THREE OXYACIDS OF PHOSPHORUS: TAUTOMERISM AND
OXIDATION MECHANISMS

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A review of the chemistry of $\text{H}_2\text{PO}_2$ ($\text{P}_1$), $\text{H}_3\text{PO}_3$ ($\text{P}_3$) and phenylphosphonic acid (PPA), and their oxidations by metal and non-metal oxidants is presented.

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Introduction

Phosphorus was the first element to be discovered in 1669 by Henning Brand in the most unusual manner by boiling 60 buckets of urine. Phosphorus is the combination of two Greek words, phos and phorus which means light bringing, because it shines in the dark when exposed to the air. Phosphorus does not exist in the elemental form. It is eleventh element in order of abundance in earth’s crust because the phosphate rocks, the source of phosphorus, occupy about 0.1% of earth’s crust. It is used in the production of insecticides or as additive of industrial oils.

The formula, structural formula, basicity, and oxidation state of P in the known oxy acids of phosphorus are as given below. The bold notations for the first three oxy acids have been used throughout the text instead of their names.

<table>
<thead>
<tr>
<th>Name of the oxy acid</th>
<th>Formula</th>
<th>Structural formula</th>
<th>Basicity</th>
<th>Oxidation state of P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hypophosphorous acid or Phosphinic acid</td>
<td>$\text{H}_3\text{PO}_2$ ($\text{P}_1$)</td>
<td>$\text{H}_2\text{PO}$(OH)</td>
<td>monobasic</td>
<td>+1</td>
</tr>
<tr>
<td>Phosphorous acid or Phosphonic acid</td>
<td>$\text{H}_3\text{PO}_3$ ($\text{P}_3$)</td>
<td>$\text{HPO}$(OH)$_2$</td>
<td>dibasic</td>
<td>+3</td>
</tr>
<tr>
<td>Phenylphosphonic acid</td>
<td>$\text{C}_6\text{H}_5\text{H}_2\text{PO}_2$ (PPA)</td>
<td>$\text{C}_6\text{H}_5\text{HPO}$(OH)</td>
<td>monobasic</td>
<td>+1</td>
</tr>
<tr>
<td>Orthophosphoric acid</td>
<td>$\text{H}_3\text{PO}_4$</td>
<td>$\text{PO}$(OH)$_3$</td>
<td>tribasic</td>
<td>+5</td>
</tr>
<tr>
<td>Metaphosphoric acid</td>
<td>$\text{HPO}_3$</td>
<td>O$\leftrightarrow$PO(OH)</td>
<td>monobasic</td>
<td>+5</td>
</tr>
<tr>
<td>Hypophosphoric acid</td>
<td>$\text{H}_2\text{P}_2\text{O}_6$</td>
<td>(HO)$_3$OP-PO(OH)$_2$</td>
<td>tetrabasic</td>
<td>+5</td>
</tr>
<tr>
<td>Pyrophosphoric acid</td>
<td>$\text{H}_3\text{P}_2\text{O}_7$</td>
<td>(HO)$_3$OP-O-PO(OH)$_2$</td>
<td>tetrabasic</td>
<td>+5</td>
</tr>
</tbody>
</table>
Its other uses are in the treatment of water, in preventing discoloration of polymers, in preserving the meat, in retrieval of precious or non-ferrous metals. It is used in bleaching agent and as antioxidant.

Thus, both hypophosphorous and phosphorous acid and their salts are reducing agents. The oxidation of these acids and their anions by different metal ions and some organic oxidants has been consistently investigated in past years. The results of such investigations are reviewed here, perhaps, for the first time.

