

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

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The rate of oxidation of *o*-toluidine by chromic acid have been measured in acetic acid-water medium. The orders in oxidant, substrate and H^+ have been obtained one in each. The effect of neutral salts, catalysts, solvent polarity and temperature on the rate of oxidation have been studied. A suitable mechanism consistent with the experimental results has been proposed.

INTRODUCTION

Chromic acid has been used as an oxidant in the study of kinetics of oxidation of some aromatic amines¹⁻⁴, though similar studies with *o*-toluidine have not been made so far. Kinetics of oxidation of *o*-toluidine have already been carried out by using different oxidants^{5,6}. The kinetics of chromic acid oxidation of *o*-toluidine have received no attention earlier. This, therefore, forms the subject matter of the present paper.

EXPERIMENTAL

All the chemicals used during the investigation were either AnalaR B.D.H., E. Merck or S. Merck of extra pure quality. Stock solution of chromic acid was prepared in distilled water and was standardised iodometrically. The reactions were studied in thermostat ($\pm 0.1^\circ C$). *o*-Toluidine was distilled under reduced pressure using a trace of zinc dust. Glacial acetic acid was used as the solvent.

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

RESULTS AND DISCUSSION

The kinetics of oxidation of *o*-toluidine by chromic acid have been studied in 10% aqueous acetic acid medium. The order of reaction with respect to chromic acid is one. The pseudo first order rate constant increases with increase in the concentration of *o*-toluidine, however, value of $k_1/[o\text{-toluidine}]$ remains constant (Table-1). This clearly indicates that the order with respect to *o*-toluidine is unity. The pseudo first order rate constant showed increase with increase in the concentration of sulphuric acid, suggesting that the reactions under study are acid catalysed (Table-1).

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The pseudo first order rate constant in chromic acid increases with increase in chromic acid concentration (Table-1). The plot of $\log(a-x)$ versus time is found linear (Fig. 1). The active oxidising species of Cr(VI) 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.

