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Journal of Advanced Scientific Research

Available online through http://www.sciensage.info

ISSN
0976-9595
Research Article

OXIDATION KINETICS AND MECHANISTIC STUDIES OF ORGANIC ACIDS BY 2-PICOLINIUM CHLOROCHROMATE

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ABSTRACT

Kinetics and mechanism of oxidation of formic and oxalic acids by 2-picolinium chlorochromate (PiCC) have been studied in dimethylsulphoxide. The main product of oxidation is carbon dioxide. The reaction is first order with respect to PiCC. 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. 76 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.

Keywords: Acids, Halochromate, Kinetics, Mechanism, Oxidation.

1. INTRODUCTION

Mild and selective oxidation of organic series of compounds under non-aqueous reaction conditions is an important reaction in synthetic organic chemistry. For this a number of different chromium (VI) reagents with various counter ions have been reported in literature [1-4]. One such reported chromium derivative is 2-picolinium chlorochromate (PiCC) [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 PiCC. Therefore, we report in this paper the kinetics of oxidation of oxalic and formic acids by PiCC in dimethylsulphoxide (DMSO) as solvent. The mechanistic aspects are discussed. A suitable mechanism has also been proposed.

2. EXPERIMENTAL

2.1. Materials and Methods:

PiCC and α-deuterioformic acid (DCO_2H 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 PiCC (× 5 or greater) was reacted with the organic acid in DMSO (100 cm^3) and the amount of residual PICC 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 (×15 or greater) of the organic acid over PICC. The temperature was kept constant to ±0.1°C. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of PICC 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 [PiCC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ± 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:

$(COOH)_2 + O_2CrClO^-PicH^+ \longrightarrow 2\ CO_2 + H_2O + OCrClO^-PicH^+$ (1)

$HCOOH + O_2CrClO^-PicH^+ \longrightarrow CO_2 + H_2O + OCrClO^-PicH^+$ (2)

PiCC undergoes two-electron change. This is in accordance with the earlier observations with structurally similar pyridinium chlorochromate (PCC) [12] and pyridinium fluorochromate (PFC) [13]. It has already been shown that both PCC and PFC act as two electron oxidants and are reduced to chromium (IV) species by determining the oxidation state of chromium by magnetic susceptibility, ESR and IR studies.

3.1. Rate Laws

The reactions were found to be first order with respect to PiCC. The reaction rate increases with an increase in [organic acid] but not linearly (Table 1). Fig. 1 depicts a typical kinetic run. A plot of 1/[organic acid] versus $1/k_{obs}$ is linear (Fig. 2) 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).

$$\text{Organic acid} + \text{PICC} \underset{k_2}{\overset{K}{\leftrightarrows}} [\text{Complex}] \quad (3)$$

$$[\text{Complex}] \rightarrow \text{Products} \quad (4)$$

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

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

10^3 [PICC] mol dm^{-3}	[Acid] mol dm^{-3}	$10^+ k_{obs}$ s^{-1}	
		(OA)	(FA)
1.00	0.10	23.4	4.03
1.00	0.20	30.7	5.99
1.00	0.40	36.5	7.92
1.00	0.60	39.0	8.88
1.00	0.80	40.3	9.45
1.00	1.00	41.2	9.83
1.00	1.50	42.4	10.4
1.00	3.00	43.7	11.6
2.00	0.20	29.7	5.76
4.00	0.20	31.5	6.21
6.00	0.20	28.8	5.85
8.00	0.20	30.6	6.03
1.00	0.40	35.1*	8.01*

