

Kinetics of oxidation of p-Toluidine by Sodium Dichromate

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ABSTRACT -The Oxidation of p-Toluidine by sodium dichromate has been studied both iodimetrically and spectrometrically (530nm) in aqueous acidic medium. The Comparison of rate constants obtained by titration method, k_t , with the rate constant obtained by absorbance method, k_A , indicated that the pseudo first order rate constant, k_A was always greater. The reaction shows a complex kinetic behavior with respect to concentrations of p-Toluidine and hydrogen ion. It is suggested that a complex, C_6 is formed between the oxidant and p-Toluidine, which breaks into two different intermediate by intramolecular electron transition leading to two different reaction paths one of which gives the closed product (P_c) and the other path gives the second product (P). The rate constants and activation parameters are calculated.

Index Terms— kinetics, oxidation, toluidine, pseudo, first order, sodium, dichromate, acidic medium

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 (1^0) aromatic amine by lead acetate has been studied by Pausacker [1]. 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 quinines. Pausacker [2] has studied the oxidation of 1^0 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 oxidation of aniline and substituted aniline by hexacyanoferrate (III) is studied by R.K. Murti and others [3-4]. The rate constants with respect to 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. Angelo [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

(I) in 50% aqueous solution of HOAc increases with the value of n. Kinetics of I(n=3) and the order of reaction indicated that the rate determining step involved the decomposition of $R'CH_2CH_2O-Cr(O)_2OH$ 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 with respect to [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. 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 303^0 K. Rate showed first order dependence on $[H^+]$. The variation of ionic strength, change in dielectric constant of medium, addition of reaction product and halide ions had no effect on reaction rate. Kaushik [8] has studied periodate oxidation of o-toluidine in acetone water medium and showed first order kinetics 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. Vijay Laxmi and her group [9] have reported the kinetic of oxidation of aniline and substituted aniline by bromated ion in acidic medium. The resultant ion complex decomposes unimolecularly in the rate determining step.

Moreover mechanism suggests that electron withdrawing group favor the reaction.

2 Materials and Methods

Kinetic experiments were performed under pseudo first order conditions employing 10 fold excess of Toluidine over sodium dichromate. Kinetic runs were reproducible within +/- 5%. Kinetic runs were carried out under varying conditions of concentrations of amines, H⁺ ions and different temperatures.

3 Results and Discussion

Kinetics and Mechanism of p-Toluidine by Sodium dichromate in acidic medium exhibits following kinetic features:

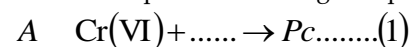
The reaction is found to be first order with respect to [Cr₂O₇]²⁻ under all experimental conditions. The reaction has been investigated by two methods:

- Titrating a definite volume of the reaction mixture against standardized sodium thio-sulfate at different time intervals. The pseudo first order rate constant, k_T has been obtained from the slope of plot of $4 + \log R_t$ vs time (R_t Represents titration reading at time).
- Reaction has also been followed spectrophotometrically at 530 nm and pseudo first order rate constant, k_A has been obtained under different conditions from the plot of in

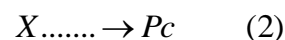
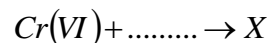
$$\frac{A_{\infty} - A_0}{A_{\infty} - A_t} \text{ vs time (where A represents}$$

absorbance at time shown by the subscript). The comparison of rate constants obtained by titration method, k_T , with the rate constants obtained by the absorbance method, k_A , indicated that the pseudo first order rate constant, k_A was always greater.

It shows that the formation of colored product (Pc) and the consumption of the oxidant do not take place in one single step.



