OXIDATION STUDIES OF SOME PHOSPHORUS OXYACIDS BY TRIPROPYLAMMONIUM CHLOROCHROMATE: ESTABLISHMENT OF REACTIVE REDUCING SPECIES

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Abstract: Oxidation of lower oxyacids of phosphorus by Tripropylammonium chlorochromate (TPACC) in dimethylsuloxide (DMSO) leads to the formation of corresponding oxyacids with phosphorus in a higher oxidation state. The reaction exhibits 1:1 stoichiometry. The reaction is first order with respect to TPACC. A Michaelis-Menten type of kinetics was observed with respect to the reductants. The reaction does not induce polymerization of acrylonitrile. Reactions are catalysed by hydrogen ions. The hydrogen-ion dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of deuteriated phosphinic and phenylphosphinic acids exhibited a substantial primary kinetic isotope effect. The oxidation was studied in nineteen different organic solvents. The solvent effects were analysed in terms of Taft's and Swain's multiparametric equations. The effect of solvent indicats the solvent polarity plays a major role in the process. It has been shown that the pentacoordinated tautomer of the phosphorus oxyacid is the reactive reductant and it has been concluded that tricoordinated forms of phosphorus oxyacids does not participate in the oxidation process. A mechanism involving transfer of a hydride ion in the rate-determining step has been proposed.

Keywords: Halochromates, Kinetics, Mechanism, Oxidation, Phosphorus acids. Reducing species

1. INTRODUCTION:

Inorganic salts of Cr(VI) are well known oxidants for the organic compounds. However these salts are rather drastic and non-selective oxidants. Further, they are insoluble in most organic solvents. Thus miscibility is a problem. To overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in organic synthesis as mild and selective oxidants in non-aqueous solvents[1-5]. Tripropylammonium chlorochromate (TPACC) is also one of such compounds used for the oxidation of primary and secondary alcohols[6]. We have been interested in the kinetic and mechanistic aspects of the oxidation by complexed Cr(VI) species and several studies on halochromates including that of TPACC, have already reported from our group[7-10]. Further the lower oxyacids are reported to exist in two tautomeric forms[11-12], and it is of interest to determine the nature and species of the oxyacid acid which is involved in the oxidation process. There seems to be no report on the oxidation of oxyacids of phosphorous by TPACC, therefore we report in this article the kinetics of oxidation of phosphinic (PA), phenylphosphinic (PPA) and phosphorous (POA) acids by TPACC in dimethylsulphoxide (DMSO) as a solvent. A suitable mechanism has also been proposed.

2. EXPERIMENTAL

2.1 Materials:

The phosphorous oxyacids were commercial products and used as received. TPACC was prepared by the reported method [6] and its purity was checked by an iodometric method and melting point determination. Deuteriated phosphinic (DPA) and phosphorus acids (DPOA) were prepared by repeatedly dissolving the acid in deuterium oxide (BARC, 99.4%) and evaporating water and the excess of deuterium oxide *in* vacuo[13]. The isotopic purity of the deuterated PA and POA, as determined from their NMR spectra, was 92±5% and 94±5% respectively. Due to the non-aqueous nature of the medium, toluene-p-sulphonic acid was used as a source of hydrogen ions. TsOH is a strong acids and in non-polar solvents like DMSO, it is likely to be completely ionized. Other solvents were purified by their usual methods.

2.2 Stoichiometry:

The oxidation of lower oxyacids of phosphorus leads to the formation of corresponding oxyacids containing phosphorus in a higher oxidation state. Reaction mixtures were prepared containing a known excess of phosphinic or phosphorous acids. On completion of the reaction, the amount of phosphorous formed in the oxidation of phosphinic acid and the residual reductant in

the oxidation of phosphorous acids were determined by reported method[14]. To determine the stoichiometry of the oxidation of PPA, a known excess of TPACC was treated with PPA and the residual TPACC was determined spectrophotometrically at 346 nm after the completion of the reaction. The oxidation state of Chromium in the completely reduced reaction mixture, determined by iodometric titration, was 3.95±0.15. The oxidation exhibited 1:1 stoicheometry and the overall reaction may therefore, be written as:

$$RPH(O)OH + O_2CrClO^-N^+(C_3H_7)_3 \longrightarrow R\ P\ H\ (O)(OH)_2 + OCrClO^-N^+(C_3H_7)_3 \qquad (1)$$

(R = H, Ph or OH)

TPACC undergoes two-electron change. This is in accordance with the earlier observations with structurally similar other halochromates also. It has already been shown that both pyridinium chlorochromate (PCC)[15] and pyridinium fluorochromate(PFC)[16] act as two electron oxidant and are reduced to chromium (IV) species determining the oxidation state of chromium by magnetic susceptibility, ESR and IR studies.

