

Effect of Primary Salt in the Kinetic Study of Oxidation of Schiff Bases of Aryl Amines and Salicylaldehyde by Ce^{4+}

VARSHA K. BANE, USHA P. FULWADHVA, CHETAN R. SHAH,
SURESH S. DODWAD*, MANZOOR M. SHAIKH
Physical Chemistry Division, The Institute of Science
15, Madam Cama Road, Fort, Bombay-400 032, India

Kinetic studies on the oxidation of Schiff bases have been made using ceric sulphate as an oxidant in the absence and presence of inert KCl with varying concentrations. The reaction showed first order kinetics. Primary salt effect has been shown to be valid for the reaction studied.

INTRODUCTION

A survey of literature shows that much work has been done on oxidation of organic compounds by $Ce(IV)^{1-5}$. Kinetics of oxidation of mandelic acid, *dl*-malic acid, lactic acid⁶, isobutyric acid⁷ and dicarboxylic acids⁸ have been studied by several workers. The present communication reports the kinetic study of oxidation of Schiff bases namely *para*-, *meta*- and *ortho*-methyl substituted salicylanils in the presence of an inert salt *viz.* KCl. An attempt has been made to establish primary salt effect for the oxidation of these Schiff bases.

EXPERIMENTAL

All chemicals used were of AnalaR Grade or of E. Merck A.R. quality. *Para*-, *meta*-, and *ortho*-methyl substituted salicylanils were prepared by the method of Schischokow⁹. Purity of the recrystallised compounds was ascertained by taking melting points and IR spectra.

Known quantity of 0.025 molar ceric sulphate solution, having 0.012 N KCl in it, was thermally equilibrated along with 0.025 molar Schiff base solution at 300 K in a thermostat with an automatic temperature control. The two solutions were then mixed and the reaction mixture was also maintained at 300 K. After every five minutes 5 mL of reaction mixture was withdrawn and poured into a conical flask containing crushed ice pieces and 10 mL of 2 N sulphuric acid. To this mixture, 3-4 drops of 2% ferroin indicator¹⁰ were added and the mixture was titrated against 0.0125 molar solution of Mohr's salt. End point of titration was from green colour to red colour.

Same procedure was adopted by taking different concentrations of KCl *viz.* 0.18 N, 0.024 N and without adding KCl. The above experiment was carried out for all the three Schiff base solutions.

RESULTS AND DISCUSSION

Oxidation of all Schiff bases is found to be a first order reaction. This has been confirmed by plotting graphs of $\log(a - x)$ against time and of $\log \frac{a}{a - x}$ against time; both the plots are linear for all concentrations of KCl. Rate constants are computed from the linear plots.

Effect of ionic strength (I) is evident as the values of rate constants increase with increase in concentration of salt solution. Further, plot of $\log(k/k_0)$ against \sqrt{I} is a straight line with a positive slope. Such a linear relation has been reported by various authors.¹¹⁻¹⁴ Values of $\log(k/k_0)$ and \sqrt{I} are presented in Table 1.

TABLE-1

| Salt strength | \sqrt{I} | $\log(k/k_0)$ | | |
|---------------|------------|---------------------------|---------------------------|---------------------------|
| | | <i>p</i> -CH ₃ | <i>m</i> -CH ₃ | <i>o</i> -CH ₃ |
| 0.000 N | 0.542 | 0.000 | 0.000 | 0.000 |
| 0.012 N | 0.553 | 0.089 | 0.086 | 0.073 |
| 0.018 N | 0.559 | 0.135 | 0.121 | 0.109 |
| 0.024 N | 0.564 | 0.177 | 0.163 | 0.147 |

Decomposition of an intermediate complex is the rate determining step of the reaction. Value of slope of the above plot for *para*-substituted Schiff base is found to be *ca.* 8.0. During the decomposition of this complex, eight positive charges are momentarily developed, which is in conformity with the slope value obtained. These eight positive charges can be accounted as, four of ionic Ce⁴⁺ and other four from the protons attached to the system as shown in Fig. 1.

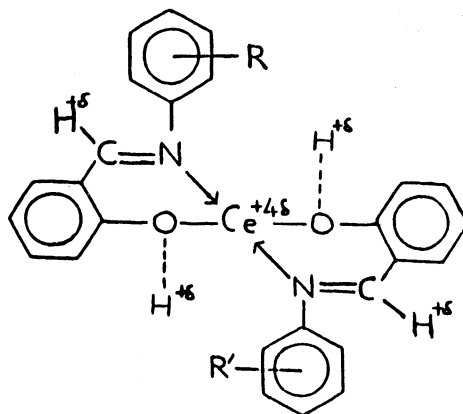


Fig. 1. Transition state

Two of these protons are from the ligand moieties, the other two being drawn from water. A review of the slope values of *meta*- and *ortho*-substituted Schiff bases reveals that they are lower than that of *para*-substituted compound. This may be probably due to the fact that momentary entry of protons from aqueous medium into the intermediate complex molecule is hindered by the substituted group.

REFERENCES

1. M.R. Ardon, J.S. Litter and M.A. Water, *J. Chem. Soc.*, 1811 (1957); *ibid.*, 2767 (1960).
2. D.L. Mathur and G.V. Bakore, *J. Indian Chem. Soc.*, **48**, 363 (1971).
3. F.R. Duke and R.F. Dremer, *J. Am. Chem. Soc.*, **73**, 5179 (1951).
4. J. Shorter and C. Hinshelwood, *J. Chem. Soc.*, 3276 (1950).
5. P. S. Sonkhla and R.N. Mehrotra, *Indian. J. Chem.*, **10**, 1977 (1972).
6. B. Krishna and K.C. Tiwari, *J. Chem. Soc.*, 3097 (1961).
7. B. Singh, M. Richards and R.K. Shukla, *J. Indian Chem. Soc.*, **53**, 751 (1976).
8. B.D. Kansal and N. Singh, *J. Indian Chem. Soc.*, **55**, 304, 618 (1978).
9. L. Schischkow, *Annalen der Chemie*, **104**, 373 rgi (1857); such Schiff, *ibid.*, 150, 194 (Bail, XII, 217).
10. A.I. Vogel, *Textbook of Quantitative Analysis*, ELBS
11. Henry, *Z. Physik. Chem.*, **10**, 96 (1892); Holmberg, *ibid.*, **80**, 587 (1912).
12. Bronsted and Pederson, *Z. Physik. Chem.*, **108**, 185 (1924).
13. Bronsted and Duns, *Z. Physik. Chem.*, **117**, 303 (1925).
14. Bronsted and King, *J. Am. Chem. Soc.*, **51**, 428 (1929).

(Received: 31 December 1994: Accepted: 30 April 1995)

AJC-983