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A Systematic Kinetic Study of Oxidation of *p*-Toluidine by Chromic Acid

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The oxidation kinetics of *p*-toluidine have been studied by chromic acid in acetic acid-water medium. The orders in oxidant, substrate and H^+ have been obtained one in each. The primary salt effect on the rate of oxidation is negligible. The effect of catalyst such as Ag^+, Cu^{2+} shows increasing effect whereas Mn^{2+} has retarded the rate. Various thermodynamic parameters have been evaluated. A probable mechanism has been suggested on the basis of kinetic results.

INTROUCTION

Chromic acid is one of the most versatile of available oxidizing agents, reacting with almost all types of oxidizable groups. Kinetic studies have been extensively carried out for various organic and inorganic compounds by using chromic acid[1–7]. The oxidation of aromatic amines has been studied by different oxidizing agents[8–12]. Further, the kinetics of oxidation of *p*-toluidine has already been carried out by using different oxidants like thallium(III)[13], sodium iodate[14], iron(III)[15] etc. by earlier workers.

The kinetics of chromic acid oxidation of *p*-toluidine have received no attention earlier. This forms the subject matter of the present paper.

MATERIALS AND METHODS

Experimental

Cr(VI) oxide (E. Merck) was twice recrystallized from conductivity water and stock solutions were prepared in conductivity water. The standardization of the Cr(IV) solution was carried out iodometrically. *p*-Toluidine was distilled under reduced pressure using a trace of Zn dust. Glacial acetic acid (S. Merck) was used as the solvent. The reaction was carried out in 10% acetic acid-water (v/v). The other chemicals employed were of B.D.H., E. Merck or S. Merck, of highest purity.

The progress of the reaction was followed by titrimetric procedure of Wiberg and Mill for the estimation of Cr(IV) iodometrically using a starch end point in a measured aliquot of the reaction mixtures at various intervals.

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RESULTS AND DISCUSSION

Dependence of reaction on reactants

The variation in chromic acid concentration (Table-1) showed that the order in chromic acid is one. The pseudo first order rate constants were calculated from the integrated first order equation. The rate of reaction increases with increase in concentration of chromic acid. The active oxidising species of Cr(IV) in the present case is in the form of H_2CrO_4, since at high concentration of chromic acid, the concentration of H_2CrO_4 will increase in the reaction mixture.

TABLE-1

[*p*-Toluidine] = 100×10^{-2} M, Temp. = 303 K, HOAc-H_2O = 10% (v/v)

[Chromic acid] × 10^3 M	1.00	1.33	2.00	2.66	4.00	5.00
$k_i \times 10^5$ s^{-1}	8.56	8.69	9.06	9.40	10.12	10.67

The variation in *p*-toluidine concentration (Table-2) showed that pseudo first order rate constants in chromic acid were directly proportional to *p*-toluidine concentration. The constancy of k_2 (= 8.74 ± 0.1007 l m^{-1} s^{-1}) values shown in last column of Table-2 clearly indicates that the reaction follows first order kinetics in *p*-toluidine.

TABLE-2

[Chromic acid] = 1.00×10^{-3} M, Temp = 303 K HOAc· H_2O = 10% (v/v)

[*p*-Toluidine] × 10^2 M	1.00	1.25	2.00	2.50	4.00	5.00
$k_1 \times 10^5$ s^{-1}	8.56	10.83	17.50	21.97	35.36	44.40
$k_2 \times 10^3$ l m^{-1} s^{-1}	8.56	8.66	8.75	8.79	8.84	8.88

$k_2 = k_1$/[p-toluidine]

Effect of sulphuric acid, neutral salts, catalysts, acetic acid and temperature

Chromic acid oxidation of *p*-toluidine was studied at different initial concentrations of sulphuric acid. The pseudo first order rate constant showed increase with increase in the concentration of acid (Table-3) suggesting that the reactions under study are acid catalysed.

The addition of salts like NaCl, KCl or Na_2SO_4 to the reaction mixture shows negligible effect on the rate of reaction, indicating that the rate determining step involves an ion and a neutral molecule. Similar observations have been also observed by Arumugam *et al.*[16] and Agrawal *et al.*[17]

The rate of reaction is influenced by the added catalytic cations like Cu^{2+}, Ag^+; however the rate of reaction is retarded by added Mn^{2+} (Table-3).

