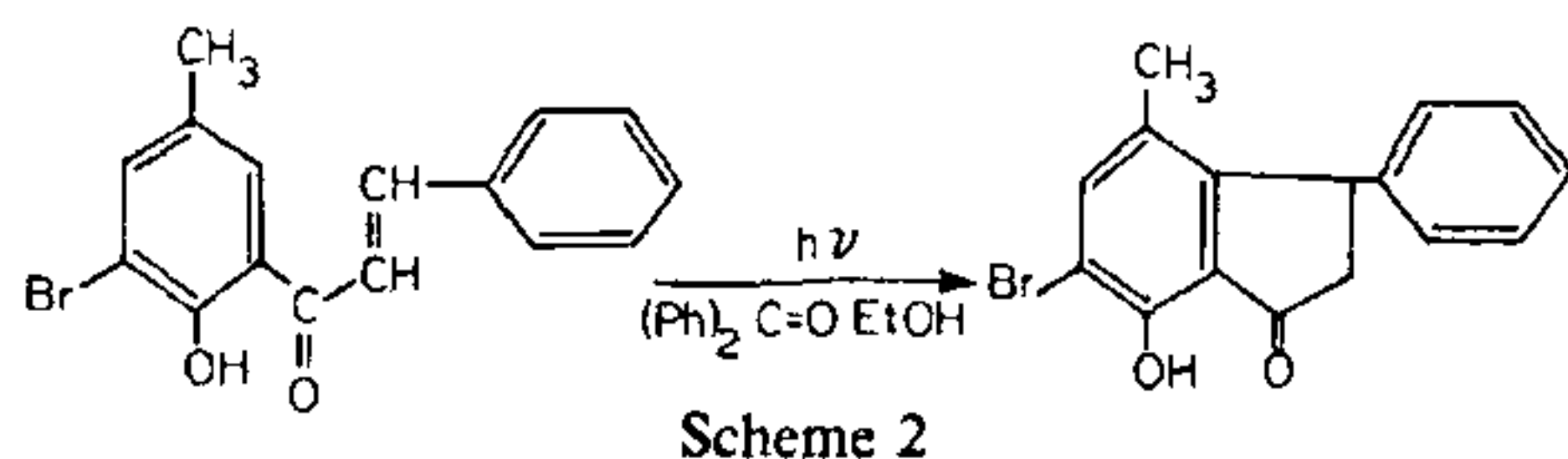


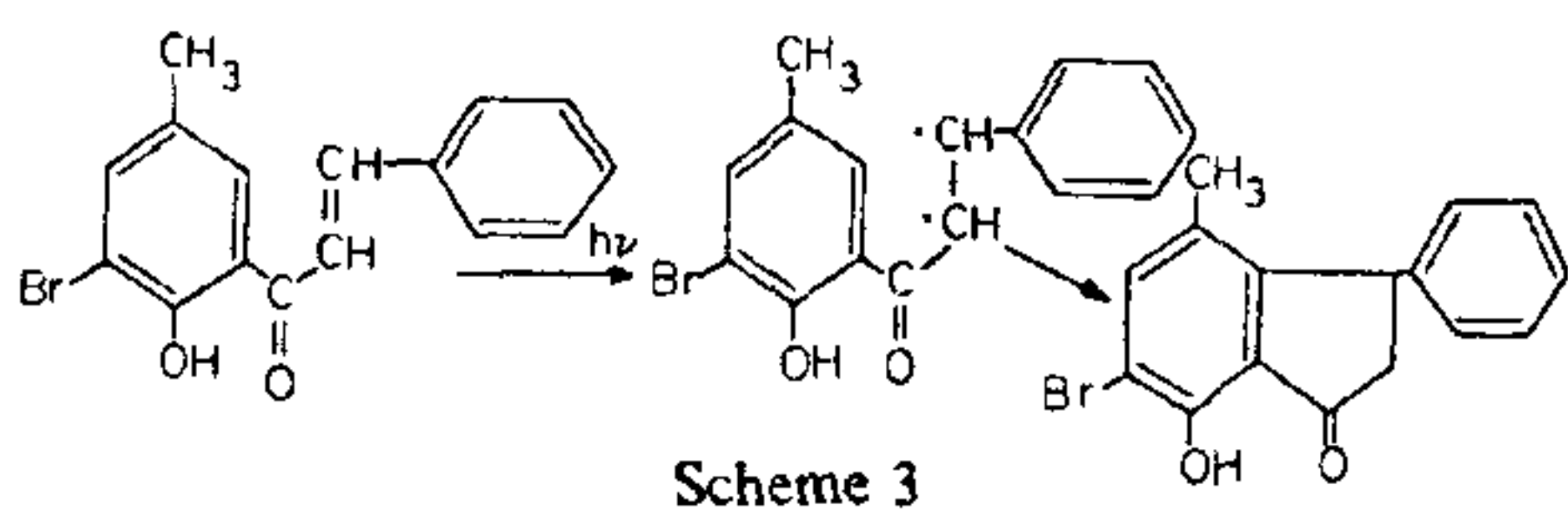
absence of benzophenone the yield was extremely poor. This clearly shows that benzophenone acts as sensitizer. On addition of alkali, the yellow colour changes to reddish orange. However, in the absence of alkali, the substrate did not dissolve and there was no reaction.

