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Kinetics of Oxidation of Toluidines by Chromic Acid

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The kinetics of oxidation of *o*, *m* and *p*-toluidines by chromic acid has been studied in acetic acid-water medium. The reactions were found to be first order with respect to [Oxidant], [Substrate] and $[H^+]$. An addition of Cu^{2+} and Ag^+ increases the rate of reaction while addition of Mn^{2+} decreases the rate of reaction in each case. An addition of neutral salts like NaCl, KCl, Na_2SO_4 and K_2SO_4 in the reaction mixture showed negligible effect. Effects of dielectric constant and temperature on the reactions were studied. Thermodynamic parameters have been evaluated and mechanism for the reactions have been proposed. The isokinetic temperature has also been evaluated.

INTRODUCTION

Reactions involving chromic acid have received limited attention, although some investigations uitlizing chromic ion oxidation kinetics in organic and inorganic compounds[1–10] have been reported. Literature survey pertaining to the above-titled reaction reveals that no attempt seems to have been made to explore the detailed kinetic study of toluidines (o^-, m^- and *p*-toluidine) by chromic acid. Thus we have conducted the present study in order to postulate a complete, concise and general mechanism of oxidation of these toluidines in aqueous acetic acid medium which has hitherto been unreported.

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(VI) solution was carried out iodometrically. Toluidines were distilled under reduced pressure using a trace of Zn dust. Glacial acetic acid (S. Merck) was used as the solvent. The kinetic studies were carried out in 10% (v/v) aqueous acetic acid under pseudo first order conditions and temperature was maintained within ±0.1°C. All the chemicals used during the investigation were either AnalaR BDH, E. Merck or S. Merck of extra pure quality. The progress of the reaction was followed by titrimetric procedure of Wiberg and Mill[11] for the estimation of Cr(VI) iodometrically using a starch end point in a measured aliquot of the reaction mixture at various intervals.

RESULTS AND DISCUSSION

The kinetic investigations were performed at several initial concentrations of chromic acid for each toluidine (Table-1) as illustrated by the linear typical plot of log (a – x) versus time (Fig. 1) which clearly reveals first order kinetics. However, with increase in [chromic acid], there is a slight increase in the value of k_{obs}. The active oxidising species of Cr(VI) in the present cases 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

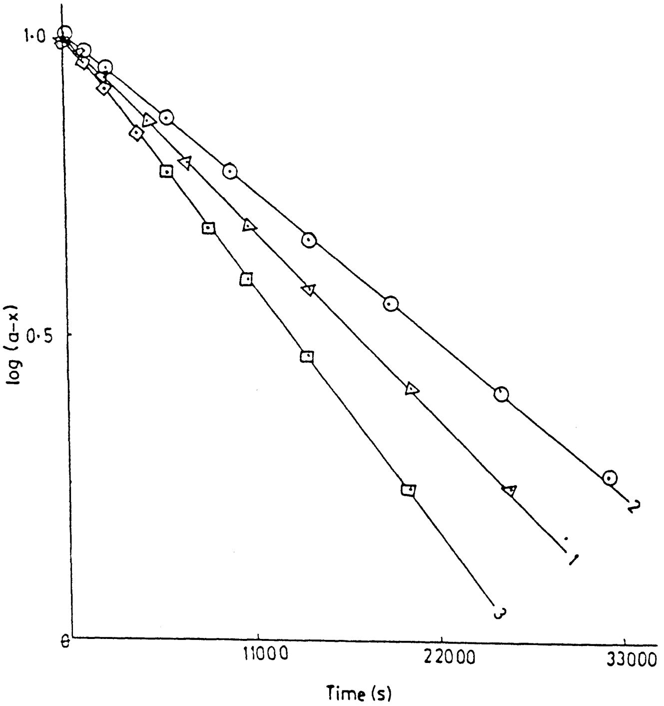

Fig. 1 Typical kinetic plot of log ($a - x$) versus time; *o*-Toluidine (1), *m*-Toluidine (2), *p*-Toludine (3) [Toludine] = 1.00×10^{-2} M (1, 2, 3); HOAc—H_2O = 10%(v/v) (1, 2, 3) Temperature = 303 K (1, 2, 3)