2.3 Kinetic measurements:

The reactions were studied under pseudo-first order conditions by keeping an excess (× 15 or greater) of the [oxyacid] over [TPACC]. The solvent was DMSO, unless specified otherwise. The reactions were studied at constant temperature (0.1 K) and were followed by monitoring the decrease in the [TPACC] spectrophotometrically at 346 nm for up to 80% reaction. Pseudo-first-order rate constants, k_{obs}, were evaluated from linear plots ($r > 0.9990$) of log[TPACC] against time. Duplicate kinetic runs showed that the rates were reproducible to within ±3%. The second order rate constants, k_2 were determined from the relation : $k_2 = k_{obs}/$ [oxyacid].

3. RESULTS AND DISCUSSION

3.1 Rate laws:

The reactions were found to be first order with respect to TPACC. The reactions exhibited the Michaelis-Menten type of kinetics with respect to the oxyacids (Table 1). A plot of 1/[oxyacid] *versus* 1/k_{obs} is linear with an intercept at the rate- ordinate (Figure 1). This indicates the following overall mechanism (equation 2 and 3) and the rate law (4).

Table 1 – Rate constants for the oxidation of Oxyacids of Phosphorous by TPACC at 298 K

10^4[TPACC] (mol dm^{-3})	[Oxyacid] (mol dm^{-3})	$10^3 k_{obs}$ PA	PPA	POA
1.00	0.10	2.03	7.54	0.70
1.00	0.20	3.23	10.9	1.08
1.00	0.40	4.51	14.1	1.48
1.00	0.60	5.20	15.6	1.69
1.00	0.80	5.62	16.4	1.81
1.00	1.00	6.03	16.9	1.89
1.00	1.50	6.36	17.9	2.03
1.00	3.00	6.87	18.8	2.17
2.00	0.40	4.68	13.5	1.51
4.00	0.40	4.32	14.4	1.44
6.00	0.40	4.41	14.0	1.53
8.00	0.40	4.59	13.9	1.35
1.00	0.20	3.42*	11.7*	1.17*
*contained 0.001 M acrylonitrile				

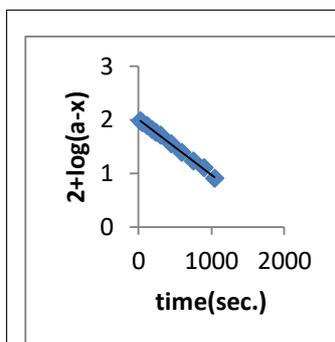Figure 1. Oxidation of POA acid by TPACC: A typical kinetic run
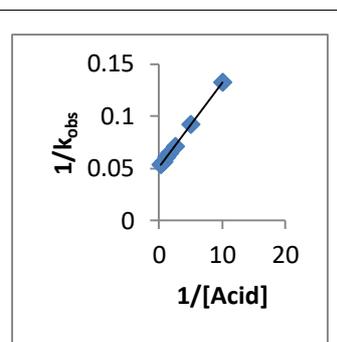
Figure 2. Oxidation of POA acid by TPACC: A double reciprocal plot

$$Oxyacid + TPACC \overset{K}{\rightleftarrows} [complex] \qquad (2)$$

$$[Complex] \overset{k_2}{\longrightarrow} products \qquad (3)$$
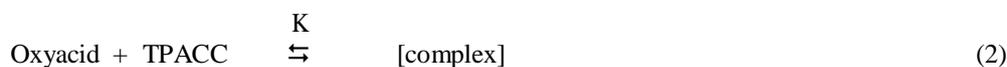
$$Rate = k_2 K [TPACC][Oxyacid]/ (1 + K [Oxyacid]) \qquad (4)$$

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

Table – 2 Formation constants and thermodynamic parameters of the aliphatic Oxyacid – TPACC complexes.