The rate of oxidation of *p*-toluidine increase with increases in percentage of acetic acid (Table-3). This can be explained by two reasons. Firstly, increase of percentage of acetic acid decreases the dielectric constant of the medium, and this decrease in dielectric constant is responsible for the increase in the rate of reaction involving an ion and a dipole. Secondly, acetic acid combines with chromic acid to form acetyl chromic acid or its protonated species which are stronger oxidising agents than chromic acid alone[18]. Similar observations have been reported by Sathyabhama[19].

TABLE-3
EFFECT OF SULPHURIC ACID AND CATALYSTS

[*p*-Toluidine] = 1.00×10^{-2} M, HOAc·H_2O = 10% (v/v)
[Chromic acid] = 1.00×10^{-3} M, Temp. = 303 K

$[H_2SO_4] \times 10^3$ M	5.00	10.0	15.0	20.0	25.0
$k_1 \times 10^5\ s^{-1}$	9.59	18.99	28.35	37.58	46.26
$[CuSO_4{\cdot}5H_2O] \times 10^3$ M		1.00	2.00	3.00	
$k_1 \times 10^5\ s^{-1}$		10.97	15.01	21.76	
$[MnSO_4{\cdot}H_2O] \times 10^3$ M		1.00	2.00	3.00	
$k_1 \times 10^5\ s^{-1}$		8.01	7.59	7.21	
$[Ag_2SO_4] \times 10^3$ M		1.00	2.00	3.00	
$k_1 \times 10^5\ s^{-1}$		8.98	9.72	10.56	

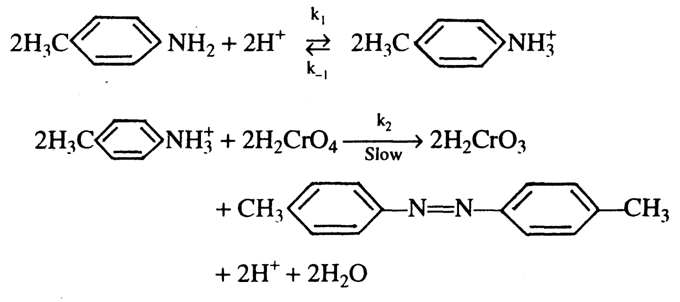
EFFECT OF ACETIC ACID [SOLVENT]
[p-Toluidine] = 1.00×10^{-2} M, Temp. = 303 K, [Chromic acid] = 1.00×10^{-3} M

HOAc·H_2O % (V/V)	10	20	30	40
$k_1 \times 10^5\ s^{-1}$	8.56	14.69	26.81	65.69

The effect of temperature was also studied and rate constants (k_1) were recorded as 8.56, 12.78, 19.58, 28.41, $42.35 \times 10^{-5}\ s^{-1}$ for *p*-toluidine [1.00×10^{-2} M] at 303, 308, 313, 318, 323 K respectively. The average value of temperature coefficient for 10°C rise in temperature was found to be 2.224 ± 0.0620. The activation parameters have been evaluated, using Arrhenius and Eyring's equations. The calculated values of energy of activation (E_a), frequency factor (A), enthalpy of activation (ΔH^*), Free energy of activation (ΔG^*) and entropy of activation (ΔS^*) are 64.92 ± 1.1474 kJ mol^{-1}, $1.35 \pm 0.01428 \times 10^7\ s^{-1}$ 62.78 ± 1.234 kJ mol^{-1}, 86.96 ± 0.6211 kJ mol^{-1} and 108.70 ± 0.2221 kJ mol^{-1} respectively.

Mechanism and Rate Expression

Based on the above experimental facts the following mechanism proposed as:



As stated above the first step in the oxidation of *p*-toluidine by chromic acid is the protonation of *p*-touidine. This reacts with H_2CrO_4 to give products. The sovent effect and salt effect substantiate the involvement of an ion and a molecule in the rate determining step.

