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Kinetics and Mechanism of Oxidation of Ethylenediamine by Chromic acid in Perchloric Acid Medium

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Kinetic studies on oxidation of ethylenediamine by chromic acid in the presence of perchloric acid have been made. The results indicate first order kinetics with respect to each chromic acid, ethylenediamine and $[H^+]$. Insignificant effect of ionic strength of the medium has been observed. Increase in chromic acid was found to show retarding effect on reaction rate. A suitable mechanism on the basis of kinetic results has been proposed.

INTRODUCTION

The chromic acid oxidation of a number of organic and inorganic substrates has been extensively studied by several workers[1–6]. Srinivasan *et al.*[1] have discerned the nature of the transition state in the oxidation of naphthyl methyl carbinols by chromic acid. Venkatasubramanian *et al.*[2] have applied Bunnett criterion in order to choose the most probable mechanism of oxidation of secondary alcohols by chromic acid. Sadagopa Ramanujam *et al.*[3] have studied the kinetics and mechanism of oxidation of hydrazine sulphate by Cr(VI) oxide in aqueous sulphuric acid and they have proved that Cr(VI) behaves as a two-electron oxidant. A survey of literature on chromic acid oxidations indicates that there is no kinetic information on reactions involving chromic acid and ethylenediamine. This paper reports the kinetic data on oxidation of ethylenediamine by chromic acid in perchloric acid medium.

EXPERIMENTAL

Aqueous solution of ethylene diamine (Fluka AG) was prepared by dissolving its weighed quantity in doubly distilled water. Chromic acid solution was prepared by dissolving a weighed quantity of chromium trioxide (BDH, AR) in known strength of perchloric acid (E. Merk) solution. All other reagents were of available pure quality (AR grade).

The kinetics of the reaction was followed as described earlier[1, 2]. The reaction was initiated by quickly adding a known volume of standard chromic acid solution to the reaction vessel containing known volumes of standard solutions of ethylenediamine and perchloric acid and maintained at desired temperature in a thermostatic water bath (± 0.1°C). The progress of the reaction was monitored by estimating an aliquot (5 ml) of the reaction mixture for unconsumed chromic acid iodometrically at different intervals of time. The reproducible results were obtained (± 2.25%).

RESULTS AND DISCUSSION

A varying ratio of excess [chromic acid] over [ethylenediamine] in perchloric acid at 35°C was maintained in four reaction vessels separately and the reaction was allowed to take place for 48 hrs. Estimation of unused chromic acid in all sets of experiments showed that two moles of chromic acid were consumed in oxidation of each mole of ethylenediamine. Accordingly following stoichiometry (1) was suggested.

$$\begin{array}{l} CH_2NH_2 \\ | \\ CH_2NH_2 \end{array} + 2H_2CrO_4 + 4H^+ \longrightarrow 2HCHO + 2NH_3 + Cr_2O_3 + 3H_2O \quad (1)$$

The end product formaldehyde was detected by conventional method[7].

First order kinetics with respect to chromic acid was observed for different initial concentrations of chromic acid. Table 1 records the kinetic data for a particular concentration of chromic acid. It is clear from the nearly constant values of first order rate constant i.e. k_1 that the reaction is first order in chromic acid.

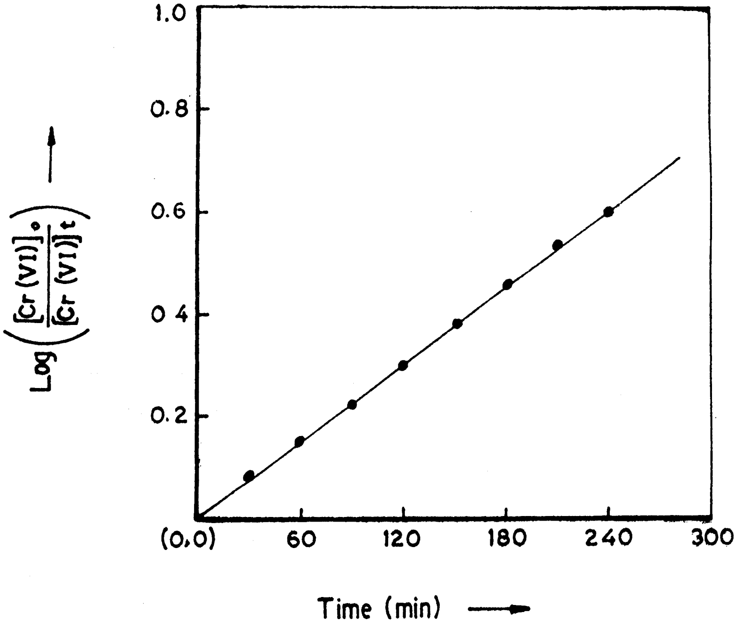

Fig. 1 Plot of log ([Cr(VI)]o/[Cr{VI}]t) against time at 65°C under the experimental conditions of Table 1

