

LETTERS TO THE EDITOR

KINETICS AND MECHANISM OF THE OXIDATION OF DIMETHYL SULPHOXIDE BY SODIUM N-CHLORO BENZENESULPHONAMIDE IN HYDROCHLORIC ACID MEDIUM

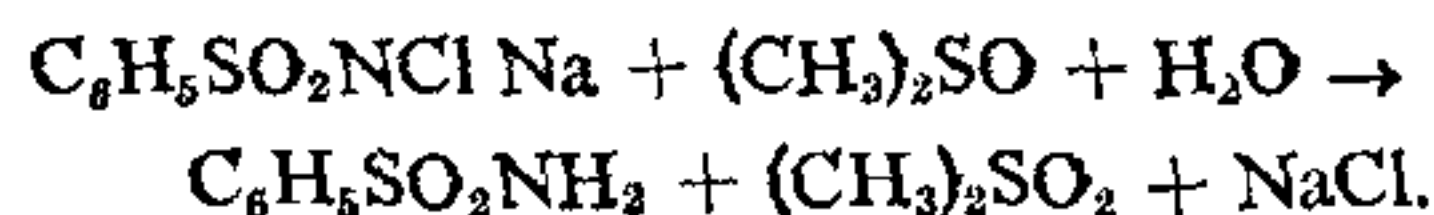
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THE kinetics of oxidation of substituted benzyl alcohols¹ and cinnamyl alcohol² by chloramine-B have been reported. Di-methyl sulphoxide (DMSO) is a versatile compound, widely used as a solvent, reaction medium and a chemical reactant. The present work reports the kinetics of oxidation of DMSO by CAB in HCl medium.

Experimental

Dimethyl sulphoxide (BDH) was distilled under reduced pressure and its aqueous solution was standardized by permanganometry³. Chloramine-B (CAB) was prepared by the method described earlier⁴. An aqueous solution of CAB was standardized by the iodometric method.

The kinetic studies were carried out at an ionic strength of 0.6 M (using NaClO₄) at 0° C under pseudo first order conditions. The rate of reaction was determined by estimating the unreacted CAB iodometrically. The stoichiometry⁵ of the reaction was found to be 1:1 and the product was dimethyl sulphone as shown by TLC (Silica gel). The reaction can be represented as



