Research Article

Kinetics of oxidation of o-toluidine by sodium dichromate

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ABSTRACT

The Oxidation kinetics of o-Toluidine by Cr (VI) has been studied both spectrophotometrically (at 640 nm) and Iodometrically in aqueous nitric acid medium. The reaction is said to follow a consecutive reaction mechanism. Mechanism with the associated reaction kinetics is assigned and discussed. The values of different kinetic parameters have been evaluated.

Key word: Kinetics, Oxidation, Catalyst.
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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 salution m-Toluidine gives pink colored throughout the course of the reaction. The product identified is azo compound by chromatiography 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. hexacynoferrate 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.

EXPERIMENTAL SECTION

o-Toluidine (Merck), Sodium dichromate (Loba Chemia), HNO_3 (Qualigens), Sodium thiosulfate (Loba Chemie), Starch (Loba Chemie), Pottassium 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 ($\sim$10x). Kinetic runs were reproducible within $\pm5\%$ of required value. Requisite amount of substrate was taken in one flask and oxidant with acid in another flask. They were thremally equilibrated for 20 mins. and then throughly mixed by skaking. The reaction was studied upto 90% of completion.

### Kinetics and Mechanism of Oxidation of o-Toluidine

In case of o-Toluidine it was observed that the minor route involves formation of colored product which is less stable and decomposes steadily. It may be observed that the absorbance at 640 nm at which the reaction was followed, passes through a maxima indicating that formation of colored product follows a consecutive reaction mechanism. Preliminary investigations indicated that the formation of colored product does not correspond to the reduction of total Cr (VI). If observed rate constant determined by titration readings ^ok is used to represent the rate constant for the formation of colored product than B_{max} which is a measure of maximum absorbance shows different pattern (i.e. time of appearance of the maxima and variation in maximum absorbance) from the observed one. It is therefore, indicated that Cr (VI) is being reduced by two different routes and only part of it is involved in the formation of colored product.

Furthermore, 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:

$$oTd + Ox \; \underset{\longleftarrow}{\overset{K_o}{\longrightarrow}} \; \overline{C} + H^+ \tag{1}$$

$$\overline{C} \xrightarrow{\;K_{11}\;} P_c \tag{2}$$

$$\overline{C} \xrightarrow{\;k_{21}\;} P \tag{3}$$

$$\overline{C} + H^+ \xrightarrow[\quad oTd^+/oTd \quad]{\overset{H^+}{k_{22}}} \tag{4}$$

$$oTd + OxH \xrightarrow[\quad oTd^+/oTd \quad]{\;k_{23}\;} P' \tag{5}$$
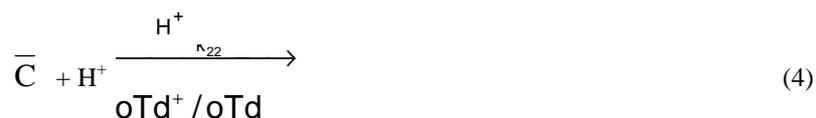
Equilibrium for oxidant and o-Toluidine are as given below:

$$Ox \; \underset{\longleftarrow}{\overset{K_1}{\longrightarrow}} \; Ox^- + H^+$$

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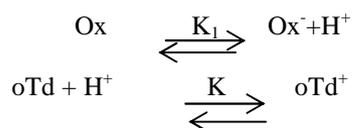
In the above mechanism, the oxidant-substrate complex, $\overline{C}$ formed in step 1 breaks down by four different routes. At low $[oTd]_o$ it is assumed that only the first route is significant. The total Cr (IV) is largely present in the form of three major species $[Ox]$, $[Ox^-]$ and $\left[\overline{C}\right]$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

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

where,

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

a.   At low $[oTd]_o$:

The oxidation rate may be expressed as:

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

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

Giving the pseudo first order rate constant, k as:

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

$$\text{where } {}^0k = \frac{k_{11}[oTd]_o}{\rho + \rho'[H^+] + [oTd]_o} \qquad\qquad (6)$$

