

Kinetics of oxidation of *m*-Toluidine by Potassium Dichromate in Absence and Presence of CTAB

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Abstract: The Oxidation of *m*-toluidine by Potassium dichromate has been studied both spectrophotometrically (640nm) and iodometrically in aqueous nitric acid medium in absence and presence of micelle (CTAB). The reaction is said to follow consecutive reaction mechanism. The reaction shows substrate inhibition at low H^+ concentration. Oxidation proceeds by two routes and both routes give the colored product. Kinetic parameters are calculated in absence of surfactant but could not be calculated in presence of surfactant because absorbance after showing maxima showed marginal dip indicating decomposition of colored product. Reaction is retarded in presence of micelle. Suitable mechanism is proposed. The rate constants, equilibrium constants and kinetic parameters are calculated.

Keywords: Kinetics, Oxidation, Catalyst, *m*-toluidine, Micelle

1. 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 primary (1) aromatic amine by lead acetate has been studied by Pausacker [1]. The medium of the reaction is acetic acid with 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. This study shows naphthyl amines result in the formation of quinones. Pausacker [2] has studied the oxidation of 1° aromatic amines by phenyliodosoacetate in benzene. It is reported that *o*-toluidine gives purple color intermediate which transforms to deep carmine color solution while *m*-toluidine gives pink color throughout the course of the reaction. The product identified is azo compound by chromatography method using alumina as stationary phase and benzene as eluent. The oxidation of aniline and substituted aniline by hexacyanoferrate (III) is studied by R.K. Murti and others [3-4]. 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]. The reactivity shows the following order *p*-toluidine > *o*-toluidine > *m*-toluidine > aniline > *p*-chloroaniline > *p*-iodoaniline > bromoaniline. Antelo [5] 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 (1) in 50% aqueous solution of HOAc increases with the value of *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 *et.al.* [6] Studied kinetics of *o*, *m* and *p*-toluidines by chromic acid in acetate acid-water medium. The reactions were found to be first order *w.r.t.* [oxidant], [Substrate] and [H⁺]. The rate of reaction is increased with addition of Cu

²⁺ or Ag⁺ while decreased with addition of Mn. Moreover an addition of neutral salts like NaCl, KCl, Na₂SO₄ and K₂SO₄ in the reaction mixture showed negligible effect. Product identified is substituted azo-benzene. Ramananda and co-workers [7] have studied kinetics of oxidation of *o*-toluidine by sodium-N-chlorobenzene sulfonamide in aqueous H₂SO₄ medium at 303° K. Rate showed first order dependence on [CAB], fractional order dependence on [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. The oxidation product was identified as dimethyl azobenzene. Kaushik [8] has studied periodate oxidation of *o*-toluidine in acetone water medium and showed that first order with respect to both oxidant and substrate. The rate of reaction rises on increasing ionic strength while decrease with decrease in dielectric constant. There is no effect of free radical scavenger on the rate of reaction, indicating main product as methyl 1, 4 benzoquinone. Vijay Laxmi and her group [9] have reported the kinetic of oxidation of aniline and substituted aniline by bromate ion in acidic medium. The resultant ion complex decomposes unimolecularly in the rate determining step and final product is azo compound formed by dimerization of nitrile formed earlier. Moreover mechanism suggests that electron withdrawing group favor the reaction. Iodine monochloride in the presence and absence of surfactant results in the iodination of anilines. The reaction has been studied by Sundaram and others [11-12] in aqueous methanol, isopropanol and dimethyl formamide 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] This paper reports kinetic of

oxidation of m-Toluidine by Potassium Dichromate by both spectrophotometrically and iodometrically in the presence of acidic medium and also indicates that oxidation proceeds by two routes and both routes give the colored product 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 HCrO₄⁻ 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.

2. Materials and Methods

Potassium dichromate (Loba Chemia), m-toluidine (Merck), HNO₃ (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.

Kinetic measurements

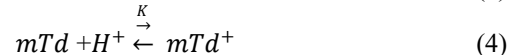
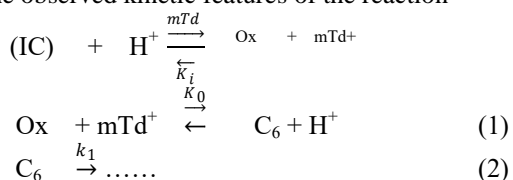
Pseudo first order conditions were maintained in all runs with excess m-toluidine (≈ 10 xs). Kinetic runs were reproducible within ±5% of required value. Requisite amount of substrate was taken in one flask and oxidant with acid in another flask. They were thermally equilibrated for 20 mins and then thoroughly mixed by shaking. The reaction was studied up to 90% of completion.