It would be in place to summarize the earlier structures assigned to hypophosphorous acid, P1. The first structure, H-P(OH)2 containing two hydroxyl groups attached to a trivalent phosphorus atom, was suggested on measurements of magnetic susceptibility of several inorganic and organic phosphorus compounds.2 The second structure, H+(H2PO2)−, was suggested on the basis of a Raman study of several oxygen containing phosphorus compounds.3 The third structure, H3P(=O)(OH), having one hydroxyl group, a phosphoryl oxygen and two P-H bonds, i.e. a pentavalent phosphorus atom, was the result of the study of NMR spin-spin splittings of aqueous H2PO2 solutions.4

A C1 molecular model with pentavalent phosphorus atom in a highly hydrogen-bonded structure was suggested by the study of the infrared spectra of crystalline P1 and D2PO3 at liquid air temperature. The KH2PO2, NaH2PO2, NH4PO2 and Ca(H2PO2)2 and the corresponding deuterated salts and the respective anions were assigned structure on the basis of C2v symmetry except the calcium salt which had a hypophosphite ion of C1 symmetry.5

**‘Active’ ‘Inactive’ Tautomers**

Steele considered equation (1) to represent the rate determining step in the iodine oxidation of P1, which was consistent with the first order dependence in P1. In the fast step, electrons were taken up by iodine to form the iodide ions consistent with the zero order dependence in iodine.6 The autocatalytic nature of the reaction with respect to H+ ions at low concentrations is self-explanatory with the formation of the H+ ion in equation (1).

\[
H_2PO_2^- + H_2O \rightarrow HPO_3^{5-} + 3H^+ + 2e^- \quad (1)
\]

The possibility of the formation of an intermediate addition compound P11 in the slow step was excluded because its assumption would have required a first order dependence in iodine which would have been inconsistent with the observed order in iodine.

In a subsequent investigation of the oxidation of P1 with I2, Mitchell concluded that these reactions were similar in nature, and that the hypothesis of the presence of free ionic charges, advanced by Steele,7 was unnecessary in view of the hypothesized equilibrium between P1 and H2PO3. The latter, formed by P1 and H2O in a small quantity, was termed as the ‘active’ form which reacted rapidly with I2. The rate determining step was the H+ ion catalyzed formation of the ‘active’ form. Mitchell provided support for this idea subsequently in a series of publications that would be discussed afterwards.

The ‘active’ form of P1 is no more represented as H2PO3. The well documented exchange studies, described hereafter, have confirmed the existence of ‘inactive’ and ‘active’ forms of P1. The respective structures are shown in equation (2).

\[
H' + HPO_3^{-} \rightarrow H_3PO_3 \quad (2)
\]

**Isotopic exchange studies**

The study of isotopic exchange of phosphorus, using radioactive P, in the system P1-P3 or H2PO2–H3PO3 in aqueous solution in the presence or absence of I or I− ion indicated that no exchange took place in several hours at room temperature or 70 °C.8 The result was unexpected because exchange between As3+ and As5+ had been observed in the I2 oxidation of H3AsO3 to H3AsO4 in acid solution using radioactive As9+ through iodine-iodide reduction.9 The contradiction was resolved by assuming the existence of two tautomeric forms, shown in equation (2). The rate of oxidation by I2 was controlled by the rate of conversion of the ‘inactive’ (normal) into the ‘active’ form which was oxidized fast. The reverse reduction of P3 followed the same mechanism.8 Thus the explanation was similar to that proposed by Mitchell.7 The kinetics of the IO3− ion oxidation of P1 also supported that the rate of conversion of the ‘inactive’ to ‘active’ form controlled the rate of oxidation.10

A study on H-D exchange between D2O and P1, P3 and their anions confirmed the presence of ‘active’ and ‘inactive’ forms, also termed as P(III) and P(V) forms respectively, in P1 but P3 and H2PO2− and H3PO3− ions did not exhibit such tautomerism. The proposed mechanism, Scheme 1, for the exchange suggested the addition of D+ to the polar O in H3P(O)OH in a preequilibrium reaction which is followed by the simultaneous elimination of H+ from the P-H bond in the rate determining step leading to the formation of ‘active form’ of the acid. The P(III) form then picks up a D+ ion to form (4) which loses to form the deuterated acid (5).

