

Oxidation Kinetics of some Lower Oxyacids of Phosphorus by Picolinium Chlorochromate: Determination of Reactive Reducing Species

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Picolinium chlorochromate (PICC) in dimethylsuloxide (DMSO) oxidizes lower oxyacids of phosphorus, forming matching oxyacids with phosphorus in a higher oxidation state. The reaction shows a stoichiometry of 1:1. In relation to PICC, the response is first order. Regarding the reductants, a kinetics of the Michaelis-Menten type was noticed. Acrylonitrile does not undergo polymerization as a result of the reaction. Hydrogen ions function as catalysts for reactions. The form of the hydrogen-ion dependency is: $k_{\text{obs}} = a + b[\text{H}^+]$. Deuterated phosphinic and phenylphosphinic acids showed a significant primary kinetic isotope impact during oxidation. Nineteen different organic solvents were used to study the oxidation. The multiparametric equations of Taft and Swain were used to analyze the solvent effects. The influence of the solvent shows that the polarity of the solvent is crucial to the process. The penta-coordinated tautomer of the phosphorus oxyacid has been shown to be the reactive reductant, and it has been determined that the tricoordinated forms of phosphorus oxyacids do not take part in the oxidation process. It has been hypothesized that the rate-determining phase involves the transfer of a hydride ion.

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 largenumber 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]. Picolinium chlorochromate (PICC) 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 PICC, have already been reported from our group [7-10]. Further, the lower oxyacids are reported to exist in two

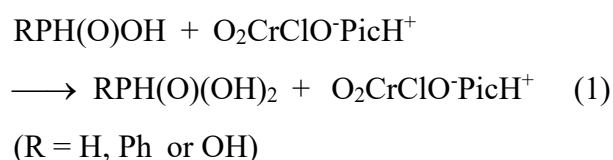
tautomeric forms [11-12], and it is of interest to determine the nature and species of the oxy-acid acid that is involved in the oxidation process. There seems to be no report on the oxidation of oxyacids of phosphorous by PICC, therefore we report in this article the kinetics of oxidation of phosphinic (PA), phenylphosphinic (PPA), and phosphorous (POA) acids by PICC in dimethylsulphoxide (DMSO) as a solvent. A suitable mechanism has also been proposed.

Experimental

Materials: The phosphorous oxyacids were commercial products and used as received. PICC was prepared by the reported method [6] and its purity was checked by an iodometric method and melting point determination. Deuteriated phosphinic (DPA) and duteriated 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 vacuum* [13]. The isotopic purity of the deuterated PA and POA, as determined from their NMR spectra, was $93\pm5\%$ and $95\pm5\%$ 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 acid and in non-polar solvents like DMSO, it is likely to be completely ionized. Other solvents were purified by their usual methods.

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 the reported method [14]. To determine the stoichiometry of the oxidation of PPA, a known excess of PICC was treated with PPA and the residual PICC was determined spectrophotometrically at 365 nm after the completion of the reaction. The oxidation state of Chromium in the completely reduced reaction mixture, determined by iodometric titration, was 3.90 ± 0.15 . The oxidation exhibited 1:1 stoichiometry and the overall reaction may, therefore, be written as:



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

Kinetic measurements: The reactions were studied under pseudo-first-order conditions by

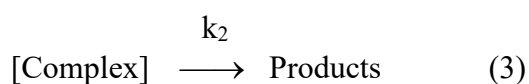
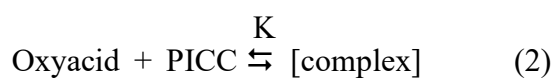
keeping an excess ($\times 15$ or greater) of the [oxy-acid] over [PICC]. The solvent was DMSO, unless specified otherwise. The reactions were studied at constant temperature (0.1 K) and were followed by monitoring the decrease in the [PICC] spectrophotometrically at 365 nm for up to 80% reaction. Pseudo-first-order rate constants, k_{obs} , were evaluated from linear plots ($r > 0.9990$) of $\log [\text{PICC}]$ against time. Duplicate kinetic runs showed that the rates were reproducible to within $\pm 3\%$.