Stoichiometry

Stoichiometry of the reaction is approximately two.
 $8RNH_2 + 5H_2CrO_4 \rightarrow 2RNO_2 + 6RN = NR + 4Cr(O)_2 + 8H_2O$

3. Results and Discussion

One of the major features of the oxidation of m-toluidine by acid dichromate as oxidizing agent is the fact that the reaction shows substrate inhibition at low [H⁺]. Secondly, it is observed that the oxidation of m-toluidine proceeds by two different routes but both the routes give the colored product as the end product. The formation of single product is also monitored by TLC tests using ethyl acetate to extract reaction product from the reaction mixtures. The TLC was run using solution of ethyl acetate with hexane as mobile phase (in the ratio of 4:1). The following mechanism justifies all the observed kinetic features of the reaction



IC represents inactive complex between m-toluidine and Cr (VI). Rate law may be obtained as: $rr = k_1 [C_6] + k_3 [mTd] [Ox][H^+]$

This gives observed rate constant, 0k_m as

$$^0k_m = \frac{k_1 K K_0 [mTd]_0 (1+K[H^+])}{\{(1+K[H^+])^2 + K_0 K [mTd]_0 (1+K[H^+]) + K_i K [mTd]_0^2\}} + \frac{k_3 [H^+] [mTd]_0 (1+K[H^+])}{\{(1+K[H^+])^2 + K_0 K [mTd]_0 (1+K[H^+]) + K_i K [mTd]_0^2\}}$$

It is assumed that at high [H⁺], the third term in denominator may be neglected in comparison to first two terms. This defines the observed rate constant $0k_m$ at high [H⁺] as

$$= \frac{\{k_1 K K_0 + k_3 [H^+]\} [mTd]_0}{(1+K[H^+]) + K_0 K [mTd]_0}$$

Taking reciprocal of the above equation

$$(^0k_{mH})^{-1} = \frac{(1+K[H^+])}{k_1 K K_0 + k_3 [H^+]} \cdot \frac{1}{[mTd]_0} + \frac{K K_0}{k_1 K K_0 + k_3 [H^+]} \quad (5)$$

The above equation has been tested by the plot of $(^0k_{mH})^{-1}$ vs $[mTd]_0^{-1}$ which is found to be linear at different [H⁺] and temperatures. Furthermore, the intercepts and slopes of these plots have been examined from the point of view of their dependence on [H⁺]. Taking reciprocal of intercept of equation [5], we get

$$(k_{iH})^{-1} = k_1 + \frac{k_3}{K K_0} [H^+] \quad (6)$$

Equation (6) is verified from the plots of $(k_{iH})^{-1}$ vs [H⁺] which are found to be linear. The intercepts of these plots give the value of k_1 at different temperatures and also the values of $k_3/K K_0$ have been obtained from the slopes, and are presented in table (1)

In the same manner the slopes of equation (5) may be rearranged as

$$^+k_{sHD} = \frac{1}{K K_0} + \frac{1}{K_0} [H^+] \quad (7)$$

$$D' = k_1 + \frac{k_3}{K_0 K} [H^+]$$

D' has been calculated at different [H⁺] using k_1 and $k_3/K K_0$ at different temperatures from table (1).

Table 1: The values of k_1 , k_3 , K and K_0 at different temperatures

Rate Constant	30°C	35°C	40°C
k_1	0.015 min ⁻¹	0.020 min ⁻¹	0.025 min ⁻¹
k_3	3.00 min ⁻¹ mol ⁻² dm ⁶	5.30 min ⁻¹ mol ⁻² dm ⁶	5.90 min ⁻¹ mol ⁻² dm ⁶
K	6.00 mol ⁻¹ dm ³	8.00 mol ⁻¹ dm ³	6.00 mol ⁻¹ dm ³
K_0	4.2	1.66	1.66

Equation (7) has been verified from the plots of $(k_{sHD})^{-1}$ vs [H⁺] which are found to be linear giving positive intercepts at different temperatures. The reciprocal of slope of these plots give the values of K_0 i.e. equilibrium constant

associated with the complex formed by the interaction of oxidant and *m*-toluidine.