![Scheme 1](image-url)
Three oxyacids of phosphorus

The absence of such tautomeric forms $H_2P(O)O^+$ ion is explained by addition of $H^+$ or $D^+$ to the $O^-$ and not to the $O$ of the $P-O$ link, which results in the formation of the normal ‘inactive’ $H_3P(O)OH$ acid.\textsuperscript{11}

The rate expression from the above mechanism would be as in equation (3).

$$k_{\text{exch}} = k_{ij}[D^+] + k_w$$ (3)

Another study had indicated a dearth of exchange in the $P-H$ links in the ‘inactive’ form of $P1$ because of the extremely slow D-H exchange in the P-H link. However, there was a rapid exchange with D both in the OH groups and in the P-H link of the ‘active’ form. Since the two forms are in equilibrium, therefore, the added D is distributed among two P-Hs and one O-H link in the ‘inactive’ form.\textsuperscript{12}

The suggested structural requirement for an atom to undergo the D-H exchange was that the atom must have an unshared electron pair and is bonded to the H atom. This explained the lack of D-H exchange in $P3$ and its anion because the P atom in either case has no unshared electron pair.\textsuperscript{13}

The differing behaviour of $P1$ and $P3$ toward D-H exchange has been attributed to the decrease in positive charge on P with the increase in the number of attached OH groups to phosphorus. This adversely causes the nucleophilic ability of $P$ to add $HO$ of $H_2O$. The free groups to phosphorus. This adversely causes the charge on $P$ with the increase in the number of attached OH groups. The exchange has been attributed to the decrease in positive charge on phosphorus.\textsuperscript{14}

Expressed differently, it was considered similar to that of oxidation reactions.\textsuperscript{15}

Specific studies

Hyphosphorous acid

The exchange of tritium between $P1$ and $H_2O$ had the rate law: 
\[ R = (k_{ij}[H^+] + k_{ij}[P1]) [P1] \]
with $k_{ij} = 0.055 \pm 0.0025$ and $k_i = 0.0483 \pm 0.0024 \text{ dm}^{-3} \text{ mol}^{-1} \text{ min}^{-1}$ at $30 ^\circ C$. $R$ is the rate at which one “undissociable” $H$ atom is exchanged per $P1$ molecule. The results were supportive of the existence of normal or ‘inactive’ and ‘active’ tautomeric forms in aqueous solution.\textsuperscript{16}

The tritium (T, radioactive hydrogen) is reported to exchange as $T^-$ or $T_2O$ with two P-H bonds of $P1$. The reaction $H_2P(O)OH + HTO \leftrightarrow HTP(O)OH + H_2O$, and the rate law for the rate limiting P-H fission was $k = k_i[P1] + k_j([H^1] + [D^1])$. The rate coefficients $k_i$ and $k_j$ equaled to 0.038 dm$^3$ mol$^{-1}$ min$^{-1}$. The exchange rate was very slow in neutral or alkaline solution. Since the rate expression for the reaction was identical with the rate law for the oxidation of $P1$ by various oxidizing agents, therefore the mechanism of exchange was considered similar to that of oxidation reactions.\textsuperscript{17}

A parallel study of the exchange between $D_2O$ and P-Hs of $P1$ was studied using NMR spectroscopy. The rate expression, $k = k_i[P1] + k_j([H^1] + [D^1])$, was similar to that observed by Jenkins and Yost,\textsuperscript{18} and referred to the P-H fission in the rate determining step of the reaction $H_2POOH + D_2O \rightarrow HDPOOH + HDO$. The $k_1 = 0.013 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ and $k_2 = 0.073 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ were reported at 16.5 $^\circ C$, and were approximately 4 and 12 times larger than the values reported by Jenkins and Yost. Such a large difference in the two values was ascribed to isotope effect.\textsuperscript{19}

Rate constants for the forward and backward reactions of acid catalyzed reaction of $P1$, equations (4) and (5), where L represents either $H$ or $D$, were determined.

