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Kinetics of Micelle catalyzed Oxidation of m-Toluidine

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ABSTRACT

The Oxidation of m-Toluidine by Cr(VI) has been studied both spectro-photometrically (640 nm) and Iodometrically in aqueous nitric acid medium in presence of micelles (CPC, Cetyl Pyridinium Chloride; Tween-20, Polyoxyethylene Sorbitan Monolaurate) and is said to follow a consecutive reaction mechanism. Kinetic parameter can not be calculated from absorbance data because absorbance after showing maximum showed marginal dip indicating that the decomposition of colored product is slow. Reaction is retarded by both the surfactant. At high concentration of detergents, the Toluidine concentration had no effect on the reaction rate. Mechanism with the associated reaction kinetics is assigned and discussed.

Keywords: Kinetics, Oxidation, Micelle, m-Toluidine, Sodium dichromate.

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INTRODUCTION

Large numbers of researchers have studied the oxidation of p-Toluidine by number of organic and inorganic oxidants [1-10]. Iodine monochloride in the presence and absence of surfactant results in the iodonation of anilines. The reaction has been studied by Sundaram and others [11-12] in aqueous methanol, isopropanal and dimethyl form amide medium. The second order rate constant for o-Toluidine is found to be greater than second order rate constant for p-Toluidine. Panigrah and others [13] have reported micelles effect in the oxidation of malic acid by chromic acid. The oxidation rate is inhibited by SDS.

The kinetics of oxidation of Orange II by Cr (VI) in the absence and presence of surfactant has been studied by Reddy and Sarada [14]. The reaction is first order w.r.t. the concentration of each of the reactants and rate increases by increases [H$^+$]. The non ionic surfactant Brij 35 inhibited the rate of oxidation nearly 10 fold while anionic micelle of SDS has no effect on the rate. The cationic micelles of CTAB strongly inhibited the rate. S. Rajagopal and his Groups [15]

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have investigated Micellar catalysis on the redox reactions of dialkyl sulphides with Cr (VI). The oxidation follows second order kinetics, first order in each reactant. SDS enhances the reaction with increase in hydrophobicity of the sulphate. CTAB inhabits the reaction due to repulsion of H^+ from the micellar surface. A.K. Das and others [16] have studied the oxidation of formaldehyde by Cr (VI) and also investigated that $HCrO_4^-$ is the main active oxidizing species in the absence of the surfactant or the presence of surfactant however. It has been reported that CPC inhibits and SDS catalyzes the reaction. Fauzia and Beg[17] have investigated the kinetics of base hydrolyses of p-nitrophenyl acetate in the presence of non-ionic surfactant (Tween 20, 40, 60 and 80), the rate of hydrolysis decreases however increase in hydrophobic chain length had no significant effect.

Literature survey pertaining to the above titled reaction reveals that no attempt seems to have been made to explore the detailed kinetic study of Toluidine in the presence of surfactant. Thus we have conducted the present study in order to postulate a complete, concise and general mechanism of oxidation of Toluidine in presence of surfactant which has hitherto been unreported.

MATERIALS AND METHODS

Sodium dichromate (Loba Chemia) m-Toluidine (Merck), HNO_3 (Qualigens), Sodium thiosulfate (Loba Chemie), Starch (Loba Chemie), Potassium Iodide (E.Merck), CPC (E.Merck), Tween-20 (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 m-Toluidine ($\sim$ 10 xs).

KINETIC MEASUREMENTS
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.

The effect of both the micelles was seen by taking measuring required amount from their stock solutions (CPC=0.25 mol dm^{-3}, Tween-20=0.045 mol dm^{-3}) and keeping other conditions constant.

Stiochiometry
Stiochiometry of the reaction is approximately two.
$$8\ RNH_2 + 5H_2CrO_4\ \text{--------->}\ RNO_2 + RN = NR + 4\ Cr\ (O)_2 + 8H_2O$$
.

RESULTS AND DISCUSSION

Kinetics of Oxidation of m-Toluidine in the presence of CPC:
The most striking difference in the kinetic behaviour of the oxidation of m-Toluidine in the presence of CPC is the fact that substrate retardation which was exhibited in the absence of surfactant is not observed [18]. However, at higher concentration of the detergent, the Toluidine concentration had no effect on the reaction rate. It is further observed that the reaction rate

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decreases with increase in [CPC] both in the premicellar region as well as in the post miceller region. It has been assumed that the detergent forms a complex (CD) with the oxidant-substrate complex. Although the complex CD represents, an unreactive species but it is important so far as mass balanced equation describing total Cr (VI) present in the reaction medium is concerned. In the presence of CPC the reactive species, however, remains unchanged. Kinetics parameters such as k_1, k_3, K and K_0 remain unchanged [18]. With the above consideration the following mechanism may be proposed.