[a] *contained 0.001 M acrylonitrile*

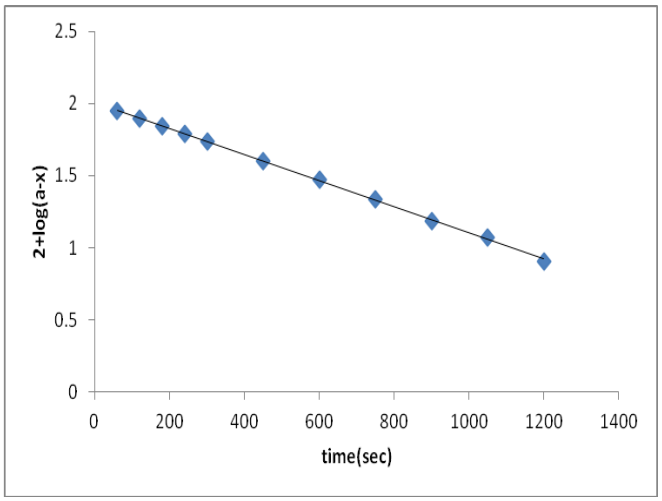


Fig. 1: Oxidation of FA by PiCC: A typical kinetic run

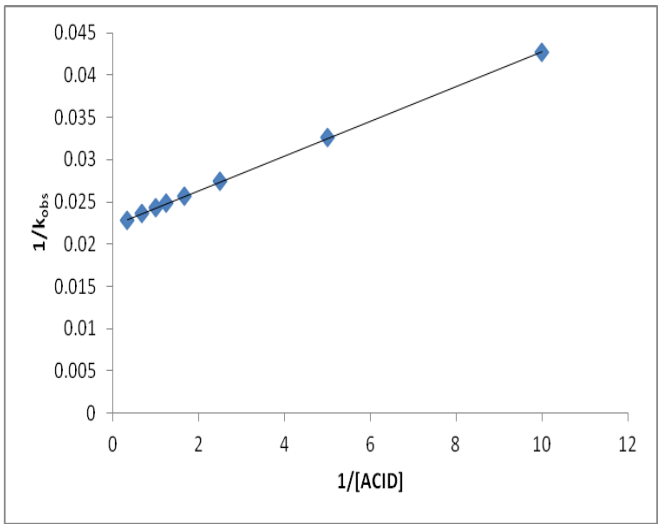


Fig. 2: Oxidation of OA by PiCC: A double reciprocal plot

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).

3.2. Effect of acidity

The reaction is catalyzed by hydrogen ions. The hydrogen-ion dependence has the form. $k_{obs} = a + b[H^+]$ (Table 4). The values of a and b, for oxalic acid, are $2.07\pm0.19 \times 10^{-3}$ s^{-1} and $8.45\pm0.31 \times 10^{-3}$ mol^{-1} dm^3 s^{-1} respectively ($r^2 = 0.9947$). The corresponding values

for the oxidation of formic acid are 0.39±0.04 x 10^{-3} and 1.51±0.06 x 10^{-3} mol^{-1} dm^3 s^{-1} (r^2 = 0.9929).

Rate = k_2 [Organic acid] [PiCC]+k_3 [Organic acid] [PiCC] [H^+] (6)

Table 2: Rate constants for the decomposition of PICC-Organic acid complexes and activation parameters

Acids	10^4 k_2 / (dm^3 mol^{-1} s^{-1})				ΔH^*	$-\Delta S^*$	ΔG^*
	288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J $mol^{-1}K^{-1}$)	(kJ mol^{-1})
OA	20.7	45.0	92.7	198	54.5±0.7	107±2	86.4±0.6
FA	5.85	11.7	22.5	42.3	47.6±0.2	142±1	89.7±0.1
DFA	0.98	2.03	4.23	8.25	51.8±0.4	142±1	94.0±0.3
k_H/k_D	5.97	5.76	5.49	5.13			

Table 3: Formation constants for the decomposition of PICC-Organic acids complexes and thermo-dynamic parameters

Acids	K (dm^3 mol^{-1})				$-\Delta H^*$	$-\Delta S^*$	$-\Delta G^*$
	288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J $mol^{-1}K^{-1}$)	(kJ mol^{-1})
OA	23.4	10.8	5.85	3.06	53.6±0.7	152±2	8.49±0.6
FA	6.03	5.25	4.41	3.63	15.4±0.6	30±2	6.55±0.5
DFA	6.12	5.35	4.50	3.71	15.2±0.7	29±2	6.60±0.5

Table 4: Dependence of the reaction rate on hydrogen-ion concentration

[PICC] = 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}	28.8	38.7	54.9	71.1	84.6	108
FA -10^4 k_{obs}/s^{-1}	5.31	6.66	10.8	12.6	16.2	18.9

3.3. Induced polymerization of acrylonitrile

The oxidation of organic acids by PICC, 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 Table 2, exhibited a substantial primary kinetic isotope effect (k_H/k_D = 5.76 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 PiCC 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.