Results

Rate laws: The reactions were found to be first order concerning PICC. The reactions exhibited the Michaelis-Mententype of kinetics for the oxyacids (**Table 1**). A plot of $1/[\text{oxy-acid}]$ versus $1/k_{\text{obs}}$ is linear with an intercept at the rate-ordinate (**Figure 1**). This indicates the following overall mechanism (Equations 2 and 3) and the rate law (4).

Table 1. Rate constants for the oxidation of Oxyacids of Phosphorous by PICC at 298 K

$10^3[\text{PICC}]$	[Oxy-acid]	$10^3 k_{\text{obs}}$		
(mol dm ⁻³)	(mol dm ⁻³)	PA	PPA	POA
1.00	0.10	2.71	9.54	0.91
1.00	0.20	4.14	13.5	1.35
1.00	0.40	5.76	18.0	1.89
1.00	0.60	6.57	19.8	2.16
1.00	0.80	7.02	20.5	2.34
1.00	1.00	7.47	21.5	2.43
1.00	1.50	7.92	22.5	2.58
1.00	3.00	8.55	23.4	2.79
2.00	0.40	5.58	17.1	1.90
4.00	0.40	5.67	17.6	1.82
6.00	0.40	5.49	18.2	1.80
8.00	0.40	5.85	17.9	1.98
1.00	0.20	4.41*	13.9*	1.41*
*contained 0.001 M acrylonitrile				



$$\text{Rate} = k_2 K [\text{PICC}][\text{Oxyacid}] / (1 + K [\text{Oxyacid}]) \quad (4)$$

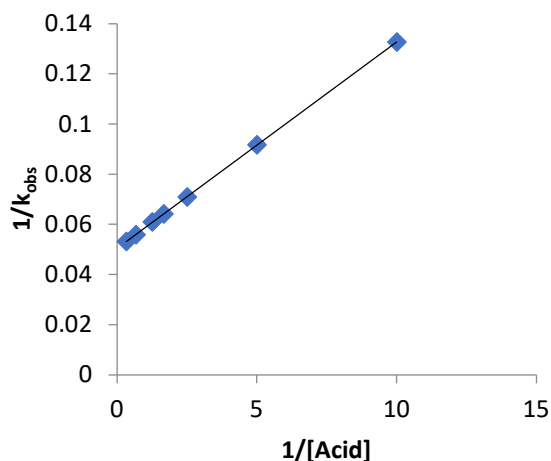


Figure 1. Oxidation of POA by PICC: A double reciprocal plot

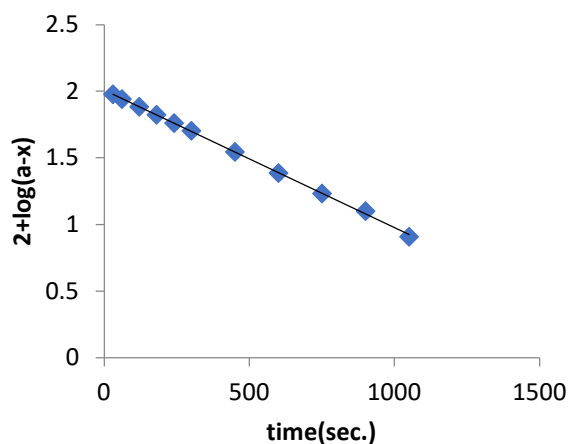


Figure 2. Oxidation of POA by PICC: A typical kinetic run

The dependence on reaction rate on reductant concentration was studied at four different temperatures and the values 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 Oxyacid – PICC complexes.

Acid	$K \text{ (dm}^3 \text{ mol}^{-1}\text{)}$				$-\Delta H^*$	$-\Delta S^*$	$-\Delta G^*$
	288 K	298 K	308 K	318 K	(kJ mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	(kJ mol ⁻¹)
PA	4.88	4.14	3.42	2.71	17.3±0.9	38±3	5.97±0.7
PPA	6.77	6.03	5.31	5.45	12.2±0.5	18±2	6.92±0.4
POA	5.03	4.23	3.69	2.97	16.4±0.7	35±2	6.07±0.6
DPA	5.22	4.50	3.81	3.06	15.9±0.7	33±2	6.18±0.6
DPOA	5.76	4.95	4.23	3.51	14.6±0.5	28±2	6.41±0.4

Table 3. Rate constants and activation parameters of the Oxy-acid – PICC complexes.