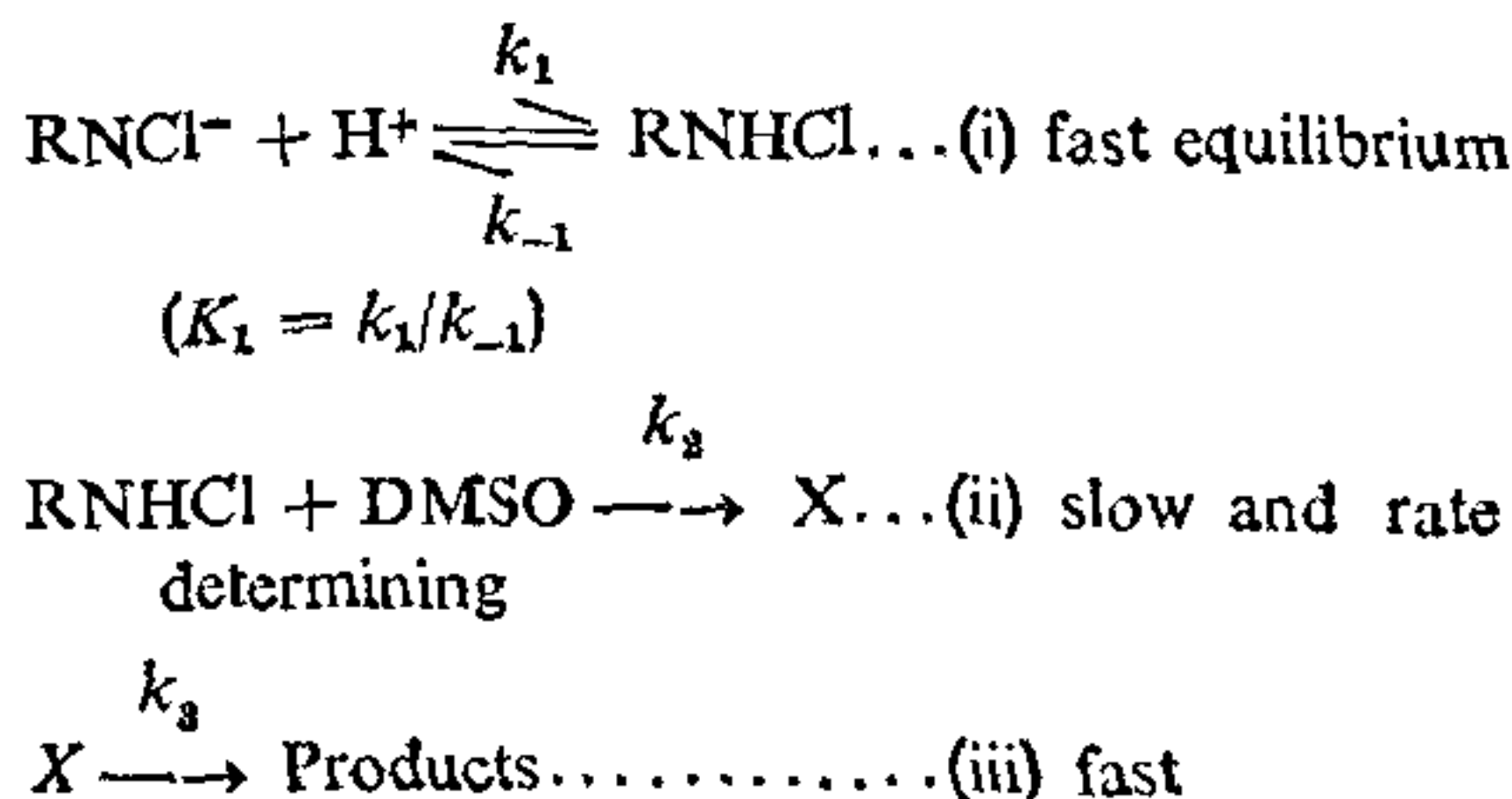
Results and Discussion

At constant [H⁺] [0.2M] and [DMSO] (0.1M), a first order dependence of the rate on [CAB] (0.003-0.007M) is noted. The pseudo first order rate constant *k_p* was 6.45 × 10⁻⁴ sec⁻¹. A plot of log *k_p* vs log [DMSO] gave a straight line of slope 0.66, indicating a fractional order dependence on substrate concentration (0.10-0.40 M). When HCl was varied from 0.15-0.40 M, a plot of log *k_p* vs. log [HCl] gave a straight line of slope 1.45. At constant [Cl⁻] (kept at 0.40 M by adding NaCl), variation of [H⁺] indicated a unit order dependence as shown by the constancy of *k_p*/[H⁺] values and also by a plot of log *k_p* vs log [H⁺]. Keeping [H⁺] constant at 0.2 M, [Cl⁻]

was varied by adding NaCl (0.20-0.50 M). A plot of log *k_p* vs log [Cl⁻] gave a straight line of slope 0.43.

Addition of the reaction product, benzene sulphoamide to the reaction mixture has no effect on the rate. Also, addition of methanol had a negligible effect on the rate indicating the absence of dielectric constant effects. Increase in the ionic strength of the medium from 0.6 to 1.2 M, increased the rate constant by about 22%, which is in the nature of a secondary salt effect, operating on equilibria encountered before the rate-determining step. Addition of acrylonitrile to the reaction mixture had no effect, indicating the absence of free radical species. The activation parameters were *E_a* = 65 kJ mole⁻¹ and Δ*S[‡]* = -82.5 JK⁻¹.

