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THE DEHYDROCHLORINATION OF 1,1-DIARYL-2,2,2-TRICHLOROETHANES

IN PROTONIC AND DIPOLE APROTONIC SOLVENTS

A THESIS
presented to the University of Auckland
for the Degree of
Doctor of Philosophy

by

RONALD JAMES WONG

University of Auckland
November 1973
When this research project was started three years ago the primary objective was to ascertain whether halide-promoted eliminations of the 1,1-diaryl-2,2,2-trichloroethanes (DDT-type compounds) in dipolar aprotic solvents are E2H rather than E2C reactions. The Hammett \( \rho \) for these reactions with chloride ion in acetone was found to be 1.31. At the time this was the largest \( \rho \) constant reported for a weak base elimination. Cristol and co-workers had reported a \( \rho \) of 2.73 for the dehydrochlorination of the DDT-type compounds with sodium hydroxide in 92.6% ethanol. However, this figure is unreliable since the base present is actually a mixture of hydroxide and ethoxide ions. In order to make a more accurate comparison between the \( \rho \) values for a halide-induced reaction and an alkoxide-induced reaction, the \( \rho \) value for the elimination of the DDT-type compounds with methanolic sodium methoxide was determined. More important however, was the deuterium isotope effect of ca. 5.2 for this reaction. This result was not in line with the reported values of 3.4 and 3.1 for the ethoxide and thiophenoxide-promoted reactions. Burnett believes that there should be more extensive proton transfer to the stronger base in E2H transition states. If this premise were to be obeyed then the isotope effects on the paeanecarbonion side should decrease as the base strength is increased along the series; thiophenoxide, methoxide, ethoxide. The full significance of the isotope effect for the methoxide reaction was not realised until the isotope effects, together with the values for the phenoxide and 4-nitrophenozone reactions, were plotted as a function of \( pK_a \) of the proton acceptor. A isotope effect maximum was obtained at ca. \( \Delta pK = 0 \). Maximal isotope effects at ca. \( \Delta pK = 0 \) have been reported for carbon acids for which proton transfer is the rate-determining step. A sole
example had been reported for an E2H reaction in which however, the isotope effect maximum did not occur at $\Delta pK = 0$. Perhaps the correlation obtained for DDT is fortuitous or perhaps it is evidence for a stepwise "irreversible" E1cB process. This mechanism had earlier been suspected for the dehydrochlorination of DDT but had not been completely proven nor discounted.

Following this lead it was found that the magnitudes of the deuterium isotope effects in methoxide-methanol and t-butoxide-t-butanol and a rate-acidity correlation reinforced the E1cB view. The most convincing piece of evidence is that the calculated rates of detritiochlorination for the DDT-type compounds versus the calculated respective $pK_a$ values fitted on the same Bronsted plot for the protodetritiation of the structurally similar fluorene derivatives. Admittedly, each single piece of evidence is in itself circumstantial. The evidence in toto however, best explained by an "irreversible" E1cB mechanism. The crucial test will be the leaving group isotope effect which has yet to be determined.

It is ironical that what was thought to be a minor digression from the main objective for comparison purposes eventually turned out to be the major mechanistic investigation. In essence, this is what research is all about and what makes it fascinating.
ABSTRACT

PART I

A general introduction is given to the mechanisms of olefin-forming \( \beta \)-elimination. The development of mechanistic criteria and their application to the various reactions is discussed. Conflicting theories concerning the nature of the transition states of E2H reactions in protic solvents as well as the Weinstein-Parker E2C-like transitions states for elimination by weak bases in dipolar aprotic solvents are described.

PART II

The use of primary deuterium isotope effects, structure-reactivity relationships, and rate-acidity correlations as mechanistic criteria for the E2 mechanism and the variants of the E1cb mechanism is reviewed. These criteria have been applied to the dehydrochlorination of the 1,1-diaryl-2,2,2-trichloroethanes (DDT-type compounds) with methoxide-methanol and t-butoxide-t-butanol. Literature comparisons indicate that the kinetic evidence for these two systems is in accord with an "irreversible" E1cb elimination pathway.

PART III

Characteristics of weak base-promoted eliminations in dipolar aprotic solvents are reviewed. The evidence is not entirely consistent with either E2C or the E2H mechanism. Deuterium isotope effects and equilibrium constants are reported for the chloride ion-promoted elimination of the 1,1-diaryl-2,2,2-trichloroethanes in dimethylformamide.
and acetone respectively. The results are in accord with an E2H mechanism.
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Reprinted Papers


'Chloride-ion Promoted Dehydrochlorination of 1,1-Diaryl-2,2,2-trichloroethanes in Dipolar Aprotic Solvents', by O. R. Jackson, D. J. McLennan, S. A. Short, and R. J. Wong, *J.C.S. Perkin II*, 1972, 2308.
PART I

GENERAL INTRODUCTION
1.1 **MECHANISMS OF ELIMINATION**

There are three basic mechanisms of olefin-forming \( \beta \)-elimination reactions in solution\(^1-^4\). These are the stepwise E1 and E1cB mechanisms and the concerted E2 mechanism.

The carbonium ion or E1 mechanism was first recognised by Hughes\(^5\) as a general mechanism of elimination. The first step of the reaction is the rate-determining heterolysis of the \( \text{C}_\alpha - \text{X} \) bond forming a carbonium ion. This can either eliminate a proton to form an olefin or react with a nucleophile to form a substitution product.

\[
\begin{array}{c}
\text{H} - \overset{\beta}{\text{C}} - \overset{\alpha}{\text{C}} - \text{X} & \text{slow} & \overset{\text{H}}{\overset{\beta}{\text{C}}} - \overset{\alpha}{\text{C}}^+ + \overset{\text{X}}{\text{X}}^- \\
\text{H} - \overset{\beta}{\text{C}} - \overset{\alpha}{\text{C}}^+ + \overset{\text{B}}{\text{B}}^- & \overset{\text{C}}{\overset{\beta}{\text{C}}} - \overset{\alpha}{\text{C}}^+ + \overset{\text{BH}}{\text{BH}} \\
\end{array}
\]

\[(1.1)\]

\[
\text{X} = \text{SR}_2^+, \text{Cl}, \text{Br}, \text{I}, \text{OSO}_2\text{R}
\]

The rate law for unimolecular elimination (no ion-pair return) is:

\[
\text{Rate} = k_1[\text{RX}]
\]

\[(1.3)\]

The E1cB mechanism involves the formation of a carbanion in the first step which can either return externally regenerating the substrate or eliminate the leaving group.
\[ B + H-\ce{C-C-X} \xleftrightarrow[k_1][]{k_{-1}} \ce{BH^+} + \ce{C-C-X} \]  
\[ \xrightarrow[k_2]{k_2} \ce{C==C} + X^- \]  
(1.4)  

A steady state analysis of these equations gives:

\[
\text{Rate} = \frac{k_1 k_2 [\text{RX}][B]}{k_{-1} [\text{BH}^+] + k_2}
\]  
(1.6)

If external return of the carbanion occurs faster than the formation of the product, that is, \( k_{-1} [\text{BH}^+] \gg k_2 \), the rate equation will be:

\[
\text{Rate} = \frac{k_2 k_1 [\text{RX}][B]}{k_{-1} [\text{BH}^+]}
\]  
(1.7)

This is the "reversible" or pre-equilibrium E1cB mechanism. The other limiting case is \( k_2 \gg k_{-1} [\text{BH}^+] \), that is, product formation occurs much faster than external return.

\[
\text{Rate} = k_1 [\text{RX}][B]
\]  
(1.8)

This is the "irreversible" E1cB mechanism.

These two mechanisms can be distinguished by two criteria. Firstly, the "reversible" E1cB mechanism obeys specific base catalysis. The rate at a constant buffer ratio is independent of the total buffer concentration. This is in contrast to the "irreversible" E1cB and E2 mechanisms which obey general base catalysis. Secondly, the external return of the carbanion in the "reversible" E1cB mechanism can be detected by hydrogen isotope exchange. The difficulty lies in distinguishing between the "irreversible" E1cB mechanism and the E2 mechanism since both are kinetically indistinguishable.
There is a third E1cB mechanism, similar to the "reversible" E1cB mechanism, involving internal return rather than external return of the carbanion. Internal return is characterized by low or even inverse primary deuterium isotope effects. The internal return mechanism is outlined below:

\[
B^- + H-C-C-C-X \xrightarrow{k_1} \xrightarrow{k_{-1}} BH \cdots \cdots C-C-X \xrightarrow{k_2} BH + C=\overset{\mathrm{\delta-}}{C} + X^- \tag{1.9}
\]

If \( k_{-1} \gg k_2 \), the rate equation will be:

\[
\text{Rate} = \frac{k_1 k_2 [RX][B^-]}{k_{-1}} \tag{1.10}
\]

The E2 mechanism, as designated by Ingold, involves the concerted breaking of the \( C_x - X \) and the \( C_\delta - H \) bonds.

\[
B^- + \overset{\mathrm{\delta-}}{C-C-C} \xrightarrow{k_{-1}} \overset{\mathrm{\delta-}}{C-C} \xrightarrow{k_2} C=\overset{\mathrm{\delta-}}{C} + BH + X^- \tag{1.11}
\]

\( X = NR_3^+, SR_2^+, OH^+, SO_2R^-, NO_2^-, OSO_2R^-, COCOR, \) halides.

\( B = CH_2, NR_3, OH^-, OR^-, OAC^-, OAr^-, NH_2^-, CO_3^{2-}, Cl^-, Br^-, I^- \).

The rate law for the E2 mechanism is:

\[
\text{Rate} = k_2[RX][B] \tag{1.12}
\]

The E2 mechanism can be distinguished from the E1cB mechanism by isotopic means and other mechanistic probes.
1.2 THE E2 TRANSITION STATE

1.2.1 THE THEORY OF THE VARIABLE E2 TRANSITION STATE

Hanhart and Ingold, \(^{13}\) in 1927, recognised that the breaking of the \(C_\alpha - X\) and \(C_\beta - H\) bonds in E2 reactions need not be synchronous. It was only in 1956 that Cram and co-workers\(^ {14}\) instigated an investigation which indicated that this presumption was correct. Although many workers\(^ {1-3}\) have verified this, it was Bunnett\(^ {2-3}\) who first developed a comprehensive theory.

The theory of the variable E2 transition state visualizes a continuum of transition states, extending from a paeneacarbonium (E1-like) extreme (I) characterized by little \(C_\beta - H\) bond breaking and a large amount of \(C_\alpha - X\) bond breaking to a paencarbanion (E1cB-like) extreme (III) with little \(C_\alpha - X\) bond breaking and considerable \(C_\beta - H\) bond breaking. In between these two extremes are the "central" transition states (II) having roughly equal amounts of \(C_\alpha - X\) and \(C_\beta - H\) bond breaking. There is very little double bond character at either extreme of the spectrum of transition states but there is a high degree of double bond character in the "central" transition states.

\[
\begin{align*}
\text{Paeneacarbonium} & \quad \quad \quad \quad \quad \text{"Central"} \quad \quad \quad \quad \quad \text{Paencarbanion} \\
(\text{I}) & \quad \quad \quad \quad \quad (\text{II}) \quad \quad \quad \quad \quad (\text{III})
\end{align*}
\]

The theory allows for the optimum adjustment of the \(C_\alpha - X\) and the
C₂ – H bonds in the transition state so that the transition state with the lowest energy is achieved. The optimization involves relatively more breaking of the weak bond and relatively less breaking of the strong bond.

This theory contravenes the Hammond postulate¹⁵ which, if applied literally to E₂ reactions, predicts that there will be more breaking of the strong bond and less breaking of the weak bond in the transition state. However, Bunnett³ has pointed out that the Hammond postulate is applicable only to reactions having one bond being made or broken or two bonds being made or broken synchronously at one reaction centre. The Hammond postulate should not be applicable to the E₂ transition state which is concerned with the concerted but not necessarily synchronous bond making and bond breaking at two reaction centres.

1.2.2 THE MORE O'FERRALL MODEL

The More O'Ferrall model¹⁶ incorporates the possibilities of reaction by the E₁ and E₁CB mechanisms as well as the E₂ mechanisms. This is represented diagrammatically in Figure 1. The out of plane axis is the potential energy.

![Diagram](image)

An E₁CB reaction is represented by translation along the abscissa to
form a carbanion followed by a vertical movement to give the products. An E1 reaction is represented by a movement along the ordinate to give a carbonium ion followed by a horizontal movement to give the products. A movement diagonally from reactants to products represents the concerted E2 mechanism.

According to the model, an increase in the stability of the product of an E2 reaction decreases the energy of the transition state and moves it closer in structure to the reactants. This is in accord with the Hammond postulate. The effect of an increase in the stability of the carbanion on an E1cb-like transition state is to move its structure towards that of the carbanion contrary to the Hammond postulate prediction. Energy changes on reactants and products act across the energy maximum of the saddle point along the reaction co-ordinate, while energy changes in the carbanion or carbonium ion act across the energy minimum of the saddle point in a direction normal to the reaction co-ordinate.

Thorton has reached similar conclusions using a model based on the direct effect of substituents upon the lengths and strengths of bonds in the transition state. Both models explain the effects of substituents and reaction conditions on the transition state in terms of the effects exerted "parallel" and "perpendicular" to the reaction co-ordinate.

1.2.3 THE E2C TRANSITION STATE

The notion that strong bases (thermodynamically speaking) were always necessary to promote elimination was refuted in 1956. Winstead and co-workers found that lithium bromide in acetone was an efficient base-solvent system in promoting elimination from cis- and trans-4-t-butyl cyclohexyl tosylate, while de la Mare and Vernon noted that thiophenoxide ion in ethanol was more efficient than ethoxide ion in ethanol, in promoting second-order elimination from t-butyl chloride.
The fact that bromide ion and mercaptide ion are weak bases led Winstein\textsuperscript{20} to postulate a transition state (or a pentacovalent intermediate) involving covalent interaction between the base and the \( \alpha \)-carbon of the substrate.

\[
\text{TsO} \quad \text{H} \quad \text{Y}^- \\
\text{TsO} \quad \text{H} \quad \text{Y}^\delta^- \\
\text{(IV)}
\]

The classical E2 mechanism was rejected on stereoelectronic grounds. In the case of the trans isomer (IV), the t-butyl group prevents the attainment of a 180\(^\circ\) dihedral angle between the tosylate group and the adjacent hydrogen atom, a requirement hitherto thought necessary for the E2 mechanism.

Winstein\textsuperscript{20,21} later modified his transition state when it failed to satisfy certain stereoechemical requirements. He has since been joined by Parker in advocating an E2C transition state\textsuperscript{21-25} for eliminations promoted by weak bases (E2C symbolizes nucleophilic attack at the \( \alpha \)-carbon atom). They visualize a spectrum of transition states with the E2H transition state (V) at one extreme and the E2C transition state (VII) at the other extreme (E2H symbolizes base attack on the \( \beta \)-hydrogen).
Winstein and Parker believe that strong bases, such as alkoxide ions in alcoholic solvents, promote E2H elimination since they are strong hydrogen nucleophiles. However, weak bases such as halide ions in dipolar aprotic solvents and mercaptide ions in alcoholic solvents promote elimination through transition states (VI) or (VII).

The E2C transition state is regarded as "loose" with considerable double bond formation, virtual sp$^2$ hybridization of the α and β carbon atoms, and with charge concentrated on B and X. The E2H transition state is "tight" with little double bond formation and with the negative charge originally on the base being well dispersed. The nature of the leaving group and the structure of the substrate and the base are thought to govern the position of any reaction in the E2H-E2C transition state spectrum.

1.3 ORIENTATION

Positional orientation refers to the position of the double bond in the products formed in the elimination of a substrate with more than one β-carbon atom. Geometrical orientation refers to the proportion of the isomeric cis and trans olefins that may be formed. The product of predominant Saytzeff elimination is the most highly substituted
olefin (VIII, IX), while the least substituted olefin (X) is the result of Hofmann elimination.

\[
\begin{align*}
RCH_2CHCH_3 X & \overset{\text{B}}{\longrightarrow} \ RCH_2CHCH_3 \ & \ H \\
& \ H \ & \ H \ & \ H \ & \ H \\
& \ C=\ & \ C=\ & \ C=\ & \ C=\ \\
& \ H \ & \ H \ & \ H \ & \ H \ & \ H \\
\text{(VIII)} & \text{(IX)} & \text{(X)} \ (1.14) \\
\end{align*}
\]

cis \quad \text{trans}

According to the Hughes–Ingold theory, \textsuperscript{26} Saytzeff elimination is controlled by the conjugative ability or the hyperconjugative ability of saturated alkyl and unsaturated aryl \( \beta \)-substituents with the developing double bond in the transition state. This interpretation is still widely accepted.

However, there is controversy over their interpretation of Hofmann orientation which has been attributed to the electron withdrawing inductive effect of the "onium" leaving group (e.g. \( \text{NR}_3^+ \), \( \text{SR}_2^+ \)). Brown\textsuperscript{27,28} has suggested that Hofmann elimination is sterically controlled. In contrast, Saunders and co-workers\textsuperscript{29} and Bartsch and Bunnett\textsuperscript{30} have found that Hofmann elimination can occur with a small leaving group (e.g. fluoride) leading Bunnett\textsuperscript{3} to conclude that steric interactions are not the primary cause. These may play a part when there are very large groups present in the substrate. According to the variable E2 transition state theory Saytzeff orientation prevails for reactions involving paenecarbonium (I) and central (II) transition states while Hofmann orientation prevails for substrates which react through paenecarbonanion transition states (III).\textsuperscript{30}

The \textbf{trans/cis} ratio is thought to be a measure of the degree of double bond character in the transition state.\textsuperscript{3} The variable E2 transition state theory predicts a decrease in the \textbf{trans/cis} ratio as the
transition state character changes from "central" towards either extreme. The eclipsing of the intended cis-alkyl groups, which retards cis olefin formation, is greater with the increase of double bond formation. This is in accord with a majority of observations.  

1.4 **STEREOCHEMISTRY**

Bimolecular E2 eliminations can follow two stereochemical pathways. In order to maximize p-orbital overlap to form the developing double bond, the hydrogen and the leaving group can either be eliminated from the same side of the developing double bond (syn elimination), or they can be eliminated from the opposite side of the developing double bond (anti elimination). Anti elimination is favored on theoretical grounds and is more often experimentally observed than is syn elimination.

Syn elimination can occur when the conformation of the substrate (e.g. alicyclic systems) is such that it prevents the attainment of an antiperiplanar conformation of the atoms to be eliminated. Sicher and co-workers found that syn elimination is favored when strong bases react to produce Hofmann orientation. This is consistent with the Hughes-Ingold idea that syn elimination is fostered by advancement of the proton transfer in the transition state, with a resulting lack of concertedness.

In contrast, stereochemical studies carried out by Winstein and co-workers on weak base-promoted eliminations indicate that these reactions are overwhelmingly Saytzeff in orientation and anti in stereochemistry. For example, more than 99.9% Saytzeff product was obtained in the chloride-promoted elimination of threo and erythro 3-p-anisyl-2-butyl chloride and tosylate. The percentage anti olefin
was greater than 99.9%.

1.5 THERMODYNAMIC BASICITY AND NUCLEOPHILICITY

According to the Bronsted theory of acids and bases, an acid is a proton donor and a base is a proton acceptor. Lewis, however, defined acids and bases in broader terms. He regarded acids as being electron pair acceptors and bases as being electron pair donors. This definition encompasses reactions other than the "classical" acid-base reactions.

There has been some confusion over the use of the terms nucleophilicity and basicity. A nucleophile was defined as an electron donor that supplies a pair of electrons to form a covalent bond with a reaction centre. This is very similar to the Bronsted and Lewis concepts of a base. Swain and Scott clarified the situation by defining nucleophilicity as the kinetic affinity of a nucleophile for a reaction centre and basicity as the thermodynamic affinity of a nucleophile for a reaction centre. Parker has qualified the basicity of a nucleophile according to its thermodynamic affinity for a particular centre. For example, carbon basicity, hydrogen basicity and sulphur basicity refer to the thermodynamic affinity of a nucleophile for a carbon, hydrogen and sulphur atom.

1.6 DIAGNOSIS OF THE QUALITY OF THE TRANSITION STATE

1.6.1 DEUTERIUM ISOTOPE EFFECTS

A primary deuterium isotope effect is expected when the bond to the isotopic atom is broken in the rate-determining step of a reaction. Theoretical calculations of deuterium isotope effects predict a maximum of about seven at 25°C. The best known theoretical model is the
Westheimer model which is based on a three-centre linear transition state. Proton tunnelling and bending vibrations are disregarded. The isotope effect should be a maximum when the transition state is symmetrical. Consider the symmetric stretching vibration for the reaction:

\[ A - H + B \rightleftharpoons [A \cdots H \cdots B]^\# \rightarrow A + HB \]  

(1.15)

The atoms A and B move in opposite directions while the H atom remains stationary in a symmetrical vibrational mode. There is no change in the zero point energy of the transition state when the hydrogen is replaced by deuterium. Therefore, the isotope effect will be dependent on the zero point energy difference of about 1.15 kcal mol\(^{-1}\) between the isotopic reactants. When the transition state is asymmetric the H atom will be in motion. This has an effect on the vibration frequency. Isotopic substitution will result in a zero point energy which is different from that for hydrogen. The zero point energy difference will be smaller, resulting in a low isotope effect.

For E2H reactions, a low isotope effect is expected for paenecarbonium and paenecarbonium transition states. A large isotope effect is expected for the "central" transition state. Observation of a low isotope effect leads to the problem of deciding on which side of "central" the transition state lies.

More O'Ferrall and Kouba\(^{46}\) have calculated theoretical isotope effects using four and five-centred transition state models. These take into account bending vibrations and proton tunnelling. The five-centre model (XI) allows for a pair of degenerate bending vibrations in the reactants and the product. This model is applied to proton transfer from a hydrogen bound to a secondary or tertiary carbon atom to a diatomic base (e.g. secondary or tertiary amine). The four-centre model (XII) is applied to proton transfer to a monatomic base (e.g. halide ions). In
this case there is no bending vibration in the product.

\[ [X \rightarrow A \cdots H \cdots B \rightarrow Y]^\ddagger \]
\[ (XI) \]
\[ [X \rightarrow A \cdots H \rightarrow B]^\ddagger \]
\[ (XII) \]

Calculations based on these two models support the conclusion based on the three-centre model that the isotope effect is a maximum for a symmetrical transition state.

More O'Ferrall\(^{47}\) extended these calculations to include non-linear transition states. He found that the isotope effect depended on the geometry of the transition state. Low isotope effects of ca. 1-2 were obtained for non-linear models. These are attributed to the isotopic sensitivity of the real stretching mode in the transition state. Model calculations on the E2C transition state indicate that a low isotope effect of ca. 2-4 would be expected.

1.6.2 LINEAR FREE ENERGY RELATIONSHIPS

Linear free energy relationships (L.F.E.R.) are valuable in correlating the reactivities of organic compounds. These are usually in the form of a linear relationship between the logarithms of the rate or equilibrium constants for one reaction series (1) and those for a second closely related reaction series (2). This relationship is in the form

\[ \log k_1 = A \log k_2 + B \]  \[ (1.16) \]

where \( k_1 \) and \( k_2 \) are the corresponding rate or equilibrium constants and \( A \) and \( B \) are constants. The relationship between the equilibrium constant for a reaction and the standard free energy change (\( \Delta G^0 \)) accompanying the reaction is given by equation (1.17).
\[
\log K = -\frac{\Delta G^0}{2.303 \text{ RT}} \tag{1.17}
\]

Similarly, the rate constant for a reaction is related to the standard free energy of activation (\(\Delta G^\ddagger\)) by

\[
\log k = -\frac{\Delta G^\ddagger}{2.303 \text{ RT}} + \log \frac{kT}{h} \tag{1.18}
\]

where \(k\) is Boltzmann's constant, \(h\) is Planck's constant and \(R\) is the Gas constant.

Substituting equations (1.17) and (1.18) into equation (1.16) we obtain:

\[
\Delta G^\ddagger = A \Delta G^0 + BRT + 2.303RT \log \frac{kT}{h} \tag{1.19}
\]

The equilibrium constant \(K\) of a compound within a series can be related to a "standard" compound with an equilibrium constant \(K_o\) by

\[
\log K - \log K_o = \frac{(\Delta G_o - \Delta G)}{2.303 \text{ RT}}
\]

\[
= \frac{\delta \Delta G}{2.303 \text{ RT}} \tag{1.20}
\]

where \(\delta\) represents the effect of a substituent change.

For the same two compounds in a second reaction a similar relationship is obtained.

\[
\log K' - \log K'_o = \frac{\delta \Delta G'}{2.303 \text{ RT}} \tag{1.21}
\]

The two reaction series are related by:

\[
\log \frac{K}{K_o} = A \log \frac{K'}{K'_o} \tag{1.22}
\]
Similarly for rate constants:

\[ \log \frac{k}{k_o} = B \log \frac{k'}{k'_o} \] (1.23)

The term \( \log(k'/k'_o) \) is termed the substituent constant. It is characteristic of the factor that is changed within a reaction series (e.g. solvent, structure etc.). The constant \( A \), termed the reaction constant, depends upon the particular reaction series that is compared with the standard series.

1.6.3 THE HAMMETT EQUATION

The best known linear free energy relationship is the Hammett equation.\(^{48-50}\) It relates the effect of meta and para substituents on aromatic side chain reactions to their effects on a standard reaction. The Hammett equation can be written as

\[ \log \frac{k}{k_o} = \sigma \rho \] (1.24)

\[ \log \frac{k}{k_o} = \sigma \rho \]

where \( k \) and \( K \) are the rate and equilibrium constants for a given substituent on the ring attached to the side chain and \( k_o \) and \( K_o \) are the rate and equilibrium constants for the standard ring substituent (hydrogen). The substituent constant \( \sigma \) measures the polar and resonance effect of the substituent relative to hydrogen. These values are based on the ionization of substituted benzoic acids in water at 25°c which is the standard reaction. The \( \sigma \) constants are positive for electron withdrawing groups and are negative for electron donating groups. The reaction constant \( \rho \) measures the sensitivity of the reaction to electronic effects. It has a value of 1.000 for the standard reaction.
Substituent constants should in principle be independent of the nature of the reaction. However, this is not entirely correct. For example, $\sigma = 0.778$ for the p-$\text{NO}_2$ substituent, based on the ionization of p-nitrobenzoic acid, was found to be inapplicable to acid-base equilibria involving phenols or anilines. An enhanced $\sigma^-$ value of 1.27 was required. This was ascribed to the cross-conjugation of the p-$\text{NO}_2$ group with the $-\text{O}^-$ or $-\text{NH}_2$ groups.

Wepster\textsuperscript{51} believes that the substituent constants depend both on the mesomeric effect of the \underline{para} substituent and the reaction constant. A sliding scale would be expected rather than a single "exalted" value. The $\sigma^R$ constant was introduced designating the normal "unexalted" value. A set of $\sigma^*$ constants for \underline{meta} substituents were taken as primary values. Only these were used to calculate the $\rho$ for a particular reaction.

Taft approached the problem differently.\textsuperscript{52,53} He suggested that the substituent constant could be separated into resonance and inductive contributions.

$$\sigma^m = \sigma^I + \alpha' \sigma^R \quad (1.25)$$

$$\sigma^p = \sigma^I + \sigma^R \quad (1.26)$$

where $\sigma^I$ is a measure of the inductive contribution and $\sigma^R$ is a measure of the resonance contribution. The relay coefficient $\alpha'$, has a value of ca. 1/3.

Substituent constants are stated to be additive for poly-substituted benzene derivatives with substituents in the meta and para positions.\textsuperscript{49} The Hammett equation is in the form

$$\log \frac{k}{k_0} = \rho \sigma^- \quad (1.27)$$
where \( \xi \sigma \) is the sum of the \( \sigma \) values for the individual substituents. Compounds with two symmetrically substituted benzene rings, such as \( \text{Ar}_2\text{CHX} \) and \( \text{Ar}_2\text{CHCCl}_3 \), should "ideally" obey a Hammett equation of the form

\[
\log \frac{k}{k_0} = n \sigma \rho \tag{1.28}
\]

where \( n \) is the number of benzene rings.

The reaction constant \( \rho \) indicates the degree of the electronic stabilization of the transition state relative to the ground state. Reactions which have rates or equilibria accelerated by electron withdrawing groups have a positive \( \rho \) value and those accelerated by electron donating groups have a negative \( \rho \) value.

1.6.4 THE BORMSTED EQUATION

The Brønsted catalysis law\(^54\) is the earliest example of a linear free energy relationship. It relates the rate of general acid or base-catalysed reactions with the thermodynamic acidity or basicity of the acid or base. The relationship is given by

\[
\log k_A = \log G_A + \alpha \log K_A \tag{1.29}
\]

\[
\log k_B = \log G_B - \beta \log K_B \tag{1.30}
\]

where \( k_A \) and \( k_B \) are the rate constants of acid and base-catalysis respectively, \( K_A \) and \( K_B \) are the dissociation constants of acid A or conjugate base B, and \( G_A \) and \( G_B \); \( \alpha \) and \( \beta \) are constants depending on the reaction conditions and on the reaction.

The selectivity coefficients \( \alpha \) and \( \beta \) are thought to be measures of the degree of proton transfer in the transition state.\(^55\) The \( \alpha \) and \( \beta \) values should be positive and less than unity. However, Bordwell and
co-workers\textsuperscript{56, 57} found $\beta$ values less than zero and greater than unity. Several groups of workers have noted discrepancies between deuterium isotope effects and $\beta$ for several unrelated systems.\textsuperscript{58-61} They conclude that $\beta$ is the less reliable criterion of transition state character for these cases.

1.6.5 ACIDITY FUNCTIONS

The pH scale, as expressed by equation (1.31) no longer becomes a valid measure of acidity for solutions of greater than ca. 0.1 M.

$$\text{pH} = -\log a_{H^+} = -\log c_{H^+} f_{H^+}$$ (1.31)

The symbol $a_{H^+}$ represents the activity of the hydrogen ion, and $c_{H^+}$ and $f_{H^+}$ are the concentration and activity coefficient respectively of the hydrogen ion.

In 1932, Hammett and Deyrup\textsuperscript{62} suggested a new acidity scale based on the extent of protonation of weakly basic indicators in concentrated acid solution. For a weak base B,

$$B + H^+ \rightleftharpoons BH^+$$ (1.32)

the dissociation constant ($pK_{BH^+}$) of its conjugate acid is given by equation (1.33).

$$pK_{BH^+} = -\log \frac{a_{H^+} a_B}{a_{BH^+}}$$ (1.33)

The extent of protonation is related to the pH by:-

$$\text{pH} = pK_{BH^+} - \log \frac{c_{BH^+}}{c_B} = -\log \frac{f_{BH^+}}{f_B}$$ (1.34)

The activity coefficients are unity in dilute solution. However, this is no longer true in more concentrated solutions and a new function $H_0$
is required to express the acidity of the medium.

\[ H_0 = -\log h_0 = -\log \frac{a_{H^+} f_B}{f_{BH^+}} \]  \hspace{1cm} (1.35)

Substituting equation (1.35) into (1.33) we obtain:

\[ H_0 = pK_{BH^+} - \log \frac{c_{BH^+}}{c_B} \]  \hspace{1cm} (1.36)

At infinite dilution \( H_0 \) becomes equivalent to pH.

A similar acidity function can be defined for concentrated base solutions. The \( H^- \) function is a measure of the ability of a negatively charged base to remove a proton from a neutral weak acid BH.

\[ B^- + H^+ \leftrightarrow BH \]  \hspace{1cm} (1.37)

\[ H^- = -\log h^- = -\log \frac{a_{H^+} f_{B^-}}{f_{BH}} \]  \hspace{1cm} (1.38)

Substituting equation (1.38) into the expression for the \( pK \) of the weak acid an expression analogous to that for the \( H_0 \) can be obtained.

\[ H^- = pK_{BH} - \log \frac{c_{BH}}{c_B} \]  \hspace{1cm} (1.39)

Acidity functions have also been determined for other solvent systems, such as methanol,\textsuperscript{63-66} t-butanol,\textsuperscript{67} water-dimethyl sulfoxide\textsuperscript{72} and alcohol-dimethyl sulfoxide mixtures.\textsuperscript{68} The interest here is mainly in the \( H^- \) acidity function for solutions of methanolic alkali metal methoxides, which refer to methanol as the standard state as far as the solvent is concerned.

\[ H^- = -\log \frac{a_{H^+} f_{B^-}}{f_{BH}} = pK^M_{BH} + \log \frac{c_{B^-}}{c_{BH}} \]  \hspace{1cm} (1.40)
\[ H_M = pK_{\text{MeOH}} + \log \frac{a_{\text{MeOH}}^{f_B} f_{\text{BH}}}{a_{\text{MeOH}}^{f_B} f_{\text{BH}}} \] (1.41)

The autoprotolysis constant of methanol \( pK_{\text{MeOH}} \) is 16.92 at 25°C.\(^1\)

The measurement of the (\( c_B^-/c_{\text{BH}} \)) ratio is straightforward provided that the acid and its conjugate base have different absorption spectra and do not show any medium effects.\(^68,69\) The \( pK \) of the weak acid \( \text{BH} \) can be determined spectrophotometrically, either directly,\(^68\) or by the stepwise comparison method.\(^62,68,70\) For a weak acid ionizing in aqueous base solution (1.42), the equilibrium constant is related to the hydroxide ion concentration by equation (1.43).

\[ \text{BH} + \text{OH}^- \rightleftharpoons \text{B}^- + \text{H}_2\text{O} \] (1.42)

\[ pK_W - pK_{\text{BH}} = \log \frac{c_{\text{B}^-}}{c_{\text{BH}}} - \log c_{\text{OH}^-} + \log \frac{a_{\text{BH}}^{f_B}/f_{\text{BH}}}{a_{\text{OH}^-}^{f_{\text{OH}^-}}} \] (1.43)

A plot of \( \log (c_{\text{B}^-}/c_{\text{BH}}) - \log c_{\text{OH}^-} \) against \( c_{\text{OH}^-} \) extrapolated to infinite dilution gives a value for \( pK_W - pK_{\text{BH}} \).\(^64\) The stepwise technique developed by Hammett and Deyrup\(^62\) involves the comparison of basicities of solutions, starting in the pH region. The method is based on the assumption that \( (f_{\text{B}^-}/f_{\text{BH}}) \) is the same for two bases of similar structure. If the \( pK \) of one of the acids is known then the \( pK \) for the other can be calculated by comparing the ratios of the indicator concentrations.

\[ pK_{\text{AH}} = pK_{\text{BH}} + \log \frac{c_{\text{B}^-}}{c_{\text{BH}}} - \log \frac{c_{\text{A}^-}}{c_{\text{AH}}} + \log \frac{f_{\text{B}^-}/f_{\text{AH}}}{f_{\text{BH}}/f_{\text{AH}}} \] (1.44)

The activity coefficient term in equation (1.44) can be neglected for acids of similar structure in solutions of high dielectric constant.\(^68\)

\[ pK_{\text{AH}} = pK_{\text{BH}} + \log \frac{c_{\text{B}^-}}{c_{\text{BH}}} - \log \frac{c_{\text{A}^-}}{c_{\text{AH}}} \] (1.45)

Similarly the \( pK \) of a third indicator can be determined from \( pK_{\text{AH}} \).\(^*\)

The acidity functions \( H_0, H_- \) and \( H_M \), have limitations in that they
are not independent of the nature of the indicators used to measure them.\textsuperscript{68-70}

The $H_-$ function based on the ionization of indigo derivatives \textsuperscript{73} in KOH and NaOH solutions is different to the acidity function based on the ionization of indoles.\textsuperscript{74} Similarly, the $H_M$ function derived from substituted phenols\textsuperscript{65} is different to the one based on carbon acids.\textsuperscript{66}

The measurement of acidity functions for concentrated acids has been reviewed thoroughly by Paul and Long\textsuperscript{69} and Rochester.\textsuperscript{68} Far less work has been done on acidity functions for solutions of concentrated bases.\textsuperscript{68,70}
PART II

ELIMINATION IN PROTIC SOLVENTS
1. INTRODUCTION

1.1 ELIMINATION FROM THE PHENETHYL AND RELATED SYSTEMS

Extensive mechanistic studies on the 2-arylethyl system (I) have supported the concept of a variable E2 transition state.²,³,⁷⁵

\[
B^- + Z \begin{array}{c} \text{-CH}_2\text{-CH}_2X \\ \text{(I)} \end{array} \rightarrow Z \begin{array}{c} \text{-CH} = \text{CH}_2 + BH + Y^- \end{array}
\] (2.1)

These include primary deuterium isotope effects,⁷⁵⁻⁸³ solvent isotope effects,¹⁷ leaving group isotope effects⁸³⁻⁸⁵ and the use of structure-reactivity relationships such as the Hammett⁷⁹⁻⁸³,⁸⁶⁻⁸⁹ and Bronsted equations.⁹⁰ Research groups led by Saunders, DePuy and Cockerill have been especially active in these investigations. Data from their investigations are summarized in Table 1. This is taken in the large part from Bunnett's review.³

<table>
<thead>
<tr>
<th>X</th>
<th>Hammett ( \rho ) value</th>
<th>( k_H/k_D )</th>
<th>Heavy atom isotope effect</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>I</td>
<td>2.07</td>
<td></td>
<td></td>
<td>86</td>
</tr>
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<td>2.14</td>
<td>7.1</td>
<td></td>
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<td>2.27</td>
<td>5.7</td>
<td></td>
<td>76, 87</td>
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<td>Cl</td>
<td>2.61</td>
<td></td>
<td></td>
<td>88</td>
</tr>
<tr>
<td>( \text{SMe}_2^+ )</td>
<td>2.75</td>
<td>5.1</td>
<td>1.0074³</td>
<td>83, 86, 87</td>
</tr>
<tr>
<td>F</td>
<td>3.12</td>
<td></td>
<td></td>
<td>88</td>
</tr>
<tr>
<td>( \text{NHMe}_3^+ )</td>
<td>3.77</td>
<td>3.0</td>
<td>1.0094²</td>
<td>79, 84, 87</td>
</tr>
<tr>
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<td>4.40⁰</td>
<td>2.75</td>
<td></td>
<td>81</td>
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</table>
a Sulphur isotope effect for reaction with hydroxide ion in water ca. 35\% of the theoretical maximum. b Nitrogen isotope effect ca. 30\% of the maximum. c For reaction with potassium t-butoxide in t-butanol.

The increase in the Hammett $\rho$ values for the 2-arylethyl system is consistent with a shift in the transition state character towards the paene-carbanion extreme of the E2 spectrum as the leaving group gets poorer.\textsuperscript{3} This is supported by a decrease in the primary deuterium isotope effect from 7.1 to 3.0. Heavy atom leaving group isotope effects have only been determined for nitrogen and sulphur.

The sulphur leaving group isotope effect has been reported by Saunders, Cockerill and co-workers\textsuperscript{78,83} for the hydroxide ion-promoted elimination of 2-phenethylidimethylsulphonium bromide in a series of water-dimethyl sulfoxide (DMSO) mixtures. The $k^{32}/k^{34}$ ratio decreased from 1.0074 in pure water to 1.0011 in ca. 20 mole \% DMSO.\textsuperscript{78} The Hammett $\rho$ value increased sharply from 2.11 to ca. 2.6 and then remained almost constant.\textsuperscript{77} The primary deuterium isotope effect increased from 5.4 in water to a maximum of 6.2 and then decreased to 5.7 as the mole percentage of DMSO was increased. The addition of DMSO desolvates the hydroxide ion thus increasing the effective base strength and shifts the transition state towards the paene-carbanion extreme. The amount of $C_{\alpha}-S$ bond rupture should decrease resulting in smaller sulphur isotope effects, as observed. Cockerill\textsuperscript{77} explained the decrease in the deuterium isotope effect on reaching ca. 60 mole \% DMSO in terms of a reactant-like shift of the transition state. However, the opposite interpretation can also be applied. The Hammett $\rho$ values are more difficult to interpret. It has been suggested that $\rho$ varies inversely with the dielectric constant. This means that $\rho$ should increase with the increasing proportion of added DMSO even if the transition state structure remains unchanged. Since the
bulk dielectric constant of the medium is not known exactly, it is not possible to determine how much of the increase in the $\rho$ value is due to the solvent change.

Ayrey, Bourns and Vyas$^{84}$ found a nitrogen leaving group isotope effect of 1.0094 for the E2 reaction of 2-phenethyltrimethylammonium bromide in ethoxide-ethanol at 60°C. The nitrogen isotope effect for the elimination of ethyltrimethylammonium bromide in ethoxide-ethanol is 1.0173. The introduction of a $\beta$-phenyl group will lower the transition state energy for E2 elimination by delocalizing the developing negative charge on the $\beta$-carbon atom. This facilitates greater $\beta$ - H bond rupture coupled with less $\alpha$ - N bond rupture. This is supported by the lowering of the primary deuterium isotope effect from ca. 6 for the ethyltrimethylammonium salt$^{84}$ to 2.98 for 2-phenethyltrimethylammonium bromide.$^{76}$

Also relevant to this study is the effect of para substituents on the nitrogen isotope effect of the ethoxide-promoted reactions of 2-p-Z-phenethyltrimethylammonium salts in ethanol at 40°C reported by Bourns and Smith.$^{85b}$ They noted a decrease in the isotope effect from 1.014 to 1.011 as the substituent Z was changed from methoxy to chloro. The addition of an electron withdrawing substituent would lead to an increase in the carbanion character at the $\beta$-carbon atom accompanied by a decrease in the amount of $\alpha$ - N bond rupture.$^{75}$

The study of E2 reactions of the 2-phenethyl system is not as extensive for the t-butoxide-t-butanol base-solvent system. The Hammet $\rho$ value of 4.4 for the elimination of 2-arylethyl methyl sulphoxide with potassium t-butoxide in t-butanol is the largest reported for the 2-phenethyl system.$^{81}$ The deuterium isotope effect is 2.7. The absence of hydrogen isotope exchange excludes the possibility of the "reversible" E1cB mechanism. It was concluded that the transition state for the
reaction has considerable carbanion character.

DePuy and Bishop found that the Hammett $\rho$ values decreased for the eliminations of 2-arylethyl bromides and iodides when the base-solvent system was changed from ethoxide-ethanol to t-butoxide-t-butanol.

The $\rho$ value decreased from 2.14 to 2.03 for the bromide compound. A similar decrease was noted for the iodide. However, the $\rho$ value for the tosylate increased from 2.27 to 3.39. Saunders and co-workers reported a Hammett $\rho$ value of 2.53 for t-butoxide-promoted elimination of 2-arylethyl bromide. On the addition of varying amounts of DMSO it was found that $\rho$ and the deuterium isotope effect of 8.1 remained constant within experimental error. The introduction of DMSO increases the polarity of the medium and alters the solvation of the base thus increasing the effective base strength. The increase in the strength of the base should shift the transition state towards the paenecarbonium extreme while the greater polarity of the solvent should shift the transition state to the paenecarbonium extreme. Blackwell et al. however, reported a Hammett $\rho$ value of 2.85 for the elimination of 2-arylethyl bromides in t-butoxide-t-butanol. The correlation of DePuy and Bishop was extended to include $p$-acetoxo and $m$-nitro substituents. It is for this reason that this value of 2.85 is believed to be the more reliable reaction constant. Deuterium isotope effects, covering a range of substituents from $p$-methoxy to $p$-nitro, have also been reported. These increase regularly from 7.00 to 9.14 as the substituent is changed from an electron donating to an electron withdrawing one. They are larger than the theoretical estimates and this has been attributed to proton tunnelling.

Cockerill and co-workers have carried out a comprehensive Hammett structure-reactivity correlation of the elimination of a series of 2-$p$-Z-phenethyl-$p$-$Y$-arenesulphonates with potassium-t-butoxide in t-butanol. The Hammett $\rho$$_Y$ value decrease from 2.49 to 2.03 ($Y$ constant,
Z varying for each correlation) as the substituent in the arenesulphonate group is changed from an electron donating to an electron withdrawing group. The decrease in the amount of C_\beta - H bond rupture is accompanied by an increase in the degree of C_\alpha - O bond rupture, that is, the transition state shifts towards the paenecarbonium extreme. The Hammett \( \rho_Y \) values (Z constant, Y varying for each correlation) measures the amount of negative charge accumulating in the sulphonate group in the transition state. They decrease from 1.24 for p-methoxy to 0.94 for m-chloro suggesting that as the C_\beta - H bond becomes more acidic, the C_\alpha - O bond rupture becomes less advanced in the transition state. It was noted that the Hammett \( \rho \) of 2.49 for the E2 reaction of 2-arylethyl tosylate in t-butoxide-t-butanol is much lower than the value reported by DePuy and Bishop.\(^87\)

This study refutes the contention that the E1cB mechanism is impossible.\(^91a\) Hoffmann believes that the greater is the \( k_{\text{UTS}}/k_{\text{Br}} \) rate ratio in an elimination the greater is the amount of C_\alpha - X bond rupture in the transition state. It was found that \( k_{\text{UTS}}/k_{\text{Br}} \) was larger for the 2-p-nitrophenethyl derivatives than for the 2-phenethyl derivatives in both t-butoxide-t-butanol and ethoxide-ethanol.\(^91b\) This led to the conclusion that greater C_\beta - H bond rupture is accompanied by greater C_\alpha - X bond rupture. Cockerill et al., however, draws the opposite conclusion from the \( \rho_Y \) values for the 2-phenethyl arenesulphonate system.\(^89\)

Saunders, Bushman and Cockerill\(^79\) found that the Hammett \( \rho \) of 3.07 for the sodium t-butoxide-promoted elimination of 2-arylethyltrimethylammonium bromide in t-butanol was much smaller than \( \rho \) of 3.77 for the ethoxide-promoted elimination. This was accompanied by a decrease in the deuterium isotope effect from 7.0 to 3.0. They conclude that there is less carbanion character in the transition state in t-butanol than in ethanol. The reaction is second-order in ethanol, but in t-butanol, the reaction
order appears to be 1.5 in substrate. It has been suggested that sodium t-butoxide, which exists as ion-pairs in solution, is converted to the more reactive free t-butoxide ion by the quarternary ammonium salt. A first-order dependence in substrate could only be obtained in the presence of the added salt, benzytrimethylammonium chloride. The Hammett correlation for the reaction in t-butanol and ethanol were based on three points, and four points respectively. Not too much reliance should be placed on the magnitudes of the reaction constants reported. It seems as if the elimination of 2-arylethyltrimethylammonium bromide is very susceptible to the polarity of the solvent.

Some interesting results have been reported by Bunnett, Davis and Tanida on the thioethoxide and methoxide-promoted elimination reactions of 1-phenyl-2-methyl-2-chloropropane(II). They obtained low β-deuterium isotope effects of 2.4 and 2.6 for the mercaptide and alkoxide ion-promoted reactions respectively. It was found that thioethoxide ion reacted about ten times as fast as methoxide ion. The transition state for both these reactions was thought to be on the paenecarbonium side of "central".