$$mTd^+ + Ox \underset{\longleftarrow}{\overset{K_0}{\longrightarrow}} C_6 + H^+ \qquad (1)$$

$$C_6 + D^+ \underset{\longleftarrow}{\overset{K_+}{\longrightarrow}} CD + H^+ \qquad (2)$$

$$C_6 \quad k_1 \qquad (3)$$

$$Ox + m\overline{Td} \overset{k_3H^+}{\longrightarrow} \qquad (4)$$

$$mTd + H^+ \underset{K}{\rightleftharpoons} mTd^+$$
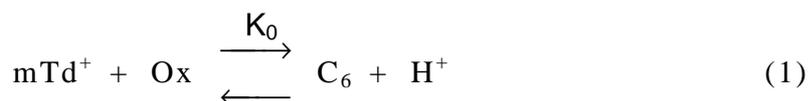
From the given mechanism the following rate, law may be obtained.

$$rr = k_1 [C_6] + k_3 [Ox] [mTd] [H^+]$$

The observed rate constant ^+k_m is given as, $^+k_m =$

$$\frac{(k_1 K_0 K + k_3)[H^+][mTd]_0}{[H^+](1 + K[H^+]) + K K_0 K_+ [D^+][mTd]_0} \qquad (5)$$

Equation (5) has been tested under two different conditions. At low [CPC], the rate is found to be dependent on $[mTd]_o$. Under these conditions reciprocal of above equation (5) gives

$$(^+k_m)^{-1} = \frac{[H^+](1 + K[H^+])}{(k_1 K_0 K + k_3)[H^+]} \frac{1}{[mTd]_0} + \frac{K K_0 K_+ [D^+]}{(k_1 K_0 K + k_3)[H^+]} \qquad (6)$$

Equation (6) is verified since the plot of $(^+k_m)^{-1}$ vs $[mTd]_0^{-1}$ are found to be linear as shown in fig (1) similar plots are obtained other temperatures and [CPC]. Intercept of these plots are given table 1. Furthermore, the intercepts of these plots (k_I) may be written as

$$k_I = \frac{K K_0 K_+ [D^+]}{(k_1 K_0 K + k_3)[H^+]} \qquad (7)$$

Equation (7) describes the dependence of k_I on $[H^+]$ and $[D^+]$. The plots of k_I vs $[D^+]$ are found to be linear passing through origin as shown in fig (2) similar plots are obtained other temperatures and $[H^+]$. The plots of k_I vs $[H^+]^{-1}$ are also found to be linear passing through the origin (vide Fig. 3) similar plots are obtained other temperatures and $[D^+]$. These observations justify the proposed mechanism at low [CPC].

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Equation (5) may be modified in the presence of higher [CPC] by ignoring the first term in the denominator, modifying ^+k_m as

$$^+k_{mH} = \frac{(k_1\, K_0\, K + k_3)[H^+]}{K\, K_0\, K_+\, [D^+]} \qquad\qquad (8)$$

Equation (8) predicts that the observed rate constant at high [CPC] should be independent of $[mTd]_0$, and should increase with increase in $[H^+]$ and decreases with increase in [CPC]. This is verified by the plot between $^+k_{mH}$ vs $[H^+]$ and $^+k_{mH}$ vs $[D^+]^{-1}$. Both these plots are linear passing through the origin as shown is Fig. (4-5) similar plots are obtained other temperatures, $[H^+]$ and $[D^+]$. From the slopes of these plots the values of K_+ i.e. equilibrium associated with the formation of complex CD has been calculated. Both the plots give the similar value of K_+ which is 1200

Table-1: Intercept (^+k_I) of plot between (^+k_m)$^{-1}$ vs [mTd]$_0^{-1}$

Temperature	30^0C^*			35^0C			40^0C		
[CPC] (moldm^{-3}) / [H$^+$] (mol dm^{-3})	9×10^{-4}	7×10^{-4}	5×10^{-4}	9×10^{-4}	7×10^{-4}	5×10^{-4}	9×10^{-4}	7×10^{-4}	5×10^{-4}
0.08	71min	60min	47min	24min	21.4min	15min	17min	14min	10.2min
0.10	60min	40min	33min	21min	17.2min	12min	14min	10.8min	8.2min
0.15	41min	30min	23min	13min	11min	8.8min	9.2min	7.4min	5.5min
0.20	31min	25min	19min	11min	8.6min	7min	8min	6.8min	4.4min
0.25	25min	18min	14min	8min	7min	5.6min	7.2min	6min	4.0min

An attempt has also been made to use the absorbance data to evaluate kinetic parameters associated with concentration leading to the formation of the colored product. However, it is observed that in the presence of the detergent the absorbance after reaching maxima shows only a marginal dip indicating that the decomposition of colored product is slow. This is further supported by the calculation of τ_{max} i.e ($^0k_m.t_{max}$) and κ. The value of τ_{max} is very high and the values of κ very low indicating that the rate constant for the formation of the coloured product is much higher than the rate constant leading to the decomposition of the colored product. Thus no attempt is made to evaluate values of maximum absorbance.