When a graph (Fig. 1) is plotted between log ([chromic acid]$_o$/[chromic acid]$_t$) and time, a straight line passing through origin and with a slope equal to $K_1/2.303$ is obtained. The k_1 value obtained from the slope (4.20×10^{-5} sec^{-1}) is close to average integral value (4.41×10^{5} sec^{-1}, Table 1) which confirms first order dependence of the reaction on chromic acid. But when chromic acid concentration is increased, the first order rate constant (k_1) decreases. This is ascribed to the decrease in concentration of oxidising species, $HCrO_4$, on account of its conversion to less powerful oxidising species, dichromate ion, on increasing the concentration of chromic acid (Table 2). The first order rate constant is thus retarded by dichromate ion.

TABLE 1

KINETIC RESULTS INDICATING CONSTANT VALUES OF FIRST ORDER RATE CONSTANT AT DIFFERENT TIMES IN AN EXPERIMENT AT 65°C

[H_2CrO_4] = 1.00×10^{-3} M,nM, [Ethylendiamine] = 3.50×10^{-1}M and [HCl] = 3.50×10^{-1}M.

Time (min)	10^4 [Chromic acid]$_t$	$k_1 \times 10^5$ sec^{-1}
0	10.00	—
30	7.84	5.85*
60	6.84	4.59
90	5.82	4.34
120	4.80	4.41
150	4.04	4.36
180	3.42	4.32
210	2.78	4.41
240	2.28	4.46

Average k_1 value (excluding) = 4.41×10^{-5} sec^{-1}

Table 2 also records the kinetic results at different concentrations of etylenediamine. The first order rate constant (k_1) increases linearly on increasing the concentration of ethylenediamine indicating first order kinetics with respect to ethylenediamine, which is also clear from nearly constant values of k_2. Effect of variation of perchloric acid concentrations on the rate constant has been shown in Table 3 which also contains the kinetic data at different ionic strengths (μ) of the medium and temperatures. First order rate dependence on [H^+] is obvious from almost constant values of k_2 (second order rate constant) at different concentrations of perchloric acid. Change in ionic strength (μ) has been affected by addition of suitable amounts of sodium perchlorate. It is evident from the kinetic data of Table 3 that first order rate constant is not influenced by variation of ionic strength of the medium.

TABLE 2
EFFECT OF VARIATION OF [REACTANT] ON RATE CONSTANT AT 65°C AND [HClO$_4$] = 3.50×10^{-1} M.

10^4 [Chromic acid] mol l^{-1}	10 [Ethylenediamine] mol l^{-1}	10^5 k_1 sec^{-1}	10^4 $k_2 = \frac{k_1}{\text{[Ethylenediamine]}}$ mol^{-1} l sec^{-1}
5.34	3.50	5.19	—
6.66	3.50	4.99	—
8.00	3.50	4.61	—
10.00	3.50	4.41	—
11.33	3.50	4.20	—
13.30	3.50	3.97	—
10.00	1.00	1.41	1.41
10.00	1.50	2.07	1.38
10.00	2.00	2.82	1.41
10.00	2.50	3.73	1.49
10.00	3.00	4.18	1.39
10.00	3.50	4.41	1.26

The reaction has been studied in the temperature range 65–80°C. The values of activation parameters viz. energy of activation (ΔE), Arrhenius factor (A), entropy of activation ($\Delta S^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) have been calculated from the measurements of rate constants at different temperatures (Table 3). The values of ΔE, A, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ for the oxidation of ethylenediamine by chromic acid in perchloric acid medium was found as 30.24 kJ/mole, 15.32 s^{-1}, −224.11 JK^{-1} mol^{-1} (at 65°C) and 105.98 kJ/mole (at 65°C) respectively.