The equation (6) may be arranged as,

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

$$= k_{LI} + k_{LS} [H^+] \qquad\qquad (7)$$

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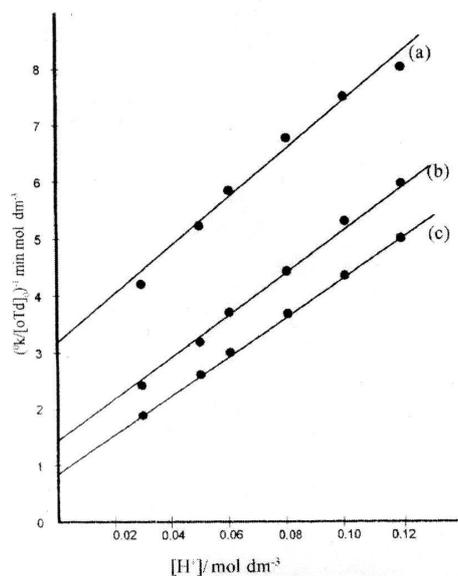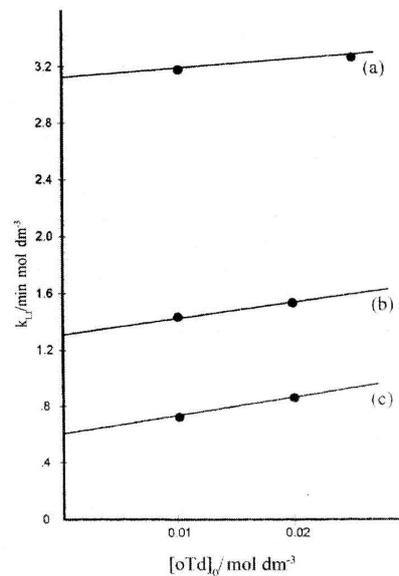

**Fig.: (1) Plots between $({}^0k/[oTd]_0^{-1}$vs$[H^+]$ Temp. (a) 45^{0}C, (b) 40^{0}C, (c) 35^{0}C, $[oTd]_0$ = 0.01 mol dm^{-3}**
Fig. (2) Plots between k_{LI} vs $[oTd]_0$ Temp. (a) 45^{0}C, (b) 40^{0}C, (c) 35^{0}C,

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 $[oTd]_o$ in Fig. (2) 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:

$$\frac{-d[Ox]_t}{dt} = k_{11}[\bar{C}] + k_{21}[H^+][\bar{C}] + k_{22}[\bar{C}][oTd^+] + k_{23}[oTd]_o[oTd]_I[O\ddot{.}H]$$

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, $\bar{C}$ 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 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. $H_3CrO_4^+$ which may be involved as minor oxidizing species in the reaction. This may be preceded by a complex formation of H_3CrO_4 with $[oTd]_I$ i.e. protonated or unprotonated species of o-Toluidine. In the above equation we put the value of $\bar{C}$ 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 $[oTd]_0$:

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

Where $k'_{23} = k''_{23}.K_3$

From the above equation the observed pseudo first order rate constant ^ok may be defined as:

$$^0k = k_c + \left\{ \frac{k_{21}[H^+][oTd]_o + k_{22}[H^+]^2[oTd]_o k_{23}[H^+]^2[oTd]_o^2}{D} \right\} \tag{8}$$

where, k_c represents,

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

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

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

Equation (8) may be further arranged as,

$$\frac{(^0k - k_c)D}{[H^+][oTd]_o} = k_I + k_s [H^+] \tag{9}$$

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 L.H.S i.e. $\frac{(^0k - k_c)D}{[H^+][oTd]_o}$ versus $[H^+]_o$

which is found to be linear at different $[oTd]_o$ as shown in Fig. (3) 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 $[oTd]_0$ in Fig. (4) 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.
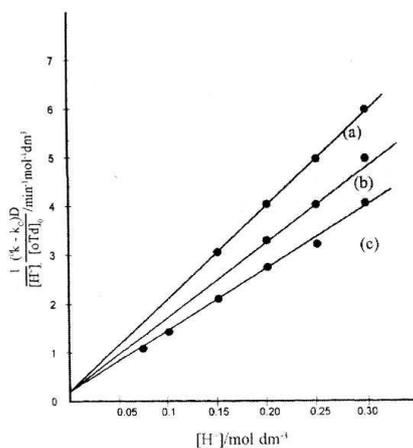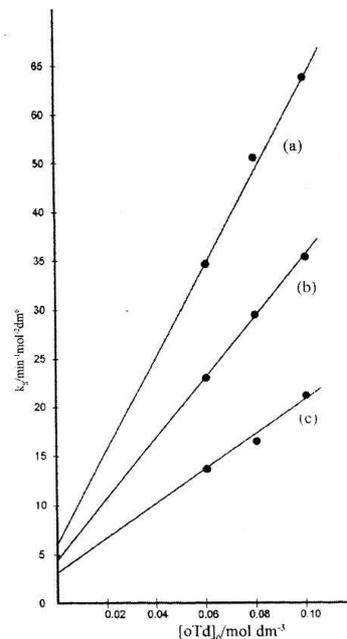

