# Oxidation of Lower Oxyacids of Phosphorus by Imidazolium Dichromate: A Kinetic and Mechanistic Approach

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## ABSTRACT

*Oxidation of lower oxyacids of phosphorus by imidazolium dichromate (IDC) in dimethylsulphoxide (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 IDC. A Michaelis-Menten type of kinetics was observed with respect to the reductants. The reaction does not induce polymerization of acrylonitrile. Reactions are catalyzed 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 indicates the solvent polarity plays a major role in the process. It has been shown that the penta-coordinated tautomer of the phosphorus oxyacid is the reactive reductant and it has been concluded that tri-coordinated 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:** Dichromate, Kinetics, Mechanism, Oxidation, Phosphorus oxyacids.
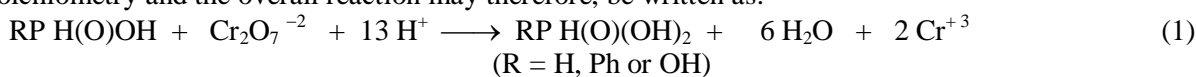
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## INTRODUCTION

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 [1-4]. One of such compounds is imidazolium dichromate (IDC) [5]. We have been interested in the kinetic and mechanistic aspects of the oxidation by complex salts of Cr (VI) and a few studies on oxidation by halochromates and dichromates are have already been reported [6-9]. It is known that mode of oxidation depends upon the nature of counter-ion attached to the chromium anion. Further the lower oxyacids of phosphorous are reported to exist in two tautomeric forms [10, 11] and it is of interest to determine the nature of the oxyacid acid involved in the oxidation process. There seems to be no report on the oxidation of oxyacids of phosphorus by IDC. Therefore, we report here the kinetics of oxidation of phosphinic (PA), phenylphosphinic (PPA) and phosphorous (POA) acids by IDC in dimethylsulphoxide (DMSO) as solvent. A suitable mechanism has also been proposed.

# MATERIALS AND METHODS

**Materials:** The phosphorus oxyacids were commercial products (Fluka) and were used as supplied. IDC was prepared by the reported method [5] 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 [12]. 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 acid and in non-polar solvents like DMSO it is likely to be completely ionised. 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 reported method [13]. To determine the stoichiometry of the oxidation of PPA, a known excess of IDC was treated with PPA and the residual IDC was determined spectrophotometrically at 354 nm after the completion of the reaction. The oxidation exhibited 1:1 Stoichiometry and the overall reaction may therefore, be written as:

$$RP\,H(O)OH\ +\ Cr_2O_7^{\,-2}\ +\ 13\,H^+\ \longrightarrow\ RP\,H(O)(OH)_2\ +\ \ 6\,H_2O\ +\ 2\,Cr^{+3} \qquad (1)$$
$$(R = H,\ Ph\ or\ OH)$$

**Kinetic measurements:** The reactions were studied under pseudo-first order conditions by keeping an excess ($\times$ 15 or greater) of the [oxyacid] over [IDC]. The solvent was DMSO, unless specified otherwise. The reactions were studied at constant temperature ($\pm 0.1$ K) and were followed by monitoring the decrease in the [IDC] spectrophotometrically at 354 nm for up to 80% reaction. Pseudo-first-order rate constants, $k_{obs}$, were evaluated from linear plots (r > 0.9990) of log [IDC] against time. Duplicate kinetic runs showed that the rates were reproducible to within $\pm 3\%$. The second order rate constants, $k_2$ were determined from the relation: $k_2 = k_{obs}/$ [oxyacid].

# RESULTS AND DISCUSSION

**Rate Laws:** The reactions were found to be first order with respect to IDC. The reactions exhibited the Michaelis-Menten type of kinetics with respect to the oxyacids (Tables 1, 2). Figure 1 depicts a typical kinetic run. A plot of 1/[oxyacid] *versus* $1/k_{obs}$ is linear with an intercept at the rate-ordinate (Figure 2). This indicates the following overall mechanism (equation 2 and 3) and the rate law (4).

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

$$\text{[Complex]} \quad \overset{k_2}{\longrightarrow} \quad \text{products} \qquad (3)$$

$$\text{Rate} \ = \ k_2\,K\,[\text{IDC}][\text{Oxyacid}]/\,(1 + K\,[\text{Oxyacid}]) \qquad (4)$$

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 3 and 4).

