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KINETICS AND MECHANISM OF OXIDATION OF 2, 4-DICHLOROBENZOIC ACID AND p-CHLOROBENZOIC ACID BY DICHROMATE IN PRESENCE AND ABSENCE OF SUCCINIC ACID

A. S. KULKARNI[a], B. K. BONGANE[a], P. G. GAVALI[a] and N. T. PATEL[*]

Yeshwant College, NANDED (M.S.) INDIA
[a]B. S. College, BASMATH (M.S.) INDIA

ABSTRACT

Kinetics of oxidation of organic acid, such as 2,4-dichlorobenzoic acid and p-chlorobenzoic acid by dichromate in acetic acid-water medium in presence of perchloric acid. The oxidising reacting species. $HCrO^{-}_{4}$ & $Cr_2O^{2-}_{7}$ participate in the reaction. The effect of varying concentration of [substrate], [oxidant], [H^+], added neutral salt have been studied. It has been found that, the order of reaction with respect to [oxidant] and [substrate] found to be unity from the slope of plots log k v/s log [sub]. The rate of reaction increases with decrease in pH of perchloric acid. Hammett's acidity function & activity of water have been studied. Effect of temperature has also been studied. Activation parameters were computed. The plot of ΔH^* vs ΔS^* is linear. The effect of substituents on the rate of reaction have been studied.

Key words: Kinetics, Oxidation, 2,4-dichlorobenzoic, p-chlorobenzoic acid, Dichromate, Succinic acid.

INTRODUCTION

The oxidation of a number of α-hydroxy acids has been studied with [Cr(VI)][1.2]. A detailed study on the oxidation of an organic acids containing substituted chloride groups at ortho and para positions has not been attempted earlier. As a part of our research programme, this work incorporates kinetic results on [Cr (VI)] oxidation of 2,4-dichlorobenzoic acid, p-chlorobenzoic acid.

EXPERIMENTAL

Materials & methods

Organic materials, substituted acids were s.d. fine (A.R.) grade glacial acetic acid

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[*] Author for correspondence; E-mail: as_kulkarni123@rediffmail.com

(A.R.) was used as the solvent. All inorganic materials including chromic acid, $HClO_4$ (60%) were A.R. grade. Doubly distilled water was used for preparing different compositions of solvent. All other chemicals used were of A.R. grade.

Kinetic measurements

The rate of consumption of [Cr(VI)] was followed colorimetrically by measuring the optical density at 420 nm on a MAC digital photoelectric colorimeter. Requisite volumes of reactants previously equilibrated at 30°C within +0.01°C were mixed & immediately transferred to the cell. The optical densities were recorded at different time of intervals. The ionic strength of the medium was adjusted by adding requisite quantity of sodium chloride. The kinetic runs were carried out under pseudo first order conditions and the first order rate constant was calculated from the slope of the linear plot of log [Cr(VI)] v/s time and values reproducible to 2-3%.

Identification of oxidation product

The reaction products ketones were identified by preparing their 2,4-DNP derivatives & spot test.

RESULTS AND DISCUSSION

Effect of varying $[H^+]$: In order to study the effect of $[H^+]$, the experiments were carried out at different $[HClO_4]$ while keeping the [substrate], [Cr(VI)] constant. The result show a proportional dependence on $[H^+]$ ions. It is observed that $[H^+]$ ions are responsible for the increase in rate[3] (Table 1). The plots of log k v/s log $[H^+]$ (Fig. 1) are found to be linear in the case of 2,4-dichlorobenzoic acid and p-chlorobenzoic acid where the slopes are significantly nearly one.