The order in substrate was computed from the slope of k_1 versus [toluidine] (Fig. 2) and it was found that reactions follow first order kinetics with respect to all toluidines. The pseudo first order rate constant increases with increase in the concentration of toluidine (Table-2)., however, the value of k_1/[toluidine] remains constant.

TABLE-1
EFFECT OF [CHROMIC ACID] ON THE RATE CONSTANT k_1

[Toluidine] = 1.00×10^{-2} M(1, 2, 3,), HOAc-H_2O = 10% (v/v)(1, 2, 3),
Temperature = 303 K (1, 2, 3)

[Chromic Acid] $M \times 10^3$	*o*-Toluidine (1)	*m*-Toluidine (2)	*p*-Toluidine (3)
		$k_1 \times 10^5\ s^{-1}$	
1.00	6.69	5.30	8.56
1.33	6.81	5.41	8.69
2.00	7.20	5.76	9.06
2.66	7.53	5.98	9.40
4.00	8.21	6.77	10.12
5.00	8.72	7.29	10.67

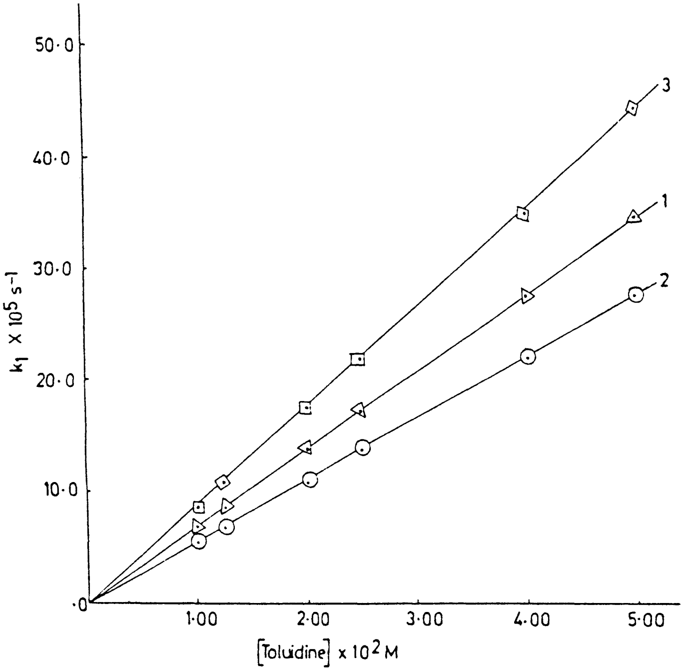

Fig. 2 Dependence of k_1 on [Toluidine]; [Chromic acid] = 1.00×10^{-3} M (1, 2, 3)
HOAc—H_2O = 10% (v/v) (1, 2, 3); Temperature = 303 K (1, 2, 3)

TABLE-2
EFFECT OF [SUBSTRATE] ON THE RATE CONSTANT k_1

[Chromic acid] = 1.00×10^{-3} M(1, 2, 3,), HOAc-H_2O = 10% (v/v)(1, 2, 3),
Temperature = 303 K (1, 2, 3)

[Substrate] M × 10^3	*o*-Toluidine (1)	*m*-Toluidine (2)	*p*-Toluidine (3)
		$k_1 \times 10^5\ s^{-1}$	
1.00	6.69	5.30	8.56
1.25	8.51	6.73	10.83
2.00	13.72	10.86	17.50
2.50	17.22	13.73	21.97
4.00	27.68	22.10	35.36
5.00	34.85	27.80	44.40

The kinetics of oxidation of toluidines by chromic acid were studied over a wide range of sulphuric acid concentration. An increase in acid concentration increases the rate of reaction proportionately (Table-3) suggesting that the reactions under study are acid catalyzed and the order with respect to sulphuric acid concentration is unity as evaluated from the unit slope values for the linear plot of k_1 versus [H_2SO_4] (Fig. 3).