**Table 1.** Rate constants for the oxidation of oxyacids of phenylphosphonic by IDC at 298 K

| $10^3$ [IDC] (mol dm$^{-3}$) | [PPA] (mol dm$^{-3}$) | [TsOH] (mol dm$^{-3}$) | $10^4$ $k_{obs}$ (mol dm$^{-3}$) |
|---|---|---|---|
| 1.0 | 0.10 | 0.00 | 11.2 |
| 1.0 | 0.20 | 0.00 | 17.0 |
| 1.0 | 0.40 | 0.00 | 22.7 |
| 1.0 | 0.60 | 0.00 | 25.5 |
| 1.0 | 0.80 | 0.00 | 27.3 |
| 1.0 | 1.00 | 0.00 | 28.4 |
| 1.0 | 1.50 | 0.00 | 30.1 |
| 1.0 | 3.00 | 0.00 | 32.0 |
| 2.0 | 0.40 | 0.00 | 22.5 |
| 4.0 | 0.40 | 0.00 | 23.4 |
| 6.0 | 0.40 | 0.00 | 21.6 |
| 8.0 | 0.40 | 0.00 | 22.0 |
| 1.0 | 0.20 | 0.00 | 18.9[*] |

[a]   contained 0.001 M acrylonitrile

**Table 2.** Rate of decomposition constants and activation parameters of the oxidation of phosphorusoxyacids – IDC complexes

| Acid | $10^3$ $k_2$ / (dm$^{-3}$ mol$^{-1}$ s$^{-1}$) | | | | $\Delta H^*$ (kJ mol$^{-1}$) | $-\Delta S^*$ (J mol$^{-1}$K$^{-1}$) | $\Delta G^*$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| | 288 K | 298 K | 308 K | 318 K | | | |
| PA | 6.21 | 12.6 | 23.4 | 44.1 | 47.0±0.4 | 144±1 | 89.6±0.3 |
| PPA | 18.9 | 34.2 | 58.5 | 99.0 | 39.4±0.1 | 161±1 | 87.1±0.1 |
| POA | 2.07 | 3.96 | 7.38 | 13.5 | 45.0±0.1 | 161±1 | 87.1±0.1 |
| DPA | 1.03 | 2.16 | 4.14 | 8.31 | 50.1±0.6 | 148±2 | 93.9±0.5 |
| DPOA | 0.35 | 0.69 | 1.34 | 2.58 | 48.1±0.5 | 164±2 | 96.7±0.4 |
| $k_H/k_D$ | 6.03 | 5.83 | 5.65 | 5.31 | | | |
| $k_H/k_D$ | 5.91 | 5.74 | 5.51 | 5.23 | | | |
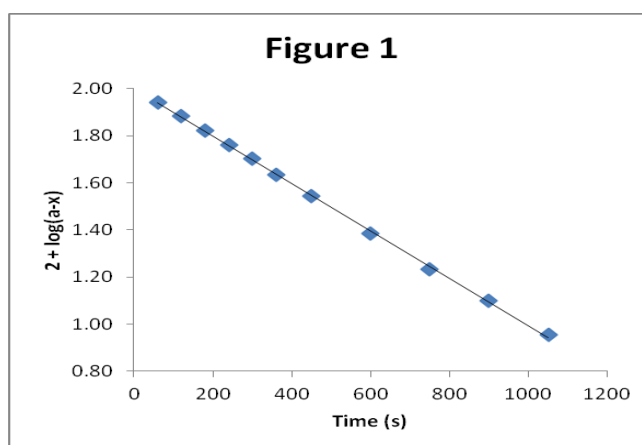


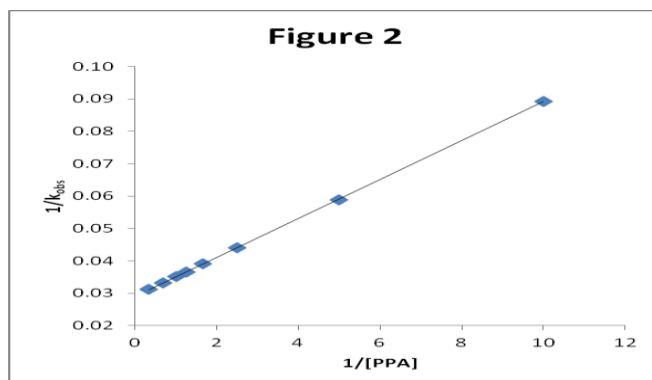**Figure 1.** Oxidation of PA by IDC: A typical kinetic run

**Figure 2.** Oxidation of PPA acid by IDC: A double reciprocal plot

**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 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$^{-3}$ of 2,6-di-t-butyl-4-methylphenol (butylated hydroxyl-toluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

**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 formation constants, K, of the intermediate complex of the deuteriated and protiated acids do not differ much, however, the rate of disproportionation of the intermediate exhibited the presence of a substantial primary kinetic isotope effect (Table 3).