K (dm³ mol⁻¹)				$-\Delta H^*$	$-\Delta S^*$	$-\Delta G^*$
Acid	288 K	298 K	308 K	318 K	(kJ mol⁻¹)	(J mol⁻¹K⁻¹)	(kJ mol⁻¹)

Acid	288 K	298 K	308 K	318 K	$-\Delta H^*$ (kJ mol⁻¹)	$-\Delta S^*$ (J mol⁻¹K⁻¹)	$-\Delta G^*$ (kJ mol⁻¹)
PA	4.41	3,81	3.15	2.58	16.2±0.6	35±2	6.61±0.3
PPA	6.84	6.15	5.40	4.70	12.0±0.4	18±1	6.69±0.2
POA	4.95	4.31	3.60	2.97	15.5±0.6	32±2	6.57±0.4
DPA	4.05	3.55	2.93	2.43	15.6±0.7	34±2	6.66±0.3
DPOA	5.58	4.90	4.32	3.70	12.8±0.4	22±1	6.42±0.3

Table – 3 Rate constants and activation parameters of the aliphatic Oxyacid – TPACC complexes.

$10^3 k_2$ / (dm³ mol⁻¹ s⁻¹)				ΔH^*	$-\Delta S^*$	ΔG^*
Acid	288 K	298 K	308 K	318 K	(kJ mol⁻¹)	(J mol⁻¹K⁻¹)	(kJ mol⁻¹)

Acid	288 K	298 K	308 K	318 K	ΔH^* (kJ mol⁻¹)	$-\Delta S^*$ (J mol⁻¹K⁻¹)	ΔG^* (kJ mol⁻¹)
PA	3.78	7.47	14.4	27.9	48.1±0.5	125±2	85.1±0.4
PPA	11.7	19.8	32.4	55.8	36.9±0.7	154±1	82.7±0.6
POA	1.26	2.34	4.50	8.28	45.4±0.6	143±2	88.0±0.5
DPA	0.61	1.27	2.62	5.37	52.6±0.6	124±2	89.5±0.5
DPOA	0.21	0.40	0.82	1.58	49.0±0.9	146±3	92.3±0.7
k_H/k_D	6.12	5.88	5.50	5.19			
k_H/k_D	6.00	5.85	5.48	5.24			

3.2 Induced polymerization of acrylonitrile/ Test for free radicals:

The oxidation of oxyacids, in an atmosphere of nitrogen, failed to induce polymerisation of acrylonitrile. Further, the addition of acrylonitrile did not affect the rate. This indicates that a one-electron oxidation, giving rise to free radicals, is unlikely in the present reaction (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⁻³of 2,6-di-t-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

3.3 Kinetic isotope effect:

To ascertain importance of the cleavage of the P-H bond in the rate-determining step, oxidation of deuteriated PA and POA was studied. Results showed the presence of a substantial primary kinetic isotope effect (Table 2).

3.4 Effect of acidity:

The reaction is catalysed by hydrogen ions (Table 4). The hydrogen ion dependence has taking the form: $k_{obs} = a + b[H^+]$. The values of a and b, for PPA, are $9.14\pm0.49 \times 10^{-4}$ s⁻¹ and $17.7\pm0.81 \times 10^{-4}$ mol⁻¹ dm³ s⁻¹ respectively at 298 K($r^2 = 0.9918$).

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

[TPACC] = 0.001 mol dm⁻³;		Oxyacids] = 1.0 mol dm⁻³;				Temp. = 298 K	
	[H⁺]/mol dm⁻³	0.10	0.20	0.40	0.60	0.80	1.00
$10^4 k_{obs}$/s⁻¹	PA	2.34	2.61	3.42	4.14	5.05	5.82
	PPA	8.55	9.72	12.6	15.3	18.9	21.6
	POA	0.81	0.90	1.17	1.44	1.75	2.03

3.5 Effect of solvents:

The oxidation of PPA was studied in 19 different organic solvents. The choice of solvents was limited due to the solubility of TPACC 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 formation constants K and decomposition constants k_2 at 298 K for the oxidation of PPA

are recorded in Table 5. The formation constant of the intermediate complex, K, did not vary much with the solvent but the rate constant, k_2, exhibited much variation in values with different solvents.