$$\text{DOL}_1 + H_2P(O)OH_{aq} \xrightarrow{k_4} \text{DHPO}_2L_{aq} + \text{HOL}_1 \quad (4)$$

$$\text{DOL}_1 + \text{DHPO}_2L_{aq} \xrightarrow{k_5} \text{D}_2\text{PO}_2L_{aq} + \text{HOL}_1 \quad (5)$$

The equilibrium constants for the reactions (4) and (5) are $K_4 (1.12 \pm 0.08)$ and $K_5 (0.305 \pm 0.015)$ at 25 $^\circ C$. The rate constants $10^4 k_4 = 4.09, 10^3 k_5 = 1.19, 10^2 k_4 = 1.87$ and $10^2 k_5 = 1.01 \text{ mol}^{-1} \text{ dm}^3$ at 25 $^\circ C$. For the acid-catalyzed, rate-determining tautomerization of ‘inactive’ $H_2P(O)OH$ to ‘active’ $HP(O)OH_2$, primary kinetic isotope effects $k_5/k_4 = 0.36$ for the forward reaction and 0.24 for the reverse reaction were obtained. The secondary isotope effect was determined to be 1.45. These isotope effects were consistent with a transition state in which proton attachment occurred with a bond order of 0.2. A free energy of tautomization = 62 $kJ$ was determined using the bond order (0.2) along with the Marcus theory of proton transfer.\textsuperscript{18}

Phosphorous acid

The exchange reaction $P-H + D \leftrightarrow P-D + H (k_i, k_i)$ in $P3$ was studied in $D_2O/H_2O$ using stretching vibrations at 2457 and 1793 cm$^{-1}$ for $P-H$ and $P-D$ respectively in the Raman spectrum (the $H$ in O-H exchanged almost instantly). $k_i$ and $k_i$ had values of $3.42 \times 10^{-3}$ and $1.67 \times 10^{-5}$ min$^{-1}$ respectively at 23 $^\circ C$. The rate of exchange increased with increasing acidity (addition of $HCl$ in $H_2O$, or $DCl$ in $D_2O$). The exchange rate in $HP(O)OH$ and $HP(O)O_2^-$ ions was very slow. An isotope effect $k_i/k_i = 5.1$, based on the stretching frequency of $P-H$ and $P-D$ bonds was predicted. A mechanism similar to the Scheme 1 was proposed except that 3 $\rightarrow$ 4 was also considered as the rate determining step in addition to the one shown there.\textsuperscript{18}

A similar study made during the I$_2$ oxidation of $P3$ using NMR spectroscopy reported that the exchange could be observed only in strong acid. The pseudo first order rate constant was $1.97 \times 10^{-5}$ min$^{-1}$ at 1.49 mol dm$^{-3}$ and 22 $^\circ C$.

There are some more exchange studies which were investigated during the oxidation of phosphorous acid. Such studies will be briefly referred to in the section dealing with the oxidation of this acid.

Phenylphosphonic acid

Phenylphosphonic acid, $C_6H_5H-P(O)OH$, is also named as phenylphosphonous acid. Tautomerism in $C_6H_5H-P(O)OH$ and its anion was studied using hydrogen isotope exchange
in aqueous and deuterium oxide solutions by infrared. The reaction was both acid and base catalyzed. The termolecular mechanisms involving both acids and bases were not significant. There was negligible exchange in the neutral or near-neutral solution. The rates of exchange of H atoms bound to P and O are different by many orders of magnitude. The acidic H atoms in P-OH groups are known to undergo extremely rapid exchange.\(^{11}\) The exchange in \(\text{C}_2\text{H}_6\text{H}-\text{P(O)OH}\) resembles more with phosphinic acid \(\text{H}_2\text{P(O)OH}\), rather more closely with that of dialkyl phosphonates (discussed below) than that of phosphorous acid \(\text{HP(O)(OH)}_2\).\(^{20}\)