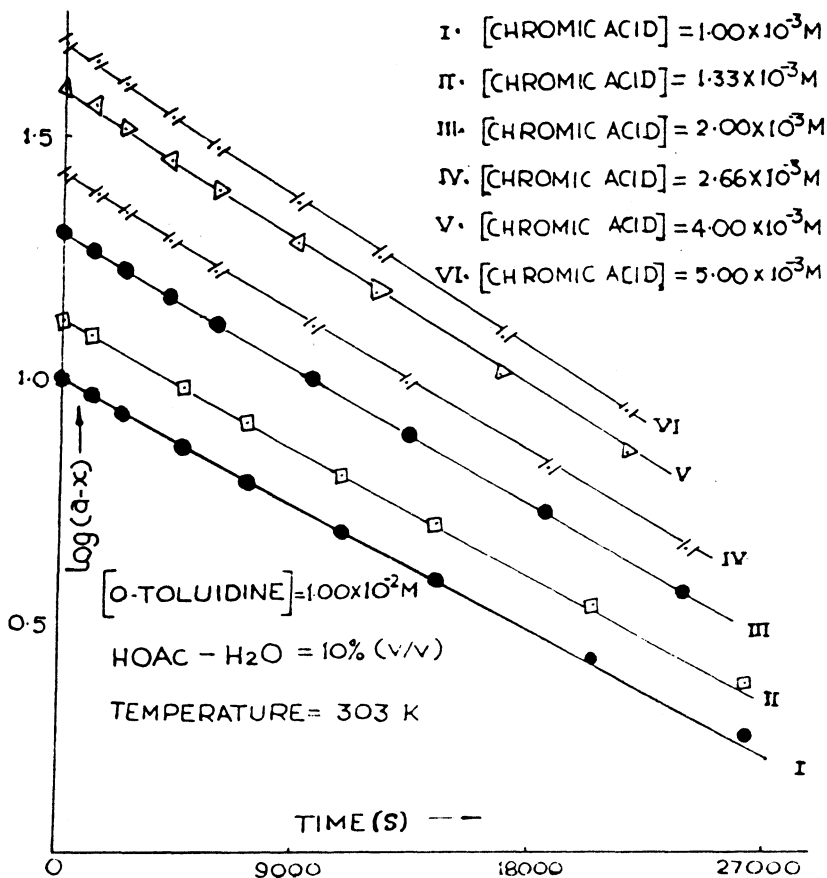


Fig. 1. Dependence of rate on chromic acid plot of $\log(a-x)$ vs time

The added salts like NaCl, KCl, Na_2SO_4 , K_2SO_4 , to the reaction mixture show negligible effect on the rate of reaction, indicating that the rate determining step involves an ion and a neutral molecule (Table-2). 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-2). The increase in the percentage of acetic acid in the reaction mixture largely enhances the reaction rate (Table-2). The plot of $\log k_1$ vs percentage composition of acetic acid, that is, $1/D$ is linear having positive slope, suggesting the reaction is positive ion-dipole type.

TABLE-1
EFFECT OF CONCENTRATION OF REACTANTS AND SULPHURIC ACID
Temp = 303 K, HOAc-H₂O = 10% (V/V)

Effect of chromic acid concentration [<i>o</i> -Toluidine] = 1.00 × 10 ⁻² M						
[Chromic acid] × 10 ³ M	1.00	1.33	2.00	2.66	4.00	5.00
k ₁ × 10 ⁵ s ⁻¹	6.69	6.81	7.20	7.53	8.21	8.72
Effect of <i>o</i> -toluidine concentration [Chromic acid] = 1.00 × 10 ⁻³ M						
[<i>o</i> -Toluidine] × 10 ² M	1.00	1.25	2.00	2.50	4.00	5.00
k ₁ × 10 ⁵ s ⁻¹	6.69	8.51	13.72	17.22	27.68	34.85
k ₂ × 10 ² l m ⁻¹ s ⁻¹	6.69	6.80	6.86	6.89	6.92	6.97
Effect of sulphuric acid concentration [<i>o</i> -Toluidine] = 1.00 × 10 ⁻² M [Chromic acid] = 1.00 × 10 ⁻³ M						
[H ₂ SO ₄] × 10 ³ M	5.00	10.00	15.00	20.00	25.00	
k ₁ × 10 ⁵ s ⁻¹	7.53	14.90	22.05	29.42	36.56	

TABLE-2
EFFECT OF CONCENTRATION OF SALTS, CATALYSTS AND ACETIC ACID

[<i>o</i> -Toluidine] = 1.00 × 10 ⁻² M, HOAc-H ₂ O = 10% (V/V) [Chromic acid] = 1.00 × 10 ⁻³ M, Temp. = 303 K				
Effect of salts concentration				
[NaCl] × 10 ³ M	4.00	6.00	8.00	
K ₁ × 10 ⁵ s ⁻¹	6.65	6.62	6.60	
[KCl] × 10 ³ M	4.00	6.00	8.00	
K ₁ × 10 ⁵ s ⁻¹	6.59	6.57	6.56	
[Na ₂ SO ₄] × 10 ³ M	1.00	2.00	3.00	
K ₁ × 10 ⁵ s ⁻¹	6.53	6.50	6.46	
[K ₂ SO ₄] × 10 ³ M	1.00	2.00	3.00	
K ₁ × 10 ⁵ s ⁻¹	6.50	6.46	6.40	
Effect of catalysts concentration				
[CuSO ₄ ·5H ₂ O] × 10 ³ M	1.00	2.00	3.00	
K ₁ × 10 ⁵ s ⁻¹	8.57	11.68	16.72	
[MnSO ₄ ·H ₂ O] × 10 ³ M	1.00	2.00	3.00	
K ₁ × 10 ⁵ s ⁻¹	6.30	6.04	5.79	
[Ag ₂ SO ₄] × 10 ³ M	1.00	2.00	3.00	
K ₁ × 10 ⁵ s ⁻¹	7.11	7.65	8.23	
Effect of percentage composition of acetic acid				
HOAc-H ₂ O% (V/V)	10	20	30	40
K ₁ × 10 ⁵ s ⁻¹	6.69	10.79	18.94	44.32