Table – 5 Effect of solvents on the oxidation of PPA by TPACC at 298 K

Solvents	K (dm^{-3} mol^{-1})	$10^4 k_{obs}$ (s^{-1})	Solvents	K (dm^{-3} mol^{-1})	$10^4 k_{obs}$ (s^{-1})
Chloroform	5.85	33.9	Toluene	4.52	12.0
1,2-Dichloroethane	4.59	51.3	Acetophenone	5.45	79.4
Dichloromethane	6.03	41.7	THF	5.49	24.5
DMSO	6.15	198	t-Butylalcohol	6.44	13.8
Acetone	5.83	47.9	1,4-Dioxane	5.39	20.9
DMF	5.76	95.5	1,2-Dimethoxyethane	5.04	11.0
Butanone	5.49	37.2	CS$_2$	4.47	5.25
Nitrobenzene	4.63	63.1	Acetic Acid	5.18	2.82
Benzene	5.72	14.8	Ethyl Acetate	5.88	17.0
Cyclohexane	4.15	0.85			

3.6 Reactive oxidizing species:

The observed hydrogen-ion dependence suggests that the reaction follows two mechanistic pathways, one is acid-independent and the other is acid dependent. The acid-catalysis may well be attributed to a protonation of TPACC to yield a protonated Cr(VI) species which is a stronger oxidant and electrophile (5).

$$[O_2CrCl\ O^-N^+(C_3H_7)_3] \quad + \quad H^+ \quad \leftrightarrows \quad [HOCrCl\ O^-N^+(C_3H_7)_3]^+ \quad\quad (5)$$

Formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar PCC[7] and QFC[8].

3.7 Solvent effect:

The rate constants of the oxidation, 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 (LESR) of Kamlet and Taft[17] (5).

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad\quad (6)$$

In this equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α 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 analysis in terms of equation (6), a biparametric equation involving π^* and β, and separately with π^* and β are given below as equations (7) – (10).

$$\log k_2 = -3.90 + 1.86\,(\pm 0.25)\,\pi^* + 0.35\,(\pm 0.21)\,\beta + 0.46\,(\pm 0.19)\,\alpha \quad\quad (7)$$
$R^2 = 0.8616;\quad sd = 0.23;\quad n = 18;\quad \psi = 0.41$

$$\log k_2 = -3.99 + 2.03\,(\pm 0.27)\,\pi^* + 0.19\,(\pm 0.22)\,\beta \quad\quad (8)$$
$R^2 = 0.8057;\quad sd = 0.26;\quad n = 18;\quad \psi = 0.47$

$$\log k_2 = -3.97 + 2.08\,(\pm 0.26)\,\pi^* \quad\quad (9)$$
$r^2 = 0.7961;\quad sd = 0.26;\quad n = 18;\quad \psi = 0.46$

$$\log k_2 = -2.83 + 0.55(\pm 0.46)\,\beta \quad\quad (10)$$
$r^2 = 0.0841;\quad sd = 0.55;\quad n = 18;\quad \psi = 0.98$

Here n is the number of data points and is the Exner's statistical parameter[18].

Kamlet's[17] triparametric equation explains *ca.* 86% of the effect of solvent on the oxidation. However, by Exner's criterion[18] the correlation is not even satisfactory (*cf.* equation (7). The major contribution is of solvent polarity. It alone accounted for *ca.* 80% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's[19] equation (11) of cation- and anion-solvating concept of the solvents also.

$$\log k_2 = aA + bB + C \qu\quad (11)$$

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 (11), separately with A and B and with (A + B).

$$\log k_2 = 0.35 (\pm 0.05) \text{ A} + 2.17 (\pm 0.03) \text{ B} - 3.85 \tag{12}$$
$$R^2 = 0.9961; \quad sd = 0.04; \quad n = 19; \quad \psi = 0.06$$

$$\log k_2 = 0.04 (\pm 0.72) \text{ A} - 2.89 \tag{13}$$
$$r^2 = 0.0002; \quad sd = 0.58; \quad n = 19; \quad \psi = 1.03$$

$$\log k_2 = 2.14 (\pm 0.07) \text{ B} - 3.68 \tag{14}$$
$$r^2 = 0.9823; \quad sd = 0.08; \quad n = 19; \quad \psi = 0.14$$

$$\log k_2 = 1.56 \pm 0.23 (\text{A} + \text{B}) - 2.67 \tag{15}$$
$$r^2 = 0.7239; \quad sd = 0.30; \quad n = 19; \quad \psi = 0.54$$

The rates of oxidation of PPA in different solvents showed an excellent correlation in Swain's equation (cf. equation 11) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 99% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.* 72% of the data. In view of the fact that solvent polarity is able to account for *ca.* 72% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of $\log k_2$ against the inverse of the relative permittivity is not linear ($r^2 = 0.5187$; $sd = 0.40$; $\psi = 0.71$).