Fig.: (3) Plots between $(^0k - k_c)D / [H^+] [oTd]_0$ vs $[H^+]$
Temp. = 35^0C, $[oTd]_0$ (a) 0.10 mol dm^{-3},   (b) 0.08 mol dm^{-3}, (C)0.06 mol dm^{-3}

Fig.: (4) Plots between k_s vs $[oTd]_0$
Temp. = (a) 45^0C,   (b) 40^0C,   (c) 35^0C

Table – 1

Rate Constant	35ºC	40ºC	45ºC
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 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_{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	$OTd + OxH \xrightarrow[oTd^-/oTd]{k_{23}} p$

Thermodynamic parameters were determined in absence of surfactant in HNO$_3$ medium at 308 K.

The kinetics of oxidation of o-Toluidine has been followed by absorbance measurement at 640 nm with time. As has been mentioned earlier the absorbance shows appearance of a maxima at different time under different experimental conditions indicating, thereby, that the colored product is formed in a consecutive reaction. In order to investigate kinetic features of this process quantitatively the observed rate constant ($^\circ k_c$ or $^\circ k_H$), may be used as rate constant of the process leading to the formation of colored product. On the basis of this assumption it is observed that the values of B_X, representing by maximum concentration of the intermediate does not match with the calculated values and also the dependence of B_X on other factors does not follow the pattern obtained by such calculations. The overall consecutive reaction in pseudo first order condition may be described as follows:

a) $\quad A+ \ldots\ldots\ldots \xrightarrow{\;k_c f\;} B_c \xrightarrow{\;k_d\;} C$

b) $\quad A+ \ldots\ldots\ldots \xrightarrow{\;k_3\;} D$
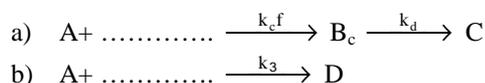
In the above scheme A represents the oxidant and B_c is the colored intermediate. It is also shown that the oxidation is being reduced by two different steps and only one of which leads to the formation of the colored intermediate.

The rate expression from the above scheme may be obtained as:

$$-\frac{d[A]}{dt} = (k_1 + k_3)[A] = {}^0k[A]$$

$$[A] = [A]_0\, e^{-{}^0 kt} = [A]_0\, e^{-b}$$

$$\frac{d[B}{dt} = k_1[A] - k_2[B]$$

where $k_c f = k_1$

solving the above differential equation we obtain

$$[B] = \frac{\kappa_1 [A]_0}{\kappa_2 - 1}\left[e^{-b} - e^{-\kappa_2 b}\right] \tag{10}$$

where $\kappa_2 = k_2/{}^0k$, $\kappa_1 = k_c/{}^0k$ and $b = {}^0kt$

In order to get the maximum value of B and τ_{max} the above may be differentiated with respect to time and set equal to zero, to give

$$\tau_{max} = \frac{1}{(\kappa_2 - 1)}\ln \kappa_2 \tag{11}$$

and the value of B_1

$$B_1 = \frac{\kappa_1}{\kappa_2 - 1}\left[e^{-\tau_{max}} - e^{-\kappa_2 \tau_{max}}\right] \tag{12}$$

For $[A_o] = 1$ and $\kappa_1 = 1$, B_x may be written as

$$Bx = \frac{1}{\kappa_2 - 1}\left[e^{-\tau_{max}} - e^{-\kappa_2 \tau_{max}}\right] \tag{13}$$

If equation (11) for τ_{max} is compared with the simple consecutive reaction there is no change. However the value of B_1 is found to be different due to the presence of κ_1 (i.e. $k_1/{k_1+k_3}$ or $k_1/{}^0k$) in the numerator which takes into account that only a fraction of oxidant is involved in this route. In order to get the value of B_x, the values of $^\circ k$ (the observed rate constant) and time of appearance of maxima (t_{max}) have been used to calculate τ_{max}.