The spectral data of the product suggest that the reaction involves synchronous hydrogen migration from C₆' to α-carbon following by bond formation between C₆' and β-carbon atom (Scheme 2).



Mechanism

This intramolecular photocyclization of 2'-hydroxy-3'-bromo-5'-methylchalcone may be explained by a free radical mechanism. The primary photoprocess may proceed by hydrogen radical at α-carbon atom, followed by cyclization between C₆' and β-carbon atom (Scheme 3). The scope, the limitation and the detailed mechanism of this reaction are under investigation.



The authors thank Dr P. K. Ramachandran, Director D.R.D.E. (Gwalior) for providing mass spectral facilities.

2 May 1983; Revised 19 October 1983

1. Blackburn, E. V. and Timmons, C. J., *Q. Rev. Chem. Soc.*, 1969, 23482.
2. Sato, T., *J. Soc. Org. Synth. Chem. Tokyo*, 1969, 27, 715.
3. Stormitz, F. R., *Org. Photochem.*, 1967, 1, 248.

4. Wenton, J. S., Ikeler, T. J. and Smyser, G. C., *J. Org. Chem.*, 1973, 38, 1157.
5. Sasaki, T., Kanematser, K. and Kakchi, A., *J. Org. Chem.*, 1972, 37, 3106.
6. Splitter, J. S., Su, T. M. and Calvin, M., *J. Am. Chem. Soc.*, 1971, 93, 4075.
7. Lewis, G. E., *Tetrahedron Lett.*, 1960, 9, 12.
8. Patrik, S. M. Emil Krochnal, Jr. and Leone, A., *J. Org. Chem.*, 1977, 42, 7.
9. Maryana, K., Kubo, Y., Machidi, M. O., Kanaoka, K. A. Y. and Kukayama, K., *J. Org. Chem.*, 1978, 43, 11.
10. Matsuura, T., Takamoto, T. and Nakashima, R., *Tetrahedron*, 1973, 29, 3337.
11. Matsuura, T., Takamoto, T. and Nakashima, R., *Tetrahedron Lett.*, 1971, 1539.

KINETICS AND MECHANISM OF THE CHLORINATION OF 2-METHYL PHENOL BY SODIUM N-CHLOROBENZENE-SULPHONAMIDE IN HYDROCHLORIC ACID MEDIUM

