Oxidation Kinetics and Mechanistic Studies of Organic Acids by Pyridinium Dichromate

[1]Radhika Rathi, [2]Arpita Vyas, [3]Anjali Purohit, [4*]Shweta Vyas and [5]Pradeep K. Sharma

[1]Research Scholar, [2]Research Scholar, [3]Research Scholar [4]Assistant Professor & Research Supervisor, [5]Sr. Professor & Research supervisor
[*]Department of Pure & Applied Chemistry, University of Kota, Kota, India
Chemical kinetics Laboratories, Department of Chemistry, J.N.V. University, Jodhpur, India

ABSTRACT: Kinetics and mechanism of oxidation of formic and oxalic acids by pyridinium dichromate (PDC) have been studied in dimethylsulphoxide. The main product of oxidation is carbon dioxide. The reaction is first order with respect to PDC. Michaelis-Menten type of kinetics were observed with respect to the reductants. The reaction is acid-catalysed and the acid dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of α-deuterio formic acid exhibits a substantial primary kinetic isotope effect ($k_H/k_D = 5.77$ at 298 K). The reaction has been studied in nineteen different organic solvents and the solvent effect has been analysed using Taft's and Swain's multiparametric equations. The temperature dependence of the kinetic isotope effect indicates the presence of a symmetrical cyclic transition state in the rate-determining step. Suitable mechanisms have been proposed.

Key words: Acids, Dichromate, Kinetics, Mechanism, Oxidation

1. INTRODUCTION:

Selective oxidation of organic compounds under non-aqueous conditions is an important reaction in synthetic organic chemistry. For this a number of different chromium (VI) derivatives have been reported [1-4]. One such reported chromium derivative is pyridinium dichromate (PDC)[5]. We have also been interested in the kinetic and mechanistic aspects of the oxidation by complexed Cr(VI) species and several reports on mechanistic aspects of organic functions have already been emanated from our laboratory[6-9]. There seems to be no report on the kinetics and mechanism of oxidation by PDC. Therefore, we report in this paper the kinetics of oxidation of oxalic and formic acids by PDC in dimethylsulphoxide (DMSO) as solvent. The mechanistic aspects are discussed. A suitable mechanism has also been proposed.

2. EXPERIMENTAL

2.1 Materials:

PDC and α-deuterioformic acid (DCO$_2$H or DFA) were prepared by the reported methods [5,10]. Due to the non-aqueous nature of the medium, toluene-p-sulphonic acid (TsOH) was used as a source of hydrogen ions. TsOH is a strong acid and in a polar solvent like DMSO it is likely to be completely ionised. Solvents were purified by the usual methods [11].
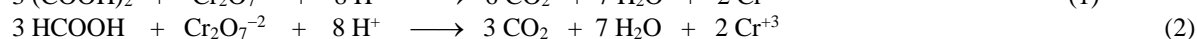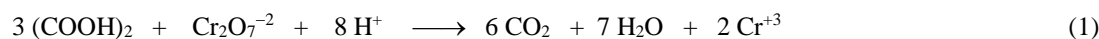
2.2 Stoichiometry:

To determine the stoichiometry, an excess of PDC ($\times 5$ or greater) was reacted with the organic acid in DMSO (100 cm^3) and the amount of residual PDC after the completion of reaction was measured spectrophotometrically at 354 nm. No quantitative determination of carbon dioxide formed was carried out.

2.3 Kinetic measurements:

The reactions were followed under pseudo-first order conditions by keeping a large excess ($\times 15$ or greater) of the organic acid over PDC. The temperature was kept constant to $\pm 0.1^\circ$C. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of PDC spectrophotometrically at 354 nm for up to 80% of the reaction. No other reactant or product has any significant absorption at this wavelength. The pseudo-first-order rate constants, k_{obs}, were evaluated from the linear (r = 0.995 - 0.999) plots of log [PDC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$.