Blackwell, Fischer and Vaughan, however, ascertained a Hammett $\rho$ of 1.00 for the formation of the Saytzeff olefin from (II) in methoxide-methanol. This result indicates that the transition state still has some carbanion character especially when compared with the $\rho$ of -1.15 for the solvolysis reaction of (II).

$$\begin{align*}
\text{H} & \quad \text{CH}_3 \\
\text{C} & \quad \text{C} \quad \text{CH}_3 \\
\text{H} & \quad \text{Cl}
\end{align*}$$

(II)

$$\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \quad \text{CH}_3 \\
\text{H} & \quad \text{X}
\end{align*}$$

(III)

A related study on the t-butoxide and ethoxide ion-promoted
eliminations of 1-aryl-2-propyl (III) and 2-aryl-1-propyl (IV) tosylates and bromides has been reported by DePuy and co-workers. For the tosylates $\rho$ was larger in the t-butoxide-t-butanol system. The converse was found for the bromides. This anomaly was explained by the greater ability of bromide, relative to tosylate, to disperse the negative charge on the benzyl carbon in the less polar t-butanol thus allowing more double bond formation in the transition state.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{CH}_3 & \quad \text{X}
\end{align*}
\]

(IV)

\[
\begin{align*}
\text{Me}_3\text{N} & \quad \text{CH}_2 \\
\text{Y} & \quad \text{phenyl}
\end{align*}
\]

(V)

Smith and Tsui found that the $\beta$-deuterium isotope effect decreased from 5.9 to 4.2 as the $\beta$-aryl substituent is changed from p-methoxy to p-trifluoromethyl for the E2 reaction of a series of 9-(4-substituted benzyl)fluorene-9-trimethylammonium ions (V) in ethoxide-ethanol. The Hammett $\rho$ for the reaction is 1.33. They claim that the decrease in the isotope effect with the increase in the electron withdrawing nature of the $\alpha$-substituent, together with the $\rho$ value, is indicative of a reactant-like transition state. It must be noted that the rates were correlated with $\sigma^-$ and good plots were obtained for protium and deuterium compounds. The decrease in the isotope effect arises from $\rho_D$ for the deuterium compounds being greater than $\rho_H$ for the protium compounds. However, $\rho_D$ is less than $\rho_H$ for the elimination of 2-arylethyl bromide in t-butoxide-t-butanol.

Little work has been carried out on the effect of $\alpha$-substituents on the rates of E2 elimination. Yoshida, Yano, and Oae have
investigated the elimination of 1-arylethyl bromide in ethoxide-ethanol, t-butoxide-t-butanol and t-butoxide-t-butanol-DMSO mixtures. The Hammett plots were positive and curved, characteristic of the type obtained for $S_N2$ reactions. The magnitude of the Hammett $\rho$ values decreased in the order of the thermodynamic basicity of the bases. The isotope effects for 1-phenethyl bromide were 3.5, 5.0, and 3.4 in t-butanol-DMSO, t-butanol, and ethanol respectively. The authors propose that the elimination reactions in t-butanol-DMSO and t-butanol proceed via paenecarbonium transition states while the reaction in ethanol was thought to go through a paenecarbonium transition state.

Smith and Tsui have reported Hammett $\rho$ values of ca. 1 for the E2 elimination of 1-arylethyltrimethylammonium ions in ethoxide-ethanol, t-butoxide-t-butanol and ethoxide-ethanol-DMSO mixtures. The $\beta$-deuterium isotope effects increased as the para substituent was changed from an electron donating to an electron withdrawing group. There was also an increase when the base-solvent system was changed from ethoxide-ethanol to t-butoxide-t-butanol. There are three points to note about the Hammett $\rho$ values. Firstly, they were linear and independent of the strength of the base while secondly, $\rho_H$ was greater than $\rho_D$. Finally, the magnitude of the $\rho$ values suggests that there is still some carbanionic charge on the benzylic carbon atom.

1.2 ELIMINATION FROM THE DIARYLETHANE SYSTEM

There have been few mechanistic studies on the diarylethane series. Willi obtained $\beta$-deuterium isotope effects of 5.27, 5.42 and 6.70 for the E2 reactions of 2,2-diphenylethyl p-X-benzenesulphonates with sodium methoxide in methyl cellosolve (for $X = p-\text{MeO}$, H and p-NO$_2$, respectively). These values, coupled with the $\rho$ of 1.11 indicate that the transition state is in the central region.
The mechanism of elimination of the 1,1-diaryl-2,2,2-trichloroethanes (VI) or DDT type compounds was first studied by Cristol and co-workers in 92.6\% ethanol with sodium hydroxide as the base.\textsuperscript{99,100} The mechanism was thought to be E2, although the E1cB mechanism is favoured structurally by α-chlorines and β-aryl groups. Compounds with one α-chlorine atom replaced by a hydrogen atom (DDD series) and with 2 α-chlorine atoms replaced by hydrogen atoms (DDM series) were also studied.\textsuperscript{100} The reactivity order was DDT > DDD > DDM and Hammett ρ values of 2.73 and 2.46 were reported for the DDT and DDD series respectively.

![Diagram](image)

(VI)

The possibility of a carbanion mechanism of elimination for the DDT series was investigated by England and McLennan.\textsuperscript{101} The lack of hydrogen isotope exchange for DDT (VI, R = Cl) in ethanol excluded the "reversible" E1cB mechanism. The thiophenoxide-promoted elimination of DDT in methanol and ethanol was general base catalysed. If the "reversible" E1cB mechanism were operating the rate should be independent of the thiophenoxide-thiophenol buffer ratio (i.e. exhibit specific base catalysis). Bronsted β values of 0.88 and 0.77 for the eliminations promoted by substituted phenoxide ions, and thiophenoxide ions respectively, together with β-deuterium isotope effects of 3.4 and 3.1 for the ethoxide-promoted and the thiophenoxide-promoted eliminations led to the conclusion that the mechanism was paenecarbanion E2. The Hammett ρ value of 2.11 for the thiophenoxide-promoted elimination in ethanol reinforced this view.\textsuperscript{102} However, evidence will be presented later which will support the "irreversible" E1cB mechanism for the base-catalysed
elimination of DDT in alcoholic solvents.

1.3 THE CARBANION MECHANISM OF \( \beta \)-ELIMINATION

Considerable interest has been shown in the E1cB mechanisms of olefin-forming \( \beta \)-eliminations.\(^6,10^3\) There are three basic types of E1cB reactions involving the "reversible", the "irreversible" and the ion-pair mechanisms. The most difficult type to identify is the "irreversible" mechanism which is kinetically and stereochemically indistinguishable from the E2 mechanism. The dependence of the rate on the nature of the leaving group should, in principle, differentiate the mechanisms.\(^3\) A list of additional criteria and their applications to E1cB reactions has been fully discussed by McLennan.\(^6\)

There have been only a few examples of "irreversible" E1cB reactions reported in the literature. Crowell et al.\(^10^4\) observed E1cB-type kinetics of the dehydrochlorination of \( \text{erythro-4,4-dichlorochalcone (VII)} \) in ethanolic acetate buffers. They found that the rate was almost independent of the acetate ion concentration at \( \text{pCH} = 8.7 \) (\( \text{pCH} = -\log [\text{H}^+] \)). At \( \text{pCH} = 10.6 \), the rate was linear with the acetate ion concentration.

No deuterium exchange was detected. This evidence pointed to the "irreversible" carbanion mechanism operating in the region of \( \text{pCH} = 10.6 \).

Bordwell and co-workers\(^10^5\) studied the methoxide ion-promoted anti and syn eliminations of acetic acid from 2-phenyl-cis-2-acet oxy-1-nitrocyclohexane (VIII) and its trans isomer (IX) and the base-promoted

\[
\begin{align*}
\text{Cl} & \quad \text{C} \quad \text{C} \quad \text{H} \\
& \quad \text{O} \quad \text{Cl} \quad \text{Cl} \\
\end{align*}
\rightarrow
\begin{align*}
\text{Cl} & \quad \text{C} \quad \text{C} \quad \text{H} \\
& \quad \text{O} \quad \text{Cl} \quad \text{Cl} \\
\end{align*}
\]

(VII)
elimination of methanol from the corresponding methoxy compounds.

(VIII)  (IX)

The methoxide ion-promoted elimination of the cis-methoxy compound was found to proceed through a nitronate anion intermediate. The appearance of the carbanion was rapid and reversible. The rates of elimination from (VIII) and (IX) were nearly identical. They were also almost identical to the rates of formation of the carbanion from the methoxy compounds. The scheme visualized is outlined below.

\[
\text{MeO}^- + \begin{array}{c}
\text{Ph} \\
\text{H} \\
\text{NO}_2
\end{array} \xrightarrow{\text{slow}} \begin{array}{c}
\text{Ph} \\
\text{H} \xrightarrow{k_1} \\
\text{NO}_2
\end{array} + \text{MeOH} \\
\downarrow \\
\begin{array}{c}
\text{Ph} \\
\text{NO}_2 \\
\text{OAc}^-
\end{array}
\]

(2.3)

Deuterium isotope effects of 8.0 were observed for both (VIII) and (IX). This was compared with the isotope effects of 7.4 and 7.5 for the elimination of 2-phenyl-trans-2-methoxycyclopentane and 2-phenyl-2-nitropropane, for which nitronate ion intermediates have been demonstrated.

The "irreversible" carbanion mechanism has been suggested for the dehydrofluorination of 2-methyl-3-phenyl-1,1,1-trifluoropropane with potassium t-butoxide in t-butanol. The deuterium isotope effect for this reaction was 1.2. No hydrogen isotope exchange was detected. Recovery of optically active starting material after partial reaction showed that no racemization had occurred.
More O'Ferrall found that the sodium t-butoxide-promoted elimination of 9-fluorenylethanol in t-butanol proceeded without hydrogen isotope exchange, in contrast to the hydroxide and methoxide ion-promoted reactions where the exchange rates exceeded the elimination rate. The deuterium isotope effect was 7.5. On the addition of 1-2% methanol it dropped to ca. 3.3. No exchange was observed. On the addition of further methanol, the rate of exchange increased. The mechanism in t-butanol was thought to be "irreversible" E1cB. The addition of a small amount of methanol leads to elimination through a slower and competing E2 pathway. In pure methanol the mechanism is "reversible" E1cB. In contrast, Spencer et al. observed general base catalysis for the triethylamine-catalysed elimination from 9-fluorenylethyl chloride in water-ethanol (9:1).

Cavestri and Fedor studied the base-catalysed elimination of 4-(p-substituted benzoyloxy)-2-butanones to give methyl vinyl ketone and p-substituted benzoic acids. The Hammett $\rho$ value of 0.13 for the hydroxide ion-catalysed reaction indicated that the reaction was insensitive to the nature of the leaving group. This, together with the Bronsted $\beta$ of 0.30, suggested the operation of an E1cB mechanism with anion formation being rate-determining.

An irreversible carbonium mechanism has been proposed for the dehydrochlorination of 1-phenyl-1,2-dichloro-2,2-difluoroethane in ethanolic sodium ethoxide. No exchange was detected and a primary deuterium isotope effect of 2.8 was reported. The Hammett $\rho$ for the reaction was 3.94. The low isotope effect suggests a highly unsymmetrical transition state or an internal return carbonium mechanism. The rate of exchange of the benzylic proton of 1-phenyl-1-chloro-2,2-trifluoroethane was faster than the rate of elimination. After applying a correction for the solvent isotope effect it was found that the primary isotope effect for dehydrofluorination was negligible. This is thought to be consistent with
considerable internal return. The Hammett $\rho$ for the dehydrofluorination was 3.74 while $\rho$ was 3.94 for the tritium exchange reaction.

Examples of the ion-pair E1cB mechanism (E1cB$_{ip}$) are also exceedingly rare. Miller and co-workers$^7$ found that the reaction between cis-dibromoethylene and trimethylamine in dimethylformamide was elimination rather than substitution. The deuterium isotope effect for the reaction was 1.0. There was no rate retardation on the addition of triethylammonium bromide or any evidence of deuterium exchange. The mechanism visualized is outlined below.

$$\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{CH} & \quad \text{CH} \\
\text{H} & \quad \text{H}
+ \quad \text{NEt}_3 & \quad \longleftarrow & \quad [\text{BrCH} = \text{CBr}^- + \text{HNEt}_3] \\
& \quad \downarrow \text{slow} \\
\text{HC} = \text{CBr}^- & \quad \text{Et}_3\text{NH}^+ & \quad \text{Br}^-
\end{align*}$$

(2.4)

Hall et al.$^8$, $^9$ studied the triethylamine-promoted eliminations of (X) and (XI) in a variety of solvents including benzene, acetonitrile and benzene–acetonitrile mixtures.

For (X), deuterium isotope effects of ca. 1.0 were obtained in each solvent. No salt effect was observed and a Bronsted $\beta$ of 0.37 was obtained.$^8$ For (XI), inverse deuterium isotope effects of ca. 0.96 were obtained using a variety of amine bases. There was also an increase in the rate as the polarity of the solvent was increased.$^9$ In each case the kinetic results were best explained by an E1cB$_{ip}$ mechanism.
The rates of the piperidine-promoted elimination from the isomers of 2-(p-tolylsulphonyl)-4-t-butylcyclohexyl sulphonates in DMF were found to be relatively insensitive to the nature of the leaving group and the stereochemistry of the leaving group and the β-hydrogen.¹¹¹ No deuterium exchange was found; however, there was a slight rate retardation in the presence of piperidine hydrochloride. The mechanism for the reaction is thought to be Et₃B⁺.¹⁰³b

A further example of the ion-pair mechanism, reported by Naso and co-workers, is remarkable in that it exhibits high syn-stereospecificity.¹¹² An inverse isotope effect of 0.8 was observed for the triethylamine-promoted elimination of hydrogen fluoride from (XII) in benzene.

\[
\begin{align*}
\text{SO}_2\text{Ph} & \quad \text{Et}_3\text{N} \quad \rightarrow \quad \text{PhSO}_2\text{C}==\text{C} \quad \text{H} \quad + \quad \text{Et}_3\text{ND}^+\text{F}^- \\
\text{H} & \quad \text{H} \quad \text{SPh} \quad \text{D} \quad \text{SPh} \\
(XII) & \\
\end{align*}
\]

The lack of a salt effect supported the notion of an intimate ion-pair intermediate.

Bordwell and co-workers¹¹ found that the leaving group effects were small for both the hydroxide and triethylamine-induced syn and anti eliminations of trans-2-(p-tolylsulphonyl)cyclohexyl arenesulphonates (XIII) and its cis isomer (XIV) in 50% dioxane-water.

\[
\begin{align*}
\text{OSO}_2\text{Ar} & \quad \text{(XIII)} \\
\text{OSO}_2\text{Ar} & \quad \text{(XIV)} \\
\end{align*}
\]

General base catalysis was observed as well as a high anti-syn rate ratio. Syn elimination was thought to be retarded by 1,2-diequatorial interactions.
distorting the chair conformation. The Hammett $\rho$ values for the syn elimination of (XIII) and the anti elimination of (XIV) are very similar, ca. 0.4-0.6. Both these compounds eliminate faster than they are calculated to undergo hydrogen exchange. If the mechanism is E1cB, it can only occur with internal return. For the elimination reaction,

$$\text{RX} + B^- \xrightarrow{k_1} \text{RX} \xrightarrow{k_{-1}} \text{HB}$$

$$\text{RX} \xrightarrow{k_2} \text{olefin} + X^- + \text{HB} \quad (2.6)$$

$$k_{\text{elim}} = \frac{k_1 k_2}{k_{-1}} \quad \text{if} \quad k_{-1} \gg k_2 \quad (2.7)$$

For the exchange reaction,

$$\text{RX} + B^- \xrightarrow{k_1} \text{RX} \xrightarrow{k_{-1}} \text{HB}$$

$$\text{RX} \xrightarrow{k_3} \text{RX} \xrightarrow{k_4} \text{DOR'}$$

$$\text{R'OD} \xrightarrow{k_4} \text{RDX} + \text{OR'} \quad (2.8)$$

$$k_{\text{exch}} = \frac{k_1 k_3}{k_{-1}} \quad \text{if} \quad k_{-1} \gg k_3 \quad (2.9)$$

The rate of elimination is greater than the rate of exchange only if $k_2 > k_3$. This must be the case since no deuterium exchange was observed. On consideration of the leaving group effects, the Hammett $\rho$ values, and comparison with other activated systems, it was concluded that the syn and anti eliminations of (XIII), and (XIV) were occurring by the same mechanism.
Another variant of the E1cB mechanism has been demonstrated by Rappoport et al.\textsuperscript{10} This has been termed the "irreversible" first order carbanion mechanism by Bordwell.\textsuperscript{103,105,113} It is characterized by rapid, irreversible formation of the carbanion, followed by the rate determining expulsion of the leaving group. Bordwell and co-workers\textsuperscript{105} found that the t-butoxide-promoted elimination of 2-phenyl-cis-2-methoxy-1-nitrocyclohexane and its trans isomer was first order in substrate and zeroth order in base. Similar behaviour was observed for the methoxide ion-promoted elimination of 2-phenyl-trans-2-methoxy-1-nitrocyclopentane and its cis isomer.\textsuperscript{113} The deuterium isotope effects for the cis- and trans-methyl-cyclohexanes and the trans-methoxycyclopentane were 8.0, 8.0 and 7.4 respectively. These are similar to the isotope effect observed for carbanion formation from 1-phenyl-2-nitropropane in t-butoxide-t-butanol.

Rappoport et al.\textsuperscript{10} reported low isotope effects of ca. 1 for the amine-promoted eliminations of hydrogen cyanide from 2,6-dimethyl-4-(\(\alpha\alpha\beta\beta\) tetracyanoethyl)-aniline (XV) in chloroform and from 2-aryl-1,1,2-tricyanopropane (XVI) in chloroform and acetonitrile.

\[
\text{Me} \quad \text{Me} \\
\begin{array}{c}
\text{NH}_2 \\
\text{C(CN)}_2-\text{CH(CN)}_2
\end{array}
\]

(XV)

\[
\begin{array}{c}
\text{CN} \\
\text{Ar} \quad \text{C} \quad \text{CN} \\
\text{CN} \quad \text{H}
\end{array}
\]

(XVI)

An isotope effect of 0.93 was obtained for the triethylamine and tri-n-butylamine-promoted eliminations of (XV). The tri-n-butylamine-promoted reaction of (XVI) was first order in base at low amine concentrations and zeroth order at high amine concentrations. The deuterium isotope effect was 1.00 for this reaction.

By far the most common olefin-forming carbanion mechanism, and the easiest to authenticate, is the "reversible" E1cB mechanism. The
demonstration of isotope exchange between the $\beta$-protons of a substrate and the solvent protons indicates the existence of a carbanion intermediate but does not necessarily prove the existence of this mechanism. It has been pointed out by Breslow that carbanion formation may be an irrelevant side reaction to an E2 elimination. This is a valid criticism, although it has been widely discounted.\textsuperscript{3,6,115} Since 1967,\textsuperscript{6} numerous examples of the "reversible" E1cB mechanism have been reported. Fedor\textsuperscript{116} observed specific base catalysis for the amine-promoted elimination of methanol from 4-methoxy-2-butanol and from 4-methoxy-4-methyl-2-pentanone in aqueous solution to give the respective $\alpha,\beta$-unsaturated ketones. The rate of exchange was faster than the rate of elimination. The overall isotope effects ($k_{\text{obs}}^H/k_{\text{obs}}^D$) were 0.37 and 0.77 respectively, for the substituted butanone and pentanone.

Crosby and Stirling\textsuperscript{117} reported isotope effects of 0.66 and 0.78 for the elimination of phenoxide from 2-phenoxyethydimethylsulphonium iodide and methyl-2-phenoxyethyl sulphoxide with aqueous sodium hydroxide. These include the solvent isotope effect as well. Rapid exchange was also observed. The Hammett $\rho$ values for the respective reactions were 2.1 and 1.7. The $\rho$ of 2.1 for the sulphones was similar to the $\rho$ of 2.32 for the t-butoxide-catalysed cyclization of ary1-3-chloropropyl sulphones for which a carbanion mechanism has been postulated. It was found that the rate of elimination of phenoxysulphones in ethoxide-ethanol was accelerated by a factor of 1.3 with the addition of an $\alpha$-phenyl substituent, in contrast to the 50-fold and 100-fold rate acceleration for the elimination of the ethyldimethyl sulphonium salt and ethyl bromide.\textsuperscript{118} This implied that the transition state had little double bond character and very little, if any, $C_\alpha - X$ bond stretching.

Hunter and Shearing\textsuperscript{119} found that elimination and exchange were in close competition in the t-butoxide-catalysed elimination reactions of 1-methoxyacenaphthalene (XVII). The stereoselectivity of both reactions
was found to change from exclusive syn to preferential trans depending on the nature of the cation. The isotope effects for the rates of elimination were in the range 1.6-1.8 with Cs⁺, K⁺ and K⁺-crown ether as cations.

Rapid hydrogen isotope exchange was reported, by More O’Ferrall and Slae, for the reaction of 9-fluorenylmethanol in aqueous sodium hydroxide. A primary deuterium isotope effect of 7.2 and a solvent isotope effect of 0.92 was observed for the elimination reaction. This was explained in terms of the "reversible" E1cB mechanism. The expected agreement between the primary isotope effect for the elimination and exchange rates, in water and deuterium oxide, did not eventuate. The same behaviour was found for the reactions in methanol and in methanol-t-butanol mixtures. These anomalous results were ascribed to the possibility of a competing E2 reaction or to internal return.

"Reversible" E1cB mechanism have also been demonstrated for 1,3 eliminations to form substituted cyclopropanes and for the hydrolysis of esters in alkaline solution.

1.4 RATE-ACIDITY CORRELATIONS OF PROTON TRANSFER REACTIONS

There have been comparatively few rate studies carried out in concentrated base solutions. Most of these investigations have been carried out in mixed media.

More O’Ferrall and Ridd correlated the rates of methanolysis
of chloroform with an \( H_M \) acidity function based on substituted phenylamines and nitroanilines.\(^{64}\) The plot of \( \log k_1 \) against \( H_M \) was curved with a mean slope of about 0.8 between 1M and 3M sodium methoxide. The rate of elimination of 2-phenethyl chloride was found to be directly proportional to the sodium methoxide concentration but increased to third order when the concentration of the base was ca. 4M. The medium effects were rationalized in terms of the difference in solvation of the initial and the transition states. The smaller the solvation difference, the greater is the dependence of the rate on the activity of the solvent. In the E1cB-like methanalysis of chloroform the base is completely neutralized before the transition state. However, the base is only partially neutralized in the transition state for the E2 elimination of 2-phenethyl chloride. The curved plot obtained for the acidity function correlation indicates that \( H_M \) based on nitrogen acids is not suitable for carbon acids.

The rates of hydrogen isotope exchange of triphenylmethane and diphenylmethane catalysed by potassium methoxide in methanol-0-d-dimethyl-sulphoxide-d\(_6\) (75:25 v/v) have been correlated with an \( H_\sim \) function.\(^{128}\) Linear correlations of slope 0.82 and 0.85 were obtained for triphenylmethane, and diphenylmethane respectively. The acidity function was based on the ionization of diphenylamines and substituted anilines in methanol\(^{63,70}\) at 25°C whereas the exchange rates were determined at 105°C in methanol-dimethyl sulphoxide.

Streitweiser and co-workers\(^{129}\) reported the rates of tritium exchange for compounds related to fluorene in methanolic sodium methoxide. Correlations with \( H_\sim \) acidity functions based on nitrogen and oxygen acids were unsatisfactory. The mean slope, using the acidity function based on nitrogen indicators, was 0.61. However, an excellent correlation, of slope 0.847, was obtained using the \( H_M \) acidity function based on the ionization of a carbon acid, 1,3-diphenyldiène, in methanol.\(^{66}\) Primary
deuterium isotope effects calculated from the tritium isotope effects for the substituted fluorenes were ca. 6.5 indicating considerable proton transfer in the transition state and negligible amounts of internal return. A Bronsted α of 0.37 was obtained for the correlation of the rates of protodetrinitiation of the fluorenyl hydrocarbons with the pK_a values derived from caesium ion-pair equilibria in cyclohexylamine. This value suggested that the central carbon atom was still essentially pyramidal in the transition state, whereas it will be sp^2-hybridized in the delocalised carbanion.

Bethell and Cockerill\textsuperscript{130} studied the t-butoxide ion-promoted elimination of hydrogen bromide from 9-bromo-9',9''-bifluorenyl in t-butanol. The rates of reaction did not parallel the equilibrium basicity of the medium, as measured by H\textsubscript{R}^\text{BuOH}. The H\textsubscript{R}^\text{BuOH} acidity function, based on the ionization of primary aromatic amines, is an empirical measure of the basicity. Rigorous functions could not be defined for alkali metal t-butoxides in t-butanol. The rate of reaction was directly proportional to the concentration of the base at low concentrations and fell below proportionality at high concentrations. The reaction was more rapid when potassium t-butoxide was substituted for sodium t-butoxide at a constant H\textsubscript{R}^\text{BuOH} value. It was concluded that the mechanism was E2 with a large amount of C\textsubscript{9} - X bond rupture. This was supported by the deuterium isotope effect of 8.0 and the fact that the rates of proton transfer from 4-nitrodi phenylmethyl chloride\textsuperscript{131} and isotope exchange at the 9-position in fluorene \textsuperscript{132} were independent of the nature of the cation at a given H\textsubscript{R}^\text{BuOH} value.

Cockerill\textsuperscript{77} correlated the rates of the hydroxide ion-promoted E2 elimination of 2-phenethyl dimethyl sulphonium bromide in dimethyl sulfoxide-water mixtures with the function H_\text{⊖} + \log C_{\text{H}_2\text{O}}. A slope of 0.98 was reported. There was a considerable enhancement of the rate on the addition of dimethyl sulfoxide. The linearity of the correlation
suggested no change in the mechanism as the basicity was changed.

The second-order rate constants of various reactions in methanol involving proton transfer have been correlated with the function

\[ H_M - pK_{MeOH} - \log \left( \frac{C_{MeOH}}{C_{MeOH}^-} \right) \]

in an attempt to semi-quantitatively relate the slope with the type of reaction.\textsuperscript{133} The reactions studied were examples of the E2, tritium exchange, S\textsubscript{N}2, E1CB and S\textsubscript{N}1 CB mechanisms. Linearity was obtained in all cases. However, there was no apparent relationship between the slope and the reaction mechanism.

1.5 VARIATION OF THE PRIMARY ISOTOPE EFFECT WITH THERMODYNAMIC BASICITY

The primary deuterium isotope effect should be a maximum when \( \Delta pK = 0 \); that is, when the pK of the acid is equal to the pK of the conjugate acid of the base abstracting the proton.\textsuperscript{44-46} This was first observed experimentally by Bell and Goodall.\textsuperscript{134} They reported a maximum in the isotope effect in the region \( \Delta pK = 0 \) for the deprotonation of a series of nitroalkanes and related compounds by various bases in water. This curve was extended in the range \( \Delta pK = -10.1 \) to \( +0.3 \) by Bordwell and Boyle.\textsuperscript{135} Longridge and Long\textsuperscript{136} observed the same behaviour for the hydrogen isotope exchange of azulenes in aqueous solution. Kresge et al.\textsuperscript{137} however, found for the hydrolysis of vinyl ethers, that the correlation between relative rates and transition state structure was destroyed on the inclusion of other reaction types.

Bell and Cox\textsuperscript{138a} measured the rates of deprotonation of (-)menthone in aqueous sodium hydroxide. The basicity of the medium was altered by the addition of varying amounts of dimethyl sulphoxide. The isotope effect had a maximum value of 6.5 in a solution containing ca. 35 mole\% dimethyl sulphoxide. This corresponded to a \( H^- \) value of approximately 19. The \( pK_a \) of menthone was estimated to be 21 by comparison with acetone. A linear Bronsted plot, of slope 0.48, was obtained suggesting a symmetrical
transition state.

The primary deuterium isotope effects for the deprotonation of ethyl nitroacetate by various nitrogen and oxygen bases in aqueous solution have been found to pass through a well defined maximum in the region of $\Delta pK = 0.138b$. The bases used covered a range of ca. 18 $pK$ units. The $pK_a$ of the proton acceptor at the isotope effect maximum is ca. 6 which corresponds very favourably with the $pK_a$ of 5.8 for the substrate. A Bronsted correlation of slope 0.65 was also reported. The only deviant point corresponded to the 2,6-lutidine reaction. The abnormally high isotope effect for this reaction is attributed to steric hindrance.

Jones et al. reported a maximal tritium isotope effect at a $H_-$ value of 16.5 for the hydroxide ion-catalysed ionization of (d)-phenylmethylacetophenone in water-dimethyl sulphoxide mixtures. The Bronsted $\beta$ was 0.49 for both isotopes. The $pK_a$ of the ketone was estimated to be 20 and $\Delta pK$ was a minimum for the isotope effect maximum.

The results of Dixon and Bruice for the primary amine catalysed ionization of nitroethane in both water and 50% dioxane-water suggest that transition state symmetry is dependent on ground state basicity. The deuterium isotope effect is a maximum for amines whose conjugate acids have $pK_a$ values of ca. 8.5. This corresponded well with the $pK_a$ of 8.5 for nitroethane in water. In 50% dioxane-water no isotope effects could be measured for amines with $pK_a$ values greater than 10 since these amines reacted rapidly with the iodine used to scavenge the carbanion. However, the results suggested that the isotope effect is a maximum of $pK_a > 10$ (c.f. $pK_a$ of 10.71 for nitroethane in 50% dioxane-water). Bronsted plots for both nitroethane and nitroethane-1-$d_2$ were roughly linear with slopes of 0.55 and 0.59 respectively. The isotope effects would be almost identical if all the experimental data fitted exactly on the Bronsted plots for $k_H$ and $k_D$. The increase and decrease of the isotope effect around
\( \Delta pK = 0 \) was reflected in the small deviations from the Bronsted plots. It was therefore concluded that the isotope effects were better indicators of transition state character than Bronsted \( \beta \) values.

The only isotope effect maximum pertaining to elimination reactions has been reported by Cockerill for the hydroxide ion-promoted elimination of 2-arylethylidimethylsulphonium bromide in water-dimethyl sulphoxide.\(^{77}\) The maximum value was reached at ca. 50 mole \% dimethyl sulphoxide. In contrast, the addition of dimethyl sulphoxide and tetramethylene sulphone had no effect on the isotope effects for the elimination of 2-phenethyl bromide\(^{78}\) and 9-bromo-9,9'-bifluorenyl\(^{130}\) with potassium t-butoxide in t-butanol. The \( pK_a \) of the sulphonium salt is not known and no estimate was made.

Examples of isotope effect maxima have also been found for diazo coupling,\(^ {140}\) proton transfer from carbon acids to organometals\(^ {141}\) and hydrogen transfer to radicals in solution.\(^ {142}\)
2. EXPERIMENTAL

2.1 ANALYTICAL METHODS

Melting points were determined on a Kofler microscope hot stage and are uncorrected. Infrared (i.r.) spectra were obtained on Perkin-Elmer 237 and 337, and Shimadzu IR-27G spectrophotometers. Ultraviolet (u.v.) spectra were recorded on a Unicam SP800A instrument using methanol as the solvent. Molar extinction coefficients (ε) were measured using a Shimadzu QV-50 spectrophotometer. Nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian Associates T-60 spectrometer with deuteriochloroform (CDCl₃) as the solvent and tetramethyldisilane (TMS) as the internal standard. The chemical shifts are expressed as parts-per-million (p.p.m.) downfield from TMS and are quoted as: position, multiplicity (s = singlet, t = triplet, q = quartet, m = multiplet), proton integration, coupling constant (J, Hz) and assignment. Low voltage (20 eV) mass spectral analyses of the deuterium content of 1,1-diaryl-2,2,2-trichloroethane-1-d were determined on a Varian Associates CH-7 low resolution mass spectrometer using the direct probe sample insertion technique at 35°C. Gas-liquid chromatography (g.l.c.) was performed on a Varian Aerograph 1400 instrument using a 5' x 1/8" stainless steel column of 5% SE-30 on Varaport 30 at 120-140°C. RDH silica gel S was used for column chromatography. Ether refers to diethyl ether.

2.2 MATERIALS

Trichloroacetyl Chloride

This compound was prepared by the method outlined by Brown.¹⁴³
Trichloroethyl Acetate

Trichloroacetic acid (112.5 g; 0.62 mol) and absolute ethanol (160.0 g, 3.48 mol) were heated under reflux for 6.0 h in the presence of a catalytic amount of concentrated hydrochloric acid (0.5 ml). The excess ethanol was distilled off and the ester (94.1 g, 73.9%) was collected at 168-169.5°C/751.2 mm (lit.144 b.p. 164.0°C/750 mm).

n.m.r. δ 1.41 (t, 3H, CH₃), 4.42 (q, 2H, CH₂)
i.r. (liq. film) 1752 s (C=O) cm⁻¹.

Trichloroacetamide

Trichloroethyl acetate (94.0 g, 0.495 mol) was dissolved in anhydrous ether and ammonia gas, dried through 4A molecular sieves, was passed through the solution until the solid amide separated out.145 This was filtered off, washed with water, and recrystallized from ethanol-water yielding colourless needles (43.4 g, 54.0%) which melted at 120-140°C (sublimation).

(lit.145 m.p. 141.0°C)
i.r. (nujol) 3370 m, 3250 m (N-H), 1680 s (C=O) cm⁻¹.

Trichloroacetonitrile

This was prepared by the method outlined by Fieser.146 Trichloroacetamide (40.0 g, 0.246 mol) was mixed thoroughly with phosphorous pentoxide (20.0 g, 0.353 mol) and heated in an oil bath. The nitrile, collected at 80-84°C was redistilled over fresh phosphorous pentoxide yielding 18.4 g (51.8%) of product, b.p. 84.0°C/758 mm (lit.144 b.p. 84.0/760 mm).
i.r. (liq. film) 2245 m (C-N) cm⁻¹.
2,2,2-Trichloroacetophenone

Method 1: This compound was prepared from trichloroacetyl chloride and benzene using the procedure outlined by Blitz. 147

Method 2: This compound was prepared by chlorinating acetophenone in acetic acid in the presence of sodium acetate using the method given by Cohen. 148

Method 3: A modification of the method outlined by Barry was used. 149 Chlorine was passed into acetophenone (120.0 g, 1.0 mol) in the presence of phosphorous trichloride (1.0 g) for 14 h. The temperature of the reaction mixture was gradually raised to, and maintained at 205°C using a 250 watt lamp and a heating mantle. The crude product was cooled, flushed with nitrogen and then dissolved in ether. The solution was washed with sodium bisulphite solution, dried over anhydrous magnesium sulphate and the ether removed under reduced pressure. The product was distilled under vacuum yielding 212.0 g (95.5%) of ketone, b.p. 87–89°C/0.6 mm (lit. 148 b.p. 99–102°C/3.5 mm).

i.r. (liq. film) 1720 s (C=O) cm⁻¹.

1-Phenyl-2,2,2-trichloroethanol (XVIII)

Method 1: This is a modification of the method outlined by Dachauer et al. 150 2,2,2-Trichloroacetophenone (3.0 g, 0.014 mol), dissolved in anhydrous ether (25 ml), was added dropwise to a solution of lithium aluminium hydride (0.18 g, 0.005 mol) in ether (30 ml). The reaction mixture was heated gently under reflux for 15 h under an atmosphere of nitrogen. Excess lithium aluminium hydride was destroyed by carefully adding wet ether (25 ml) and 2M sulphuric acid (20 ml). The ether layer was then separated, washed with two portions of 10% sodium bicarbonate solution (20 ml), dried over anhydrous magnesium sulphate and the
solvent removed under reduced pressure. The crude product, chromatographed on silica gel and eluted with n-hexane-benzene mixtures of increasing polarity, yielded 2.54 g of alcohol (83.0%).

\[ \text{n.m.r. } \delta 3.40 \text{ (s, 1H, OH)}, \ 5.21 \text{ (s, 1H, C-1 aliphatic H)}, \ 7.42 \text{ (m, 5H, aromatic H)}. \]

i.r. (liq. film) 3640 m, 3550 s, 3435 s (O-H), 2895 (C-H) cm\(^{-1}\).

Method 2: This compound was prepared by the method of Galun and Kailir.\textsuperscript{151}

1-Phenyl-2,2,2-trichloroethanol-1-d

This compound was prepared by reducing 2,2,2-trichloroacetophenone with Fluka lithium aluminium deuteride (>99 atom %) under the conditions given for (XVIII).

\[ \text{n.m.r. } \delta 3.39 \text{ (s, 1H, OH)}, \ 7.41 \text{ (m, 5H, aromatic H)}. \]

i.r. (liq. film) 3650 m, 3545 s, 3430 s (O-H), 2170 (C-D) cm\(^{-1}\).

1,1-Diphenyl-2,2,2-trichloroethane (XIX)

Method 1: 1-Phenyl-2,2,2-trichloroethanol (3.2 g, 0.014 mol) and benzene (5.2 ml, 0.029 mol) were cooled to 0°C in an ice bath and a 5:1 mixture of concentrated sulphuric acid and oleum (26.5 ml) was added dropwise. The reaction mixture was stirred for 2.5 h and then poured onto ice (200 g). The crude product was filtered off, melted in hot water (200 ml) and stirred vigorously to remove any occluded acid. On cooling, the product was filtered off and recrystallized several times from methanol yielding colourless plates (2.73 g, 67.1%), m.p. 64.5-65.5°C (lit.\textsuperscript{152} m.p. 65°C).

\[ \text{n.m.r. } \delta 5.06 \text{ (s, 1H, C-1 aliphatic H)}, \ 7.46 \text{ (m, 10H, aromatic H)}. \]

lit.\textsuperscript{153} \delta 5.05.
u.v. $\lambda_{\text{max}} = 231$ nm $\log \varepsilon = 4.314$.

i.r. (CS$_2$) 2910 (C-H, aliphatic) cm$^{-1}$.

Method 2: Benzene (2 equivs.) was added dropwise to a solution of 2,2,2-trichloroethandiol (1 equiv.) in concentrated sulphuric acid.$^{102}$ The reaction mixture was stirred for 2.5 h and worked up in the manner outlined in method 1.

1,1-Diphenyl-2,2,2-trichloroethane-1-d (XIXa)

This compound was prepared from 1-phenyl-2,2,2-trichloroethanol-1-d using the conditions outlined in Method 1 for the preparation of the undeuterated substrate. Colourless plates (59.8% yield) were obtained with a m.p. and mixed m.p. 64.5-65.5°C (lit.$^{152}$ m.p. 65°C) and a deuterium content of 99.0 atom %.

n.m.r. $\delta$ 7.45 (m,10H, aromatic H).

i.r. (CS$_2$) 2160 (C-d) cm$^{-1}$.

1,1-Di-(p-nitrophenyl)-2,2,2-trichloroethane (XX)

Method 1: This compound was prepared by nitrating (XIX) with fuming nitric acid using the procedure outlined by Haskelberg and Lavic.$^{154}$

Method 2: This is a modification of the procedure given by Delaby and Baronnet.$^{155}$ 1,1-Diphenyl-2,2,2-trichloroethane (3.0 g, 0.0103 mol) was added in portions over a period of 1 h to a mixture of fuming nitric acid (8.9 ml) and acetic anhydride (8.0 ml). A few crystals of urea were added. The reaction mixture, immersed in a chloroform-hexane-dry ice mixture, was stirred for 2.5 h. The mixture was then poured onto ice (100 g) and allowed to stand overnight. The crude product was filtered off and recrystallized repeatedly from methanol and from glacial acetic
acid as yellow needles (1.49 g, 39.5%), m.p. 169-170°C (lit. 154 m.p. 169°C).

\[ \delta \] 5.36 (s, 1H, C-1 aliphatic H), 8.03 (q, 8H, J = 9.0 Hz, aromatic protons). Lit. 152 \[ \delta \] 5.35

\( \lambda_{\text{max}} \) 272 nm \( \log \varepsilon = 4.346 \)

\( \text{i.r. (CS}_2 \) 2850 (C-H cm}^{-1}. \)

1,1-Di-(p-nitrophenyl)-2,2,2-trichloroethane-1-d (XXa)

This compound was prepared by nitrating (XIXa) according to method 2 outlined for the preparation of (XX). Yellow needles were obtained (42.2%) with m.p. and mixed m.p. 169-170°C (lit. 154 m.p. 169°C) and a deuterium content of 98.8 atom %.

\( \text{i.r. (CS}_2 \) 2155 (C-H cm}^{-1}. \)

2,2,2,4'-Tetrachloroacetophenone (XXI)

This compound was prepared by the method outlined by Barry. 149

\( \text{i.r. (liq. film) 1710 s (C=O) cm}^{-1}. \)

1-(p-Chlorophenyl)-2,2,2-trichloroethanol (XXII)

This compound was prepared by reducing (XXI) under the conditions outlined for the preparation of (XVIII).

\( \delta \) 3.33 (s, 1H, CH), 5.12 (s, 1H, C-1 aliphatic H),

7.38 (q, 4H, J_{AB} = 9.0 Hz, aromatic H).

\( \text{i.r. (liq. film) 3630 m, 3530 s, 3345 s (O-H), 2880 (C-H cm}^{-1}. \)

1-(p-Chlorophenyl)-2,2,2-trichloroethanol-1-d (XXIIa)

This compound was prepared by reducing the ketone (XXI) with lithium aluminium deuteride using the procedure outlined for the preparation of
(XVIII).

n.m.r. δ 3.70 (s, 1H, OH), 7.38 (q, 4H, J_{AB} = 9.0 Hz, aromatic H).
i.r. (liq. film) 3640 m, 3535 s, 3395 s (O-H), 2170 (C-D) cm^{-1}.

1,1-Di-(p-chlorophenyl)-2,2,2-trichloroethane (XXIII)

Method 1: This compound was prepared by condensing (XXII) with chlorobenzene using method 1 outlined for the preparation of (XIX).

Colourless needles were obtained, m.p. 108-109°C (lit.\textsuperscript{152} m.p. 108-109°C).

n.m.r. δ 5.02 (s, 1H, C-1 aliphatic H), 7.42 (q, 8H, J = 9.0 Hz, aromatic H). lit.\textsuperscript{153} δ 5.02

u.v. \(\lambda_{max} = 237 \text{ nm} \quad \log \epsilon = 4.305\).
i.r. (CS\textsubscript{2}) 2925 m (C-H) cm\textsuperscript{-1}.

Method 2: 2,2,2-Trichloroethanediol was condensed with chlorobenzene according to the procedure outlined in method 2 for the preparation of (XIX).

1,1-Di-(p-chlorophenyl)-2,2,2-trichloroethane-1-d (XXIIIa)

This compound was prepared from (XXIIa) by method 1 outlined for the preparation of (XIX). Colourless needles were obtained (63.8%), with m.p. and mixed m.p. 108-109°C (lit.\textsuperscript{152} m.p. 108-109°C) and a deuterium content of 98.3 atom %.

n.m.r. δ 7.41 (q, 4H, J_{AB} = 9.0 Hz, aromatic H).
i.r. (CS\textsubscript{2}) 2165 (C-D) cm\textsuperscript{-1}.

2,2,2-Trichloro-4'-methoxyacetophenone (XXIV)

This compound was prepared by the method outlined by Houben and Fischer.\textsuperscript{145} Anhydrous hydrogen chloride was passed through a solution of anisole (10.8 g, 0.100 mol), trichloroacetonitrile (16.0 g, 0.110 mol)
and anhydrous ether (50 ml) in the presence of anhydrous zinc chloride, for two days. The ether was removed under reduced pressure and the reaction mixture was hydrolysed in warm water. The crude product was chromatographed twice on silica gel (eluted with benzene and then n-hexane) yielding a pale yellow oil (6.70 g, 27.0%).

n.m.r. δ 3.84 (t, 3H, OMe), 7.55 (q, 4H, J_{AB} = 9.5 Hz, aromatic protons).

i.r. (liq. film) 1695 s (C=O) cm^{-1}.

1-p-Anisyl-2,2,2-trichloroethanol-1-d

This compound was prepared by reducing (XXIV) with lithium aluminium deuteride using the method outlined for the preparation of (XVIII).

n.m.r. δ 3.39 (s, 1H, OH), 3.80 (t, 3H, OMe), 7.18 (q, 4H, J_{AB} = 9.5 Hz, aromatic H).

i.r. (liq. film) 3550 s, 3430 s (O-H), 2045 (C-D) cm^{-1}.

1,1-Di(p-anisyl)-2,2,2-trichloroethane (XXV)

This compound was prepared by condensing 2,2,2-trichloroethanediol and anisole in a mixture of concentrated sulphuric and glacial acetic acid. Recrystallization from n-hexane yielded colourless prisms (48.2%), m.p. 89-90°C (lit. m.p. 87-88°C).

n.m.r. δ 3.81 (t, 6H, OMe), 4.96 (s, 1H, C-H aliphatic H), 7.17 (q, 8H, J_{AB} = 8.5 Hz, aromatic H).

i.r. (KCl-P) 2304 (C-H) cm^{-1}.

u.v. λ_{max} = 230 nm log ε = 4.204.

1,1-Di(p-anisyl)-2,2,2-trichloroethane-1-d (XXVa)

Concentrated sulphuric acid (25.0 ml) was added dropwise to a
solution of anisole (5.0 g, 0.049 mol) and 1-p-anisyl-2,2,2-trichloroethanol-1-d (6.30 g, 0.025 mol) in glacial acetic acid (25.0 ml). The reaction mixture was stirred for 2.0 h at 0°C and 0.75 h at room temperature. It was then worked up as usual. Several recrystallizations from n-hexane yielded colourless prisms (4.75 g, 55.2%) with a m.p. and mixed m.p. 87.5-88.5°C (lit. 99 m.p. 87-88°C) and a deuterium content of 99.1 atom %.

\[ \delta \] 3.79 (t, 6H, OMe), 7.18 (q, 8H, J\text{AB} = 9.0 Hz, aromatic H).

i.r. (KBr) 2110 (C-D) cm\(^{-1}\).

1,1-Di(p-bromophenyl)-2,2,2-trichloroethane

This compound was prepared by condensing bromobenzene (2 equivs.) with 2,2,2-trichloroethanediol (1 equiv.) under the conditions outlined in method 2 for the preparation of (XIX). Recrystallization from ethanol yielded colourless needles with m.p. 142.5-143.5°C (lit. 99 142.9-143.6°C).

\[ \delta \] 4.98 (s, 1H, C-1 aliphatic H), 7.47 (q, 8H, aromatic H).

\begin{align*}
\text{litr.} & \quad 153 \delta 4.97.
\end{align*}

u.v. \( \lambda_{\text{max}} = 2.41 \text{ nm} \quad \log \varepsilon = 4.456.\)

i.r. (CS\(_2\)) 2940 m (C-H) cm\(^{-1}\).

1,1-Di(p-tolyl)-2,2,2-trichloroethane

This compound was prepared by condensing toluene (2 equivs.) with 2,2,2-trichloroethanediol under the conditions outlined in method 2 for the preparation of (XIX). Colourless plates were obtained with a m.p. 90-91°C (lit. 152 m.p. 92°C).

\[ \delta \] 2.28 (t, 6H, Me), 4.99 (s, 1H, C-1 aliphatic H),
\[ \quad \] 7.31 (q, 8H, J\text{AB} = 8.5 Hz, aromatic H).

\begin{align*}
\text{u.v.} & \quad \lambda_{\text{max}} = 236 \text{ nm} \quad \log \varepsilon = 4.413 \\
\text{i.r.} & \quad (\text{CS}_2) 2914 \text{ m (C-H) cm}^{-1}.\end{align*}
1,1-Di(p-fluorophenyl)-2,2,2-trichloroethane

A sample supplied by Mr S. A. Short, recrystallized from chloroform-benzene, had m.p. 38.5-43.0°C (lit. 43-45°C).

**Attempted Preparation of 2-Bromo-2,2-dichloroacetophenone**

2,2-Dichloroacetophenone was prepared by the method outlined by Aston et al. (Better yields were obtained by doubling the chlorination time). This was photobrominated under the conditions outlined for 2,2,2-trichloroacetophenone using phosphorous tribromide as a catalyst. A t.l.c. of the crude product revealed starting material and product. G.l.c. indicated two major products, one of which was 2,2,2-trichloroacetophenone. Qualitative elemental analysis showed the presence of bromine in the crude product. Vacuum distillation and chromatography on silica gel (eluted with benzene) failed to separate the two products.