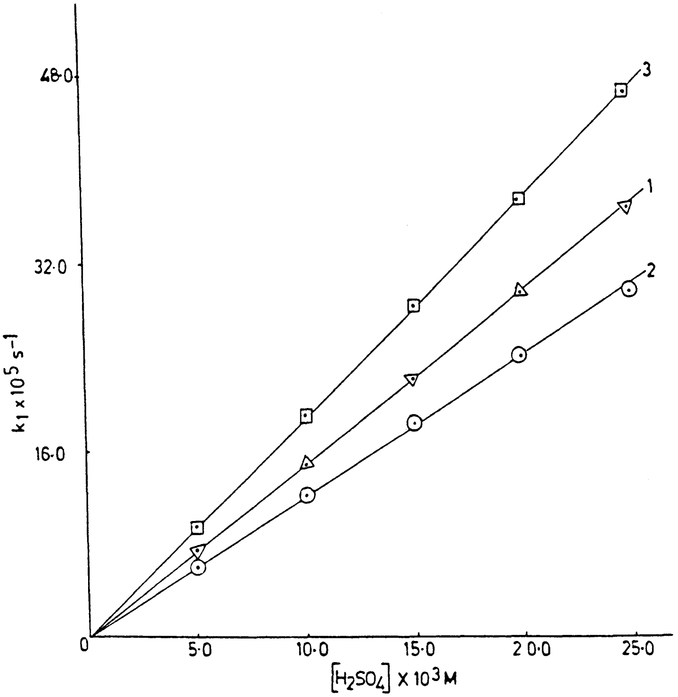

Fig. 3 Dependence of k_1 on H_2SO_4, [Toludine] = 1.00×10^{-2} M (1, 2, 3)
HOAc—H_2O = 10% (v/v) (1, 2, 3); [Chromic acid] = 100×10^{-3} M (1, 2, 3);
Temperature = 303 K (1, 2, 3)

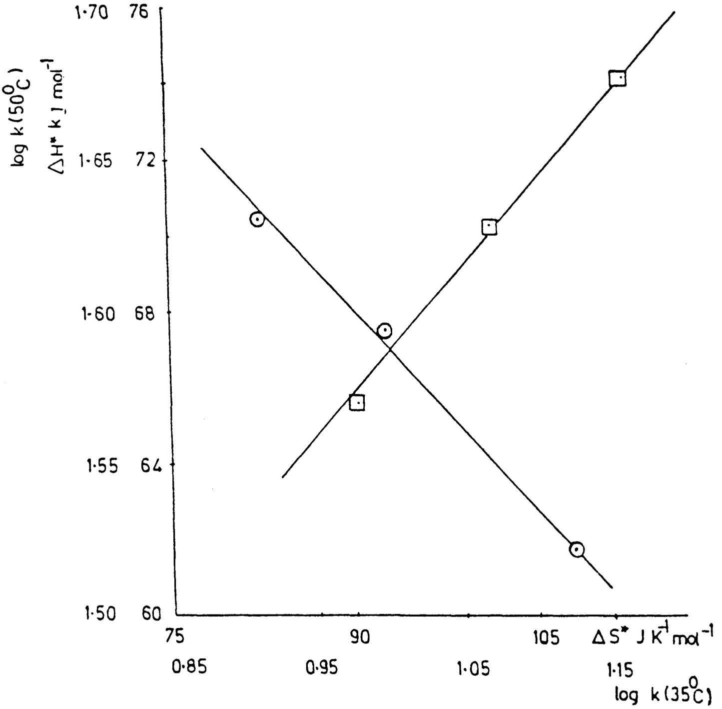

Fig. 4. Reactions between toluidines and chromic acid

⊙ Isokinetic plot: ΔH^* versus ΔS^*

◇ Exner plot: log k (35°C) versus log k (50°C)