3. RESULTS AND DISCUSSION:

The oxidation of organic acids leads to the formation of carbon dioxide. The stoichiometric determination indicated the following overall reactions:

$$3\,(COOH)_2 \;+\; Cr_2O_7^{-2} \;+\; 8\,H^+ \;\longrightarrow\; 6\,CO_2 \;+\; 7\,H_2O \;+\; 2\,Cr^{+3} \qquad\qquad (1)$$
$$3\,HCOOH \;+\; Cr_2O_7^{-2} \;+\; 8\,H^+ \;\longrightarrow\; 3\,CO_2 \;+\; 7\,H_2O \;+\; 2\,Cr^{+3} \qquad\qquad (2)$$

3.1 Rate Laws:

The reactions were found to be first order with respect to PDC. The reaction rate increases with an increase in [organic acid] but not linearly (Table 1). A plot of 1/[organic acid] versus $1/k_{obs}$ is linear (Figure 1) with an intercept on the rate ordinate. Thus the reactions exhibited Michaelis-Menten type kinetics with respect to the organic acids. This indicates the following overall mechanism (3) and (4) and the rate law (5).

Table 1. Rate constants for the oxidation of oxalic and formic acids by PDC at 298 K

10^3 [PDC] mol dm^{-3}	[Acid] mol dm^{-3}	$10^4\ k_{obs}$ s^{-1} (OA)	(FA)
1.00	0.10	26.7	4.71
1.00	0.20	34.7	6.98
1.00	0.40	40.8	9.20
1.00	0.60	43.3	10.3
1.00	0.80	44.7	10.9
1.00	1.00	45.6	11.4
1.00	1.50	46.8	12.0
1.00	3.00	48.1	12.7
2.00	0.20	35.1	7.02
4.00	0.20	34.2	6.57
6.00	0.20	36.0	7.38
8.00	0.20	35.5	6.75
1.00	0.40	42.3*	9.54*

[a]   contained 0.001 M acrylonitrile
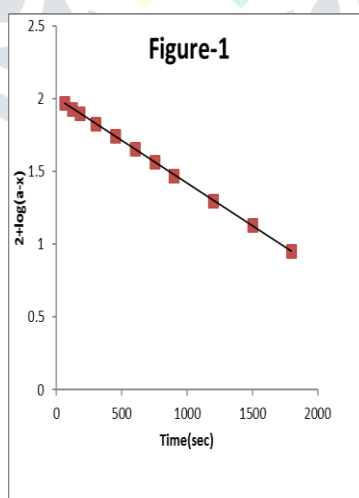
Figure 1. Oxidation of FA acid by PDC: A typical kinetic run

$$\text{Organic acid} \quad + \quad \text{PDC} \quad \overset{K}{\rightleftharpoons} \quad [\text{Complex}] \tag{3}$$

$$[\text{Complex}] \quad \overset{k_2}{\rightarrow} \quad \text{Products} \tag{4}$$

$$\text{Rate} \ = \ k_2\ K[\text{PDC}]\ [\text{Organic acid}]/(1 + K[\text{Organic acid}]) \tag{5}$$

The dependence of the reaction rate on reductant concentration was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. The thermodynamic and activation parameters, at 298 K, were also calculated from the values of K and k_2 respectively, at four different temperatures (Tables 2 and 3). Figure 2 depicts a typical kinetic run.

Table 2. Rate constants for the decomposition of PDC−Organic acid complexes and activation parameters

Acid	$10^4\ k_2\ /\ (\ dm^3\ mol^{-1}\ s^{-1}\ )$				ΔH^* (kJ mol^{-1})	$-\Delta S^*$ (J mol^{-1}K^{-1})	ΔG^* (kJ mol^{-1})
	288 K	298 K	308 K	318 K			
OA	22.5	49.5	99.9	207	53.5±0.5	110±1	86.2±0.4
FA	6.39	13.5	25.2	46.8	47.7±0.5	140±2	89.5±0.4
DFA	1.06	2.34	4.56	9.00	51.4±0.5	143±2	93.8±0.4
k_H/k_D	6.03	5.77	5.53	5.20			

Table 3. Formation constants for the decomposition of PDC−Organic acids complexes and thermodynamic parameters

