THE REACTION OF OLEFINS WITH SULPHUR MONOCHLORIDE

by

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A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY LONDON UNIVERSITY

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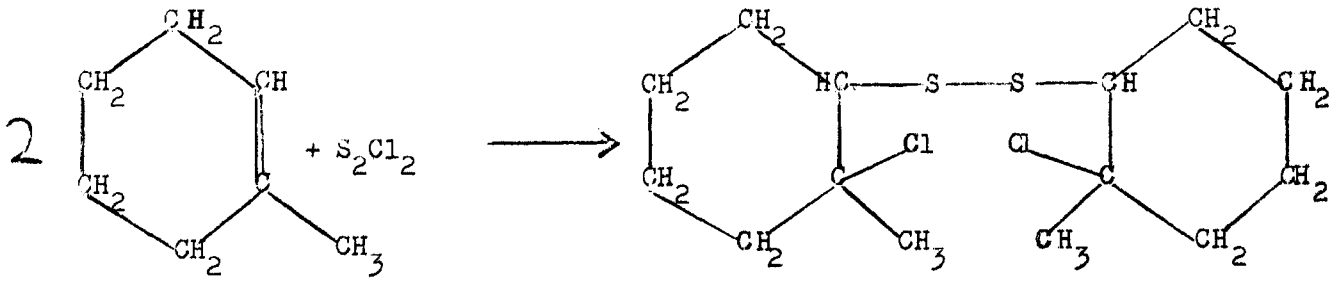
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ABSTRACT OF THE THESIS

"REACTIONS OF OLEFINS WITH SULPHUR MONOCHLORIDE"

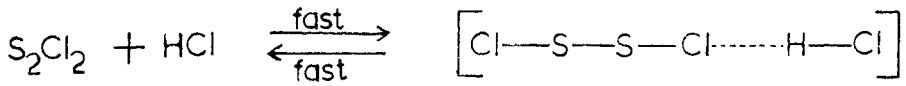
The thesis entails the study of the reaction of 1-methyl-cyclohexene with sulphur monochloride in solvent. The main reaction product is identified as 1,1'-dimethyl-1,1'-dichlorodicyclohexyl-2,2'--disulphide, and the reaction may be represented stoicheiometrically as

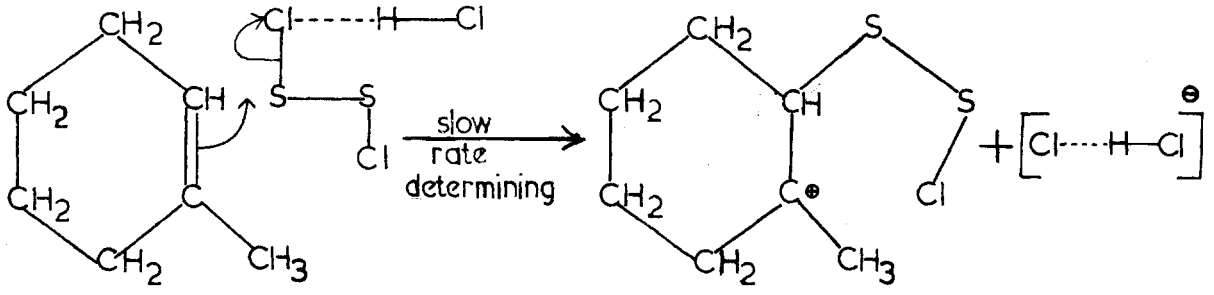


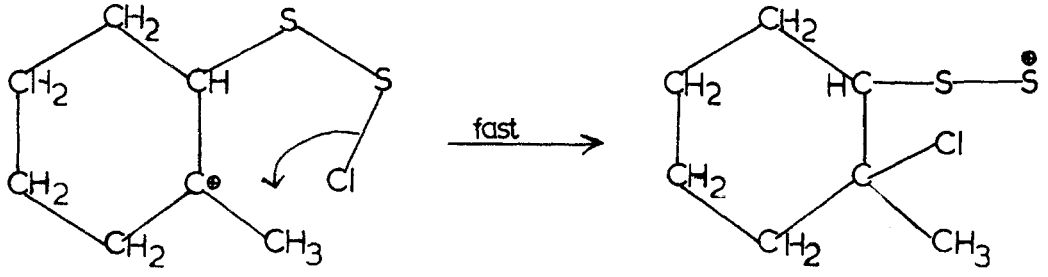
The kinetics of the reaction are studied using a dilatometric technique. The reaction is found to obey overall second order kinetics, being first order with respect to each of the reactants: sulphur monochloride and 1-methylcyclohexene.

