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Kinetics and Mechanism of Oxidation of Phosphinic, Phenylphosphinic, and Phosphonic Acids by Pyridinium Chlorochromate

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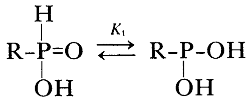
Oxidation of the lower oxyacids of phosphorus by pyridinium chlorochromate (PCC) results in the formation of the corresponding higher oxyacids of phosphorus. The reaction is of first order with respect to PCC and the oxyacid. The reaction is catalyzed by hydrogen ions, $k_{obs}=a+b[H^+]$. The reaction exhibited a substantial primary kinetic isotope effect. The rates in 19 different organic solvents have been analyzed using Kamlet–Taft's and Swain's equations. It has been found that the cation-solvating power of the solvents plays a predominant role. It is proposed that the "inactive" tautomer of the phosphorus oxyacids is the reactive species. Transfer of a hydride ion from the P–H bond to PCC, in the rate-determining step, has been proposed.

The three lower oxyacids of phosphorus viz, phosphinic (**1**), phenylphosphinic (**2**), and phosphonic (**3**) are known to exhibit tautomerism (Reaction 1).[1,2]



$$\mathrm{R{-}\overset{\displaystyle H}{\underset{\displaystyle OH}{P}}{=}O} \underset{}{\overset{K_t}{\rightleftharpoons}} \mathrm{R{-}\underset{\displaystyle OH}{P}{-}OH} \qquad (1)$$

(A) (B)

1: R = H; **2**: R = Ph; **3**: R = OH

Generally, tautomer (A) is called the "inactive" tautomer and (B) the "active" one. The equilibrium constant, K_t, has[3] a value ca. 10^{-12}. Chromic acid[4] oxidation of **1** has been reported to involve the "active" form as the reactive species. Recently, however, Sharma and Mehrotra[5] reported that in the chromic acid oxidation of **2**, it is not possible to pinpoint the reactive form of the oxyacid. Moreover, in several oxidations the participation of the "inactive" form has been proposed e.g., oxidation by permanganate[6] and vanadium(V).[7] Pyridinium chlorochromate (PCC) is a versatile oxidant.[8] We have previously reported the kinetics of oxidation of alcohols[9] and hydroxy acids[10] by PCC. There seems to be no report on the mechanism of oxidation of phosphorus compounds by PCC. In this paper, we report the kinetics of the oxidation of the three lower oxyacids of phosphorus by PCC in dimethyl sulfoxide (DMSO) as a solvent. The mechanistic aspects are discussed.

Experimental

Materials. The oxyacids were commercial products (Fluka) and were used as such. Their solution in DMSO was standardized, after dilution with water, by alkalimetry. PCC was prepared and purified as reported.[8] *p*-Toluenesulfonic acid (TsOH) was as a source of hydrogen ions. Organic solvents were purified by the usual methods.[11]

The P–H bonds in **1** and **3** were deuteriated by dissolving the acid in deuterium oxide (BARC, 99.4% purity) and evaporationg the excess of deuterium oxide and water in vacuo.[12] The isotopic purity of deuteriated **1** and **3** as determined by their NMR spectra, were 91±5 and 93±4 percents respectively.

Stoichiometry. The oxidation of lower oxyacids of phosphorus by PCC leads to the formation of the corresponding higher oxyacids of phosphorus. Reaction mixtures, containing a known excess of **1** or **2**, were prepared. After the completion of the reaction, phosphonic and phenylphosphonic acid formed was determined by the reported method.[13] To determine the stoichiometry of the oxidation of **3**, reaction mixtures containing a know excess of PCC were prepared and after completion of the reaction, residual PCC was determined iodometrically.

Kinetic Measurements. Pseudo-first-order conditions were attained by keeping a large excess of the phosphorus compound over PCC. The solvent was DMSO, unless specified otherwise. The reactions were followed at constant temperature (±0.1 K), by monitoring the decrease in the concentration of PCC at 352 nm. Pseudo-first-order rate constants, k_{obs}, were evaluated from the least squares plots of log[PCC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. The second order rate constants, k_2, were evaluated from the relation $k_2=k_{obs}/[\text{oxyacid}]$. Corrections were applied to the rate constants of the deuteriated compounds for the ordinary hydrogen content.

Results and Discussion

The oxidation of **1** results in the formation of **3**. **1** is oxidized at ca. five times the rate of oxidation of **3**. To reduce the effect of further oxidation of **3** on the kinetics and stoichiometry of the oxidation of **1**, the [oxyacid] was always kept in large excess over [PCC].

