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Kinetics of Oxidation of Propyl Ester of 3-Phenylacrylic Acid by Acid Dichromate

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Kinetics of oxidation of propyl ester of 3-phenyl acrylic acid by acid dichromate ions are studied. The order of reaction with respect to chromium(IV), ester and the hydrogen ions is one in each case. The rate decreases in the presence of manganous ions. Oxidation products of the ester (i) when the ester is in excess are benzaldehyde and propyl glyoxalate and (ii) when acid dichromate is in excess it is benzoic acid. The effect of temperature on rates is studied and thermodynamic parameters are calculated. A probable mechanism for the reaction is suggested on the basis of the product analysis.

INTRODUCTION

It is believed that oxidation of olefins by acid permanganate is quite different in nature from the oxidation of olefin by chromium(VI)[1]. A work published by Lee and Brownridge[2] has studied the kinetics and mechanism of oxidation of 3-phenylacrylic acid by acid permanganate which prompted us to undertake the study of the oxidation of 3-phenylacrylic acid[3] and its aryl and alkyl derivatives[4, 5] by acid dichromate.

EXPERIMENTAL

Propyl ester of 3-phenylacrylic acid was prepared by Fischer-Speier method[6] using 3-phenylacrylic acid of Schimmel & Co., German make. The product was confirmed by its b.p. Potassium dichromate and sulphuric acid used were of AR grade. Acetic acid used in the study was first distilled over anhydrous chromium trioxide to remove reducible matter. Other chemicals used during titrations, *viz.*, sodium thiosulphate and potassium iodide were of BDH make. The indicator starch used in the work was of E. Merck of German make. The solutions of all the reactants, except propyl ester of 3-phenyl acrylic acid, were prepared in distilled water obtained from all glass joint apparatus. The ester solution was prepared in acetic acid. Pure distilled acetic acid is used in preparing various concentrations of the ester keeping HOAc : H_2O ratio in the mixture as 60 : 40.

During the kinetic studies, solutions of all the reactants were brought to the thermostat temperature. The reaction was initiated by adding dichromate. Aliquot portions were withdrawn at definite intervals of time and the reaction was quenched in ice. The rate of reaction was followed by estimating the unreacted dichromate ions by the iodometric procedure of Kolthoff and Carr[7]. Due precautions were taken to minimize the air oxidation iodide[8].

The stoichiometry of the reaction was determined when concentration of the acid dichromate was in excess. The reaction mixture was kept for 96 h in a closed reaction vessel. The amount of dichromate ions left was estimated by the usual procedure[7]. One mole of ester reacted with 1.37 moles of Cr(VI). It was not possible to determine the stoichiometry of the reaction under the condition when ester was in excess. The procedures adopted for the product analysis when (i) ester is in excess over the acid dichromate and (ii) acid dichromate is in excess over the ester are as follows:

Under condition (i) after the reactions were over, the solution was divided into two parts. One part of the solution was extracted with ether. The ethereal layer was first treated with dilute sodium hydroxide solution and then washed with water. The layer was then passed over anhydrous sodium sulphate to remove traces of water. After evaporation of the ether, the liquid left behind was identified as benzaldehyde (confirmed by its 2,3-dinitrophenylhydrazine derivative). The other part of the solution was also extracted with ether. The aqueous layer, left after extraction with ether, was treated with sodium hydroxide which on boiling gave precipitate of $Cr(OH)_3$. The precipitate was removed by filtration. The filtrate was then acidified and tested for the ester. From boiling point test it was identified as propyl ester of glyoxalic acid. Under condition (ii) after the reactions were over, the solution was extracted with ether. The ethereal layer was then treated with dilute sodium hydroxide solution, washed with water and then passed through anhydrous sodium sulphate. The ether was then allowed to evaporate. No traceable amount was left in the container. The aqueous layer of the reaction mixture left out on extraction with ether was then acidified which gave white precipitate. The precipitate was identified as benzoic acid (confirmed by its m.p.).

The reactions can be written as:

1. $$3\,C_6H_5CH{=}CHCOOCH_2CH_2CH_3 + 2\,Cr_2O_7^{2-} + 16\,H^+ \rightarrow 3\,C_6H_5CHO + 3\,CHO{\cdot}COOCH_2CH_2CH_3 + 4\,Cr^{3+} + 8\,H_2O$$

2. $$3\,C_6H_5CH{=}CH{\cdot}COOCH_2CH_2CH_3 + 4\,Cr_2O_7^{2-} + 32\,H^+ \rightarrow 3\,C_6H_5COOH + 3\,CH_3CH_2CH_2COOH + 3\,CO_2 + 16\,H_2O + 8\,Cr^{3+}$$

Reaction (2) corresponds to the observed stoichiometry $[Cr_2O_7^{2-}]/[\text{Ester}] = 1.37$, when acid dichromate is in excess over the ester.