Using equation (12) for simple consecutive reaction a theoretical plot between τ_{max} and B_X was obtained. And similarly a plot between τ_{max} and κ_2 was also done. These plots were used to read the values of κ_2 and B_X at a particular value of τ_{max} ($= t_{max}.{}^\circ k$) and are presented in Tables3-5. From the values of B_x, the values of B_c is obtained

by multiplying by a factor $k_c/_ok$ where k_c represents the values of the rate constant associated with the process leading to formation of the colored product. In the present case, the first term appearing in equation (8) is used k_c:

$$k_c = \frac{k_{11}[oTd]_0}{\rho + \rho'[H^+][oTd]_0}$$

under different conditions of $[H^+]$, $[oTd]_0$ and temperatures. It has been noted that if the rate constants involved in second, third and fourth terms of equation (8) are used for calculating B_c individually or in combination of one another they give unsatisfactory values of B_c. The unsatisfactory values signify that the variation in B_c with $[H^+]$ or temperature is in one direction (say increases) then the observed values are in opposite direction (i.e. decreases). Therefore the value of k_{21}, k_{22} and k_{23} have not been used as a measure of formation of colored product. After obtaining the values of B_c an attempt has been made to relate the values of B_c with observed maximum absorbance (A_{max}). It was expected that multiplying B_c by a fixed number signifying molar absorption coefficient should give the value of maximum absorbance. This was not found to be applicable in this case. It is empirically found that the value of B_1 and maximum absorbance fit into the following equation;

$$A_{max} = B_c \times 1.16 \times 10^6 \times [oTd]_0 \qquad\qquad (14)$$
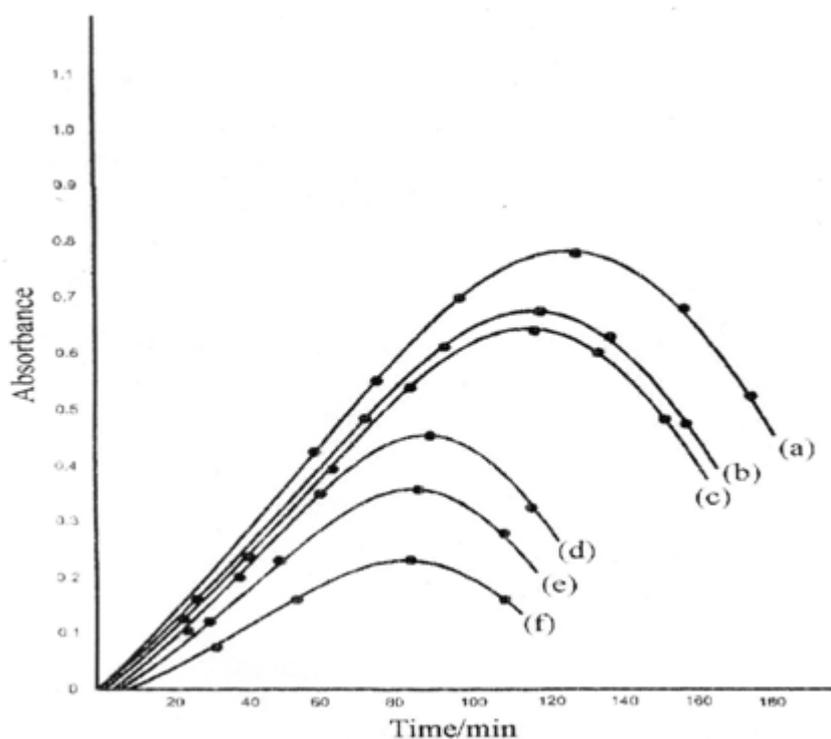
Fig.: A(1)

It is not possible to give a complete description of the relationship between B_c and absorbance. This may however, be due to complex formation between B_c and Toluidine. The values of A_{max} calculated by using equation (14) is presented in column (11) in Tables3-5, which compare well with the observed values shown in column (12). Plots of Absorbance (observed) vs Time are given in Fig. : A (1-2) at temperature 35^0C. Similar plots are obtained at other $[oTd]_0$, $[H^+]$ and temperature.