The exchange of P-H bond in \(\text{C}_6\text{H}_5\text{H}-\text{P(O)OH}\) in \(\text{D}_2\text{O}\) to \(\text{P-D}\), studied in acidified \(\text{EtOH-}\text{H}_2\text{O}\) mixture and aqueous alkaline solution by following the decreasing intensity of the P-H doublet in NMR spectroscopy, was acid-base catalyzed. The reaction had a first order dependence in \(\text{H}^+\) and \(\text{OH}^-\) ions and \(\text{C}_2\text{H}_6\text{H}-\text{P(O)OH}\). The rates in acid solutions were faster than those in alkaline solution. The exchange of O-H to O-D was rapid,\(^{11}\) and no exchange of O-18 between phenylphosphonous acid and \(\text{H}_2\text{O}^{18}\) was detected under the conditions in which H exchange was studied. The proposed mechanism of the acid catalyzed exchange was similar to that shown in Scheme I. The \(\text{OH}^-\) ion catalyzed exchange presumably proceeded by direct proton abstraction. The rate law for the acid catalyzed reaction was \(k = k_{\text{d}}[\text{H}^+] + k_w\) where \(k_w\) is the rate coefficient for the acid independent reaction.\(^{21}\)

### Ester of Phosphonic Acid

The reactions between dialkyl esters and cuprous halide,\(^{22}\) phenylazide,\(^{23}\) and diazomethane\(^{24}\) had been suggestive of equilibrium between the pentavalent ‘inactive’ and trivalent ‘active’ tautomeric form of the dialkyl esters of phosphorous acid. However, the existence of normal keto or ‘inactive’ form of the esters was suggested by the Raman,\(^{25}\) ultraviolet,\(^{26}\) NMR and infrared,\(^{27,28,29}\) spectral studies.

However, the study of the acid catalyzed exchange of H bonded to P of dimethyl-, diethyl- and di-n-propylphosphonate with D in \(\text{D}_2\text{O}\), followed by the decreasing intensity of the P-H doublet in NMR spectrometer. The reaction first order in phosphonates and the rate law was: \(k = k_{\text{d}}[\text{H}^+] + k_w\) where \(k_w\) is the specific rate constant and \(k_w\) is the catalytic constant for the spontaneous acid-independent exchange. \(10^2k_{\text{d}}\) (± 10%) and \(10^2k_w\) (± 30%) at 23 ± 1 °C were 6.6, 8 (dimethyl-), 6.2 (diethyl-) and 5.8, 7 (di-n-propyl) phosphonate respectively. Although some acid-catalyzed hydrolysis of dialkyl phosphonate was observed but the extent of such hydrolysis was negligible. Since the rate law happened to be identical with the rate law for the oxidation of these esters with iodine,\(^{30}\) it suggested that the phosphite form of the dialkyl phosphonates, \(6\), was a common intermediate for both the exchange and oxidation reactions.\(^{31}\)

Luz and Silver\(^{31}\) re-investigated the exchange of the P bonded H with D in \(\text{D}_2\text{O}\) in dimethyl- and diethyl phosphonate in presence of acetate buffer using the same method to follow the reaction. The rate law for the reaction was \(k = k_{\text{AcO}^-}[\text{AcO}^-] + k_{\text{AcOH}}[\text{AcOH}] + k_w\). The hydrolysis of dialkyl phosphonates under the experimental conditions was negligible.\(^{32}\) The \(10^2k_{\text{AcO}^-}\) (± 10%) was 52 and 7.5 dm\(^{-3}\) mol\(^{-1}\) min\(^{-1}\) for dimethyl and diethyl phosphonate at 21.5 ± 0.5 °C was much greater than the values of \(k_w\) for the similar phosphonates.\(^{33}\) The \(\text{AcO}^-\) ion was considered as the catalyst. Based on the similarity of the rate law with the rate law for the oxidation under similar conditions,\(^{30}\) the Scheme 2 for the catalyzed exchange was suggested. It was further suggested that the substitution of D for the phosphorus bonded H in diethylphosphonate had a negligible effect on the oxidation rate.\(^{35}\)

The infrared study of deuterium exchange between di-n-butyl phosphonate and \(n\)-butylalcohol-\(d\), in the presence of acids or bases as well as in neutral solution indicated the existence of mobile prototropic equilibrium between the ester and acidic species present in the reaction mixture. The exchange was catalyzed by both acid and base. In the absence of catalysts, the reaction proceeded in a manner similar to that for acetone.\(^{34}\)

### Oxidation Studies

In this section the kinetics of oxidation of \(\text{P}_1\), \(\text{P}_3\) and \(\text{PH}_2\text{PO}_2\) (hereafter abbreviated to \(\text{P}_1\), \(\text{P}_3\) and \(\text{PPA}\) respectively) are discussed for each metal separately. However, if identical mechanisms were reported for other oxidants then these oxidations have been grouped at one place for brevity. The first order in the oxidant and the oxy-acids and negative tests for the free radicals are not mentioned. No mention is made if the oxy-acid reacted in its ‘inactive’ form.

#### Chromium(VI)

Mitchell, while examining the effect of \(\text{P}_1\) on titration of \(\text{FeSO}_4\) by \(\text{K}_2\text{Cr}_2\text{O}_7\), probably, for the first time postulated two reactions. The reaction between \(\text{Cr}_2\text{O}_7^{2-}\) and \(\text{HP(O)(OH)}_2\), the ‘active’ form, is unimolecular with respect to each and did not involve \(\text{H}^+\) ions. The rate determining \((r.d.)\) reaction (6) is followed by the reaction (7). Velocity coefficients varied inversely as the 1/7 power of the initial concentration of the \(\text{H}_2\text{CrO}_4\).\(^{35}\)

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} + \text{HPO(OH)}_2 & \xrightarrow{r.d.} \text{H}_2\text{PO}_3 + \text{Cr}_2\text{O}_6^{2-} \quad \text{(6)} \\
\text{Cr}_2\text{O}_6^{2-} + 2\text{H}_2\text{PO}_2 + 8\text{H}^+ & \xrightarrow{\text{fast}} 2\text{Cr}^{3+} + 2\text{H}_3\text{PO}_4 + 4\text{H}_2\text{O} \quad \text{(7)}
\end{align*}
\]

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**Scheme 2**

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The oxidation of P₃ in concentrated solutions of HClO₄, H₂SO₄ and HCl acids is reported without any formal rate law presuming CrO₄²⁻ ion to be the reacting species because it was present in excess.³⁶

The intermediacy of the ‘active form’, H₃P(OH)₃, equation (8), and HCrO₄⁻ ion, equation (9) was proposed assuming rapid reduction of CrO₄²⁻ to Cr(III) in the mechanism. The kₙ/k₀, had an estimated value of 466 at 25 °C.³⁷

\[ \text{H}_2\text{PO}_3 \xrightarrow{k_{\text{a}}} \text{HP(OH)_2} \quad (8) \]

H₃PO₄ + H⁺ + 2HCrO₄⁻ → \[ k \] \[ \text{H}_2\text{PCrO}_6⁻ + \text{H}_2\text{O} \quad (9) \]

H₃PO₄ was not oxidized in acetate buffer over several days at 25 °C, but it slowly oxidized at 100 °C to H₂PO₄⁻ ion. H-P bond of H₂PO₃⁻ was inhibited the oxidation. However, P₃ oxidized fast in 1 M H⁺ ion. The spectrometric equilibrium constant K for the equation (10) had a value 26. Although the rate law in equation (11) was given, yet the mechanism was not suggested. The values of k₁ and k₂ were \( \approx 10^{-4} \) mol dm⁻³ s⁻¹. C′ formed CrOCl⁻ which inhibited the reaction.³⁸

\[ \text{H}_3\text{PO}_3 + \text{HCrO}_4⁻ \rightarrow \text{H}_2\text{PCrO}_6⁻ + \text{H}_2\text{O} \quad (10) \]

\[ \text{rate}= \frac{(k_1+k_2[H_3PO_3])[H_3PO_3][Cr(VI)]\text{[H}^+]}{1+K[H_3PO_3]} \quad (11) \]