The kinetics of oxidation of *o*-toluidine by chromic acid have been studied at different temperatures and rate constants (k_1) were recorded as 6.69, 10.30, 16.35, 24.53, $37.78 \times 10^{-5} \text{ s}^{-1}$. Logarithmic plots of $\log a/(a-x)$ versus time were also obtained and showed excellent straight lines at temperatures 303 K, 308 K, 318 K, 323 K (Fig. 2). The average value of temperature coefficient for 10°C rise

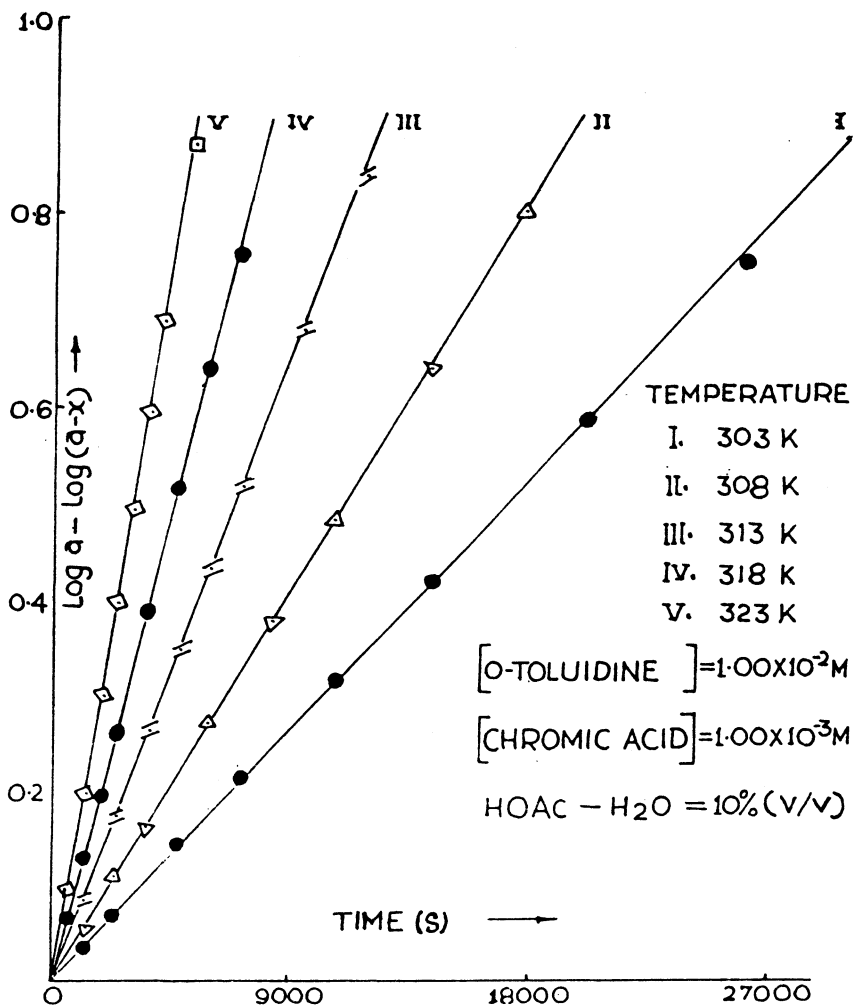
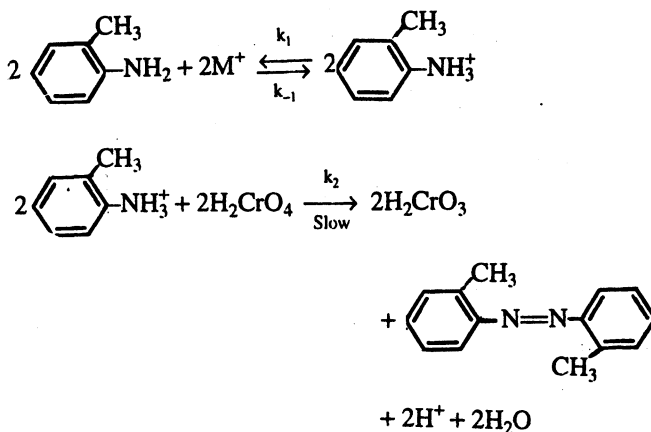