3.8 Reactive reducing species:

Lower oxyacids of phosphorus are reported to exist in two tautomeric forms[11,12]. The predominant species is the penta-coordinated form (A). The value[20] of the equilibrium constant, K_t, in aqueous solutions, is of the order of 10^{-12}.

$$\underset{\text{(A)}}{\text{RPH(O)OH}} \quad \overset{K_t}{\rightleftarrows} \quad \underset{\text{(B)}}{\text{R} - \text{P} - (\text{OH})_2} \tag{16}$$

Hence two alternative broad mechanisms can be formulated. Assuming in the first instance pentacoordinated tautomer (A) as the reactive reducing species, the following mechanism may be proposed which leads to the rate law (19).

$$\text{TPACC} + \text{RPH(O)OH} \quad \overset{K_a}{\rightleftarrows} \quad [\text{complex}] \tag{17}$$

$$[\text{complex}] \quad \overset{k_a}{\longrightarrow} \quad \text{Products} \tag{18}$$

$$\text{Rate} = k_a K_a [\text{Oxyacid}]_0 [\text{TPACC}]/ 1 + K_t K_a [\text{oxyacid}]_0 \tag{19}$$

Where $[\text{oxyacid}]_0$ represents the initial concentration of the oxyacid. Equation (19) can be reduced to (20) as $1 \gg K_t$.

$$\text{Rate} = k_a K_a [\text{Oxyacid}]_0 [\text{TPACC}]/ 1 + K_a [\text{oxyacid}]_0 \tag{20}$$

Another mechanism can be formulated assuming the tricoordinated form (B) as the reactive reducing species.

$$\text{TPACC} + \text{RP(OH)}_2 \quad \overset{K_b}{\rightleftarrows} \quad [\text{complex}] \tag{21}$$

$$[\text{complex}] \quad \overset{k_b}{\longrightarrow} \quad \text{Products} \tag{22}$$

$$\text{Rate} = k_b K_b K_t [\text{Oxyacid}]_0 [\text{TPACC}]/ 1 + K_t + K_t K_b [\text{oxyacid}]_0 \tag{23}$$

This mechanism leads to the rate law (24), which can be reduced to (20), again acknowledging

$$1 \gg K_t. \text{Rate} = k_b K_b K_t [\text{Oxyacid}]_0 [\text{TPACC}]/1 + K_t K_b [\text{oxyacid}]_0 \tag{24}$$

Therefore, in the plots of $1/k_{obs}$ versus $1/[\text{oxyacid}]$, the slope and the intercept are equivalent to the values given below. Slope = $(k_b K_b K_t)^{-1}$, intercept = $1/k_b$, intercept/slope = $K_b K_t$.

It is thus seen that $k_2 = k_a = k_b$, which means that the rate constant for the decomposition of the complex is not affected by the reactive form of the phosphorus oxyacid. However, $K = K_t K_b$, so that $K_b = 10^{-12} K$ or K_b for PPA should have value of the order of 10^{12}. Generally chromium (VI) does not give rise to extensive and highly stable series of complexes[21]. Further, the reported values[22,23] of the formation constant for the chromic acid-PPA complexes are 6.12 ± 0.3, 11 ± 2 and 19 ± 4 dm^3 mol^{-1}. Similarly, the formation constant of complex[24] between triethylamine and Cr(VI) diperoxide derivative is 0.0014 dm^3 mol^{-1}. Thus the very high value of formation constant of present oxidant-phosphorus oxyacid complex is improbable, and it is highly unlikely that the tricoordinated form is involved in the oxidation process.

4. MECHANISM

The absence of any effect of the radical scavenger on the reaction rate and the failure to induce polymerization of acrylonitrile point against a one-electron oxidation giving rise to free radicals. The presence of a substantial kinetic isotope effect confirms the cleavage of a P–H bond in the rate-determining step. A preferential cleavage of a P–H bond, in the rate-determining step, is likely in view of the relatively high bond dissociation energy of the O-H bond. The mean value of the bond dissociation energy of an O-H bobd[25] is 460 kJ mol^{-1}, while that for a P-H bond[26] is 321 kj mol^{-1}. Therefore, a hydride transfer mechanism may be proposed for the oxidation of these oxyacids. The proposed mechanism involving the hydride ion transfer in the rate determining step is also supported by theobserved major role of cation-solvating power of the solvents.

It has already been shown that both PCC[15] and PFC[16] 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.

In the chromic acid oxidation of phosphinic acid Sengupta and Chakaldar[23] postulated the participation of tricoordinatedtautomer. However, no evidence has been presented and author did not take into consideration the small value of K_t. However, Sharma an Mehrotra[22] reported that in the chromic acid oxidation, it is not possible to point the reactive form of the compound. The formation of a phosphinium ion in the rate determining step has been postulated by the earlier workers[22,23].

