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

IN PROTIC AND DIPOLAR APROTIC SOLVENTS

A THESIS

presented to the University of Auckland

for the Degree of

Doctor of Philosophy

by

RONALD JAMES WONG

University of Auckland

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PREFACE

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. Bunnett 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 paenecarbanion 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-nitrophenoxide 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 is 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 Winstein-Parker E2C-like transition 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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TABLE OF CONTENTS

	PAGE
<u>Preface</u>	ii
<u>Abstract</u>	iv
<u>Acknowledgements</u>	vi
<u>PART I</u> General Introduction	1
1.1 Mechanisms of Elimination	2
1.2 The E2 Transition State	5
1.2.1 The Theory of the Variable E2 Transition State	5
1.2.2 The More O'Ferrall Model	6
1.2.3 The E2C Transition State	7
1.3 Orientation	9
1.4 Stereochemistry	11
1.5 Thermodynamic Basicity and Nucleophilicity	12
1.6 Diagnosis of the Quality of the Transition State	12
1.6.1 Deuterium Isotope Effects	12
1.6.2 Linear Free Energy Relationships	14
1.6.3 The Hammett Equation	16
1.6.4 The Bronsted Equation	18
1.6.5 Acidity Functions	19
<u>PART II</u> Elimination in Protic Solvents	23
1. <u>Introduction</u>	24
1.1 Elimination From the Phenethyl and Related Systems	24
1.2 Elimination From the Diarylethane System	31
1.3 The Carbanion Mechanism of $\beta$ -Elimination	33



TABLE OF CONTENTS CONTD

	PAGE
1.4 Rate-Acidity Correlations of Proton Transfer Reactions	41
1.5 Variation of the Primary Isotope Effect with Thermodynamic Basicity	44
2. <u>Experimental</u>	47
2.1 Analytical Methods	47
2.2 Materials	47
2.3 Products	56
2.4 Reagents and Solvents	57
2.5 Stoichiometry	58
2.6 Kinetics	60
3. <u>Results</u>	64
4. <u>Discussion</u>	73
4.1 Hammett Correlations	73
4.2 The Effect of the Base Strength on the Deuterium Isotope Effect	89
4.3 The Effect of the Acidity of the Substrate on the Isotope Effect	99
4.4 Rate-Acidity Correlations	111
4.5 Rate of Carbanion Formation	119
4.6 The Nature of the Transition State	125
4.7 Reactants and Products	130
5. <u>Conclusion</u>	133

TABLE OF CONTENTS CONTD

PAGE

<u>PART III</u> Elimination in Dipolar Aprotic Solvents	136
1. <u>Introduction</u>	137
1.1 The E2C Mechanism	137
1.2 The E2H Mechanism	144
2. <u>Experimental</u>	149
2.1 Materials and Reagents	149
2.2 Stoichiometry	150
2.3 Kinetics	156
3. <u>Results</u>	158
4. <u>Discussion</u>	161
4.1 Reactions in Dimethylformamide	161
4.2 Reactions in Acetone	164
4.3 The DDT:DDD Rate Ratio	167
5. <u>Conclusion</u>	172
<u>References</u>	173
<u>Appendices</u>	189
I Details of Individual Kinetic Runs	189
II Precision of L.F.E.R. Correlations	203
III Calculation of the DDT:DDD Rate Ratio	206
IV Estimation of $pK_a$ for 1,1-Di(p-nitrophenyl)-2,2,2-trichloroethane	208

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