**Table 3.** Formation constants and thermodynamic parameters of the oxidation of phosphorus-oxyacids – IDC complexes

| 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 | | | |
| PA | 5.94 | 5.25 | 4.52 | 3.78 | 13.9±0.6 | 25±2 | 6.56±0.5 |
| PPA | 5.67 | 4.92 | 4.25 | 3.51 | 14.5±0.6 | 28±2 | 6.42±0.5 |
| POA | 5.58 | 4.86 | 4.17 | 3.42 | 14.8±0.7 | 28±2 | 6.37±0.5 |
| DPA | 6.12 | 5.64 | 4.65 | 3.96 | 13.6±0.5 | 24±2 | 6.64±0.4 |
| DPOA | 5.76 | 5.07 | 4.32 | 3.63 | 14.2±0.5 | 27±2 | 6.47±0.4 |

**Effect of acidity:** The reaction is catalyzed by hydrogen ions (Table 4). The hydrogen- ion dependence has the following form $k_{obs} = a + b\ [H^+]$. The values of a, b; for PPA, are 11.6±0.50 × 10$^{-3}$ s$^{-1}$ and 21.4±0.82 ×10$^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$ respectively at 298 K (r$^2$ = 0.9942).

**Table 4.** Effect of hydrogen ion concentration on the oxidation of PPA by IDC

| [IDC] =  0.001 mol dm$^{-3}$; | | [PPA] = 1.0 mol dm$^{-3}$; | | | Temp. = 298 K | |
|------|------|------|------|------|------|------|
| [H$^+$]/mol  dm$^{-3}$ | 0.10 | 0.20 | 0.40 | 0.60 | 0.80 | 1.00 |
| PPA | 13.5 | 16.2 | 20.7 | 23.4 | 28.8 | 33.3 |

**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 IDC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen.  The kinetics was 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 phenylphosphinic acid by IDC 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 | 5.58 | 51.3 | Toluene | 6.00 | 22.4 |
| 1,2-Dichloroethane | 5.76 | 63.1 | Acetophenone | 5.31 | 79.4 |
| Dichloromethane | 6.03 | 58.9 | THF | 6.15 | 33.9 |
| DMSO | 5.25 | 126 | t-Butylalcohol | 5.90 | 25.7 |
| Acetone | 6.11 | 47.9 | 1,4-Dioxane | 6.31 | 38.9 |
| DMF | 5.89 | 87.1 | 1,2-Dimethoxyethane | 5.44 | 19.9 |
| Butanone | 5.77 | 41.7 | CS$_2$ | 5.88 | 14.8 |
| Nitrobenzene | 5.94 | 70.8 | Acetic Acid | 5.98 | 12.0 |
| Benzene | 5.66 | 27.5 | Ethyl Acetate | 5.47 | 32.4 |
| Cyclohexane | 5.45 | 5.25 | | | |

**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 [14] (5).

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

In this equation, $\pi^*$ represents the solvent polarity, $\beta$ the hydrogen bond acceptor basicities and $\alpha$ 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 $\alpha$. The results of correlation analyses in terms of equation (6), a biparametric equation involving $\pi^*$ and $\beta$, and seperately with $\pi^*$ and $\beta$ are given below as equations (6) - (9).

$$\log k_2 = -3.21 + 1.16 (\pm 0.15) \pi^* + 0.13 (\pm 0.12) \beta + 0.20 (\pm 0.12) \alpha \qquad (6)$$
$$R^2 = 0.8538; \quad sd = 0.14; \quad n = 18; \quad \psi = 0.42$$
$$\log k_2 = -3.26 + 1.24 (\pm 0.15) \pi^* + 0.06 (\pm 0.13) \beta \qquad (7)$$
$$R^2 = 0.8229; \quad sd = 0.15; \quad n = 18; \quad \psi = 0.45$$
$$\log k_2 = -3.25 + 1.25 (\pm 0.15) \pi^* \qquad (8)$$
$$r^2 = 0.8204; \quad sd = 0.14; \quad n = 18; \quad \psi = 0.44$$
$$\log k_2 = -2.53 + 0.28 (\pm 0.28) \beta \qquad (9)$$
$$r^2 = 0.0608; \quad sd = 0.33; \quad n = 18; \quad \psi = 1.00$$

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

Kamlet's [14] triparametric equation explains *ca.* 85% of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not even satisfactory (*cf.* equation (6). The major contribution is of solvent polarity. It alone accounted for *ca.* 82% of the data. Both $\beta$ and $\alpha$ play relatively minor roles.