Hammett's acidity function represents the ability of a solvent to donate a proton to neutral base. In dilute solution $H_0 = -\log a_H^+ = pH$, therefore for pure water $H_0 = pH = 7$ at 25°C. As the acidity of the solution increases, the value of H_0 decreases in order to get a mechanistic interpretations of acid catalysed reactions, the Hammett's acidity function (H_0) is used. According to Zucker & Hammett[4], involvement of water in the slow step of the reaction mechanism can be formulated.

$$
\begin{aligned}
S + H^+ &\rightleftharpoons SH^+ \\
SH^+ &\xrightarrow{\text{Slow}} X^+ \\
X^+ &\xrightarrow{\text{Fast}} \text{Product} + H^+
\end{aligned}
$$

A linear plot between log k_{obs} vs $-H_0$ for both uni-molecular & bimolecular gives unit slopes. This hypothesissis known as Zucker-Hammett hypothesis[5]. Plot of [log k + H_0] v/s log a_w gives a straight line, positive value of parameter "ω" (Fig. 1) greater than +3.3, indicates that water behaves as proton transfer agent in the rate controlling step[6].

Table 1: Effect of varying [H^+] on reaction rate [Cr(VI)] = 5 x 10^4 M, constant μ=0.3030 M, [HOAc] = 2 0% Temp. 30°C

[H^+] M	log a_w	H_o	2,4-dichlorobenzoic		p-chlorobenzoic	
			k x 10^3	H_0 + log k	k x 10^3	H_0 + log k
0.730	-0.0120	+0.30	10.01	-1.6996	7.09	-1.8490
0.909	-0.0165	+0.05	11.51	-1.8890	8.86	-2.0030
1.090	-0.0200	-0.12	12.12	-2.0360	10.47	-2.1005
1.273	-0.0240	-0.25	14.39	-2.0920	12.80	-2.1431
1.455	-0.0280	-0.40	16.44	-2.1840	15.35	-2.2139
1.818	-0.0380	-0.60	20.94	-2.2790	19.19	-2.3170

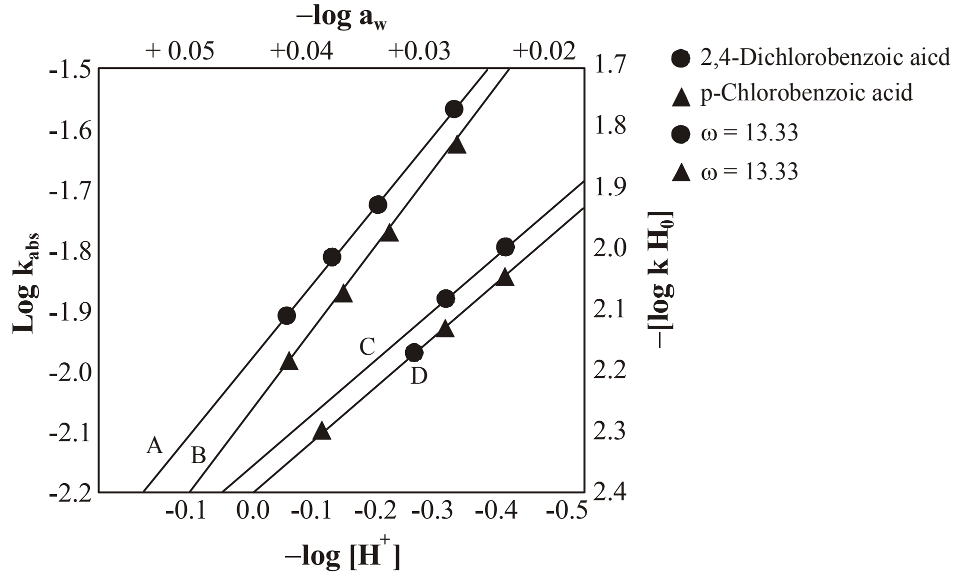


Fig. 1: A, B Plot of log k_{abs} vs log [H^+] and C, D plot of –[log k + H_0] v/s = log a_W

Effect of varying [oxidant]

The reaction was studied at varying oxidant concentrations and the order with respect to oxidant was found to be one. The first order rate constant showed that rate constant decreases with increasing the initial [Cr(VI)] (Table 2). This suggests that $HCrO_4^-$ is oxidising reacting species of Cr(VI)[7,8].