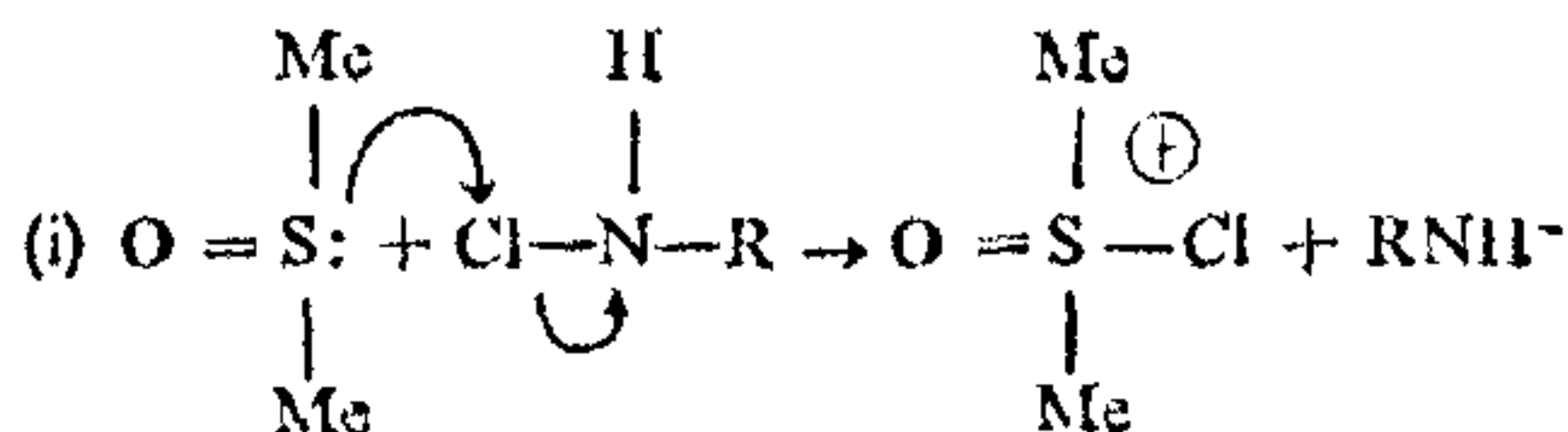
In an acidified solution of CAB, the possible oxidizing species^{1,2} are dichloramine-B (RNCl₂), protonated CAB (RNHCl) and HOCl. If RNCl₂ or HOCl were to be the active species, then the rate law will be contrary to experimental observations. It is likely that RNHCl oxidizes the substrate under the present conditions. The following scheme accounts for the experimental results:

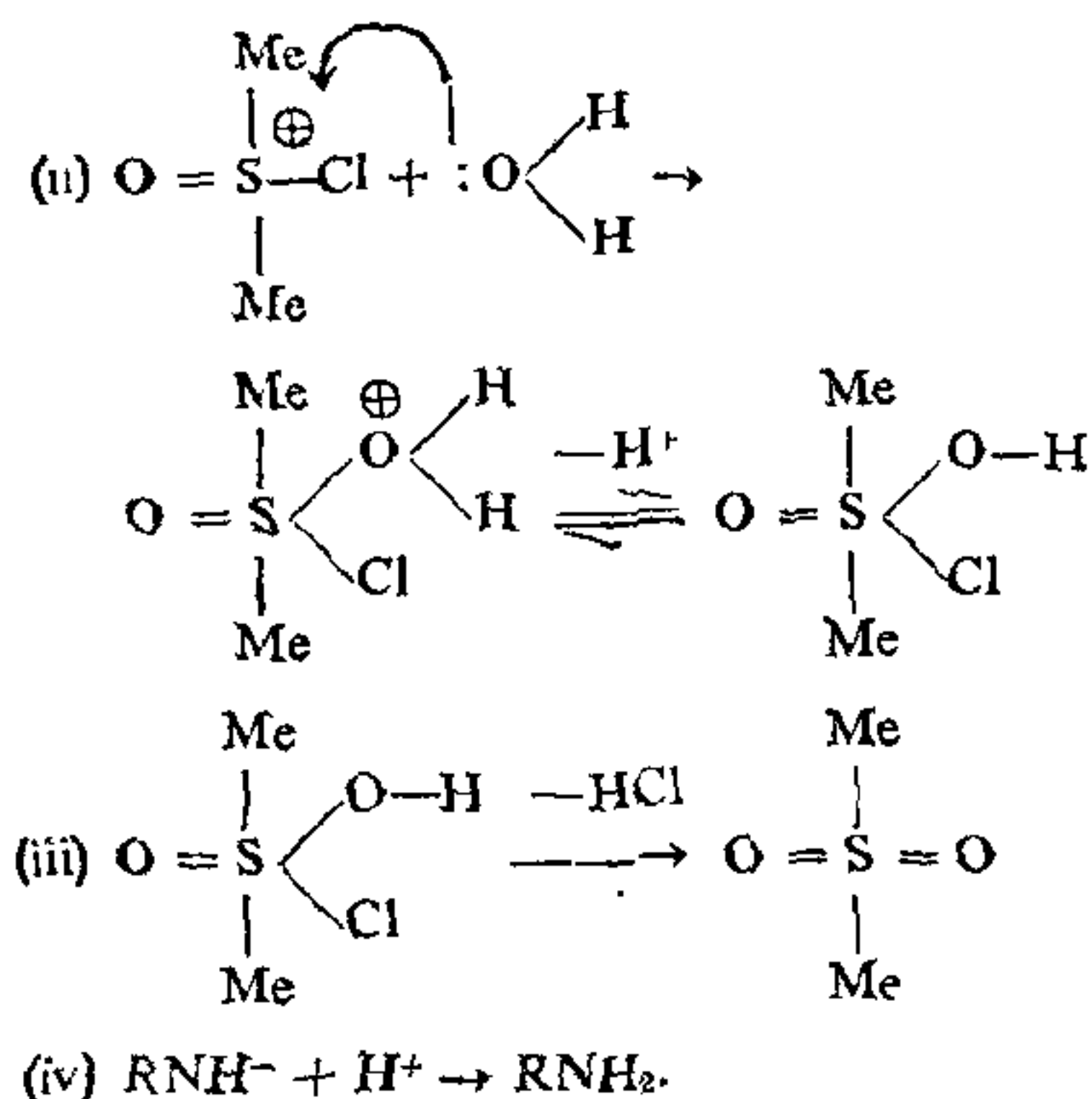


Assuming steady state conditions for RNHCl, rate law (1) is derived.

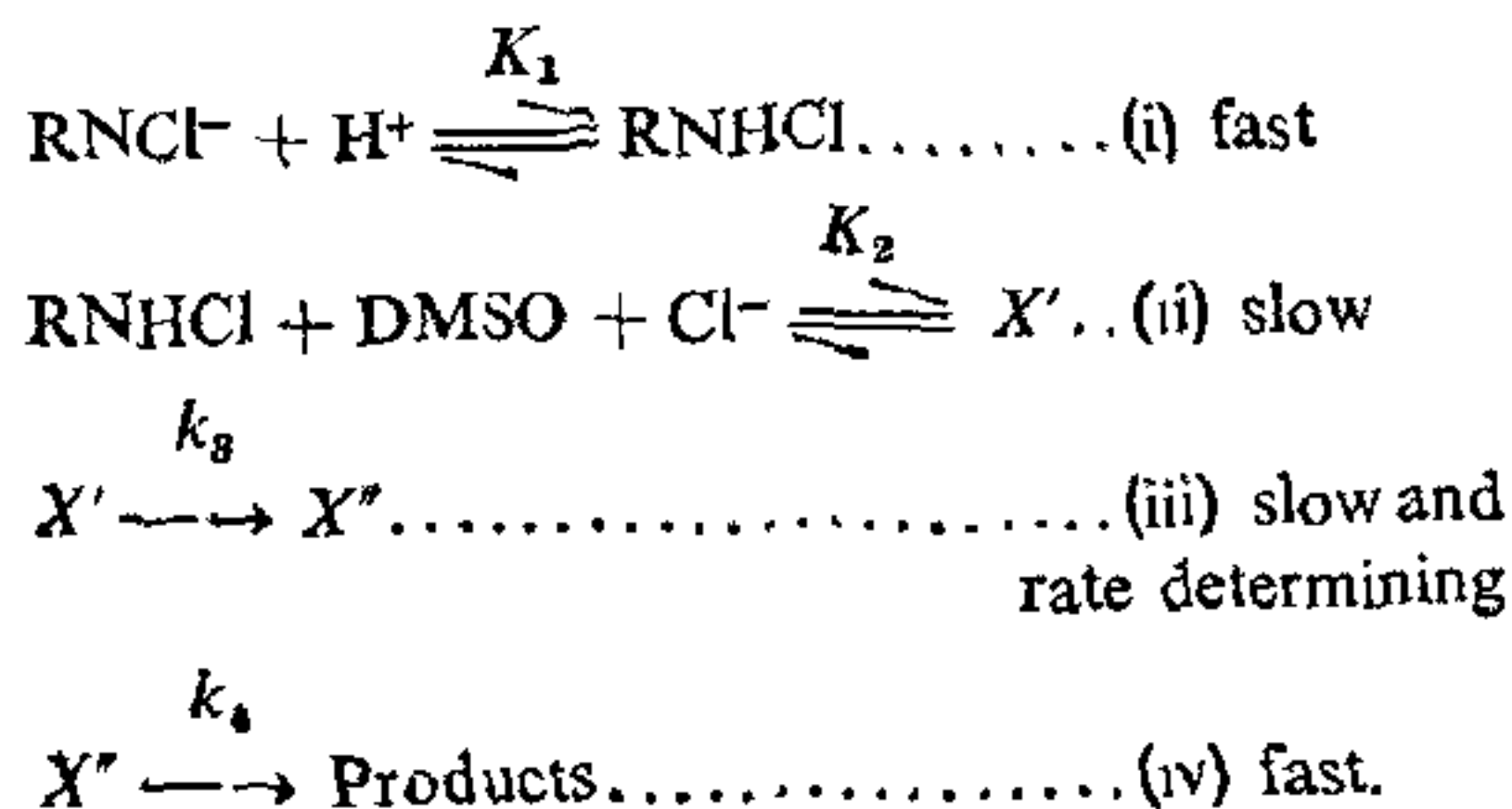
$$-\frac{d[CAB]}{dt} = \frac{k_2 [DMSO] [H^+]}{\frac{1}{K_1} + \frac{k_3}{k_1} [DMSO]} \quad (1)$$