$10^3 k_2 / (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$					ΔH^*	$-\Delta S^*$	ΔG^*
Acid	288 K	298 K	308 K	318 K	(kJ mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	(kJ mol ⁻¹)
PA	4.66	9.17	17.1	32.4	46.4±0.5	148±2	90.3±0.4
PPA	14.4	25.0	42.3	73.8	38.7±0.6	165±2	87.8±0.5
POA	1.53	2.98	5.67	10.8	47.0±0.5	155±2	83.1±0.4
DPA	0.79	1.61	3.20	6.35	50.2±0.5	149±2	94.6±0.4
DPOA	0.27	0.57	1.10	2.15	49.2±0.5	162±2	97.2±0.4
$k_H/k_D(\text{PA})$	5.90	5.70	5.34	5.10			
$k_H/k_D(\text{POA})$	5.67	5.21	5.15	5.02			

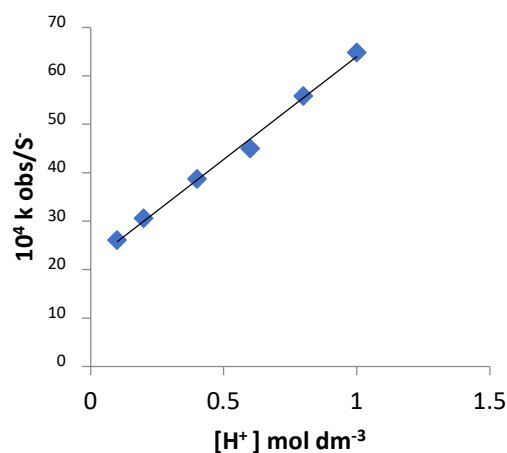
Induced polymerization of acrylonitrile/
Test for free radicals: The oxidation of oxyacids, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile did not affect the rate. This indicates that one-electron oxidation, giving rise to free radicals,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

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

Effect of acidity: the reaction is catalyzed by hydrogen ions (Table 4). The hydrogen ion dependence has taken the form: $k_{\text{obs}} = a + b[\text{H}^+]$. The values of *a* and *b*, for PPA, are $9.14 \pm 0.49 \times 10^{-3} \text{ s}^{-1}$ and $17.7 \pm 0.81 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ respectively at 298 K ($r^2 = 0.9918$) (**Figure 3**).

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

[PICC] = 0.001 mol dm ⁻³ ;		[PPA] = 1.0 mol dm ⁻³ ;		Temp. = 288 K			
[H ⁺]/mol dm ⁻³		0.10	0.20	0.40	0.60	0.80	1.00
10 ⁴ k _{obs} /s ⁻¹		26.1	30.6	38.7	45.0	55.8	64.8

**Figure 3.** Effect of Acidity on the Oxidation of PPA by PICC

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 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 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.

Discussions:

Solvent effects:

The rate constants of the oxidation, k_2 , in eighteen solvents (CS₂ 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] (Equation 5).

$$\log k_2 = A_0 + \rho\pi^* + b\beta + a\alpha \quad (5)$$

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. The results of correlation analysis in terms of equation (5), a bi-parametric equation involving π^* and β , and separately with π^* and β are given below as equations (6) – (9).

Table 5. Effect of solvents on the oxidation of PPA by PICC at 288 K

Solvents	K (dm ⁻³ mol ⁻¹)	10 ⁴ k ₂ (dm ³ mol ⁻¹ s ⁻¹)	Solvents	K (dm ⁻³ mol ⁻¹)	10 ⁴ k ₂ (dm ³ mol ⁻¹ s ⁻¹)
Chloroform	5.58	27.5	Toluene	4.59	7.94
1,2-Dichloroethane	4.95	36.3	Acetophenone	5.44	60.2
Dichloromethane	6.12	41.7	Tetrahydrofuran	5.94	15.5
DMSO	6.75	144	t-Butylalcohol	6.03	9.12
Acetone	5.85	33.9	1,4-Dioxane	5.96	18.2
DMF	5.67	63.1	1,2-Dimethoxyethane	5.40	7.08
Butanone	5.94	22.4	Carbondisulfide	4.77	4.26
Nitrobenzene	4.68	51.3	Acetic Acid	5.88	3.16
Benzene	5.76	12.0	Ethyl Acetate	5.80	13.2
Cyclohexane	4.14	0.71			

