



Kinetics of oxidation of *m*-Toluidine by Sodium Dichromate

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ABSTRACT

The Oxidation of *m*-toluidine by sodium dichromate has been studied both spectrophotometrically (640nm) and iodometrically in aqueous nitric acid medium. 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. Suitable mechanism is proposed. The rate constants, equilibrium constants and kinetic parameters are calculated.

Key word: Kinetics, Oxidation, Catalyst, *m*-toluidine, Sodium Dichromate.

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 colour 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^{2+} . Moreover an addition of neutral salts like NaCl, KCl, Na_2SO_4 and K_2SO_4 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 H_2SO_4 medium at $303^\circ K$. Rate showed first order dependence on [CAB], fractional order dependence on [*o*Td] 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. This paper reports kinetic of oxidation of *m*-Toluidine by Sodium 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.

MATERIALS AND METHODS

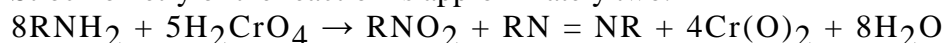
Sodium dichromate (Loba Chemia), *m*-toluidine (Merck), HNO_3 (Qualigens), sodium thiosulfate (Loba Chemie), starch (Loba Chemie), potassium iodide (E. Merck) were used without purification. Solutions of all reagents were prepared in doubly distilled water. The oxidant concentration of $0.0002 \text{ mol dm}^{-3}$ was maintained throughout the kinetic runs.

Kinetic measurements

Pseudo first order conditions were maintained in all runs with excess *m*-toluidine ($\approx 10x$). 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.

Stoichiometry

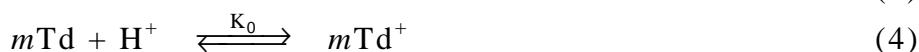
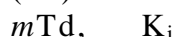
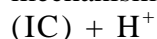
Stoichiometry of the reaction is approximately two.



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 a

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:

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

This gives observed rate constant 0k_m as

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

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 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 a plot of $({}^0k_{mH})^{-1}$ vs $[mTd]_0^{-1}$ which is found to be linear at different $[H^+]$ and temperatures as shown in fig (1) similar plots are obtained at other 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 as shown in fig (2) similar plots are obtained at other temperatures. The intercepts of these plots give the value of k_1 at different temperatures and also the values of k_3/KK_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

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

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

D' has been calculated at different $[H^+]$ using k_1 and k_3/KK_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	4.20	1.66	1.66

Equation (7) has been verified from the plots of $(k_{sH} D')$ vs $[H^+]$ which are found to be linear giving positive intercepts at different temperatures as shown in fig (3) similar plots are obtained at other 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 sodium dichromate 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_1	44.62	84.83	42.10	-0.141	$C_6 \xrightarrow{k_1} \dots\dots\dots$
k_3	88.27	71.51	85.75	0.047	$mTd^+ + O_x \xrightarrow{k_3, H^+} \dots\dots\dots$

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

At low $[H^+]$, the observed rate constant 0k_m is given as

$$k_{mL} = \frac{\{k_1 K K_0 + k_3 [H^+]\} [mTd]_0 (1 + K[H^+])}{(1 + K[H^+])^2 + K_0 K [mTd]_0 (1 + K[H^+]) + K_1 K [mTd]_0^2}$$

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

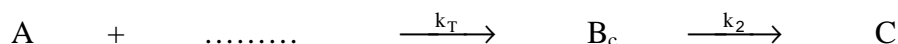
$$^0k_{mL} = \frac{\{k_1 K K_0 + k_3 [H^+]\} [mTd]_0 (1 + K[H^+])}{(1 + 2K[H^+]) + K_0 K [mTd]_0 (1 + K[H^+]) + K_1 K [mTd]_0^2} \quad (8)$$