Acid	K (dm^3 mol^{-1})				$-\Delta H^*$ (kJ mol^{-1})	$-\Delta S^*$ (J mol^{-1}K^{-1})	$-\Delta G^*$ (kJ mol^{-1})
	288 K	298 K	308 K	318 K			
OA	25.2	11.7	6.03	3.24	54.0±0.5	154±2	8.65±0.4
FA	6.12	5.35	4.53	3.69	15.3±0.7	30±2	6.60±0.6
DFA	6.39	5.61	4.77	3.98	14.5±0.6	27±2	6.72±0.4
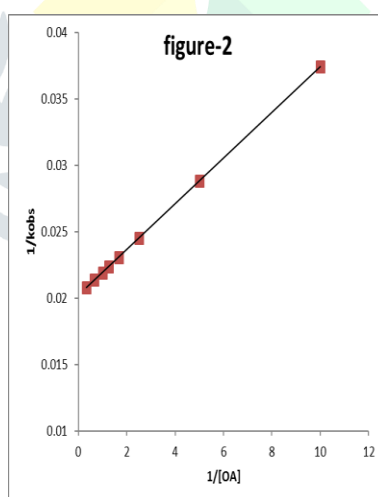
Figure 2. Oxidation of OA acid by PDC: A double reciprocal plot

3.2 Effect of acidity:

The reaction is catalyzed by hydrogen ions. The hydrogen-ion dependence has the form. $k_{obs} = a + b\ [H^+]$ (Table4). The values of a and b, for oxalic acid, are 2.32±0.29 x 10^{-3} s^{-1} and 9.82±0.47 x 10^{-3} mol^{-1} dm^3 s^{-1} respectively ($r^2 = 0.9908$). The corresponding values for the oxidation of formic acid are 0.45±0.03 x 10^{-3} and 1.74±0.05 x 10^{-3} mol^{-1} dm^3 s^{-1} ($r^2 = 0.9982$).

$$\text{Rate} = k_2\ [\text{Organic acid}]\ [\text{PDC}] + k_3\ [\text{Organic acid}]\ [\text{PDC}]\ [H^+] \tag{6}$$

Table 4. Dependence of the reaction rate on hydrogen−ion concentration

[PDC] = 0.001 mol dm^{-3};		[Acid] = 1.0 mol dm^{-3};			Temp. = 298 K	
[H$^+$]/mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00
OA - $10^4 k_{obs}$/s^{-1}	33.3	44.1	63.0	81.0	96.3	126
FA - $10^4 k_{obs}$/s^{-1}	6.21	7.83	11.7	14.4	18.9	21.6

3.3 Induced polymerization of acrylonitrile:

The oxidation of organic acids by PDC, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Further, rate of oxidation was not affected by the addition of acrylonitrile (Table 1). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm^{-3} of 2,6-di-t-butyl-4-methylphenol (butylated hydroxyltoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively. Thus a one-electron oxidation giving rise to free radials is unlikely.

3.4 Kinetic isotope effect:

To ascertain the importance of the cleavage of the α-C-H bond in the rate-determining step, the oxidation of α−deuterioformic acid (DFA) was studied. The results recorded in Tables 2, exhibited a substantial primary kinetic isotope effect (k_H/k_D = 5.77 at 298 K).

3.5 Effect of solvents:

The oxidation of formic acid was studied in 19 different organic solvents. The choice of solvents was limited due to the solubility of PDC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics were similar in all the solvents. The values of formation constants K and the decomposition constants k_2 are recorded in Table 5.

Table 5. Effect of solvents on the oxidation of formic acid by PDC at 298 K

Solvents	K (dm^{-3} mol^{-1})	$10^5 k_{obs}$ (s^{-1})	Solvents	K (dm^{-3} mol^{-1})	$10^5 k_{obs}$ (s^{-1})
Chloroform	5.92	45.7	Toluene	5.58	7.94
1,2-Dichloroethane	5.86	42.6	Acetophenone	5.50	49.0
Dichloromethane	6.03	37.1	THF	5.90	16.6
DMSO	5.35	135	t-Butylalcohol	5.33	18.2
Acetone	6.03	35.5	1,4-Dioxane	5.52	14.8
DMF	5.29	58.9	1,2-Dimethoxyethane	5.39	7.58
Butanone	5.25	22.4	CS$_2$	5.96	3.47
Nitrobenzene	5.88	51.3	Acetic Acid	5.59	17.4
Benzene	5.63	9.77	Ethyl Acetate	5.88	12.9
Cyclohexane	6.12	1.51			

Solvent effect: The rate constants, k_2, in eighteen solvents (CS$_2$ was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (7) of Kamlet et al [12].