$$\log k_2 = -2.97 + 1.92 (\pm 0.23) \pi^* + 0.21 (\pm 0.19) \beta + 0.32 (\pm 0.18) \alpha \quad (6)$$

$$R^2 = 0.8744; \quad sd = 0.21; \quad n = 18; \quad \psi = 0.39$$

$$\log k_2 = -2.90 + 2.04 (\pm 0.23) \pi^* + 1.01 (\pm 0.19) \beta \quad (7)$$

$$R^2 = 0.8455; \quad sd = 0.22; \quad n = 18; \quad \psi = 0.42$$

$$\log k_2 = -2.92 + 2.06 (\pm 0.22) \pi^* \quad (8)$$

$$r^2 = 0.8427; \quad sd = 0.22; \quad n = 18; \quad \psi = 0.41$$

$$\log k_2 = -1.92 + 0.47 (\pm 0.45) \beta \quad (9)$$

$$r^2 = 0.0637; \quad sd = 0.54; \quad n = 18; \quad \psi = 0.99$$

Here n is the number of data points and ψ is the Exner's statistical parameter [18]. Kamlet's¹³ tri-parametric equation explains *ca.*

87% of the effect of solvent on oxidation. However, by Exner's criterion [18] the correlation is not even satisfactory (*cf.* equation (6)). The major contribution is solvent polarity. It alone accounted for *ca.* 84% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analyzed in terms of Swain's [19] equation (10) of cation- and anion-solvating concept of the solvents.

$$\log k_2 = aA + bB + C \quad (10)$$

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 analyzed in terms of equation (10), separately with A and B and with (A + B).

$$\log k_2 = 0.50 (\pm 0.05) A + 2.08 (\pm 0.04) B - 2.74 \quad (11)$$

$$R^2 = 0.9953; \text{sd} = 0.04; n = 19; \psi = 0.07$$

$$\log k_2 = 0.21 (\pm 0.69) A - 1.83 \quad (12)$$

$$r^2 = 0.0053; \text{sd} = 0.56; n = 19; \psi = 1.02$$

$$\log k_2 = 2.05 (\pm 0.10) B - 2.90 \quad (13)$$

$$r^2 = 0.9643; \text{sd} = 0.11; n = 19; \psi = 0.19$$

$$\log k_2 = 1.56 \pm 0.20 (A + B) - 2.79 \quad (14)$$

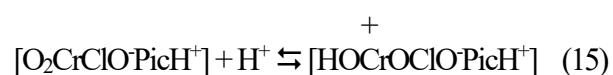
$$r^2 = 0.7748; \text{sd} = 0.26; n = 19; \psi = 0.49$$

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.* 77% of the data. In view of the fact that solvent polarity is able to account for *ca.* 77% 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 ($r^2 = 0.5096$; $\text{sd} = 0.39$; $\psi = 0.72$).

Reactive Species:

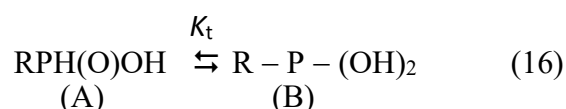
Reactive oxidizing species: The observed hydrogen-ion dependence suggests

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 PICC to yield a protonated Cr (VI) species which is a stronger oxidant and electrophile (15).

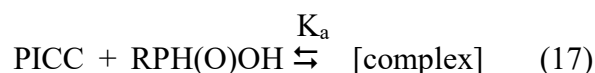


Formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar pyridinium chlorochromate (PCC) [7] and quinolinium fluorochromate (QFC) [8].

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} .