TABLE-3

EFFECT OF $[H_2SO_4]$ ON THE RATE CONSTANT k_1

[Toluidine] = 1.00×10^{-2} M(1,2,3,), HoAc-H_2O = 10% (v/v)(1,2,3), Temperature = 303 K (1,2,3)

$[H_2SO_4]$ $M \times 10^3$	*o*-Toluidine (1)	*m*-Toluidine (2)	*p*-Toluidine (3)
		$k_1 \times 10^5\ s^{-1}$	
5.00	7.53	6.18	9.59
10.00	14.90	12.23	18.99
15.00	22.05	18.35	28.35
20.00	29.42	24.03	37.58
25.00	36.56	29.59	46.26

The rates of oxidation increase with increase in percentage of acetic acid in all toluidines (Table-4). 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 the reactions 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.[12] Similar observations have been reported by Sathyabhama *et al.*[13]

TABLE-4
EFFECT OF SOLVENT COMPOSITION ON THE RATE CONSTANT k_1

[Toluidine] = 1.00×10^{-2} M (1, 2, 3), [Chromic acid] = 1.00×10^{-3} M (1, 2, 3),
Temperature = 303 k (1, 2, 3)

HOAc-H$_2$O % (v/v)	o-Toluidine (1)	m-Toluidine (2)	p-Toluidine (3)
	$k_1 \times 10^5$ s^{-1}		
10	6.69	5.30	8.56
20	10.79	8.02	14.69
30	18.94	12.28	26.81
40	44.32	24.52	65.69

The added salts like NaCl, KCl, Na_2SO_4 and 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. The rate of reaction is influenced by the added catalytic cations like Cu^{2+}, Ag^+; however, the rate of reaction is retarded by adding Mn^{2+} for all toluidines. Copper catalysed reactions have been studied by various workers, using different oxidants. On the basis of these studies, it has been suggested that Cu^{2+} ion catalysis is characteristic in case where it can form a complex with substrate. Similarly the possiblility due to which Ag^+ ions can increase the rate of reaction, is the complex formation between Ag^+ ions and the substrate. The retarding effect of Mn^{2+} ions is explained by assuming that in presence of Mn^{2+} ions, two different oxidising species of chromium are involved. They are Cr(V) and Cr(IV). These species can oxidise Mn^{2+} ions with the result that lesser chromium is available for the oxidation of substrate and hence the rate decreases.

The values of various Arrhenius and Eyring parameters were computed from the study of rate measurements within the temperature range 303, 308, 313, 318 and 323 K, respectively, and are reported in Table-5.

TABLE-5
ACTIVATION PARAMETERS OF TOLUIDINE-CHROMIC ACID SYSTEM

Activation parameters	[o-Toluidine]	[m-Toluidine]	[p-Toluidine]
Ea kJ mol^{-1}	70.22 ± 0.2655	74.12 ± 0.07385	64.91 ± 0.2022
Graphical value	69.99 ± 0.9162	73.83 ± 0.0913	64.85 ± 1.6014
A s^{-1}	$(8.93 \pm 0.1135) \times 10^7$	$(3.26 \pm 0.0399) \times 10^8$	$(1.49 \pm 0.0125) \times 10^7$
ΔH^* kJ mol^{-1}	67.64 ± 0.4706	70.30 ± 0.2578	61.74 ± 1.2482
ΔG^* kJ mol^{-1}	87.42 ± 0.5013	87.89 ± 0.4141	86.95 ± 0.6224
ΔS^* J K^{-1} mol^{-1}	-93.02 ± 0.2196	-82.25 ± 0.2123	-107.92 ± 0.2182