Based on these facts, the following general mechanism and rate expression is proposed:

$$S + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SH^+ \quad \text{(Fast)} \tag{1}$$

where, S stands for *p*-toluidine

$$SH^+ + H_2CrO_4 \xrightarrow[\text{Slow}]{k_2} \text{Products} \tag{2}$$

$$\text{Rate of reaction} = k_2[SH^+][H_2CrO_4] \tag{3}$$

On applying the steady state approximation,

$$-\frac{d}{dt}[SH^+] = 0 = k_1[S][H^+] - k_{-1}[SH^+]\,1 - k_2[SH^+][H_2CrO_4]$$

$$[SH^+] = \frac{k_1[S][H^+]}{k_{-1} + k_2[H_2CrO_4]}$$

Substituting the value of $[SH^+]$ in equation (3), we get

$$\text{Rate of reaction} = \frac{k_2k_1[S][H^+][H_2CrO_4]}{k_{-1} + k_2[H_2CrO_4]}$$

Since $k_{-1} >> k_2$,

$$\therefore \quad \text{Rate of reaction} = \frac{k_2k_1[S][H^+][H_2CrO_4]}{k_{-1}}$$

$$= k_2k[S][H^+][H_2CrO_4]$$

where $k = k_1/k_{-1}$.

The derived rate law explains all the observed experimental facts.

Product analysis

The oxidation product has been identified as *p, p′* dimethylazobenzene[13, 14, 20] by the method of Pausacker and Scroggie[8].

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REFERENCES

1. S.K. Tandon, K.K. Banerjee and G.V. Bakore, *Indian J. Chem.*, **10**, 677 (1971).
2. V. Balliah amd P.V.V. Satyanarayana, *Indian J. Chem.*, **17A**, 966 (1978).

3. H.C.S. Senthlage, *Recl. Trav. Chim. Phys. Bas. Belg.*, **59**, 111 (1940); **61**, 213 (1942).
4. S. Senet, F. Mata and J.M. Leal, *Z. Phys. Chem. Leipzig*, **258**, 187 (1977).
5. F. Hasan and J. Rocek, *Tetrahedron*, **30**, 24 (1974).
6. D.R. Nagarajan, S. Sundaram and N. Venkatasubramanian Indian, *J. Chem.*, **18A**, 335 (1979).
7. P.S. Subramanian and D.R. Nagarajan, *Indian J. Chem.*, **18A**, (1979).
8. K.H. Pausacher and J.C. Seorogie, *J. Chem. Soc.*, 4003 (1954).
9. R. Edwards, *J. Am. Chem. Soc.*, **80**, 3591 (1958).
10. P.B.D. Dela Mare A.D. Kettery and C.A. Vernon, *J. Chem. Soc.*, 1290 (1954).
11. P.S. Radhakrishnamurti and M.D. Prasad Rao, *Indian J. Chem.*, **15A**, 485 (1976).
12. P.S. Radhakrishnamurti and S.N. Sahu, *Indian J. Chem.*, **15A**, 898 (1976).
13. P.S. Radhakrishnamurti and S.N. Pati, *Indian J. Chem.*, **19A**, 980 (1980).
14. M.D. Prasada Rao and J. Padmanabha, *Indian J. Chem.*, **19A**, 984 (1980).
15. K.V. Subbaiah, P.S.N. Murty, B.A.N. Murty and P.V. Subba Rao, *J. Indian Chem. Soc.*, **56**, 1213 (1979).
16. N. Arumugam, C. Shrinivasan and P. Kuthalingam, *Indian J. Chem.*, **17**, 478 (1978).
17. G.L. Agrawal and A.K. Bhattacharya, *Indian J. Chem.*, **17A**, 900 (1978).
18. K.B. Wiberg and H. Schaffer, *J. Am. Chem. Soc.*, **91**, 927 (1969).
19. V. Sathyabhama and S.V. Ananthakrishnan, *Indian J. Chem.*, **9**, 1963 (1972).
20. K.V. Subbaiah, P.S.N. Murty, B.A.N. Murty and P.V. Subba Rao, *J. Indian Chem. Soc.*, **56**, 1213 (1979).

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