The ratio of slope / intercept gives the value of K at different temperatures. The values of k_1 , k_3 , K and K_0 have been presented in table 1 and activation parameters related to k_1 and k_3 , have also been presented in table 2.

Table 2: Kinetic data for the oxidation of *m*-toluidine by potassium dichromate in acid medium

Rate constant	Ea/KJ mol ⁻¹	ΔG [#] /KJ mol ⁻¹	ΔH/KJ mol ⁻¹	ΔS/KJ mol ⁻¹	Nature of rate constant
k_1	44.62	84.83	42.1	-0.141	C6 →.....
k_3	88.27	71.51	85.75	0.047	k_3, H^+ <i>m</i> Td +Ox →.....

Thermodynamic parameters were determined in absence of surfactant in HNO₃ medium at 303 K.

At low [H⁺], the observed rate constant $^0k_{mL}$ is given as

$$^0k_{mL} = \frac{\{k_1 K K_0 + K_3 [H^+]\} [mTd]_0 (1 + K [H^+])}{(1 + K [H^+])^2 + K_0 K [mTd]_0 (1 + K [H^+]) + K_1 k [mTd]_0^2}$$

The first term in the denominator may be equated as (1+2K[H⁺]) assuming [H⁺]² to be negligible, this gives

$$^0k_{mL} = \frac{\{k_1 K K_0 + K_3 [H^+]\} [mTd]_0 (1 + K [H^+])}{(1 + 2K [H^+]) + K_0 K [mTd]_0 (1 + K [H^+]) + K_1 k [mTd]_0^2} \quad (8)$$

Rearranging equation (8) taking reciprocal and again rearranging we get,

$$\left\{ \left(\frac{^0k_{mL}}{[mTd]_0} \right)^{-1} - F_H \right\} \frac{1}{[mTd]_0} = \frac{K_0 K (1 + K [H^+])}{\{k_1 K K_0 + K_3 [H^+]\}} + \frac{K_1 k [mTd]_0}{\{k_1 K K_0 + K_3 [H^+]\} (1 + K [H^+])} \quad (9)$$

Where $F_H = \frac{1 + 2K [H^+]}{\{k_1 K K_0 + K_3 [H^+]\} (1 + K [H^+])}$ (10)

Since the values of k_1 , k_3 , K and K_0 are known at different temperatures, the values of function F_H has been obtained at different [H⁺] and temperatures using equation (10). Equation (9) has been tested by making a plot of L.H.S. of the equation vs [mTd]₀ which is found to be linear (Fig.1)

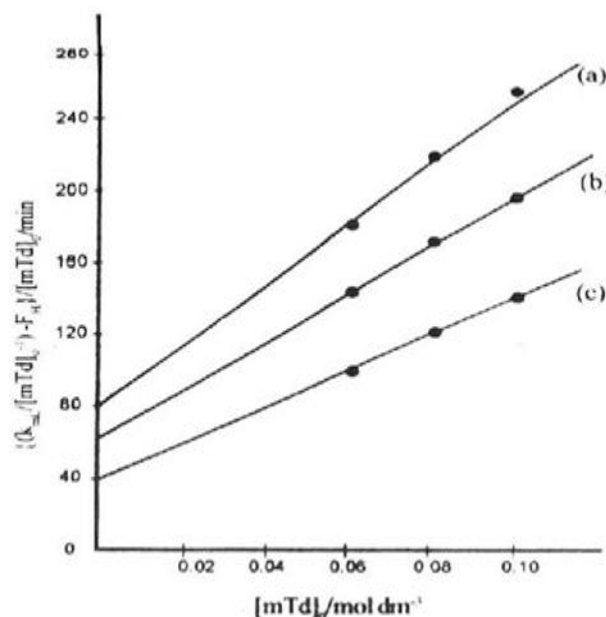
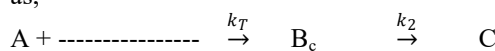


Figure 1: Plot of $\left\{ \left(\frac{^0k_{mL}}{[mTd]_0} \right)^{-1} - F_H \right\} \frac{1}{[mTd]_0}$ vs $[mTd]_0$ at 30°C

Since the reaction has been studied in pseudo first order condition, the formation of colored product may be written as,



Where 'A' represents the oxidant. If total Cr (VI) is reduced by steps leading to the formation of the colored product then the observed pseudo first order rate constant 0k_m should represent rate constant for the formation of colored product and may be used to get the values of τ_{max} , B_x , κ from the established equation of consecutive reaction.