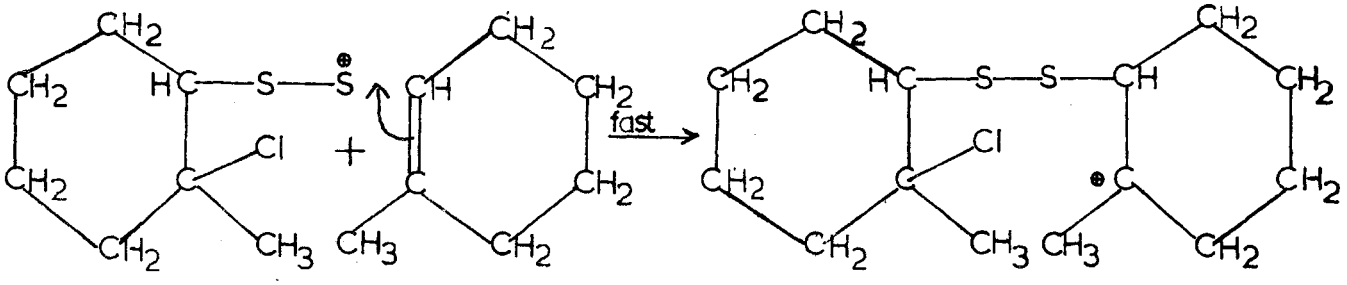
The marked dependence of the reaction rate upon the dielectric constant of the solvent leads to the conclusion that the reaction is polar or ionic.

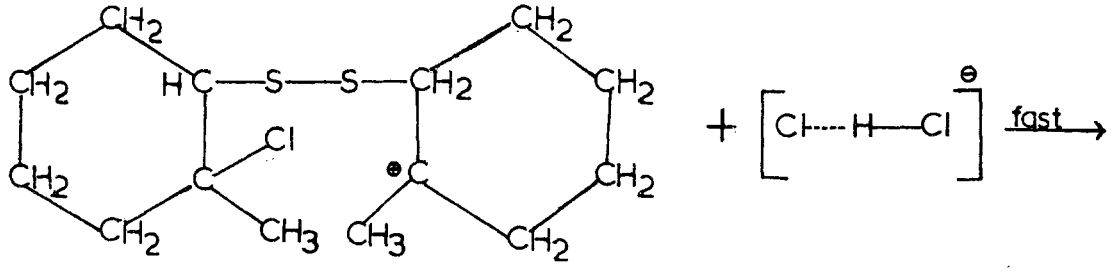
A mechanism for this reaction is suggested, comprising a complex/ionic reaction scheme, whose rate determining step is polar but not ionic. It is suggested that the sulphur monochloride reacts in the form of a complex with hydrogen chloride in trace amounts. The proposed reaction scheme is as shown below:

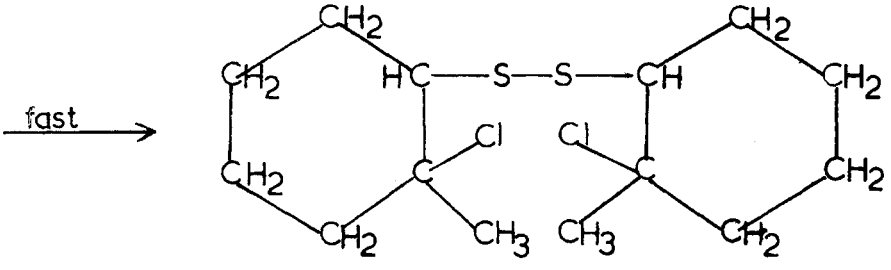

S_2Cl_2 + HCl
fast
fast
Cl—S—S—Cl·····H—Cl


slow
rate
determining


fast


fast


fast


fast

One novel aspect of this reaction scheme is the recognition that hydrogen chloride catalyses the reaction and that the effective reagent in the rate determining stage is a complex of sulphur monochloride and hydrogen chloride. The catalytic role of the hydrogen chloride appears to be paralleled by the catalytic activity exhibited by several ionized or ionogenic chlorides (quaternary ammonium chlorides, ferric chloride and hydrogen chloride). The postulation of a pre-equilibrium, leading to the formation of a complex of sulphur monochloride and hydrogen chloride, is required by the low Arrhenius activation energy (ca. 5 k.cal.mole^{-1}) observed for the overall reaction.

Another novel aspect of the reaction scheme is the view that one of the component stages involves an intra-molecular electrophilic attack by a carbonium ion on a sulphur-chlorine bond, thus:

