THE RADIOLYSIS OF AQUEOUS SOLUTIONS OF CYSTEINE

by

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For BRENDA.

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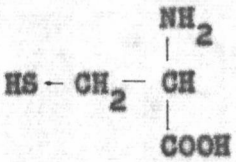
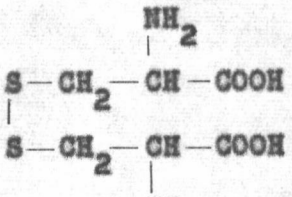
NOTE

Throughout this thesis the following abbreviated formulae are used for convenience:-

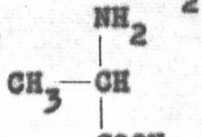
RSH cysteine



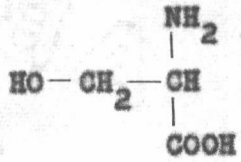
RSSR cystine



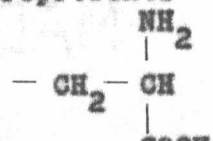
RH alanine



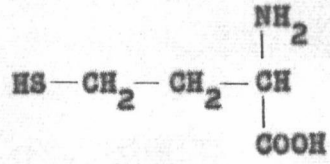
ROH serine



R, as used in RSOH, RSOOH etc., represents



R'SH homocysteine



ABSTRACT

The radiolysis of cysteine in both deaerated and oxygenated solution at pH 7 has been studied.

In deaerated solution the mechanism of the reaction appears to be the same as that at pH 5 - 6. The rate constant for the reaction

$$\cdot OH + RSH \longrightarrow RS\cdot + H_2O$$

has been measured by competition with paranitrosodimethylaniline. A value of 9×10^9 was found, which though not absolutely accurate (for reasons described in the text) is sufficiently accurate to show that the reaction is fast. The rate constant of the reaction

$$e_{aq} + RSH \longrightarrow R\cdot + SH^-$$

has been measured by competition with oxygen, and a value of $(4.0 \pm 0.2) \times 10^9$ was found. This compares well with values found by other methods.

From the values of G(-RSH), G(RSSR), and $G(H_2O_2)$ in oxygenated solution, and from the effects of the scavengers nitrous oxide and acetone or these values a mechanism has been proposed in which RS radicals produced by attack of primary species on cysteine propagate a chain, the rate of the propagation reaction depending on the cysteine concentration.

The autoxidation of cysteine has been studied briefly, the rate being found proportional to oxygen concentration. The mechanism is believed to be the same as that for the radiolysis.

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LIST OF FIGURES