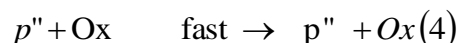
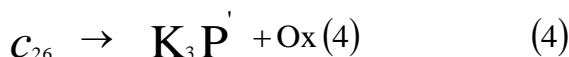
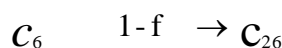
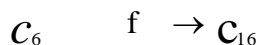
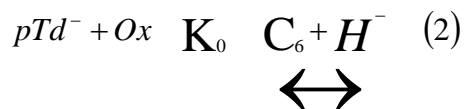
In such a case k_T should be equal to k_A under all conditions of experiments. Furthermore, it may also be argued that the formation of colored product (Pc) is not dependent on some intermediate species formed by the reduction of Cr (VI) preceding the formation of Pc because in such a case k_A should be less than k_T ,



In view of the fact, that k_A is always greater than k_T , the possibility of reaction paths given above (1' and 2') are ruled out i.e. the reduction of Cr (VI) does not precede or occur concurrently with the formation of the colored product. It may be emphasized that titration by sodium thio-sulfate represents a measure of reduction of Cr (IV) and includes all oxidation states of chromium other than Cr (III). Whereas absorbance represents the formation of colored product. It is a unique observed feature of oxidation of p-Toluidine. The reaction also shows a compels kinetic behavior with respect to concentrations of p-Toluidine and hydrogen ion. In order to accommodate the above kinetic features, it is suggested that a complex is formed between the oxidant and p-Toluidine, C_6 (C_6 represents the complex where oxidation state of chromium remains unchanged). The complex, C_6 breaks down into two different intermediate by intermolecular electron transitions leading to two different reaction paths one of which gives the colored product (Pc) and the other path gives the second product (P). It may further be added that the second reaction path consumes more oxidant/mole of product formed in comparison to first reaction path. This assumption is based on the fact that the reduction of Cr (VI) cannot be significantly shared between two reactions paths otherwise the two rate constants would not be so different.

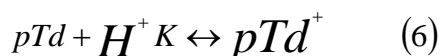
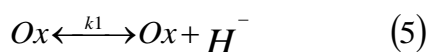
The reduction of Cr (VI) is exclusively determined by the second reaction path and the first reaction path represents a minor route by which colored product is obtained and the reduction of Cr (VI) is also minimal. On the basis of above features the following mechanism has been proposed assuming

that a fraction f of the complex is involved in route 1:



In the above mechanism, the terms C_{16} and C_{26} represent two different reaction intermediate produced by C_6 without change of oxidation state of chromium. Other terms used have already been explained. A suitable rate expression may be obtained from the above mechanism as given below:

It is assumed that major species of Cr (VI) present at any time in the reaction medium are $[Ox]$, $[Ox^-]$ and $[C_6]$.



Using the following mass-balanced equation the concentration of these species can be obtained in terms of concentration of p-Toluidine and $[H^+]$.

$$\begin{aligned} [Ox]_t &= [Ox] + [Ox^-] + [C_{16}] + [C_{26}] \\ &= [Ox] + [Ox^-] + C_6 \end{aligned}$$

$$\begin{aligned} &= \frac{C_6[H^+]}{K_0[pTd^+]} + \frac{K_1}{[H^+]} \frac{C_6[H^+]}{K_0[pTd^+]} + C_6 \\ &= C_6 \left(\frac{[H^+]}{K_0[pTd^+]} + \frac{K_1}{[H^+]} \right) \quad (7) \end{aligned}$$

For p-Toluidine the following mass balanced equation may be written.

$$\begin{aligned} [pTd]_0 &= [pTd] + [pTd^+] \\ [pTd]^+ &= \frac{K[H^+][pTd]_0}{K[H^+] + 1} \quad (8) \end{aligned}$$

And p-Toluidine is largely present in protonated form.

Putting the value of $[pTd^+]$ from equation (8) into (7) we get

$$[Ox]_t = C_6 \left\{ \frac{[H^+]}{K_0} + K_1 \right\} \frac{K[H^+] + 1}{K[H^+] + 1} \quad (9)$$

$$[C_6] = \frac{KK_0[H^+][pTd]_0}{K_1 + (1 + KK_1)[H^+] + KK_0[H^+][pTd]_0} [Ox]_t \quad (9)$$

It has been mentioned that the complex; C_6 breaks down into two different intermediate C_{16} and C_{26} . The two different reaction paths are determined by the slow decomposition of these intermediates. C_{16} which is a small fraction of C_6 gives rise to the colored product. The rate of the reaction for this path may be obtained as given below-

A. Rate expression for route 1

From step 3, the rate of reaction may be written as,

$$R_1 = f k_1 [C_6] [H^+] \quad (10)$$

Where f represents the fraction of the complex C_6 , which is involved in route 1.