A reinvestigation confirmed almost all the above findings and additionally probed the oxidation of P₁. A common mechanism for the oxidations of H₂PO₃⁻, P₁ and P₃ was proposed as given in Scheme 3, which depicted the mechanism for P₃ oxidation. The P₃ and HCrO₄⁻ formed an anhydride, equation (12). The abstraction of a proton from the protonated anhydride, protonation could be effected either by H⁺ or P₃, by bases H₂O and H₂PO₃, were the conjectural rate limiting steps based on analogy with Westheimer mechanisms of alcohol oxidations.³⁹ The derived rate equation (13) was slightly different from the equation (11) with \( k_1 = kK_1 \) and \( k_2 = k'K_2K_3 \), where \( K_2 \) is the dissociation constant of the respective acid. A \( k_2/k_0 = 4 \) suggested breaking of P-H bond in the rate determining step. H₂PO₂ formed another anhydride at pH 4 or was oxidized by HCrO₄⁻. The 10⁴k₁ = 1.7, and \( K_1 = 16 \) were reported for P₃ at 25 °C. The corresponding values for P₁ were 6.0 and 11 respectively.⁴⁰

\[ \text{H}_2\text{PO}_4⁻ + \text{H}_2\text{PO}_3 \rightarrow \text{O}_4\text{Cr-Ph(OH)OH} \quad (12) \]

\[ \text{H}^+ + \text{O}_4\text{Cr-Ph(OH)OH} \rightarrow \text{O}_4\text{Cr-Ph(OH)OH}_2 \quad (i) \]

\[ \text{O}_4\text{Cr-Ph(OH)OH}_2 + \text{H}_2\text{O} \rightarrow \text{O}_4\text{Cr-Ph(OH)OH} + \text{H}_2\text{O} \quad (ii) \]

\[ \text{O}_4\text{Cr-Ph(OH)OH}_2 + \text{H}_2\text{PO}_3⁻ \rightarrow \text{O}_4\text{Cr-Ph(OH)OH}_2 + \text{H}_2\text{PO}_3⁻ \quad (iii) \]

\[ \text{Cr}^{IV} + \text{Cr}^{IV} \rightarrow 2\text{Cr}^{IV} \quad (iv) \]

\[ \text{Cr}^{V} + \text{H}_2\text{PO}_3 \rightarrow \text{Cr}^{IV} + \text{H}_2\text{PO}_4 \quad (v) \]

\[ \frac{-d[\text{Cr(VI)}]}{dt} = \left( kK_1[H^+] + k'K_2K_3[H_3PO_3] \right)[Cr(VI)][H_3PO_3] \quad (13) \]

Another study reported \( K_1 = 13 \) in addition to \( K_9 = 0.101 \) in perchlorate media. Though the results agreed with the above mechanism, yet the rate equation (14) had two new terms, \( k_9 \) and \( k_2[H^+] \), in addition to the terms appearing in equation (13). The \( k_9 \) may correspond either to the reaction of unprotonated complex having unknown number of solvent molecules or to abstraction of a phosphoric proton by OH⁻ ion from the neutral protonated complex. The \( k_2[H^+] \) term is attributed to the formation of doubly protonated complex H₃PCrO₆, followed by proton abstraction by water.⁴¹

\[ \text{rate}= \left( k_9+k_1[H^+]+k_2[H^+]^2+k_3[H_3PO_3][\text{CrO}_4⁻][\text{H}_3\text{PO}_3] \right) \quad (14) \]