**2.3 PRODUCTS**

The 1,1-diaryl-2,2,2-trichloroethanes were heated under reflux with methanolic sodium methoxide and the products were recovered as before. The melting points and ultraviolet spectra of the products were identical to the appropriate 1,1-diaryl-2,2-dichloroethenes. The m.p.s. and molar extinction coefficients have been reported before, and are summarised in Table 1.
TABLE 1.

M.p.s. and U.v. Spectra of 1,1-Diaryl-2,2-dichloroethenes

<table>
<thead>
<tr>
<th>para-substituent</th>
<th>M.p. °C</th>
<th>Lit. m.p. °C</th>
<th>λmax</th>
<th>log ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO</td>
<td>109-110.5</td>
<td>109 (152)</td>
<td>253</td>
<td>4.133</td>
</tr>
<tr>
<td>Me</td>
<td>85.5-87</td>
<td>87 (152)</td>
<td>246</td>
<td>4.352</td>
</tr>
<tr>
<td>H</td>
<td>78-79</td>
<td>80 (152)</td>
<td>247</td>
<td>4.243</td>
</tr>
<tr>
<td>F</td>
<td>37-39.5</td>
<td>34.5(99)</td>
<td>248</td>
<td>4.016</td>
</tr>
<tr>
<td>Cl</td>
<td>89-90.5</td>
<td>87.5-88 (101)</td>
<td>245</td>
<td>4.243</td>
</tr>
<tr>
<td>Br</td>
<td>121-121.5</td>
<td>121 (152)</td>
<td>249</td>
<td>4.235</td>
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<tr>
<td>NO₂</td>
<td>172-173</td>
<td>172-173 (158)</td>
<td>290</td>
<td>4.290</td>
</tr>
</tbody>
</table>

2.4 REAGENTS AND SOLVENTS

Methanol

Commercial methanol was dried over magnesium turnings according to the procedure outlined by Vogel and stored over 4A molecular sieves.

t-Butanol

Fluka t-butanol was dried over potassium according to the method outlined by Saunders et al. and stored over 4A molecular sieves.

Sodium Hydroxide

Sodium metal was washed in n-hexane and anhydrous ether to remove any adhering paraffin oil. It was allowed to react with a portion of anhydrous methanol in order to remove the oxide coating, transferred into a flask containing anhydrous methanol and dissolved under a nitrogen atmosphere. The stock solution was diluted to the required concentration and standardized against standard hydrochloric acid using bromothymol
blue as the indicator.

**Potassium t-Butoxide**

This was prepared by the method outlined for the preparation of sodium methoxide.

**Hydrochloric Acid**

BDH standard concentrated volumetric solutions were used to make up standard solutions of the appropriate concentrations.

**Zinc Chloride**

BDH laboratory grade zinc chloride was dried by the method outlined by Perrin et al.\(^{160}\)

### 2.5 STOICHIOMETRY

All reactions proceeded by the stoichiometry of equation (2.1).

\[
\begin{align*}
\text{R} & \quad \text{CH-CCl}_3 + B^- \quad \rightarrow \quad \text{R} \\
\text{R} & \quad \text{C=CCl}_2 + BH + \text{Cl}^- \\
\end{align*}
\]

They have been found to obey second-order kinetics.\(^ {99-102}\)

\[
\text{Rate} = \frac{dx}{dt} = k_2[\text{Ar}_2\text{CHCCl}_3][B^-] = k_2(a - x)(b - x)
\]

where
- \(a\) = initial concentration of the substrate
- \(b\) = initial concentration of the base
- \(x\) = concentration of the olefin at time \(t\).
Integrating equation (2.3) and rearranging:

\[ k_2 = \frac{2.303}{l(b-a)} \log \frac{a(b-x)}{b(a-x)} \]  \hspace{1cm} (2.4)

Under pseudo-first-order conditions, \([B^-] \gg [Ar_2CHCCl_3]\), therefore, 
\((b - a) \approx b\) and \(\frac{b-x}{b} \approx 1\). Equation (2.4) becomes

\[ k_2 = \frac{2.303}{bt} \log \frac{a}{a-x} \]

or 
\[ k_1 t = 2.303 \log \frac{a}{a-x} \]  \hspace{1cm} (2.5)

where \(k_1\) is the observed first-order rate constant (\(= k_2 b\)).

If the progress of the reaction is followed spectrophotometrically, the absorbance at time \(t\) is given by equation (2.6):

\[ A_t = (a-x) \varepsilon_a l + x \varepsilon_c l \]  \hspace{1cm} (2.6)

\[ A_0 = a \varepsilon_a l \]  \hspace{1cm} (2.7)

\[ A_\infty = a \varepsilon_c l \]  \hspace{1cm} (2.8)

The symbol \(l\) is the path length of the cell (1 cm), \(\varepsilon_a\) and \(\varepsilon_c\) are the molar extinction coefficients of the substrate and the olefin, and \(A_0\) and \(A_\infty\) are the absorbances at zero time and infinity.

It follows from equations (2.6), (2.7) and (2.8) that as long as \(\varepsilon_a \neq \varepsilon_c\),

\[ x = \frac{A_t - A_0}{A_\infty - A_0} \]  \hspace{1cm} (2.9)

Substituting the value of \(x\) into equation (2.5) we obtain:

\[ 2.303 \log \frac{A_\infty - A_0}{A_\infty - A_t} = k_1 t \]  \hspace{1cm} (2.10)
\[ \log (A_\infty - A_t) = -\frac{k_1 t}{2.303} + \log (A_\infty - A_0) \]  

(2.11)

If \( A_\infty \) and \( A_0 \) are known then equation (2.10) is applicable otherwise equation (2.11) is used. The observed first-order rate constant \( (k_1) \) is obtained from the slope of the plot of \( \log (A_\infty - A_t) \) versus time. The second-order rate constant \( (k_2) \) is calculated by dividing \( k_1 \) by the stoichiometric base concentration.

\[ k_2 = \frac{k_1}{[B^-]} \]  

(2.12)

2.6 KINETICS

Water baths were of conventional design with a Gallenkamp mercury contact thermometer, heating element and stirrer. Temperatures were maintained to within ± 0.02°C of the required value. A layer of polystyrene foam chips was placed on the surface of the water to minimize evaporation. The thermometers used in the investigation were calibrated against a standard set (checked by the Auckland Industrial Development Division, D.S.I.R., 5th Nov. 1971). A Heuer stopwatch was used to time reactions lasting less than 1h. This was checked against a Lab-cron mains timer. For the other reactions, the laboratory electric clocks were used.

All kinetic runs were performed under pseudo-first-order conditions (using at least 20-fold excess of base) at the wavelengths given in Table 2. The rate of olefin formation was followed at a wavelength where the absorbance of the reactant is minimal.
Solutions of substrate and alkoxide were made up under an atmosphere of nitrogen just prior to the commencement of a kinetic run. The stock solutions of the alkoxides were stored in a dry box.

Several different procedures were used to follow the reactions depending on the rate. The stoppered flask technique was used for the slower reactions. Solutions of substrate (50 ml) and alkoxide (50 ml) of the appropriate concentration were mixed after being thermostated separately for 0.5 h. Aliquots (10 ml) were withdrawn at various intervals, quenched with a few drops of concentrated hydrochloric acid dissolved in methanol, diluted 10-fold with distilled methanol and the absorbance measured using a Shimadzu UV-50 spectrophotometer. The reactions were usually followed to 3 half lives. Infinity readings were obtained after 10 half-lives had elapsed. These were in agreement with the theoretical infinities. U.v. spectra of the infinities showed that the olefin was the sole product.
Reactions which were too fast to be followed by the stoppered flask technique, were carried out in Y-tubes. Solutions of substrate and base were placed in the separate arms of an inverted Y-tube, thermostated for 0.5 h, mixed rapidly and quenched at various time intervals. These were diluted 10-fold with methanol and analysed as before.

The reaction of 1,1-diphenyl-2,2,2-trichloroethane with varying concentrations of methanolic sodium methoxide was following using the stoppered cell technique. Base (2 ml) and substrate (2 ml) were thermostated in the two arms of a Y-tube. They were mixed thoroughly and rapidly transferred to a stoppered quartz cell placed in the cell compartment of a Unicam SP3000 automatic spectrophotometer. This instrument was fitted with a timer and a SP3001 automatic digital printer. The cell compartment was thermostated at 30\(^\circ\)C +0.05\(^\circ\)C using a Grant SC10 circulation unit. Rate constants of check runs obtained using this technique were in agreement with those obtained by the flask technique. The experimental inferences varied according to the concentration of the base in the reaction. The sensitivity of the spectrophotometer was such that it could not handle dense solutions in the blank pathlength. If the blank contained metal alkoxide of ca. greater than 0.4M, the attenuator limit of the instrument was reached and the automatic slit width adjustment programmer had to be overridden.

The reactions of 1,1-di(4-nitrophenyl)-2,2,2-trichloroethane with methoxide-methanol and t-butoxide-t-butanol at 30\(^\circ\) and 45\(^\circ\)C were followed on a Durum-Gibson D-110 stopped-flow spectrophotometer fitted with a Hewlett Packard 1418 oscilloscope. The maximum mixing dead time of the instrument is 2 x 10\(^{-3}\) s. Constant temperature water was circulated through the reservoir containing the drive syringes. The substrate and base solutions were allowed to equilibrate to the required temperature.
They were then mixed and the absorbance changes determined at 305 nm.
The oscilloscope traces were photographed on Ilford FP4 film, developed
for 6 min. in Microphen, and enlarged onto graph paper.

The reactions at 0°C were carried out using the Y-tube technique.
The aliquots were quenched and diluted as previously outlined and analysed
on the Shimadzu QV-50 spectrophotometer. A Grant R 86F freezing unit
was used to maintain the temperature at 0°C ± 0.1°C.
3. RESULTS

Second-order rate constants for the reactions of the 1,1-diaryl-2,2,2-trichloroethanes and the 1-deuterated analogues with sodium methoxide in methanol and potassium t-butoxide in t-butanol are shown in Tables 1 and 2. They are in the main part the mean of two or more concordant results. Details of individual kinetic runs are presented in the Appendix.

**TABLE 1.**

Rate Constants for the Reactions of Ar₂CH·CCl₃ and Ar₂CD·CCl₃ with Sodium Methoxide in Methanol

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Temp. °C</th>
<th>10⁵ k₂ (1 mol⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p-MeOC₆H₄)₂CH·CCl₃</td>
<td>30</td>
<td>8.71</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>50.4</td>
</tr>
<tr>
<td>(p-MeOC₆H₄)₂CD·CCl₃</td>
<td>30</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>10.4</td>
</tr>
<tr>
<td>(p-MeC₆H₄)₂CH·CCl₃</td>
<td>30</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>77.6</td>
</tr>
<tr>
<td>Ph₂CH·CCl₃</td>
<td>30</td>
<td>47.6</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>197</td>
</tr>
<tr>
<td>Ph₂CD·CCl₃</td>
<td>30</td>
<td>9.37</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>42.8</td>
</tr>
<tr>
<td>(p-F C₆H₄)₂CH·CCl₃</td>
<td>30</td>
<td>181.5</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>1080</td>
</tr>
</tbody>
</table>
TABLE 1. continued

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Temp. °C</th>
<th>$10^5 k_2$ (1 mol⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(p-ClC_6H_4)_2CH·CCL_3$</td>
<td>-1.5</td>
<td>32.4</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1130</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>5230b</td>
</tr>
<tr>
<td>$(p-ClC_6H_4)_2CD·CCL_3$</td>
<td>-1.5</td>
<td>4.39</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>219</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>1100</td>
</tr>
<tr>
<td>$(p-BrC_6H_4)_2CH·CCL_3$</td>
<td>30</td>
<td>1230</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>6810</td>
</tr>
<tr>
<td>$(p-NO_2C_6H_4)_2CH·CCL_3$</td>
<td>-0.5</td>
<td>109000</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>605000</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>251000</td>
</tr>
<tr>
<td>$(p-NO_2C_6H_4)_2CD·CCL_3$</td>
<td>-0.4</td>
<td>10100</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>122000</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>545000</td>
</tr>
</tbody>
</table>

a Uncorrected for solvent expansion

b Reference 101 reports $k_2 = 5140 \times 10^{-5}$ 1 mol⁻¹ s⁻¹.

All the kinetic runs were followed spectrophotometrically under pseudo first-order conditions. The observed first-order rate constant was determined by graphical estimation and converted into the second-order rate constant by dividing by the stoichiometric base concentration. The substrate concentration was usually ca. $8 \times 10^{-4}$ M. However, the concentration of the base was varied from ca. 0.01-0.5 M depending on the
reactivity of the substrate. Isotope effects were calculated for the protium and deuterium compounds using rate constants calculated from kinetic runs carried out under the same base concentrations.

Rate constants for $1,1$-di($p$-nitrophenyl)-$2,2,2$-trichloroethane at $30^\circ$ and $45^\circ$C and its $1$-deuterated analogue at $30^\circ$C were measured by the stopped-flow technique. Spurious results were obtained for the deuterated analogue at $45^\circ$. There was insufficient time to repeat these experiments so the rate constant for this compound was extrapolated from the rates at $-0.4^\circ$C and $30^\circ$C. No induction periods were obtained for any of the reactions of $1,1$-diaryl-$2,2,2$-trichloroethane-$1$-$d$ with alcoholic metal alkoxide, indicating that no hydrogen isotope exchange was competing with elimination.\textsuperscript{120}

A quantitative treatment of why an induction period should be observed, if elimination and exchange are occurring at similar rates, is outlined below. This is a simplified version of the More O’Ferrall and Slae model.\textsuperscript{120}

Let C be the carbanion and P be the olefinic product. For $1,1$-di($p$-chlorophenyl)-$2,2,2$-trichloroethane-$1$-$d$ (DDT-$d$) in methoxide-methanol:

\[
\begin{align*}
\text{DDT-}d + \text{MeO}^- & \xrightleftharpoons[k_{-1}^D]{k_1^D} C \\
& \xrightleftharpoons[k_{-1}^H]{k_1^H} \text{DDT} + \text{MeO}^- \\
& \xrightarrow[k_2]{D} P
\end{align*}
\]

(2.13)

Now \[
\frac{d[P]}{dt} = k_2[C] \quad (2.14)
\]

and \[
\frac{d[C]}{dt} = (k_1^D[\text{DDT-}d] + k_1^H[\text{DDT}]) [\text{MeO}^-] - k_{-1}^H[C] - k_{-1}^D[C] - k_2[C] = 0 \quad (2.15)
\]
Substituting equation (2.14) into equation (2.15) we obtain:

\[
\frac{d[P]}{dt} = \frac{k_2(k_1^D[DDT-d] + k_1^H[DDT])[MeO^-]}{k_1^H + k_1^D + k_2}
\] (2.16)

The \( k_{-1} \) terms will actually be of the form: \( k_{-1}^H[MeOH] \) and \( k_{-1}^D[MeOD] \). As the concentration of methanol-0-d (MeOD) will be small, this term is neglected. At times approaching \( t = 0 \), the concentration of DDT will be small so this term is also neglected.

\[
\therefore \frac{d[P]}{dt} = \frac{k_1^Dk_2[DDT-d][MeO^-]}{k_1^H + k_2}
\] (2.17)

Since \([MeO^-] \gg [DDT-d]\)

\[
\frac{d[P]}{dt} = k_{obs}[DDT-d]
\] (2.18)

where \( k_{obs} = \frac{k_1^Dk_2}{k_1^H + k_2} \) (2.19)

When \([DDT-d]\) is small, i.e. at large reaction times:

\[
\frac{d[P]}{dt} = \frac{k_1^Hk_2[DDT][MeO^-]}{k_1^H + k_2}
\] (2.20)

and \( k_{obs} = \frac{k_1^Hk_2}{k_1^H + k_2} \) (2.21)
As \( k_1^H > k_1^D \), the slope of \( \log(A_0 - A_t) \) versus \( t \) will be greater at long reaction times than at short reaction times. Hence there is an induction period if elimination and exchange proceed at similar rates.

If exchange proceeds much faster than elimination then \( (k_{\text{obs}})_H = (k_{\text{obs}})_D \). Since all the deuterium compound will be converted to protium compound before product formation is significant the isotope effect \( (k_H/k_D) \) is unity.

From equation (2.16), \( k_{-1}^H[\text{MeOH}] + k_{-1}^D[\text{MeOD}] \gg k_2 \)

\[
\therefore \frac{d[P]}{dt} = \frac{k_2(k_1^H[D\text{DT}^+] + k_1^D[D\text{DT-d}])[\text{MeO}^-]}{k_{-1}^H[\text{MeOH}]} \tag{2.22}
\]

Since \( [\text{MeOH}] \gg [\text{MeOD}] \) and \( k_{-1}^H \div k_{-1}^D \) (both at diffusion level)

\[
\therefore \frac{d[P]}{dt} = \frac{k_1^H k_2[D\text{DT}][\text{MeO}^-]}{k_{-1}^H[\text{MeOH}]} + \frac{k_1^D k_2[D\text{DT-d}][\text{MeO}^-]}{k_{-1}^D[\text{MeOH}]} \tag{2.23}
\]

Now \( \frac{k_1^D}{k_{-1}^D} = \frac{[C][\text{MeOD}]}{[D\text{DT-d}][\text{MeO}^-]} \tag{2.24} \)

\[
\therefore \frac{d[P]}{dt} = \frac{k_1^H k_2[D\text{DT}][\text{MeO}^-]}{k_{-1}^H[\text{MeOH}]} + \frac{k_2[C][\text{MeOD}]}{[\text{MeOH}]} \tag{2.25}
\]

Since \( [\text{MeOD}]/[\text{MeOH}] \) is very small, therefore:

\[
\frac{d[P]}{dt} = \frac{k_1^H k_2[D\text{DT}][\text{MeO}^-]}{k_{-1}^H[\text{MeOH}]} \tag{2.26}
\]

and \( \frac{(k_{\text{obs}})_D}{k_{-1}^H[\text{MeOH}]} = \frac{(k_{\text{obs}})_H}{k_{-1}^H[\text{MeOH}]} \tag{2.27} \)
If there is no exchange \((k_{\text{obs}})_H \neq (k_{\text{obs}})_D\), there is no induction period and \((k_{\text{obs}})_H/(k_{\text{obs}})_D = k_1^H/k_1^D\). Since \(k_2 \gg k_{-1}^H [\text{MeOH}] + k_{-1}^D [\text{MeOD}]\), equation (2.16) becomes:

\[
\frac{d[P]}{dt} = (k_1^D[\text{DDT-d}] + k_1^H[\text{DDT}]) [\text{MeO}^-] \tag{2.28}
\]

Now \([\text{DDT}]\) is very small.

\[
\therefore \frac{d[P]}{dt} = k_1^D[\text{DDT-d}] \tag{2.29}
\]

\[
\therefore (k_{\text{obs}})_D = k_1^D \tag{2.30}
\]

and \((k_{\text{obs}})_H = k_1^H\) \tag{2.31}
TABLE 2.
Rate Constants for the Reactions of Ar<sub>2</sub>CH·CCl<sub>3</sub> and Ar<sub>2</sub>CD·CCl<sub>3</sub> With Potassium t-Butoxide in t-Butanol

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Temp °C</th>
<th>10&lt;sup&gt;5&lt;/sup&gt; k&lt;sub&gt;2&lt;/sub&gt; (1 mol&lt;sup&gt;-1&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p-MeOC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH·CCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>30</td>
<td>94.8</td>
</tr>
<tr>
<td>(p-MeOC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CD·CCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>30</td>
<td>26.7</td>
</tr>
<tr>
<td>(p-MeC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH·CCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>30</td>
<td>113</td>
</tr>
<tr>
<td>Ph&lt;sub&gt;2&lt;/sub&gt;CH·CCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>30</td>
<td>262&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ph&lt;sub&gt;2&lt;/sub&gt;CD·CCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>30</td>
<td>66.6&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>(p-FC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH·CCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>30</td>
<td>2005</td>
</tr>
<tr>
<td>(p-ClC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH·CCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>30</td>
<td>22200</td>
</tr>
<tr>
<td>(p-ClC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CD·CCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>30</td>
<td>6850</td>
</tr>
<tr>
<td>(p-NO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH·CCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>30</td>
<td>21900000&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>(p-NO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CD·CCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>30</td>
<td>5730000&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> From competitive run with deuterium compound also present.

<sup>b</sup> From competitive run with protium compound also present.

The kinetic runs in Table 2 were carried out using a substrate concentration of ca. 8 x 10<sup>-4</sup> M and base concentrations of ca. 0.01-0.2 M. The reactions of 1,1-di(p-nitrophenyl)-2,2,2-trichloroethane and its 1-deuterated analogue were also followed by stopped-flow spectrophotometry. These reactions were found to be very sensitive to trace amounts of basic impurities in the solvent. Rate constants varied markedly between different solvent batches. Erratic results were also obtained for the
reaction of 1,1-diphenyl-2,2,2-trichloroethane and its 1-deuterated analogue with t-butoxide in t-butanol. A competitive technique was therefore used to obtain the rate constants and isotope effects for these compounds. A mixture of the protium and deuterium compounds (1:2) was allowed to react with the alkoxide and the rate of formation of olefin was monitored continuously or at various intervals of time. The isotope effects obtained by this method are considered to be as accurate as the ones calculated from separate runs. However, there is greater uncertainty in the actual rate constants obtained.

The effect of varying concentrations of sodium methoxide on the rate of elimination of 1,1-diphenyl-2,2,2-trichloroethane in methanol at 30°C is shown in Table 3.

**Table 3.**

Reactions of Ph₂CHCl · With Sodium Methoxide in Methanol at 30°C

<table>
<thead>
<tr>
<th>[NaOMe]M</th>
<th>10⁴ k₁ (s⁻¹)</th>
<th>10⁴ k₂ (l mol⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.112</td>
<td>0.487</td>
<td>4.37</td>
</tr>
<tr>
<td>0.226</td>
<td>0.993</td>
<td>4.39</td>
</tr>
<tr>
<td>0.472</td>
<td>2.27</td>
<td>4.76</td>
</tr>
<tr>
<td>0.707</td>
<td>3.46</td>
<td>4.89</td>
</tr>
<tr>
<td>0.944</td>
<td>5.39</td>
<td>5.70</td>
</tr>
<tr>
<td>1.410</td>
<td>11.5</td>
<td>8.13</td>
</tr>
<tr>
<td>1.838</td>
<td>20.5</td>
<td>10.85</td>
</tr>
</tbody>
</table>
The rate constants are the mean of two or more concordant results.

The second-order rate coefficients were determined by dividing the observed first-order rate constant by the stoichiometric base concentration. The substrate concentration was $1.05 \times 10^{-4}$ M for all runs.
4. **DISCUSSION**

4.1 **HAMMETT CORRELATIONS**

The second-order rate constants for the dehydrochlorination of the 1,1-diaryl-2,2,2-trichloroethanes with methoxide-methanol and t-butoxide-t-butanol have been correlated with the Hammett equation (Tables 1 and 2, Figures 1 and 2).

**TABLE 1.**

Rate Constants and Substituent Parameters for the Reactions of Ar₂CH·CCl₃ With NaOH-MeOH and t-BuOK-t-BuOH

<table>
<thead>
<tr>
<th>Substituent</th>
<th>log k₂</th>
<th>2α₁ b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T=30° (MeOH)</td>
<td>T=45° (MeOH)</td>
</tr>
<tr>
<td>p-NO₂</td>
<td>0.7818</td>
<td>1.3947</td>
</tr>
<tr>
<td>p-Br</td>
<td>-1.9101</td>
<td>-1.1669</td>
</tr>
<tr>
<td>p-Cl</td>
<td>-1.9469</td>
<td>-1.2815</td>
</tr>
<tr>
<td>p-F</td>
<td>-2.7411</td>
<td>-1.9666</td>
</tr>
<tr>
<td>H</td>
<td>-3.3224</td>
<td>-2.7055</td>
</tr>
<tr>
<td>p-MeO</td>
<td>-4.0600</td>
<td>-3.2976</td>
</tr>
</tbody>
</table>

a Rate constants obtained by extrapolating the individual rate constants at 30° and 45°C to 65°C.

b From ref. 55.
The magnitude of the Hammett $\rho$ values are large in both solvent-base systems indicating a considerable amount of negative charge at the $\beta$-carbon atom in the transition state. However, $\sigma^-$ was required to correlate the reactivity of the p-nitro compound. This suggests that there is little direct resonance stabilization of this charge.

**TABLE 2**

Hammett Correlations of the Reactions of Ar$_2$CH.CCl$_3$ with Various Bases in Various Solvents

<table>
<thead>
<tr>
<th>Base</th>
<th>Solvent</th>
<th>Temp $^\circ$C</th>
<th>$\rho$</th>
<th>$r^a$</th>
<th>$s^b$</th>
<th>$\alpha$</th>
<th>$\log k_0^C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOME</td>
<td>MeOH</td>
<td>30</td>
<td>2.40</td>
<td>0.995</td>
<td>0.09</td>
<td>1.00</td>
<td>-3.033</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>2.54</td>
<td>0.998</td>
<td>0.07</td>
<td>0.76</td>
<td>-3.193</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>2.33</td>
<td>0.992</td>
<td>0.11</td>
<td>1.00</td>
<td>-2.307</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>2.49</td>
<td>0.996</td>
<td>0.08</td>
<td>0.72</td>
<td>-2.504</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65</td>
<td>2.09</td>
<td>0.987</td>
<td>0.13</td>
<td>1.00</td>
<td>-1.336</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65</td>
<td>2.30</td>
<td>0.995</td>
<td>0.08</td>
<td>0.60</td>
<td>-1.579</td>
</tr>
<tr>
<td>t-BuOK</td>
<td>t-BuOH</td>
<td>30</td>
<td>2.73</td>
<td>0.986</td>
<td>0.17</td>
<td>1.00</td>
<td>-1.968</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>2.99</td>
<td>0.993</td>
<td>0.14</td>
<td>0.62</td>
<td>-2.269</td>
</tr>
<tr>
<td>NaSPh</td>
<td>EtOH$^d$</td>
<td>65</td>
<td>1.79</td>
<td>0.980</td>
<td>0.14</td>
<td>1.00</td>
<td>-4.490</td>
</tr>
<tr>
<td>d</td>
<td></td>
<td>65</td>
<td>2.11</td>
<td>0.999</td>
<td>0.02</td>
<td>0.37</td>
<td>-4.850</td>
</tr>
</tbody>
</table>

$^a$ Correlation coefficient.

$^b$ Standard deviation of slope.

$^c$ Theoretical rate constant for the unsubstituted compound.

$^d$ From ref. 102.
Figure 2

Hammett Correlation of $\text{Ar}_2\text{Cl} \cdot \text{CCl}_3 / \text{t-BuO}^+ / \text{t-BuOH}/30^\circ$

- NO$_2$
- Br
- Cl
- H
- Me
- iPr
- --

$\sigma^*$ vs. $\log k$
The assumption that substituent constants are additive gives rise to
not particularly satisfactory correlations in all cases. For each \( \sigma - \rho \)
correlation there are marked derivations from linearity for
1,1-diphenyl-2,2,2-trichloroethane and the p-methoxy analogue (Figure 1
and 2). The same behaviour has been noted previously for the elimination
reactions of these compounds with chloride ion in acetone and
dimethylformamide,\(^{162}\) thiophenoxide in ethanol,\(^{102}\) and sodium hydroxide
in ethanol.\(^{99,100}\)

In these earlier studies it was found that the substituents exhibiting
the greatest deviations from the regression line were those which had
the strongest resonance interactions with the reaction centre.\(^{102,162}\)
The substituents can exert their effect (i.e. additive) only if the two
aryl rings are coplanar in the transition state. In this case the
Hammett equation will be in the form of:

\[
\log \frac{k}{k_0} = 2 \sigma \rho 
\]  

(2.32)

This equation will also hold if the same degree of non-coplanarity in
the initial and transition states is retained. The Hammett substituent
constants can be split into inductive and resonance contributions.\(^{52,53}\)

\[
\sigma_M = \sigma_I + \alpha \sigma_R 
\]  

(2.33)

\[
\sigma_P = \sigma_I + \sigma_R 
\]  

(2.34)

The inductive (field) contribution should be independent of the geometry
of the two aryl rings in the initial and transition states so the total
contribution will be \(2\sigma_I\). The total resonance contribution will be
\(2\sigma_R\) if the two rings are coplanar. However, if one aryl ring is
orientated such that the full resonance contribution is \(\sigma_R\) (i.e., coplanar
with the sigma skeleton of the developing double bond) and the other
ring cannot achieve this optimum orientation for steric reasons, the
total resonance contribution will be \((1 + a)\sigma_R\) where \(a\) is a parameter
with values between zero and unity. The parameter \(a\) is a qualitative
measure of the resonance contribution to the reaction centre.
Alternatively, it can be viewed as the degree of twist of the rings in
passing from the initial to the transition state. The total substituent
effect is \(2\sigma_I + (1 + a)\sigma_R\) and the appropriate form of the Hammett
equation is:

\[
\log \frac{k}{k_0} = (2\sigma_I + (1 + a)\sigma_R)\rho 
\]  

(2.35)

New sets of substituent constants were calculated, for various values
of \(a\), using the Taft \(\sigma_I\) and \(\sigma_R\) substituent parameters (Table 3).

**TABLE 3.**

Taft Inductive and Resonance Substituent Parameters\(^a\)

<table>
<thead>
<tr>
<th>Substituent</th>
<th>(\sigma_I)</th>
<th>(\sigma_R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-NO(_2)</td>
<td>0.63</td>
<td>0.15</td>
</tr>
<tr>
<td>p-Br</td>
<td>0.45</td>
<td>-0.22</td>
</tr>
<tr>
<td>p-Cl</td>
<td>0.47</td>
<td>-0.24</td>
</tr>
<tr>
<td>p-F</td>
<td>1.04</td>
<td>-0.92</td>
</tr>
<tr>
<td>H</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>p-Me</td>
<td>-0.05</td>
<td>-0.12</td>
</tr>
<tr>
<td>p-MeO</td>
<td>0.30</td>
<td>-0.57</td>
</tr>
</tbody>
</table>

\(^a\)Ref. 163.
These were correlated with the second-order rate constants. Least squares iterations were carried out using a Burrough B 6700 and I.B.M. 1130 computer. The optimum correlation was determined by a clear minimum in the standard deviation of the slope. In all cases the line of best fit was improved (Table 2, Figures 3 and 4). The noteworthy effect of the "alpha" treatment is that the Hammett $\rho$ constant is increased, with a corresponding decrease in the standard deviation.

Cockerill and Lamper$^{164}$ obtained an unsatisfactory Hammett correlation for the $pK_a$ values of a series of 9-arylfluorenes in dimethyl sulfoxide-water mixtures. It was concluded that the substituents in the 9-phenyl ring could not exert their full influence on the fluorenyl moiety. They independently put forward an identical treatment compensating for twisting of the phenyl ring away from the plane of the fluorene nucleus. The transmission coefficient $n$ ($\alpha$ in our case) is theoretically related to the degree of non-coplanarity of the aromatic rings by equation (2.36),$^{165}$

$$n' = n_0 \cos^2 \phi$$

(2.36)

where $n_0 = 1$ for the total resonance contribution when the aromatic rings are coplanar, and $n$ is the resonance contribution when the phenyl ring is twisted at an angle $\phi$ from the plane.

An attempt$^{102}$ was made earlier to correlate $\alpha$ with the degree of non-coplanarity of the aryl rings in the reaction of 1,1-diaryl-2,2,2-trichloroethanes with thiophenoxide ion in ethanol using equation (2.36). It was found that $\alpha = 0.37$ corresponded to an angle of $50^\circ$ in the transition state which was intermediate between the measured angles of $45^\circ$ and $55^\circ$ for the reactant and product respectively.$^{166}$ However, Table 2 shows that this correlation is fortuitous. The parameter $\alpha$ is not a unique quantity describing only the degree of non-coplanarity of the two aryl rings, but may merely be a parameter expressing qualitatively
Figure 3

Modified Hammett Correlation of \( \text{Ar}_2\text{CH} \cdot \text{CCl}_3 / \text{MeO}^- / \text{MeOH} / 30^\circ \)

The diagram shows a linear relationship between \( \log k_2 \) and \( 2 \sigma_I + 1.76 \sigma_R \). The symbols represent different substituents: Me, MeO, F, Br, Cl, and NO₂.
Figure 4

Modified Hammett Correlation of $\text{Ar}_2\text{CH} \cdot \text{CCl}_2/\text{t-BuO}^-/\text{t-BuOH}/30^\circ$

\[ \log k_2 = 2\sigma^- I + 1.62\sigma^- R \]
the amount of charge delocalisation in the transition state.

The breakdown of the assumption that substituent effects are additive has been noted by several workers \(^{167-171}\). Several methods, related to the present study, have been used to correct for the non-linearity of the linear free energy relationships (L.F.E.R.).

Dubois and co-workers \(^{167,168}\) obtained a curved Hammett plot for the bromination of 1,1-diarylethenes. They noted that the p-methoxy and p-methyl derivatives were more reactive than expected. It was calculated that the equal twisting of both aryl rings by ca. 30° would result in a 2% drop in the resonance contribution by each ring. Use of equation (2.37) gives a good correlation.

\[
\log \frac{k}{k_0} = \rho (\sigma^+ + \sigma) \quad (2.37)
\]

Rausse and Dubois \(^{169}\) found that if the bromination of substituted stilbenes was regarded as going through two discrete reaction centres a linear correlation could be obtained. A modified L.F.E.R. of the form in equation (2.38)

\[
\log \left( \frac{k_x + k_y}{k_0} \right) = \log \left( 10^{\rho_\alpha \sigma^+} + 10^{\rho_\beta \sigma} \right) \quad (2.38)
\]

was used, where \(\rho_\alpha\) is the reaction constant for the C\(_x\) carbonium ion centre \(\alpha\) to the substituted ring and \(\rho_\beta\) is the reaction constant for C\(_y\). This method is mathematically more rigorous than the "alpha" method. However, the end result is the same. The advantage of the present method is that a single reaction constant is required to express the effect of substituents.

The correlations of the rates of solvolysis of di- and polysubstituted benzhydryl chlorides in methanol, ethanol and 2-propanol, with \(\rho^+\), exhibited some marked deviations from linearity. \(^{170}\) This was especially
noticeable for the p-methoxy and the p-dimethyl derivatives. Similar
behaviour was observed by Berliner and Malter for the solvolysis of
$4,4'$-disubstituted benzhydrol chlorides in acetone-water mixtures.$^{171}$
A method similar to that used in the present research was used to
correct the Hammett correlation of the $\mathbf{pK}_a$ values with $\sigma^+$ for the
protonation of substituted benzhydrols.$^{172}$

However, it must be noted that the Hammett correlation of the
vinylc nucleophilic substitution in the 1,1-diaryl-2-halogenoethylene
series was linear when $2\sigma^-$ was used.$^{173,174}$ The formation of a carbanion
is the rate-determining step in this reaction. The hybridization at the
$\beta$-carbon atom remains the same in going from the initial to the transition
state. Therefore the relative orientation of the rings need not change,
in contrast to the 1,1-diaryl-2,2,2-trichloroethane system. A further
illustration of this is that no correction was needed for the Hammett
correlation of the $S_{II}$ reaction of the 1,1-diaryl-2,2-dichloroethanes with
thiophenoxide ion in ethanol,$^{102}$ where $C_\beta$ remains $sp^3$ hybridized throughout.

The salient feature of the modified Hammett correlations of the
reactions of the 1,1-diaryl-2,2,2-trichloroethanes in methanol and
t-butanol is that $\sigma^-_R$ derived from $\sigma$ for the p-nitro substituent gave a
much better fit than the parameter derived from $\sigma^-$. This suggests that
there is no direct resonance interaction between the p-nitro group and
the developing negative charge at the $\beta$-carbon atom in the transition
state. The $\beta$-carbon atom may therefore be predominantly pyramidal
although the carbanion intermediate is delocalized. The lone pair in the
$sp^3$ orbital cannot overlap with the p orbitals of the aryl rings even
though the rings might be as coplanar as the ortho hydrogen interactions
will allow.

A similar interpretation has been placed on the tritium exchange rates
in the diarylmethane system.$^{175,176}$ The magnitude of the primary
deuterium isotope effects suggest a symmetrical transition state while the Bronsted β of OMe suggests only ca. 31% C-H bond rupture, if literally interpreted. Consequently, the extent of the reaction as measured by the degree of proton transfer is different from that measured by the amount of charge delocalization. The extended Hammond postulate\(^{177}\) is inapplicable in this case since the transition state does not fit into a "smooth" structural and electronic reorganization involving the reactants changing to products.\(^{176}\) However, the Hammett ρ values for the reactions of the 1,1-diaryl-2,2,2-trichloroethanes in methoxide-methanol and t-butoxide-t-butanol are adjusted for the non-coplanarity of the aryl rings in the largely pyramidal transition state.

The Hammond postulate\(^{15}\) is applicable to highly endothermic or highly exothermic reactions (i.e. \(\Delta G^0 \gg \Delta G^\ddagger\)) whilst the extended Hammond postulate\(^{177}\) seeks to help assign transition state character to reactions where \(\Delta G^\ddagger\) and \(\Delta G^0\) are comparable. It incorporates the idea that the stabilization of products by structural changes is accompanied by stabilization of the transition state along the whole reaction coordinate.

The enthalpies and entropies of activation for the reactions of the 1,1-diaryl-2,2,2-trichloroethanes in methanolic sodium methoxide are shown in Table 4. The energies of activation (\(E_a\)) were calculated from two point Arrhenius plots over a 15°C temperature range using equation (2.39).\(^{178}\)

\[
\log k_2 = \frac{E_a}{2.303 \text{ RT}} + \text{ constant} \tag{2.39}
\]

The enthalpies of activation (\(\Delta H^\ddagger\)) were calculated from equation (2.40) where \(T\) is the mid-point of the temperature range employed.

\[
\Delta H^\ddagger = E_a - RT \tag{2.40}
\]
The entropies of activation (ΔS‡) were calculated from a standardized form of the Eyring Equation,179

\[
\frac{\Delta S^\ddagger}{4.576} = \log k_2 - 10.753 - \log T + \frac{\Delta H^\ddagger}{4.576T}
\]

(2.41)

where log \(k_2\) is the rate constant at temperature \(T\), the mid-point of the temperature range.

**TABLE 4.**

Activation Parameters for the Reactions of \(\text{Ar}_2\text{CH} \cdot \text{CCl}_3\) and \(\text{Ar}_2\text{CD} \cdot \text{CCl}_3\) With \(\text{NaOMe-MeOH}\)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>(\Delta H^\ddagger) (kcal mol(^{-1}))</th>
<th>(\Delta S^\ddagger) (cal K(^{-1})mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p-MeOC(_6)(_4))(_2)CH\cdot\text{CCl}_3</td>
<td>21.8</td>
<td>-2.6</td>
</tr>
<tr>
<td>(p-MeOC(_6)(_4))(_2)CD\cdot\text{CCl}_3</td>
<td>22.7</td>
<td>-2.8</td>
</tr>
<tr>
<td>(p-MeC(_6)(_4))(_2)CH\cdot\text{CCl}_3</td>
<td>22.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Ph(_2)CH\cdot\text{CCl}_3</td>
<td>17.5</td>
<td>-13.4</td>
</tr>
<tr>
<td>Ph(_2)CD\cdot\text{CCl}_3</td>
<td>18.8</td>
<td>-12.5</td>
</tr>
<tr>
<td>(p-FC(_6)(_4))(_2)CH\cdot\text{CCl}_3</td>
<td>22.2</td>
<td>4.7</td>
</tr>
<tr>
<td>(p-CIC(_6)(_4))(_2)CH\cdot\text{CCl}_3</td>
<td>18.8</td>
<td>-2.7</td>
</tr>
<tr>
<td>(p-CIC(_6)(_4))(_2)CD\cdot\text{CCl}_3</td>
<td>20.0</td>
<td>-2.1</td>
</tr>
<tr>
<td>(p-BrC(_6)(_4))(_2)CH\cdot\text{CCl}_3</td>
<td>21.2</td>
<td>5.4</td>
</tr>
<tr>
<td>(p-NO(_2)C(_6)(_4))(_2)CH\cdot\text{CCl}_3</td>
<td>17.8</td>
<td>5.9</td>
</tr>
<tr>
<td>(p-NO(_2)C(_6)(_4))(_2)CD\cdot\text{CCl}_3</td>
<td>18.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

\(^a\) Ref. 101 reports \(\Delta H^\ddagger = 18.0\) kcal mol\(^{-1}\), \(\Delta S^\ddagger = -10.2\) cal K\(^{-1}\)mol\(^{-1}\).

based on three rate constants measured over a 20°C temperature range.
Understandably, the errors in the activation parameters are large, \( \text{ca.} \pm 1 \text{ kcal mol}^{-1} \) in \( \Delta H^\ddagger \) and \( \text{ca.} \pm 2.5 \text{ cal mol}^{-1} \) in \( \Delta S^\ddagger \). However, notwithstanding this, it can be seen that there is no correlation between the reactivities of the compounds and the activation parameters. Also there is no isokinetic relationship. Previously it was thought that \( \Delta S^\ddagger \) values of \( \text{ca.} -10 \) to \(-20 \text{ cal mol}^{-1} \) for hydrogen exchange reactions indicated rate-determining proton transfer whereas \( \Delta S^\ddagger \) values of \( \text{ca.} \) zero indicated the occurrence of internal return.\(^{12,180}\) Consider the mechanism of hydrogen isotope exchange visualized by Cram and Kollmeyer.\(^{12}\)

\[
\begin{align*}
A & \quad \text{DOMe} \quad \stackrel{k_1}{\longrightarrow} \quad C^- \quad \text{HOME} \\
B & \quad \text{OME} \quad \stackrel{k_2}{\longrightarrow} \quad C^- \quad \text{DOMe} \\
C \quad & \quad \text{C-D} \quad (2.42)
\end{align*}
\]

A steady state analysis of the mechanism gives:

\[
k_{\text{obs}} = \frac{k_1 k_2}{k_1 + k_2} \quad (2.43)
\]

If internal return occurs \((k_1 \gg k_2)\) then \(k_{\text{obs}} = \frac{k_1 k_2}{k_1} \). The transition state is \((B \rightarrow C)^\ddagger\) where one hydrogen bond is replaced by a deuterium bond. The negative charge on the central carbon is largely delocalized.

If there is no internal return \((k_2 \gg k_1)\) then \(k_{\text{obs}} = k_1 \). This corresponds to transition state \((A \rightarrow B)^\ddagger\) where a covalent bond is broken and one hydrogen bond is being made. In this case the negative charge is partially localized on the oxygen and more solvent is expected to be "frozen out" than in \((B \rightarrow C)^\ddagger\). This was thought to be consistent with the large negative \(\Delta S^\ddagger\) values while the \(\Delta S^\ddagger\) values around zero were
thought to be consistent with \((B \rightarrow C)^\ddagger\). However, this has proved to be an oversimplification since the activation parameters for the protodetritiation of fluorenes and indenes, where internal return is not important,\(^{129}\) and diaryl and triarylmethanes where internal return is significant,\(^{175}\) do not exhibit this grouping of \(\Delta S^\ddagger\) values. There is also no mechanistic significance in the \(\Delta S^\ddagger\) values for the dehydrochlorination of the 1,1-diaryl-2,2,2-trichloroethanes although the deviation of the diphenyl analogue from the Hammett correlations may be due to the anomalous \(\Delta S^\ddagger\) value.

Although all the Hammett \(\rho\) values in Table 2 are large, they are not as high as some of the values obtained for the E2 reactions of the 2-arylethyl derivatives.\(^{79-82,86-88}\) This can be attributed to the trichloromethyl group lowering the charge density on the benzylic carbon, a process that of course cannot operate in the 2-arylethyl series. The Hammett \(\rho\) value increases as the base strength is increased along the series thiophenoxide, methoxide \(t\)-butoxide. However, not too much significance should be placed on the fact that \(\rho\) for the \(t\)-butoxide-promoted reaction is greater than \(\rho\) for the methoxide-promoted reaction. Part of the increase is due to the differences in the polarities of the solvents.\(^{181}\) Equation (2.44) relates the \(\rho\) value to the dielectric constant of the solvent.

\[
\rho_s = \rho_\infty + \frac{L}{D_s} \tag{2.44}
\]

where \(\rho_\infty\) is the reaction constant in a solvent of infinite dielectric constant, \(L\) is a parameter independent of the substrate and \(D_s\) is the dielectric constant of the solvent \(s\). The dielectric constants of methanol and \(t\)-butanol are 32.6 and 12.2 respectively.\(^{182}\) No-one has attempted to separate the \(\rho\) value into solvent polarity and base strength contributions. A similar order of \(\rho\) values has been noted for the E2
reactions of 2-arylethyl tosylates\(^87,89\) and bromides,\(^80,82,87\) although the opposite trend has been observed for the 2-arylethyl iodide\(^87\) and trimethylammonium salts.\(^79\)

It is noteworthy however, that \(\rho\) for the methoxide-methanol reaction is greater than \(\rho\) for the thiophenoxide-ethanol reaction. Notwithstanding the change in solvent (\(\rho\) for the thiophenoxide-methanol reaction should be less than 2.11\(^{181}\)), this suggests more negative charge at the \(\beta\)-carbon atom in the transition state for the stronger base (i.e. more \(C_\beta-H\) bond rupture). This observation is in contradiction to an extension of the Hammond postulate, which would require that the strongest bond be the most broken in the transition state. A linear three-centre proton transfer model has 3N-5 degrees of freedom and requires a three-dimensional potential energy surface to describe it when bending motions are neglected. Therefore the Hammond postulate may not be applicable. If the effect of changing base strength acts on the vibrational modes parallel to the reaction co-ordinate the behaviour will be in accord with the prediction of the postulate. However, if this acts on the mode perpendicular to the reaction co-ordinate "anti-Hammond" behaviour is predicted.\(^16,17\)

There is evidence to suggest that perpendicular effects may be more important than parallel effects in some systems. Yano and Oae\(^183\) noted an increase in the Hammett \(\rho\) values with increasing basicity for the elimination of \(p\)-X-phenyl-2-chloroethyl sulphones in acetonitrile promoted by various tertiary amines. The primary deuterium isotope effect determined for the tosylate derivative remained constant for the same series of bases. The Bronsted \(\beta\) coefficients for the E2 eliminations of \(p\)-nitrophenethyl bromide and phenethyl bromide, promoted by substituted phenoxide ions, are 0.67 and 0.54 respectively.\(^90\) Although some doubt has been cast on the validity of \(\beta\) parameters as transition state criteria in certain cases,\(^56-61\) the \(\beta\) values suggest a greater degree of proton
transfer for the more acidic compound, the p-nitro derivative.

If highly exoenergetic proton transfer reactions (ΔpK negative) have reactant-like transition state structures whilst endoenergetic reactions (ΔpK positive) have product-like transition state as required by the extended Hammond postulate, it follows that, as the base strength of the proton acceptor is progressively decreased, the Bronsted β and the Hammett ρ should increase as ΔpK approaches zero from the negative side.\textsuperscript{134} However, observations contrary to these predictions were made for the deprotonation of arylnitroalkanes and related carbon acids,\textsuperscript{57} meaning either that the L.F.E.R. slopes are not good indices of transition state character or that the extended Hammond postulate (a "parallel effect" prediction) is not applicable in these cases.

