Kinetics of oxidation of o-toluidine by potassium dichromate

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Abstract- The Oxidation kinetics of o-Toluidine by Cr (VI) has been studied Iodometrically in aqueous sulphuric acid medium. The reaction follows complex kinetic behavior with respect to concentration. Mechanism with the associated reaction kinetics is assigned and discussed all kinetic and thermodynamic parameters are calculated.

Index Terms- Kinetics, Oxidation, Catalyst.

I. INTRODUCTION

The metabolism of nitrogen compounds by oxygenation was established in the beginning of last century. Further, interest was developed in such type of reactions in view of involvement of product of N-Oxidation in Certain pharmacological and toxicological processes, effecting physiological changes in the body. Oxidation of 1^0 aromatic amine by lead acetate has been studied by Pausacker[1]. The medium of the reaction is acetic acid as benzene it is assumed that the reaction mechanism with lead tetra-acetate remains analogous to that proposed for phenyl iodo-acetate. It is established that o-Toluidine and m-Toluidine give better yield of azo compound with both the oxidants in comparison to p-toluidine. Pausacker[2] has studied the oxidation of 1^0 aromatic amines by phenyliodosocetate in benzene. It is reported that o-Toluidine gives purple color intermediate which transforms to deep carmine color solution m-Toluidine gives pink colored throughout the course of the reaction. The product identified is azo compound by chromatography method using alumina as stationary phase and benzyne as stationary phase and benzene as eluent.The oxidation of aniline and substituted aniline by hexocyanoferate (111) is studied by R.K. Murti[3] and others. The rate constants w.r.t. hexacyanoferrate is pseudo first order under all conditions. The reaction is first order in [substrate] also. The reaction rate is independent of [alkali]. Antelo[4] and others have investigated oxidation of ethanol amines with Cr(VI) in acetic acid. The rate of $K_2Cr_2O_7$ oxidation of ethanol amine

$[HOCH_2CH_2O)_n$ NH_{3-n} (n=1-3) (1) in 50% aquous HOAc increases with n. Kinetics of 1(n=3) and the order of reaction indicated that the rate determining step involved the decomposition of $R'CH_2CH_2O$ $Cr(O_2)OH$ formed by protonation. Mishra[5] others have studied kinetics of o, m and p-toluidines by Chromic acid has been studied in acetate acid-water medium. The reactions were found to be first order w.r.t. (oxidant), [Substrate] and [H+]. An addition of Cu^{2+} and Ag^+ increases the rate of reaction while addition of Mn^{2+} decreases the rate. An addition of neutral salts like NaCl, KCl, Na_2SO_4 and K_2SO_4 in the reaction mixture showed negligible effect.Ramananda[6]and others have studied kinetics of

oxidation of o-Toluidine by NaN-Chlorobenzene sulfonaamide in aqueous H_2SO_4 medium at 303 K. Rate showed first order dependence on [CAB], fractional order in [oTd] and increase first order dependence on [H^+]. The variation of ionic strength, change in dielectric constant of the medium, addition of reaction product and halide ions had no effect on reaction rate. Kaushik[7] and others have studied periodate oxidation of o-Toluidine in acetone water medium. Order with respect to both oxidant and substrate is one.
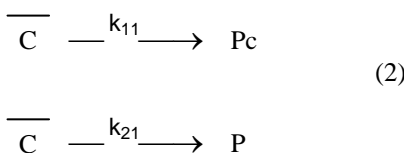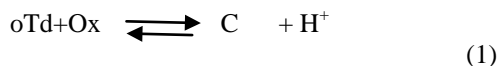
II. EXPERIMENTAL SECTION

o-Toluidine (Merck), Potassium dichromate (Loba Chemia), H_2SO_4 (Qualigens), Sodium thiosulfate (Loba Chemie), Starch (Loba Chemie), Potassium Iodide (E.Merck) where used without purification. Solutions of all reagents were prepared in doubly distilled water. The oxidant concentration of 0.0002 mol dm^{-3} was maintained throughout the kinetic runs. Pseudo first order conditions were maintained in all runs with excess o-Toluidine (~10x). Kinetic runs were reproducible within $\pm$5% of required value. Requisite amount of substrate was taken in one flask and oxidant with acid in another flask. They were thermally equilibrated for 20 mins. and then thoroughly mixed by shaking. The reaction was studied up to 90% of completion.
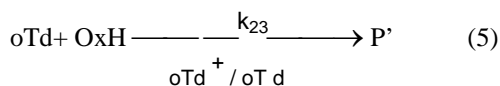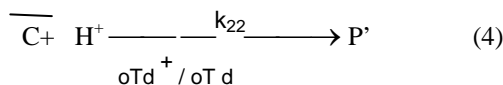
Kinetics of Oxidation of o-Toluidine