It has been noted that the extent of color formation does not change significantly under

different conditions. For example, a change in $[H^+]$ from 0.10 to 0.60 mol dm^{-3} does not result in the change of absorbance at the end of the reaction by more than 10%. Route 1 is a minor reaction path but is fast in comparison to the route 2 and furthermore, Cr (VI) reduced by this reaction path is insignificant in comparison to Cr (VI) consumed by the reaction path (2)

The complete rate law for this reaction path may be obtained by putting the value of C_6 from equation (9) into equation (10) and further, replacing fk_1 as k'_1 we may write-

$$\frac{-d[Ox]_t}{dt} = \frac{k_1[H^+]KK_0[H^+][pTd]_0}{(K_1 + (1 + KK_1)[H^+] + KK_0[H^+][pTd]_0)}[Ox]_t$$

Since it has been assumed that a particular fraction of the total oxidant is converted into the colored product. The above rate law may be expressed in terms of absorbance by the following procedure.

$$f[Ox]_0 \propto [Pc]_{\infty} \propto (A_{\infty} - A_0)$$

Also, $f \{ [Ox]_0 - [Ox]_t \} \propto [Ox]_t \propto [Pc]_t \propto A$ (A signifies Absorbance at time t).

Substituting the values of concentration of oxidant in terms of absorbance of product we get-

$$\frac{d[A]}{dt} = \frac{KK_0k_1[H^+]^2[pTd]_0(A_{\infty} - A)}{(K_1 + (1 + KK_1)[H^+])KK_0[H^+][pTd]_0}$$

Giving

$$\ln \frac{A_{\infty} - A_0}{A_{\infty} - A} = {}^0k_A t$$

$$\text{where } {}^0k_A = \frac{KK_0k'_1[H^+]^2[pTd]_0}{(K_1 + (1 + KK_1)[H^+] + KK_0[H^+][pTd]_0)}$$

The reciprocal of the above equation gives

$$({}^0k_A)^{-1} = \frac{K_1 + (1 + KK_1)[H^+]}{KK_0k_1[H^+]^2[pTd]_0} + \frac{1}{k_1[H^+]} \quad (12)$$

$$= k'_s \frac{1}{[pTd]_0} + k_1$$

The above equation predicates that the between $({}^0k_A)^{-1}$ vs $[pTd]_0^{-1}$ should be linear giving a positive intercept at different $[H^+]$. Furthermore, the inverse of the intercepts of these plots, $[K_1]^{-1}$ have been plotted against $[H^+]$, which passes through origin, the slopes of plots give k'_1 at different temperatures. The dependence of the slopes of plots gives k'_1 at different temperatures. The dependence of the slopes of equation (12) on $[H^+]$ has also been verified.

$$k'_s = \frac{K_1 + (1 + KK_1)[H^+]}{KK_0k'_1[H^+]^2}$$

Which can be arranged as

$$k'_s [H^+]^2 = \frac{K_1}{KK_0k_1} + \frac{(1 + KK_1)[H^+]}{KK_0k'_1}$$

The plot of $k'_s [H^+]^2$ vs $[H^+]$ is found to be linear giving a positive intercept (vide figure P_A:1). However, the values of equilibrium constants K_0 , K_1 and K could not be assessed from the kinetic data. It is also not possible, to use values of these constants from the literature because their specific dependence on temperature and ionic strength are not available.