The following equilibria[8, 9] are known to exist in acidic solution of chromic acid.

$$Cr_2O_7^{2-} + H_2O \rightleftarrows 2HCrO_4^- \tag{2}$$

$$HCrO_4^- + H_3O^+ \rightleftarrows H_2CrO_4 + H_2O \tag{3}$$

First order dependence of the reaction on hydrogen ions indicates that $HCrO_4$ is reactive species of chromic acid. This is, further, confirmed by decreasing effect of chromic acid which is explained on the basis of conversion of oxidising species, $HCrO_4^-$ to $Cr_2O_7^{2-}$ in equilibrium (2). Dichromate ion is less powerful oxidising species[10] than $HCrO_4^-$, thus causing retardation in the rate constant. Hence under the experimental conditions $HCrO_4^-$ has been assumed to be oxidising species of chromic acid on the basis of kinetic observations. Although molecular chromic acid, H_2CrO_4 or its conjugate acid ($H_3CrO_4^+$) have also been taken as oxidising species in oxidation of ketones[11], but in our case these species yield the rate law incapable of explaining the kinetic results. Hence these have been ruled out as oxidising species.

TABLE 3

EFFECT OF VARIATION OF [PERCHLORIC ACID], IONIC STRENGTH (μ) OF THE MEDIUM AND TEMPERATURE ON REACTION RATE

[Chromic acid] = 1.00×10^{-3}M and [Ethylenediamine] = 3.50×10^{-1}M

Temp. °C	10 [$HClO_4$] mol l^{-1}	10 (μ) mol l^{-1}	$k_1 \times 10^5$ sec^{-1}	$10^4\ k_2 = \frac{k_1}{[HClO_4]}$ $mol^{-1}\ l\ sec^{-1}$
65	3.50	14.03	4.41	1.26
65	4.00	14.03	4.99	1.25
65	4.50	14.03	6.00	1.33
65	5.00	14.03	7.10	1.42
65	5.50	14.03	7.72	1.40
65	7.00	14.03	9.18	1.31
65	10.50	14.03	14.42	1.37
65	14.00	14.03	19.00	1.35
65	3.50	3.53	4.41	—
65	3.50	4.53	4.40	—
65	3.50	6.53	4.42	—
65	3.50	8.53	4.40	—
65	3.50	10.53	4.43	—
65	3.50	12.53	4.39	—
65	3.50	14.53	4.40	—
70	3.50	3.53	6.19	—
75	3.50	3.53	8.80	—
80	3.50	3.53	12.52	—

On the basis of above statement and other kinetic results the following reaction steps are suggested.

$$\underset{(C_1)}{HCrO_4^-} + H^+ \overset{K_1}{\rightleftarrows} \underset{(C_2)}{H_2CrO_4} \qquad \text{(i)}$$

$$S + H_2CrO_4 \overset{K_2}{\rightleftarrows} \underset{(C_3)}{\text{Intermediate}} \qquad \text{(ii)}$$

where S stands for ethylenediamine

$$C_3 \xrightarrow{kd} \text{Products} \qquad \text{(iii)}$$

slow and rate determining step

The rate of oxidation of ethylenediamine in terms of loss of [chromic acid] i.e. [Cr(VI)] may be expressed as equation (4)

$$\frac{-d[Cr(VI)]}{dt} = kd\,[C_3] \qquad (4)$$

The total concentration of chromic acid i.e. $[Cr(VI)]_T$ may be written as equation (5)

$$[Cr(VI)]_T = [C_1] + [C_2] + [C_3] \tag{5}$$

On solving equation (5) with the help of steps (i) and (ii) we have equation (6)

$$[C_3] = \frac{K_1K_2[S][H^+][Cr(VI)]_T}{1 + K_1[H^+](1 + K_2[S])} \tag{6}$$

On comparing equations (5) and (6), we get equation (7)

$$\frac{-d[Cr(VI)]_T}{dt} = \frac{kd\, K_1K_2[S][H^+][Cr(VI)]_T}{1 + K_1[H^+](1 + K_2[S])} \tag{7}$$

where $K_2 = (k_2/k_{-2})$

Further, on assuming $1 \gg K_1[H^+](1 + K_2[S])$ in the rate law (7), we have equation (8).

$$\frac{-d[Cr(VI)]_T}{dt} = kd\, K_1K_2[S][H^+][Cr(VI)]_T \tag{8}$$

The rate law (8) is in agreement with observed kinetic results. This also explains negligible effect of ionic strength of the medium as slow and rate determining step is decomposition of the intermediate which is formed as a result of interaction of two neutral molecules i.e. ethylenediamine and neutral molecular chromic acid (H_2CrO_4).

The proposed mechanism is also supported by large value of free energy of activation (ΔG^{*}) and large negative value of entropy of activation (ΔS^{*}). The large value of free energy of activation suggests that transition state is highly solvated while large negative value of entropy suggests that degree of freedom in the transition state is decreased.

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