The data on the solvent effect were analysed  in  terms of Swain's [16] equation (10) of cation-  and  anion-solvating  concept of the solvents also.

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

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).

$$\log k_2 = 0.30 (\pm 0.04) A + 1.29 (\pm 0.03) B - 3.36 \qquad (11)$$
$$R^2 = 0.9917; \ sd = 0.03; \ n = 19; \quad \psi = 0.10$$
$$\log k_2 = 0.11 (\pm 0.42) A - 2.48 \qquad (12)$$

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$r^2 = 0.0043$; sd = 0.34; n = 19; $\psi = 1.02$

$\log k_2 = 1.26(\pm 0.06)\ B - 3.27$ 　　　　　　　　　　　　　　　　　　　(13)

$r^2 = 0.9633$; sd = 0.07; n = 19; $\psi = 0.20$

$\log k_2 = 0.96 \pm 0.13\ (A + B) - 3.83$ 　　　　　　　　　　　　　　　　(14)
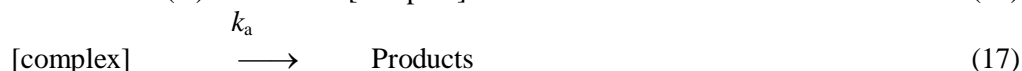
$r^2 = 0.7656$; sd = 0.17; n = 19; $\psi = 0.50$

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.* 76% of the data. In view of the fact that solvent polarity is able to account for *ca.* 74% 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 ($r^2 = 0.4952$; sd = 0.24; $\psi = 0.73$).

**Reactive reducing species:** Lower oxyacids of phosphorus are reported to exist in two tautomeric forms [10, 11]. The predominant species is the pentacoordinated form (A). The value [17] of the equilibrium constant, $K_t$ is of the order of $10^{-12}$.

$$RPH(O)OH \quad \overset{K_t}{\leftrightarrows} \quad R - P - (OH)_2 \qquad\qquad (15)$$
$$\text{(A)} \qquad\qquad\qquad \text{(B)}$$
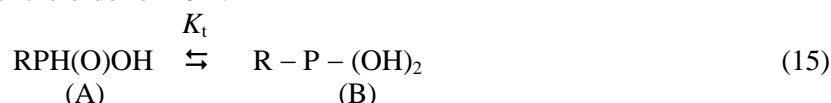
Hence two alternative broad mechanisms can be formulated. Assuming in the first instance pentacoordinated tautomer (A) as the reactive reducing species, the following mechanism may be proposed which leads to the rate law (19).

$$IDC + RPH(O)OH \quad \overset{K_a}{\leftrightarrows} \quad [\text{complex}] \qquad\qquad (16)$$

$$[\text{complex}] \quad \overset{k_a}{\longrightarrow} \quad \text{Products} \qquad\qquad (17)$$

$$\text{Rate} = k_a\ K_a\ [\text{Oxyacid}]_0\ [\text{IDC}]/\ 1 + K_t\ K_a\ [\text{oxyacid}]_0 \qquad\qquad (18)$$

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

$$\text{Rate} = k_a\ K_a\ [\text{Oxyacid}]_0\ [\text{IDC}]/\ 1 + K_a\ [\text{oxyacid}]_0 \qquad\qquad (19)$$

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

$$IDC + RP(OH)_2 \quad \overset{K_b}{\leftrightarrows} \quad [\text{complex}] \qquad\qquad (20)$$

$$[\text{complex}] \quad \overset{k_b}{\longrightarrow} \quad \text{Products} \qquad\qquad (21)$$

$$\text{Rate} = k_b\ K_b\ K_t\ [\text{Oxyacid}]_0\ [\text{IDC}]/\ 1 + K_t + K_t\ K_b\ [\text{oxyacid}]_0 \qquad\qquad (22)$$

This mechanism leads to the rate law (23), which can be reduced to (10), again acknowledging $1 \gg K_t$.

$$\text{Rate} = k_b\ K_b\ K_t\ [\text{Oxyacid}]_0\ [\text{IDC}]/1 + K_t\ K_b\ [\text{oxyacid}]_0 \qquad\qquad (23)$$

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 [18]. Further, the reported values [19, 20] of the formation constant for the chromic acid-PPA complexes are $6.12\pm0.3$, $11\pm2$ and $19\pm4$ $dm^3\ mol^{-1}$. Similarly, the