Table 3: Comparison of calculated absorbance with maximum observed absorbance

$[oTd]_0$ mol dm^{-3}	$[H^+]$ (mol dm^{-3})	^ok (min^{-1})	t_{max} (min)	τ_{max}	Bx (mol dm^{-3})	k_c (min^{-1})	$B_c x10^{-4}$ (mol dm^{-3})	κ_2	k_2 (min^{-1})	Abs Calculated (nm)	Abs. Observed (nm)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
0.02	0.03	0.0100	130	1.30	0.460	0.0100	0.4600	0.59	0.0059	0.92	0.78
	0.05	0.0064	120	0.77	0.290	0.0064	0.2900	1.60	0.010	0.67	0.67
	0.06	0.0061	119	0.72	0.270	0.0061	0.2700	1.82	0.011	0.63	0.65
	0.08	0.0052	90	0.47	0.150	0.0052	0.1500	4.03	0.021	0.35	0.47
	0.10	0.0041	85	0.35	0.104	0.0041	0.1040	6.40	0.026	0.24	0.35
	0.12	0.0035	85	0.29	0.0806	0.0035	0.0806	8.68	0.030	0.18	0.24
0.08	0.20	0.0280	32	0.90	0.34	0.0085	0.1030	1.20	0.034	0.96	0.99
	0.25	0.0320	29	0.90	0.35	0.0074	0.0810	1.20	0.038	0.75	0.81
	0.30	0.0400	37	1.08	0.39	0.0062	0.0600	0.80	0.032	0.56	0.63
0.06	0.08	0.0125	60	0.75	0.27	0.0130	0.280	1.70	0.021	1.95	1.40
	0.10	0.0135	50	0.67	0.24	0.0116	0.206	2.10	0.028	1.44	1.28
	0.15	0.0168	45	0.75	0.27	0.0082	0.130	1.70	0.028	0.90	0.99
	0.20	0.0180	45	0.81	0.29	0.0069	0.110	1.50	0.027	0.76	0.81
	0.25	0.0200	40	0.80	0.29	0.0056	0.081	1.50	0.030	0.56	0.63
	0.30	0.0250	30	0.75	0.27	0.0047	0.052	1.70	0.042	0.36	0.45
0.10	0.15	0.0350	30	1.05	0.38	0.0136	0.147	0.90	0.032	1.70	1.39
	0.20	0.040	25	1.00	0.37	0.0107	0.099	0.90	0.360	1.14	1.16
	0.25	0.0500	20	1.00	0.37	0.0093	0.072	0.90	0.450	0.83	0.87
	0.30	0.0580	18	1.04	0.44	0.0077	0.058	0.90	0.052	0.67	0.70

$$Temp = 35^oC, \ [Na_2Cr_2O_7] = 2x10^{-4} \ mol \ dm^{-3}, \qquad l$$

Table 4: comparison of calculated absorbance with maximum observed absorbance

$[oTd]_0$ (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	^ok (min^{-1})	t_{max} (min)	τ_{max}	Bx (mol dm^{-3})	k_c (min^{-1})	$B_c x10^{-4}$ (mol dm^{-3})	κ_2	k_2 (min^{-1})	Abs Calculated (nm)	Abs. Observed (nm)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
0.02	0.03	0.0079	139	1.09	0.40	0.0079	0.40	0.84	0.0066	0.93	0.80
	0.05	0.0061	140	0.85	0.31	0.0061	0.31	1.37	0.0084	0.72	0.73
	0.06	0.0054	139	0.75	0.28	0.0054	0.28	1.69	0.0091	0.65	0.68
	0.08	0.0044	100	0.44	0.14	0.0044	0.14	4.46	0.0190	0.32	0.43
	0.10	0.0038	90	0.34	0.10	0.0038	0.10	6.77	0.0260	0.23	0.28
	0.12	0.0032	90	0.29	0.08	0.0032	0.08	2.71	0.0280	0.18	0.21
0.06	0.10	0.0184	40	0.73	0.26	0.0110	0.150	1.80	0.033	1.04	0.87
	0.15	0.0210	35	0.73	0.26	0.0082	0.100	1.80	0.038	0.70	0.76
	0.20	0.0250	30	0.75	0.27	0.0064	0.082	1.70	0.043	0.57	0.54
	0.25	0.0320	30	0.96	0.35	0.0053	0.074	1.10	0.035	0.31	0.39
	0.30	0.0370	30	1.11	0.41	0.0045	0.050	0.80	0.030	0.35	0.34
0.08	0.15	0.028	30	0.84	0.30	0.0106	0.110	1.40	0.039	1.02	0.87
	0.20	0.034	22	0.75	0.27	0.0084	0.067	1.70	0.058	0.61	0.74
	0.25	0.043	18	0.77	0.27	0.0087	0.055	1.70	0.073	0.51	0.56
	0.30	0.053	18	0.95	0.35	0.0059	0.039	1.10	0.058	0.36	0.47
0.10	0.15	0.0460	24	1.10	0.40	0.0129	0.110	0.80	0.037	1.28	1.10
	0.20	0.0570	20	1.14	0.41	0.0100	0.072	0.80	0.045	0.83	0.81
	0.25	0.6400	18	1.15	0.41	0.0084	0.054	0.80	0.051	0.63	0.67
	0.30	0.6800	16	1.08	0.44	0.0073	0.047	0.90	0.075	0.54	0.54