The oxidation exhibited a 1 : 1 stoichiometry (Table 1) and the overall reaction may be written as Eq. 2.

$$\mathrm{RH_2PO_2 + C_5H_5NHCrO_3Cl \longrightarrow RH_2PO_3 + C_5H_5NHCrO_2Cl} \qquad (2)$$

The oxidation is first order with respect to PCC. The individual kinetic runs follow first order kinetics. Further, k_{obs} is independent of the initial concentration of PCC. The reaction is of first order with respect to the substrate also. The reaction is catalyzed by hydrogen ions (Tables 2—4) and the hydrogen ion dependence has the following form (Eq. 3).

Table 1. Stoichiometry of the Oxidation of Phosphorus Oxyacids by PCC

[PCC] mol dm^{-3}	[Oxyacid] mol dm^{-3}	[Product] mol dm^{-3}	[Product] / [PCC]
	Phosphinic acid		
0.020	0.50	0.019	0.95
0.040	0.50	0.046	1.15
0.050	0.50	0.056	1.12
	Mean=1.07±0.10		
	Phenylphosphinic acid		
0.020	0.50	0.020	1.00
0.050	0.50	0.061	1.22
0.080	0.50	0.086	1.08
	Mean=1.10±0.13		
[PCC] mol dm^{-3}	[Oxyacid] mol dm^{-3}	[Residual PCC] mol dm^{-3}	Δ[PCC] / [Oxyacid]
	Phosphonic acid		
0.300	0.05	0.246	1.08
0.300	0.07	0.228	1.03
0.300	0.10	0.202	0.98
	Mean=1.03±0.05		

Table 2. Rate Constants of Oxidation of Phosphinic Acid by PCC at 298 K

[H_3PO_2] mol dm^{-3}	10^3[PCC] mol dm^{-3}	[TsOH] mol dm^{-3}	10^5k_{obs} s^{-1}
0.1	1.0	0.0	12.0
0.2	1.0	0.0	25.0
0.3	1.0	0.0	35.2
0.5	1.0	0.0	60.8
0.7	1.0	0.0	83.2
1.0	1.0	0.0	122
0.5	2.0	0.0	62.3
0.5	4.0	0.0	58.7
0.5	6.0	0.0	60.3
0.5	8.0	0.0	61.2
0.5	10.0	0.0	62.0
0.1	1.0	0.1	21.3
0.1	1.0	0.2	31.0
0.1	1.0	0.4	48.7
0.1	1.0	0.6	67.8
0.1	1.0	0.8	87.3
0.1	1.0	1.0	104
0.1	1.0	1.0	107[a]

a) Contained 0.02 mol dm^{-3} acrylonitrile.

$$k_{obs} = a + b[H^+]. \tag{3}$$

The acid catalysis can be attributed to a protonation of PCC to yield a protonated Cr(VI) species which is a better oxidant and electrophile.[9,10]

The oxidation of deuteriated **1** and **3** indicated the presence of a substantial primary kinetic isotope effect (Table 5) indicating the rupture of a P-H bond in the rate-determining step.

The oxidation of the oxyacids, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further the rate is not affected by the addition of acrylonitrile. Therefore, a one-electron oxidation,

Table 3. Rate Constants of Oxidation of Phenylphosphinic Acid by PCC at 298 K

[PhH_2PO_2] mol dm^{-3}	10^3[PCC] mol dm^{-3}	[TsOH] mol dm^{-3}	10^4k_{obs} s^{-1}
0.02	1.0	0.0	2.31
0.04	1.0	0.0	4.57
0.06	1.0	0.0	7.02
0.08	1.0	0.0	9.25
0.12	1.0	0.0	14.0
0.16	1.0	0.0	18.4
0.20	1.0	0.0	23.5
0.20	2.0	0.0	23.0
0.20	4.0	0.0	23.7
0.20	6.0	0.0	22.2
0.20	8.0	0.0	23.2
0.20	10.0	0.0	22.3
0.02	1.0	0.1	3.85
0.02	1.0	0.2	5.40
0.02	1.0	0.3	6.80
0.02	1.0	0.5	10.3
0.02	1.0	0.7	12.8
0.02	1.0	1.0	18.0
0.04	1.0	0.0	4.35[a]

a) Contained 0.02 mol dm^{-3} acrylonitrile.