Kinetics of oxidation of m-Toludine in the presence of Tween 20:

Kinetic features of oxidation of m-Toluidine in the presence of Tween 20 are similar to those observed in the presence of CPC, namely

1) The reaction is first order w.r.t. Cr (VI) concentration.
2) There is no substrate retardation.
3) The reaction rate becomes independent of $[mTd]_o$.
4) The reaction rate increase with increase in $[mTd]_0$

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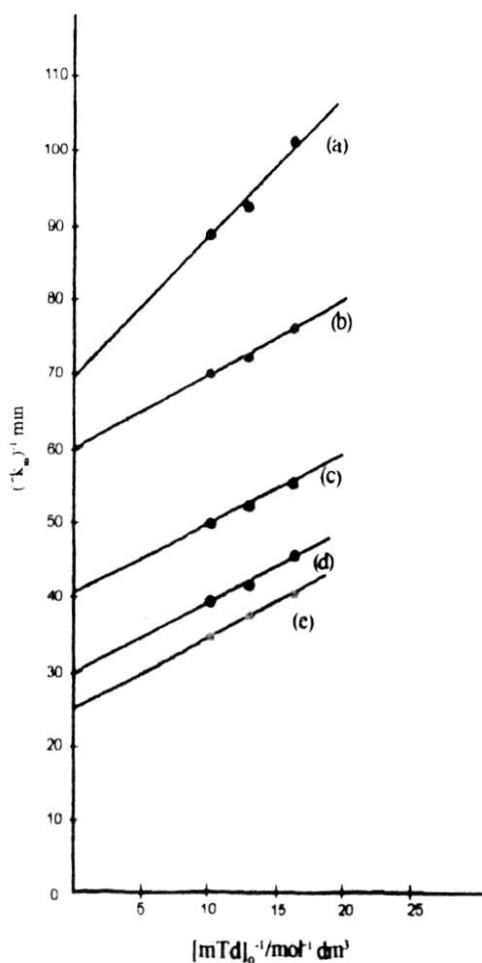
Fig.: (1) Plots between $(^tk_m)^{-1}$ vs $[mTd]_0^{-1}$ in the presence of CPC
Temp. = 30°C, [H⁺] (a) 0.08 mol dm⁻³, (b) 0.10 mol dm⁻³,
(c) 0.15 mol dm⁻³, (d) 0.20 mol dm⁻³, (e) 0.25 mol dm⁻³,
[CPC] = 9.0x10⁻⁴ mol dm⁻³, [Na₂Cr₂O₇] = 2x10⁻⁴ mol dm⁻³
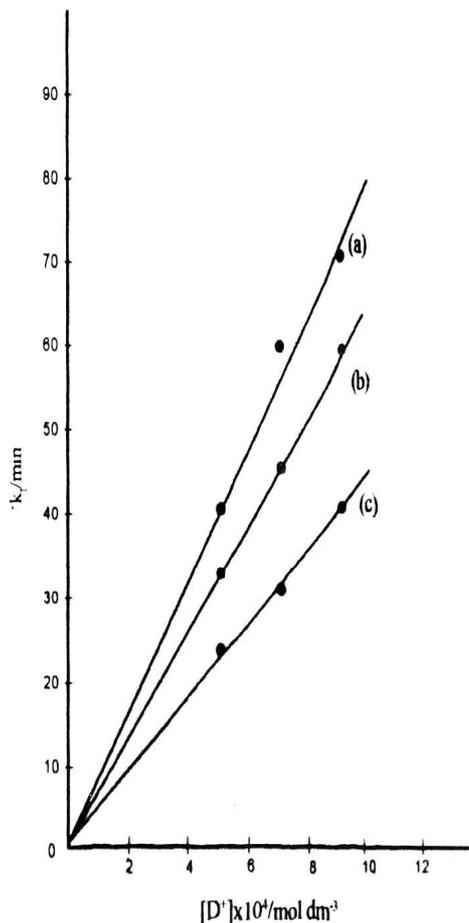
Fig.: (2) Plots between $^tk_1$ vs $[D^+]$,
Temp. = 30°C, [H⁺] (a) 0.08 mol dm⁻³, (b) 0.10 mol dm⁻³,
(b) 0.15 mol dm⁻³
Note : $^tk_1$ is the intercept of the plot between $(^tk_m)^{-1}$ vs $[mTd]_0^{-1}$