RESULTS AND DISCUSSION

The reaction is attended with an induction period and then follows first order rate law. First order plots were obtained for about 70% of the reaction. The rate is first order with respect to propyl ester of 3-phenylacrylic acid (Table-1) and hydrogen ions (Table-2). The variation of rate with concentration of acid dichromate is found decreased with the increase of Cr(VI) concentration, while the ratio K_1 (rate constant) $\times [Cr(VI)]/[HCrO_4^-]$ remaining constant (Table-3) confirms the existence of $HCrO_4^-$ species[9] in the set under the studied conditions. The concentration of $HCrO_4^-$ is calculated on the basis of the equation:

$$[HCrO_4^-] = \frac{K}{4}\left[-1 + \left\{1 + \frac{8[Cr(VI)]}{K}\right\}^{1/2}\right]$$

Further, the equilibrium position of the reaction $H_2O + Cr_2O_7^{2-} \rightleftharpoons 2HCrO_4^-$ is independent of pH as $HCrO_4^-$ and $Cr_2O_7^{2-}$ have approximately the same absorption spectra on the basis of the observations made by Westheimer[10], and the value reported for K of the above reaction in acetic acid medium is the same as considered for the studied mixed solvent medium.

TABLE-1

VARIATION OF RATE WITH CONCENTRATION OF PROPYL ESTER OF 3-PHENYL ACRYLIC ACID

Solvent: 60% (v/v) aqueous acetic acid

10^3 [Cr(VI)] = 5.0 M; [H^+] = 2.0 M; Temp = 303 K

10^2 [Ester] moles litre^{-1}	10^5 K_1 sec^{-1}	10^3 K_1 [Ester] mole^{-1} litre sec^{-1}
1.0	4.415	4.415
1.5	6.570	4.380
2.0	9.598	4.799
2.5	11.050	4.421

TABLE-2

VARIATION OF RATE WITH CONCENTRATION OF HYDROGEN IONS

Solvent: 60% (v/v) aqueous acetic acid

10^3 [Cr(VI)] = 5.0 M; [H^+] = 2.0 M; Temp = 303 K

[H^+] moles litre^{-1}	10^5 K_1 sec^{-1}	10^3 K_1 [Ester] mole^{-1} litre sec^{-1}
1.2	5.383	4.486
1.6	6.716	4.198
2.0	9.414	4.708
2.4	10.540	4.394

TABLE-3

VARIATION OF RATE WITH CONCENTRATION OF ACID DICHROMATE

Solvent: 60% (v/v) aqueous acetic acid

10^3 [Cr(VI)] = 5.0 M; [H^+] = 2.0 M; Temp = 303 K

10^2 [Cr(VI)] moles litre^{-1}	10^2 [HCrO]	10^5 K_1 sec^{-1}	10^3 K_1 [Ester][$HCrO_4^-$]
3.0	2.484	9.646	11.44
4.0	3.161	9.298	11.77
5.0	3.797	9.098	11.99
6.0	4.351	8.702	11.90

The results in connection with the effect of manganous ions on the rate of oxidation have shown the following characteristic features of the reaction (Table-4): (a) The induction period in the early stages of the reaction is eliminated. (b) The rate in the presence of manganous ions is nearly the same in the early parts of the induction period in absence of Mn^{2+} ions. (c) The effect of Mn^{2+} on rate constant with its lower concentration, *i.e.*, below 4×10^{-4} M was not remarkable. (d) The rate of oxidation has reached a limiting value when concentration of manganous ions is $\geq 1.6 \times 10^{-3}$ M and under these conditions the rate of oxidation in presence of manganous ions has decreased nearly to one-third of the rate, after the induction period, in the absence of manganous ions.

TABLE-4

EFFECT OF MANGANOUS IONS ON THE RATE OF OXIDATION

Solvent: 60% (v/v) aqueous acetic acid

10^2 [Ester] = 2.0 M; 10^3 [Cr(VI)] = 5.0 M; [H^+] = 2.0 M; Temp = 303K

10^2 [Mn^{2+}] moles litre^{-1}	10^5 K_1 sec^{-1}
–	9.598
4.0	4.166
8.0	3.861
12.0	3.533
16.0	3.014

The decrease in the rate of oxidation of the ester in presence of Mn^{2+} is in accordance with the observations made by Bakore and Narain[9] during their study of oxidation of α-hydroxy carboxylic acid by chromic acid.