$$\text{Rate law: } \frac{-d\,[\mathrm{Cr\ (VI)}]}{dt} = k\,[(\mathrm{Cr\ (VI)}]\,[\mathrm{Substrate}]$$

The decreasing trend in the rate constant may be due to the hydrolytic equilibrium between $Cr_2O_7^{2-}$ and $HCrO_4^-$. The molecular identity of [Cr(VI)] species present in the solution as given below :

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

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

$$HCrO_4^- + 2H^+ \rightleftarrows HCrO_3^+ + H_2O$$

In addition to the above species there may be other species, since the reaction has been carried out in acetic acid-water medium, [Cr(VI)] is also expected to exist in the form of an acetyl chromate $AcOCrO_3^-$.

Table 2: Effect of varying [Cr(VI)] on reaction rate

$[Cr(VI)] \times 10^4$ M	2,4-dichlorobenzoic acid $k \times 10^3$ min^{-1}	p-chlorobenzoic acid $k \times 10^3$ min^{-1}
2.87	5.23	4.19
2.72	6.58	5.12
2.57	7.68	5.62
2.42	8.85	7.68
2.27	9.21	8.86
2.12	10.90	10.45
1.96	11.23	11.52
1.81	13.55	14.40

Effect of varying [Substrate]

The rate of oxidation increased with increasing concentration of the substrate. The plots of 1/k v/s 1/[sub] are linear and do not pass through the origin but show definite intercepts at 1/k $_{obs}$ axis (Fig. 2 and slope = 1, of line A & B). This indicates evidence for complex formation between the oxidant and the substrate[9].

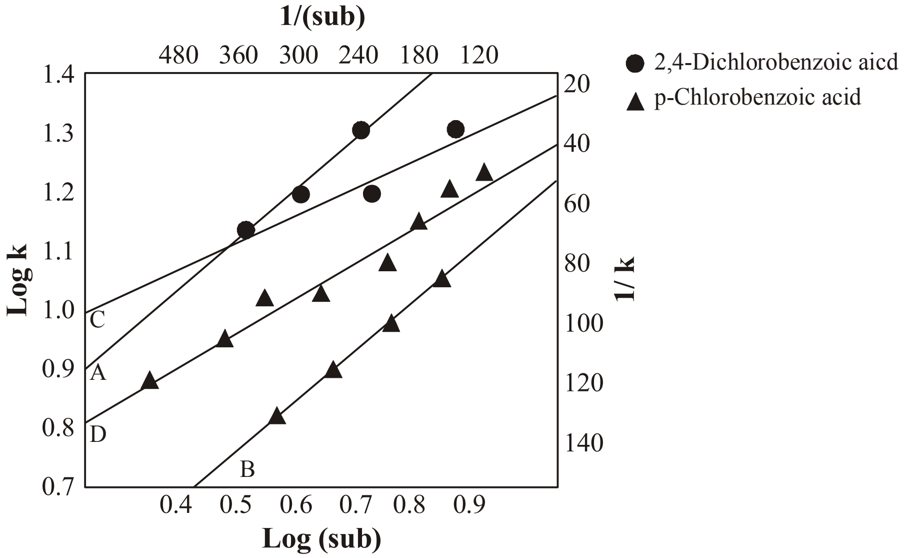


Fig. 2: A, B Plot of log k v/s log [sub] and C, D plot of 1/k v/s 1/(sub)

Effect of varying Ionic Strength

On increasing ionic strength by adding sodium chloride the rate decreases. The plot of [log k-log k_0] v/s $\sqrt{\mu}$, indicates that the reaction is between oppositely charged reactants[10]. The acid chromate-dichromate equilibrium constant is a function of the ionic strength, increase in ionic strength will favour the formation of the dichromate ion and this will decrease the rate of reaction.

Effect of varying [Solvent]

It is observed that the rate of oxidation increases with the increasing percentage of acetic acid in water. The reaction has been carried out in acetic acid medium, [Cr (VI)] dissolved in high percentage of acetic acid may also exist in the form of an acetyl chromate ion ($AcOCrO_3^-$). Solvent dependence on rate indicates a superior oxidising species. The plots of log k v/s 1/ D (Fig. 3) are linearly related as expected for ion-dipole reaction[11]. The attacking species is considered to be $HCrO_3^+$.