Table 4. Rate Constants of Oxidation of Phosphonic Acid by PCC at 308 K

[H_3PO_3] mol dm^{-3}	10^3[PCC] mol dm^{-3}	[TsOH] mol dm^{-3}	10^5k_{obs} s^{-1}
0.1	1.0	0.0	7.42
0.2	1.0	0.0	14.7
0.3	1.0	0.0	22.2
0.4	1.0	0.0	28.9
0.6	1.0	0.0	44.1
0.8	1.0	0.0	58.3
1.0	1.0	0.0	73.0
0.3	2.0	0.0	21.3
0.3	4.0	0.0	23.1
0.3	6.0	0.0	22.7
0.3	8.0	0.0	21.8
0.3	10.0	0.0	22.0
0.3	1.0	0.1	34.5
0.3	1.0	0.2	46.2
0.3	1.0	0.3	60.9
0.3	1.0	0.5	83.7
0.3	1.0	0.7	110
0.3	1.0	1.0	147
0.3	1.0	0.0	22.7[a]

a) Contained 0.02 mol dm^{-3} acrylonitrile.

Table 5. Kinetic Isotope Effect in the Oxidation of **1** and **3** [PCC] 0.001 mol dm^{-3}, [**1**] 0.50 mol dm^{-3}, [**3**] 0.80 mol dm^{-3}, temp 298 K

Acid	10^5k_{obs}/s^{-1} H	 D	k_H/k_D
1	61.1	10.3	5.90
3	58.3	9.10	6.41

Table 6. Rate Constants at Different Temperatures and Activation Parameters

Acid	10^4k_2/dm^3 mol^{-1} s^{-1}				ΔH^*	ΔS^*	ΔG^*
	298 K	308 K	318 K	323 K	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}
1	12.0	25.8	50.2	65.6	52.2±0.9	−126±3	89.6±0.7
2	115	221	402	530	46.4±0.2	−127±1	84.1±0.2
3	2.50	7.35	20.0	30.3	77.8±0.7	− 53±2	93.5±1.0

giving rise to free radicals, is highly unlikely.

The rate of the oxidation was determined at different temperatures and the activation parameters were calculated (Table 6).

The oxidation of **2** was studied in 19 different organic solvents. The choice of solvents was limited by the solubility of PCC and its reaction with primary and secondary alcolols. There was no noticeable reaction with the solvents used. The kinetics are similar in all the solvents. The values of second order rate constants, k_2, are recorded in Table 7.

The analysis of rate constant of oxidation, k_2, in 17 solvents (CS_2 and acetic acid were not cosidered as the complete range of the solvent parameters were not available) in terms of linear solvation energy relationship (LSER) of Kamlet and Taft,[14] failed to yield any significant correlation.

The data on solvent effect was analyzed in terms of Swain's equation[15] of cation-solvating and anion-solvating concept also Eq. 4.

$$\log k_2 = aA + bB + C. \quad (4)$$

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.[15] The results of correlation analysis in terms of Eq. 4, individually with A and B, and with $(A+B)$ are given in Eqs. 5—8.

Table 7. Effect of Solvent on the Oxidation of Phenylphosphinic Acid by PCC at 298 K

Solvent	10^5k_2/dm^3 mol^{-1} s^{-1}
Chloroform	802
Carbon disulfide	11.2
1,2-Dichloroethane	161
Dichloromethane	156
DMSO	1150
Acetone	160
N,*N*-Dimethylformamide	444
2-Butanone	117
Nitrobenzene	236
Benzene	48.1
Cyclohexane	1.30
Toluene	28.8
Acetophenone	330
Tetrahydrofuran	73.1
t-Butyl alcohol	28.4
Dioxane	82.7
1,2-Dimethoxyethane	23.1
Acetic acid	3.75
Ethyl acetate	45.5

$$\log k_2 = 0.44\,A + 2.82\,B - 0.09 \quad (5)$$

$r^2 = 0.9373$; sd $= 0.20$; $n = 19$; $\psi = 0.19$

$$\log k_2 = 2.03\,(A+B) - 1.93 \quad (6)$$

$r_2 = 0.6788$; sd $= 0.44$; $n = 19$; $\psi = 0.55$

$$\log k_2 = 0.04\,A + 1.85 \quad (7)$$

$r^2 = 0.0001$; sd $= 0.78$; $n = 19$; $\psi = 1.63$

$$\log k_2 = 2.79\,B + 0.05 \quad (8)$$

$r^2 = 0.9252$; sd $= 0.21$; $n = 19$; $\psi = 0.20$

Here n is the number of data points and ψ is Exner's statistical parameter.[16]

The analysis in terms of Swain's equation[15] indicated that ca. 94% of the data is explained on the basis of Eq. 4. A comparison of Eqs. 5 and 8 indicates that the cation-solvating power of the solvents plays the major role. B alone accounts for ca. 93% of the data. The value of Exner's ψ points to a fair correlation in both Eqs. 5 and 8.