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \tag{7}$$

In this equation, π^* represents the solvent polarity, α the hydrogen bond acceptor basicities and β is the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of the 18 solvents, 12 have a value of zero for α. The results of correlation analyses in terms of equation (4), a biparametric equation involving π^* and β, and separately with π^* and β are given below as equation (8) - (11).

$$\log k_2 = -4.14 + 1.71 (\pm 0.20) \pi^* + 0.13 (\pm 0.16) \beta + 0.26 (\pm 0.16) \alpha \tag{8}$$
$$R^2 = 0.8617; \quad sd = 0.18; \quad n = 18; \quad \psi = 0.41$$

$$\log k_2 = -4.20 + 1.62 \,(\pm 0.20)\, \pi^* + 0.21 \,(\pm 0.16)\, \beta \qquad (9)$$
$$R^2 = 0.8342; \quad sd = 0.19; \quad n = 18; \quad \psi = 0.43$$

$$\log k_2 = -4.24 + 1.67 \,(\pm 0.20)\, \pi^* \qquad (10)$$
$$r^2 = 0.8152; \quad sd = 0.24; \quad n = 18; \quad \psi = 0.44$$

$$\log k_2 = -2.86 + 0.50 \,(\pm 0.36)\, \beta \qquad (11)$$
$$r^2 = 0.1100; \quad sd = 0.43; \quad n = 18; \quad \psi = 0.97$$

Here n is the number of data points and ψ is the Exner's statistical parameter [13].

Kamlet's[12] triparametric equation explains ca. 86% of the effect of solvent on the oxidation. However, by Exner's[13] criterion the correlation is not even satisfactory. (cf. equation 8). The major contribution is of solvent polarity. It alone accounts for 81% of the data. Both β and α play relatively minor roles.

The data on solvent effect were also analyzed in terms of Swain's equation [14] of cation- and anion-solvating concept of the solvents also (12).

$$\log k_2 = aA + bB + C \qquad (12)$$

Here A represents the anion-solvating power of the solvent and B the cation-solvating power. C is the intercept term. $(A + B)$ is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of equation (12), separately with A and B and with $(A + B)$.

$$\log k_2 = 1.23 \,(\pm 0.08)\, A + 1.63 \,(\pm 0.06)\, B - 3.89 \qquad (13)$$
$$R^2 = 0.9831; \quad sd = 0.06; \quad n = 19; \quad \psi = 0.14$$

$$\log k_2 = 0.99 \,(\pm 0.54)\, A - 2.98 \qquad (14)$$
$$r^2 = 0.1643; \quad sd = 0.44; \quad n = 19; \quad \psi = 0.94$$

$$\log k_2 = 1.54 \,(\pm 0.22)\, B - 3.47 \qquad (15)$$
$$r^2 = 0.7357; \quad sd = 0.29; \quad n = 19; \quad \psi = 0.53$$

$$\log k_2 = 1.50 \pm 0.07 \,(A + B) - 3.91 \qquad (16)$$
$$r^2 = 0.9634; \quad sd = 0.09; \quad n = 19; \quad \psi = 0.20$$

The rates of decomposition of the complex in different solvents showed an excellent correlation in Swain's equation [cf. eqn.(09)] with the cation- solvating power playing the major role. In fact, the cation-solvation alone account for ca. 73% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A+B), also accounted for ca. 96% of the data. In view of the fact that solvent polarity is able to account for ca. 96% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of log (rate) against the inverse of the relative permittivity is not linear ($r^2 = 0.5364$; $sd = 0.33$; $\psi = 0.70$).