Taking the above observation into consideration, the mechanism in the presence of CPC has been applied in this case also with slight modification as given below.

$$mTd^+ + Ox \rightleftharpoons C_6 + H^+ \qquad\qquad (9)$$

$$C_6 + D_n \underset{}{\overset{K_n}{\rightleftharpoons}} CD_n + H^+ \qquad\qquad (10)$$

$$[C_6] \xrightarrow{k_1} \ldots\ldots\ldots \qquad\qquad (11)$$

$$[Ox] + [mTd] \xrightarrow{k_3H^+} \ldots\ldots\ldots \qquad\qquad (12)$$

$$mTd + H^+ \rightleftharpoons mTd^+$$

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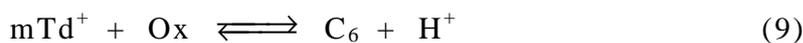
Appling the similar procedure as has been done in the presence of CPC; the rate law in the presence of Tween-20 is expressed as:

$$rr = k_1[C_6] + k_3 [Ox] [mTd] [H^+]$$
$$= {}^n k_m [Ox]_t$$

Giving,

$${}^n k_m = \frac{(k_1 K_o K + k_3)[H^+][mTd]_o}{[H^+](1 + K[H^+]) + K K_0 K_n[Dn][mTd]_o}$$

At low [Tween-20], the rate is $[mTd]_0$ dependent under these conditions reciprocal of the above equation gives

$$\left({}^n k_m\right)^{-1} = \frac{[H^+](1 + K[H^+])}{(k_1 K_0 K + k_3)[H^+]} \bullet \frac{1}{[mTd]_0} + \frac{K K_0 K_n[Dn]}{(k_1 K_0 K + k_3)[H^+]} \qquad (13)$$

Equation 13 is verified since the plots of $({}^n k_m)^{-1}$ vs. $[mTd]_0^{-1}$ are found to be linear vide figure (6) similar plots are obtained other temperatures, [Dn] and $[H^+]$. Intercepts of these plots are given in table 5. Furthermore, the intercepts of these plots (k_I) may be written as

$$k_I = \frac{K K_0 K_n[Dn]}{(k_1 K_0 K + k_3)[H^+]} \qquad (14)$$

The plots of k_I vs. [Dn] and k_I vs $[H^+]^{-1}$ are found to be linear passing through origin vide figure (7-8) similar plots are obtained other temperatures, [Dn] and $[H^+]$.
At high concentration of Tween-20,

$${}^n k_{mH} = \frac{(k_1 K_o K + k_3)[H^+]}{K K_o K_n[Dn]_o} \qquad (15)$$

Equation 15 is verified by plots between ${}^n k_{mH}$ vs. $[Dn]^{-1}$ and ${}^n k_{mH}$ vs. $[H^+]$. Both these plots are linear passing through the origin vide figure (9-10) similar plots are obtained other temperatures, [Dn] and $[H^+]$.

However, from the slopes of plots between ${}^n k_{mH}$ versus $[Dn]^{-1}$ and ${}^n k_{mH}$ versus $[H^+]$ values of K_n have been evaluated at different temperatures which is 12000.

It has been observed that the absorbance of the colored product passes through a maximum but the decomposition of the colored product is very slow as has been observed in the presence of CPC. In view of this fact the kinetic parameters associated with the consecutive reactions have not be evaluated.

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Table-2: Intercept (^nk_I) of plot between (^nk_m)$^{-1}$ vs [mTd]$_0$$^{-1}$

Temperature	30^0C*			35^0C			40^0C		
[Tween-20] (mol dm^{-3}) / [H$^+$] (mol dm^{-3})	0.000100	0.000045	0.000085	0.000100	0.000045	0.000085	0.000100	0.000045	0.000085
0.08	85min	77min	39min	24min	17.6min	9.2min	30min	24.6min	12.8min
0.10	67min	57min	31min	18min	13min	7min	25.2min	20min	11min
0.15	48min	39min	21min	11min	9min	5min	16.4min	14min	5min
0.20	36min	33min	16min	8min	7min	4.4min	12min	11min	7min
0.25	28min	28min	12min	7min	6min	3.6min	10min	8min	5min

CONCLUSION

The reaction is studied in presence of micelles (CPC, Cetyl Pyridinium Chloride; Tween-20, Polyoxyethylene Sorbitan Monolaurate) and is said to follow a consecutive reaction mechanism. Kinetic parameter can not be calculated from absorbance data because absorbance after showing maximum showed marginal dip indicating that the decomposition of colored product is slow. Reaction is retarded by both the surfactant. At high concentration of detergents, the Toluidine concentration had no effect on the reaction rate.

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