Dependence of ^ok (pseudo first order rate constant determined by titer values at time t) on [H^+] and [oTd] gives a complexed rate law consisting of four terms. An attempt has been made to identify which of these four routes are involved in producing the colored product and which ones are involved in the formation of uncolored product. This has been done in following manner.
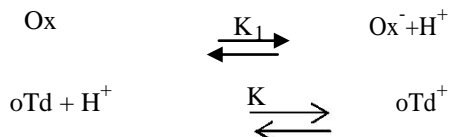
It is observed that at very low [oTd]$_o$(intial concentration of o-Toluidine) the oxidation rate decreases with increasing [H^+]. However, at moderate and high [oTd]$_o$ the trend is reversed. This and other kinetic features of the reaction are satisfied by the following proposed mechanism:

$$oTd + Ox \rightleftharpoons C + H^+ \qquad (1)$$

$$\overline{C} \xrightarrow{k_{11}} Pc \qquad (2)$$

$$\overline{C} \xrightarrow{k_{21}} P$$

(3)

$$\overline{C} + H^+ \xrightarrow[\text{oTd}^+ / \text{oT d}]{k_{22}} P' \qquad (4)$$

$$\text{oTd} + \text{OxH} \xrightarrow[\text{oTd}^+ / \text{oT d}]{k_{23}} P' \qquad (5)$$

Equilibrium for oxidant and o-Toluidine are as given below:

$$\text{Ox} \xrightleftharpoons{K_1} \text{Ox}^- + \text{H}^+$$

$$\text{oTd} + \text{H}^+ \xrightleftharpoons{K} \text{oTd}^+$$

In the above mechanism, the oxidant-substrate complex, $\overline{C}$ formed in step 1 breaks down by four different routes. At low formed [oTd]o it is assumed that only the first route is significant. The total Cr (IV) is largely present in the form of three major species [Ox], [Ox-] and [$\overline{C}$] from the mass-balanced equation for [Ox]t, giving

$$= [\text{oTd}]_o [\text{Ox}]_t / \rho + \rho' [\text{H}^+] + [\text{oTd}]_o$$

where,

$$\rho = K_1 / K_o \qquad \text{and } \rho' = (1 + KK_1) / K_o [\text{H}^+]$$

a.   At low [oTd]$_o$:

The oxidation rate may be expressed as:

$$\frac{-d[\text{Ox}]_t}{dt} = k_{11} [\overline{C}]$$

$$= \frac{k_{11}[\text{oTd}]_o [\text{Ox}]_t}{\rho + \rho'[\text{H}^+] + [\text{oTd}]_o}$$

Giving the pseudo first order rate constant, k as:

$$\text{In } R_o/R_t = {}^0kt$$

$$\text{where } {}^0k = \frac{k_{11}[\text{oTd}]_o}{\rho + \rho'[\text{H}^+] + [\text{oTd}]_o}$$

The equation (6) may be arranged as,

$$\left(\frac{{}^0k}{[\text{oTd}]_o}\right)^{-1} = \frac{\rho + [\text{oTd}]0}{k_{11}} + \frac{\rho'[\text{H}^+]}{k_{11}}$$

$$= k_{LI} + k_{LS} [\text{H}^+]$$

Equation (7) has been verified from the plots of L.H.S. i.e. $\left({}^0k/[\text{oTd}]_o\right)^{-1}$ Vs [H$^+$] which are found to be linear From these plots, intercept, k_{LI} and the slope, k_{LS} have been determined at different temperatures and [oTd]$_o$.