Table 3: Comparison of calculated absorbance with maximum observed absorbance ($[K_2Cr_2O_7] = 2 \times 10^{-4}$ mol dm⁻³ [Surfactant]= Nil

Temp	[H ⁺] (mol dm ⁻³)	[mTd] ₀ [H ⁺] (mol dm ⁻³)	Km (min ⁻¹)	Tmax (min)	τ_{max}	$B_c \times 10^{-4}$ (mol dm ⁻³)	κ_2	k_2 (min ⁻¹)	Abs Cal (nm)	Abs Obs (nm)
1	2	3	4	5	6	7	8	9	10	11
400C	0.25	0.06	0.035	40	1.40	0.49	0.51	0.0178	0.88	0.80
		0.08	0.047	27	1.20	0.43	0.70	0.0316	0.77	0.75
		0.10	0.055	20	1.10	0.40	0.83	0.0458	0.72	0.80
	0.20	0.06	0.028	48	1.34	0.48	0.55	0.0154	0.80	0.80
		0.08	0.034	35	1.19	0.43	0.71	0.0240	0.80	0.75
		0.10	0.042	25	1.05	0.38	0.92	0.0386	0.70	0.75
	0.15	0.06	0.023	57	1.31	0.47	0.57	0.0132	0.85	0.80

		0.08	0.030	45	1.35	0.48	0.54	0.0163	0.86	0.85
		0.10	0.033	45	1.48	0.52	0.44	0.0146	0.93	0.90
350C	0.25	0.06	0.027	45	1.20	0.43	0.70	0.0189	0.77	0.75
		0.08	0.033	30	0.99	0.36	1.03	0.0340	0.65	0.70
		0.10	0.038	25	0.95	0.35	1.10	0.0420	0.63	0.65
	0.20	0.06	0.024	55	1.32	0.47	0.57	0.0137	0.85	0.85
		0.08	0.028	40	1.12	0.40	0.82	0.0230	0.72	0.75
		0.10	0.033	30	0.99	0.36	1.03	0.0340	0.65	0.70
	0.15	0.06	0.0217	62	1.34	0.48	0.55	0.0120	0.86	0.85
		0.08	0.0260	50	1.30	0.46	0.59	0.0155	0.83	0.85
		0.10	0.0280	48	1.34	0.48	0.55	0.0153	0.86	0.90
300C	0.25	0.06	0.018	60	1.08	0.39	0.87	0.0156	0.70	0.80
		0.08	0.022	45	0.99	0.36	1.03	0.0226	0.55	0.75
		0.10	0.025	38	0.95	0.35	1.10	0.0270	0.63	0.70
	0.20	0.06	0.0125	70	0.87	0.32	1.31	0.0164	0.58	0.70
		0.08	0.0147	55	0.81	0.30	1.48	0.0218	0.54	0.65
		0.10	0.0160	45	0.72	0.28	1.77	0.0282	0.50	0.65
	0.15	0.06	0.0120	80	0.96	0.35	1.09	0.0130	0.63	0.70
		0.08	0.0100	72	0.72	0.27	1.82	0.0182	0.48	0.54
		0.10	0.0150	70	1.05	0.39	0.89	0.0134	0.70	0.80

In the case of m-toluidine it is found that the observed rate constant k_{obs} gives a reasonably good value of Bx (maximum value of concentration of colored product). Its variation with $[H^+]$ shows the same trend as observed by maximum absorbance at 640 nm. With molar absorption coefficient as $1.8 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ the values of maximum absorbance have been calculated. These values along with the observed ones have been presented in tables 3 in column 10 and 11 respectively. Whereas, the calculated

absorbance matches satisfactorily with observed ones at 35°C and 40°C at different $[H^+]$ but at 30°C the calculated values are found to be rather low in comparison to corresponding observed values. Plots of Absorbance (observed) vs Time are given in Fig. B (1) similar plots are obtained at other temperatures and $[H^+]$.