Scheme - 1
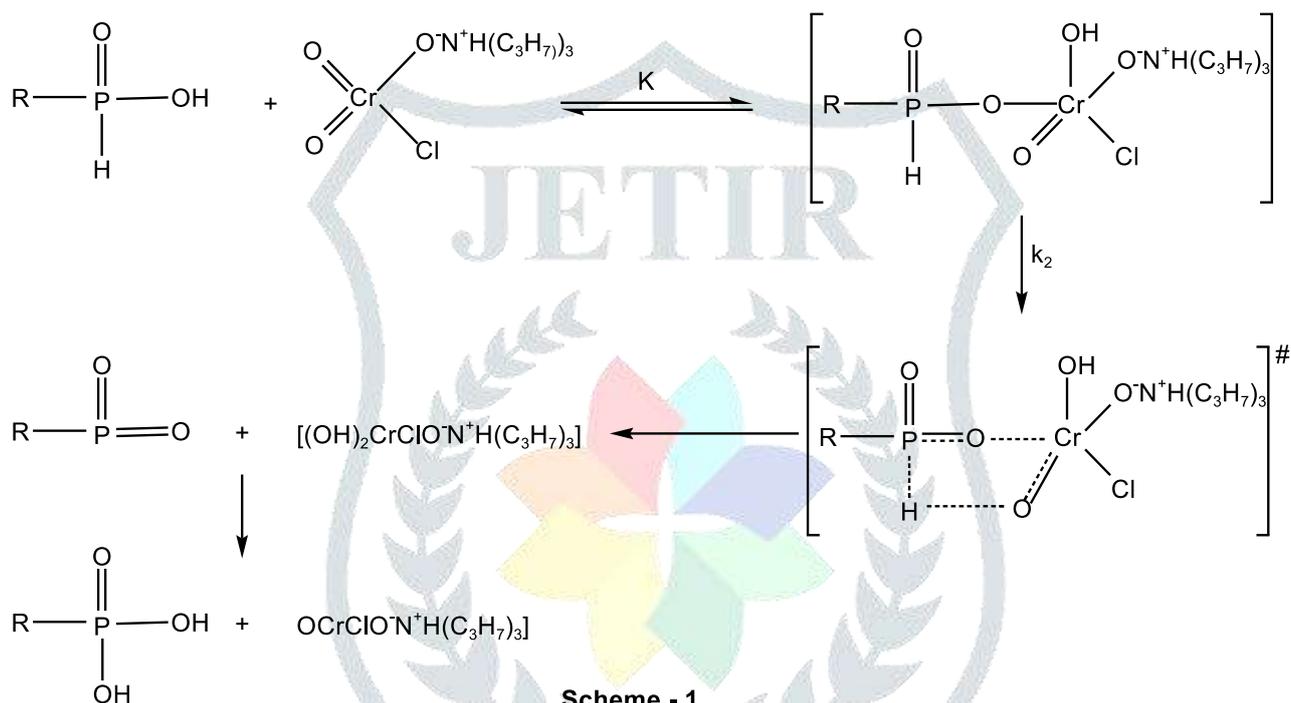
The rate of oxidation follows the order PPA > PA > POA. The faster rate of PPA could be explained on the basis of stabilisation of a positively polarized phosphorus, in the transition state, by the phenyl group through resonance. The slower rate of POA may well be due to the electron-withdrawing nature of hydroxyl group causing an electron-deficiency at the phosphorus atom. This makes the departure of an anion more difficult. A perusal of the activation parameters in Table 3 revealed that the reaction ratesare controlled mainly by the entropy of activation.

It is of interest to compare the mode of oxidation of lower oxyacids of phosphorus by PFC[27], PCC[28] and TPACC. Theoxidation by PCC exhibited the second order kinetics, first with respect to each reactant. The oxidation by PFC and TPACC presented similar kinetic picture i.e. Michaelis-Menten type of kinetics. The rate-law, acid dependence, kinetic isotope effect aresimilar in both the cases. In all the three oxidations, excellent correlation were obtained in terms of Swain's equation with the cationsolvating power of the solvents playing the major role.

5. CONCLUSION

The oxidation of lower oxyacids of phosphorus involve the hydride ion transfer in the rate determining step, further it is also supported by the observed major role of cation-solvating power of the solvents.

6. ACKNOWLEDGEMENTS

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