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

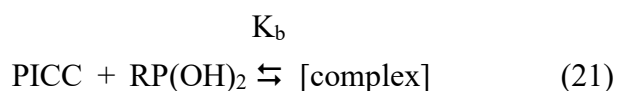


$$\text{Rate} = \frac{k_a K_a [\text{Oxy-acid}]_0 [\text{PICC}]}{1 + K_t K_a [\text{oxy-acid}]_0} \quad (19)$$

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

$$\text{Rate} = k_a K_a [\text{Oxy-acid}]_0 [\text{PICC}] / 1 + K_a [\text{Oxy-acid}]_0 \quad (20)$$

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



$$\text{Rate} = k_b K_b K_t [\text{Oxy-acid}]_0 [\text{PICC}] / 1 + K_t + K_t K_b [\text{Oxy-acid}]_0 \quad (23)$$

This mechanism leads to the rate law (24), which can be reduced to (20), again acknowledging $1 \gg K_t$.

$$\text{Rate} = k_b K_b K_t [\text{Oxy-acid}]_0 [\text{PICC}] / 1 + K_t K_b [\text{Oxy-acid}]_0 \quad (24)$$

Therefore, in the plots of $1/k_{\text{obs}}$ versus $1/[\text{Oxy-acid}]$, 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 oxy-acid. However, $K = K_t K_b$, so that $K_b = 10^{-12} K$ or K_b for PPA should have a value of the order of 10^{12} . Generally, chromium (VI) does not give rise to an 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 $19 \pm 4 \text{ dm}^3 \text{ mol}^{-1}$. Similarly, the formation constant of complex [24] between tri-ethylamine and Cr(VI) di-peroxide derivative is $0.0014 \text{ dm}^3 \text{ mol}^{-1}$. Thus the very high value of the formation constant of the present oxidant-phosphorus oxy-acid complex is improbable, and it is highly unlikely that the tri-coordinated form is involved in the oxidation process.

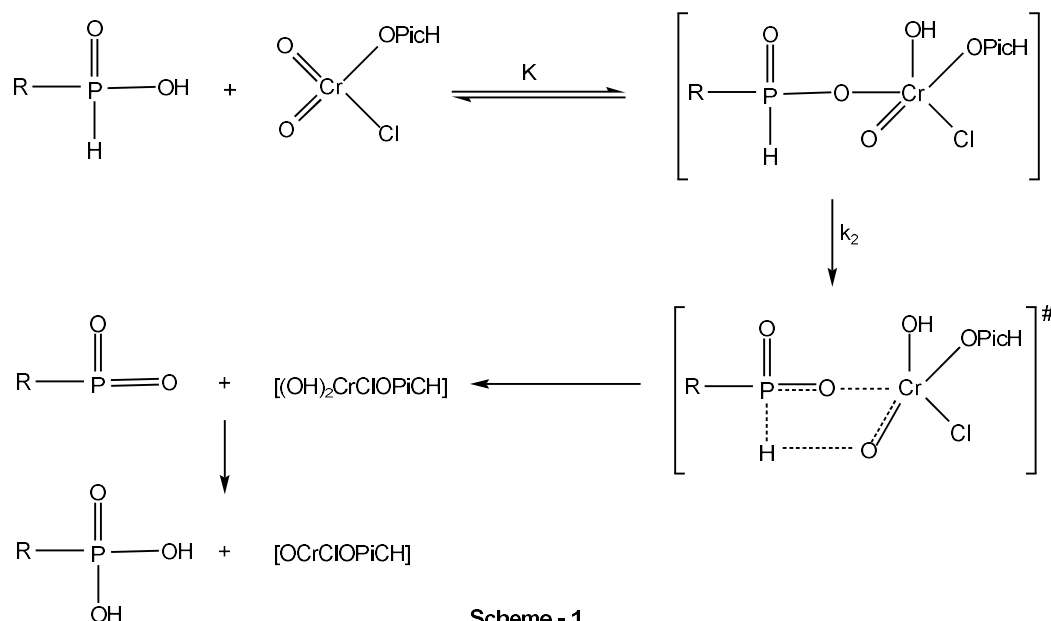
Mechanism

The absence of any effect of the radical scavenger on the reaction rate and the failure to induce polymerization of acrylonitrile point against one-electron oxidation give 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 bond [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 the observed major role of the cation-solvating power of the solvents.

It has already been shown that both PCC

[15] and PFC [16] act as two electron-changed 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 tri-coordinated tautomer. However, no evidence has been

presented and the author did not take into consideration the small value of K_t . However, Sharma and Mehrotra [22] reported that in 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 rates of oxidation follow the order $\text{PPA} > \text{PA} > \text{POA}$. The faster rate of PPA could be explained based on the stabilization of 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 the 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 rates are controlled mainly by the entropy of activation.

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

Conclusion

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

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