In view of the fact that the reaction becomes very slow at low [oTd]$_o$ the reaction has been studied only at two different concentrations of o-Toluidine. Secondly, the plots of intercepts k_{LI} vs [oTd]$_o$ have been used to evaluate the values of k_{11} and ρ and putting the values of k_{11}, the values of ρ' have been obtained at different temperatures and these values have been presented in Table-3.

b.   At moderate and high concentration of o-Toluidine

At [oTd] above 0.06 mol dm^{-3}, the oxidation rate shows a complex dependence on [H$^+$] and [oTd]$_o$. It appears that in the concentration range 0.06 mol dm^{-3} and above all the four routes as proposed in the mechanism come into play. The overall oxidation rate may be expressed as:

$$\frac{-d[Ox]t}{dt} = k_{11}[C] + k_{21}[H^+][\overline{C}] + k_{22}\overline{[c]}[\text{oTd}^+]$$
$$+ k_{23}[\text{oTd}]_0[\text{oTd}][\text{OXH}]$$

The first term represents the minor reaction path by which the colored product is formed at different [H$^+$] and [oTd]$_o$. The second term is hydrogen ion catalyzed and leads to the formation of other product. It appears that the complex, C may form an intermediate with protonated o-Toluidine, [oTd$^+$] or the unprotonated o-Toluidine, [oTd],which breaks down in route 3 to give the uncolored product. [oTd] in the third and fourth term represents that both protonated and unprotonated, o-Toluidine may be involved in similar steps. The fourth term represents the oxidation of o-Toluidine by OXH i.e. H$_3$CrO$_4$$^+$ which may be involved as minor oxidizing species in the reaction. This may be preceded by a complex formation of H$_3$CrO$_4$ with [oTd]$_I$ i.e. protonated or unprotonated species of o-Toluidine. In the above equation we put the value of C on the assumption that overall mass balanced equation for Cr(VI) is not altered although the presence of other complexes as reaction intermediate cannot be ruled out. The overall rate law may be obtained by fitting the values of [C] and [oTd] in terms of [oTd]$_0$:

$$\frac{-d[Ox]t}{dt} = \frac{\left[k_{11}[\text{oTd}]0 + k_{21}[\text{oTd}]0[H^+] + k_{22}\ [H^+]^2[\text{oTd}]_0 + k'_{23}\ [\text{oTd}]_0^2\ [H^+][Ox]_t\right]}{\rho + \rho'[H^+] + [\text{oTd}]_0}$$

Where k'$_{23}$ = k''$_{23}$. K$_3$

From the above equation the observed pseudo first order rate constant ^{0}k may be defined as:

$$^0k = k_c + \left\{\frac{k_{21}[H^+][OTd]_0 + K_{22}[H^+]^2[OTd]_0\ K_{23}[H^+]^2[OTd]_0^2}{D}\right\}$$

Where k_c represents

(7)

$$k_c = \frac{k_{11}[\text{oTd}]_o}{\rho + \rho'[\text{H}^+] + [\text{oTd}]_o} \text{ and}$$

$$D = \square + \square' [H^+] + [oTd]_o$$

The values of k_c at different $[H^+]$, $[oTd]$, and temperatures have been evaluated using the values of $\square$, $\square'$ and k_{11} from table-2. Also D values have been a calculated using values of $\square$ and $\square'$ from table under different conditions.

Equation (8) may be further arranged as,

$$\frac{\square^0 k \square k_c}{\square D}$$

$$\overline{[H^\square][oTd]_o} \quad \square k_I + k_s [H] \qquad (9)$$

where, $k_I = k_{21}$ and $k_s = (k_{22} + k_{23} [oTd]_0)$

Equation (9) has been tested at different temperatures by using a plot of by by using
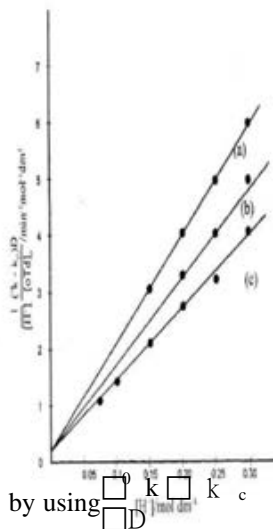
a plot of L.H.S i.e. $\dfrac{(^0k - k_c)D}{[H^+][oTd]_o}$ vs $[H^+]_0$
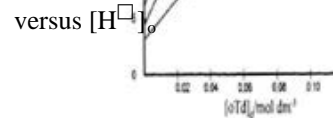
which is found to be linear at different $[oTd]_o$ as shown in Fig. (1) at Temp. 35^0C similar plots are obtained at other temperatures. It may be observed that these plots give same intercepts at different concentrations of o-Toluidine. Intercept of these plots give the value of k_{21}. The slopes of these plots k_s have been tested for their dependence on $[oTd]_0$ and are tabulated in table 1. It is observed that the plot of k_s verses $[oTd]_o$ in Fig. (2) are linear giving a positive intercept from which the values of k_{22} have been obtained whereas slopes of these plot give the values of k_{23}. All kinetic parameters have been evaluated at different temperatures and are presented in Table-2 along with their activation parameters in Table 3