The behaviour of Mn(II) in the reaction is complex; however, the results of rate constant of the ester in presence of Mn^{2+} indicate that some intermediate species of chromium, *viz.*, Cr(V) or Cr(IV)[8, 10, 11] oxidises the ester. The induction period seen in Table-4 is likely to be due to the following reaction of Mn(II) with either Cr(V) or (IV) or both:

$$\text{Cr(V)} + \text{Mn(II)} \rightarrow \text{Mn(IV)} + \text{Cr(III)}$$

or

$$\text{Cr(V)} + 2\text{Mn(II)} \rightarrow 2\text{Mn(III)} + \text{Cr(III)}$$

and

$$\text{Cr(IV)} + \text{Mn(II)} \rightarrow \text{Mn(III)} + \text{Cr(III)}$$

or

$$\text{Cr(IV)} + \tfrac{1}{2}\text{Mn(III)} \rightarrow \tfrac{1}{2}\text{Mn(IV)} + \text{Cr(III)}$$

The existence of induction period in the initial stages and the decrease of rate constant to 1/3 the initial rate constant in presence of Mn(II) in the later stages is probably due to higher activation energy required in forming Mn(II)-Cr(V) or Cr(IV) intermediate complex in aqueous HOAc solution which created low concentration of the active reaction species of chromium in the solution and as a result showing a decrease in the value of rate constant. A similar behaviour was found[12] in the oxidation of oxalate ions by permanganate ions. A plot of log K_1

vs. inverse of absolute temperature (Table-5) gives a straight line. The Arrhenius equation is therefore valid. The energy of activation (E_a) for the overall reaction calculated from rate constants data has value 54.60 kJ mole^{-1} and enthalpies of activation ($\Delta H^{\neq}$) at different temperatures were determined using the relation $\Delta H^{\neq} = E_a - RT$.[13] Table-5 represents various values of rate constants, enthalpy of activation ($\Delta H^{\neq}$), entropy of activation ($\Delta S^{\neq}$) and free energy of activation ($\Delta G^{\neq}$).

TABLE-5
EFFECT OF TEMPERATURE ON RATE

10^2 [Ester] = 2.0 M; [H^+] = 2.0 M; 10^3 [Cr(VI)]= 5.0 M
Solvent : 60% (v/v) aqueous acetic acid

Temperature (K)	10^5 K_1 sec^{-1}	$\Delta H^{\neq}$ kJ moles^{-1}	$\Delta S^{\neq}$ J moles $^{-1}$	$\Delta G^{\neq}$ kJ moles^{-1}
303	9.800	51.51	-151.79	97.50
308	13.750	51.47	-151.87	98.26
313	18.170	51.43	-152.36	99.11
318	26.350	51.39	-151.99	99.72

The value of entropy of activation found was higher than the value reported by previous workers[14] for 3-phenyl acrylic acid. This might be due to some influence of inductive effects of —C_3H_7 group as compared to —COOH group and of solvent composition on the rate. Further, the mechanism suggested is also different.

The oxidation of styrene by CrO_2Cl_2 exhibits an isotope effect which suggests that the rate determining step produces a carbonium ion[15]. On the other hand, the isotope effects observed in the oxidation of cinnamic acid by acid permanganate are more consistent with the formation of a cyclic ester[2].

It is believed that chromic acid oxidation of olefinic compounds probably involves $[HCrO_3]^+$ as the active oxidant species[1]. If $[HCrO_3]^+$ were the active oxidant species in the present case, the rate would depend on the square of the hydrogen ion concentration. The fact that the rate depends only on the first power of the concentration of hydrogen ions (Table-2) would require that the active oxidant species is H_2CrO_4:

$$H^+ + HCrO_4^- \rightleftharpoons H_2CrO_4$$

The rate determining step is

$$C_6H_5CH{=}CH{\cdot}COO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + H_2CrO_4 \longrightarrow$$

and this is followed by a number of fast steps in which intermediate products of ester are oxidised.

The rate laws and the results of product study suggest that the following mechanism might be operative:

$$S + O \xrightarrow[\text{Determining (slow step)}]{\text{Rate}} \text{Cr(IV) ester} \xrightarrow{H_2O} \text{Intermediate Complex}$$

$$\xrightarrow[\text{(fast step)}]{H_2CrO_4} P + \text{Cr(IV)}$$

and Cr(IV) on further reaction with Cr(IV) (in acid media) and intermittent product is transformed to Cr(III) (S = substrate, O = oxidant, P = product).

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