$$Temp = 40^oC, \qquad [Na_2Cr_2O_7] = 2x10^{-4} \ mol \ dm^{-3},$$

TABLE 5: Comparison of calculated absorbance with maximum observed absorbance

$[oTd]_0$ mol dm^{-3}	$[H^+]$ (mol dm^{-3})	^ok (min^{-1})	t_{max} (min)	τ_{max}	Bx (mol dm^{-3})	k_c (min^{-1})	$B_c x10^{-4}$ (mol dm^{-3})	κ_2	k_2 (min^{-1})	Abs Calculated (nm)	Abs. Observed (nm)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
0.02	0.03	0.0044	160	0.70	0.2700	0.0044	0.2700	1.87	0.0082	0.62	0.51
	0.05	0.0035	140	0.50	0.1600	0.0035	0.1600	3.66	0.1280	0.37	0.44
	0.06	0.0031	140	0.43	0.1300	0.0031	0.1300	4.74	0.0147	0.30	0.39
	0.08	0.0028	120	0.34	0.1000	0.0028	0.1000	6.77	0.0189	0.23	0.30
	0.10	0.0025	120	0.30	0.0806	0.0025	0.0806	6.39	0.0210	0.18	0.25
	0.12	0.0021	110	0.23	0.0600	0.0021	0.0600	12.20	0.0250	0.14	0.19
0.06	0.08	0.0175	55	0.96	0.35	0.0092	0.018	1.10	0.019	1.25	1.04
	0.10	0.0200	40	0.80	0.29	0.0082	0.120	1.50	0.030	0.83	0.81
	0.15	0.0270	32	0.86	0.31	0.0064	0.073	1.40	0.038	0.51	0.58
	0.20	0.0370	28	1.03	0.44	0.0053	0.063	0.90	0.033	0.43	0.46
	0.25	0.0410	25	1.02	0.44	0.0045	0.048	0.90	0.037	0.32	0.35

	0.30	0.0480	25	1.20	0.48	0.0039	0.039	0.55	0.026	0.27	0.29
0.08	0.10	0.032	35	1.12	0.40	0.0100	0.125	0.80	0.260	1.16	1.10
	0.15	0.045	20	0.90	0.33	0.0084	0.076	1.20	0.054	0.71	0.79
	0.20	0.065	16	1.17	0.46	0.0069	0.049	0.70	0.045	0.46	0.56
	0.25	0.078	16	1.24	0.48	0.0059	0.036	0.60	0.047	0.32	0.44
	0.30	0.092	18	1.65	0.58	0.0051	0.032	0.35	0.320	0.30	0.35
0.10	0.15	0.0640	18	1.15	0.44	0.0100	0.069	0.70	0.045	0.80	0.87
	0.20	0.0850	16	1.36	0.52	0.0085	0.052	0.50	0.043	0.60	0.70
	0.25	0.1050	14	1.45	0.32	0.0073	0.036	0.50	0.052	0.42	0.46
	0.30	0.1200	13	1.56	0.56	0.0063	0.029	0.40	0.048	0.35	0.42

$Temp = 45^oC,$ $[Na_2Cr_2O_7] = 2x10^{-4} mol\ dm^{-3},$

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