$$\frac{\square^0 k \square k_c}{\square D}$$

$$\overline{[H^\square][oTd]_o}$$

fig-1

versus $[H^\square]_o$

fig-2

Fig.: (i) Plots between $(^0k - k_c)D / [H^+] [oTd]_0$ vs $[H^+]$
Temp. $= 35^0C$, $[oTd]_0$ (a) 0.10 mol dm^{-3}, (b) 0.08 mol dm^{-3}, (C)0.06 mol dm^{-3}

Fig.: (2) Plots between k_s vs $[oTd]_0$
Temp. $= (a)$ 45^0C, (b) 40^0C, (c) 35^0C

Table – 1

Rate Constant	35°C	40°C	45°C
k_{11}	0.13 min	0.14 min	0.16 min
k_{21}	0.30 min^{-1} mol^{-1} dm^3	0.60 min^{-1} mol^{-1} dm^3	2.22 min^{-1} mol^{-1} dm^3
k_{22}	3.50 min^{-1} mol^{-2} dm^6	5.00 min^{-1} mol^{-2} dm^6	6.50 min^{-1} mol^{-2} dm^6
k_{23}	175 min^{-1} mol dm^3	300 min^{-1} mol dm^3	600 min^{-1} mol dm^3
ρ	0.09	0.19	0.46
ρ'	5.2	5.6	6.4

Table – 2: Kinetic data for the oxidation of o-toluidine by Potassiumdichromate in acid medium

Rate constant	Ea/KJ mol^{-1}	$\Delta G^\#$/KJ mol^{-1}	ΔH/KJ mol^{-1}	ΔS/KJ mol^{-1}	Nature of rate constant
k_{11}	11.87	80.62	9.32	-0.231	$\bar{c} \xrightarrow{k_{11}} P_c$
k_{21}	111.06	78.57	108.49	0.097	$\bar{c} \xrightarrow[H^+]{k_{21}} p$
k_{22}	57.15	72.31	54.69	-0.057	$\bar{c}+H^+ \xrightarrow[oTd/oTd]{k_{22}} p$
k_{23}	86.36	62.29	83.80	0.069	$OTd+OxH \xrightarrow[oTd/oTd]{k_{23}} p$

III. CONCLUSION

A complexed rate law consisting of four routes is been assigned. At low $[oTd_o]$, the oxidation rate decreases with increase in $[H^+]$. At moderate and high $[oTd_o]$, oxidation rate is in reversed order and over all oxidation rate is expressed as some

of four terms. The first term represents the minor reaction path by which the colored product is formed at different [H+] and [oTd]o. The second term is hydrogen ion catalyzed and leads to the formation of other product. It appears that the complex,C may form an intermediate with protonated o-Toluidine, [oTd+] or the unprotonated o-Toluidine, [oTd],which breaks down in route 3 to give the uncolored product. [oTd]I in the third and fourth term represent that both protonated and unprotonated, o-Toluidine may be involved in similar steps. The fourth term represents the oxidation of o-Toluidine by OXH i.e. H3CrO4+ which may be involved as minor oxidizing species in the reaction. This may be preceded by a complex formation of H3CrO4 with [oTd]I i.e. protonated or unprotonated species of o-Toluidine.

REFERENCES

[1]   K.H.Pausacker; J.G. Scroggie. *J. Chem. Soc*. **1954**, 4003.

[2]   K.H.Pausacker. *J. Chem. Soc*. 1953, **1989**.

[3]   R.K.Murti; R.K. Panda. *Indian J. Chem*. **1971**, 1247**.**

[4]   Antelo, "*Acta Cient Compostelana*".**1977**, 14(1), 375.

[5]   R.Singh; S.K. Mishra. *Asian J. Chem*. **1998**, 10(4), 749.

[6]   M.G.Ramananda; S.Ananda. *Asian J. Chem*.**1999**, 11(4), 1348.

[7]   R.D.Kaushik; VIPIN Kumar; R.K. Arya. *Asian J. chem***2000**, 12(4) 1123.

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