3.6. 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 [14].

$$log\ k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad (7)$$

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 eqn. (7), a biparametric equation involving π* and β, and separately with π* and β are given below as equation (8)-(11).

Table 5: Effect of solvents on the oxidation of formic acid by PICC 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	5.39	44.7	Toluene	5.50	8.71
1,2-Dichloroethane	5.88	41.7	Acetophenone	5.96	45.7
Dichloromethane	6.01	37.2	THF	5.82	15.1
DMSO	5.25	117	t-Butylalcohol	5.62	21.4
Acetone	6.12	31.6	1,4-Dioxane	5.99	16.2
DMF	5.79	63.1	1,2-Dimethoxyethane	5.90	11.2
Butanone	5.84	22.4	CS_2	5.69	4.47
Nitrobenzene	5.58	47.9	Acetic Acid	5.55	17.4
Benzene	5.39	11.2	Ethyl Acetate	5.49	14.8
Cyclohexane	6.00	1.44			

$\log k_2 = -4.14 + 1.71 (\pm 0.20) \pi^* + 0.13 (\pm 0.16) \beta + 0.26 (\pm 0.16) \alpha$ (8)

$R^2 = 0.8617$; sd = 0.18; n = 18; $\psi = 0.41$

$\log k_2 = - 4.20 + 1.62 (\pm 0.20) \pi^* + 0.21 (\pm 0.16) \beta$ (9)

$R^2 = 0.8342$; sd = 0.19; n = 18; $\psi = 0.43$

$\log k_2 = - 4.24 + 1.67 (\pm 0.20) \pi^*$ (10)

$r^2 = 0.8152$; sd = 0.24; n = 18; $\psi = 0.44$

$\log k_2 = - 2.86 + 0.50 (\pm 0.36) \beta$ (11)

$r^2 = 0.1100$; sd = 0.43; n =18; $\psi = 0.97$

Here n is the number of data points and ψ is the Exner's statistical parameter [15].

Kamlet's [14] triparametric equation explains ca. 86% of the effect of solvent on the oxidation. However, by Exner's [15] criterion the correlation is not even satisfactory. (cf. eq. 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 [16] of cation- and anion-solvating concept of the solvents also (12).

$\log k_2 = aA + bB + C$ (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).

$\log k_2 = 1.23 (\pm 0.08) A + 1.63 (\pm 0.06) B - 3.8$ (13)

$R^2 = 0.9831$; sd = 0.06; n = 19; $\psi = 0.14$

$\log k_2 = 0.99 (\pm 0.54) A - 2.98$ (14)

$r^2 = 0.1643$; sd = 0.44; n = 19; $\psi = 0.94$

$\log k_2 = 1.54 (\pm 0.22) B - 3.47$ (15)

$r^2 = 0.7357$; sd = 0.29; n = 19; $\psi = 0.53$

$\log k_2 = 1.50 \pm 0.07 (A + B) - 3.91$ (16)

$r^2 = 0.9634$; sd = 0.09; n = 19; $\psi = 0.20$

The rates of decomposition of the complex in different solvents showed an excellent correlation in Swain's equation [cf. eqn.(12)] 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; ψ = 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-PICC 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 [17]. The value of formation constant, 9.5dm^3 mol^{-1}, reported by Hassan and Rocek [17] compares favorably with the values obtained in this investigation. The