Observations such as the above are in line with Bunnett's intuitive predictions as to the effect of base strength on transition state character\textsuperscript{3} which have been recently justified theoretically by Critchlow.\textsuperscript{184}

4.2 THE EFFECT OF THE BASE STRENGTH ON THE DEUTERIUM ISOTOPE EFFECT

The primary deuterium isotope effects for the reaction of 1,1-di(p-chlorophenyl)-2,2,2-trichloroethane (DDT) with various bases in ethanol are shown in Table 5. The isotope effect for the methoxide-methanol reaction is also included in the table since methanolic sodium methoxide is slightly less basic than ethanolic sodium ethoxide as measured by their respective H+ acidity functions.\textsuperscript{70} The rates of elimination are similar in both solvents.\textsuperscript{101}
TABLE 5.
Deuterium Isotope Effects for the Reactions of Various Bases With
DDT in Ethanol at 45°C

<table>
<thead>
<tr>
<th>Base</th>
<th>Isotope Effect</th>
<th>$pK_a$ (BH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhS⁻</td>
<td>3.13</td>
<td>9.3ᵇ</td>
</tr>
<tr>
<td>p-NO₂C₆H₄O⁻</td>
<td>4.83</td>
<td>13.3ᶜ,d</td>
</tr>
<tr>
<td>PhO⁻</td>
<td>6.21</td>
<td>15.8ᶜ,e</td>
</tr>
<tr>
<td>MeO⁻</td>
<td>4.75</td>
<td>18.3ᵃ,f</td>
</tr>
<tr>
<td>EtO⁻</td>
<td>3.40</td>
<td>20.3ᵇ,g</td>
</tr>
</tbody>
</table>

ᵃ In methanol solvent.
ᵇ From ref. 101.
ᶜ From ref. 185.
ᵈ From ref. 186.
ᵉ From ref. 187.
ᶠ From ref. 71.
ᵍ From ref. 188.

The deuterium isotope effect reaches a definite maximum as the base strength increases (Figure 5). The maximum is reasonably sharp at $pK_a \approx 16$ which corresponds to the $pK_a$ for phenol. A maximal isotope effect is predicted when $\Delta pK = 0$, that is, when the force constants of the partial C...H and B...H bonds in the transition state are equal. ⁴⁴-⁴⁷ This can be shown semi-quantitively in the following manner.

The proton transfer equilibrium shown in equation (2.45) can be dissected into a thermodynamic cycle,
\[
AH + B^- \leftrightarrow A^- + HB \\
A - H \rightarrow A^- + H^+ \\
A^- + e^- \rightarrow A^- \\
H^- \rightarrow H^+ + e^- \\
B^- + H^- \rightarrow B^- + e^- \\
H^+ + e^- \rightarrow H^+ \\
\]

\text{Energy}
\[
D_{AH} \\
(E.A^-)_A \\
(I.P^-)_B \\
(I.P^-)_A \\
\]

where \(E.A^-\) and \(I.P^-\) are the electron affinity and the ionization potential respectively. Since \((E.A^-)_B = -(I.P^-)_B\) and \((I.P^-)_B = -(E.A^-)_A\)
the total free energy change is obtained by adding the individual energies of the thermodynamic cycle.

\[
\Delta G = (D_{AH} - D_{BH}) + [(E.A^-)_A - (E.A^-)_B] \\
\]

At \(\Delta pK = 0\), \(\Delta G = 0\).

\[
D_{AH} - D_{BH} = (E.A^-)_A - (E.A^-)_B \\
\]

Assume R.H.S. = 0. Therefore \(D_{AH} = D_{BH}\) at \(\Delta pK = 0\). Since the bond dissociation energies are related to the force constants the isotope effect is at a maximum. If \(A^-\) and \(B^-\) are identical then the assumption is true. In all other cases it would hold by coincidence. Thus in real cases\(^{60,134-139}\) it is not surprising that the isotope effect maximum occurs near to, but not exactly at \(\Delta pK = 0\). For example, Dixon and Bruice\(^{60}\) observed an isotope effect maximum for the deprotonation of nitroethane at \(\Delta pK = 0\). The \(pK_a\) of the proton acceptor is ca. 8.5 which
is in good agreement with the pK\textsubscript{a} of 8.5 for the substrate in water. Bell and co-workers have reported isotope effect maxima at ca. \( \Delta \text{pK} = 0 \) for the deprotonation of a series of nitroalkanes and related compounds\textsuperscript{134} (-)-menthone\textsuperscript{138a} and ethyl nitroacetate\textsuperscript{138b} in aqueous solution. In each case the pK\textsubscript{a} of the proton acceptor corresponded closely to the pK\textsubscript{a} of the substrate.

The pK\textsubscript{a} of DDT and its analogues cannot be measured but can be estimated by an L.F.E.R. method. The pK\textsubscript{a} of diphenylmethane (Ph\textsubscript{2}CH\textsubscript{2}) is 30.2 in methanol.\textsuperscript{12} It is assumed to be numerically the same in ethanol by analogy with the behaviour of acetic acid,\textsuperscript{189} phenol\textsuperscript{187} and thiophenol\textsuperscript{101} in the two solvents. Assuming the additivity of substituent effects, the pK\textsubscript{a} values of the appropriate para disubstituted diphenyl methanes can be calculated using equation (2.48).

\[
\log K\textsubscript{a} (Ar\textsubscript{2}CH\textsubscript{2}) - \log K\textsubscript{a} (Ph\textsubscript{2}CH\textsubscript{2}) = 2 \sigma \rho \quad (2.48)
\]

The additivity assumption is not the best approximation.\textsuperscript{102,162} However, it cannot be avoided since \( \rho \) for the ionization of the diarylmethanes is not known.

A \( \rho \) value of 5.0 for the anionic polymerization of substituted styrenes has been reported by Swarc and co-workers.\textsuperscript{190} This reaction involves the formation of benzyl carbamion intermediates. Bowden, Cockerill, and Gilbert reported a Hammett \( \rho \) of 6.3 for the ionization of 2-substituted fluorenes in DMSO-water mixtures\textsuperscript{191} while a \( \rho \) of 4.0 was noted for the ionization of phenyl substituted 2-hydro-2-phenylethoxfluoropropanes in DMSO-methanol.\textsuperscript{192} Furthermore, a \( \rho \) of 5.0 can be calculated from the pK\textsubscript{a} values of di-\textit{p}-tolylmethane and diphenylmethane in cyclohexylamine.\textsuperscript{193}

On comparison with these systems it is therefore reasonable to assume a \( \rho \) of 5.0 for the ionization of diarylmethanes in ethanol. The pK\textsubscript{a} values of the substituted diarylmethanes can now be calculated from equation (2.48) using the appropriate \( \sigma \) constants. The pK\textsubscript{a} values of
the 1,1-diaryl-2,2,2-trichloroethanes are calculated from the Taft equation.

\[
 p_{K_a}(\text{Ar}_2\text{CH} \cdot \text{CCl}_3) = p_{K_a}(\text{Ar}_2\text{CH}_2) - \rho^* (\sigma_{\text{CCl}_3} - \sigma_\text{H}^*) \tag{2.49}
\]

A \( \rho^* \) value has to be estimated for carbanion formation. Bowden et al.\textsuperscript{191} calculated a \( \rho^* \) of 4.6 for the ionization of 9-substituted fluorenes in DMSO-water. A \( \rho^* \) of 4.55 was reported for the ionization of 9-alkylfluorenes in cyclohexylamine.\textsuperscript{194} An estimate of \textit{ca.} 5.0 again seems appropriate for our case. The Taft \( \sigma^* \) substituent constants for \(-\text{CCl}_3\) and \(-\text{H}\) are 2.65 and 0.49 respectively.\textsuperscript{195} The calculated \( p_{K_a} \) values for the 1,1-diaryl-2,2,2-trichloroethanes are shown in Table 6.

\begin{center}
\textbf{TABLE 6.}
\end{center}

\textit{Calculated }\( p_{K_a} \textit{ Values for } \text{Ar}_2\text{CH} \cdot \text{CCl}_3 \textit{ in Ethanol} \)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( p_{K_a} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>((p-\text{MeOC}_6\text{H}_4)_2\text{CH} \cdot \text{CCl}_3)</td>
<td>22.1</td>
</tr>
<tr>
<td>(\text{Ph}_2\text{CH} \cdot \text{CCl}_3)</td>
<td>19.4</td>
</tr>
<tr>
<td>((p-\text{ClC}_6\text{H}_4)_2\text{CH} \cdot \text{CCl}_3)</td>
<td>17.1</td>
</tr>
<tr>
<td>((p-\text{NO}_2_C_6\text{H}_4)_2\text{CH} \cdot \text{CCl}_3)</td>
<td>6.7 - 11.6</td>
</tr>
</tbody>
</table>

No quantitative estimate can be made of the error in the \( p_{K_a} \) values. The assumption that the \( p_{K_a} \) values of the carbon acids are the same in ethanol and methanol may give rise to an error of \textit{ca.} 1.5 \( p_{K} \) units (by comparison with oxygen and sulphur acids). Furthermore, if \( \rho \) and \( \rho^* \) are given values of 5.0±1.0, this increases the error to ±2.5 \( p_{K} \) units. The estimated \( p_{K_a} \) for the dinitro analogue lies between 6.7 and 11.6
because of doubt as to whether $\sigma^+$ or $\sigma^-$ is the appropriate substituent constant for the ionization of di-\textit{p}-nitrophenylmethane.

The L.P.E.R. estimate of the $pK_a$ for DDT is within the "kinetic" estimate determined from the $pK_a$ of phenol at $\Delta pK = 0$ (Table 5). This implies that the rate-determining step of the dehydrochlorination of the 1,1-diaryl-2,2,2-trichloroethanes is simple proton transfer, by analogy with the behaviour of other carbon acids.\textsuperscript{134-139} This is not proof of the "irreversible" E1cB mechanism. However, it strongly suggests that the mechanism is a likely possibility.

The only example of a maximal isotope effect observed for an E2 reaction is for the elimination of 2-phenethylidimethylsulphonium bromide with hydroxide ion in DMSO-water mixtures.\textsuperscript{77} There is a possibility that the isotope effect is a maximum at $\Delta pK = 0$. The $pK_a$ of the substrate is not known but it can be calculated using the L.P.E.R. method.

The $pK_a$ of toluene\textsuperscript{176} is 40.9. Although it was calculated from caesium cyclohexylamide-cyclohexylamine equilibria the $pK_a$ is referred to dilute aqueous solution as standard state. The Taft $\sigma^*$ constant for the $-\text{CH}_2\text{SMe}_2^+$ group is calculated from the $\sigma_I$ value\textsuperscript{123b} of 0.58 using equation (2.50).

$$\sigma_I = 0.45 \sigma^* \quad (2.50)$$

Assuming that $\rho^*$ is 5 and substituting $\rho^* = 0.49$ for $-\text{H}$ into equation (2.51) gives an estimate of 36.8 for the $pK_a$ of 2-phenethylidimethylsulphonium ion in water.

$$pK_a(\text{PhCH}_2\text{CH}_2\text{SMe}_2^+) = pK_a(\text{PhCH}_3) - \rho^*(\sigma^*_{\text{CH}_2\text{SMe}_2^+} - \sigma^*_{\text{H}}) \quad (2.51)$$

The values of $\Delta pK$ are calculated from equation (2.52) using the method of Bell and Cox.\textsuperscript{138a}
\[ \Delta pK = pK_a(\text{PhCH}_2\cdot\text{CH}_2\cdot\text{SMe}_2^+) - H - \log \frac{c_{\text{H}_2\text{O}}}{55.5c_{\text{OH}^-}} \] (2.52)

The isotope effects and the calculated \( \Delta pK \) values are shown in Table 7.

**TABLE 7.**

Isotope Effects as a Function of \( \Delta pK \) for the Hydroxide ion-Promoted Elimination of \( \text{PhCH}_2\cdot\text{CH}_2\cdot\text{SMe}_2^+ \) in DMSO-Water Mixtures

<table>
<thead>
<tr>
<th>Mole % DMSO</th>
<th>Isotope Effect(^a)</th>
<th>( \Delta pK )(^b)</th>
<th>( \Delta pK )(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.03</td>
<td>24.4</td>
<td>23.3</td>
</tr>
<tr>
<td>19.4</td>
<td>5.29</td>
<td>22.3</td>
<td>21.2</td>
</tr>
<tr>
<td>26.3</td>
<td>5.55</td>
<td>21.8</td>
<td>20.7</td>
</tr>
<tr>
<td>38.0</td>
<td>5.73</td>
<td>21.0</td>
<td>19.9</td>
</tr>
<tr>
<td>50.2</td>
<td>5.61</td>
<td>20.1</td>
<td>19.0</td>
</tr>
<tr>
<td>60.3</td>
<td>5.63</td>
<td>19.2</td>
<td>18.2</td>
</tr>
<tr>
<td>71.8</td>
<td>4.79</td>
<td>18.2</td>
<td>17.1</td>
</tr>
</tbody>
</table>

\( a \) From ref. 77, at 50\(^\circ\)C.

\( b \) Based on \( H^- \) scale of ref. 70.

\( c \) Based on \( H^- \) scale of ref. 196.

The isotope effect maximum does not pass through \( \Delta pK = 0 \). This must be a consequence of proton transfer being coupled to other bond-breaking and bond-making processes in the E2 transition state. Based on the sole example of the effect of varying base strength on the isotope effect for E2 reactions, it seems unlikely that the 1,1-diaryl-2,2,2-trichloroethanes would eliminate by the same mechanism.
The third variant of the E1CB mechanism, which involves internal return, can be rejected. Deuterium isotope effects close to unity are observed for internal return. For example, Miller reported an isotope effect of 1.00 for the triethylamine-promoted elimination of cis-dibromoethylene in dimethylformamide. Hall and Naso observed inverse isotope effects for the E1CB mechanism. An exception is the hydrogen isotope exchange of triphenylmethane with lithium cyclohexylamide in cyclohexylamine. Internal return was demonstrated for this system. However, a primary deuterium isotope effect of 11 was reported. Further evidence refuting the E1CB mechanism will be presented later.

There is an alternative interpretation for the varying isotope effects shown in Table 5. There may be a change in the mechanism over the range of bases employed. Some bases may promote an E2 reaction while the rest promote an E1CB reaction. The essential similarity of the Hammett $\rho$ values of 2.11 for the thiophenoxide-promoted reaction and 2.30 for the methoxide-promoted elimination suggest that the overall mechanism is identical for both bases, even considering the difference in basicity of 9 pK units. The small difference in the $\rho$ values can be explained in terms of small variations in transition state structure in the rate-determining step of the same basic mechanism. Previously it was thought that the similarity of the isotope effects for the ethoxide and thiophenoxide-promoted reactions was indicative of similar transition states. However, it is apparent that two different transition states are involved; one with the proton more than half transferred and the other with the proton less than half transferred.

There are several anomalies that require an explanation. The isotope effect of 6.2 for the phenoxide-promoted elimination suggests a symmetrical transition state (i.e. the proton is half transferred). On the other hand, the Bronsted $\beta$ parameter of 0.88 for the substituted phenoxide-promoted
reaction suggests more considerable proton transfer in the transition state. Similarly, the isotope effect of 3.1 for the thiophenoxide-promoted reaction indicates little proton transfer while the Bronsted $\beta$ value of 0.77 and the Hammett $\rho$ value of 2.11 indicate extensive proton transfer in the transition state.

In several cases it has been noted that there is little correspondence between Bronsted $\beta$ values and other transition state criteria, leading to the conclusion that $\beta$ is the less reliable criterion. The Bronsted $\beta$ values for DDT were determined by correlating the rates of deprotonation of a carbon acid with the $pK_d$ values for a series of oxygen or sulphur bases. These $pK_d$ values refer to proton transfer equilibria, involving the solvent ethanol which is an oxygen acid. There are intrinsic differences between carbon and oxygen acids. The rates of proton transfer from carbon acids are much slower than from oxygen acids because a greater amount of solvent and internal geometrical reorganization is required. These rearrangements contribute to the activation energies for carbon acid ionization but not to oxygen acids because of the great differences in the abilities of the respective conjugate bases to accept hydrogen bonds and hence to be stabilized. The fact that $\beta$ cannot be interpreted literally as a degree of proton transfer index therefore is not contrary to expectations.

The disparity between the deuterium isotope effect and the Hammett $\rho$ for the thiophenoxide-promoted reaction can be explained by realizing that $\rho$ is a measure of the extent of proton transfer in geometrical terms while the isotope effect is a measure of the force constants of the partial $\text{C}_\beta \cdots \text{H}$ and $\text{H} \cdots \text{S}$ bonds. More O'Ferrall and Kouba have shown that a symmetrical transition (in the geometrical sense) for proton transfer to sulphur does not correspond to an isotope effect maximum. This is because the carbon-hydrogen bond is stronger than the sulphur-hydrogen bond. This is illustrated in Table 8 which shows the theoretical isotope
effects for varying degrees of proton transfer to sulphur and oxygen bases.

TABLE 8.

Isotope Effects for Proton Transfer to Methoxide and Thiomethoxide ions

<table>
<thead>
<tr>
<th>x</th>
<th>Isotope Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MeO⁻</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.875</td>
<td>3.3</td>
</tr>
<tr>
<td>0.75</td>
<td>5.2</td>
</tr>
<tr>
<td>0.625</td>
<td>7.1</td>
</tr>
<tr>
<td>0.5</td>
<td>7.2</td>
</tr>
<tr>
<td>0.375</td>
<td>5.6</td>
</tr>
<tr>
<td>0.25</td>
<td>4.3</td>
</tr>
<tr>
<td>0.125</td>
<td>3.3</td>
</tr>
<tr>
<td>0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

From ref. 46.

The structure of the transition state is expressed in terms of \( x(0.5\frac{x}{1-x}) \).

4.3 EFFECT OF THE ACIDITY OF THE SUBSTRATE ON THE ISOTOPE EFFECT

Primary deuterium isotope effects for the reactions of the 1,1-diaryl-2,2,2-trichloroethanes with sodium methoxide in methanol and potassium t-butoxide in t-butanol are shown in Table 9.
Isotope Effects for the Reactions of $\text{Ar}_2\text{CH} \cdot \text{CCl}_3$ with $\text{MeO}^- \cdot \text{MeOH}$ and $\text{t-BuO}^- \cdot \text{t-BuOH}$

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Isotope Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{MeO}^- \cdot \text{MeOH}$ (30°)</td>
</tr>
<tr>
<td>$(p\text{-MeOC}_6\text{H}_4)\text{CH} \cdot \text{CCl}_3$</td>
<td>5.21</td>
</tr>
<tr>
<td>$\text{Ph}_2\text{CH} \cdot \text{CCl}_3$</td>
<td>5.08</td>
</tr>
<tr>
<td>$(p\text{-ClC}_6\text{H}_4)\text{CH} \cdot \text{CCl}_3$</td>
<td>5.16</td>
</tr>
<tr>
<td>$(p\text{-NO}_2\text{C}_6\text{H}_4)\text{CH} \cdot \text{CCl}_3$</td>
<td>4.95</td>
</tr>
</tbody>
</table>

The noteworthy point is that the isotope effects are invariant within experimental error as the substituent is changed from $p$-methoxy to $p$-nitro. This encompasses a substrate acidity range of at least 11 pK units (Table 6). Fry suggested that a maximal isotope effect may be observed as the substituent in the benzene ring is changed from an electron donating to an electron withdrawing group.\(^{75}\) This has not been observed in several other cases.\(^{82,95,97,199}\)

The $\Delta \text{pK}$ values for the 1,1-diaryl-2,2,2-trichloroethanes (Table 10) can be calculated from equation (2.53) using the pK\(_a\) of 18.3 for methanol and the pK\(_a\) values of the substrates given in Table 6.

$$\Delta \text{pK} = \text{pK}_a(\text{MeOH}) - \text{pK}_a(\text{Ar}_2\text{CH} \cdot \text{CCl}_3) \quad (2.53)$$

The pK\(_a\) values of the substrates refer to methanol since they are based on the ionization of diphenylmethane in methanol.
TABLE 10.

ΔpK Values for Ar₂CH.CCl₃ in Methanol

<table>
<thead>
<tr>
<th>Substrate</th>
<th>ΔpK</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p-MeOC₆H₄)₂CH.CCl₃</td>
<td>-3.8</td>
</tr>
<tr>
<td>Ph₂CH.CCl₃</td>
<td>-1.1</td>
</tr>
<tr>
<td>(p-ClC₆H₄)₂CH.CCl₃</td>
<td>+0.8</td>
</tr>
<tr>
<td>(p-NO₂C₆H₄)₂CH.CCl₃</td>
<td>+6.7</td>
</tr>
</tbody>
</table>

The deuterium isotope effects do not pass through a maximum even though ΔpK = 0 is within the substrate acidity range. One supposition is that the rate constants for both the deuterated and undeuterated substrates obey the same L.F.E.R., that is $\rho_H \frac{1}{\rho_D}$. Theoretical calculations\(^{200}\) show this to be a correct assumption.

Consider the reaction

$$AH + A^- \rightarrow A^- + AH$$  \hspace{1cm} (2.54)

and assume the Bronsted equation holds for a given series of bases, A:

$$\left(\log k_H\right)_A = \beta_H pK_{AH} + C$$  \hspace{1cm} (2.55)

For a series of bases B reacting with AH:

$$\left(\log k_B\right)_B = \beta_H pK_{BH} + C$$  \hspace{1cm} (2.56)

Subtracting equation (2.55) from (2.56)

$$\left(\log k_H\right)_B - \left(\log k_H\right)_A = \beta_H \Delta pK_H$$  \hspace{1cm} (2.57)

where

$$\Delta pK_H = pK_{BH} - pK_{AH}$$  \hspace{1cm} (2.58)
Similarly for the acid AD reacting with bases A and B:

\[(\log k_D)_B - (\log k_D)_A = \beta_D \Delta pK_D\]  \hspace{1cm} (2.59)

\[\therefore \log \left[\frac{k_H}{k_D}\right]_B = \log \left[\frac{k_H}{k_D}\right]_A + \beta_H \Delta pK_H - \beta_D \Delta pK_D\]  \hspace{1cm} (2.60)

It has been shown that \(\Delta pK_H \equiv \Delta pK_D\) for a related series of oxygen and sulphur bases.\(^{201}\) Therefore equation (2.60) reduces to:

\[\log \left[\frac{k_H}{k_D}\right]_B = \log \left[\frac{k_H}{k_D}\right]_A + \Delta pK (\beta_H - \beta_D)\]  \hspace{1cm} (2.61)

At \(\Delta pK = 0\) the transition state will be symmetrical, thus

\[\log \left[\frac{k_H}{k_D}\right]_B = \log \left[\frac{k_H}{k_D}\right]_A\]  \hspace{1cm} (2.62)

Differentiating equation (2.62) with respect to \(\Delta pK:\)

\[
\frac{\partial \log \left[\frac{k_H}{k_D}\right]}{\partial (\Delta pK)}_B = \beta_H - \beta_D = \text{const.}\]  \hspace{1cm} (2.63)

This means that a plot of \(\log (k_H/k_D)\) against \(\Delta pK\) should be linear. The isotope effect will either increase with increasing \(pK (\beta_H > \beta_D)\) or decrease \((\beta_H < \beta_D)\). It will not go through a maximum. If \(\beta_H = \beta_D\), the isotope effect will be invariant with changing \(\Delta pK\). A similar treatment can be based on the Hammett equation.

Therefore, if an L.F.E.R. holds there will be no isotope effect maximum. This is the case for the E2 reaction of 2-aryl ethyl bromides in t-butoxide-t-butanol\(^{82}\) where \(\rho_H > \rho_D\). The isotope effect increases with increasing \(\sigma\). The same behaviour was also found for the E2 reactions of 1-aryl ethyltrimethylammonium salts in ethoxide-ethanol and t-butoxide-t-butanol.\(^{97}\) The isotope effect should decrease if
$\rho_H < \rho_D$ as was found for the protodetrinitiation of acetophenones in aqueous solution.\textsuperscript{199} This trend was also observed for the E2 reaction of 9-(4-substituted benzyl)fluorene-9-trimethylammonium salts in ethoxide-ethanol.\textsuperscript{95}

If an L.F.E.R. does not hold for the deuterated and the undeuterated compounds, or if there are irregularities in the L.F.E.R.,\textsuperscript{60,77,140} observation of an isotope effect maximum is a possibility. It was found that small deviations in the Bronsted plots for the deprotonation of nitroethane and nitroethane-$1-d_2$ are reflected in the rise and fall of the isotope effect around the region of $\Delta pK = 0$.\textsuperscript{60} The same behaviour is also noted for the Bronsted plot of the diazo-coupling reaction of 2-aminophenol-4-sulphonic acid with 1-naphthol-2-sulphonic acid in aqueous buffer solution\textsuperscript{140} and the L.F.E.R. plot of log $k_2$ against $H^- + \log c_{H_2O}$ for the E2 reaction of 2-phenethylidimethylsulphonium bromide with hydroxide ion in DMSO-water mixtures.\textsuperscript{77}

The effect of irregularities in L.F.E.R. plots on the isotope effects can be demonstrated in a hypothetical case. Consider a Hammett series of acids reacting with a base. Let the $\sigma$ constants of the substituents be: 0, 0.2, 0.4, 0.6 and 0.8. If the phenyl compound is assigned a rate constant ($k_H^H$) of 1.00 and $\rho$ for the reaction series is assigned a value of 1.00 then the other $k_H$ values can be calculated. Assume the isotope effect passes through a maximum. This enables the corresponding $k_D$ values to be calculated. The relevant data is shown in Table 11.
TABLE 11.
The Effect of Irregularities in the Hammett Correlations of H and D Compounds on the Isotope Effects

<table>
<thead>
<tr>
<th>σ</th>
<th>$k_H$</th>
<th>$k_H/k_D$</th>
<th>$k_D$</th>
<th>log $k_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00</td>
<td>3.0</td>
<td>0.333</td>
<td>-0.478</td>
</tr>
<tr>
<td>0.2</td>
<td>1.58</td>
<td>5.0</td>
<td>0.316</td>
<td>-0.500</td>
</tr>
<tr>
<td>0.4</td>
<td>2.51</td>
<td>7.0</td>
<td>0.359</td>
<td>-0.445</td>
</tr>
<tr>
<td>0.6</td>
<td>3.98</td>
<td>5.0</td>
<td>0.786</td>
<td>-0.105</td>
</tr>
<tr>
<td>0.8</td>
<td>6.31</td>
<td>3.0</td>
<td>2.10</td>
<td>0.322</td>
</tr>
</tbody>
</table>

Figure 6 shows that the deviation from linearity is most marked.

Small deviations from L.F.E.R. plots are impossible to explain.

It is difficult enough to explain the existence of regular plots, which, in the case of the Hammett equation, should arise when the reaction series are isoenthalpic, isoentropic, or have enthalpy changes directly proportional to entropy changes. The latter phenomenon is observed for the standard reaction series (benzoic ionization in water). However, a majority of reaction series fall in none of these categories even though they yield good Hammett plots.

In the present work there is, however, no linear Bronsted plot for log $k_H$ versus $pK_a$ pertaining to a series of bases or log $k_D$ versus $pK_a$.

Figure 7 shows a Bronsted plot for the reaction of DDT with a series of sulphur bases ($PhS^-$, p-MeO$_2$C$_6$H$_4S^-$) and oxygen bases (p-$NO_2$C$_6$H$_4O^-$, $PhO^-$, p-MeOC$_6$H$_4O^-$, MeO$^-$-MeOH, EtO$^-$) in ethanol. It is not surprising that linearity is not attained for a series of structurally unrelated bases. Therefore, it is in principle possible that the isotope effect will go through a maximum when $\Delta pK$ is changed by varying the base strength along.

* Data from ref. 101 and 185.
The Effect of Irregularities in Hammett Correlations of H and D Compounds on Isotope Effects
Figure 7

Bronsted Correlation of the dehydrochlorination of DDT with Various bases in Ethanol

- PhS⁻
- p-MeC₆H₄S⁻
- PhO⁻
- p-MeOC₆H₄O⁻
- p-NO₂C₆H₄O⁻
- MeO⁻
- EtO⁻
a series of unrelated bases, as observed. The isotope effect seems to be very insensitive to the variation in $\Delta pK$ for a series of closely related carbon acids. Here, the acidities are manifested by merely altering the para ring substituent.

The enthalpies and entropies of activation for the reactions of the 1,1-diaryl-2,2,2-trichloroethanes and the deuterated analogues are shown in Table 4. Although the errors in the activation parameters are large (2 point Arrhenius plots), it can be seen that the isotope effects are determined mainly by changes in $\Delta H^+$ rather than $\Delta S^+$. This implies that quantum mechanical tunnelling is not the determining factor of the isotope effects.203

Little information of the transition state can be gained solely from the isotope effects. It is significant that the isotope effects for all the substrates decrease as the base-solvent system is changed from methoxide-methanol to t-butoxide-t-butanol. Behaviour of this type has never been observed for any E2 reactions. The reverse trend has in fact been observed for all cases. Prior to this study, no isotope effects have been reported for E1cB reactions in both t-butanol and methanol or ethanol. In Table 12 is listed all the examples of isotope effect studies of E2 reactions carried out in both solvents.

The E2 mechanism has been verified for many of these reactions, using a variety of mechanistic criteria. For example, in reaction 1 the nitrogen leaving group isotope effect decreased from 1.0182 to 1.0154 on changing the base-solvent system from ethoxide-ethanol to t-butoxide-t-butanol.204 There are substantial Br : Cl leaving group rate ratios for the 5,7 and 6,8 pairs of reactions. Changing the solvent from methanol to t-butanol lowers the rate ratio.205

It must be noted that the deuterium isotope effects for the E2 reaction of 2-arylethylidimethylsulphonium ions decreases from 5.93 to 5.07
TABLE 12.
Isotope Effects of E2 Reactions in Ethanol and t-Butanol at 30°C

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Substrate</th>
<th>Isotope Effects</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>E₂O⁻-EtOH</td>
<td>t-BuO⁻-t-BuOH⁻</td>
</tr>
<tr>
<td>1</td>
<td>PhCH₂·ONO₂⁻</td>
<td>5.94</td>
<td>6.41</td>
</tr>
<tr>
<td>2</td>
<td>PhCH₂·CH₂·NMe₃⁺</td>
<td>2.95b</td>
<td>7.03</td>
</tr>
<tr>
<td>3</td>
<td>PhCH₂·CH₂·Br</td>
<td>7.11</td>
<td>8.0</td>
</tr>
<tr>
<td>4</td>
<td>PhCH₂·CH₂·OTs</td>
<td>5.66</td>
<td>8.01</td>
</tr>
<tr>
<td>5</td>
<td>cis-PhCH=CHBr</td>
<td>2.9c</td>
<td>4.6</td>
</tr>
<tr>
<td>6</td>
<td>cis-p-NO₂C₆H₄CH=CHBr</td>
<td>2.2c</td>
<td>4.3</td>
</tr>
<tr>
<td>7</td>
<td>cis-PhCH=CHCl</td>
<td>2.2c</td>
<td>3.2</td>
</tr>
<tr>
<td>8</td>
<td>cis-p-NO₂C₆H₄CH=CHCl</td>
<td>1.6c</td>
<td>3.5</td>
</tr>
<tr>
<td>9</td>
<td>cyclo-C₆H₁₁·OTs</td>
<td>4.2</td>
<td>6.3</td>
</tr>
<tr>
<td>10</td>
<td>PhCH(Br)CH₃</td>
<td>3.4</td>
<td>5.0</td>
</tr>
<tr>
<td>11</td>
<td>m-BrC₆H₄CH(CH₂)CH₂·OTs</td>
<td>4.71</td>
<td>6.29</td>
</tr>
<tr>
<td>12</td>
<td>p-MeC₆H₄CH(CH₂)CH₂·OTs</td>
<td>4.09</td>
<td>6.20</td>
</tr>
<tr>
<td>13</td>
<td>m-BrC₆H₄CH(CH₂)CH₂·Br</td>
<td>7.04</td>
<td>7.73</td>
</tr>
<tr>
<td>14</td>
<td>p-MeC₆H₄CH(CH₃)CH₂·Br</td>
<td>6.35</td>
<td>6.71</td>
</tr>
<tr>
<td>15</td>
<td>9-bromo-9,9'-bifluorenyl</td>
<td>6.2f</td>
<td>8.0</td>
</tr>
<tr>
<td>16</td>
<td>PhCH(NMe₃⁺)CH₃</td>
<td>4.46</td>
<td>4.63g</td>
</tr>
<tr>
<td>17</td>
<td>p-CF₃C₆H₄CH(NMe₃⁺)CH₃</td>
<td>4.84</td>
<td>5.15g</td>
</tr>
</tbody>
</table>

a Carbonyl-forming E₂CO₂ elimination; PhCHO and NO₂⁻ are the products.
b At 50°C. c In MeO⁻-MeOH. d Cyclohexyl toluene-p-sulphonate at 50°C.
e At 50°C. f MeO⁻ in t-BuOH. g Extrapolated to 70°C.
as the base-solvent system is changed from hydroxide-water to ethoxide-ethanol.\textsuperscript{207} Although the increase in the amount of $C_\beta - H$ bond rupture seems to parallel the increase in the basicity of the medium this is not mechanistically significant because of the great change in the solvent polarity on going from water to ethanol as compared with the change in polarity on going from ethanol to t-butanol.

It seems that the isotope effects for the reactions of the 1,1-diaryl-2,2,2-trichloroethanes in methanol and t-butanol show a trend contrary to those exhibited by E2 reactions in these solvents. This anomaly implies that the elimination mechanism for these compounds is not paenecarbonian E2. The isotope effect behaviour is so distinct that it may prove useful as a criterion of mechanism.

An alternative explanation for the low deuterium isotope effects of the reactions in t-butoxide-t-butanol is that ion-pair return of the carbanion is involved. Consider the scheme:

\begin{equation}
\begin{align*}
\text{DDT} + \text{B}^- & \xrightarrow{k_1} \text{DDT}^- \cdots \cdots \cdots \text{H-B} \\
& \xleftarrow{k_2} \text{DDT}^- \cdots \cdots \cdots \text{H-B} \\
& \xrightarrow{k_2} \text{DDT}^- + \text{HB} \\
& \xleftarrow{k_2} \text{DDT}^- \cdots \cdots \cdots \text{H-B} \\
& \xrightarrow{k_3} \text{product}
\end{align*}
\end{equation}

\begin{equation}
k_2 \neq 0 \text{ since no tritium exchange is observed.}\textsuperscript{101}
\end{equation}

A steady state analysis of the mechanism gives:

\begin{equation}
k_{\text{obs}} = \frac{k_1 k_2}{k_1 + k_2}
\end{equation}
If $k_{-1} \gg k_2$ then:

$$k_{	ext{obs}} = \frac{k_1k_2}{k_{-1}} = k_e k_2$$  \hspace{1cm} (2.67)

A small equilibrium isotope effect on $k_e$ and a small isotope effect on $k_2$ would be expected since the latter applies to a rate process involving the breaking of a weak hydrogen bond. Therefore the observed isotope effect will be small if internal return is important. This would be observed when $\Delta pK = pK_{DDT} - pK_{BH}$ is large, that is, if BH is the stronger acid it will undergo internal return more readily than a weaker acid.\(^{12}\) This is illustrated by the data in Table 13.

**TABLE 13.**

Tritium Isotope Effects for the Reaction of Hydrocarbon Acids in Methoxide-Methanol

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Base-Solvent</th>
<th>$\Delta pK$</th>
<th>$k_\text{H}/k_\text{T}$ (obs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-Ph-Fluorene</td>
<td>OMe$^-$/MeOH</td>
<td>0.4</td>
<td>16.1(^a)</td>
</tr>
<tr>
<td>Triphenylmethane</td>
<td>&quot;</td>
<td>11.4</td>
<td>1.77(^b)</td>
</tr>
</tbody>
</table>

\(^{a}\) From ref. 129.

\(^{b}\) From ref. 175.

The $\Delta pK$ value for DDT in methoxide-methanol is -0.8. Therefore little internal return is expected. The lack of internal return is confirmed by the excellent correlation of the 1,1-diaryl-2,2,2-trichloroethanes with the Bronsted correlation\(^{129}\) for the substituted fluorenes (Section 4.5). The $pK_a$ of t-butanol is not known but it is certainly a weaker acid than
methanol. The $\Delta pK$ values in t-butoxide-butanol will be smaller and internal return will be even of less consequence.

4.4 RATE-ACIDITY CORRELATIONS

The Zucker-Hamnett hypothesis$^{208}$ enables correlations of the rates of acid-catalysed reactions with acidity functions. A corresponding relationship can be derived for reactions in strongly basic solutions.$^{68,128}$ The B1 mechanism, as classified by More O’Ferrall and Ridd,$^{127}$ involves the formation of a carbanion in a pre-equilibrium step followed by the rate-determining step to form products.

$$
\begin{align*}
\text{RH} + \text{MeO}^- & \xrightleftharpoons{K_a} \text{R}^- + \text{MeOH} \\
\text{R}^- & \xrightarrow{k_2} \text{products} \\
\text{slow}
\end{align*}
$$

(2.68)

According to the Bronsted-Bjerrum treatment of the influence of ionic strength on reaction rates,$^{209}$ the rate equation for the B1 mechanism is given by:

$$
\frac{-d(c_{R^-} + c_{RH})}{dt} = k_2 \frac{c_R}{c_{+}} \frac{c_{R^-}}{c_{+}}
$$

(2.69)

where $c_{+}$ is the activity coefficient of the transition state leading to the formation of the products. The observed first-order rate constant $k_1$ is defined by equation (2.70).

$$
k_1 = -\frac{1}{(c_{R^-} + c_{RH})} \cdot \frac{d}{dt} (c_{R^-} + c_{RH})
$$

$$
= \frac{c_{R^-}}{(c_{R^-} + c_{RH})} \cdot k_2 \frac{f_{R^-}}{f_{+}}
$$

(2.70)
The equilibrium between the intermediate and the reactants may be expressed as:

$$K_a = \frac{a_{R^-} a_{MeOH}}{a_{RH} a_{MeO^-}}$$  \hspace{1cm} (2.71)

Substituting equation (2.71) into (2.70) and taking logarithms we obtain:

$$\log k_1 = \log K_a k_2 + \frac{a_{MeO^-} f_{RH}}{a_{MeOH} f^*}$$  \hspace{1cm} (2.72)

The methoxide ion activity is related to the $H_M$ acidity function via equation (2.73),\textsuperscript{127} when $B^-, BH$ is the indicator pair used to establish the $H_M$ function.

$$H_M = pK_{MeOH} + \log \frac{a_{MeO^-} f_{BH}}{a_{MeOH} f_{B^-}}$$  \hspace{1cm} (2.73)

This is related to equation (2.72) by:

$$\log k_1 = \log \left( \frac{c_{RH}}{c_R^- + c_{BH}} \right) + H_M + \log K_a k_2 -$$

$$pK_{MeOH} + \log \frac{f_{RH} f_{B^-}}{f_{BH} f^*}$$  \hspace{1cm} (2.74)

An approximation of the Zucker–Hammett hypothesis is that the activity coefficient ratios ($f_{RH}/f^*$) and ($f_{B^-}/f_{BH}$) are equal.\textsuperscript{203} Assuming that $RH$ is a weak acid, that is $c_{RH} \gg c_R^-$ and $\log \left( \frac{c_{RH}}{c_{RH} + c_R^-} \right) = 0$

equation (2.74) simplifies to:

$$\log k_1 = H_M + \text{constant}$$  \hspace{1cm} (2.75)

For any reaction obeying this relationship $\log k_1$ will be a linear function of $H_M$ with unit slope.
Another mechanistic possibility is the rate-determining formation of the carbanion followed by a fast step to give products. This corresponds to the "irreversible" E1cB mechanism.

\[
\text{RH} + \text{MeO}^- \xrightarrow{k_a \text{ slow}} \text{R}^- + \text{MeOH} \\
\text{R}^- \xrightarrow{\text{fast}} \text{products}
\] (2.76)

\[
\text{Rate} = k_i c_{\text{RH}} c_{\text{MeO}^-} \cdot \frac{f_{\text{RH}} f_{\text{MeO}^-}}{f^*}
\] (2.77)

The observed first-order rate constant is given by equation (2.78).

\[
\log k_i = \log k_a + \log c_{\text{MeO}^-} + \log \frac{f_{\text{RH}} f_{\text{MeO}^-}}{f^*}
\] (2.78)

Combining this with equation (2.73) gives:

\[
\log k_i = H_W + \log k_a - pK_{\text{MeOH}} + \log a_{\text{MeOH}} + \log \frac{f_{\text{RH}} f_{\text{B}^-}}{f_{\text{B}H} f^*}
\] (2.79)

Assuming that the activity coefficient term is unity,\textsuperscript{208} equation (2.79) simplifies to

\[
\log k_i = H_W + \text{constant}
\] (2.80)

which is the same as equation (2.75) obtained for the pre-equilibrium case. However, the two mechanisms can be distinguished by hydrogen isotope exchange.

A slightly different derivation of the L.F.E.R. has been given by Kollmeyer and Cram.\textsuperscript{128} Their treatment takes into account the solvation of all species in solution, as well as the activity of the solvent.

Previous attempts to correlate the rates of proton-transfer reactions with the basicity of the medium have only been moderately successful.
More O'Ferrall and Ridd\textsuperscript{127} found that the rates of the E2 reaction of 2-phenethyl bromide in methanolic sodium methoxide correlated with the stoichiometric base concentration. The rates of the carbanionic α-elimination of chloroform, in the same medium, increased sharply with the concentration of the base. An L.F.E.R. correlation with an $H_\infty$ function based on substituted amines produced a curved plot with a mean slope of 0.8, suggesting that the indicators behaved differently from the substrate in the same media. It had been hoped that the behaviour of the rates with changing concentration of the base, as opposed to the behaviour with changing $H_\infty$, would serve as a criterion for distinguishing between bimolecular E2 elimination where proton transfer is coupled with other bond breaking and bond making processes, and reactions where proton-transfer is the sole process in the rate-determining step.

In theory, if the Zucker-Hammett hypothesis holds, the logarithm of the observed first-order rate constant should vary linearly with the appropriate acidity function and have unit slope.\textsuperscript{68,127,208} The major drawback with the rate-acidity correlations reported for reactions in strongly basic media has been the lack of a suitable acidity function scale. The $H_\infty$ scales based on the ionization of nitrogen acids\textsuperscript{63,64,70} and oxygen acids\textsuperscript{65} are not properly suited to reactions involving proton transfer from carbon acids. The protodetritiation of fluorene-9-t in sodium methoxide-methanol, studied by Streitweiser \textit{et al.}\textsuperscript{129} illustrates this point nicely. Poor L.F.E.R. plots of slope ca. 0.61 were obtained using acidity functions based on nitrogen and oxygen indicators. However, an excellent linear correlation of slope 0.847±0.006 was obtained using the $H_M$ function based on the ionization of 1,3-diphenylindene (a structurally similar carbon acid) in methanol.

The above protodetritiation has been chosen as a model reaction for the dehydrochlorination of the 1,1-diaryl-2,2,2-trichloroethanes since
it involves simple proton transfer (with insignificant internal return) in the rate-determining step. This is identical to the rate-determining step of the "irreversible" E1cB mechanism. Fluorene is also structurally similar. The ideal model substrate would have been diphenylmethane. However, proton transfer in methanolic sodium methoxide is accompanied here by internal return.12,175,176

The effect of the base concentration on the rates of elimination of 1,1-diphenyl-2,2,2-trichloroethane in the methanolic sodium methoxide is shown in Table 14. The second-order rate constants are calculated by dividing the observed first-order rate constants with the stoichiometric base concentration. Figure 8 shows that the second-order rate constant $k_2$ is linear with the sodium methoxide concentration at low concentrations (less than ca. 0.2M). The curvature of the plot is reminiscent of those obtained for the methanolysis of chloroform127 and the protodetritiation of fluorene-9-t.129

**TABLE 14.**

Reactions of Ph₂CH·CCl₃ with Methanolic Sodium Methoxide at 30°C.

<table>
<thead>
<tr>
<th>[NaOMe] M</th>
<th>$10^4 k_1$ (s⁻¹)</th>
<th>$10^4 k_2$ (1 mol⁻¹s⁻¹)</th>
<th>log $k_1$</th>
<th>$H_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.112</td>
<td>0.487</td>
<td>4.37</td>
<td>-4.3116</td>
<td>16.04</td>
</tr>
<tr>
<td>0.226</td>
<td>0.993</td>
<td>4.39</td>
<td>-4.0310</td>
<td>16.36</td>
</tr>
<tr>
<td>0.472</td>
<td>2.27</td>
<td>4.76</td>
<td>-3.6498</td>
<td>16.79</td>
</tr>
<tr>
<td>0.707</td>
<td>3.46</td>
<td>4.89</td>
<td>-3.4609</td>
<td>17.06</td>
</tr>
<tr>
<td>0.944</td>
<td>5.39</td>
<td>5.70</td>
<td>-3.2684</td>
<td>17.27</td>
</tr>
<tr>
<td>1.410</td>
<td>11.5</td>
<td>8.13</td>
<td>-2.9393</td>
<td>17.63</td>
</tr>
<tr>
<td>1.888</td>
<td>20.5</td>
<td>10.85</td>
<td>-2.6382</td>
<td>17.94</td>
</tr>
</tbody>
</table>
Figure 8
Second-Order rate Constants for the Dehydrochlorination of Ph₂CH·CCl₃ with NaOMe-MeOH as a Function of base Concentration
Figure 9

Observed First-Order rate Constants for the Dehydrochlorination of \( \text{Ph}_2\text{CH} \cdot \text{CCl}_3 \) with

\[ \text{NaOMe-MeOH} \] versus \( H_M \)
The plot of log $k_1$ against $H_M$ gives a slope of $0.853 \pm 0.008$ and a correlation coefficient of 1.000 (Figure 9). Figure 10 shows the relationship between $H_M$ and the sodium methoxide concentration.

Linearity of the L.F.E.R. is not a significant criterion in itself, since the correlations of the rates of a series of E2, $S_N^2$, E1cB and hydrogen isotope exchange reactions studied by More O'Ferrall are also linear with respect to this $H_M$ function. The noteworthy feature is that the slope for the rate-acidity correlation of 1,1-diphenyl-2,2,2-trichloroethane is identical to that obtained for fluorene-9-t, thus implying identical rate-determining steps.

Any suggestion of the "irreversible" E1cB mechanism being accompanied by internal return can be further dispelled by comparison with the hydrogen isotope exchange of polyfluorobenzenes. These have been shown to exchange through a mechanism complicated by internal return. A slope of 1.125 is obtained for the L.F.E.R. correlation of the hydrogen isotope exchange of 1,2,3,5-tetrafluorobenzene with sodium methoxide-methanol-0-t. This slope is vastly different to the one obtained for the elimination of 1,1-diphenyl-2,2,2-trichloroethane.

This is not of course definitive evidence for the operation of the "irreversible" E1cB mechanism. When the observed first-order rate constants for the E2 reactions of 2-phenethyl tosylate in methanolic sodium methoxide are plotted against $H_M$, a slope of 0.853 results. The dangers inherent in assuming mechanistic identity from L.F.E.R. plots of identical slopes has been clearly demonstrated by Fryor. Thus the identity of the slopes in the 1,1-diphenyl-2,2,2-trichloroethane and fluorene-9-t plots is a necessary but not a sufficient condition for assuming mechanistic similarity.