Fig. 2. Dependence of rate on temperature plot of $\log a/(a-x)$ vs time

in temperature was found to be 2.378 ± 0.0665 . 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 $70.27 \pm 0.8322 \text{ kJ mol}^{-1}$, $8.82 \pm 0.1026 \times 10^7 \text{ s}^{-1}$, $67.88 \pm 0.5045 \text{ kJ mol}^{-1}$, $87.44 \pm 0.4961 \text{ kJ mol}^{-1}$, $-93.12 \pm 0.2198 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively.

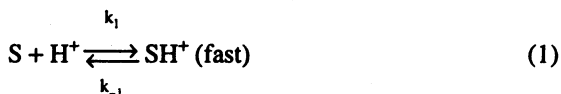
Mechanism and rate expression

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

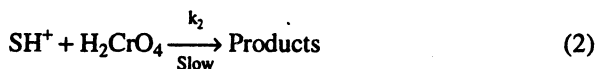


As stated above the first step in the oxidation of *o*-toluidine by chromic acid is the protonation of *o*-toluidine. This reacts with H_2CrO_4 to give products. The solvent effect and salt effect substantiate the involvement of an ion and a molecule in the rate determining step.

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



where S stands for *o*-toluidine



$$\text{Rate of reaction} = k_2[\text{SH}^+][\text{H}_2\text{CrO}_4] \quad (3)$$

On applying the steady state approximation,

$$-\frac{d}{dt} [\text{SH}^+] = 0 = k_1[\text{S}][\text{H}^+] - k_{-1}[\text{SH}^+] - k_2[\text{SH}^+][\text{H}_2\text{CrO}_4]$$

$$[\text{SH}^+] = \frac{k_1[\text{S}][\text{H}^+]}{k_{-1} + k_2[\text{H}_2\text{CrO}_4]}$$

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

$$\text{Rate of reaction} = \frac{k_2 k_1 [\text{S}][\text{H}^+][\text{H}_2\text{CrO}_4]}{k_{-1} + k_2[\text{H}_2\text{CrO}_4]}$$

Since $k_{-1} \gg k_2$,

$$\begin{aligned}\text{Rate of reaction} &= \frac{k_2 k_1 [S][H^+][H_2CrO_4]}{k_{-1}} \\ &= k_2 k [S][H^+][H_2CrO_4]\end{aligned}$$

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 O,O'-dimethylazobenzene^{5,6} by the method of Pausacker and Scroggie⁷.

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REFERENCES

1. Ranveer Singh and K.B.L. Shrivastava, *Asian J. Chem.*, **8**, 293 (1996).
2. _____, *Asian J. Chem.*, **8**, 649 (1996).
3. K.B.L. Shrivastava and Ranveer Singh, *Asian J. Chem.*, **7**, 767 (1995).
4. K.B.L. Shrivastava, Ranveer Singh and K.S. Tiwari, *Asian J. Pure & Appl. Chem.*, **1**, 46 (1995).
5. P.S. Radhakrishnamurti and S.N. Pati, *Indian J. Chem.*, **19A**, 980 (1980).
6. B.S. Rawat and M.C. Agrawal, *Indian J. Chem.*, **17A**, 299 (1979).
7. K.H. Pausacher and J.C. Seorogie *J. Chem. Soc.*, 4003 (1954).

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