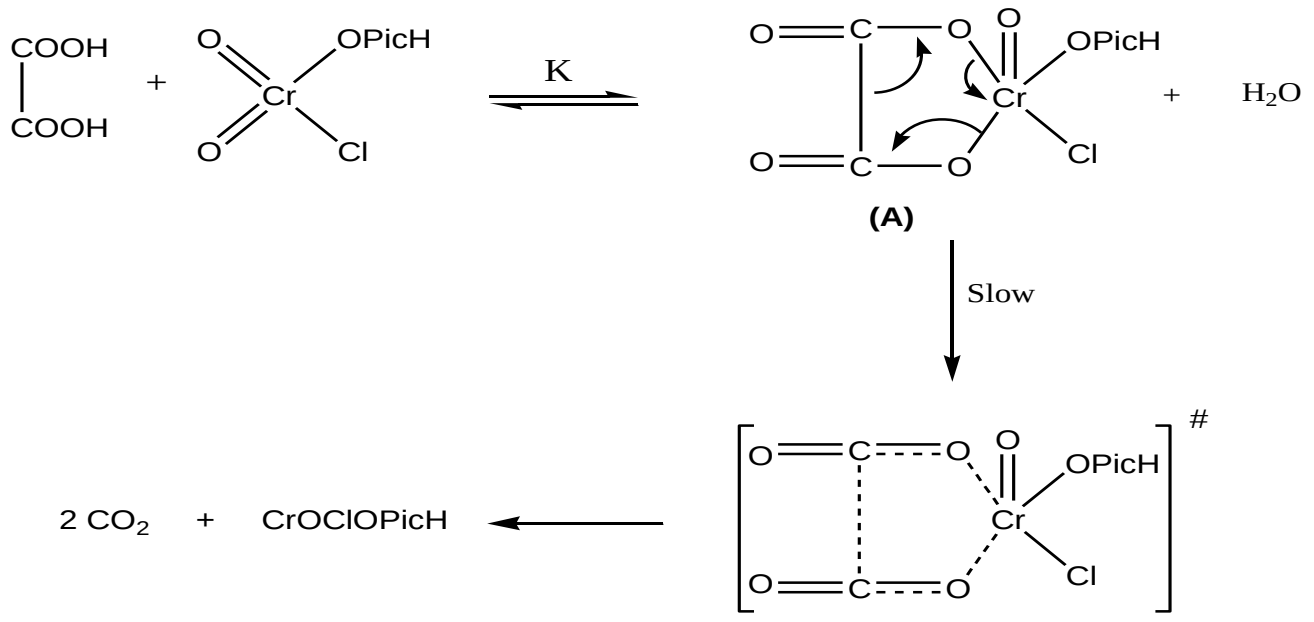
absence of any effect of a radical scavenger, acrylonitrile, indicates that a hydrogen abstraction mechanism, giving rise to free radicals, is unlikely.

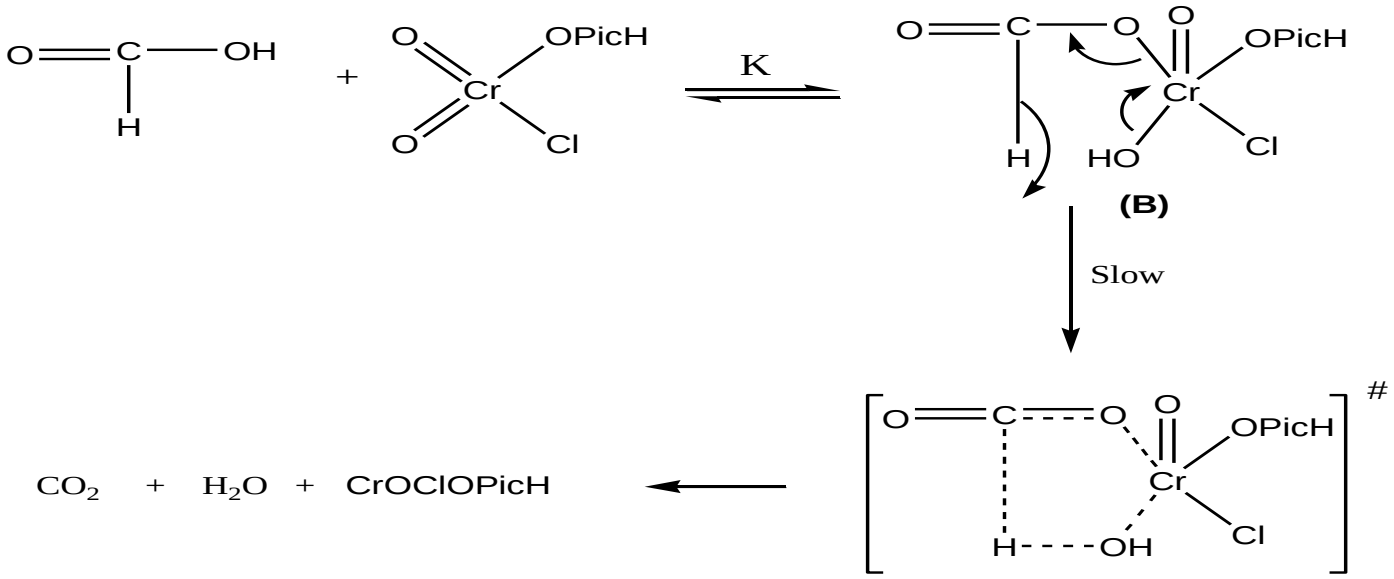
For the formic acid oxidation, the cation-solvating power of the solvents plays a relatively more important role. Therefore, formation of an electron-deficient carbon centre in the transition state is indicated. Thus the decomposition of PiCC-formic acid complex may involve a hydride ion transfer via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