4.5 RATES OF CARBANION FORMATION

Streitweiser and co-workers reported a Bronsted correlation for
the protodetritiation of indene and substituted fluorenes in methanolic sodium methoxide at 45°C. Although the rates were correlated against the corresponding pKₐ values measured with respect to caesium cyclohexylamide in cyclohexylamine (CsCHA-CHA) the pKₐ values refer to dilute aqueous solution as the standard state. On consideration of the Bronsted α of 0.369 and the tritium and deuterium isotope effects it was concluded that the rate-determining step was deprotonation to form the carbanion. The high deuterium isotope effect of ca. 6.5 was not consistent with significant internal return.129

If the dehydrochlorination of the 1,1-diaryl-2,2,2-trichloroethanes proceeds via an "irreversible" E1cb mechanism, the rates of elimination and carbanion formation should be identical. The rates of carbanion formation have not been determined but can be calculated with reasonable accuracy. The pKₐ values of the 1,1-diaryl-2,2,2-trichloroethanes relative to dilute aqueous solution are calculated using the L.F.E.R. method outlined in section (4.2). A pKₐ of 31.15 is calculated for di-p-chlorophenylmethane assuming ρ is 5.0 for the ionization of the diarylmethanes and using the pKₐ of 33.45 for diphenylmethane in water.129 The ρ* value of 5.0 for the ionization of the diarylmethanes and the σ* values of 2.65 and 0.49 for the -CCl₃ and -H groups then gives a value of 20.35 for the pKₐ of DDT. The pKₐ values for the DDT analogues are shown in Table 15.
TABLE 15

Calculated $pK_a$ Values of $\text{Ar}_2\text{CH.CCl}_3$ and the Rates of Detritiochlorination in MeO$^-$.MeOH at 45$^\circ$C

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$pK_a$ ($\text{CsCHA-CHA}$)</th>
<th>log $k_2^T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(p-\text{MeOC}_6\text{H}_4)_2\text{CH.CCl}_3$</td>
<td>25.4</td>
<td>-4.269</td>
</tr>
<tr>
<td>$\text{Ph}_2\text{CH.CCl}_3$</td>
<td>22.7</td>
<td>-3.660</td>
</tr>
<tr>
<td>$(p-\text{ClC}_6\text{H}_4)_2\text{CH.CCl}_3$</td>
<td>20.4</td>
<td>-2.254</td>
</tr>
<tr>
<td>$(p-\text{NO}_2\text{C}_6\text{H}_4)_2\text{CH.CCl}_3$</td>
<td>9.9-14.8</td>
<td>0.446</td>
</tr>
</tbody>
</table>

The rate constants for the methoxide-promoted detritiochlorination of the 1,1-diaryl-2,2,2-trichloroethanes in methanol at 45$^\circ$C have not been measured but can be calculated from the primary deuterium isotope effects and the rates of dehydrochlorination at this temperature using the Swain-Schaad relationship.\textsuperscript{211}

$$\log \frac{k_H}{k_T} = 1.44 \log \frac{k_H}{k_D}$$ \hspace{1cm} (2.81)

These are shown in Table 15. Figure 11 shows the Bronsted plot for the protodetritiation of the substituted indenes and fluorenes with methanolic sodium methoxide at 45$^\circ$. The relevant points for the detritiochlorination of the 1,1-diaryl-2,2,2-trichloroethanes are also included.

The original least squares line for the hydrocarbons is:

$$\log k_2^T = 5.1085 \pm 0.47 - (0.369 \pm 0.024) pK$$ with a correlation coefficient $r$ of 0.986 and the standard deviation of fit = 0.200. With the inclusion of the data for DDT, the diphenyl and the p-methoxy analogues the least
squares line is: 
\[ \log k_2^T = 5.285 \pm 0.396 - (0.379 \pm 0.019) pK \]
with a correlation coefficient \( r \) of 0.985 and the standard deviation of fit = 0.194.

The point for 1,1-diphenyl-2,2,2-trichloroethane deviates from the regression line. Similar behaviour has been noted for this compound in other L.F.E.R. correlations. The deviation could be a consequence of the low entropy of activation (Table 4). The Bronsted correlation is improved overall with the inclusion of our detritiochlorination data. Although the correlation coefficient implies a poorer fit, the decrease in the standard deviation of the slope and the standard deviation of fit suggests a better correlation. It has been noted previously that the standard deviation is the more accurate criterion of fit. Providing that the \( pK_a \) values are realistic estimates it can be concluded that the rates of elimination and carbonion formation are identical.

The large error in the \( pK_a \) for 1,1-di(p-nitrophenyl)-2,2,2-trichloroethane arises from the uncertainty as to whether \( \sigma^- (0.778) \) or \( \sigma^- (1.27) \) is the appropriate substituent constant for the L.F.E.R. estimate. Therefore no conclusion can be drawn for this compound. It is significant to note that the regression line passes through the middle of the \( pK_a \) range (Figure 11). The problem of deciding which substituent constant is appropriate for p-NO\(_2\) in L.F.E.R. correlations is not unusual. Saunders and co-workers\(^{80}\) found that \( \sigma^- \) was necessary to correlate the rates of elimination of p-nitrophenethyl bromide in t-butoxide-t-butanol. However, Blackwell and co-workers\(^{82}\) noted that a derived value of 1.15 was necessary to correlate this reaction. Bordwell and Anderson\(^{212}\) used a \( \sigma^- \) value of 1.00 to correlate the \( pK_a \) of p-nitrophenol in 48% ethanol. This seems more applicable to our calculations. In several cases derived substituent constants outside the normal limits have been required.\(^{51}\)

The \( \sigma \) of 0.379, taken literally, suggests that the C-T bond is 38%
Figure 11

Bronsted Correlation for the Protodetritiation of Fluorenyl Hydrocarbons
and the Detritiochlorination of $\text{Ar}_2\text{CH} \cdot \text{CCl}_3$ with $\text{NaOMe-MeOH}$ at 45°
broken in the transition states. The deuterium isotope effects suggest a symmetrical transition state. Subsequent reports indicate that the central carbon atom is still pyramidal. This has considerable negative charge but only a portion of this can be delocalized. Differences in the charge distribution in the transition state and the carbanion can result in a variety of $\alpha$ values including some less than zero and greater than unity. In these cases $\alpha$ is no longer a valid measure of proton transfer and the extended Hammond postulate is inapplicable.

The $pK_a$ values of DDT (17.1) and phenol (15.8) are very similar. However, the rates of proton transfer from these substrates are vastly different. For example, the second-order rate constant $k_2$ for the deprotonation of phenol with aqueous hydroxide ion is $1.4 \times 10^{10} \text{ mol}^{-1} \text{s}^{-1}$. The rate of deprotonation of DDT with methanolic sodium methoxide at $45^\circ\text{C}$ is $5.23 \times 10^{-2} \text{ mol}^{-1} \text{s}^{-1}$ so there is a $10^{12}$ difference in the rates. p-Nitrophenol and DDT also have comparable acidities. The rate of the p-nitrophenoxide-catalysed deprotonation of DDT is $1.45 \times 10^{-6} \text{ mol}^{-1} \text{s}^{-1}$ at $45^\circ\text{C}$ whilst the rate of proton transfer between p-nitrophenol and p-nitrophenoxide in methanol is $4.3 \times 10^6 \text{ mol}^{-1} \text{s}^{-1}$ at $-80^\circ\text{C}$. Once again there is a $10^{12}$ difference in the rate. This is the consequence of the inherent difference between carbon acids and oxygen acids. Proton transfer reactions are slower from carbon acids because greater solvent reorientation is required going to the transition state.

Internal geometrical rearrangements contribute to the activation energies of the carbon acids but not to oxygen acids. In the reactions of oxygen acids and bases the hydrogen bonding is strong enough to provide energy for the usually minimal geometric rearrangements on going to the transition states. This is not the case for carbon acids which have a weaker ability to hydrogen bond to the attacking base.
4.6 THE NATURE OF THE TRANSITION STATE

The Hammond postulate, as originally stated, applies only to highly exothermic and highly endothermic reactions. The literal interpretation of the postulate is that transition states of reactions with small activation energies (highly exothermic reactions) closely resemble the reactants where as transition states for highly endothermic reactions resemble the products. The Hammond postulate should not be applicable to the dehydrochlorination of the 1,1-diaryl-2,2,2-trichloroethanes since the carbanions formed are low energy species relative to the reactants. Therefore the transition states will not resemble the carbanions closely in the structural sense since they do not resemble them energetically.

The equilibrium constant for the reaction

$$\text{DDT} + \text{B}^- \rightleftharpoons \text{DDT}^- + \text{BH} \quad (2.82)$$

is given by equation (2.83)

$$K_e = \frac{K_{\text{DDT}^-}}{K_{\text{BH}}} \quad (2.83)$$

where $K_{\text{DDT}^-}$ is the acidity constant of DDT and $K_{\text{BH}}$ is the acidity constant of the conjugate acid of the base.

$$-2.303 \, RT \, \log K_e = 2.303 \, RT \, (pK_{\text{DDT}} - pK_{\text{BH}})$$

$$\Delta G^0 = 2.303 \, RT \, (pK_{\text{DDT}} - pK_{\text{BH}}) \quad (2.84)$$

The standard free energy change ($\Delta G^0$) for the deprotonation of DDT can be calculated for various bases from the $pK_a$ of 17.1 for DDT and the $pK_a$ values of the various bases (Table 5) using equation (2.84). The free energy of activation ($\Delta G^\ddagger$) is calculated from equation (2.85).
\[ \Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \]  

Values for \( \Delta G^0 \) and \( \Delta G^\ddagger \) for proton transfer to phenoxide, methoxide and ethoxide are shown in Table 16. Partial reaction profiles constructed from this data are shown in Figure 12.

### Table 16

Free Energy Parameters for the Reactions of Various Bases with \((p-ClC_6H_4)_2CH_2CCl_3\)

<table>
<thead>
<tr>
<th>Base</th>
<th>( pK_a )</th>
<th>( \Delta G^0 ) (kcal mol(^{-1}))</th>
<th>( \Delta G^\ddagger ) (kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhS(^-)</td>
<td>9.3</td>
<td>11.3</td>
<td>25.6(^a)</td>
</tr>
<tr>
<td>MeO(^-)</td>
<td>18.3</td>
<td>-1.6</td>
<td>19.6</td>
</tr>
<tr>
<td>EtO(^-)</td>
<td>20.3</td>
<td>-4.7</td>
<td>19.9(^a)</td>
</tr>
</tbody>
</table>

\(^a\) Ref. 101.

The free energy of activation for the thiophenoxide reaction is 25.6 kcal mol\(^{-1}\) while the standard free energy change is 11.3 kcal mol\(^{-1}\). This means that reprotonation is activation controlled. Carbanion formation for the methoxide and ethoxide reactions is exoenergetic since \( \Delta G^0 \) is -1.6 and -4.7 kcal mol\(^{-1}\) respectively. Consequently, there is no necessary resemblance between transition states and products. The extended Hammond postulate\(^{177}\) is also inapplicable on the grounds outlined previously.

Therefore the notion that stronger bases are associated with more C-H bond rupture in the transition state may be valid for carbanion-forming reactions and is not a contradiction of the Hammond postulate. The Hammett \( \rho \) values for the elimination of 1,1-diary1-2,2,2-trichloroethane in methoxide-methanol and t-butoxide-t-butanol are 2.54 and 2.99 respectively.
Figure 12
Partial Reaction Profiles of DDT with PhS\(^{-}\) and EtO\(^{-}\)

Potential Energy (kcal mol\(^{-1}\))

- DD\(_T\)\(^{-}\) + PhSH: 19.9 kcal/mol
- DD\(_T\)\(^{-}\) + EtOH: 11.3 kcal/mol
- DD\(_T\)\(^{-}\) + MeOH: 1.6 kcal/mol

Reaction Coordinate
The deuterium isotope effects are \textit{ca.} 5.1 for the reactions in methanol and \textit{ca.} 3.4-3.8 in t-butanol. The large Hammett \( \rho \) value and the isotope effect for the methoxide reactions suggests that the proton is about half transferred in the transition state. The lower isotope effect for the t-butoxide reactions then indicates that the proton is more extensively transferred in the more basic medium. The isotope effect order is contrary to the trend observed for E2 reactions but is in accord with the notion outlined previously.\textsuperscript{3} However, the opposite view has also been expressed.\textsuperscript{77-83,89,95,97}

The E2 results can be rationalized if we consider for the moment that changing the base from methoxide to t-butoxide has no effect on the degree of proton transfer in the E2 transition state, although the change to the less polar solvent is accompanied by less \( C_a - X \) bond rupture.\textsuperscript{79,204,205} The transition states for these reactions are then:

\begin{align*}
\text{(I)} & \quad \begin{array}{c}
\delta-\text{OMe} \\
\text{H} \\
\text{C} \quad \text{C} \\
\text{X}^\text{\delta-}
\end{array} \\
\text{(II)} & \quad \begin{array}{c}
\delta-\text{OBut} \\
\text{H} \\
\text{C} \quad \text{C} \\
\text{X}
\end{array}
\end{align*}

Transition state (I) has more double bond character than (II). Using the Westheimer 3-centre model\textsuperscript{45} it is predicted that the isotope effect is the same for both transition states. Proton transfer is also coupled to other bond-breaking and bond-making processes in these transition states. Theoretical calculations on the E2 reaction of ethyl-dimethyl sulphonium ion with hydroxide ion show that the isotope effect, for a
given degree of proton transfer, will decrease as the motion of the proton becomes more coupled with double bond formation and C\textsubscript{a} - X bond rupture.\textsuperscript{214} This confirmed earlier calculations by More O’Ferrall and Kouba\textsuperscript{46}, who found that isotope effects calculated on the three-centre transition state model were higher than those based on more complex models. Transition state (I) is more coupled than is (II) and so a reaction involving (II) should display the greater isotope effect.

The isotope effects for the E2 reactions can thus be explained if the coupling effect dominates the degree of proton transfer effect.

The gas phase acidities of the relevant species show that t-butoxide (in the absence of solvent) is intrinsically a weaker base than methoxide.\textsuperscript{215} t-Butoxide in t-butanol is a stronger base (in the kinetic and thermodynamic sense) than methoxide in methanol because of the greater solvation of the methoxide ion in the more polar solvent. Thus the greater basicity or reactivity of t-butoxide is a consequence of an initial state solvation effect. The energy barrier is lower because of a higher initial state for t-butoxide rather than a lower transition state energy level. This is borne out by the work of Smith and Pollock.\textsuperscript{204} They found that the nitrogen leaving group isotope effect for the E\textsubscript{CO\textsuperscript{2}} reaction of benzyl nitrate increased with the increasing amount of water present in the ethanol-water solvent. In the region of 100 to 65\% ethanol-water the isotope effect remained constant. This led to the conclusion that the transition state remained constant over this solvent range and that the rate increase was a manifestation of the initial state solvation effect. Saunders et al.\textsuperscript{80} noted that \( \rho \) and the deuterium isotope effect for the E2 reaction of 2-arylethyl bromide with potassium t-butoxide remained constant in certain t-butanol-DMSO solvent mixtures and reached similar conclusions.

In the E2 transition state the bases are partially neutralized.
This represents a situation where the intrinsic base strengths of t-butoxide and methoxide may be similar and where the basicity order changes. In this position the coupling effect can dominate since the differential degree of proton transfer effect will be small. t-Butoxide will have slightly greater control over the proton (as required by the E1cB results mentioned earlier).

4.7 REACTANTS AND PRODUCTS

The synthesis of 2,2,2-trichloroacetophenone, under the conditions outlined by Cohen et al.,\textsuperscript{148} yielded ca. 25-30% product (cf. reported yield of 93.4%). The chlorination of acetophenone in acetic acid proceeds readily to form 2,2-dichloroacetophenone. However, it is relatively difficult to replace the remaining hydrogen. Cohen used anhydrous sodium acetate to facilitate this. When the synthesis was repeated, 2-chloro-, 2,2-dichloro- and 2,2,2-trichloroacetophenones were obtained together with a small amount of starting material. A sample of 2,2-dichloroacetophenone was prepared by the method outlined by Aston.\textsuperscript{157} This was then chlorinated in acetic acid in the presence of anhydrous sodium acetate under Cohen's conditions. The products were 2-chloroacetophenone, 2,2,2-trichloroacetophenone and acetophenone. Starting material was also present. It seems that the equilibrium

\[
\text{PhCO} \cdot \text{CHCl}_2 + \text{Cl}_2 \rightleftharpoons \text{PhCO} \cdot \text{CCl}_3 + \text{HCl}
\]  

may be in favour of the reactants even in the presence of sodium acetate. The corresponding 2,2,2-tribromoacetophenone is used as a selective brominating agent for methyl ketones.\textsuperscript{146,216}

\[
\text{PhCO} \cdot \text{CBr}_3 + \text{PhCO} \cdot \text{CH}_3 \rightleftharpoons \text{PhCO} \cdot \text{CH}_2\text{Br} + \text{PhCO} \cdot \text{CHBr}_2
\]
The products can disproportionate according to:

\[
2\text{PhCO.CH}_2\text{Br} \xrightleftharpoons{\text{HBr}} \text{PhCO.CHBr}_2 + \text{PhCO.CH}_3 \quad (2.88)
\]

\[
2\text{PhCO.CHBr}_2 \xrightleftharpoons{\text{HBr}} \text{PhCO.CBr}_3 + \text{PhCO.CH}_2\text{Br} \quad (2.89)
\]

It is conceivable that similar disproportionation reactions could occur for the chloroacetophenones, and the presence of PhCOCH\(_3\) and PhCOCH\(_2\)Cl in the product mixture from chlorination of PhCOCHCl\(_2\) can be taken as evidence for this.

The Friedal-Crafts acylation of benzene with trichloroacetyl chloride\(^{147}\) yielded ca. 30% 2,2,2-trichloroacetophenone. The major product of the reaction is 1-hydroxy-1,2,2-triphenylethene. However, the photochlorination of acetophenone produced almost a quantitative yield of 2,2,2-trichloroacetophenone.

The analogous photochlorination of anisole produced an intractable tar. G.l.c. indicated the presence of ca. thirty products.

2,2,2-Trichloro-4'-methoxyacetophenone was prepared by the method of Houben and Fischer.\(^{145}\) Anisole was reacted with trichloroacetonitrile in the presence of zinc chloride and dry hydrogen chloride according to the scheme:

\[
\text{MeO-} + \text{CCl}_3\text{CN} \xrightarrow{\text{ZnCl}_2, \text{HCl}} \text{MeO-} \xrightarrow{\text{NH}_3, \text{HCl}, \text{H}_2\text{O}} \text{MeO-} \quad (2.90)
\]

Zinc chloride probably reacts with trichloroacetonitrile in the following way.
\[
\text{ZnCl}_2 + \text{CCl}_3\text{CN} \xrightarrow{\text{HCl}} \left[\text{CCl}_3\text{C}=\text{NH}\right]^+ \left[\text{ZnCl}_3^-\right]
\] (2.91)

Stable infinity absorbance readings could not be obtained for several kinetic runs involving the reactions of 1,1-diaryl-2,2,2-trichloroethanes with t-butoxide-t-butanol using the stoppered cell technique. The possibility that the olefin may undergo nucleophilic vinylic substitution was checked. However, no chloride ion was detected in a preparative run involving the olefin and potassium t-butoxide. The erroneous absorbance values were eventually attributed to the t-butoxide reacting with atmospheric carbon dioxide. This was prevented by storing the stoppered cell in a dessicator until ten half-lives had elapsed.

The effect of the leaving group on the rate of elimination is the most definitive test for an E1cb reaction. The synthesis of 2-bromo-2,2-dichloroacetophenone (the precursor of 2,2-diphenyl-1-bromo-1,1-dichloroethane) was only partially successful. Preliminary separation procedures were unsatisfactory and there was not sufficient time available to isolate the product.
5. CONCLUSION

Kinetic evidence has been presented which suggests that the mechanism of dehydrochlorination of 1,1-diaryl-2,2,2-trichloroethane in protic solvents is not paenecarbanion E2, as previously thought, but "irreversible" E1cB. The magnitude of the Hammett $\rho$ values for the methoxide and t-butoxide-promoted reactions are large, indicating a considerable amount of negative charge on the $\beta$-carbon atom. The primary deuterium isotope effects pass through a maximum as the basicity is increased along a series of oxygen and sulphur bases. This phenomenon has been observed for proton transfer from carbon acids.\(^{134-142}\) In each of these cases the isotope effect maximum occurred at $\Delta pK = 0$ (i.e. when the $pK_a$ of substrate = $pK_a$ of conjugate acid of the base). Only one example involving an E2 reaction has been reported.\(^{77}\)

Calculations of $\Delta pK$ values for this reaction show that the isotope effect maximum is nowhere near $\Delta pK = 0$. The magnitudes of the isotope effects for the reactions with methoxide-methanol and t-butoxide-t-butanol are not affected by the variation in substrate acidity. This is believed to be a consequence of the rates for the protium and deuterium compounds obeying the same L.F.E.R. In all cases the isotope effects were smaller for t-butoxide than for methoxide. This is contrary to the trend reported for E2 reactions.

The protodetrinitiation of fluorene-9-t with methoxide-methanol\(^{129}\) at 45$^\circ$C was chosen as a model for the "irreversible" E1cB mechanism. The rate-determining step of this reaction is simple proton transfer. Internal return was insignificant. Furthermore, fluorene is structurally similar to the 1,1-diaryl-2,2,2-trichloroethanes. The effect of the
increasing basicity of the medium on the rate of elimination of
1,1-diphenyl-2,2,2-trichloroethane in methanol has been reported.
The slope of the correlation of the observed first-order rate constants
with $H_M$ is identical to that obtained for the model reaction. This
implies that the rate-determining steps of both reactions may be
identical.

The rates of elimination and carbanion formation are identical
if the mechanism of dehydrochlorination is "irreversible" E1cB. The
rates of detritiochlorination at $45^\circ$ of the 1,1-diaryl-2,2,2-trichloroethanes
were calculated from the deuterium isotope effects using the Swain-Schaad
equation\(^{211}\) while the $pK_a$ values of the substrates in dilute aqueous
solution were calculated using an L.F.E.R. method (Section 4.2). These
data have been included in the Bronsted correlation\(^{129}\) of the rates of
protodetritiation of substituted fluorene and indene hydrocarbons in
methoxide-methanol at $45^\circ$C and the hydrocarbon $pK_a$ values in water.
The fit of the data is excellent, suggesting that carbanion formation and
elimination proceed at the same rate. This is perhaps the strongest
piece of evidence in favour of the "irreversible" E1cB mechanism.

The internal return E1cB mechanism has been discounted by comparisons
with data reported in the literature. Although evidence for the
"irreversible" E1cB mechanism is circumstantial and somewhat ambiguous,
it is favoured because it is the only mechanism that explains all the
kinetic data.

The deuterium isotope effects and Hammett $\rho$ values for the reactions
in methoxide-methanol and t-butoxide-t-butanol can be taken as evidence
for "anti-Hammond" behaviour. This is in line with Bunnett's predictions.\(^3\)
The $\beta$-carbon in the transition state is thought to be largely pyramidal.
In this case the extended Hammond postulate\(^{177}\) does not apply.\(^{176}\)

The "irreversible" E1cB mechanism also explains the anomalous
solvent effects on the rates of base-catalysed dehydrochlorination of DDT in methanol–water mixtures. The rates decreased as the water content of the solvent was increased. This is contrary to the trend noted for E2 reactions. The hydrogen nucleophilicity order for DDT must therefore follow the thermodynamic basicity order (OH⁻ > OMe⁻) and not the E2 reactivity order (OMe⁻ > OH⁻). A correlation of this type would be expected if the rate-determining step of the elimination mechanism was solely proton transfer.
PART III

ELIMINATION IN DIPOLAR APROTIC SOLVENTS
1. INTRODUCTION

1.1 THE E2C MECHANISM

In 1956 it was noted that weak bases, such as halide ions in acetone\(^{18}\) and mercaptide ions in alcoholic solvents,\(^{19}\) were remarkably effective in promoting second-order elimination. These weak bases are also very strong carbon nucleophiles and it had been suggested that their efficiency as eliminating agents is related to the nucleophilicity.\(^{20-25}\) A "merged" substitution-elimination mechanism was originally proposed.\(^{18,219}\) This was later rejected on stereoelectronic grounds.\(^{20,21}\) However, a modified transition state (termed the E2C transition state, where "C" designates B\(\cdots\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\) interaction) was presented\(^{21-25}\) which involved covalent interaction between the base and the \(\alpha\)-carbon of the substrate (II or III).

![Diagram](Image)

This interaction was invoked to compensate for the weak thermodynamic basicity of the base. Elimination promoted by strong bases (such as alkoxides and substituted phenoxides) are thought to proceed via the classical E2 mechanism. This mechanism is now termed E2H (I) by
The E2C transition state is as described by the latter workers "loose" with considerable double bond formation. There is little charge residing on the α- and β-carbon atoms, most of which is on the leaving group and the attacking base. The $C_\alpha - X$ and $C_\beta - H$ bonds are largely broken. The products of elimination promoted by weak bases in dipolar aprotic solvents arise from a strong preference for Saytzeff orientation from almost an exclusive anti pathway, which is a consequence of the $S_N^2$ rule demanding inversion of configuration at $C_\alpha$.

Winstein, Parker and co-workers reported that the chloride ion-promoted elimination of three-3-p-anisyl-2-butyl brosylate (IVa) and its erythro isomer (Va) in acetone, produced $> 99.9\%$ Saytzeff olefins.

![Diagram](https://via.placeholder.com/150)

The elimination pathway was $> 99.9\%$ anti since the erythro isomer gave this proportion of the cis-butene and the three-isomer gave the same proportion of the corresponding trans-butene. The reaction of (Vb) with chloride ion in acetone is $> 98\%$ anti- and the reaction of (IVb) is $> 80\%$ anti. This suggests a different transition state for (IVb) and (Vb), and is evidence against the "merged" mechanism which requires a common transition state for both stereoisomers and therefore a common product.

The reaction of menthyl tosylate (VI) with tetra-n-butylammonium
chloride in acetone produces almost exclusively the $\Delta^2$-menthene (> 98.2% Hofmann product).\textsuperscript{20,21} The reaction cannot give the $\Delta^3$-menthene by anti elimination. Therefore, the least stable olefin is produced. Neomenthyl tosy late (VII), however, produced the $\Delta^3$-olefin (97%) via an anti pathway.

\begin{align*}
\text{H} \\
\text{OTs} & \quad \text{anti-ee} \\
\text{H} & \quad \text{anti-aa} \\
\end{align*}

\begin{align*}
\text{H} & \quad \text{anti-ee} \\
\text{H} & \quad \text{anti-aa} \\
\text{OTs} & \quad \Delta^2\text{-menthene} \\
\text{VII} & \quad \Delta^3\text{-menthene} \\
\end{align*}

The effect of changes in solvent, base, substituents, and leaving group on the reactions of the cyclohexyl and cyclopentyl systems suggest that the E2C transition state is "loose".\textsuperscript{25} A noteworthy point is that the rates of elimination from a given substrate are faster in acetone than in t-butanol. Table 1 shows the rate constants for the dehydratosylation of cyclohexyl tosylate.

\textbf{TABLE 1.}

Rate Constants for the Elimination of Cyclohexyl Tosylate in Acetone\textsuperscript{25}

<table>
<thead>
<tr>
<th>Base\textsuperscript{a}</th>
<th>$10^4 k_2 E \text{ (1 mol}^{-1} \text{s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBr</td>
<td>7.25</td>
</tr>
<tr>
<td>n-\text{Bu}_4\text{NCl}</td>
<td>53.7</td>
</tr>
<tr>
<td>n-\text{Bu}_4\text{NBr}\textsuperscript{b}</td>
<td>5.13</td>
</tr>
<tr>
<td>n-\text{Bu}_4\text{NCl}\textsuperscript{b}</td>
<td>9.12</td>
</tr>
<tr>
<td>t-\text{BuOK}\textsuperscript{b}</td>
<td>5.89</td>
</tr>
</tbody>
</table>

\textsuperscript{a} In the presence of 2,6-lutidine. \textsuperscript{b} In t-butanol.
The rates of elimination promoted by halides in t-butanol and by t-butoxide in the same solvent are very similar. This seems to suggest that t-butanol can be regarded as an aprotic rather than a protic solvent. These results seem strange when it is realised that tetra-n-butylammonium chloride is ca. $10^{15}$ times less basic than potassium t-butoxide.

The rates of elimination and substitution of several cyclohexyl derivatives with a series of bases were correlated\textsuperscript{25} with a Swain-Scott type linear free energy relationship (L.F.E.R.).

$$\log k^E = n \log k^S + \text{constant} \tag{3.3}$$

The parameters $k^E$ and $k^S$ are the rate constants for the elimination and substitution reactions respectively. Linear correlations were obtained for the reactions of cyclohexyl tosylate, cyclohexyl bromide, and cis-2-methylcyclohexyl tosylate even though the slope was set at unity; an extra restriction on the L.F.E.R. On this basis the authors conclude that there is interaction between the base and the $\alpha$-carbon in the E2C transition state, emphasizing the $S_n^1$-2-like bonding at $C_\alpha$. Furthermore, the Bronsted correlation of the rates of elimination of cyclohexyl tosylate in acetone with the $pK_a$ values (in dimethylformamide) of the conjugate acids of the attacking bases was a scatter plot. The $pK_a$ values in acetone are not known but they should be linearly related to the values in dimethylformamide. The lack of a Bronsted correlation purportedly suggests that the rates of elimination of cyclohexyl derivatives with weak bases in acetone correlate with the carbon nucleophilicity order and not the hydrogen basicity order.\textsuperscript{25} A prerequisite for a good Bronsted correlation is that a series of structurally similar bases be used.\textsuperscript{220} A linear plot would not be expected for cyclohexyl tosylate since oxygen, sulphur, and halide bases are included in the series.\textsuperscript{25}
The effect of the leaving group on the rates of elimination and substitution of cyclohexyl compounds with tetra-n-butylammonium chloride in acetone\textsuperscript{25} was also correlated by equation (3.3). A slope of approximately unity was obtained from which it was concluded that changes at the $\alpha$-carbon in the $S_N2$ and E2C transition states are similar. However, Pryor\textsuperscript{210} has pointed out that good L.F.E.R. correlations do not necessarily imply similarity of mechanism.

Large $k_{\text{OTs}}/k_{\text{Br}}$ ratios were obtained for the elimination of cyclohexyl and cis-2-bromocyclohexyl derivatives with chloride and bromide ions in acetone.\textsuperscript{25} These ratios decreased as the thermodynamic basicity of the base was increased along the series: bromide, chloride, 4-nitrothiophenoxide, azide, acetate, 4-nitrophenoxide. It has been contended that large values of $k_{\text{OTs}}/k_{\text{Br}}$ suggest a "loose" transition state whilst small values indicate a "tight" transition state.\textsuperscript{91} However, $k_{\text{OTs}}/k_{\text{Br}}$ ratios are not now considered a reliable criterion of transition state character.\textsuperscript{89,221}

In a related paper Winstead, Parker, and co-workers\textsuperscript{22} reported the effect of substituents on the rates of elimination of acyclic systems. They found that E2C-like reactions of (VIII) and (IX) were accelerated up to 100-fold on the addition of a $\beta$-methyl group in contrast to the small effect on rates of E2H reactions.

\[(\text{VIII}) \quad \text{X = OTs, Br} \quad (\text{IX}) \quad \text{Y = H, Me}\]
The addition of a $\beta$-phenyl group in place of a $\beta$-methyl group increased the rate of $\text{E2H}$ reactions by up to $10^6$-fold while the rates of $\text{E2C}$ reactions are increased slightly. In fact phenyl and 4-methoxyphenyl have the same effect. This implied that there is little negative charge on the $\beta$-carbon atom, while the rate acceleration by all aryl groups implied a well-developed double bond in the transition state. However, the small rate effect of phenyl over methyl is not consistent with strong double bond development.

The addition of $\alpha$- and $\beta$-alkyl groups retard $\text{S}_\text{N2}$ reactions considerably, $\text{E2H}$ reactions are slightly retarded, but $\text{E2C}$ reactions are accelerated (in the absence of cis effects). The main effect of an $\alpha$-alkyl group on $\text{E2H}$ reactions is due to the non-bonded interactions. The effect of $\alpha$-methyl, ethyl, isopropyl, and t-butyl groups on $\text{E2C}$ rates of secondary and tertiary substrates is very similar. The rate acceleration is attributed to the non-bonded cis interactions being relieved on hybridization of the $\alpha$-carbon from $sp^3$ to partial $sp^2$ in the $\text{E2C}$ transition state. $\alpha$-Phenyl substituents accelerate $\text{E2H}$ reactions slightly compared with $\beta$-substituents. The rate enhancement of phenyl over methyl for these reactions is ca. 10-fold. In $\text{E2C}$ reactions phenyl and 4-nitrophenyl $\alpha$-substituents have approximately the same effect. The phenyl group should accelerate the rate more than the 4-nitrophenyl group if there were any positive charge development at the $\alpha$-carbon. It was noted that $\alpha$-methyl and $\alpha$-phenyl have similar effects on the rates. This also suggested that there is little positive charge development in the $\text{E2C}$ transition state.

Winston, Parker, and co-workers reported a trans/cis ratio of 5.8 for the formation of but-2-enes from 2-butyl bromide with bromide ion in acetone. In contrast Bartsch and co-workers reported trans/cis ratios of 3.36, 3.14, and 1.47 for the $\text{E2H}$ reactions of 2-butyl bromide.
with methoxide-methanol, ethoxide-ethanol, and t-butoxide-t-butanol respectively. These values are vastly different to that reported for 2-butyl bromide under weak base conditions and it was proposed that the greater degree of double bond character in E2C transition states gave rise to the higher trans/cis ratios.²²

The rates of dehydrobromination of t-butyl bromide with various bases in acetone were correlated with the rates of bimolecular substitution of cyclohexyl tosylate and n-butyl bromide²³ using equation (3.3). A slope of 1.66 was obtained for the correlation against the reactions of cyclohexyl tosylate. This suggested that the S₂ transition state for this compound is "looser" than the E2C transition state for t-butyl bromide. A poor correlation was obtained with the reactions of n-butyl bromide which have a "tight" S₂ transition state. Furthermore there was no Bronsted correlation. Winstein and Parker conclude that the rates of reaction of t-butyl bromide with a series of bases follow the carbon nucleophilicity order for a "loose" transition state. However, it must be noted once again that a linear Bronsted plot would not be expected since a series of unrelated bases was used.

Kevill, Weiler, and Cromwell²²²,²²⁴ reported Hammett ρ values for the dehydrobromination of p-substituted 2-benzyl-2-bromo-1-indanone (X) using tetraethylammonium chloride and bromide in acetonitrile (formation of exocyclic olefin).

![Chemical Structure](image)
Curved plots were obtained. However, average slopes of 0.42 and 0.16 were calculated for the chloride ion and bromide ion-promoted eliminations respectively. A deuterium isotope effect of 3.4 was reported for 

Primary deuterium isotope effects were reported for the chloride ion-promoted dehydratosylation of several alkyl tosylates.\textsuperscript{24} These were in the range of 2.3-3.2. For example, the isotope effects for 3-methyl-2-butyl tosylate and trans-4-t-butylcyclohexyl tosylate are 2.7 and 3.2 respectively. These values are well within the theoretical isotope effects of 2-4 calculated by More O’Ferrall\textsuperscript{47} as appropriate for E2C transition states.

1.2 THE E2H MECHANISM

An alternative view of weak base-promoted eliminations is that they can be explained by the E2H spectrum of transition states (XI-XIII).\textsuperscript{3,162,225-227}

![Diagram](image)

If the E2C transition state has B...C\textsubscript{\alpha} interaction similar to that in a S\textsubscript{N}2 transition state then it should be sensitive to steric hindrance at the \textalpha-carbon atom.

With this in mind Bunnett and Eck\textsuperscript{225-227} applied this mechanistic criterion to the elimination of secondary and tertiary alkyl bromides and
tosylates. They first examined the chloride ion-promoted elimination of t-butyl bromide (XIV) and 2-bromo-2,3,3-trimethylbutane (XV) in acetone and dioxane.\textsuperscript{225}

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{C} \quad \text{CH}_3 \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

(XIV)

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{C} \quad \text{C} \quad \text{CH}_3 \\
\text{Br} & \quad \text{Br} \quad \text{CH}_3
\end{align*}
\]

(XV)

The rate of elimination from (XV), which is the sterically hindered neopentyllic substrate, was twice as fast as that from (XIV) in either solvent. This was compared with the rates of bimolecular substitution of neopentyl bromide which reacts 240,000-fold more slowly than ethyl bromide with sodium ethoxide in ethanol\textsuperscript{228} and 160,000-fold more slowly with lithium chloride in dimethylformamide.\textsuperscript{229} It was concluded that the transition state for (XV) did not involve any B\cdots C\alpha interaction.

This was refuted by Cook and Parker\textsuperscript{22,230} who argued that there should be less neopentyllic effect on $S_N^2$ reactions at a tertiary than at a primary carbon. This was supported by the fact that the $S_N^2$ reaction of isopropyl bromide (XVI) is only 500 times faster than that for 2-bromo-3,3-dimethylbutane (XVII).

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{C} \quad \text{CH}_3 \\
\text{Br} & \quad \text{Br} \quad \text{CH}_3
\end{align*}
\]

(XVI)

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{C} \quad \text{C} \quad \text{CH}_3 \\
\text{Br} & \quad \text{Br} \quad \text{CH}_3
\end{align*}
\]

(XVII)

A similar rate difference was noted for the corresponding tosylate derivatives.\textsuperscript{22} They also reported that the $S_N^2$ reaction of (XV) with
azide ion in acetone was ca. 5 times slower than that for (XIV). There is some uncertainty about this data since it is based on a 3.5% difference in titres. 230

Bunnell and Eck 226 found that the rate of elimination of cyclohexyl tosylate with chloride ion in acetone is only 12 times faster than its 2,2-dimethyl analogue. There was no substitution reaction detected for the dimethyl analogue. These results are in contrast to the retardation of ca. 10^3 expected for a transition state involving B···Cα interaction. The 12-fold rate retardation is understandable in terms of the E2H mechanism. This can be attributed to 1,3-diaxial interaction between a methyl group and the base attacking the β-hydrogen.

Mercaptide:alkoxide rate ratios (K_{ETS}/K_{MeO}) of 0.55 and 1.7 were reported for the elimination of (XVI) and (XVII) respectively. 227 The predominant reaction for (XVI) was S_N2. However, no substitution product was detected for (XVII). It was estimated that the S_N2 reaction of (XVII) was slower than that of (XVI) by at least 1300-fold with methoxide ion and 28,000-fold with thioethoxide ion. This is based on a hypothetical rate constant of about 1% of the elimination rate constant. It was concluded that the transition state for the mercaptide-promoted elimination does not involve any B···Cα interaction.

Bunnell, Davis, and Tanida 231 reported deuterium isotope effects of 2.4-2.6 for the dehydrochlorination of 2-chloro-2-methyl-1-phenyl propane (XVIII) with sodium methoxide and sodium thioethoxide in methanol.

\[
\begin{align*}
\text{H} & \quad \text{CH}_3 \\
\text{H} & \quad \text{Cl} \\
\text{(XVIII)}
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{X} \\
\text{(XIX)} & \quad \text{X, a = Cl} \\
& \quad \text{b = Br}
\end{align*}
\]
Winstein and Parker\textsuperscript{24} have classified this reaction as E2C-like. However, the Hammett $\rho$ of 1.00 (for the formation of the Saytzeff olefin) for the elimination of (XVIII) with methoxide–methanol\textsuperscript{93} suggests a substantial amount of negative charge at the $\beta$-carbon.

Hayami, Ono, and Kaji\textsuperscript{232,233} reported that tetraethylammonium fluoride in acetonitrile promoted elimination from 2-phenethyl chloride (XIXa) 800 times faster than did ethoxide–ethanol. Hammett $\rho$ values of 2.03 and 1.88, and deuterium isotope effects of 3.99 and 5.03 were reported for (XIXa) and (XIXb) respectively. The Hammett $\rho$ values are the largest reported for halide-promoted eliminations in dipolar aprotic solvents and are vastly different from the $\rho$ of 0.57 for the $S_n^2$ reaction of (XIXa) with chloride ion ($^{36}\text{Cl}^-$) in acetonitrile.\textsuperscript{234}

The notion\textsuperscript{22} that only halide-promoted eliminations give high trans/cis ratios was discounted by Feit and co-workers\textsuperscript{235}. They found that as the base strength was increased along the series: bromide, fluoride, t-butoxide in acetone or dimethylformamide, the trans/cis ratio for 2-pentyl bromide increased from 4.2 to 5.8. These observations point out that high trans/cis ratios can no longer be regarded as a criterion of an E2C transition state.

Bartsch and co-workers\textsuperscript{236} reported recently that trans/cis ratios for weak base-promoted eliminations are not anomalously high. Instead the ratios in t-butoxide–t-butanol are anomalously low due to ion-pair association.

1.3 INTRODUCTION TO THE PRESENT RESEARCH

It was previously thought that the dehydrochlorination of 1,1-diaryl-2,2,2-trichloroethanes with strong bases in protic solvents were paenecarbonion E2H reaction.\textsuperscript{99-101} This conclusion was based on
the Hammett $\rho$ of 2.73 for the reaction with sodium hydroxide-ethanol,\textsuperscript{99,100} the deuterium isotope effect of 3.4 for the ethoxide-promoted reaction of 1,1-di(p-chlorophenyl)-2,2,2-trichloroethane (DDT) and the Bronsted $\beta$ of 0.88 for the substituted phenoxide-promoted reaction of the same compound in ethanol.\textsuperscript{101} The Bronsted $\beta$ of 0.77, the deuterium isotope effect of 3.1, and the Hammett $\rho$ of 2.11 for the thiophenoxide-promoted reaction led to similar conclusions.\textsuperscript{101,102}

The halide-promoted elimination of DDT was first studied by England and co-workers\textsuperscript{237} using tetra-n-butylammonium chloride in acetone. The reaction was found to be second-order in the presence of 2,6-lutidine which was used to scavenge eliminated hydrogen chloride. The Hammett $\rho$ value for this reaction\textsuperscript{162,238} is 1.31. At the time, this was the highest $\rho$ value reported for a halide-promoted reaction. It was concluded that the chloride ion-promoted elimination of the 1,1-diaryl-2,2,2-trichloroethanes was E2H on comparison with the $\rho$ values for the reactions in protic solvents. However, this comparison is now invalid since there is evidence to suggest that elimination promoted by alkoxides and mercaptide ions in alcoholic solvents proceed through an "irreversible" E1cB mechanism (see Part II, present research). The problem of mechanism is now approached from a different direction, using isotope effects as a guide.
2. EXPERIMENTAL

2.1 MATERIALS AND REAGENTS

The preparation of the 1,1-diaryl-2,2,2-trichloroethanes, the 1-deuterated analogues, and the isolation of the products have been outlined previously (see Part II, Experimental 2.2 and J.C.S. Perkin II, 1972, 2308).

Product Analysis of 1,1-di(p-chlorophenyl)-2,2,2-trichloroethane with Lithium Bromide in Dimethylformamide

A solution of 1,1-di(p-chlorophenyl)-2,2,2-trichloroethane (0.37 g, 0.052 mol) and lithium bromide (0.117 g, 0.067 mol) in dimethylformamide (20 ml) was allowed to react at 65° for 96 h. The reaction mixture was poured into 250 ml of water and the crude product filtered off. T.l.c. of the product indicated ca. 50% olefin. A mass spectral analysis showed no m/e 399 peak characteristic of the substitution product.

Tetra-n-butylammonium Chloride

Eastman Kodak laboratory grade tetra-n-butylammonium chloride was purified by the method outlined by Kay et al.\textsuperscript{239}

Tetra-n-butylammonium Perchlorate

This was prepared by the method outlined by Lloyd.\textsuperscript{240} A solution of sodium perchlorate (38 g) in 800 ml water was added slowly to tetra-n-butylammonium bromide (50 g) in 600 ml water. The precipitated salt was filtered off, washed with water, and recrystallized from methanol-water and anhydrous acetone-ether. The crystals were dried over phosphorous pentoxide at room temperature.
Lithium Chloride

BDH laboratory reagent anhydrous lithium chloride was recrystallized from anhydrous acetone. 241

Lithium Bromide

BDH laboratory reagent anhydrous lithium bromide was recrystallized from anhydrous acetone. 241

Potassium Chloride

RDH analytical reagent grade material was dried at 120°C for 24h before being used to make up standard solutions.

Silver Nitrate

AnalaR silver nitrate was dried at 120°C for 24h before being used to make up standard solutions.

Acetone

AnalaR acetone was dried over 4A molecular sieves and used without further purification.

Dimethylformamide

BDH laboratory reagent dimethylformamide was purified by the method outlined by Perrin et al. 160

Methanol

Commercial grade methanol was distilled prior to being used for spectroscopic analyses.

2.2 STOICHIOMETRY

The stoichiometry of the chloride ion-promoted elimination of
1,1-diaryl-2,2,2-trichloroethanes in acetone is shown in equation (3.4),

\[
\begin{align*}
\text{Ar} & \text{CH-CCl}_3 + \text{Cl}^- \rightarrow \text{Ar} \text{C=CCl}_2 + \text{HCl} + \text{Cl}^- \\
\text{Ar} & \text{Ar}
\end{align*}
\] (3.4)

when excess 2,4,6-collidine (or 2,6-lutidine) is used as a hydrogen chloride scavenger.\(^{162,237,238}\) 2,4,6-Collidine has no effect on the kinetics. In its absence the reaction reaches equilibrium rather than proceeding to completion.\(^{237}\) The reaction was found to obey pseudo first-order kinetics as given by equation (3.5) up to one half life.

\[
\text{Rate} = k_{\text{obs}} [\text{Ar}_2\text{CH:CCl}_3] \\
\] (3.5)

It thus appears that collidinium chloride remains as tight ion-pairs, releasing little, if any chloride ions for autocatalysis. Therefore, the concentration of free chloride ions in solution remains constant. The second-order rate constants \((k_2)\) are calculated from equation (3.6)

\[
k_2 = \frac{k_{\text{obs}}}{[\text{Cl}^-]_0} \\
\] (3.6)

After ca. 1 half life the observed first-order rate constants drift downwards. This has been attributed to the acid-catalysed condensation of acetone.\(^{242}\) The equilibrium constant for reaction (3.4) is given by equation (3.7):

\[
K = \frac{[\text{Ar}_2\text{C:CCl}_2][\text{HCl}^-]}{[\text{Ar}_2\text{CH:CCl}_3][\text{Cl}^-]} \\
\] (3.7)

The stoichiometry of the lithium chloride-promoted elimination of the 1,1-diaryl-2,2,2-trichloroethanes in dimethylformamide is the same as shown in equation (3.4). A hydrogen chloride scavenger is not necessary since no back-addition was detected when 1,1-di(p-chlorophenyl)-2,2-dichloroethene was exposed to dry hydrogen chloride in dimethylformamide.
over a period of several half-lives. Assuming that the reaction is autocatalytic, the rate equation for the reaction is given by equation (3.8)

\[
\frac{dx}{dt} = \text{Rate} = k_2'[Ar_2CH_2CCl_3][Cl^-] = k_2'(a - x)(a + x)
\]

where \(a\) is the initial concentration of the substrate and the base, and \(x\) is the concentration of the olefin at time \(t\). Integrating equation (3.9) and rearranging:

\[
k_2' = \frac{1}{2at} \ln \frac{a+x}{a-x}
\]

Rate coefficients \(k_2'\) calculated from equation (3.10) drifted downwards. Furthermore, second-order rate coefficients calculated on the basis of no autocatalysis were also not constant. 