Mechanism. Compounds **1** to **3** exist in two tautomeric forms.[1,2] A mechanism can be written assuming the "inactive" form to be reactive species (Eq. 9).

$$\mathrm{RHP(O)OH} + \mathrm{PCC} \xrightarrow{k_{2a}} \mathrm{Products}. \quad (9)$$

The reaction sequence in Eqs. 1 and 9 leads to the rate Eq. 10.

$$\frac{-\mathrm{d[PCC]}}{\mathrm{d}t} = \frac{k_{2a}\mathrm{[PCC]\,[RHP(O)OH]_0}}{1+K_t}, \quad (10)$$

where $\mathrm{[RHP(O)OH]_0}$ represents the initial concentration of the phosphorus oxyacid. Since $1 \gg K_t$, Eq. 10 is reduced to Eq. 11.

$$-\mathrm{d[PCC]/dt} = k_{2a}\mathrm{[PCC]\,[RHP(O)OH]_0}. \quad (11)$$

Eq. 12 represents the alternate mechanism involving the "active" tautomer

$$\mathrm{PCC} + \mathrm{RP(OH)_2} \longrightarrow \mathrm{Products}. \quad (12)$$

The rate law for Eqs. 1 and 12 is given by Eq. 13.

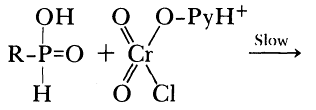
$$\frac{-\mathrm{d[PCC]}}{\mathrm{d}t} = \frac{k_{2b}K_t\mathrm{[PCC]\,[RHP(O)OH]_0}}{1+K_t}, \quad (13)$$

In view of the relation $1 \gg K_t$, Eq. 13 is reduced to Eq. 14.

$$-\mathrm{d[PCC]/d}t = k_{2b}K_t\mathrm{[PCC]\,[RHP(O)OH]_0}. \quad (14)$$

The two rate equations are thus experimentally indistinguishable and confirm to the observed rate law. If Eq. 12 represents the mode of oxidation of the oxyacids of phosphorus by PCC, then the experimental second order rate constant, $k_2=k_{2b}K_t$. The value of K_t is of the order of 10^{-12}. Thus the value of rate limiting constant k_{2b} should be of the order of 10^{10} to 10^{12}. This rate constant thus exceeds/equals the rate constants of diffusion-controlled reactions.[17] Hence it is highly unlikely that the "active" form of the oxyacids participates in the oxidation process. Further, the rate constant for the conversion (A) to (B) (Eq. 1) is likely to be smaller than the rate of oxidation.

The presence of a substantial primary kinetic isotope effect in the oxidation of **1** and **3** confirms the rupture of the P-H bond in the rate-determining step. A one-electron oxidation, giving rise to the free radicals, is not likely, in view of the failure to induce polymerization of acrylonitrile. The analysis of solvent effect indicated the importance of cation-solvating power of the solvent. Therefore, it is proposed that the rate-determing decomposition of the complex involves transfer of a hydride ion from the substrate to PCC (Eq. 15). The large value of the primary kinetic isotope effect supports an intermolecular hydride ion transfer in the rate-determining step.



$$\text{R-}\overset{\text{OH}}{\underset{\text{H}}{\text{P}}}\text{=O} + \overset{\text{O}\quad\text{O-PyH}^+}{\underset{\text{O}\quad\text{Cl}}{\text{Cr}}} \xrightarrow{\text{Slow}} \text{R-}\overset{+}{\text{P}}\text{(O)OH} + \underset{\text{Cr(IV)}}{(\text{HOCrOClOPyH})^-} \qquad (15)$$

$$\text{R-}\overset{+}{\text{P}}\text{(O)OH} + (\text{HOCrOClOPyH})^- \xrightarrow{\text{Fast}} \text{RP(O)(OH)}_2 + \text{CrOClOPyH} \qquad (16)$$

It has been shown that both PCC[18] and pyridinium fluorochromate (PFC)[19] act as two-electron oxidants and are reduced to Cr(IV) species. The nature of the reduction products of PFC and PCC were established as Cr(IV) species by determining the oxidation state of chromium, magnetic susceptibility, ESR, and IR studies.[18,19]

In the chromic acid oxidation of phosphinic acid, Sen Gupta and Chakaldar[4] postulated the participation of the "active" tautomer in the oxidation process. However, no evidence has been presented and the authors have not taken into consideration the small value of K_t. Recently Sharma and Mehrotra[5] reported that in Cr(IV) oxidation, it is not possible to pinpoint the reactive form of **2**. Formation of a phosphonium ion in the rate-determining step has been postulated by earlier workers.[4,5]

The faster rate of oxidation of phenylphosphinic acid can be attributed to the stabilization of the phosphonium ion by phenyl group through resonance. The lower rate of oxidation of phosphonic acid may well be attributed to the electron-withdrawing nature of a hydroxyl group.

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