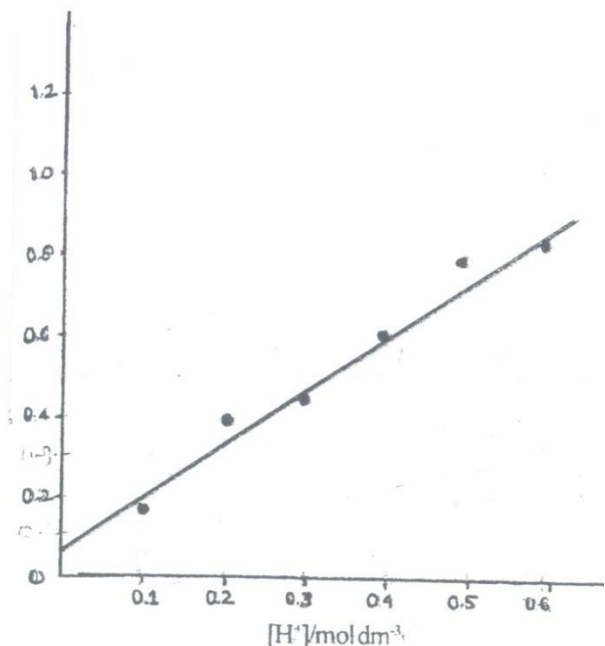


Fig (PA:1) Plot between ${}^0k'_s [H^+]$ vs $[H^+]$
Temp = 35°C

So far as route 2 is concerned it has been investigated by titration method because most of the oxidant is consumed by Route 2. It has been assumed that a fraction (f) of complex C_6 is consumed by Route 1 whereas the fraction (1-f) of the complex C_6 is consumed by route 2. It may also be noted that the end product by this route is obtained by reduction of more oxidants in fast steps. These two factors when taken into account ensure that the oxidant is more or less consumed by this reaction path and reduction of Cr (VI) by route 1 may be ignored, giving,

$$\begin{aligned} r_2 &= (1-f) k_3 [C_6] \text{ (if f is small)} \\ &= k_3 [C_6] \end{aligned} \quad (13)$$

$$\frac{-d[Ox]_t}{dt} = \frac{k_3 K K_0 [H^+] [pTd]_0 \cdot [Ox]_t}{K_1 + (1 + K K_1) [H^+] + K K_0 [H^+] [pTd]_0}$$

The rate constant ${}^0k_{rt}$, may be obtained as,
In $R_0/R_t = {}^0k_{rt}$ (where R_0 and R_t represent titration reading at zero time and at time t and ${}^0k_{rt}$ is

$${}^0k_T = \frac{k_3 K K_0 [H^+] [pTd]_0}{K_1 + (1 + K K_1) [H^+] + K K_0 [H^+] [pTd]_0}$$

The reciprocal of above equation gives:

$$\begin{aligned} ({}^0k_T)^{-1} &= \frac{K_1 + (1 + K K_1) [H^+]}{k_3 K K_0 [H^+]} \frac{1}{[pTd]_0} + \frac{1}{k_3} \quad (14) \\ &= k_s \frac{1}{[pTd]_0} + k_1 \quad (15) \end{aligned}$$

The above equation has been experimentally verified as the plots of $({}^0k_T)^{-1}$ vs $[pTd]_0^{-1}$ are found to be linear giving positive intercepts as shown in Fig. (Pr 1) at different temperature and $[H^+]$. The reciprocal of intercepts give k_3 which have been obtained. It is also noted that the plots in fig (Pr1) give same intercepts at different $[H^+]$ which is different from the plots obtained by using the absorbance data in Route 1.

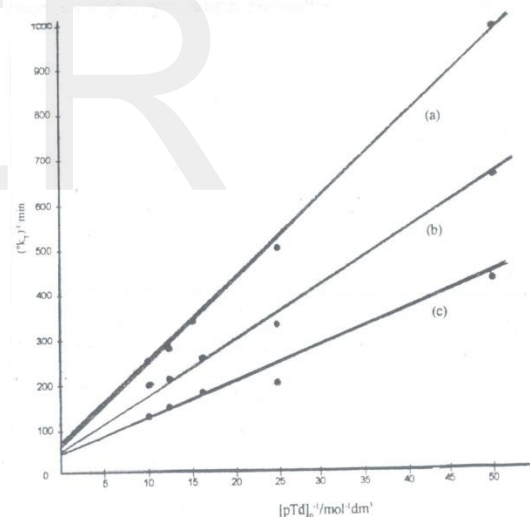


Fig. (Pr:3) Plots between $({}^0k_T)^{-1}$ vs $[pTd]_0^{-1}$
Temp. = (a) 35°C, (b) 40°C, (c) 45°C, $[H^+] = 0.10 \text{ mol dm}^{-3}$