B. N. USHA, H. S. YATHIRAJAN and RANGASWAMY

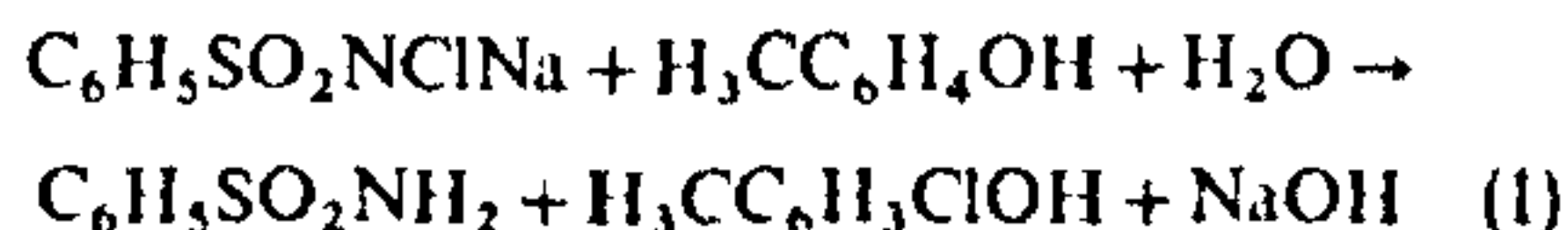
Department of Chemistry, University of Mysore, Manasagangothri, Mysore 570 006, India.

THE kinetics of oxidation of substituted benzyl alcohols¹, unsaturated alcohols^{2,3} and dimethylsulphoxide⁴ by chloramine-B (CAB) have been reported.

2-Methyl phenol (Naarden, b.p. 191°C) was distilled under reduced pressure. The requisite amount of phenol was accurately weighed and dissolved in ethanol. Aqueous solution of chloramine-B was standardized by iodometry. All the other chemicals used were of analytical grade.

The kinetic studies were carried out at an ionic strength of 0.5 M (using NaClO₄) at 35°C under pseudo first order conditions. The reaction rate was determined by estimating the unreacted CAB iodometrically. The stoichiometry of the reaction was 1:1 and the product was 2-chloro-6-methyl phenol as shown by TLC.

The reaction can be represented as:



At constant [H⁺] (0.05 M) and [phenol] (0.1 M), a first order dependence of the rate on [CAB] (0.003-0.007 M) is noted. The pseudo first order rate

constant $k\psi$ was $6.43 \times 10^{-4} \text{ sec}^{-1}$. The pseudo first order rate constants in CAB are independent of the substrate concentration (0.05–0.25 M). Hence, the reaction is zero order with respect to substrate. When HCl was varied from 0.05–0.1 M, a plot of $\log k\psi$ vs $\log [\text{HCl}]$ gave a straight line of slope 2. At constant $[\text{Cl}^-]$ (kept at 0.1 M by adding NaCl), variation of $[\text{H}^+]$ indicated a slope of 1.2 by the plot of $\log k\psi$ vs $\log [\text{H}^+]$. Keeping $[\text{H}^+]$ constant at 0.05 M, $[\text{Cl}^-]$ was varied by adding NaCl (0.05–0.1 M). A plot of $\log k\psi$ vs $\log [\text{Cl}^-]$ gave a straight line of slope 0.8.

Addition of the reaction product benzene-sulphonamide and variation of ionic strength (0.5–1 M) have no significant effect on the rate of reaction. An increase in the reaction rate was noticed by changing ethanol composition of the reaction mixture (30–70%). Addition of acrylonitrile to the reaction mixture had no effect, indicating the absence of free radical species.