The mechanism of oxidation includes an electrophilic attack by the positive chlorine in RNHCl at the sulphur site of the substrate since the *pπ* - *dπ* overlap of the S-O bond leads to a considerable electron density. The reaction intermediate hydrolyzes through a fast step.





Increase in the rate of reaction by the addition of chloride ion is similar to its effect observed in the Orton re-arrangement of N-haloamides⁶. The latter refers to the migration of chlorine from the side chain of an N-haloamide or a ring substituted derivative of chloroamide to the ring, in the presence of H^+ and Cl^- ions. The present results can be explained by the following scheme, where an electrophilic attack by Cl^- ion on RNHCl is assumed, accounting for the catalytic effect of chloride ions:



If $[\text{CAB}]_T = [\text{RNCl}^-] + [\text{RNHCl}] + \text{X}'$, then the rate law at constant $[\text{H}^+]$ would be

$$\text{Rate} = \frac{kK_2k_3[\text{CAB}]_T[\text{DMSO}][\text{Cl}^-]}{1 + k + kK_2[\text{DMSO}][\text{Cl}^-]} \quad (2)$$

where $k = K_1[\text{H}^+]$.

When catalysis is effected simultaneously by H^+ and Cl^- , an order of 1.45 on the gross concentration of HCl is observed. This may be traced to a mixed order kinetics following the rate law:

$$-\frac{d[\text{CAB}]}{dt} = k'[\text{CAB}][\text{H}^+][\text{DMSO}]^{0.66} + k''[\text{CAB}][\text{Cl}^-]^{0.43}[\text{DMSO}]^{0.66} \quad (3)$$

In the composite rate law, the first term accounts for H^+ catalysis and the second for Cl^- catalysis.

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1. Mukherjee, J. and Banerji, K. K., *J. Chem. Soc. Perkin II*, 1980, 4, 676.
2. Rangaswamy and Yathirajan, H. S., Paper presented at the Annual Convention of Chemists, 1979.
3. Douglas, T. B., *J. Am. Chem. Soc.*, 1945, 68, 1072.
4. Rangaswamy, Yathirajan, H. S. and Mahadevappa, D. S., *Curr. Sci.*, 1980, 49, 342.
5. —, — and —, *Indian J. Chem.*, 1979, 17A, 602.
6. Gould, E. S., *Mechanism and Structure in Organic Chemistry*, Holt, Rinehart and Winston, New York, 1964, p. 650.

SYNTHESIS WITH DIAZOALKANES AND *o*-BENZOYL BENZOYL CHLORIDE

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o-BENZOYL benzoyl chloride contains two sites of reactivity, the carbonyl group and an acid chloride group, both of which are susceptible towards diazoalkanes. By using different amounts of diazoalkanes it is possible to attack either one or both the sites present. The action of 2 moles of diazoalkanes on one mole of the acid chloride attacked only the acid chloride group while the carbonyl group, the other site, was also affected when 3 moles of diazoalkanes were used, resulting the α -diazoketones.

ω -diazo- ω -alkyl-*o*-benzoyl acetophenone (I) and ω -diazo- ω -alkyl-*o*-1-alkyl-2-phenyl-1,2-epoxy-ethyl acetophenone(II) were synthesised by the action of 2 and 3 moles of diazoalkanes on *o*-benzoyl benzoyl chloride (1 mol).

By adopting the method of Arndt, Eistert and Partale^{2,7} the action of 2 moles of diazomethane, diazoethane, diazopropane, diazo-*n*-butane and phenyl diazomethane on *o*-benzoyl benzoyl chloride in ether at 0° C was studied and diazoketone I (R = -H, -CH₃, -C₂H₅, -*n*-C₃H₇, and -C₆H₅) was obtained. When 3 moles of diazoalkanes were used the carbonyl group¹ was also attacked, resulting in the formation of II (R = -H, -CH₃, -C₂H₅, -*n*-C₃H₇, and -C₆H₅).

All these diazoketones were found to be orange or brown liquids, which could not be purified by distilla-