It was thought that some of the catalytically active free chloride ion could be rendered inactive by forming a hydrogen bonded complex or an ion-pair with the protonated solvent molecule thereby causing imperfect autocatalysis.

\[
\text{DMF} \cdot H^+ + Cl^- \rightarrow \text{DMF} \cdot H^+ \cdot Cl^- \quad (3.11)
\]

The equilibrium constant for this is:

\[
K = \frac{[\text{DMF} \cdot H^+] [Cl^-]}{[\text{DMF} \cdot H^+ \cdot Cl^-]} \quad (3.12)
\]

The amount of active catalyst is given by:

\[
[Cl^-]_{\text{free}} = [Cl^-]_{\text{total}} - [\text{DMF} \cdot H^+ \cdot Cl^-] = [Cl^-]_{\text{total}} - \frac{[\text{DMF} \cdot H^+] [Cl^-]_{\text{free}}}{K} \quad (3.13)
\]

Since \([\text{DMF} \cdot H^+] = x\)
\[ [\text{Cl}^-]_{\text{total}} = a - x + 2x = a + x \quad (3.14) \]

and \[ [\text{Cl}^-]_{\text{free}} = \frac{a + x}{1 + x/K} \quad (3.15) \]

Substituting this into a revised form of equation (3.9)

\[ \frac{dx}{dt} = \frac{k_2(a - x)(a + x)K}{(k + x)} \quad (3.16) \]

or

\[ k_2t = \int_0^x \frac{dx}{a^2 - x^2} + K \int_0^x \frac{x \, dx}{a^2 - x^2} \quad (3.18) \]

Integrating equation (3.18) gives

\[ k_2 = \frac{1}{2at} \ln \frac{a + x}{a - x} + \frac{1}{kt} \ln \frac{a}{a^2 - x^2} \quad (3.19) \]

or

\[ k_2 = k_2' + \frac{1}{kt} \ln \frac{a}{a^2 - x^2} \quad (3.20) \]

where \( k_2 \) is the true rate constant.

The true values of \( k_2 \) and the equilibrium constant \( K \) are not known but are calculated by an iterative process. This method employs the drifting \( k_2' \) values to estimate values of \( K \) which give consistent \( k_2 \) values. These are further refined by least squares. The value of \( K \) needed for convergence must of course be independent of the substrate used. However, \( K \) is susceptible to experimental errors and values ranging from 0.5 to 0.9 mol l\(^{-1}\) were obtained. A mean value of 0.7 mol l\(^{-1}\) based on data from 17 substrates was used in the final calculations.

The reactions were followed spectrophotometrically. If \( A_0 \), \( A_t \) and \( A_\infty \) are the absorbances at time zero, \( t \), and infinity respectively, and \( \epsilon_s \) and \( \epsilon_p \) are the molar extinction coefficients of the substrate and
product respectively then:

\[ A_0 = a \varepsilon_s l \]  \hspace{1cm} (3.21)

\[ A_\infty = a \varepsilon_p l \]  \hspace{1cm} \text{l = 1 cm}  \hspace{1cm} (3.22)

\[ A_t = (\varepsilon_s c_s + \varepsilon_p c_p) \]
\[ = \frac{A_0(a - x) + A_\infty x}{a} \]  \hspace{1cm} (3.23)

Rearranging equation (3.23)

\[ x = \frac{a(A_t - A_0)}{(A_\infty - A_0)} \]  \hspace{1cm} (3.24)

\[ a + x = \frac{(A_\infty + A_t - 2A_0)}{A_\infty - A_0} \]  \hspace{1cm} (3.25)

\[ a - x = \frac{A_\infty - A_t}{A_\infty - A_0} \]  \hspace{1cm} (3.26)

Substituting equations (3.24-6) into equation (3.20) gives:

\[ k_2 = \frac{1}{2at} \ln \left( \frac{A_\infty + A_t - 2A_0}{A_\infty - A_0} \right) + \frac{1}{kt} \ln \left( \frac{1}{a(1 - (A_t - A_0)^2)/(A_\infty - A_0)^2} \right) \]  \hspace{1cm} (3.27)

The lithium bromide-promoted elimination of the 1,1-diaryl-2,2,2-trichloroethanes in dimethylformamide involve a competitive-consecutive second-order reaction sequence. Exact integration is not possible.

\[ \text{Ar} / \text{CH-CCl}_3 + \text{Br}^- \xrightarrow{k_1} \text{Ar} / \text{C=CCl}_2 + \text{H}^+ + \text{Br}^- + \text{Cl}^- \]  \hspace{1cm} (3.28)
The rate equation is given by:

\[- \frac{d[Ar_2CH_3CCl_3]}{dt} = k_1[Ar_2CH_3CCl_3][Br^-] + k_2[Ar_2CH_3CCl_3][Cl^-]\]  \hspace{1cm} (3.30)

\[- \frac{d[Ar_2CH_3CCl_3]}{[Ar_2CH_3CCl_3]} = k_1[Br^-]dt + k_2[Cl^-]dt\]  \hspace{1cm} (3.31)

\[\int_0^t \frac{d[Ar_2CH_3CCl_3]}{[Ar_2CH_3CCl_3]} = k_1 \int_0^t [Br^-]dt + k_2 \int_0^t [Cl^-]dt\]  \hspace{1cm} (3.32)

\[\ln \frac{[Ar_2CH_3CCl_3]_o}{[Ar_2CH_3CCl_3]_t} = k_1 \int_0^t [Br^-]dt + k_2 \int_0^t [Cl^-]dt\]  \hspace{1cm} (3.33)

To solve the simultaneous equations (3.32) and (3.33), the concentrations of the substrate, bromide ion, and chloride ion must be known at least two times, \(t\), and \(t_2\). Saville\(^{244}\) has developed a method of estimating the concentration-time integrals by graphical means. The rate constant \(k_2\) for the chloride ion-promoted elimination is known independently and the bromide ion concentration is constant with respect to time. Therefore, the concentration of chloride ion with respect to time is the only integral required to be solved. The amount of chloride ion liberated is given by:

\[[Cl^-]_t = [Ar_2CH_3CCl_3]_o - [Ar_2CH_3CCl_3]_t\]  \hspace{1cm} (3.34)

Equation (3.31) becomes:

\[\ln \frac{[Ar_2CH_3CCl_3]_o}{[Ar_2CH_3CCl_3]_o-[Cl^-]_t} = k_1[Br^-]_o t + k_2 \int_0^t [Cl^-]dt\]  \hspace{1cm} (3.35)
The amount of chloride and bromide ion is analysed by potentiometric titration.

2.3 KINETICS

Runs in acetone and dimethylformamide at 65°C were carried out using 10 ml sealed ampoules. Approximately equimolar quantities of substrate and tetra-n-butylammonium chloride (ca. 0.02M) were used for the reactions in acetone. The ionic strength of the medium was maintained by adding ca. 0.4M tetra-n-butylammonium perchlorate. The reaction mixture of the required concentrations was made up under a stream of dry nitrogen and ca. 5 ml aliquots were pipetted into 10 ml ampoules. These were sealed and thermostated. Samples were removed and the reaction was quenched by immersing the ampoules in an ice bath. A 5 ml aliquot was pipetted out and the amount of chloride ion determined by potentiometric titration against standard silver nitrate solution using a Radiometer TTT1d automatic titrator coupled to a SBR2c recorder. The electrodes were a silver indicator electrode and a calomel reference electrode. The electrical circuit was completed by a potassium nitrate-agar salt bridge.

The lithium chloride-promoted eliminations in dimethylformamide were followed spectrophotometrically using a Shimadzu QV-50 spectrophotometer. The reaction mixtures were made up under a stream of nitrogen and ca. 5 ml was transferred into ampoules. These were sealed and thermostated. Samples were removed at various intervals of time and quenched. A 1 ml aliquot was removed, using 1 ml A grade pipette, and transferred to a 250 ml volumetric flask. The sample was diluted to 250 ml using distilled methanol and analysed at the wavelengths given previously (Part II, Experimental 2.5). Blank solutions contained 1 ml of solvent diluted to 250 ml with methanol. Zero time was taken to be 2 min. after
the ampoules were thermostated. The u.v. spectra of the infinity samples were identical to those of the authentic olefins. Experimental infinities measured after ten half-lives were in agreement with the calculated infinities.

The lithium bromide-promoted reactions were followed potentiometrically. Samples (4 ml) were titrated against standard silver nitrate in the presence of 10% barium nitrate solution added to prevent, as far as possible, co-precipitation of silver bromide and silver chloride.\textsuperscript{23}
3. RESULTS

Second-order rate constants for the reaction of the 1,1-diaryl-2,2,2-trichloroethanes and 1-deuterated analogues with lithium chloride in dimethylformamide are shown in Table 1. Details of individual runs are shown in the Appendix.

TABLE 1.

Rate Constants for the Elimination of Ar₂CH ·CCl₃ and Ar₂CD·CCl₃ with LiCl in DMF

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Temp °C</th>
<th>$10^5 k_2$ (1 mol⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p-NO₂C₆H₄)₂CH·CCl₃</td>
<td>55</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>408</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>1160</td>
</tr>
<tr>
<td>(p-NO₂C₆H₄)₂CD·CCl₃</td>
<td>65</td>
<td>77.7</td>
</tr>
<tr>
<td>(p-ClC₆H₄)₂CH·CCl₃</td>
<td>65</td>
<td>54.6</td>
</tr>
<tr>
<td>(p-ClC₆H₄)₂CD·CCl₃</td>
<td>65</td>
<td>9.74</td>
</tr>
<tr>
<td>Ph₂CH·CCl₃</td>
<td>65</td>
<td>9.54</td>
</tr>
<tr>
<td>Ph₂CD·CCl₃</td>
<td>65</td>
<td>2.22</td>
</tr>
<tr>
<td>(p-CH₃C₆H₄)₂CH·CCl₃</td>
<td>65</td>
<td>9.23</td>
</tr>
<tr>
<td>(p-CH₃C₆H₄)₂CD·CCl₃</td>
<td>65</td>
<td>1.77</td>
</tr>
</tbody>
</table>

\(^a\) Ref. 162 reports $\Delta H^\ddagger = 22.5$ k cal mol⁻¹, $\Delta S^\ddagger = -10.1$ cal K⁻¹ mol⁻¹

\(^b\) Ref. 162 reports $\Delta H^\ddagger = 21.8$ k cal mol⁻¹, $\Delta S^\ddagger = -14.7$ cal K⁻¹ mol⁻¹

All the rate constants are corrected for imperfect autocatalysis and are the mean of two or more concordant runs. The lithium chloride and
the substrate concentrations were 0.0200M in all cases. The activation parameters for 1,1-di(p-nitrophenyl)-2,2,2-trichloroethane, as calculated from a nicely linear Arrhenius plot are; $\Delta H^\ddagger = 23.4 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -2.7 \text{ cal K}^{-1} \text{ mol}^{-1}$.

In Table 2 are shown the equilibrium constants for the reaction of the 1,1-diaryl-2,2,2-trichloroethanes with tetra-n-butylammonium chloride in acetone at 65°C.

### TABLE 2.

Equilibrium Constants for the Reaction of $\text{Ar}_2\text{CH} \cdot \text{CCl}_3$ with $\text{n-Bu}_4\text{NCl}$

in Acetone at 65°C

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$X^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p-$\text{NO}_2\text{C}_6\text{H}_4$)$_2\text{CH} \cdot \text{CCl}_3$</td>
<td>27.1</td>
</tr>
<tr>
<td>(p-$\text{BrC}_6\text{H}_4$)$_2\text{CH} \cdot \text{CCl}_3$</td>
<td>35.5</td>
</tr>
<tr>
<td>(p-$\text{ClC}_6\text{H}_4$)$_2\text{CH} \cdot \text{CCl}_3$</td>
<td>27.9</td>
</tr>
<tr>
<td>$\text{Ph}_2\text{CH} \cdot \text{CCl}_3$</td>
<td>0.399</td>
</tr>
<tr>
<td>(p-$\text{MeC}_6\text{H}_4$)$_2\text{CH} \cdot \text{CCl}_3$</td>
<td>0.148</td>
</tr>
<tr>
<td>(p-$\text{MeOC}_6\text{H}_4$)$_2\text{CH} \cdot \text{CCl}_3$</td>
<td>0.145</td>
</tr>
</tbody>
</table>

$a$ $\text{ca. } 0.02M$

$b$ In the presence of $0.406\text{M n-Bu}_4\text{NClO}_4$

These values are the average of two or more concordant runs.

Aliquots were analysed after thermostating for $\text{ca. } 8$ days. In each case the solvent acetone was coloured dark yellow indicating acid-catalysed condensation had occurred.

No rate constants have been reported for the lithium bromide-
promoted reactions of the 1,1-diaryl-2,2,2-trichloroethanes, since a satisfactory analytical technique for determining the chloride ion concentration in the presence of bromide ion could not be developed. The potentiometric titrations of the mixed halides in the presence of 10% barium nitrate solution produced erroneous results. With 0.1 M each of bromide and chloride ions, silver chloride should begin precipitating out when:

$$\dfrac{[Ag^+]}{[Cl^-]} = \dfrac{K_{AgCl}}{0.1} = 1.7 \times 10^{-10}$$  \hspace{1cm} (3.36)

$$= 1.7 \times 10^{-9} \text{M}$$

The bromide ion concentration at this point is:

$$\dfrac{[Br^-]}{[Ag^+]} = \dfrac{K_{AgBr}}{1.7 \times 10^{-9}} = 3.3 \times 10^{-13}$$  \hspace{1cm} (3.37)

$$= 1.9 \times 10^{-4} \text{M}$$

This is 0.19% of the initial bromide ion concentration. In practice the titration of mixed halides is not as accurate as predicted. Even under the most favourable conditions with equal concentrations of halide ions the titration errors are ca. 2%. These errors become larger when the bromide ion concentration is increased relative to that of chlorine ion.
4. DISCUSSION

4.1 REACTIONS IN DIMETHYLFORMAMIDE

Primary deuterium isotope effects calculated from individual rate constants for the dehydrochlorination of the 1,1-diaryl-2,2,2-trichloroethanes and their 1-deuterated analogues with lithium chloride in dimethylformamide are shown in Table 1.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Isotope Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-NO₂</td>
<td>5.26</td>
</tr>
<tr>
<td>p-Cl</td>
<td>5.60</td>
</tr>
<tr>
<td>H</td>
<td>4.50</td>
</tr>
<tr>
<td>p-MeO</td>
<td>5.20</td>
</tr>
</tbody>
</table>

The isotope effect for 1,1-diphenyl-2,2,2-trichloroethane is lower than the values for the other derivatives. It is estimated that the rate constants may be in error by up to 6%, so that the errors in the isotope effects will be of the order ± 12%. Thus, within experimental uncertainty the isotope effects are insensitive to the change in para substituent. This means that the rate constants for the protium and deuterium compounds are described by the same L.F.E.R. It was suggested that an isotope effect maximum may be observed as β-aryl substituents are changed from electron donating to electron withdrawing ones. 75
However, this was not observed in the isotope effects for the alkoxide-promoted eliminations of the 1,1-diaryl-2,2,2-trichloroethanes nor in several other cases. 82,95,97,199

The theoretical maximum isotope effect\textsuperscript{45,46} for a linear, three-centre proton transfer, at 25°C is about 7.0. The isotope effect for the chloride ion-promoted elimination of the 1,1-diaryl-2,2,2-trichloroethanes at 65°C corresponds to a value of ca. 6.8 at 25°C. This figure is calculated from equation (3.39) which can be derived from equation (3.38),

\[ \log k = - \frac{E_a}{2.303 \, RT} + \text{constant} \tag{3.38} \]

\[ \log \frac{k_1^H}{k_1^D} - \log \frac{k_2^H}{k_2^D} = \frac{E_D - E_H}{2.303 \, R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \tag{3.39} \]

The activation energy for the deuterium compound has not been measured but \(E_D - E_H\) is assumed to be equal to zero point energy difference which in turn is assumed to be 1.15 kcal mol\textsuperscript{-1}. The isotope effects for the 1,1-diaryl-2,2,2-trichloroethanes are much greater than the theoretical values of 2–4 calculated by More O’Ferrall for the E2C transition state.\textsuperscript{47}

The calculations were based on a 5-centre model,

\[ \begin{array}{c}
0.5 \\
H \\
\beta \\
0.5 \\
C \\
\end{array} \]

with bond orders of 0.1, 0.5, and 0.5 for the partial C\textsubscript{a} – S, S – H and C\textsubscript{β} – H bonds respectively. Isotope effects calculated for proton transfer to alkoxide, mercaptide and chloride ions are shown in Table 2.


On comparison with the data in Table 2 it is clear that the transition state for the dehydrochlorination of the 1,1-diaryl-2,2,2-trichloroethanes is predominantly linear with the proton approximately half-transferred. The Hammett $\rho$ value for this reaction in dimethylformamide $^{162}$ is 0.99. This indicates that a substantial amount of negative charge resides on the $\beta$-carbon. This in turn implies a small amount of double bond character in the transition state. If there was extensive double bond formation coupled with the large Hammett $\rho$ value then a lower isotope effect would be expected on the basis of a greater degree of coupling of the atomic motions of the proton, the central carbons, and the leaving group. $^{214}$

The $\rho$ values for the fluoride ion-promoted elimination of 2-arylethyl bromides and the corresponding chlorides in acetonitrile are $^{232,233}$ 1.88 and 2.03 respectively. The primary deuterium isotope effects for these reactions are 5.03 ($5.0^\circ C$) and 3.99 ($35.0^\circ C$) respectively. This leads to the conclusion that the mechanism for fluoride ion-promoted eliminations of the 2-arylethyl halides is E2H on comparison with the $\rho$ values of 2.14 and 2.61 for the reactions of the bromide
and the chloride in ethoxide-ethanol. Furthermore the isotope effects for the reactions in acetonitrile are of a magnitude expected for an E2H reaction, disregarding temperature effects. The $\rho$ value for the chloride ion-promoted eliminations of the 1,1-diaryl-2,2,2-trichloroethanes is approximately half of that obtained for the fluoride ion-promoted of the 2-arylethyl halides. This is expected since the three electronegative chlorines on the $\alpha$-carbon of the former compounds would reduce the electron density at the $\beta$-carbon. Also, fluoride ion is a stronger base than chloride ion in dipolar aprotic solvents. Therefore a greater degree of proton transfer to the stronger base would be expected.$^3$ The Hammett $\rho$ for the halide-induced eliminations of the 2-arylethyl halides and the 1,1-diaryl-2,2,2-trichloroethanes are, like the isotope effects, out of line with those reported for elimination of "loose" substrates such as 2-benzyl-2-bromo-1-indanone$^{223,224}$ for which the E2C mechanism has been proposed.

4.2 REACTIONS IN ACETONE

The equilibrium constants for the reaction

$$\text{Ar}_2\text{CH-CCl}_3 + \text{Cl}^- \rightarrow \text{Ar}_2\text{C} = \text{CCl}_2 \cdot + \text{HCl}_2^- \quad (3.40)$$

in acetone in the absence of 2,4,6-collidine show a large substituent effect (Table 2, Results). The data plotted against $2\sigma^-$ or against the rate constants for the dehydrochlorination in the presence of 2,4,6-collidine$^{162,238}$ produce scatter diagrams.

The pattern of equilibrium constants for reaction (3.40) is contrary to the results reported for the acid-catalysed equilibration of 1,3-diarylallyl alcohols$^{245,247}$ and the acid-catalysed hydration of substituted styrenes.$^{248}$ Bernstein$^{246}$ reported rate and equilibrium constants for the reaction of 1,3-diarylallyl alcohols catalysed by
hydrochloric acid in 60% aqueous dioxane.

\[ \text{\begin{align*}
\text{OH} & \quad \text{H}^+ & \quad \text{OH} \\
\text{X} & \quad \text{X}
\end{align*}} \]

The equilibrium constants are approximately unity for the substituents p-nitro, bromo, and methoxy. Neither is there any change when the phenyl group is replaced by \( \alpha- \) or \( \beta- \) naphthyl groups.\(^{247}\) Therefore, there is no differential interaction between the substituents and the C = C double bond as opposed to the C – C single bond in the ground state. However, as far as the rates of rearrangement in the forward direction are concerned,\(^{246}\) \( \rho^* \) is -2.7, indicating a substantial substituent effect on the rate, and therefore a strong differential interaction in the initial and transition states.

Schubert and Keeffe\(^{248}\) found that an equilibrium amount of styrene of ca. 2.5–2.9\% was obtained for the acid-catalysed hydration of styrenes.

\[ \text{ArCH=CH}_2 \xrightarrow{\text{H}_2\text{O}} \text{Ar-CH-CH}_3 \xrightarrow{-\text{H}_2\text{O}} \text{Ar-CH-CH}_3 \text{OH} \] (3.42)

This proportion was invariant as the substituent was changed from p-methoxy to p-chloro. The kinetic \( \rho^* \) is -3.6 for the hydration.

The anomalous equilibrium constants in the present case are possibly a consequence of the acid-catalysed condensation of acetone.\(^{242}\) Another important factor is the decomposition of tetra-n-butylammonium chloride to form 1-butene, tributylamine, butyl chloride, and hydrogen chloride. The rate constant for this reaction in acetone\(^{25}\) is \(8.5 \times 10^{-7} \text{ mol}^{-1} \text{s}^{-1}\) at 75\(^\circ\)C. This decomposition would definitely interfere with the rate of dehydrochlorination of 1,1-di(p-tolyl)-2,2,2-trichloroethane and the
p-methoxy analogue.

England and Ang\textsuperscript{237a} found that the equilibrium constant for the reaction between 1,1-di(p-chlorophenyl)-2,2,2-trichloroethane (DDT) and chloride ion in acetone varied between 12 and 29 according to the chloride ion concentration. These reactions were carried out in the absence of 2,6-lutidine or 2,4,6-collidine and of tetra-n-butylammonium perchlorate. The variation in the equilibrium constant may be due to a salt effect, as well as to the condensation of the solvent and to the decomposition of tetra-n-butylammonium chloride.

The effect of solvent condensation and base decomposition will be less pronounced the more rapidly is the equilibrium attained. It is therefore noteworthy that the equilibrium constants for the three most reactive substrates in Table 2 of the previous section are in fact almost identical. If this is the case, $\rho(\text{equilibrium}) \approx 0$, while $\rho(\text{rate})$ is 1.31. The conclusion that can then be drawn is that the transition state in the forward reaction does not resemble the olefinic products. The Parker-Winstein E\textsubscript{2}C transition state, as has been previously mentioned is held to be largely olefin-like, and so, with reservations, it may be concluded that the equilibrium study provides further evidence against an E\textsubscript{2}C process in the chloride ion-promoted eliminations of the 1,1-diaryl-trichloroethanes.

If the dehydrochlorination of the 1,1-diaryl-2,2,2-trichloroethanes is E\textsubscript{2}H then the back-addition of hydrogen chloride to the olefins has to be termolecular since the principle of microscopic reversibility requires the reverse addition reaction to go through the same transition state as the forward reaction.\textsuperscript{249} There is a precedent for a mechanism of this type. A termolecular process has been proposed for the \underline{anti} addition of hydrogen chloride to cyclohexene and 1,2-dimethylcyclohexene\textsuperscript{250} in acetic acid. In both these cases the rate equation was found to contain
both a second-order and a third-order term. The third-order term is dominant at high concentrations of added chloride. This is thought to be mechanistically consistent with a trans, termolecular addition process utilizing a transition state of the form:

\[
\begin{array}{c}
\text{Cl}^- \\
\text{H}^+ \\
\text{C}^+ \\
\text{C} \quad \text{C}^+ \\
\text{Cl}^-
\end{array}
\]

However, not all hydrogen chloride addition reactions follow this process. The addition of this reagent to 1-methylcyclopentene in nitromethane is a non-synchronous process.\textsuperscript{251} This is in accord with a carbonium ion mechanism while the addition of hydrogen chloride to t-butylethylene in acetic acid involves an ion-pair intermediate.\textsuperscript{252}

4.3 THE DDT:DDD RATE RATIO

Winston, Parker, et al.\textsuperscript{22} noted that the rates of E2C-like reactions were accelerated by bulky α- and β-substituents. The enhancement of the rate was attributed to non-bonded interactions being relieved on changing from sp\textsuperscript{3} hybridization in the initial state to near-sp\textsuperscript{2} hybridization in the transition state. On this basis 1,1-di(p-chlorophenyl)-2,2,2-trichloroethane (DDT) should be more reactive than 1,1-di(p-chlorophenyl)-2,2-dichloroethane (DDD) in E2C reactions.

On the other hand, the opposite prediction can be made on the basis of a different premise. The E2C transition state is S\textsubscript{N}2-like as far as the bonding situation at the α-carbon is concerned. It is known
that an accumulation of \( \alpha \)-bound halogens retard \( S_{N2} \) rates,\(^{254} \) so it might be expected that DDT would be less reactive than DDD were the E2C mechanism operative.

It was deduced that the DDT:DDD elimination rate ratio is at least 23 per labile chlorine.\(^{102} \) This is based on the rates of reaction of thiophenoxyde with DDT and DDD, and on the fact that < 0.5% olefin is produced in the reaction of DDD with thiophenoxyde. Similarly the DDT:DDD rate ratio with chloride ion is at least 70 per chlorine. The DDT:DDD elimination rate ratio with ethoxide-ethanol\(^{101,253} \) is 3.6 at 45°C. However, the DDD:DDT \( S_{N2} \) rate ratio with thiophenoxyde ion is at least \( 1.5 \times 10^{5} \) suggesting on the basis of the effects of \( \alpha \)-halogens on \( S_{N2} \) rates that the reaction of DDT with thiophenoxyde* and chloride ions is E2H rather than E2C.

Since the observed DDT:DDD rate ratio is also in accord with the E2C mechanism, potential energy calculations have been carried out in order to estimate the extent of the potential-energy changes (\( \Delta W \)) when non-bonded interactions are relieved in the E2C transition states for DDT and DDD. The model situations at \( C_{\alpha} \) are taken as:

\[
\begin{align*}
\text{CCl}_2(sp^3) & \rightarrow \text{CCl}_2(sp^2) \\
\text{CHCl}(sp^3) & \rightarrow \text{CHCl}(sp^2)
\end{align*}
\]

(3.43) (3.44)

The potential energy equation used in the calculations is:

\[
W = W(\text{dispersion}) + W(\text{van der Waals}) + W(\text{dipole-dipole})
\]

(3.45)

This is similar to the one used for calculating steric contributions to the rates of \( S_{N2} \) reactions.\(^{255} \) However, the ion-dipole interaction

* This mechanism is now thought to be "irreversible" E1cB, which may be regarded as an extreme case of the E2H mechanism.
term in the latter is replaced by a dipole-dipole interaction term.\(^{256}\)

For the system

\[\begin{align*}
\mu_x \text{ and } \mu_y \text{ are the dipole moments of } C - X \text{ and } C - Y, \alpha_x \text{ and } \alpha_y \text{ are the} \\
\text{atomic polarizabilities of } X \text{ and } Y, \text{ and } I_x \text{ and } I_y \text{ are the ionization} \\
\text{potentials of } X \text{ and } Y. \text{ The London dispersion force}^{257} \text{ of interaction} \\
\text{(attractive) is given by:}
\end{align*}\]

\[W(\text{dispersion}) = \frac{3}{2} \times \frac{2.1 \times \alpha_x \alpha_y I_x I_y}{r^6 (I_x + I_y)} \quad (3.46)\]

The van der Waals repulsive force\(^{255}\) is given by

\[W(\text{van der Waals}) = B e^{-r/0.345} \quad (3.47)\]

where the empirical factor \(B\) is obtained by setting \(\delta n/\delta r = 0\) and

substituting the sum of the appropriate van der Waals radius for \(r\).

The dipole-dipole interaction term\(^{256}\) is:

\[W(\text{d-d}) = \frac{2 \mu_x \mu_y}{r^3} \left(2 \cos \theta_x \cos \theta_y + \sin \theta_x \sin \theta_y \right) \quad (3.48)\]

Assuming that the \(sp^2\) configurations refer to the \(E2C\) transition

states, and that all other things in the hypothetical DDT and DDD \(E2C\)

transition states are equivalent, then equation (3.49) gives the

theoretical rate ratio.

\[
\frac{\Delta W_{\text{DDD}} - \Delta W_{\text{DDT}}}{2.303 \ \text{RT}} = \frac{\Delta G^c_{\text{DDD}} - \Delta G^c_{\text{DDT}}}{2.303 \ \text{RT}}
\]
\[ \log \frac{k_{\text{DDT}}}{k_{\text{DDD}}} \]  

(3.49)

Two sets of DDT:DDD rate ratios are reported. The first set shown in Table 3 is based on average covalent radii for C–Cl and C–H bonds attached to sp$^3$ and sp$^2$ carbon atoms.\textsuperscript{258} The r values are calculated from these bond lengths and from the appropriate bond angles. The appropriate dipole moments, atomic polarizabilities, and ionization potentials used in both sets of calculations are given in the Appendix.

**TABLE 3.**

Potential Energy Changes for the Dehydrochlorination of DDT and DDD

<table>
<thead>
<tr>
<th></th>
<th>DDT</th>
<th>DDE</th>
<th>DDD</th>
<th>DDDE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(r=2.87 Å)</td>
<td>(r=2.86 Å)</td>
<td>(r=2.33 Å)</td>
<td>(r=2.27 Å)</td>
</tr>
<tr>
<td>Dispersion</td>
<td>4.689</td>
<td>4.788</td>
<td>3.082</td>
<td>3.604</td>
</tr>
<tr>
<td>van der Waals</td>
<td>4.560</td>
<td>4.694</td>
<td>6.533</td>
<td>7.774</td>
</tr>
<tr>
<td>W</td>
<td>8.316</td>
<td>8.957</td>
<td>0.515</td>
<td>0.787</td>
</tr>
<tr>
<td>ΔW</td>
<td>0.641</td>
<td></td>
<td>0.272</td>
<td></td>
</tr>
</tbody>
</table>

In this case:

\[ \frac{k_{\text{DDT}}}{k_{\text{DDD}}} = 0.882 \text{ (at } 65^\circ\text{C)} \]

In the second set shown in Table 4 measured bond lengths\textsuperscript{259} in compounds such as CH$_2$=CHCl, CH$_3$–CCL$_2$, CH$_3$–CHCl$_2$ and CH$_2$=CCL$_2$ are used.
TABLE 4.

Potential Energy Changes for the Dehydrochlorination of DDT and DDD

<table>
<thead>
<tr>
<th>P.E.</th>
<th>DDT  (r=2.89 Å)</th>
<th>DDE  (r=2.93 Å)</th>
<th>DDD  (r=2.34 Å)</th>
<th>DDDE (r=2.44 Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipole-dipole</td>
<td>8.271</td>
<td>8.418</td>
<td>-2.899</td>
<td>-2.724</td>
</tr>
<tr>
<td>Dispersion</td>
<td>4.497</td>
<td>4.141</td>
<td>3.004</td>
<td>2.336</td>
</tr>
<tr>
<td>van der Waals</td>
<td>4.303</td>
<td>3.832</td>
<td>6.346</td>
<td>5.635</td>
</tr>
<tr>
<td>W</td>
<td>8.077</td>
<td>8.108</td>
<td>0.443</td>
<td>0.575</td>
</tr>
<tr>
<td>ΔW</td>
<td>0.031</td>
<td></td>
<td></td>
<td>0.132</td>
</tr>
</tbody>
</table>

\[ \frac{k_{DDT}}{k_{DDD}} = 1.16 \text{ (at 65°)} \]

In both cases the rate ratios are small. The latter set is probably the most realistic since the atoms X and Y are further apart in the sp² cases. The dipole-dipole and van der Waals interactions are almost balanced by the London forces. There is no correspondence between the calculated rate ratios and the experimental values. It thus may be concluded on the basis of these admittedly imperfect calculations that the increase in the number of α-chlorines has no effect on the rate if the α-carbon is almost sp² hybridized. They should have little effect on the β-carbon in an E2C transition state since C₂ is held to bear little if any negative charge in such a species. Hence DDT and DDD should react at much the same rate were the elimination mechanism E2C. This is contrary to the fact as far as the use of chloride ions in acetone is concerned, and so a further line of evidence against the operation of the E2C mechanism in the reactions under consideration.
5. CONCLUSION

The primary deuterium isotope effects for the chloride ion-promoted elimination of the 1,1-diaryl-2,2,2-trichloroethanes in dimethylformamide are outside the range of those calculated for an E2C transition state.\(^{47}\) Previously\(^{102,238}\) it was estimated that \(\rho\) for an E2C reaction is ca. 0.5. The chloride ion-promoted elimination of 2-benzyl-2-bromoindan-1-ones in acetonitrile has a \(\rho\) of 0.44 while \(\rho\) is 0.17 for the corresponding bromide promoted reaction.\(^{223}\) The \(\rho\) value for the bromide-induced dehydrobromination of 1-aryl-2-bromopropanes in acetone is 0.48.\(^{240}\) Also \(\rho\) for the \(S_N^2\) chloride isotope exchange reaction of 2-arylethyl chloride in acetonitrile\(^{234}\) is 0.57. These values are different to the \(\rho\) values of 0.99 and 1.31 reported for the chloride ion-induced elimination of the 1,1-diaryl-2,2,2-trichloroethanes in dimethylformamide and acetone respectively.

The equilibrium constants measured for the reaction of the 1,1-diaryl-2,2,2-trichloroethanes with chloride ion in acetone in the absence of 2,4,6-collidine run contrary to the trends reported in similar studies. This anomaly is attributed partly to the condensations of the solvent and to the decomposition of tetra-n-butylammonium chloride, but a suggestion that the transition state is not olefin-like has been made. A termolecular mechanism is proposed for the back-addition reaction. This would be consistent with an E2H mechanism for the dehydrochlorination reaction. The hydrochlorination is anti-Markownikoff since the starting material is regenerated. This could be taken as evidence for an addition mechanism that does not follow the normal electrophilic pathway.
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APPENDIX I

DETAILS OF REPRESENTATIVE KINETIC RUNS

All rate constants are uncorrected for solvent expansion. The concentrations quoted at the beginning of each run are those of the reactants at zero time. All concentrations are in moles per litre (M).

Run 44  \((p-\text{MeOC}_6\text{H}_4)_2\text{CHCCl}_3/\text{NaOMe/MeOH}/30^\circ\text{C}\)

\([\text{Ar}_2\text{CHCCl}_3] = 9.34 \times 10^{-4}\)  \([\text{NaOMe}] = 0.474\)

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorbance</th>
<th>(-\log (A_\infty - A_t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.242</td>
<td>0.0665</td>
</tr>
<tr>
<td>60</td>
<td>0.301</td>
<td>0.0975</td>
</tr>
<tr>
<td>130</td>
<td>0.450</td>
<td>0.1871</td>
</tr>
<tr>
<td>190</td>
<td>0.548</td>
<td>0.2581</td>
</tr>
<tr>
<td>240</td>
<td>0.585</td>
<td>0.2882</td>
</tr>
<tr>
<td>300</td>
<td>0.668</td>
<td>0.3645</td>
</tr>
<tr>
<td>370</td>
<td>0.732</td>
<td>0.4342</td>
</tr>
<tr>
<td>420</td>
<td>0.780</td>
<td>0.4949</td>
</tr>
<tr>
<td>(\infty)</td>
<td>1.10</td>
<td>—</td>
</tr>
</tbody>
</table>

\(k_1 = 4.20 \times 10^{-5} \text{ s}^{-1}\)

\(k_2 = 8.86 \times 10^{-5} \text{ mol}^{-1} \text{ s}^{-1}\)
Run 57 \((p\text{-Me}_6\text{C}_4)\text{H}_2\text{CH}\cdot\text{CCl}_3/\text{NaOMe/MeOH}/30.0^\circ\)

\[
[\text{Ar}_2\text{CH} \cdot \text{CCl}_3] = 9.21 \times 10^{-4} \quad \quad [\text{NaOMe}] = 0.474
\]

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorbance</th>
<th>(-\log (A_\infty - A_t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.180</td>
<td>0.0315</td>
</tr>
<tr>
<td>40</td>
<td>0.236</td>
<td>0.0585</td>
</tr>
<tr>
<td>80</td>
<td>0.348</td>
<td>0.1180</td>
</tr>
<tr>
<td>120</td>
<td>0.450</td>
<td>0.1805</td>
</tr>
<tr>
<td>160</td>
<td>0.542</td>
<td>0.2457</td>
</tr>
<tr>
<td>200</td>
<td>0.606</td>
<td>0.2976</td>
</tr>
<tr>
<td>240</td>
<td>0.683</td>
<td>0.3696</td>
</tr>
<tr>
<td>280</td>
<td>0.742</td>
<td>0.4342</td>
</tr>
<tr>
<td>(\infty)</td>
<td>1.11</td>
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</tbody>
</table>

\[k_1 = 5.98 \times 10^{-5} \text{ s}^{-1}\]

\[k_2 = 1.26 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}\]
<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorbance</th>
<th>$-\log (A_\infty - A_t)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.224</td>
<td>0.0287</td>
</tr>
<tr>
<td>120</td>
<td>0.346</td>
<td>0.0894</td>
</tr>
<tr>
<td>180</td>
<td>0.462</td>
<td>0.1561</td>
</tr>
<tr>
<td>240</td>
<td>0.568</td>
<td>0.2277</td>
</tr>
<tr>
<td>300</td>
<td>0.664</td>
<td>0.3045</td>
</tr>
<tr>
<td>375</td>
<td>0.736</td>
<td>0.3726</td>
</tr>
<tr>
<td>465</td>
<td>0.832</td>
<td>0.4841</td>
</tr>
<tr>
<td>540</td>
<td>0.900</td>
<td>0.5850</td>
</tr>
<tr>
<td>$\infty$</td>
<td>1.16</td>
<td></td>
</tr>
</tbody>
</table>

$k_1 = 4.45 \times 10^{-5} \text{ s}^{-1}$

$k_2 = 9.42 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$
Run 155  \( \text{Ph}_2\text{CH-CCl}_3/\text{NaOMe/M} \text{eOH/30.0}^\circ \) (stoppered cell technique)

\[ [\text{Ar}_2\text{CH-CCl}_3] = 1.05 \times 10^{-4} \quad [\text{NaOMe}] = 1.888 \]

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorbance</th>
<th>(-\log (A_\infty - A_t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.852</td>
<td>0.0186</td>
</tr>
<tr>
<td>2.08</td>
<td>0.975</td>
<td>0.0783</td>
</tr>
<tr>
<td>3.91</td>
<td>1.140</td>
<td>0.1739</td>
</tr>
<tr>
<td>5.00</td>
<td>1.220</td>
<td>0.2291</td>
</tr>
<tr>
<td>6.42</td>
<td>1.320</td>
<td>0.3098</td>
</tr>
<tr>
<td>7.09</td>
<td>1.360</td>
<td>0.3468</td>
</tr>
<tr>
<td>8.00</td>
<td>1.400</td>
<td>0.3872</td>
</tr>
<tr>
<td>9.00</td>
<td>1.450</td>
<td>0.4437</td>
</tr>
<tr>
<td>10.00</td>
<td>1.490</td>
<td>0.4949</td>
</tr>
<tr>
<td>11.00</td>
<td>1.530</td>
<td>0.5328</td>
</tr>
<tr>
<td>( \infty )</td>
<td>1.810</td>
<td></td>
</tr>
</tbody>
</table>

\[ k_1 = 2.04 \times 10^{-3} \text{ s}^{-1} \]

\[ k_2 = 1.08 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1} \]
Run 103  \((p-\text{ClC}_6\text{H}_4)\text{CH}_2\text{CCl}_3/\text{NaOMe/MeOH/45.0}^\circ\text{C}\) (Y-tube technique)

\[ [\text{Ar}_2\text{CH}_2\text{CCl}_3] = 8.29 \times 10^{-4} \quad [\text{NaOMe}] = 0.0274 \]

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorbance</th>
<th>(-\log (A_\infty - A_t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.475</td>
<td>0.1221</td>
</tr>
<tr>
<td>3.0</td>
<td>0.590</td>
<td>0.1938</td>
</tr>
<tr>
<td>4.5</td>
<td>0.680</td>
<td>0.2596</td>
</tr>
<tr>
<td>6.0</td>
<td>0.730</td>
<td>0.3010</td>
</tr>
<tr>
<td>7.5</td>
<td>0.780</td>
<td>0.3468</td>
</tr>
<tr>
<td>9.0</td>
<td>0.842</td>
<td>0.4112</td>
</tr>
<tr>
<td>10.5</td>
<td>0.878</td>
<td>0.4535</td>
</tr>
<tr>
<td>12.0</td>
<td>0.912</td>
<td>0.4976</td>
</tr>
<tr>
<td>(\infty)</td>
<td>1.23</td>
<td></td>
</tr>
</tbody>
</table>

\[ k_1 = 1.41 \times 10^{-3} \text{ s}^{-1} \]

\[ k_2 = 5.13 \times 10^{-2} \text{ mol}^{-1} \text{ s}^{-1} \]
Run 106: (p-ClC₆H₄)₂CD·CCl₃/NaOMe/MeOH/45.0°C

\[ [\text{Ar}_2\text{CD·CCl}_3] = 8.04 \times 10^{-4} \quad \text{[NaOMe]} = 0.0477 \]

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorbance</th>
<th>(-\log(A_{\infty} - A_t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.225</td>
<td>0.0386</td>
</tr>
<tr>
<td>10</td>
<td>0.353</td>
<td>0.1040</td>
</tr>
<tr>
<td>15</td>
<td>0.452</td>
<td>0.1624</td>
</tr>
<tr>
<td>20</td>
<td>0.562</td>
<td>0.2381</td>
</tr>
<tr>
<td>25</td>
<td>0.622</td>
<td>0.2857</td>
</tr>
<tr>
<td>30</td>
<td>0.665</td>
<td>0.3233</td>
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<tr>
<td>35</td>
<td>0.780</td>
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<tr>
<td>40</td>
<td>0.815</td>
<td>0.4881</td>
</tr>
<tr>
<td>(\infty)</td>
<td>1.14</td>
<td></td>
</tr>
</tbody>
</table>

\(k_1 = 5.16 \times 10^{-4} \text{ s}^{-1}\)

\(k_2 = 1.08 \times 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}\)
Run 91 \((p-FC_6H_4)_2CH\cdot CCl_3/NaOMe/H_2O/45.0^\circ\)

\([Ar_2CH\cdot CCl_3] = 1.02 \times 10^{-3}\)  \([NaOMe] = 0.0238\)

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorbance</th>
<th>(-\log (A_\infty - A_t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.238</td>
<td>0.0851</td>
</tr>
<tr>
<td>20</td>
<td>0.356</td>
<td>0.1524</td>
</tr>
<tr>
<td>30</td>
<td>0.439</td>
<td>0.2069</td>
</tr>
<tr>
<td>40</td>
<td>0.522</td>
<td>0.2692</td>
</tr>
<tr>
<td>55</td>
<td>0.619</td>
<td>0.3555</td>
</tr>
<tr>
<td>71</td>
<td>0.728</td>
<td>0.4789</td>
</tr>
<tr>
<td>85</td>
<td>0.796</td>
<td>0.5784</td>
</tr>
<tr>
<td>100</td>
<td>0.840</td>
<td>0.6576</td>
</tr>
<tr>
<td>(\infty)</td>
<td>1.06</td>
<td>--</td>
</tr>
</tbody>
</table>

\(k_1 = 2.52 \times 10^{-4} \text{ s}^{-1}\)

\(k_2 = 1.06 \times 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}\)
Run 233 \((p-\text{NO}_2\text{C}_6\text{H}_4)\text{C}_2\text{H}_2\text{Cl}_3\text{NaOMe/McOH/30.5}^\circ\) (Stopped-flow)

\[
[A_{2\text{CH} \cdot \text{Cl}_3}] = 2.91 \times 10^{-5} \quad [\text{NaOMe}] = 0.1525
\]

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Absorbance</th>
<th>(-\log (A_{\infty} - A_t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.137</td>
<td>0.6861</td>
</tr>
<tr>
<td>0.4</td>
<td>0.168</td>
<td>0.7570</td>
</tr>
<tr>
<td>0.6</td>
<td>0.198</td>
<td>0.8386</td>
</tr>
<tr>
<td>0.8</td>
<td>0.223</td>
<td>0.9208</td>
</tr>
<tr>
<td>1.0</td>
<td>0.243</td>
<td>1.000</td>
</tr>
<tr>
<td>1.2</td>
<td>0.260</td>
<td>1.081</td>
</tr>
<tr>
<td>1.4</td>
<td>0.273</td>
<td>1.155</td>
</tr>
<tr>
<td>1.6</td>
<td>0.286</td>
<td>1.244</td>
</tr>
<tr>
<td>1.8</td>
<td>0.295</td>
<td>1.319</td>
</tr>
<tr>
<td>(\infty)</td>
<td>0.343</td>
<td></td>
</tr>
</tbody>
</table>

\[k_1 = 0.921 \text{ s}^{-1}\]

\[k_2 = 6.03 \text{ l mol}^{-1} \text{ s}^{-1}\]
Run 222 \((p-\text{NO}_2\text{C}_6\text{H}_4)_2\text{CH} \cdot \text{CCl}_3/\text{NaOMe/MeOH}/45.5^\circ\) (Stopped-flow)

\[ [\text{Ar}_2\text{CH} \cdot \text{CCl}_3] = 2.91 \times 10^{-5} \quad [\text{NaOMe}] = 0.1525 \]

<table>
<thead>
<tr>
<th>(10^2) Time (s)</th>
<th>Absorbance</th>
<th>(-\log (A_\infty - A_t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.132</td>
<td>0.6615</td>
</tr>
<tr>
<td>10</td>
<td>0.168</td>
<td>0.7399</td>
</tr>
<tr>
<td>15</td>
<td>0.197</td>
<td>0.8153</td>
</tr>
<tr>
<td>20</td>
<td>0.225</td>
<td>0.9031</td>
</tr>
<tr>
<td>25</td>
<td>0.247</td>
<td>0.9872</td>
</tr>
<tr>
<td>30</td>
<td>0.265</td>
<td>1.071</td>
</tr>
<tr>
<td>35</td>
<td>0.280</td>
<td>1.155</td>
</tr>
<tr>
<td>40</td>
<td>0.292</td>
<td>1.237</td>
</tr>
<tr>
<td>45</td>
<td>0.302</td>
<td>1.319</td>
</tr>
<tr>
<td>(\infty)</td>
<td>0.350</td>
<td>—</td>
</tr>
</tbody>
</table>

\(k_1 = 3.82 \text{ s}^{-1}\)

\(k_2 = 25.0 \text{ l mol}^{-1} \text{ s}^{-1}\)
Run 123 \( (p-\text{BrC}_6\text{H}_4)_2\text{CH} \cdot \text{CCl}_3/t-\text{BuOK}/t-\text{BuOH}/30.0^\circ \) (Y-tube technique)

\[
\left[\text{Ar}_2\text{CH} \cdot \text{CCl}_3\right] = 1.03 \times 10^{-3} \quad \left[t-\text{BuOK}\right] = 0.0179
\]

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorbance</th>
<th>(-\log (A_\infty - A_t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>0.445</td>
<td>0.2041</td>
</tr>
<tr>
<td>2.0</td>
<td>0.522</td>
<td>0.2612</td>
</tr>
<tr>
<td>3.0</td>
<td>0.689</td>
<td>0.4191</td>
</tr>
<tr>
<td>4.0</td>
<td>0.799</td>
<td>0.5670</td>
</tr>
<tr>
<td>5.0</td>
<td>0.882</td>
<td>0.7258</td>
</tr>
<tr>
<td>6.0</td>
<td>0.930</td>
<td>0.8529</td>
</tr>
<tr>
<td>7.0</td>
<td>0.979</td>
<td>1.041</td>
</tr>
<tr>
<td>8.0</td>
<td>0.998</td>
<td>1.143</td>
</tr>
<tr>
<td>(\infty)</td>
<td>1.07</td>
<td></td>
</tr>
</tbody>
</table>

\[ k_1 = 5.51 \times 10^{-3} \text{ s}^{-1} \]

\[ k_2 = 3.08 \times 10^{-1} \text{ l mol}^{-1} \text{ s}^{-1} \]
Run 193 $\text{Ph}_2\text{CH} \cdot \text{CCl}_3 / \text{Ph}_2\text{CD} \cdot \text{CCl}_3 / \text{t-BuOK} / \text{t-BuOH} / 30.0^\circ$  
(Stoppered cell technique, mixed run)