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

$$\left\{ \left(\frac{^0k_{mL}}{[mTd]_0} \right)^{-1} - F_H \right\} \frac{1}{[mTd]_0} = \frac{K_0 K (1 + K[H^+])}{\{k_1 K K_0 + k_3 [H^+]\}} + \frac{K_1 K [mTd]_0}{\{k_1 K K_0 + k_3 [H^+]\} (1 + K[H^+])} \quad (9)$$

$$\text{where } F_H = \frac{1 + 2K[H^+]}{\{k_1K K_0 + k_3[H^+]\}(1 + K[H^+])} \quad (10)$$

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 at different temperatures as shown in fig (4) similar plots are obtained at other temperatures. 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 ($[Na_2Cr_2O_7] = 2 \times 10^{-4}$ mol dm^{-3} [Surfactant] = Nil)

Temp	$[H^+]$ (mol dm^{-3})	$[mTd]_0 [H^+]$ (mol dm^{-3})	0k_m (min^{-1})	t_{max} (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
40°C	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
35°C	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
30°C	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

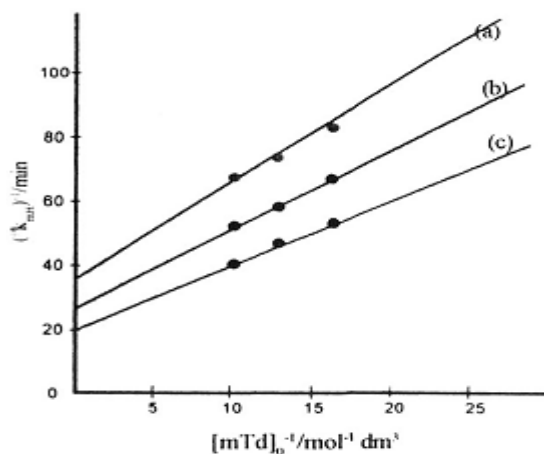


Fig.: (1) Plots between $(k_{\text{obs}})^{-1}$ vs $[\text{mTd}]_0^{-1}$ in the absence of any surfactant
Temp. = 30°C, $[\text{H}^+]$ (a) 0.15 mol dm⁻³, (b) 0.20 mol dm⁻³, (c) 0.25 mol dm⁻³, $[\text{Na}_2\text{Cr}_2\text{O}_7] = 2 \times 10^{-4}$ mol dm⁻³

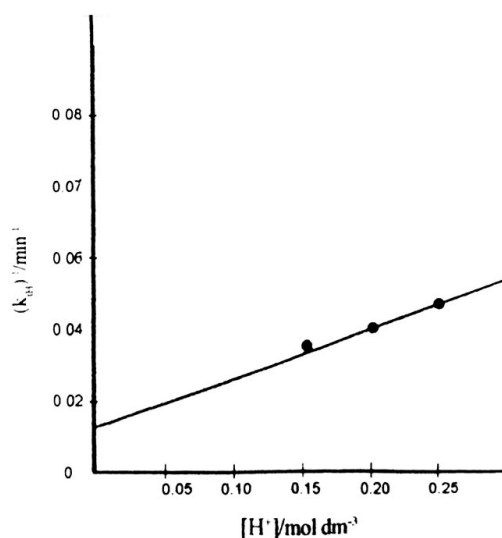


Fig.: (2) Plot between $(k_{\text{obs}})^{-1}$ vs $[\text{H}^+]$, in the absence of any surfactant
Temp. = 30°C

Note : (k_{int}) is of intercept of plot between $(k_{\text{obs}})^{-1}$ vs $(\text{mTd})_0^{-1}$

In the case of m-toluidine it is found that the observed rate constant 0k_m gives a reasonably good value of B_c (maximum value of concentration of colored product). Its variation with $[\text{H}^+]$ 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 $[\text{H}^+]$ 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 $[\text{H}^+]$.