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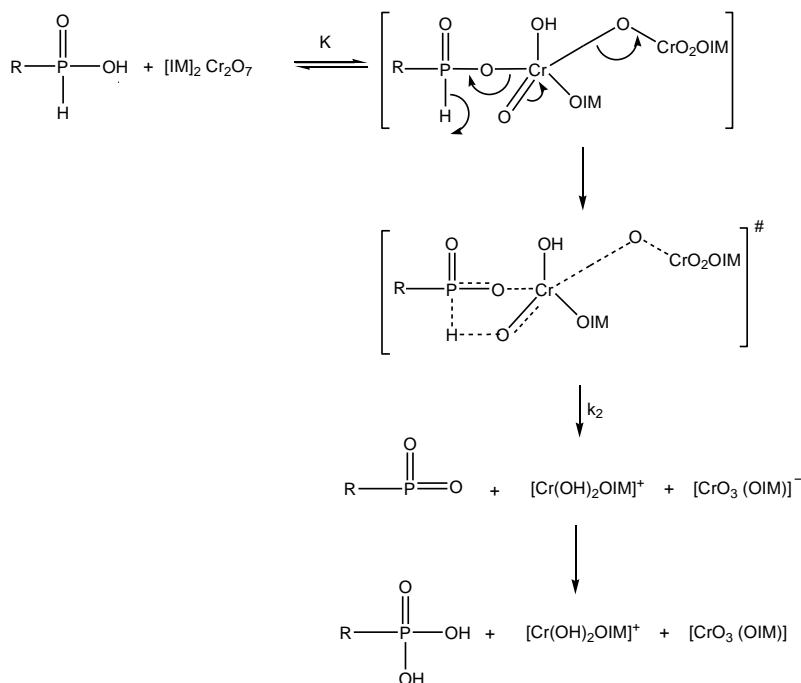
formation constant of complex [21] between triethylamine and Cr (VI) diperoxide derivative is 0.0014 dm$^3$ mol$^{-1}$. Thus the very high value of formation constant of present oxidant-phosphorus oxyacid complex is improbable, and it is highly unlikely that the tricoordinated form is involved in the oxidation process.

**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 bond [22] is 460 kJ mol$^{-1}$, while that for a P−H bond [23] is 321 kJ mol$^{-1}$. Therefore, a hydride ion 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 cation-solvating power of the solvents.
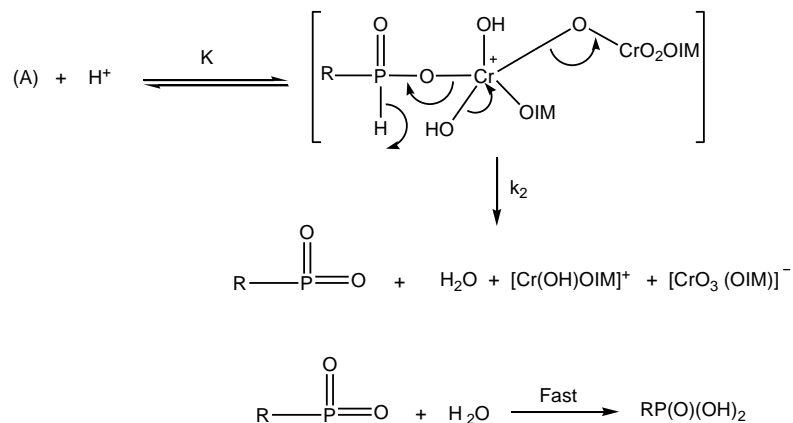
In the chromic acid oxidation of phosphinic acid Sengupta and Chakaldar [19] postulated the participation of tricoordinated tautomer. However, no evidence has been presented and author did not take into consideration the small value of $K_t$. However, Sharma and Mehrotra [20] reported that in the chromic acid oxidation it is not possible to pinpoint the reactive form of the compound. The formation of a phosphinium ion in the rate determining step has been postulated by the earlier workers [19,20].

The rate of oxidation follows the order PPA > PA > POA. The faster rate of PPA could be explained on the basis of stabilisation 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 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. Reaction Schemes 1,2 given below.

**Acid-independent Path (Scheme -1)**

**Acid-dependent Path (Scheme - 2)**

$$(A) + H^+ \underset{K}{\overset{}{\rightleftharpoons}} \left[ \begin{array}{c} \text{...} \end{array} \right] \xrightarrow{k_2}$$

$$R-P(=O)=O + H_2O + [Cr(OH)OIM]^+ + [CrO_3(OIM)]^-$$

$$R-P(=O)=O + H_2O \xrightarrow{Fast} RP(O)(OH)_2$$

## CONCLUSIONS

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.

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