Effect of varying temperature

The pseudo first order rate constants of oxidation of 2,4-dichlorobenzoic acid and p-chlorobenzoic acid were determined at different temperatures. The plots of log k v/s 1/T (Fig. 3) are linear and the heat of activation were calculated from these plots. The reactions are as a whole characterized by a wide range of parameters. The activation parameters E_a, ΔH^*, ΔS^*, ΔG^*, were evaluated (Table 3).

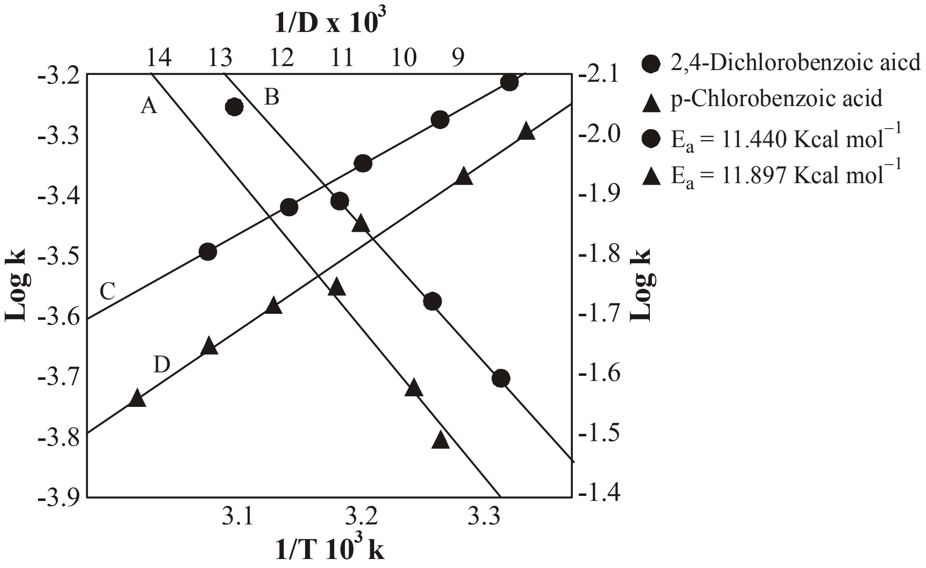


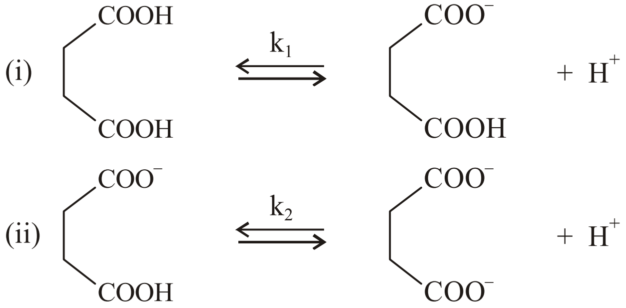
Fig. 3: A, B Plot of log v/s 1/T 10^3 k and C, D plot of log k v/s 1/D

Table 3: Activation parameters

	2, 4-dichlorobenzoic acid	**p-chlorobenzoic acid**
E_a Kcal mol^{-1}	11.44	11.897
ΔH^* kcal mol^{-1}	10.80	11.294
ΔS^* e.u.	-39.96	-38.752
ΔG kcal mol^{-1}	22.91	23.040
A sec^{-1}	3.176×10^4	5.80×10^4

Effect of varying [Succinic acid]

The kinetic of oxidation of organic acid in presence of succinic acid ionize into two steps & increase the acidity of the reaction, in order to enhance the reaction.



Hence the increase in concentration of succinic acid, increases the rate of reaction because of the electron-withdrawing effect of second-COOH group enhances the acidity of the first COOH[12].