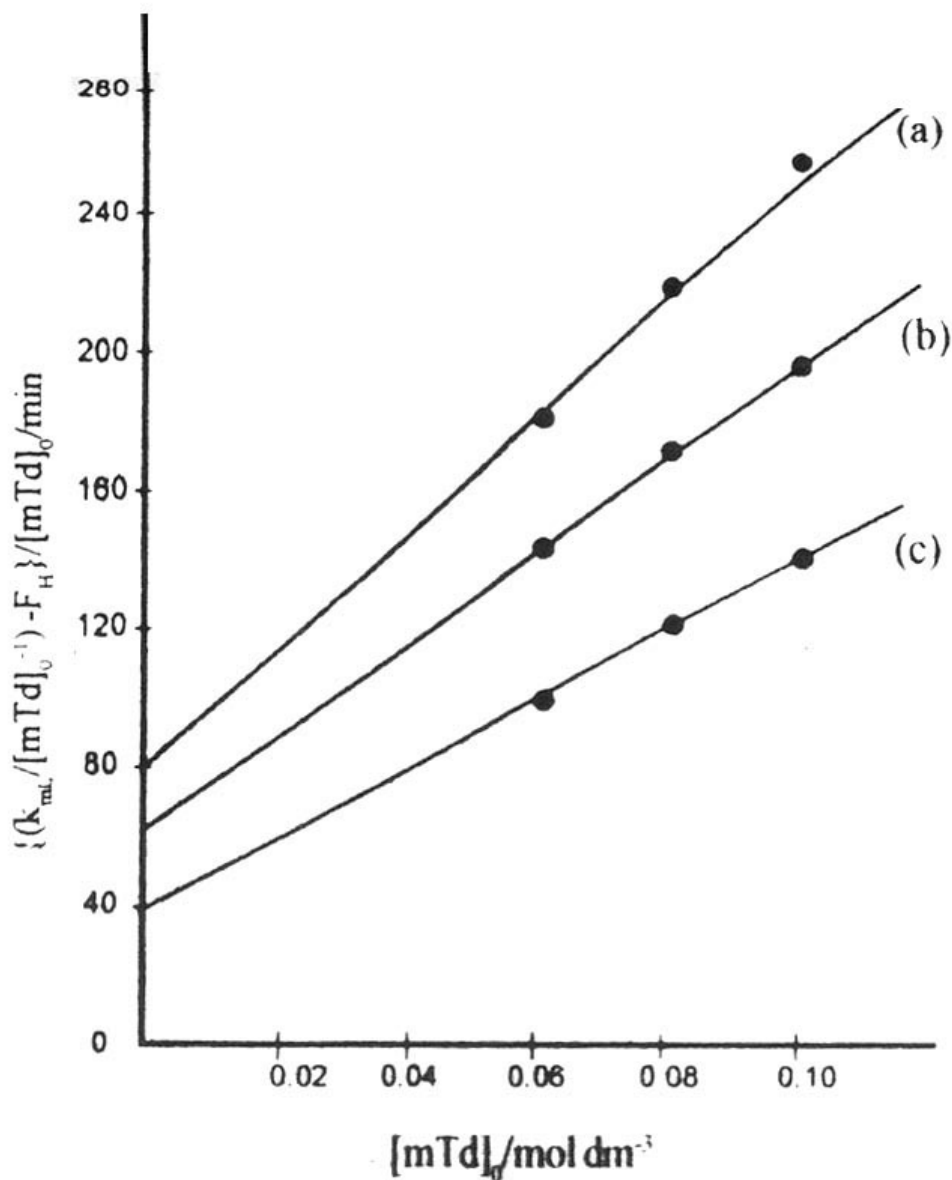


Fig.: (4) Plots between $\{(k_{m_{d_0}}/[mTd]_0^{-1}) - F_{H^+}\}/[mTd]_0$ vs $[mTd]_0$ in the absence of any surfactant
 Temp. = 30°C, $[H^+]$ (a) 0.05 mol dm⁻³, (b) 0.06 mol dm⁻³,
 (c) 0.08 mol dm⁻³, $[Na_2Cr_2O_7] = 2 \times 10^{-4}$ mol dm⁻³