$[\text{Ph}_2\text{CH} \cdot \text{CCl}_3] = 3.92 \times 10^{-5}$ \hspace{1cm} $[\text{Ph}_2\text{CD} \cdot \text{CCl}_3] = 7.16 \times 10^{-5}$

$[\text{t-BuOK}] = 0.0915$

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorbance</th>
<th>$-\log (A_\infty - A_t)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.540</td>
<td>-0.0531</td>
</tr>
<tr>
<td>16</td>
<td>0.758</td>
<td>0.0400</td>
</tr>
<tr>
<td>26</td>
<td>0.891</td>
<td>0.1085</td>
</tr>
<tr>
<td>36</td>
<td>0.985</td>
<td>0.1643</td>
</tr>
<tr>
<td>46</td>
<td>1.050</td>
<td>0.2076</td>
</tr>
<tr>
<td>56</td>
<td>1.108</td>
<td>0.2503</td>
</tr>
<tr>
<td>66</td>
<td>1.158</td>
<td>0.2907</td>
</tr>
<tr>
<td>76</td>
<td>1.200</td>
<td>0.3279</td>
</tr>
<tr>
<td>86</td>
<td>1.230</td>
<td>0.3565</td>
</tr>
<tr>
<td>96</td>
<td>1.260</td>
<td>0.3872</td>
</tr>
<tr>
<td>106</td>
<td>1.280</td>
<td>0.4084</td>
</tr>
<tr>
<td>116</td>
<td>1.310</td>
<td>0.4437</td>
</tr>
<tr>
<td>126</td>
<td>1.340</td>
<td>0.4815</td>
</tr>
<tr>
<td>136</td>
<td>1.360</td>
<td>0.5086</td>
</tr>
<tr>
<td>141</td>
<td>1.370</td>
<td>0.5229</td>
</tr>
<tr>
<td>156</td>
<td>1.390</td>
<td>0.5528</td>
</tr>
<tr>
<td>166</td>
<td>1.410</td>
<td>0.5850</td>
</tr>
<tr>
<td>176</td>
<td>1.420</td>
<td>0.6021</td>
</tr>
<tr>
<td>186</td>
<td>1.430</td>
<td>0.6198</td>
</tr>
<tr>
<td>196</td>
<td>1.450</td>
<td>0.6576</td>
</tr>
<tr>
<td>216</td>
<td>1.460</td>
<td>0.6778</td>
</tr>
<tr>
<td>226</td>
<td>1.470</td>
<td>0.6990</td>
</tr>
<tr>
<td>236</td>
<td>1.480</td>
<td>0.7212</td>
</tr>
</tbody>
</table>
Run 193 continued

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorbance</th>
<th>(-\log (A_\infty - A_t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>246</td>
<td>1.490</td>
<td>0.7447</td>
</tr>
<tr>
<td>266</td>
<td>1.500</td>
<td>0.7696</td>
</tr>
<tr>
<td>286</td>
<td>1.510</td>
<td>0.7959</td>
</tr>
<tr>
<td>306</td>
<td>1.520</td>
<td>0.8239</td>
</tr>
<tr>
<td>316</td>
<td>1.520</td>
<td>0.8239</td>
</tr>
<tr>
<td>(\infty)</td>
<td>1.670</td>
<td>--</td>
</tr>
</tbody>
</table>

\[ k_D^1 = 6.02 \times 10^{-5} \text{ s}^{-1} \]
\[ k_D^2 = 6.59 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1} \]
\[ k_H^1 = 2.39 \times 10^{-4} \text{ s}^{-1} \]
\[ k_H^2 = 2.62 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1} \]
Run 20 \((p\text{-MeOC}_{6}H_{4})_{2}\text{CH} \cdot \text{CCl}_{3}/\text{LiCl}/\text{DMF}/64.95^\circ\)

\[ [\text{Ar}_2\text{CH} \cdot \text{CCl}_3] = [\text{LiCl}] = 0.0200 \quad K = 0.7 \text{ mol } \text{l}^{-1} \]

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorbance</th>
<th>$10^5 k_2^t (\text{l mol}^{-1} \text{s}^{-1})$</th>
<th>$10^5 k_2 (\text{l mol}^{-1} \text{s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.154</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1200</td>
<td>0.262</td>
<td>8.51</td>
<td>9.40</td>
</tr>
<tr>
<td>2580</td>
<td>0.370</td>
<td>8.04</td>
<td>9.73</td>
</tr>
<tr>
<td>3180</td>
<td>0.401</td>
<td>7.50</td>
<td>9.32</td>
</tr>
<tr>
<td>4110</td>
<td>0.450</td>
<td>7.04</td>
<td>9.10</td>
</tr>
<tr>
<td>5460</td>
<td>0.520</td>
<td>6.70</td>
<td>9.15</td>
</tr>
<tr>
<td>6160</td>
<td>0.541</td>
<td>6.33</td>
<td>8.79</td>
</tr>
<tr>
<td>7320</td>
<td>0.608</td>
<td>6.44</td>
<td>9.41</td>
</tr>
<tr>
<td>8760</td>
<td>0.650</td>
<td>6.02</td>
<td>9.08</td>
</tr>
<tr>
<td>10,140</td>
<td>0.673</td>
<td>5.52</td>
<td>(8.48)</td>
</tr>
<tr>
<td>(\infty)</td>
<td>1.040</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Mean $k_2 = (9.25 \pm 0.28) \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$
Run 76  \((p-\text{ClC}_6\text{H}_4)\text{CH} \cdot \text{CCl}_3/n-\text{Bu}_4\text{NCl}/n-\text{Bu}_4\text{NClO}_4/\text{Me}_2\text{CO}/64.95\)

\[
\begin{align*}
\text{[Ar}_2\text{CH} \cdot \text{CCl}_3\text{]} &= 0.02069 \\
\text{[Bu}_4\text{NClO}_4\text{]} &= 0.406 \\
\text{[AgNO}_3\text{]} &= 0.0449 \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Titre (ml)</th>
<th>(10^2[\text{Cl}^-])</th>
<th>(10^2[\text{DDT}])</th>
<th>(10^2[\text{DDE}])</th>
<th>(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.120</td>
<td>1.903</td>
<td>2.069</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>8580</td>
<td>3.490</td>
<td>3.140</td>
<td>0.832</td>
<td>1.237</td>
<td>27.65</td>
</tr>
<tr>
<td>10,080</td>
<td>3.490</td>
<td>3.140</td>
<td>0.832</td>
<td>1.237</td>
<td>27.65</td>
</tr>
<tr>
<td>11,610</td>
<td>3.495</td>
<td>3.142</td>
<td>0.830</td>
<td>1.239</td>
<td>27.85</td>
</tr>
</tbody>
</table>
APPENDIX II

THE PRECISION OF L.F.E.R. CORRELATIONS

The criteria of correlations is expressed in terms of correlation coefficient \((r)\) and standard deviation \((s)\). Jaffe\(^{49}\) regarded a correlation coefficient of \(0.99 \leq r \leq 1\) as excellent, \(0.95 < r < 0.99\) as satisfactory and \(0.90 < r < 0.95\) as a fair correlation. Wepster \textit{et al.}\(^{51}\) employed tighter criteria in that they correlated rates of reactions only with the substituents; m-methyl, m-fluoro, m-chloro, m-iodo, m-acetoxy, m-nitro, p-acetoxy, and p-nitro. These "primary" substituent constants were based on the ionization of substituted benzoic acids for which resonance interaction was assumed to be negligible. Charton, however, has employed confidence levels as a criterion of fit.\(^{261}\) These are the probability of finding a linear correlation in the limits of a confidence interval. The relationship between the correlation coefficient and the confidence level is shown in the following Table.
### TABLE 1.

Relationship Between Confidence Levels and Correlation Coefficients

<table>
<thead>
<tr>
<th>Degrees of Freedom (m-2)</th>
<th>Confidence Levels</th>
<th>90%</th>
<th>95%</th>
<th>98%</th>
<th>99%</th>
<th>99.9%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.988</td>
<td>0.997</td>
<td>0.999</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.900</td>
<td>0.950</td>
<td>0.980</td>
<td>0.990</td>
<td>0.999</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.805</td>
<td>0.878</td>
<td>0.934</td>
<td>0.959</td>
<td>0.992</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.729</td>
<td>0.811</td>
<td>0.882</td>
<td>0.917</td>
<td>0.974</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.669</td>
<td>0.754</td>
<td>0.833</td>
<td>0.874</td>
<td>0.951</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>0.621</td>
<td>0.707</td>
<td>0.789</td>
<td>0.834</td>
<td>0.925</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>0.582</td>
<td>0.666</td>
<td>0.750</td>
<td>0.798</td>
<td>0.898</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>0.549</td>
<td>0.632</td>
<td>0.716</td>
<td>0.765</td>
<td>0.872</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>0.521</td>
<td>0.602</td>
<td>0.685</td>
<td>0.735</td>
<td>0.847</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>0.497</td>
<td>0.576</td>
<td>0.658</td>
<td>0.708</td>
<td>0.823</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>0.476</td>
<td>0.553</td>
<td>0.634</td>
<td>0.684</td>
<td>0.801</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>0.457</td>
<td>0.532</td>
<td>0.612</td>
<td>0.661</td>
<td>0.780</td>
</tr>
</tbody>
</table>

*a* Taken from ref. 262. The data in the body of the table are correlation coefficients and m is the number of points in the correlation.

Data for "bad" Hammett correlations obtained for the dehydrochlorination of the 1,1-diaryl-2,2,2-trichloroethanes with various bases in various solvents are shown in Table 2.
TABLE 2.
Elimination of Ar₂CH₂CCl₃ with Various Base-Solvent Systems.

<table>
<thead>
<tr>
<th>Base</th>
<th>Solvent</th>
<th>m</th>
<th>r</th>
<th>Confidence level</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₅⁻</td>
<td>EtOH</td>
<td>7</td>
<td>0.980</td>
<td>99.9</td>
<td>102</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>Me₂CO</td>
<td>6</td>
<td>0.981</td>
<td>99.9</td>
<td>162</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>DMF</td>
<td>13</td>
<td>0.938</td>
<td>99.9</td>
<td>162</td>
</tr>
<tr>
<td>t-BuOH⁻</td>
<td>t-BuOH</td>
<td>7</td>
<td>0.986</td>
<td>99.9</td>
<td>a</td>
</tr>
<tr>
<td>NaOH</td>
<td>EtOH</td>
<td>8</td>
<td>0.969</td>
<td>99.9</td>
<td>99,100</td>
</tr>
</tbody>
</table>

*Present research.*

It is evident that all of the untreated Hammett plots \((\alpha = 1.0)\) of the present research have a confidence level of \(> 99.9\%\). Therefore, it seems that the correlation coefficient and standard deviation provide better criteria of fit in these cases.
APPENDIX III

CALCULATION OF THE DDT:DDD RATE RATIO

The relevant data for the potential energy calculations of the non-bonded interactions in E2C reactions of DDT and DDD are given in the following Table.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DDT</th>
<th>DDE&lt;sup&gt;d&lt;/sup&gt;</th>
<th>DDD</th>
<th>DDE&lt;sup&gt;e&lt;/sup&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>μ&lt;sub&gt;x&lt;/sub&gt;</td>
<td>2.05x10&lt;sup&gt;-18&lt;/sup&gt; e.s.u.</td>
<td>2.05x10&lt;sup&gt;-18&lt;/sup&gt;</td>
<td>2.05x10&lt;sup&gt;-18&lt;/sup&gt;</td>
<td>2.05x10&lt;sup&gt;-18&lt;/sup&gt;</td>
<td>263</td>
</tr>
<tr>
<td>μ&lt;sub&gt;y&lt;/sub&gt;</td>
<td>2.05x10&lt;sup&gt;-18&lt;/sup&gt; e.s.u.</td>
<td>2.05x10&lt;sup&gt;-18&lt;/sup&gt;</td>
<td>0.43x10&lt;sup&gt;-18&lt;/sup&gt;</td>
<td>0.43x10&lt;sup&gt;-18&lt;/sup&gt;</td>
<td>263</td>
</tr>
<tr>
<td>θ&lt;sub&gt;x&lt;/sub&gt;</td>
<td>35°16′</td>
<td>30°</td>
<td>25°07′</td>
<td>39°</td>
<td>a</td>
</tr>
<tr>
<td>θ&lt;sub&gt;y&lt;/sub&gt;</td>
<td>39°16′</td>
<td>30°</td>
<td>45°25′</td>
<td>21°</td>
<td>a</td>
</tr>
<tr>
<td>a&lt;sub&gt;x&lt;/sub&gt;</td>
<td>2.355x10&lt;sup&gt;-24&lt;/sup&gt; cm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>2.355x10&lt;sup&gt;-24&lt;/sup&gt;</td>
<td>2.355x10&lt;sup&gt;-24&lt;/sup&gt;</td>
<td>2.355x10&lt;sup&gt;-24&lt;/sup&gt;</td>
<td>258</td>
</tr>
<tr>
<td>a&lt;sub&gt;y&lt;/sub&gt;</td>
<td>2.355x10&lt;sup&gt;-24&lt;/sup&gt; cm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>2.355x10&lt;sup&gt;-24&lt;/sup&gt;</td>
<td>4.34x10&lt;sup&gt;-25&lt;/sup&gt;</td>
<td>4.34x10&lt;sup&gt;-25&lt;/sup&gt;</td>
<td>258</td>
</tr>
<tr>
<td>I&lt;sub&gt;x&lt;/sub&gt;</td>
<td>3.0x10&lt;sup&gt;6&lt;/sup&gt; cal</td>
<td>3.0x10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>3.0x10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>3.0x10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>260</td>
</tr>
<tr>
<td>I&lt;sub&gt;y&lt;/sub&gt;</td>
<td>3.0x10&lt;sup&gt;6&lt;/sup&gt; cal</td>
<td>3.0x10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>3.13x10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>3.13x10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>260</td>
</tr>
<tr>
<td>r&lt;sub&gt;1&lt;/sub&gt;</td>
<td>2.87x10&lt;sup&gt;-8&lt;/sup&gt; cm</td>
<td>2.86x10&lt;sup&gt;-8&lt;/sup&gt;</td>
<td>2.33x10&lt;sup&gt;-8&lt;/sup&gt;</td>
<td>2.27x10&lt;sup&gt;-8&lt;/sup&gt;</td>
<td>b</td>
</tr>
<tr>
<td>r&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.89x10&lt;sup&gt;-8&lt;/sup&gt; cm</td>
<td>2.93x10&lt;sup&gt;-8&lt;/sup&gt;</td>
<td>2.34x10&lt;sup&gt;-8&lt;/sup&gt;</td>
<td>2.44x10&lt;sup&gt;-8&lt;/sup&gt;</td>
<td>c</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated from bond angles of 109°28′ and 120° for sp<sup>3</sup> and sp<sup>2</sup> carbon atoms.

<sup>b</sup> Covalent radii from ref. 258.

<sup>c</sup> Covalent radii from ref. 259.

<sup>d</sup> 1,1-di(p-chlorophenyl)-2,2-dichloroethene

<sup>e</sup> 1,1-di(p-chlorophenyl)-2-chloroethene.

The dispersion energy is given by:<sup>257</sup>

\[
W(\text{dispersion}) = 2.1 \times \frac{3 \alpha_a \alpha_b \beta \beta_y}{2r^6} \frac{I_x I_y}{(I_x + I_y)}
\]
The 2.1 factor is used to give a better agreement between the theoretical and experimental values for the viscosities of rare gases of high atomic weight.

The empirical factor $B$ in the van der Waals repulsion term[^255] is calculated by substituting

$$W(\text{van der Waals}) = B e^{-\frac{r}{\sigma_{345}}}$$

the sum of the appropriate van der Waals radii into the function $\frac{dn}{dr} = 0$. The van der Waals radii for chlorine and hydrogen are $1.8 \times 10^{-8}$ and $1.2 \times 10^{-8}$ cm respectively[^260]. The empirical $0.345$ factor in the exponent is based on the properties of alkali halide crystals.

The dipole-dipole interaction term has to be multiplied by a factor of $1.4396 \times 10^{16}$ to convert the units of the dipole moments into calories.
ESTIMATION OF $pK_a$ FOR 1,1-DI(p-NITROPHENYL)-2,2,2-TRICHLOOROETHANE

There is considerable uncertainty in the estimation of the $pK_a$ value of 1,1-di(p-nitrophenyl)-2,2,2-trichloroethane in water (Part II, Discussion 4.5). The L.F.E.R. $pK_a$ range given in the text was based on the estimation of $pK_a$ values of di-p-nitrophenylmethane using either $\sigma^-$ or $\sigma^-$ substituent constants for $p$-nitro. However, these values in themselves are approximate. Further approximations are needed with this particular compound and so its L.F.E.R. $pK_a$ is subject to even greater uncertainty.

Streitweiser et al.,\textsuperscript{193} reported $pK_a$ values of 35.1 and 33.4 respectively for di-p-tolylmethane and diphenylmethane in water based on measurements in cyclohexylamine. These correspond to a $\rho$ of 4.85.

The $pK_a$ values of di-p-nitrophenylmethane and 3,4'-dinitrodiphenylmethane are 15.85 and 17.62 respectively.\textsuperscript{264} These are based on Hammett calculations in ethanolic dimethyl sulfoxide. No linear Hammett plot correlates the 4 $pK_a$ values since the methods of extrapolation are different even though the values refer to water as the standard state solvent.

The $\rho$ value for the dinitrophenylmethanes is 25.2 based on $2\sigma^+_p$ as the total substituent constant for the di-p-nitro compound, and $\sigma^+_p + \sigma^-_m$ for the 3,4' analogue. However, $\rho$ is 3.16 using $2\sigma^-_p$ for the di-p-nitro compound and $\sigma^+_p + \sigma^-_m$ for the 3,4' compound. If $\sigma^+_p$ (effective) is taken as 1.08 for $p$-nitro in diaryl methane ionization a $\rho$ of 4.85 is obtained. This is in agreement with Streitweiser's value.

Using the $pK_a$ of 33.4 for diphenylmethane and $\sigma^-_p = 1.08$ for $p$-nitro $pK_a$'s of 22.6 and 11.8 can be calculated for di-p-nitrophenyl-
methane and 1,1-di(p-nitrophenyl)-2,2,2-trichloroethane respectively. The Bronsted equation for the detritiochlorination of the 1,1-diaryl-2,2,2-trichloroethanes and the protodetritiation of the substituted fluorenes and indenes in methanol at 45°C is

$$\log k^T_2 = 5.285 - 0.379 \, pK_a$$

Using this we can calculate a "kinetic" $pK_a$ of 12.8 for 1,1-di(p-nitrophenyl)-2,2,2-trichloroethane which compares nicely with the L.P.E.R. value of 11.8.
ISOTÖPE EFFECTS FOR THE BASE-PROMOTED DEHYDROCHLORINATION
OF DDT IN PROTIc SOLVENTS. EVIDENCE FOR ElcB ELIMINATION.

D.J. McLennan and R.J. Wong

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(Received in UK 31 May 1972; accepted for publication 7 June 1972)

For a number of years we have been interested in the mechanism of the dehydro-
chlorination of DDT ($\text{Ar}_2\text{CHCCl}_3$, where $\text{Ar} = \text{p-ClC}_6\text{H}_4$) and its analogues in a variety of
base-solvent systems.\textsuperscript{1-4} It has always been assumed that the mechanism is the normal
concerted E2 process, in which proton transfer from $\text{C}_\beta$ and chloride loss from $\text{C}_\alpha$ occur
simultaneously. The pre-equilibrium carbanionic mechanism\textsuperscript{5} (ElcB Mechanism I) was rejected
on the grounds that general rather than specific base catalysis was observed for reactions in

ElcB Mechanism I

$$\begin{align*}
\text{Ar}_2\text{CHCCl}_3 + \text{B}^- & \leftrightharpoons \text{Ar}_2\text{CH}_{\beta}^-\text{CCl}_3 + \text{BH}^- \\
\text{Ar}_2\text{CH}_{\beta}^-\text{CCl}_3 & \rightarrow \text{Ar}_2\text{C=CCl}_2 + \text{Cl}^- \quad \text{(slow)}
\end{align*}$$

ethanolic PhS\textsuperscript{-}/PhSH buffers, and further, that no isotopic hydrogen exchange between
substrate and hydroxylic solvent could be detected.\textsuperscript{1}

Not so easily dismissed however is a variant of the stepwise carbanionic mechanism (ElcB
Mechanism II) in which carbanion formation is irreversible and rate-determining, since general
base catalysis and no hydrogen exchange are predicted for this process.\textsuperscript{5} We now present

ElcB Mechanism II

$$\begin{align*}
\text{Ar}_2\text{CHCCl}_3 + \text{B}^- & \rightarrow \text{Ar}_2\text{CH}_{\beta}^-\text{CCl}_3 + \text{BH}^- \\
\text{Ar}_2\text{CH}_{\beta}^-\text{CCl}_3 & \rightarrow \text{Ar}_2\text{C=CCl}_2 + \text{Cl}^- \quad \text{(fast)}
\end{align*}$$

evidence which strongly suggests that the latter mechanism in fact operates in protic solvents.

Primary deuterium isotope effects have been measured for the dehydrochlorination of DDT
by a variety of anionic bases in ethanol (and by methoxide ion in methanol). Some of the
results have been reported previously,\textsuperscript{1} and are collected with more recent data in the Table.
The isotope effect clearly rises to a maximum and then decreases as the base strength is
increased. The maximum in a plot of $k_H/k_D$ vs. $pK_a$ (see Figure) is reasonably sharp.\textsuperscript{8}
TABLE

Isotope Effects For the Dehydrochlorination
of Ar₂CH(D)CCl₃ in Ethanol.

<table>
<thead>
<tr>
<th>Base</th>
<th>Temp. (°C)</th>
<th>(10^5k_H^b)</th>
<th>(10^5k_D^b)</th>
<th>(k_H/k_D)</th>
<th>(pK_a^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhS⁻</td>
<td>45</td>
<td>2.61</td>
<td>0.834</td>
<td>3.1</td>
<td>9.3</td>
</tr>
<tr>
<td>p-NO₂C₆H₄O⁻</td>
<td>45</td>
<td>0.145</td>
<td>0.030</td>
<td>4.8</td>
<td>13.3</td>
</tr>
<tr>
<td>PhO⁻</td>
<td>45</td>
<td>17.4</td>
<td>2.77</td>
<td>6.3</td>
<td>15.8</td>
</tr>
<tr>
<td>MeO⁻</td>
<td>30</td>
<td>1130</td>
<td>210</td>
<td>5.4</td>
<td>18.1</td>
</tr>
<tr>
<td>EtO⁻</td>
<td>45</td>
<td>36100</td>
<td>10600</td>
<td>3.4</td>
<td>20.3</td>
</tr>
</tbody>
</table>

Ar₂CCCl₃ is (100±1)% deuterated on C-1. \(\text{In } 1 \text{ mol}^{-1} \text{s}^{-1}\). \(pK_a\) of conjugate acid in EtOH, from refs. 1 and 6. \(\text{In methanol.}\) \(pK_a\) in methanol solvent. Basicity function measurements show that MeO⁻/MeOH is less basic than EtO⁻/EtOH (ref. 7).

Such an effect is theoretically respectable but has only rarely been observed, and only a single report pertaining to elimination reactions exists, albeit for slightly different circumstances. It is generally agreed that for reactions in which proton transfer is rate-determining, \(k_H/k_D\) should reach a maximum when the \(pK_a\) of the substrate is equal to the \(pK_a\) of the conjugate acid of the base producing the maximum isotope effect. If DDT dehydrochlorination in fact proceeds by ElcB Mechanism II, the \(pK_a\) of DDT would thus be approximately 16. An uncertainty of one \(pK\) unit would appear to be reasonable (Figure).

The \(pK_a\) of DDT can be independently estimated. The \(pK_a\) of Ph₂CH₂ in methanol is 30.2. If the reasonable assumption of a Hammett \(\rho\) value of 5.0 for diphenylmethane ionization is made, the \(pK_a\) of Ar₂CH₂ can be calculated to be 27.9. If the Taft \(\sigma^*\) value is assumed to be 5.0 for diarylmethane ionization (again a reasonable estimate), use of \(\sigma^* = 2.65\) for -CCl₃ and \(\sigma^* = 0.490\) for -H leads to \(pK_a = 17.1\) for Ar₂CHCCl₃.

The agreement between the "kinetic" and L.P.E.R. estimates for the \(pK_a\) of DDT is remarkably good. It is not direct proof for the rate-determining step in DDT dehydrochlorination being carbocation formation, but it is strongly suggestive.
A third variant of the carbanionic mechanism, similar to ElcB Mechanism I but involving internal rather than external return for carbanion reprotonation\(^{16}\) can be easily rejected. Internal return invariably results in the observation of small (and even inverse) primary hydrogen isotope effects\(^{12,16(a-d)}\) and there is no suggestion of these in the present system. These results, together with those in the accompanying communication,\(^{17}\) point to simple deprotonation of DDT being rate-determining. Discussion of the nature of the transition states in our reactions, and of isotope effects for other ring-substituted DDT-type compounds in further base-solvent systems, is deferred to the full paper.

Acknowledgement. We thank Dr P.D. Woodgate for mass spectral analyses.

REFERENCES

15. If $\rho$ and $\sigma^*$ are assigned values of $5 \pm 1$, the L.P.E.R. $pX_a = 17.1 \pm 2.6$.
RATE-ACIDITY CORRELATION FOR THE BASE-PROMOTED
DEHYDROCHLORINATION OF DDT IN METHANOL.
EVIDENCE FOR E1cb ELIMINATION.

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(Received in UK 31 May 1972; accepted for publication 7 June 1972)

Straitwieser and co-workers\(^1\) have recently shown that a Brønsted-type correlation exists
between \(\log k'_a\), the rate constants for second-order detritiation of tritiated indene and
fluorene-type hydrocarbons in MeO\(^-\)/MeOH at 45\(^\circ\)C, and the hydrocarbon \(pK_a\) values relative to
cæsium cyclohexylamidine in cyclohexylamine (CsCHA/CHA). The rate-determining step was
identified as simple proton transfer to form the carbonan, from consideration of the
magnitude of the Brønsted \(\beta\) parameter (0.369) and the hydrogen isotope effects. Internal
return was found to be unimportant.

It follows that if the dehydrochlorination of DDT (Ar\(_2\)CHOCCl\(_3\), where Ar = (p-CIC\(_6\)H\(_4\))
proceeds via the "irreversible" carbonan or E1cb mechanism\(^2\) as previously proposed,\(^3\) the
point pertaining to the rate constant for elimination from tritiated DDT in MeO\(^-\)/MeOH at

\[
\begin{align*}
\text{Ar}_2\text{CHOCCl}_3 + \text{B}^- &\rightarrow \text{Ar}_2^+\text{COCCl}_2 + \text{BH}^- \quad \text{(slow)} \\
\text{Ar}_2^+\text{COCCl}_2 &\rightarrow \text{Ar}_2^+\text{COCCl}_2 + \text{Cl}^- \quad \text{(fast)}
\end{align*}
\]

45\(^\circ\)C and the \(pK_a\) of DDT relative to CsCHA/CHA should lie on the Straitwieser Brønsted plot, as
the rate-determining step is carbonan formation. Neither of these quantities has been
measured but they can be estimated with reasonable precision.

The primary deuterium isotope effect for DDT dehydrochlorination by MeO\(^-\)/MeOH at -0.1\(^\circ\)C is
7.5 \((k_H = 3.24 \times 10^{-4} \text{ mol}^{-1} \text{ s}^{-1}; k_D = 4.31 \times 10^{-5} \text{ mol}^{-1} \text{ s}^{-1})\). From the 30\(^\circ\)C rate constants
quoted,\(^3\) the \(k_H/k_D\) value at 45\(^\circ\)C can be calculated as 4.7. The tritium isotope effect \(k_H/k_D\) can be
obtained from this latter figure using the Swain-Schaad equation\(^4\) (Eq. 1), and is found to be
9.3 at 45\(^\circ\)C. The rate constant for dehydrochlorination of Ar\(_2\)CHOCCl\(_3\) by MeO\(^-\)/MeOH at 45\(^\circ\)C is\(^5\)

\[
\log(k_H/k_D) = 1.44 \log(k_H/k_D) \quad \text{..................(1)}
\]
5.14 \times 10^{-2} \text{ mol}^{-1} \text{ s}^{-1} \text{ and so } k_T, \text{ the rate constant for detritiochlorination of } \text{Ar}_2\text{CCl}_3 \text{ at this temperature is } 5.53 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}.

The pK_a of DDT relative to CsCHA/CHA can be calculated as before. The pK_a of Ph_2\text{CH}_2 relative to CsCHA/CHA is 33.45. The reasonable assumption of a Hammett ρ value of 5 leads to pK_a = 31.15 for Ar_2\text{CH}_2. If a Taft ρ* value of 5 is then assumed and σ* values of 2.65 (-\text{CCl}_3) and 0.490 (-\text{H}) employed, the relevant pK_a of DDT is calculated to be 20.35.

The log k_T vs. pK_a point for DDT is shown, together with Streitwieser's hydrocarbon data, in the Figure. It is clear that the DDT point lies on the line, as the deviation of 0.14 log units (rate) is well within the standard deviation of fit (0.200). From the Brönsted equation pertaining to Streitwieser's least-squares plot we may calculate k_T = 4.0 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}; a result which compares most favourably with the value calculated independently above. This is of course not direct evidence for the rate-determining step in DDT dehydrochlorination being irreversible deprotonation, but it is strongly suggestive, especially in view of the fact that the previous approach to the question yields the same conclusion. Only arguments invoking coincidence could justify retention of our earlier assumption of a concerted E2 elimination in protic solvents.

However, our previous conclusions based on the E2 mechanism require little modification, as it has always been recognised that the transition state has considerable carbonic character at Cβ and a poorly broken C=Cl bond. High R^+:ES^- rate ratios, high Hammett ρ values (2.11 for PhS^-/EtOH; 2.37 for MeO^-/MeOH; 2.64 for EtO^-/EtOH, the similarity indicating mechanistic similarity) and somewhat anomalous solvent effects pertaining to alkaline MeOH/H_2O mixtures can be explained equally well if not better by an E1cB mechanism as by a paenecarbanion E2 process. However one apparent anomaly remains. Our isotope effects suggest that the proton is about half-transferred, in force constant terms rather than geometrically, in the transition state when phenoxide ion in ethanol is the base. On the other hand, the Brönsted β value for the DDT/\text{RC}_6\text{H}_4O^- reaction series in ethanol (0.88) implies an almost completely transferred proton. Such discrepancies between k_H/k_D and β have been noted previously for disparate systems, and in all cases it has been concluded that β is the less reliable criterion of transition state structure.

Bordwell has suggested that all β-eliminations from activated substrates should involve
the intermediacy of carbanions,\textsuperscript{12} and the present conclusions agree with his view. Whether a mechanistic extrapolation can be made to non-activated substrates such as simple alkyl halides and arenensulphonates is another matter however. Indirect evidence as presented here, and more direct evidence of the type adduced by Bordell and his co-workers for nitro- and sulphonyl-activated substrates\textsuperscript{13} is lacking for simpler systems. In fact it seems clear that the chloride ion induced dehydrochlorination of DDT in acetone and DME is a single-step E2 process, since the Hammett $\rho$ values (1.31 for acetone and 0.99 for DME)\textsuperscript{14} are very much lower than those expected for carbanion formation.

The approaches to the identification of E1cB dehydrochlorination in this and the preceding paper are somewhat similar to one employed by Hine and Ramsey.\textsuperscript{15}

REFERENCES


Eliminations promoted by Thiolate Ions. Part IV. A Hammett Equation Study of the Reactions of 1,1-Diaryl-2,2,2-trichloro- and 1,1-Diaryl-2,2-dichloro-ethane with Benzenethiolate Ions in Ethanol

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1972
Eliminations promoted by Thiolate Ions. Part IV.¹ A Hammett Equation Study of the Reactions of 1,1-Diaryl-2,2,2-trichloro- and 1,1-Diaryl-2,2-dichloro-ethane with Benzenethiolate Ions in Ethanol

By D. J. McLennan * and R. J. Wong, Department of Chemistry, University of Auckland, Auckland, New Zealand

The Hammett ϕ value for the benzenethiolate-promoted dehydrochlorination of 1,1-diaryl-2,2,2-trichloroethane (DDT-type) compounds in ethanol is 2.11 at 65 °C. For Sn2 substitution of benzenethiolate for chloride in the 1,1-diaryl-2,2-dichloroethane (DDC) series, ϕ = 0.41. Comparison of the former value with that for the conventional E2 reaction promoted by ethoxide in ethanol (2.34) suggests that the transition state for the benzenethiolate-promoted reaction is of the normal E2H variety, and is not an E2C-like transition state. The DDD Sn2 reaction series has been chosen as a model for possible E2C dehydrochlorination of DDT, and the disparity between the two ϕ values indicates that the DDT transition state has considerably more β-carbanionic character than does the DDD transition state.

The fact that DDT is dehydrochlorinated by weak bases such as benzenethiolate and chloride ions more readily than DDD is also taken as evidence in favour of the E2H mechanism. Potential-energy calculations, based on the assumption that both DDT and DDD eliminate via E2C transition states, give theoretical DDT:DDD rate ratios close to unity, which are widely different from the experimental values.

The assumption of additivity of substituent constants in diarylmethyl Hammett series is questioned and a novel method of obtaining linear plots is described.

In Part I² it was shown that the bimolecular dehydrochlorination of the DDT (1c) in ethanol [equation (1)] was some 8000 times slower at 65 °C when benzenethiolate (pKb = 9.8 in ethanol)² was used as base than

\[(\rho - RC_6H_4)_2CH\cdot CCl_3 + B^- \rightarrow (I)\]

\[(\rho - RC_6H_4)_2CCl_3 + BH + Cl^- (I)

(a) R = OMe  (e) R = Cl  
(b) R = Me  (f) R = Br  
(c) R = H  (g) R = NO₂

(d) R = F

with the strong base ethoxide. This is hardly surprising

⁵ D. J. McLennan, J. Chem. Soc. (B), 1966, 705.

character (V), to which class DDT-type compounds properly belong.\textsuperscript{2}

\[ \begin{align*}
\text{B}^- & \quad \text{B}^- \\
\text{H} & \quad \text{C} \\
\text{X} & \quad \text{C} \\
\text{(III)} & \quad \text{(IV)} & \quad \text{(V)}
\end{align*} \]

However, other possible explanations are provided by recent studies by Parker, Weinstein, and their co-workers.\textsuperscript{6,8,13} They have suggested another dimension to the E2 transition-state spectrum (VI–VIII) to be utilized by weak bases which are also strong carbon nucleophiles,\textsuperscript{14} such as halide ions in dipolar aprotic solvents and thiolate ions. Such species are held to react via E2C-like transition states (VI) or (VII) whilst

\[ \begin{align*}
\text{H}^+ & \quad \text{B}^- \\
\text{B}^- & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{(VI)} & \quad \text{(VII)} & \quad \text{(VIII)}
\end{align*} \]

strong bases utilize conventional E2H transition states such as (VIII). The similarity of E2C to S\textsubscript{N}2 transition states, as far as the bonding situation at C\textsubscript{4} is concerned, is clear. Substrates such as DDT, which have the leaving group in a poor environment for departure, would obviously not react readily in E2C thiolate-promoted eliminations as the ‘tighter’ transition state\textsuperscript{14,13} is not the ideal type for such reactions.

We have argued\textsuperscript{13} that most of the experimental evidence presented in favour of the E2C mechanism for halide-promoted elimination from ‘loose’ substrates such as t-butyl chloride and cyclohexyl toluene-\textsubscript{p}-sulphonate can equally well be interpreted in terms of paenecarbonium E2H transition states such as (III).

Lloyd and Parker however have recently found that the rates of such reactions are fairly insensitive to the electronic effects of \textit{para}-substituents on \textit{a}-bound aryl groups,\textsuperscript{16} and this result is incompatible with electron deficiency at C\textsubscript{4} in the transition state. If this is the case, the E2C mechanism seems to have been adequately demonstrated for halide-promoted elimination, and by analogy for thiolate-promoted elimination, from ‘looser’ substrates.

It thus becomes necessary to reopen the question of the mechanism of the benzenothiolate-promoted dehydrochlorination of DDT since the low \( \beta \)-deuterium isotope effect (3·1 at 45 °C) and the low RS\textsuperscript{−}:RO\textsuperscript{−} rate ratio are also compatible with a ‘tight’ four-centre E2C transition state.\textsuperscript{14,17,18} Such tightness could also account for the high Bronsted \( \beta \) value (0·77) which could be diagnostic of a situation in which the nucleophile is strongly bound to both C\textsubscript{4} and H\textsubscript{3} in an E2C transition state as well as to an E2H paenecarbonian transition state.

RESULTS

The solvent throughout was magnesium-dried ethanol. Temperatures in the kinetic runs were controlled to within 0·1 °C. All rate constants have units of mol\textsuperscript{−1} s\textsuperscript{−1}.

<p>| Table 1 |
| Rate constants ( * ) for the reaction of ((p-RC\textsubscript{6}H\textsubscript{4}H\textsubscript{2})_2\text{CH}\cdot\text{CHCl}_2) compounds ((ca. : 0·01M)) with sodium benzenothiolate ((ca. : 0·03M)) ( b ) in ethanol at 65·0 °C |</p>
<table>
<thead>
<tr>
<th>R</th>
<th>MeO</th>
<th>Me</th>
<th>H</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>NO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>10\textsuperscript{4}</td>
<td>0·55</td>
<td>0·40</td>
<td>1·45</td>
<td>10·7</td>
<td>26·4 ( ^e )</td>
<td>28·8</td>
<td>1880</td>
</tr>
<tr>
<td>* Mean of two or more concordant runs. ( ^e ) [PhSH] ca. 0·001M. ( ^2 ) Ref. 2.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

shows rate constants for the second-order reactions of \( p \)-substituted DDT-type compounds with sodium benzenothiolate. All reactions proceeded by the stoichiometry of equation (1).

The \( S\textsubscript{N}\textsubscript{2} \) reactions\textsuperscript{19} of other 1,1-diaryl-2,2-dichloroethanes with sodium benzenethiolate were also examined.

Except for the \( p \)-nitro-compound (IXf), the stoichiometry of the reactions of these derivatives with benzenethiolate in ethanol was as shown in equation (2). The sole organic products of all such reactions (X) were identical

\[ (p-RC\textsubscript{6}H\textsubscript{4}H\textsubscript{2})_2\text{CH}\cdot\text{CHCl}_2 + 2\text{PhS}^- \rightarrow (IX) \]

\[ (p-RC\textsubscript{6}H\textsubscript{4}H\textsubscript{2})_2\text{C}\cdot\text{CHSPh} + 2\text{Cl}^- + \text{PhSH} \quad (2) \]

(a) R = OMe (d) R = Cl
(b) R = Me (e) R = Br
(c) R = H (f) R = NO\textsubscript{2}

to the products of the reactions of \((p-RC\textsubscript{6}H\textsubscript{4}H\textsubscript{2})_2\text{CCHHal}\) with

\begin{align*}
\text{D. J. McLennan and R. J. Wong, Tetrahedron Letters, 1970, 5829.} \\
\text{R. F. Hudson, Chimia (Switz.), 1962, 16, 175.} \\
\end{align*}
PhS\(^-\) in dimethylformamide\(^{30}\) or to have properties similar to those of the products of the reactions of \((p-RC_6H_4)CHCHHal\) with \(p-MeC_6H_4S^-\) in dimethylformamide.\(^{21}\) The reaction kinetics were strictly of the second-order, first-order in both substrate and benzenethiolate. In all cases the rate of production of PhSH lagged behind the rate of destruction of substrate indicating that, as is the case for compound (IId),\(^9\) the actual product is \((p-RC_6H_4)CHCH(SH)Ph\), which slowly eliminates thiophenol. G.l.c. failed to detect any olefin of the type \((p-RC_6H_4)CHCHCl\) (XI) under conditions where 0-5% would have been observed. It is known however that the chloro-olefin (XI; \(R = Cl\)) is unstable in the presence of both PhS\(^-\) and PhSH and forms (XId)\(^9\). But at an early stage of the reaction between PhS\(^-\) and (IXd), when the benzenethiol concentration was low and where a control experiment showed that the chloro-olefin was largely stable, no such product was actually observed under conditions where an amount corresponding to an overall yield of 0-5% would have been detectable. The anomalous reactions of the \(p\)-nitro-compound (IXf) are described in the Experimental section. Table 2 shows the second-order rate constants for the Sc\(^2\) reactions of the DDD-type compounds with benzenethiolate.

### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>(k \times 10^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R)</td>
<td>(MeO)</td>
</tr>
<tr>
<td>10(^3)</td>
<td>50-1</td>
</tr>
</tbody>
</table>

\(^{31}\) Mean of two or more concordant runs. \(^{32}\) [PhSH] ca. 0-001 M. \(^{33}\) Extrapolation of rate constants in ref. 19 to 65 °C gives a rate constant of 127 \(\times 10^{-4}\) M\(^{-1}\) s\(^{-1}\).

### DISCUSSION

**The DDT Reactions.**—The Hammett plot of log \(k_2\) for the reactions of \(Ar_2CH-CCl_4\) compounds against \(2\sigma\) (\(\sigma\) values from Leffler and Grasswald\(^{23}\)) is shown in Figure 1. The least-squares line gives a \(\rho\) value of 1.79 with standard deviation (\(s\)) of 0.14 and correlation coefficient (\(r\)) of 0.980. The fit of the data to the least-squares line is not particularly good and, most seriously, the \(p\)-methoxy-compound (\(\sigma = -0.27\)) is more reactive than the \(p\)-tolyl derivative (\(\sigma = -0.17\)). The rate constants for three other compounds also deviate significantly. Similar irregular behaviour can be found in other work involving multiple substitution in both rings of \(Ar_2^C^-\) systems.\(^{24-25}\) The assumption that \(2\sigma\) adequately represents the total substituent effect, i.e., that substituents affect the rate independently and additively, must therefore be questioned.\(^{26}\)

\(^*\) The real stereochemical situation will obviously not be as suggested here, but it will be equivalent to our model as we are principally concerned with the orientation of one benzene ring relative to the other.


In improving the Hammett plot and in finding an adequate substituent parameter,\(^{36}\) we note that generally the greatest deviations occur with those substituents having the strongest resonance interactions with the reaction centre. If it is assumed that the inductive (field) effects of the substituents are not dependent on the relative orientation of the two benzene rings in the initial and transition states, the relevant total inductive parameter will be \(2\sigma_1\) where \(\sigma_1\) is the inductive component of the Hammett \(para\)-substituent constant.\(^{27}\) On the other hand, if one benzene ring is oriented so that the full resonance effect of its substituent can be felt at the reaction centre, i.e., with its plane perpendicular to the lobes of the developing \(p\)-orbital on \(C_5\), the other ring cannot adopt such an orientation for steric reasons, and the full resonance effect of the substituent on the latter ring can therefore not be felt at the reaction centre.* The relevant total resonance parameter is thus not \(2\sigma_2\) (where \(\sigma_2\) is the resonance component of the Hammett \(para\)-substituent constant\(^ {27}\)) but rather \((1 + \alpha)\sigma_2\) where \(\alpha\) is a parameter, with possible values between zero and unity, which is a measure of the inability of both substituents to exert their full resonance electron-donating or -withdrawing powers on the reaction centre because of the inability of the rings to achieve coplanarity. It has recently been shown that the benzene rings in both DDT and its dehydrochlorination product (Ile) in solution are far from being coplanar.\(^ {28}\)

Consequently, \(2\sigma_1 + (1 + \alpha)\sigma_2\) should best represent the total substituent effect, and we have computed plots of log \(k_2\) against this quantity for various values of \(\alpha\). The best plot (Figure 2), as judged by a clear minimum in the standard deviation of the slope, is found for \(\alpha = 0.37\). The \(\rho\) value arising from this much-improved Hammett plot is 2-11, with \(s = 0.02\), and \(r = 0.999\).

Cockerill and Lamper\(^{29}\) have recently and independently used this method to correlate the acids


\(^{26}\) R. J. Wong, MSc Thesis, University of Auckland, 1970.


of 9-arylfluorenes. Their procedure for calculating the angle between the rings in a non-coplanar aromatic system as applied to the present results enables us to estimate that the angle between the planes of the rings in the DDT–PhS⁻ transition state is 50°. This is nicely in between the measured angle in the reactant molecule (40°) and in the product (55°). Unpublished results on the Ar₂C₆H₄–B₃H₅–NCI reaction in acetone and the Ar₂C₆H₄–LiCl reaction in dimethylformamide reveals the necessity for the modified Hammett treatment. We note that although the assumption is made that direct resonance interaction between the reaction centre and the substituents occurs, use of a σᵢ value based on σ特色的p-nitro results in a poorer correlation in all cases.

Cristol et al. obtained only a fair Hammett plot of log k against 2σ for the Ar₂C₆H₄–CCl₃–OEt⁻ dehydrochlorination in EtOH; φ = 2.34 ± 0.24; r = 0.908 at 65°C. The p-methoxy-point exhibited a positive deviation from the least-squares line.

![Figure 2](image-url) Modified Hammett plot of log k against (2σ₂ + 1.37σ₃) for the reaction of Ar₂C₆H₄–CCl₃ with PhS⁻.

It is noteworthy that in one reaction series, involving vinylic nucleophilic substitution in compounds of the type Ar₃C≡CHHal, plots of log k against 2σ are clearly linear. In such a system the hybridization of Cβ remains sp³ on going from the initial to the transition state and hence the relative orientation of the two rings need not change, whereas in our system and in other badly behaved reactions, the hybridization of the carbon atom to which both rings are bonded changes from sp³ in the initial state to partial sp² in the transition state. This factor appears to be a condition for the success of our treatment, which is somewhat equivalent to one in which a different ρ value is associated with each ring. An advantage of the present method is that a single reaction parameter can be used to describe the overall sensitivity of the reaction to substituent effects.

The ρ value for DDT dehydrochlorination by benzenethiolate (2:11) is comparable with that (2:34 at 65°C) obtained when the base is ethoxide in 95% ethanol. The latter reaction, involving a strong base reacting with an ‘acidic’ substrate which has the leaving group in poor environment for departure, almost certainly proceeds through a benzoecarbanion E2H transition state, and the relatively large ρ value supports this view. Similarly, the comparable ρ value for the benzene-thiolate-promoted elimination seems to be diagnostic of a large amount of negative charge at Cβ in the transition state. On the other hand, E2C-like transition states as visualized by Winston and Parker, have little negative charge residing on Cβ and little positive charge on Cα. They are characterized instead by a large degree of double-bond development.

On this basis it appears that the DDT–PhS⁻ reaction does indeed pass through a benzoecarbanion E2H transition state as previously supposed. The large Bronsted β and low deuterium isotope effect thus point to a linear three-centre proton transfer process with the proton closer to the base than to Cβ instead of to a fourcentre E2C transition state having a well-formed S···Cα partial bond. The ring substituents appear to have a small but significant influence on the character of this E2H transition state. Values of k₄(PhS⁻)/k₄(OEt⁻) at 65°C, with the ethoxide rate constants having been extrapolated from data pertaining to 95% ethanol as solvent at lower temperatures, are, for R = MeO, 4.15 × 10⁻¹⁴; for R = H, 3.04 × 10⁻¹⁴; and for R = Br, 1.35 × 10⁻¹⁴. Such a decrease is consistent with the transition state’s becoming more benzoecarbanionic as the substituents are made more electron-demanding. This interpretation is in agreement with the observation that the Bronsted coefficient for the E₂ reaction series of p-NO₂-C₆H₄CH₂CH₂Br with ArO⁻ is greater than that for the PhCH₂CH₂Br–ArO⁻ series, and both these results can be reconciled with More O’Ferrall’s theory on the effect of substituents on transition-state geometry.