4. MECHANISM

A one-electron oxidation, giving rise to free radicals, is not likely to be operative in this reaction, in view of the failure to induce polymerization of acrylonitrile and recovery of unchanged BHT. The presence of a substantial kinetic isotopic effect confirmed that an α-C-H bond is cleaved in the rate-determining step. The observed kinetics indicate the formation of an intermediate complex in a rapid pre-equilibrium. However, the highly unfavorable entropy term obtained in the complex formation of oxalic acid-PDC reaction suggests that oxalic acid acts as a bidentate ligand and forms a cyclic intermediate complex. In the chromic acid oxidation also, the formation of a cyclic anhydride intermediate, oxalyl chromate, has been postulated [15]. The value of formation constant, $9.5 \, dm^3 \, mol^{-1}$, reported by Hassan and Rocek [15] compares favorably with the values obtained in this investigation. The absence of any effect of a radical scavenger, acrylonitrile, indicates that a hydrogen abstraction mechanism, giving rise to free radicals, is unlikely.

For the formic acid oxidation, the cation-solvating power of the solvents plays a relatively more important role. Therefore, formation of an electron-deficient carbon centre in the transition state is indicated. Thus the decomposition of PDC-formic acid complex may involve a hydride ion transfer via an anhydride intermediate (Scheme 1).

Acid-independent Path (Scheme -1)

$$[Py]_2 Cr_2 O_7 \; + \; HCOOH \rightleftharpoons \left[\; \right] \; (A)$$

Slow

$$H^+ + CO_2 + CrO(OH)OPy + [CrO_3(OPy)]^- \longleftarrow \left[\; \right]^{\#}$$

$$[Py]_2 Cr_2 O_7 \; + \; (COOH)_2 \rightleftharpoons \left[\; \right] \; (B)$$

Slow

$$H^+ + 2CO_2 + CrO(OH)OPy + [CrO_3(OPy)]^-$$

This hydride ion transfer may take place either via an anhydride or by an acyclic process. The involvement of a concerted cyclic process is supported by a study of the temperature dependence of the kinetic isotope effect[16]. The data for protio- and deuterio- formic acids when fitted in the familiar expression $k_H/k_D = A_H/A_D \exp(-\Delta H^*/RT)$ show a direct correspondence with the properties of a symmetrically transition state in which the differences in the activation energies for the protio and deuterio compounds are equal to the differences in the zero point energies of the corresponding C-H and C-D bonds (ca. 4.5 kJ mol^{-1}) and the entropies of the activation of the respective reactions are almost equal [17,18]. Similar phenomena were observed earlier in the oxidation of aliphatic alcohols by butyltriphenyl phosphonium dichromate [19] and of diols by 2,2'-bipyridinium chlorochromate[20]. Bordwell [21] has documented a very cogent evidence against the occurrence of concerted one-step bimolecular processes by hydrogen transfer and it is evident that in the present studies also the hydrogen transfer does not occur by an acyclic biomolecular process. It is well established that intrinsically concerted sigmatropic reactions, characterised by transfer of hydrogen in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen transfer [22]. Littler [23] has also shown that a cyclic hydride transfer, in the oxidation of alcohols by Cr(VI), involves six electrons and, being a Huckel-type system, is an allowed process. Thus a transition state having a planar, cyclic and symmetrical structure can be envisaged for the decomposition of the ester intermediate. Therefore, in the oxidation of organic acids by PDC, the overall mechanism is proposed to involve the formation of a chromate anhydride in a fast pre-equilibrium step and then a decomposition of the anhydride in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (Schemes 1 and 2).

Acid-dependent Path (Scheme - 2)

$$(A) \; + \; H^+ \rightleftharpoons \left[\; \right]$$

Slow

$$H^+ + CO_2 + CrO(OH)OPy + [CrO_3(OPy)]^-$$

$$(B) \; + \; H^+ \rightleftharpoons \left[\; \right]$$

Slow

$$H^+ + 2CO_2 + [Cr(OH)_2 OPy]^+ + [CrO_3(OPy)]^-$$

The observed negative value of entropy of activation also supports the proposed mechanism. As the charge separation takes place in the transition state, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy [24].

Initially Cr(VI) is reduced to Cr(IV). It is likely to react with another Cr(VI) to generate Cr(V) which is then reduced in a fast step to the ultimate product Cr(III). Such a sequence of reactions in Cr(VI) oxidations is well known.[25]

5. ACKNOWLEDGEMENTS

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