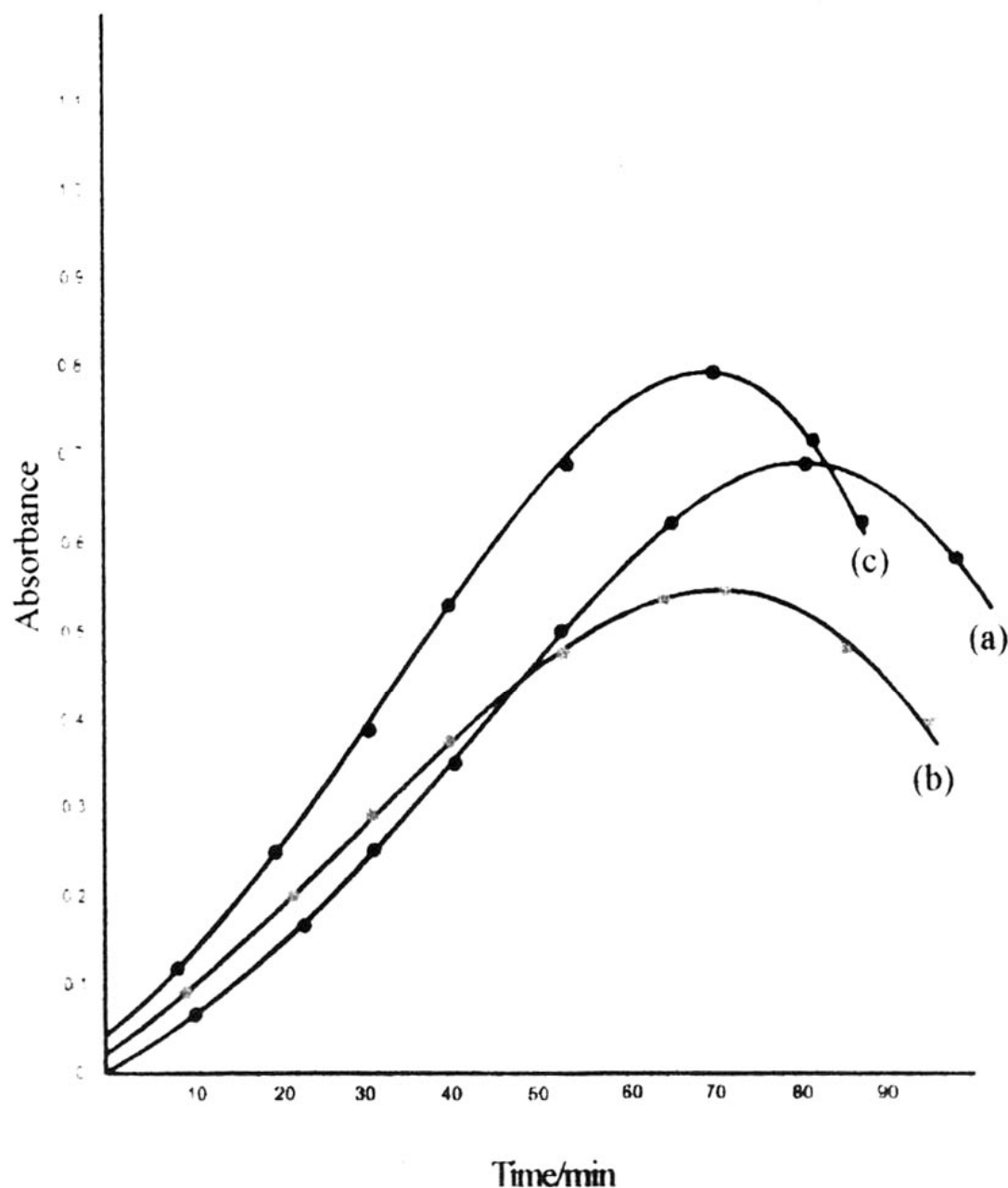


Fig.: B (1) Plots between Absorbance vs Time in the absence of any surfactant
Temp. = 30°C, [H⁺] = 0.15 mol dm⁻³, [mTd]₀ (a) 0.06 mol dm⁻³,
(b) 0.08 mol dm⁻³, (c) 0.10 mol dm⁻³, [Na₂Cr₂O₇] = 2x10⁻⁴ mol dm⁻³

CONCLUSION

The Oxidation of *m*-toluidine by sodium dichromate has been studied both spectrophotometrically (640nm) and iodometrically in aqueous nitric acid medium. 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

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