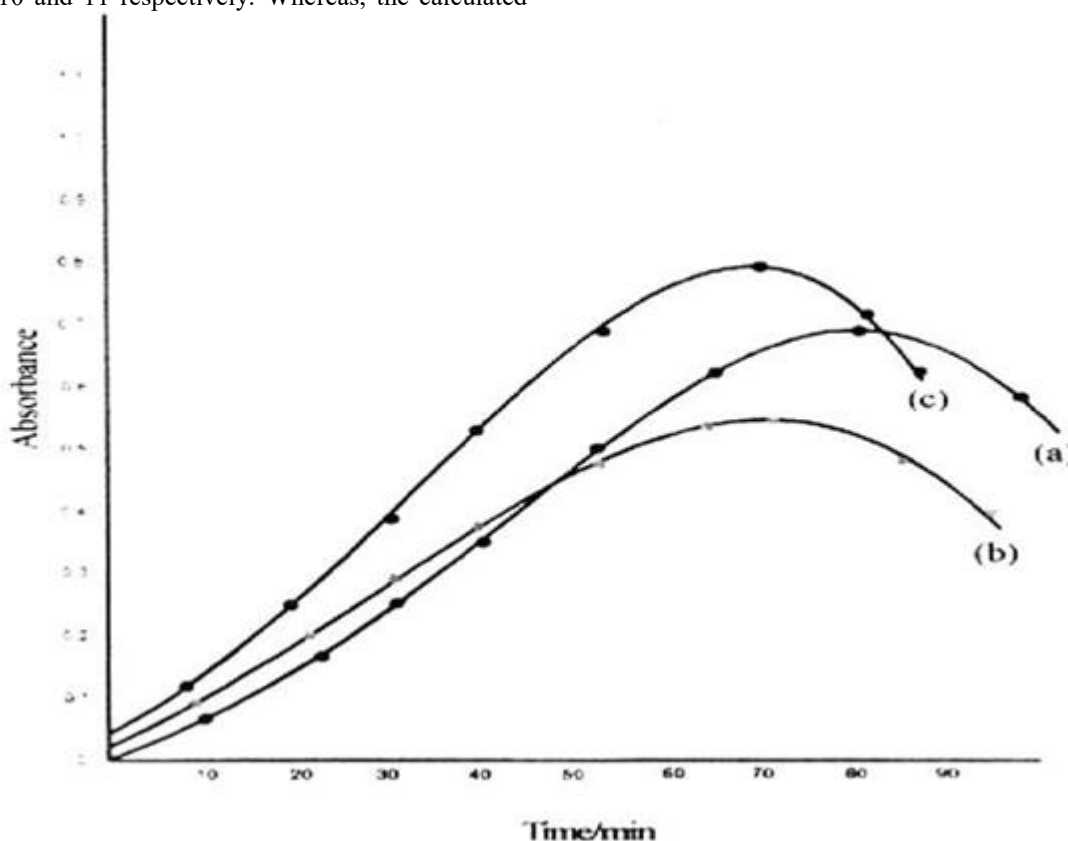


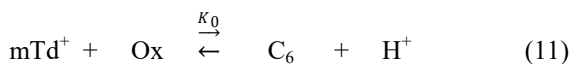
Figure B (1) Plots of Absorbance vs Time at 30°C

Kinetics of Oxidation of m-Toluidine in the presence of CTAB:

The most striking difference in the kinetic behavior of the oxidation of m-Toluidine in the presence of CTAB is the

fact that substrate retardation which was exhibited in the absence of surfactant is not observed. 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 decreases with increase in [CTAB] both in the premicellar region as well as in the post micellar 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 CTAB the reactive species, however, remains unchanged. Kinetics parameters such as k_1 , k_3 , K and K_0 remain unchanged. With the above consideration the following mechanism may be proposed.



From the given mechanism rate law is obtained as
 $rr = k_1 [C_6] + k_3 [Ox] [mTd] [H^+]$

The observed rate constant ^+k_m is given as,

$$^+k_m = \frac{(k_1 K_0 K + k_3) [H^+] [mTd]_0}{[H^+] (1 + K [H^+]) + K K_0 K_+ [D^+] [mTd]_0} \quad (16)$$

Equation (16) has been tested under two different conditions. At low [CTAB], the rate is found to be dependent on [mTd]₀. Under these conditions reciprocal of above equation (16) gives

$$(^+k_m)^{-1} = \frac{[H^+] (1 + K [H^+])}{(k_1 K_0 K + k_3) [H^+]} \frac{1}{[mTd]_0} + \frac{K K_0 K_+ [D^+]}{(k_1 K_0 K + k_3) [H^+]} \quad (17)$$

Equation (17) is verified since the plot of $(+km)^{-1}$ vs $[mTd]_0^{-1}$ are found to be linear. Intercept of these plots are given table 1. Furthermore, the intercepts of these plots (k_1) may be written as

$$k_1 = \frac{K K_0 K_+ [D^+]}{(k_1 K_0 K + k_3) [H^+]} \quad (18)$$

Equation (18) describes the dependence of k_1 on $[H^+]$ and $[D^+]$. The plots of k_1 vs $[D^+]$ are found to be linear passing through origin. The plots of k_1 vs $[H^+]^{-1}$ are also found to be linear passing through the origin. These observations justify the proposed mechanism at low [CTAB].