The values of k_1 and k_3 at different temperatures have been tabulated and their activation parameters have been evaluated as shown in Table 1 and table 1A respectively.

TABLE 1

Rate Constant	35°C	40°C	45°C
k_1	$0.10 \text{ min}^{-1} \text{ mol}^{-1} \text{ dm}^3$	$0.14 \text{ min}^{-1} \text{ mol}^{-1} \text{ dm}^3$	$0.23 \text{ min}^{-1} \text{ mol}^{-1} \text{ dm}^3$
k_3	0.017 min^{-1}	0.020 min^{-1}	0.025 min^{-1}

Table 1A

Rate Constant	$E_a/\text{KJ mol}^{-1}$	$\Delta G^\ddagger/\text{KJ mol}^{-1}$	$\Delta H^\ddagger/\text{KJ mol}^{-1}$	$\Delta S^\ddagger/\text{KJ mol}^{-1}$	Nature of rate constant
k_1	81.39	53.91	51.35	-0.097	C16 $\xrightarrow{k_1 H^+}$ Pc+Ox (4)

Thermodynamic parameters were determined in H_2SO_4 medium at 308 K.

The slopes of equation (14) have been tested for its dependence on $[\text{H}^+]$ by rearranging the equation as given below:

$$k_s = \frac{K_1 + (1 + KK_1)[\text{H}^+]}{k_3 KK_0 [\text{H}^+]}$$

$$k_s [\text{H}^+] = \frac{K_1}{k_3 KK_0} + \frac{(1 + KK_1)[\text{H}^+]}{k_3 KK_0} \quad (16)$$

The above equation shows that plot of $k_s [\text{H}^+]$ vs $[\text{H}^+]$ should be linear. This is verified by plots in Fig (P_T 2). Unfortunately, this investigation also does not yield the values of different equilibrium constants involved in the reaction mechanism.

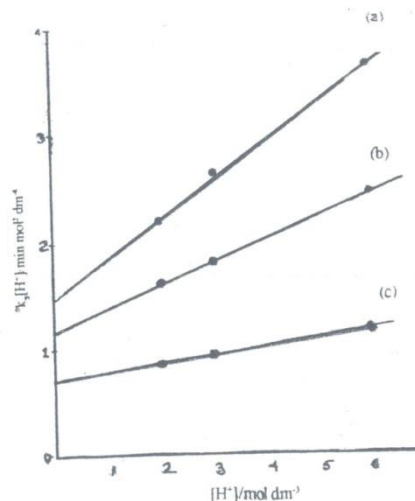


Fig. (P_T:3) Plots between $\log k_s [\text{H}^+]$ vs $[\text{H}^+]$
Temp. = (a) 35°C, (b) 40°C, (c) 45°C,

Conclusion

In order to accommodate the above kinetic features, it is suggested that a complex is formed between the oxidant and p-Toluidine, C_6 this complex breaks down into two different intermediate by intermolecular electron transitions leading to two different reaction paths one of which gives the colored product (Pc) and the other path gives the second product (P). It may further be added that the second reaction path consumes more oxidant/mole of product formed in comparison to first reaction path. This assumption is based on the fact that the reduction of Cr (VI) cannot be significantly shared between two reactions paths otherwise the two rate constants would not be so different. The reduction of Cr (VI) is exclusively determined by the second reaction path and the first reaction path represents a minor route by which colored product is obtained and the reduction of Cr (VI) is also minimal

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