It is also noteworthy that as the base strength is increased along the series Cl⁻, PhS⁻, OEt⁻ the Hammett φ value increases for the dehydrochlorination of Ar₂C₆H₄–CCl₃ compounds. This is in accord with Burnett’s prediction and with the recent results of Yano and Oae.

The DDT Reactions.—What should be the magnitude of ρ in E2C elimination of HX from compounds having the skeleton Ar–CH–CX? Chloride-promoted dehydrobromination of 2-benzyl-2-bromoindan-1-ones in acetonitrile has a ρ value of 0.44, whilst ρ = 0.17 is obtained for the bromide-induced reaction. These low values are comparable with those found for Sₓ₂ elimination of X from compounds having the above skeleton. The analogy between Sₓ₂ and E2C-like transition states for competitive substitution and elimination from a given substrate has been demonstrated. This type of analysis cannot be used for DDT since no substitution can be detected. However the dichloro-analogue of DDT, namely DDD, reacts with benzenethiolate by an
The structural similarity of the two compounds makes the Ar₂(CH–CHCl₂–Ph) series an attractive model for the possible E2C reaction of DDT.

A plot of log k₂ (Table 2) against 2e is accurately linear, with p = 0.41, r = 0.988, s = 0.03. The fit of the points is not improved by using the treatment employed for the DDT series (i.e., a = 1-00).

Several important implications arise from this result. First, since the Hammett p is very much different from that found for E2H dehydrochlorination of Ar₂CH–CHCl₂ compounds (2.19 at 65°C with OEt⁻ in EtOH),³¹ the rate-determining step of the benzethiolate-promoted reaction is not dehydrochlorination, in accordance with other evidence.¹⁹ This suggestion is substantiated by the non-observation of dehydrochlorination products. Secondly, the Hammett plot is linear, indicating that the balance between bond-making and bond-breaking in the S₂2 transition states is largely unaffected by the substituents. This is not always the case.¹⁶,³⁶,³⁸

Most importantly from the point of view of the DDT–PhS reactions, the p value for the S₂2 reactions of a closely related series is about five times smaller than that for the elimination. A plot of log k₂ for the DDT reactions against log k₂ for the corresponding DDD compounds is a scatter diagram. The conclusions are that the S₂2 and E2 transition states are quite dissimilar and that the latter have no significant E2C character. A similar conclusion is reached when the p value for the fluoride-induced dehydrochlorination of 2-arylethyl chlorides (2.03) is compared with that for the S₂2 chloride exchange (0.57) in acetonitrile.³⁹

The DDT: DDD E2 Rate Ratio.—From the observation that the DDD–PhS reaction produces <0.5% dehydrochlorination product and from the rate constants²,¹⁹ for the DDD–PhS and DDT–PhS reactions at 45°C, it can be deduced that the DDT: DDD dehydrochlorination rate ratio is at least 23 per chlorine (ΔG² = 2.40 kcal mol⁻¹ in favour of DDT) when PhS⁻ is the hydrogen nucleophile. It can also be calculated, albeit roughly, on the basis that DDT is not visibly dehydrochlorinated by Bu₄NCl after 5-5 h under reflux in acetone containing 2,4,6-collidine,¹⁵ that the DDT: DDD E2 rate ratio with Cl⁻ is at least 70 per chlorine at 65°C (ΔG² = 3.1 kcal mol⁻¹ in favour of DDT). The DDT: DDD E2H rate ratio (ethoxide in ethanol)²,¹⁹ is 3.6 at 45°C. On the other hand, rates of S₂2 reactions are known to be retarded by α-halogen substituents,⁴⁰ and this is confirmed by the DDD: DDT S₂2 rate ratio for reaction with PhS⁻, which is at least 1.5 × 10⁶. These rate ratios suggest that the DDT–PhS– and DDT–Cl⁻ reactions do not proceed through S₂2-like transition states (such as E2C), but through E2H transition states as does the DDT–OEt⁻ elimination.

Parker and his co-workers however have reported that large α- and β-bound groups accelerate E2C-like reactions¹¹ and have suggested that non-bonded repulsions between such groups are relieved as the initial state sp³ hybridization changes to near-sp³ in the E2C transition state. This consideration applied to DDT and DDD leads to the conclusion that the former should be more reactive than the latter in E2C reactions. Thus the observed rate ratio is apparently also qualitatively consistent with the E2C mechanism.

In an attempt to resolve this ambiguity we have carried out potential-energy calculations. We have calculated the potential-energy changes (ΔW) caused by interaction of non-bonded and non-reacting atoms for the processes in equations (3) and (4) which are taken as models for

\[ \text{CCl}_4 (sp^3) \rightarrow \text{CCl}_4 (sp^2) \] (3)

\[ \text{CHCl} (sp^3) \rightarrow \text{CHCl} (sp^2) \] (4)

the situation at C₄ in E2C reactions of DDT and DDD respectively. The potential function chosen was that so successfully employed by Hughes, Ingold, and their co-workers for calculation of steric contributions to S₂2 rates,⁴¹ except that we have replaced their ion-dipole interaction term with a dipole–dipole interaction.⁴² The calculations were performed, in the case of the system represented by equation (3), by computing W with r, the distance between the two chlorines, being calculated from sp³ C–Cl bond lengths and the appropriate bond angle. A value of r and hence of W was then computed for the CCl₄ (sp²) system by use of sp² bond lengths and an angle of 120°, and ΔW was taken as the difference between the latter and former energy values. The same procedure was followed for the system represented by equation (4).

If r values are calculated by adding the appropriate covalent radii,⁴³ it is found that ΔW = 0.641 kcal mol⁻¹ for the CCl₄ system and is 0.272 kcal mol⁻¹ for the CHCl system. Values of r have also been calculated from measured bond lengths and angles in suitable model compounds⁴⁴ and lead to ΔW values of 0.031 and 0.132 kcal mol⁻¹ respectively. Intermediate values of r produce intermediate energy changes.

If all other things in the hypothetical DDT and DDD E2C transition states are equal, these potential energy changes can be equated to contributions from non-bonded interactions at C₄ to the free energy of activation. From the first pair of energies mentioned above we calculate, via the ΔG² value, that as far as the situation at C₄ is concerned, DDD should be 1-13 times more reactive than DDT. Use of the second pair of energies gives the result that DDT should be only 1-16 times more reactive than DDD. Intermediate values of r produce

³⁷ Ref. 22, p. 191.
⁴¹ (a) I. Dostrovsky, E. D. Hughes, and C. L. Ingold, J. Chem. Soc., 1946, 177; (b) P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. L. Ingold, and J. D. H. Mackie, ibid., 1955, 3200.
⁴⁴ 'Tables of Interatomic Distances and Configuration in Molecules and Ions,' Chem. Soc. Special Publ., 1958, No. 11.
intermediate values of the rate ratio. Thus non-bonded interactions at \( C_2 \) appear to have a negligible effect on the DDT:DDD E2C rate ratio. The not obvious reasons for this are that London forces almost balance the effects of dipole-dipole and van der Waals interactions as the hybridization at \( C_2 \) is changed from \( sp^3 \) to \( sp^2 \), and that the increase in the bond angle from 109° 28' to 120° is accompanied by a decrease in C-Cl and C-H bond lengths, so that the overall change in \( r \) is small. It should be noted that we have neglected phenyl-clorine, phenyl-hydrogen, nucleophile-chlorine, and nucleophile-hydrogen interactions in our calculations. These are longer-range forces than those already mentioned, and rough calculations based on estimated distances show that the DDT:DDD rate ratio is increased by only ca. 20% by their inclusion.

The calculated and experimental rate ratios do not agree. The conclusion is that the DDT and DDD transition states do not have near- \( sp^2 \) hybridization at \( C_2 \) and are therefore not E2C-like. This conclusion is based on the assumptions that (i) the potential function is a good one and (ii) the hypothetical DDT and DDD E2C transition states are identical in all respects except at \( C_2 \). Concerning (i), the suitability of this type of potential function has been amply demonstrated for systems more complex than used here,\(^{41,46} \) even though the dipole term is more appropriate for long-range interactions.\(^{42} \) Assumption (ii) is reasonable for E2C-like transition states with a well developed double bond, since little negative charge is permitted at \( C_2 \) and hence the inductive effect of the extra \( \alpha \)-chlorine in DDT should be of little consequence. It is probably the primary cause of DDT being more reactive than DDD under E2H conditions, but even with these paenecarbonian transition states the acceleration is small (3-6-fold)\(^{4,19} \) and not enough to account for the present discrepancy.

**Conclusion:** Our conclusion that the reaction of DDT with PhS\(^{-} \) is E2H rests on firm experimental grounds. Thus the decrease in RS\(^{-} \): RO\(^{-} \) E2 rate ratios as substrates are changed from the t-butyl chloride type to the DDT type seems, on the basis of evidence available, to be caused by the RS\(^{-} \) transition states shifting from the E2C- to the E2H-type.

The potential-energy calculations indicate that the DDT:PhS\(^{-} \) and DDT:Cl E2 transition states are not E2C-like.

### EXPERIMENTAL

N.m.r. spectra were run on a Varian Instruments T-60 instrument with CDCl\(_3\) as solvent. Analytical g.l.c. was performed on a Varian Aerograph Model 1400 instrument with a column of SE-30 on Varaport 30 at 200 °C. U.V. absorption spectra of solutes in 95% ethanol were obtained on a Unicam SP800 instrument.


**Materials.**—DDT (Ic) (Aldrich) was recrystallized repeatedly from ethanol. Compounds (Ia) and (Ib) were prepared by dissolving 1 equiv. of 2,2,2-trichloroethanol in a 1:1 HOAc-H\(_2\)SO\(_4\) mixture and adding 2 equivs. of anisole and toluene respectively, dropwise at 0 °C. Compound (Ia) was recrystallized from n-hexane and (Ib) from methanol. Compounds (Ic) and (Id), the latter prepared by Mr S. A. Short, were obtained by condensing 1 equiv. of 2,2,2-trichloroethanol with 2 equivs. of benzene and fluorobenzene respectively, in concentrated H\(_2\)SO\(_4\) at 0 °C. Compound (Ic) was recrystallized from ethanol and (Id) from chloroform-benzene. The latter melted over a wider range than usual, but t.l.c. and the n.m.r. spectrum revealed no impurity. Compound (If) was prepared in the same way as were (Ic) and (Id) except that portions of oleum were added to the mixture during the addition of bromobenzene. It was recrystallized from ethanol. Compound (If) resulted from the nitration of (Ic) with fuming nitric acid according to Haskelberg and Lavié.\(^{44} \) It was recrystallized from glacial acetic acid. M.p. and n.m.r. data for all compounds are in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.p. (°C)</th>
<th>Lit. m.p. (°C)</th>
<th>N.m.r. δ*</th>
<th>Lit. n.m.r. δ*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ia)</td>
<td>89–90</td>
<td>87–88 (31)</td>
<td>4.96</td>
<td>4.93</td>
</tr>
<tr>
<td>(Ib)</td>
<td>90–91</td>
<td>92 (49)</td>
<td>4.99</td>
<td></td>
</tr>
<tr>
<td>(Ic)</td>
<td>64.5–65.5</td>
<td>65 (49)</td>
<td>5.06</td>
<td>5.05</td>
</tr>
<tr>
<td>(Id)</td>
<td>38.5–43</td>
<td>42–45 (31)</td>
<td>5.00</td>
<td>5.03</td>
</tr>
<tr>
<td>(Ie)</td>
<td>108–109</td>
<td>108–109 (31)</td>
<td>5.02</td>
<td>5.02</td>
</tr>
<tr>
<td>(If)</td>
<td>142.5–143.5</td>
<td>142.9–143.6 (31)</td>
<td>4.98</td>
<td>4.97</td>
</tr>
<tr>
<td>(Ig)</td>
<td>168–169</td>
<td>169 (48)</td>
<td>5.36</td>
<td>5.35</td>
</tr>
</tbody>
</table>

* Chemical shift of benzylic proton downfield from tetramethysilane in p.p.m. \(^{4} \) Ref. 47.

### Dichloroacetal (1,1-dichloro-2,2-dihydroxyethane) was prepared by the method of van Dorp and his co-workers.\(^{48} \) DDD (IxI) (Aldrich) was recrystallized repeatedly from ethanol. Compounds (Ixa), (Ixb), (Ixc), and (Ixe) were prepared from dichloroacetal and anisole, toluene, benzene, and bromobenzene respectively, by use of a method similar to that employed for their trichloro-analogues. Yields and ease of product isolation were improved by adding acid to a stirred mixture of dichloroacetal and the appropriate arene at 0 °C. Nitration of (Ixc) according to the method of Delaby and Baronnet\(^{49} \) afforded compound (Ixf). All compounds were recrystallized from ethanol except for (Ixf), for which glacial acetic acid was employed. M.p. and n.m.r. data for all the above compounds are in Table 4. Satisfactory microanalytical results for several of the compounds in Tables 3 and 4 were obtained.

The above DDT and DDD compounds, with the exception of (Ixf), were dehydrochlorinated by a previously described method.\(^{2} \) Compound (Ixf) was dehydrochlorinated at 0 °C instead of under reflux. Properties of the resulting olefins, most of which were recrystallised from methanol or


ethanol, are shown in Table 5. Satisfactory micro-analyses were obtained for several of these oleins.

**Table 4**

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.p. (°C)</th>
<th>Lit. m.p. (°C)</th>
<th>N.m.r.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(IXa)</td>
<td>114–115</td>
<td>114–5–115 (31)</td>
<td>4.48</td>
</tr>
<tr>
<td>(IXb)</td>
<td>78–65–70</td>
<td>78–5–70 (31)</td>
<td>4.47</td>
</tr>
<tr>
<td>(IXc)</td>
<td>78–77–5</td>
<td>75–7–58 (31)</td>
<td>4.50</td>
</tr>
<tr>
<td>(IXd)</td>
<td>109–110</td>
<td>109–5–110 (19)</td>
<td>4.50</td>
</tr>
<tr>
<td>(IXe)</td>
<td>134–135</td>
<td>134–135 (31)</td>
<td>4.45</td>
</tr>
<tr>
<td>(IXf)</td>
<td>177–178</td>
<td>178–5–48 (48)</td>
<td>4.83</td>
</tr>
</tbody>
</table>

* Chemical shift of benzylic proton downfield from tetramethylsilane in p.p.m.  
* Ref. 47 reports 8 6.3 Hz.

**Table 5**

Dehydrochlorination products of substituted DDT- and DDT-type compounds

<table>
<thead>
<tr>
<th>Olefin</th>
<th>M.p. (°C)</th>
<th>Lit. m.p. (°C)</th>
<th>N.m.r.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ia)</td>
<td>110–130</td>
<td>109 (49)</td>
<td>254</td>
</tr>
<tr>
<td>(Ib)</td>
<td>85–65</td>
<td>87 (49)</td>
<td>247</td>
</tr>
<tr>
<td>(Ic)</td>
<td>78–79</td>
<td>80 (49)</td>
<td>247</td>
</tr>
<tr>
<td>(Id)</td>
<td>37–105</td>
<td>30–5 (31)</td>
<td>246</td>
</tr>
<tr>
<td>(Ie)</td>
<td>89–91</td>
<td>87–58 (22)</td>
<td>245</td>
</tr>
<tr>
<td>(If)</td>
<td>121–121</td>
<td>121 (49)</td>
<td>240</td>
</tr>
<tr>
<td>(Ig)</td>
<td>172–172</td>
<td>127–173 (51)</td>
<td>240</td>
</tr>
<tr>
<td>(XI)</td>
<td>80–81</td>
<td>80–81 (31)</td>
<td>250</td>
</tr>
<tr>
<td>(XII)</td>
<td>66–67</td>
<td>67 (52)</td>
<td>240</td>
</tr>
</tbody>
</table>

Ethanol was dried with magnesium turnings and sodium benzenethiolate solutions were prepared as before. Benzenethiol was purified as before.

**Table 6**

Products of the reaction of DDT-type compounds with benzeneethiolate in ethanol

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.p. (°C)</th>
<th>Lit. m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Xa)</td>
<td>65–69</td>
<td>69 (20)</td>
</tr>
<tr>
<td>(Xb)</td>
<td>72–72–73</td>
<td>72–73 (20)</td>
</tr>
<tr>
<td>(Xc)</td>
<td>70–71</td>
<td>70–71 (19)</td>
</tr>
<tr>
<td>(Xd)</td>
<td>99–101</td>
<td>99–101 (19)</td>
</tr>
</tbody>
</table>

Experiments with use of t.l.c. for detection showed that the starting materials were stable during work-up.

Compound (IXf) was heated under reflux with 2 equivs. of NaSPh and 1 equiv. of PhSH in ethanol for 48 h. Normal work-up produced a dark red gum which was chromatographed on silica gel using a graded series of n-hexane-ether mixtures for elution. Products obtained were: diphenyl disulphide (86%), m.p. 60–61 °C (lit. 61 °C); the olefin (XI; R = NO2) (8%), m.p. and mixed m.p. with an authentic sample, 145–146 °C (lit. 146–147 °C); d{i} (p-nitrophenyl)acetylene (10%), m.p. and mixed m.p. with an authentic sample 212–214 °C (lit. 214 °C); and an intractable dark red tar which resisted elution and which failed to yield crystals from a variety of solvents. The combined aqueous extracts from work-up, which contained a water-soluble compound exhibiting the properties of an acid–base indicator, were acidified with dilute nitric acid, volumetrically diluted, and a sample was titrated with a silver nitrate solution. The amount of chloride ion corresponded to 1:91 equivs. per equiv. of starting material.

**Kineti**cs.—The reactions of Ar3CH·Cl3 with PhS− and of Ar3CH·CHCl3 with PhS− were followed as before. In all runs of the latter set, iodometric analysis for (PhS− + PhSH) was performed on a sample taken at ca. 50% reaction (as indicated by chloride-ion analysis). In all cases the production of benzenethiol lagged behind that of chloride ion.

A sample of mixture, taken from the reaction of compound (IXd) with PhS− at a time when 10% of the substrate

21 K. Brand and D. Krucke-Ameling, Ber., 1939, 72, B, 1029.
had been consumed as indicated by chloride-ion analysis and when 2% of the theoretical amount of benzenethiol had been produced as indicated by iodometric titration, was subjected to normal product work-up and g.l.c. analysis. No olefin (XI; R = Cl) was observed where an amount corresponding to a yield of 0.05% would have been detectable. Results of a parallel run involving the reaction of a small quantity of the chloro-olefin with PhS⁻ and PhSH, both at similar concentrations to those in the previous run, showed that the chloro-olefin was stable and detectable at this stage of the reaction. The conclusion is that it is formed to the overall extent of 0.5% or less.

We thank Dr. A. J. Parker for discussions and both him and Dr. R. A. More O’Ferrall for showing us manuscripts in advance of publication. We also thank Dr. A. D. Campbell, University of Otago, for microanalyses, and Mr. S. A. Short for some preparations.

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Chloride-ion Promoted Dehydrochlorination of 1,1-Diaryl-2,2,2-trichloroethanes in Dipolar Aprotic Solvents

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Chloride-ion Promoted Dehydrochlorination of 1,1-Diaryl-2,2,2-trichloroethanes in Dipolar Aprotic Solvents

By O. R. Jackson, D. J. McLennan, S. A. Short, and R. J. Wong, Department of Chemistry, University of Auckland, Auckland, New Zealand

Rate constants are reported for the second-order dehydrochlorination reactions of $\text{Ar}_2\text{CHCl}_2$ compounds promoted by $\text{Bu}_4\text{NCl}$ in acetone and by $\text{LiCl}$ in dimethylformamide. Rate data for the dehydrochlorination reactions of $\text{Ar}(\text{Ph})\text{CHCl}_2$ compounds in the latter system are also presented. A modified Hammett-equation analysis yields $p$ values of 1.31 (acetone) and 0.99 (dimethylformamide). It is considered that these parameters are diagnostic of a significant degree of $\beta$-carbonionic character in the $E2$ transition states, and that the system provides the first clear example of a halide-promoted $E2$H reaction. The $E2C$ mechanism can be definitely rejected for this particular case.

Second-order olefin-forming eliminations of organic halides and sulphonate esters do not necessarily require the agency of a strong base. Weakly basic systems such as halide ions in dipolar aprotic solvents$^{1-8}$ and thiolate ions in both protic$^9$ and dipolar aprotic$^9,10,11$ solvents are often more effective in promoting such eliminations than are conventionally strong bases such as alkoxide ions in alcohol.

A controversy has arisen as to the nature of the transition:

1. J. C. S. Perkin II

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tion state in eliminations promoted by weak bases. One view is that the transition states belong to the normal $E2H$ spectrum of $E2$ transition states (I)–(III) and (IV)–(VI) in which the weak bases utilize the $E2C$-like transition states (V) and (VI) with suitable substrates.

They characterize $E2C$-like transition states as having well-developed double bonds, with most of the charge residing on B and X with little if any charge at Cα and Cr ('loose' transition states).

However the picture is incomplete. The substrates that have so far been investigated with respect to halide-promoted eliminations are those (mainly secondary and tertiary alkyl halides and arenediazonium salts) which would, under $E2H$ conditions (alkoxide ions in alcohol) be predisposed to react via ene carbenium transition states such as (I). We do not imply deliberate omission, for the fact is that the weak bases of interest do not usually promote olefin formation from the more 'acidic' substrates that would be expected to react through ene carbenium transition states (III) under $E2H$ conditions. For instance, the 2-arylethyl system Ar-CH$_2$-CH$_2$-X has been widely employed for $E2H$ investigations and transition-state character appears to vary from central (II) to ene carbenium (III) depending on the choice of base, solvent, and leaving group. However the reaction of 2-phenethyl bromide with benzenethiolate ions in ethanol yields only the product of nucleophilic substitution.

The dehydrochlorination of 1,1-diaryl-2,2,2-trichloroethanes (DDT-type compounds) with strong bases in protic solvents has been held to proceed via ene carbenion $E2H$ transition states. We have previously found that benzenethiolate ions also promote these reactions, although at a slow rate, as the multiplicity of halogens at C$_3$ retards possible competition by $S_N2$ reactions. With this fact in mind, the late B. D. England and his students investigated the reaction between 1,1,1-trichloro-2,2-bis-p-chlorophenylethane (DDT) and chloride ions (from tetra-n-butylammonium chloride) in acetone and found that dehydrochlorination occurred. Kinetics were of the second order when 2,6-lutidine was used to scavenge eliminated HCl. Substitution reactions that may be occurring in competition with the elimination are of course invisible in this system and do not consume the substrate.

We now take up the question of the mechanism of this $E2$ reaction between halide ions and an 'acidic' substrate. Our recent Hammett $\rho$-$\sigma$ analysis of the reaction between Ar$_3$CH-CCl$_3$ compounds and benzenethiolate ions in ethanol gave results which suggested an $E2H$ process, with the transition state having somewhat less carbanion character than that for ethoxide-promoted elimination. We now apply the same method to the reactions of Ar$_3$CH-CCl$_3$ compounds with chloride ions.

In fact there is now good evidence, arising from comparison of the measured elimination rate constant with an interpolated rate constant for deprotonation, that both the reactions of OR$^-$ in ROH and of PhS$^-$ in EtOH proceed via an $E1cB$ mechanism involving the intermediacy of an irreversibly-formed carbanion. Our previous basic conclusion, to the effect that the reactions possessed carbanion-like transition states, is thus unaltered, but comparison of Hammett $\rho$ values for the chloride-promoted and alkoxide-promoted reactions is now invalid.

RESULTS

The reactions between DDT-type compounds (VII) and Bu$_3$NCl in dry acetone displayed the stoichiometry of equation (I) when excess of 2,4,6-collidine was used as an

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$^{17}$ B. D. England, P. Ang, and P. R. Fawcett, unpublished results; P. Ang (1968), and P. R. Fawcett (1969), MSc. Theses, Victoria University of Wellington.
HCl scavenger. The hindered base has no effect on the rate constants but the reaction proceeds to equilibrium

\[(p-RCH\textsubscript{2})\textsubscript{2}CH\cdot CC\left\{Cl\right\}_2 + Cl^- \rightarrow (p-RCH\textsubscript{2})\textsubscript{2}CH\cdot CC\left\{Cl\right\}_2 + HCl + Cl^- \]

(VII) (VIII)

\[
a; \ R = OMe \\
b; \ R = Me \\
c; \ R = H \\
d; \ R = F \\
e; \ R = Cl \\
f; \ R = Br \\
g; \ R = NO\textsubscript{2}
\]

rather than to completion in its absence. All reactions obeyed first-order kinetics: rate = \(k_{obs}/[Cl\textsubscript{2}]\), up to about one half-life, consistent with the collidine chloride existing as tight ion-pairs, so that the concentration of free chloride ion does not change during the reaction. After allowance is made for small and regular salt effects, second-order rate coefficients calculated from \(k_2 = k_{obs}/[Cl\textsubscript{2}]\) are in fact constant. All further runs were carried out at the same initial salt concentration. The requisite olefins (VIII) were isolated in good yield from all runs and their identity established by comparison with authentic samples.

After about one half-life has elapsed for the slower reactions, \(k_{obs}\) values begin drifting downwards. This behaviour has been observed in similar systems and has been attributed to acid-catalysed condensation reactions of acetone. Hence the second-order rate constants in Table I apply to the first 50% of reaction.

### Table 1

<table>
<thead>
<tr>
<th>R</th>
<th>MeO</th>
<th>Me</th>
<th>H</th>
<th>Cl</th>
<th>Br</th>
<th>NO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>10(^{4})k\textsubscript{2}/mol\textsuperscript{-1} s\textsuperscript{-1}</td>
<td>8-11</td>
<td>7-62</td>
<td>15-6</td>
<td>83-8</td>
<td>113-1430</td>
</tr>
</tbody>
</table>

* Mean of two or more concordant runs. 2,4,6-Collidine (ca. 0-02% in acetone) present.

The above reactions were also studied with lithium chloride as the base in dimethylformamide solvent. At the concentration used, LiCl is about 90% dissociated. The stoichiometry was as in equation (1). It was not necessary to add an HCl scavenger as dry hydrogen chloride in dimethylformamide did not react with olefin (VIIe) during a period equivalent to several half-lives of the dehydrochlorination of (VIIe). The dehydrochlorination was expected to be autocatalytic with kinetics given by equations (2) and (3) in which \(a\) is the initial concentration of olefin at time \(t\). However, values of the second-order rate coefficient \(k_2\) so calculated drifted downwards during all runs. Second-order rate coefficients calculated on the assumption of no autocatalysis were also not constant, and it was assumed that the drift was caused by somewhat imperfect autocatalysis.

In correcting the drifting \(k_2\) values from equation (3) we assume that only free chloride ions are catalytically active, and that some equilibrium process consequent to the dehydrochlorination partially deactivates liberated chloride ions. The process could be that in equation (4) in which the Me\textsubscript{2}N-CHO.HCl complex is presumed to exist as both free ions and a hydrogen-bonded complex or ion-pairs. If the equilibrium constant for reaction (4) is \(K\), we can modify the \((a + x)\) term in equation (3) so that it refers to the Me\textsubscript{2}N-CHO.H\textsuperscript{+}Cl\textsuperscript{-} concentration of free chloride ions rather than to the total chloride concentration. The pertinent rate equation is thus (5) which on integration yields equations (6) or (7). In these equations, \(k_2\) is the true second-order rate constant. It can easily be shown that \(k_2 > k_2\) for all \(x, (a > x)\), so that \(k_2\) should indeed drift downwards. The true \(k_2\) values were therefore calculated from equation (7) by an iterative procedure which employs the drift of \(k_2\) values and calculates the value of \(K\) necessary for constancy of \(k_2\). The \(K\) needed for convergence should be independent of the substrate and this was found to be the case, within the bounds of the rather large error engendered by the smallness of the drift in \(k_2\). \(K\) values for convergence ranged between 0-5 and 0-9 mol\textsuperscript{-1} and a mean value of 0-7 mol\textsuperscript{-1} calculated from data for 17 substrates, was finally employed in the calculations for all substrates. A specimen run is shown in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Time/min</th>
<th>Absorbance * 10(^{4})k\textsubscript{2}/mol\textsuperscript{-1} s\textsuperscript{-1}</th>
<th>10(^{4})k\textsubscript{2}/mol\textsuperscript{-1} s\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0-154</td>
<td>9-40</td>
</tr>
<tr>
<td>1200</td>
<td>0-262</td>
<td>8-51</td>
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<td>2580</td>
<td>0-370</td>
<td>8-04</td>
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<tr>
<td>3180</td>
<td>0-401</td>
<td>7-50</td>
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<td>4110</td>
<td>0-450</td>
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<td>5460</td>
<td>0-520</td>
<td>6-70</td>
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<td>6160</td>
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<td>7320</td>
<td>0-608</td>
<td>6-44</td>
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<tr>
<td>8760</td>
<td>0-650</td>
<td>6-02</td>
</tr>
<tr>
<td>10,140</td>
<td>0-673</td>
<td>5-52</td>
</tr>
<tr>
<td>∞</td>
<td>1-040</td>
<td>8-48</td>
</tr>
</tbody>
</table>

* U.v. absorbance of sample, diluted 250-fold with methanol, at 283 nm. 2 Observed second-order rate constant, calculated from equation (9) (Experimental section). 3 Calculated from equation (7) by use of the appropriate \(k_2\) value and \(K = 0-7\) mol\textsuperscript{-1}. 4 Uncertainty expressed as standard deviation.

Also investigated were the reactions of substrates having only one para-substituted benzene ring (equation 8).

\[(p-RCH\textsubscript{2})\textsubscript{2}CH\cdot CC\left\{Cl\right\}_2 + Cl^- \rightarrow (p-RCH\textsubscript{2})\textsubscript{2}CH\cdot CC\left\{Cl\right\}_2 + HCl + Cl^- \]

IX

\[\text{(IX)}\]

\[
a; \ R = OMe \\
b; \ R = Me \\
c; \ R = Cl \\
d; \ R = Br
\]

Unfortunately we were unable to prepare the para-nitro-compound by our standard method. The unsymmetrically disubstituted compound 1,1,1-trichloro-2-p-chlorophenyl-2-p-methoxyphenylethane (XI) was also subjected to dehydrochlorination with LiCl in dimethylformamide. All rate constants for this base-solvent system are shown in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate Constant</th>
<th>λ/µm</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO</td>
<td>MeO</td>
<td>9:66</td>
<td>283</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>5:29</td>
<td>262</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>9:90</td>
<td>250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>25:2</td>
<td>248</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>55:2</td>
<td>260</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>36:3</td>
<td>277</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_3$</td>
<td>NO$_3$</td>
<td>406</td>
<td>305</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>MeO</td>
<td>7:44</td>
<td>255</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>F</td>
<td>17:6</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>Cl</td>
<td>23:0</td>
<td>265</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>Br</td>
<td>24:1</td>
<td>265</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>MeO</td>
<td>19:5</td>
<td>265</td>
<td></td>
</tr>
</tbody>
</table>

- Mean of two or more concordant runs.
- Runs at other temperatures establish ΔH° = 21:8 kcal mol$^{-1}$; ΔS° = −14:7 cal mol$^{-1}$ K$^{-1}$.
- Runs at other temperatures establish ΔH° = 22:5 kcal mol$^{-1}$; ΔS° = −10:1 cal mol$^{-1}$ K$^{-1}$.
- Wavelength used for spectrophotometric kinetics.

It was found that (p-C$_6$H$_4$)$_2$CH-CHCl$_2$ (DDD) was quite unreactive when refluxed in acetone containing Bu$_3$NCl and 2,4,6-collidine for 5-5 h. No olefin could be isolated or detected. We therefore estimate that the DDT/DDD rate ratio is at least 70 (per chloride) at 65°C.

**DISCUSSION**

**Reactions in Acetone.**—A Hammett plot of log $k_2$ against 2σ with use of the results in Table 1 is not satisfactorily linear (Figure 1). The least-squares parameters are: $\rho = 1:16$; $r$ (correlation coefficient) = 0:981; $s$ (standard deviation in slope) = 0:19. We have noted almost identical behaviour previously,$^{17}$ and following our earlier analysis and one employed by$^{23}$


Cockerill and Lamper,$^{22}$ we find that optimum linearity is obtained by plotting log $k_2$ against 2σ + 1:45σ$_R$, whence $\rho = 1:31$, $r = 0:998$, $s = 0:03$ (Figure 2). The causes of this non-additivity of substituent effects have been discussed.$^{17,22}$

We have previously estimated that a Hammett $\rho$ of ca. 0-5 would be appropriate for the E2C dehydrohalogenation of a β-aryl substituted halide.$^{1,17}$ To the examples cited in support of this figure can be added the $\rho$ value of 0-48 for the bromide-promoted dehydrobromination of 1-aryl-2-bromopropanes in acetone.$^{23}$ Thus our $\rho$ of 1-31 is significantly different from those for E2C-like processes. It is also significantly different from that for the E1CB dehydrochlorination$^{19}$ of Ar$_2$CH-CCl$_3$ compounds by ethoxide in ethanol (234 at 65°C).$^{14}$ The obvious interpretation is that while the transition state for the chloride-promoted reaction is E2H-like, and has carbanionic charge at C$_B$, it is not as carbanionic as the transition state in the E1CB ethoxide-promoted reaction. A consequence of this interpretation is that an increase in basicity might shift the character of E2H transition states towards the paenecarbanion extreme, and while current theory is ambiguous on this point,$^{24}$ recent results of Yano and Oae$^{25}$ indicate that, for the ArSO$_2$CH$_2$-CH$_2$-Clamine system at least, this is the case. The conclusion that can be drawn however is that the chloride-promoted reactions are not E1CB, as the $\rho$ values seem to be too small to permit consideration of this process.

Can the present results be accommodated within the framework of the E2C spectrum? A superficially attractive explanation is available when it is recalled that E2C-like transition states are believed to be largely olefinic in character,$^{4,24}$ with C$_B$ and C$_A$ hybridization being nearly sp$^2$. The dipole-dipole repulsion energy between two identical aryl groups on C$_B$ having parallel dipoles should be relieved in an sp$^2$-like transition state relative to an sp$^3$ initial state, and so all of the Ar$_2$CH-CCl$_3$ compounds should be more reactive than the unsubstituted compound. This is not quite the case (Table 1) but the poorness of the unadorned Hammett plot could be a result of the superimposition of such

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dipole–dipole effects on the small electronic effect expected for an E2C reaction. The question of the E2H as opposed to the E2C explanation is resolved in the next section.

Similarly the greater reactivity of Ar₂CH·CCl₃ than of Ar₂CH·CHCl₂ reactivity order may be interpreted qualitatively in terms of both E2H and E2C mechanisms. However, theoretical calculations involving estimation of steric interactions between non-reacting chlorine atoms and hydrogen atoms in the transition state give results which are not in accord with an E2C transition state.

Reactions in Dimethylformamide.—In order to resolve the above ambiguity, we have attempted to evaluate the ‘true’ electronic effect on the system by carrying out a Hammett equation study of the dehydrochlorination of monosubstituted Ar(Ph)CH·CCl₃ compounds using LiCl in dimethylformamide. The dipole–dipole repulsion factor should be much less important in this series. As usual an unmodified Hammett plot of log \( k_2 \) against \( \sigma \) poorly fits the data \( (\rho = 0.88, r = 0.938, s = 0.17) \), but an excellent plot of log \( k_2 \) against \( \sigma + 0.67\sigma_R \) yields the following parameters: \( \rho = 1.10, r = 0.997, s = 0.08 \). The \( \rho \) value is a little lower than that for the reaction in acetone but it is still larger than that expected to apply to the electronic substituent effect on an E2C reaction. In support of our contention that rate changes in the Ar₂CH·CCl₃ system represent primarily an electronic effect is the observation that a plot of log \( k_2 \) against \( \Sigma \sigma + 0.67\Sigma\sigma_R \) for both the Ar₂CH·CCl₃ and Ar(Ph)CH·CCl₃ systems is clearly linear (Figure 3), whence \( \rho = 0.99, r = 0.997, s = 0.03 \). That the rate constants for both linearly and disubstituted derivatives fit the same line are hardly related to the symmetrical disubstituted compound (XI) lies on this line. The inductive and resonance effects of the methoxy- and chloro-substituents are clearly governing the reactivity of this compound relative to the unsymmetrical com-

If however dipole–dipole repulsions in an E2C transition state as opposed to those in the initial state were the most important determinants of reactivity, it could be expected that (XI) would be less reactive than the unsubstituted compound. This is not so (Table 3) and the \( \rho \) values of 1.31 (acetone) and 0.99 (Me₂N·CHO) thus primarily represent electronic effects. Our assignment of carbamionic E2H transition states to the chloride-promoted eliminations is thus in order.

It follows that chloride ions in dipolar aprotic solvents are sufficiently strong as bases in the kinetic sense (hydrogen nucleophiles) to promote E2H elimination from suitable acidic substrates. This should not be surprising as chloride ion acts as a base (thermodynamically) in dimethylformamide although it is quite weak. It would be surprising however to observe an E2H reaction promoted by chloride ions in protic solvents. There is a danger in equating thermodynamic basicity (or the lack of it) with hydrogen nucleophilicity (or the lack of it) in proton transfer reactions, and the extension of this warning to E2 reactions, where the transfer is coupled to other bond-making and bond-breaking processes, is clear even for E2H reactions involving conventionally strong bases in protic solvents.

It is thus not sufficient to cite the comparatively low basicity of halide ions as prima facie evidence for the non-operation of E2H mechanisms in any particular case. Weinstein and Parker have clearly pointed out that substrate acidity is also a factor in determining where a transition state should lie on the E2H–E2C spectrum but of course when acidic substrates such as DDT are involved, halide ions in dipolar aprotic solvents are inferior to alkoxide ions in alcohol as dehydrohalogenating agents.

**EXPERIMENTAL**

**Materials.**—Acetone and dimethylformamide were purified and dried by standard methods. Anhydrous LiCl was recrystallized from dry acetone. Bu₄N·Cl was precipitated from a cold dry acetone solution by addition of ether and was recrystallized from dry acetone. Potentiometric titration for chloride ion indicated a purity of 99.15%. All operations involving this salt were performed under nitrogen in a dry-box. Commercial 2,4,6-collidine was distilled from KOH pellets and fractionally distilled. The preparation and properties of substrates (VIIa–g), 1,1-dichloro-2,2-bis-p-chlorophenylethane, the olefins (VIIa–g), and the olefin 2-chloro-1,1-bis-p-chlorophenylethane have been described.

2,2,2-Trichloro-1-phenylethanol was prepared by the method of Galun and Kalir. Condensation of bromobenzene and chlorobenzene with this alcohol as described yielded compounds (IXe) and (IXd) respectively. Addition of concentrated sulphuric acid to a mixture of the alcohol and toluene at 0 °C and stirring for 6 h produced the p-tolyl

**Figure 3** Modified Hammett plot for the reactions between \((p-
YC₄H₄)(p-ZC₄H₄)CH·CCl₃\) compounds and LiCl in dimethylformamide

0.67\( \sigma_R \) yields the following parameters: \( \rho = 1.10, r = 0.997, s = 0.03 \). The \( \rho \) value is a little lower than that for the reaction in acetone but it is still larger than that expected to apply to the electronic substituent effect on an E2C reaction. In support of our contention that rate changes in the Ar₂CH·CCl₃ system represent primarily an electronic effect is the observation that a plot of log \( k_2 \) against \( \Sigma \sigma + 0.67\Sigma\sigma_R \) for both the Ar₂CH·CCl₃ and Ar(Ph)CH·CCl₃ systems is clearly linear (Figure 3), whence \( \rho = 0.99, r = 0.997, s = 0.03 \). That the rate constants for both linearly and disubstituted derivatives fit the same line are hardly related to the symmetrical disubstituted compound (XI) lies on this line. The inductive and resonance effects of the methoxy- and chloro-substituents are clearly governing the reactivity of this compound relative to the unsubstituted com-

* This experiment was kindly suggested to us by Dr. A. J. Parker.

**References**


derivative (IXb), which was recrystallized from ethanol. A similar method was employed for the \( p \)-fluoro-compound (IXc) by use of fluorobenzene. Chromatographic separation of the crude product on silica gel was followed by recrystallization from ethanol.

The method of Reeve and Fine was used to prepare \( 2,2,2 \)-trichloro-1-\( p \)-methoxyphenylethanol from \( p \)-anisaldehyde, chloroform, and potassium t-butoxide in t-butyl alcohol. The product was recrystallized from benzene and had m.p. 58–60 °C (lit., 55–56 °C). A solution of the alcohol (5 g) in benzene (10 ml) was added dropwise to a cooled and stirred mixture of benzene (20 ml) and concentrated \( \text{H}_2\text{SO}_4 \) (25 ml) during 1 h. The mixture was stirred for a further 15 min and was then poured on ice. The crude oil obtained after ether extraction and solvent evaporation was chromatographed on a silica gel column with \( n \)-hexane for development and elution. After recrystallization from ethanol a yield of 11–13% of compound (IXa) was obtained.

The major product appeared to be a trimeric compound, 1,\( \text{H} \)-methoxy-2,2,2-trichloro-1-\( p \)-methoxyphenylethyl)-4-(2,2,2-trichloro-1-\( p \)-methoxyphenylethyl)benzene, m.p. 104–108 °C, \( \text{S} 3 \)-72 (3H, s, MeO); 3-76 (3H, s, MeO); 5-05 (1H, s, benzylic); 5-67 (1H, s, benzylic); 6-7-7-8 (12H, aromatic) (Found: C, 51-7; H, 3-7; Cl, 38-6. Calc. for \( \text{C}_{14}\text{H}_{14}\text{Cl}_{2} \): C, 52-1; H, 3-6; Cl, 38-5%). This compound may be formed by attack of the carbonium ion derived from the alcohol at a ring position ortho to the methoxy-group of another alcohol molecule, followed by normal condensation with benzene. The unsymmetrically substituted compound (XI) was prepared in exactly the same manner as compound (IXa) except that chlorobenzene was used in place of benzene.

Attempted preparations of 1,1,1-trichloro-2-\( p \)-nitrophenyl-2-phenylethylene by condensation of benzene with 2,2,2-trichloro-1-\( p \)-nitrophenylethanol were unsuccessful.

Samples of product olefins were obtained by dissolving the diaryltrichloroethanes (0-4 g) in ethanol (50 ml) containing dissolved KOH (0-6 g) and allowing reaction to proceed for 48 h at room temperature. The olefins were isolated after normal work-up and recrystallized from ethanol. Data for the substrates are in Table 4, properties of the

**Kinetics.** The reactions between \( \text{Ar-CH-Cl} \) compounds and \( \text{Be}^{2+}\text{Cl} \) in acetone were followed by acid–base titration (Radiometer titrigraph) for the liberated acid. The reaction mixture was contained in sealed ampoules which were cooled and opened at various times, and the contents were washed into water. Organic material was quantitatively extracted with carbon tetrachloride before titration.

### Table 5

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lit. m.p./°C</th>
<th>( \lambda_{\max } /\text{nm} )</th>
<th>log ( \varepsilon )</th>
</tr>
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<tbody>
<tr>
<td>(IXa)</td>
<td>84–85-5</td>
<td>247</td>
<td>4-12</td>
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<tr>
<td>(IXb)</td>
<td>89–90</td>
<td>87-5 (c)</td>
<td>243</td>
</tr>
<tr>
<td>(IXc)</td>
<td>54–55-5</td>
<td></td>
<td>245</td>
</tr>
<tr>
<td>(IXd)</td>
<td>109–110</td>
<td>110–111 (d)</td>
<td>243</td>
</tr>
<tr>
<td>(IXe)</td>
<td>112–113</td>
<td>113 (c)</td>
<td>244</td>
</tr>
<tr>
<td>(XI)</td>
<td>59–60</td>
<td>251</td>
<td>4-336</td>
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</tbody>
</table>


### Table 6

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found (%)</th>
<th>Required (%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>(IXa)</td>
<td>57-2</td>
<td>4-3</td>
</tr>
<tr>
<td>(IXb)</td>
<td>51-3</td>
<td>3-4</td>
</tr>
<tr>
<td>(IXc)</td>
<td>64-4</td>
<td>4-5</td>
</tr>
<tr>
<td>(IXd)</td>
<td>63-0</td>
<td>3-5</td>
</tr>
<tr>
<td>(XI)</td>
<td>57-8</td>
<td>3-7</td>
</tr>
</tbody>
</table>

The reactions involving \( \text{LiCl} \) in dimethylformamide were followed spectrophotometrically. The reaction mixture (5 ml samples) was contained in sealed ampoules, which were opened at various times, and 1 ml was pipetted into a 250 ml volumetric flask containing redistilled methanol. The solution was made up to the mark with methanol and the u.v. absorbance of a sample of this solution was measured with a Shimadzu QV50 spectrophotometer. Blank solutions were prepared by dissolving 1 ml of dimethylformamide in methanol and making up to 250 ml. The wavelengths chosen for each compound were close to those of maximum absorption of the corresponding product olefin, but in all cases the substrate had negligible absorbance at these wavelengths. If \( A_0 \), \( A_p \) and \( A_\infty \) are the respective absorbances at time \( t \), and infinity respectively, equation (3) can be modified to (9). The latter was used in calculating individual values of \( A_\infty / A_p \) of compound (IXa). Equation (8) was similarly modified to allow calculation of \( k_2 \) directly from the absorbance

\[
\frac{1}{2a} \ln \frac{A_\infty + A_p - 2A_2}{A_\infty - A_p} = k_2 t
\]

The u.v. spectra of all infinity samples were identical to those of the authentic olefins. In several cases the product was isolated from an 'infinity' ampoule and its identity confirmed by m.p. and mixed m.p. with an authentic sample. When olefin (VIIIa) (ca. 0-02tm) and dry hydrogen chloride (ca. 0-02tm) in dimethylformamide were mixed and left at 65 °C for several days, no change in u.v. absorbance at 245 nm was observed.

### Table 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.p./°C</th>
<th>Lit. m.p./°C (ref.)</th>
<th>( \alpha )</th>
</tr>
</thead>
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<tr>
<td>(IXa)</td>
<td>50–51-5</td>
<td>5-90 *</td>
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</tr>
<tr>
<td>(IXb)</td>
<td>81–82-5</td>
<td>72-5 (d)</td>
<td>5-02 *</td>
</tr>
<tr>
<td>(IXc)</td>
<td>53–55</td>
<td>50–52 (e)</td>
<td>5-02 *</td>
</tr>
<tr>
<td>(IXd)</td>
<td>78–79</td>
<td>77–77-5 (14a)</td>
<td>5-02 *</td>
</tr>
<tr>
<td>(IXe)</td>
<td>96–100</td>
<td>95–96 (30)</td>
<td>5-00 *</td>
</tr>
<tr>
<td>(XI)</td>
<td>104–106</td>
<td></td>
<td>4-98 *</td>
</tr>
</tbody>
</table>


olefinic products are shown in Table 5, and Table 6 gives microanalytical results for new compounds. M.p.s are uncorrected.

1,1-Dichloro-2,2-bis-\( p \)-chlorophenylethane (0.01 mol) was refluxed for 5.5 h in dry acetone containing \( \text{Bu}_4\text{NCl} \) (0.01 mol) and 2,4,6-collidine (0.01 mol). An ether extract of the reaction mixture after normal work-up was examined by g.l.c. and t.l.c. No compound other than the starting material was detected, even though check experiments showed that an amount of the olefin 2-chloro-1,1-bis-\( p \)-chlorophenylethylene corresponding to a 5% yield was easily detectable. Starting material was recovered from the extract in 90% yield.

We thank Dr. A. J. Parker for discussions and Dr. A. D. Campbell, University of Otago, for microanalyses.

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