Table 1: Intercept ($^+k_1$) of plot between $(^+km)^{-1}$ vs $[mTd]_0$.

Temperature [H ⁺]	30 °C			35 °C			40 °C		
	CTAB 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	10.6min	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
.025	25min	18min	14min	8min	7min	5.6min	7.2min	6min	4.0min

Concentration of H^+ and CTAB are taken in mol dm⁻³

Equation (16) may be modified in the presence of higher [CTAB] by ignoring the first term in the denominator, modifying ^+k_m as

$$^+k_{mH} = \frac{(k_1 K_0 K + k_3) [H^+]}{K K_0 K_+ [D^+]} \quad (19)$$

Equation (19) predicts that the observed rate constant at high [CTAB] should be independent of [mTd]₀, and should increase with increase in $[H^+]$ and decreases with increase in [CTAB]. 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. (2-3) 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

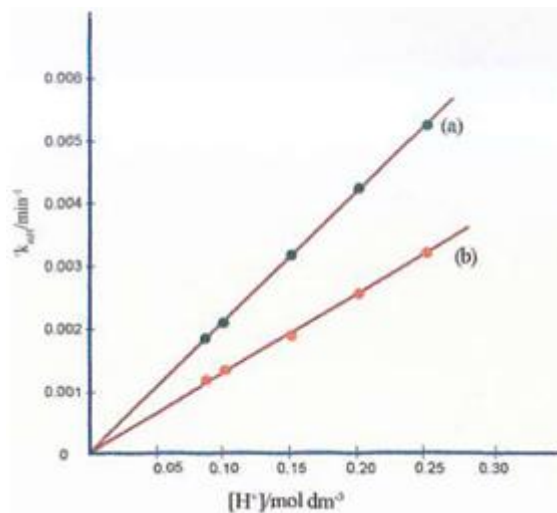


Figure 2: Plot of $^+k_{mH}$ vs $[H^+]$ at 30°C

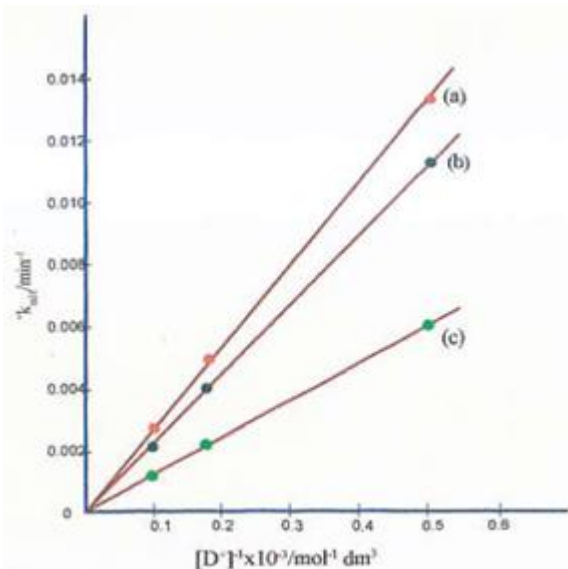


Figure 3: Plot of k_{obs} vs $[D^+]^{-1}$ at 30°C

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. $(0/k_{\text{m}} \cdot \tau_{\text{max}})$ and k_{d} . The value of τ_{max} is very high and the values of k_{d} very low indicating that the rate constant for the formation of the colored 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.

4. Conclusion

The oxidation of m-toluidine by potassium dichromate has been studied both spectrophotometrically (640nm) and iodometrically in aqueous nitric acid medium. The reaction is said to follow consecutive reaction mechanism. Oxidation proceeds by two routes and the both the routes give colored products. The reaction shows inhibition at low $[\text{H}^+]$ in absence of surfactant but this inhibition does not occur in presence of CTAB. Kinetic parameter were calculated in absence of surfactant but in presence kinetic parameter could not be calculated because absorbance after showing maximum showed margin dip indicating that the decomposition of colored product is slow. Reaction is retarded in presence CTAB. At high concentration of detergents, the toluidine concentration had no effect on the reaction rate.

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