CONCLUSION

The positive values of enthalpy of activation (kΔH^*) indicates the reaction are endothermic in nature. The activation energy is highest for the slowest reaction suggesting that the oxidation reactions are enthaply controlled[13]. The negative entropy of activation (kΔS^*) indicates the oxidation of these reactions are entropy controlled[13]. The plot of ΔH^* v/s ΔS^* is linear.

In the oxidation of 2,4-dichlorobenzoic acid & p-chlorobenzoic acid by chromic acid, the frequency factor lies in the ranges of 3.176×10^4 to 5.8×10^4. Hence, reactions can be described as normal reactions and to suggest that the reactions are not of bimolecular type[14].

The effect of substituents on the rate of oxidation

The reaction products ketones were identified by preparing their 2,4-DNP derivatives and spot test. The kinetic of oxidation of 2, 4-dichlorobenzoic acid is found to have higher than p-chlorobenzoic acid. This is because of resonance effect is stronger than the inductive effect and causes net electron release at para and ortho positions, causes more activation and higher the rate of reaction. The reactivity is thus controlled by stronger resonance effect.[15]

Mechanism

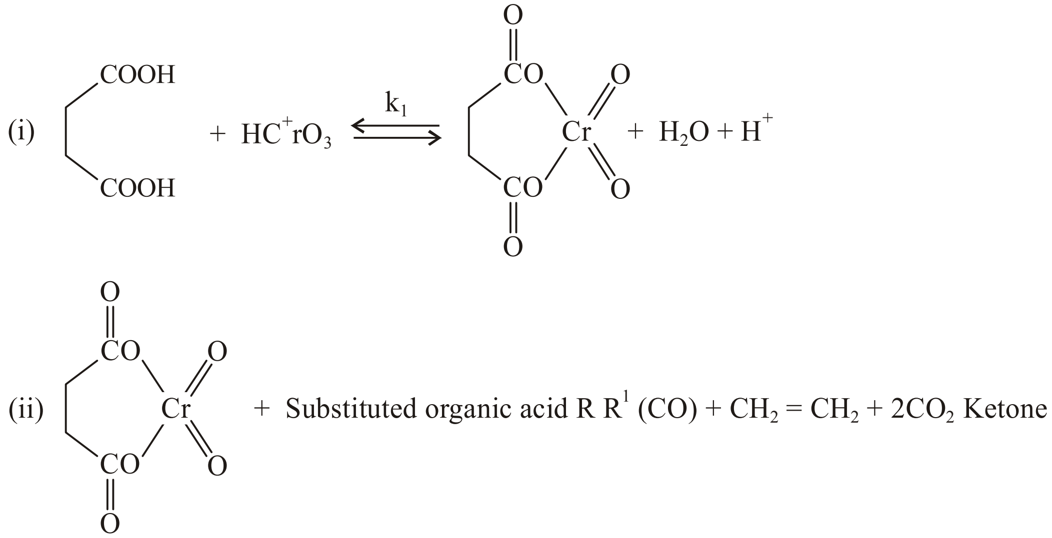
The formation of free radical was neither indicated in the initial stage of the reaction nor at the later stage by addition of mercuric chloride in the rate-determining step. It is therefore reasonable to assume that the reaction of acid dichromate with 2,4-dichlorobenzoic acid and p-chlorobenzoic acid proceeds through simple two electron transfer oxidant.

In consideration of the above discussions stoichiometry and products formed, the reaction mechanism of 2,4-dichlorobenzoic acid and p-chlorobenzoic acid with $HCrO_4^-$ can be explained by much simpler mechanism shown in **Scheme 1**.

(i) 2, 4-dichlorobenzoic or p-chlorobenzoic acid $+ H^+ + HCrO_4^- \xrightleftharpoons{k_1}$ Intermediate complex fast

(ii) Intermediate complex $\xrightleftharpoons[\text{Slow}]{k_1}$ Ketone + H_2CrO_3

Scheme 1



Scheme 2: (In presence of succinic)

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