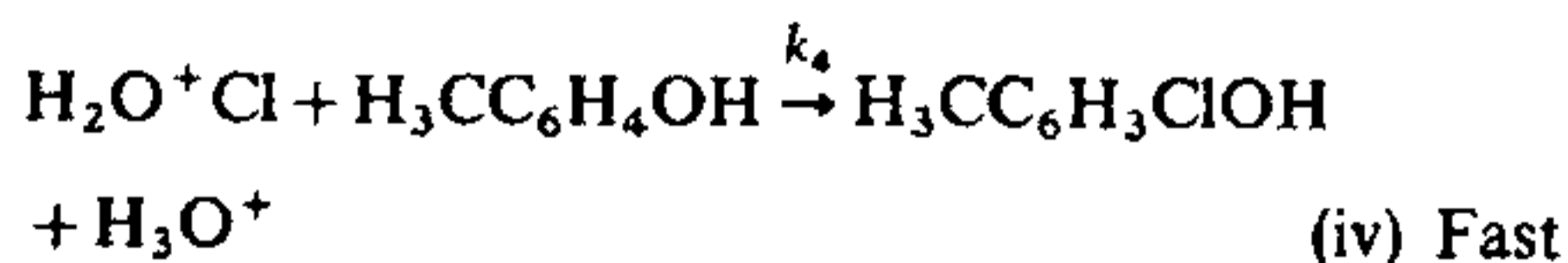
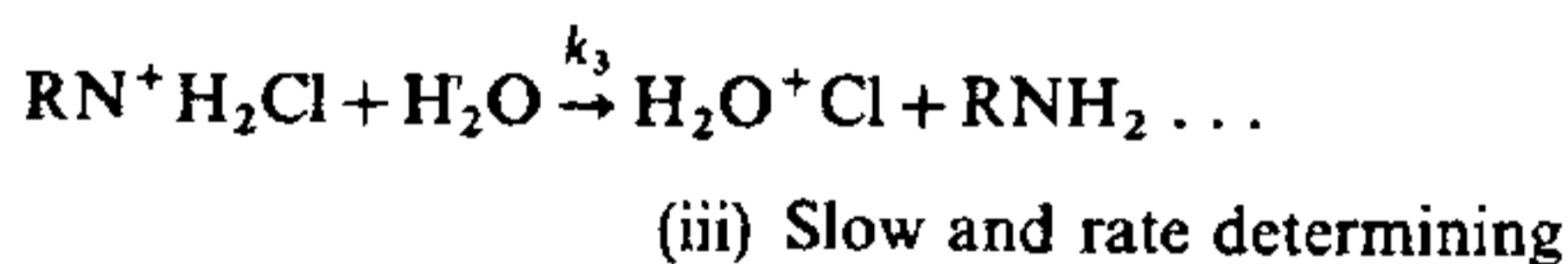
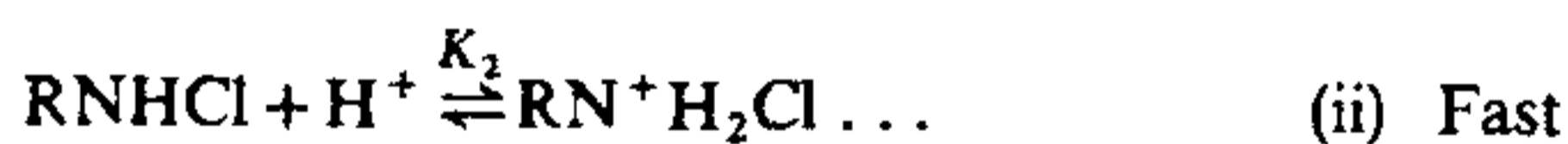
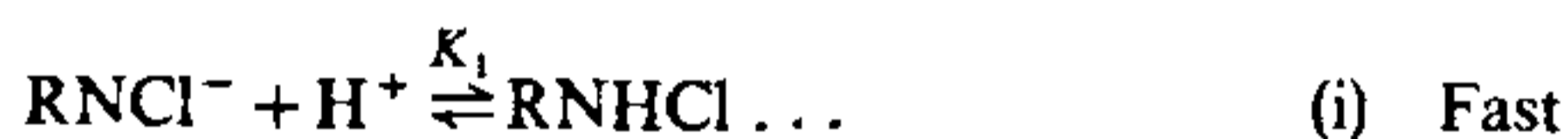
It is interesting to note that the overall rate law for the chlorination of phenol by CAB in the presence of HCl is of the form:

$$-\frac{d[\text{CAB}]}{dt} = k[\text{CAB}][\text{H}^+]^2 \quad (2)$$

while the composite rate law takes the form

$$-\frac{d[\text{CAB}]}{dt} = k'[\text{CAB}][\text{H}^+]^{1.2} + k''[\text{CAB}][\text{Cl}^-]^{0.8} \quad (3)$$

The following scheme accounts for the observed kinetics:



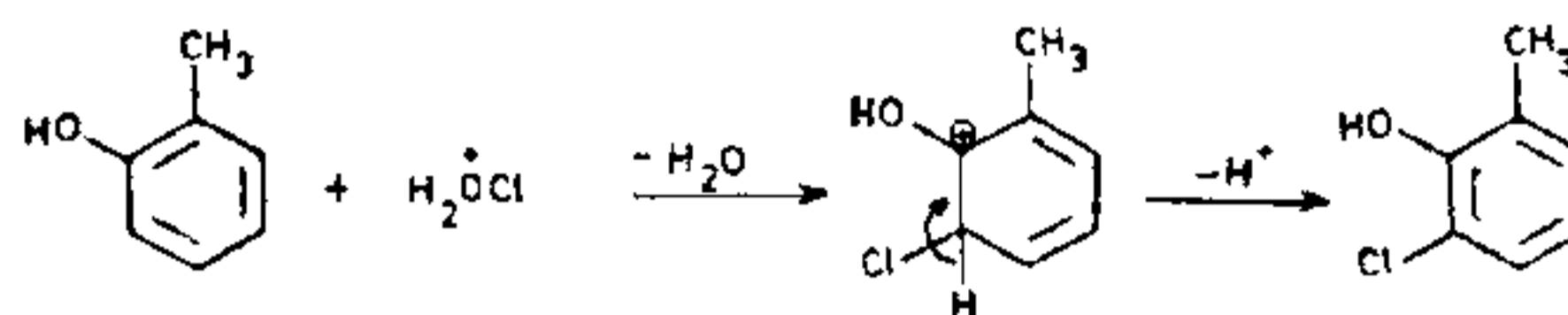
Scheme 1

If $[\text{CAB}]_T = [\text{RNCl}^-] + [\text{RNHCl}] + [\text{RN}^+\text{H}_2\text{Cl}]$, then the rate law would be

$$-\frac{d[\text{CAB}]}{dt} = \frac{K_1 K_2 k_3 [\text{CAB}]_T [\text{H}^+]^2}{1 + K_1 [\text{H}^+] \{1 + K_2 [\text{H}^+]\}} \quad (4)$$

Equation (4) explains the fractional order dependence on $[\text{H}^+]$ in accordance with the experimental results.

The positive ion $\text{H}_2\text{O}^+\text{Cl}$ is powerfully electrophilic and is considered to be the reactive chlorinating agent, the mechanism of which is given in scheme 2.



Scheme 2

Addition of chloride ion increases the reaction rate and a fractional order dependence on $[\text{Cl}^-]$ is observed. Such behaviour has been noted in the Orton rearrangement⁵ involving N-haloamides.

The present results can be explained by assuming an electrophilic attack by Cl^- on $\text{RN}^+\text{H}_2\text{Cl}$, accounting for the catalytic effect of chloride ions.

When catalysis is effected simultaneously by H^+ and Cl^- , an order of 2 on the gross concentration of HCl is observed. This may be traced to a mixed order kinetics and in the composite rate law (3), the first term accounts for H^+ catalysis and the second for Cl^- catalysis.

The authors are grateful to Prof. D. S. Mahadevappa and Dr S. Y. Ambekar for helpful discussions. BNU thanks UGC, New Delhi for the award of a fellowship.

7 April 1983; Revised 12 October 1983

1. Mukherjee, J. and Banerji, K. K., *J. Chem. Soc. Perkin II*, 1980, 4, 676.
2. Rangaswamy, Yathirajan, H. S. and Mahadevappa, D. S., *Rev. Roum. Chim.*, 1981, 26, 565.
3. Yathirajan, H. S., Rangaswamy and Mahadevappa, D. S., *Coll. Czech. Chem. Comm.*, 1982, 47, 1826.
4. Rangaswamy and Yathirajan, H. S., *Curr. Sci.*, 1981, 50, 757.
5. Gould, E. S., *Mechanism and structure in organic chemistry*, (Holt, Rinehard and Winston, New York), 1964, p. 650.