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 [18]. 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 [19, 20]. Similar phenomena were observed earlier in the oxidation of aliphatic alcohols by butyltriphenyl phosphonium dichromate [21] and of diols by 2,2'-bipyridinium chlorochromate [22]. Bordwell [23] 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 [24]. Littler [25] 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 PiCC, 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).

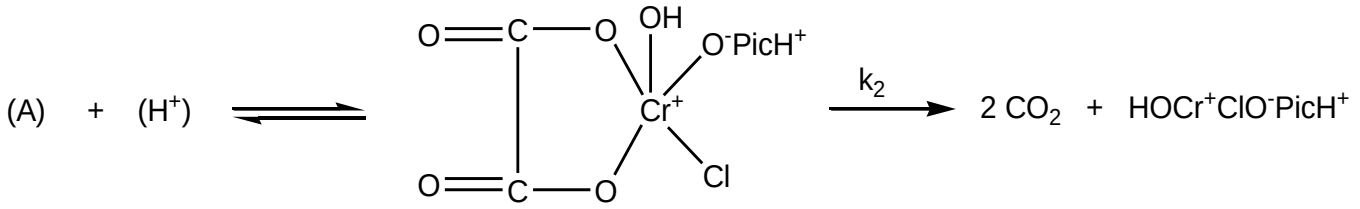
The observed negative value of entropy of activation also supports the proposed mechanism. As the charge separation takes place in the transition state, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy [26].

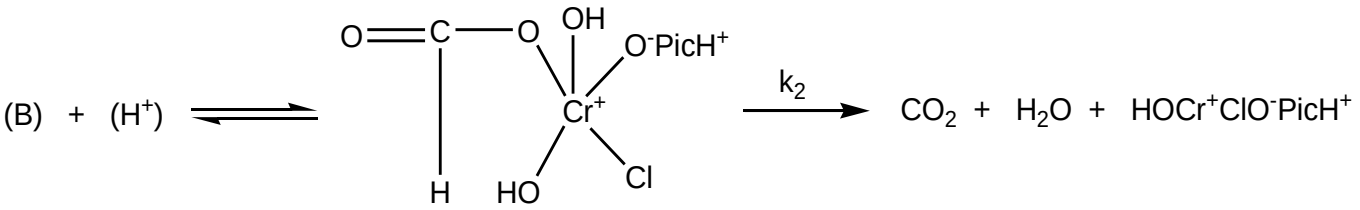
Scheme - 1 - Acid - Independent Path





Scheme - 2 - Acid - Dependent Path





5. CONCLUSION

The present reaction is proposed to proceed through a hydride-ion transfer from reductant to the oxidant through an anhydride intermediate in the rate-determining step. A α-C-H bond in formic acid is cleaved in the rate-determining step. Both protonated and unprotonated PiCC are the reactive oxidising species.

6. ACKNOWLEDGEMENTS

Thanks are due to UGC, New Delhi, India for financial support in the form of JRF to DK, UGC-BSR-One Time Grant to AC and to Head, Department of Chemistry, J.N.V. University, Jodhpur for necessary facilities.

Conflict of interest

None declared

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