The stoichiometry of each reaction under investigation has been determined by equilibrating the reaction mixture containing an excess of chromic acid over toluidine in varying ratio at the experimental temperature for five days. The result of the experiment on stoichiometry indicated that 2 moles of substrate were consumed per 2 moles of the chromic acid for the completion of the reaction. The stoichiometric equation overall for each reaction under investigation can be, therefore, written as

$$2CH_3—C_6H_4—NH_2 + 2H_2CrO_4 \\ \rightarrow 2H_2CrO_3 + CH_3—C_6H_4—N{=}N—C_6H_4—CH_3 + 2H_2O$$

The oxidation products have been identified to be substituted azobenzenes by the TLC method as reported by Pausacher *et al.*[16]

Mechanism and rate expression

The authors propose the following mechanism to account for their kinetic results:

$$\underset{(o^-, m^- \text{ or } p^-\text{-toluidine})}{2Ar-NH_2} + 2H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Ar-NH_3^+$$

$$2Ar-NH_3^+ + 2H_2CrO_4 \xrightarrow[\text{slow}]{k_2} 2H_2CrO_3 + Ar—N{=}N—Ar + 2H^+ + 2H_2O$$

The order of reactivity observed was in the following sequence:

p-Toluidine > *o*-Toluidine > *m*-Toluidine

Similar results have been reported by Radhakrishnamurti *et al.*[14] and Prasada Rao *et al.*[15] in their works.

Kinetic thermodynamic and mechanistic evidences support the proposed mechanism of the reaction under investigation. It was found that the respective kinetic findings are almost similar in all the cases; therefore it is suggested that for all the oxidations of toluidines, the mechanism should be similar. If the mechanism is similar, the intermediates and kinetic parameters should also be similar.

Mechanism of the reaction reveals that after the initial protonation of toluidine, a protonated species is generated which exists in equilibrium with initial toluidine. When H_2CrO_4 oxidation species is introduced during midway of the reaction, it immediately changes the course of reaction and lowers down the rate of reaction which ultimately favours the formation of the final reaction product.

Now as per the rates of reaction observed for toluidines, *p*-toluidine shows the fastest rate whereas *m*-toluidine the slowest. This order can be explained on the basis of their respective structures, molecular geometry, electron donating influence of CH_3 substituents and of course the vicinity of substituent from the actual reaction site in the toluidine molecule.

In case of *p*-toluidine, besides CH_3 being the electron donating group, which interacts with mesomeric π-electron system of the molecules and enhances the electron density at $—NH_2$ and ultimately favours the rapid attack of proton and consequently the Ar—NH_3^+ species. Molecular symmetry in the case of *p*-toluidine enhances the rate of reaction; therefore the rate of reaction is faster in *p*-toluidine, *o*-derivatives lose symmetry but the vicinity of CH_3 group to —NH_2 puts it in the second place when the rate of reaction is studied.

Based on the above experimental facts, the following general mechanism is proposed:

$$S + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ \qquad \text{(Fast)} \qquad (1)$$

where, S stands for toluidine

$$SH^+ + H_2CrO_4 \xrightarrow{k_2} \text{Products} \qquad \text{(Slow)} \qquad (2)$$

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

On applying the steady state approximation,

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

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

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

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

Since $k_{-1} \gg k_2$

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

$$= k_2k[S][H^+][H_2CrO_4], \qquad \text{where, } k = k_1/k_{-1}$$

The derived rate law explains all the observed experimental facts obtained in the oxidation reactions.

Conclusion

The activation energy is highest for the slowest reaction and vice-versa suggesting that the reactions are enthalpy controlled. The linear plot of ΔH^* versus ΔS^*, and the fairly constant value of ΔG^* suggest that a similar mechanism prevails for all toluidines. The isokinetic temperature β was found to be 350.74 K (Fig. 4) which is in good agreement with the value 354.65 K obtained from the Exner plot[17] (Fig. 4).

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