The oxidation of H₂PO₃⁻ by Cr⁵⁺ chelate (I), formed with (C₂H₅)₂C(OH)CO₂H (lig), in buffered solution (buff) of the lig and its Na-salt, to H₃PO₄ and Cr³⁺ proceeded through bridged transition state (II) in which the mobilization of protons bound to P is favored by strongly acidic Cr⁵⁺ or Cr⁷⁺. The reaction towards the later stages becomes autocatalyzed, which was attributed to Cr⁷⁺ and had been explained by suggesting the following sequence of the reactions (Scheme 4). The reactions (a) and (b) control the initial stage of the reaction till Cr⁵⁺ starts getting accumulated when the reaction (c) becomes significant producing more free radical that reacts more rapidly with Cr⁵⁺ compared to Cr⁷⁺ in reaction (d). This explains the catalysis of Cr⁷⁺ in the later part of the reaction. The \( k_1 \) and \( k_2 \) had the values (0.049 ± 0.006) and (0.18 ± 0.04) dm³ mol⁻¹ s⁻¹ respectively whereas ratio \( k_2/k_4 \) was (2.32 ± 0.35).⁴²

\[ \text{Cr}^{V} + \text{H}_2\text{PO}_3⁻ \xrightarrow{k_1} \text{Cr}^{IV} + \text{H}_2\text{POO}⁻ \quad (a) \]

\[ \text{Cr}^{V} + \text{H}_2\text{POO}⁻ \xrightarrow{k_2} \text{Cr}^{IV} + \text{H}_2\text{PO}_3⁻ \quad (b) \]

\[ \text{Cr}^{IV} + \text{H}_2\text{PO}_2⁻ \xrightarrow{k_3} \text{Cr}^{III} + \text{H}_2\text{PO}_3⁻ \quad (c) \]

\[ \text{Cr}^{IV} + \text{H}_2\text{POO}⁻ \xrightarrow{k_4} \text{Cr}^{III} + \text{H}_2\text{PO}_3⁻ \quad (d) \]

Scheme 4

The oxidation of H₂PO₃⁻ by Cr⁷⁺, chelated with the lig, in the buff at pH 2.7 and excess Cl(NH₃)₅Co²⁺, a scavenger for Cr(II), had shown the parallel formation of Cr⁵⁺ and Cr⁷⁺, stabilized by the lig, by competing le and 2e⁻ paths (see below). The reduction of Cr⁷⁺ to Cr⁵⁺ and of Cr⁷⁺ to Cr⁵⁺ involved hydride shifts from H₂PO₂⁻ to the Cr(=O), whereas formation of Cr⁵⁺ and its reduction to Cr⁵⁺ involved preliminary coordination of H₂PO₄⁻ to the chromium center.

followed by P-H to O-H tautomerization (see (11)) within the biunimolecular complex and then transfer of a single-electron from P to the Cr center. The rates of formation of CrV and CrIV from CrVI were (2.58 ± 0.9) × 10⁻⁸ and (4.52 ± 0.08) × 10⁻⁸ mol dm⁻³ s⁻¹ respectively at 25 °C. The formation of CrIV had the rate law, k(obs) = (k₁ + k₂[ZP]) [H₃PO₂]⁻[H⁺][Cr(OH)₂CO₃]⁻, with k₁ = (15.3 ± 0.2) M⁻¹ s⁻¹ and k₂ = (2.5 ± 0.2) × 10⁴ M⁻¹ s⁻¹. The k₁/k₂ = 3.9 and 2.2, kD(O)/kD(H₂O) = 2.2 and 1.7 were observed for generation of CrIV and CrV respectively. The formation of CrII indicated that the more usual state CrIII was bypassed.43

A very confusing paper on the oxidation of P3, which missed on the above mentioned references, mentions that Cr₂O₇²⁻ is the predominant CrVI species but considers HCrO₄⁻ as the reactive species in the mechanism consisting of reactions (i)-(vii), Scheme 5, where X = HSO₄ or ClO₄⁻. The dimerization of the free radical (OH₂)P(O) to H₃P₂O₆ was not substantiated. The unsubstantiated formation of higher esters is stated to be more rapid than the rate-limiting intermediate with (ZP). However, their role in the mechanism was not explained. The reported rate law (viii), where kobs is perhaps equal to Kk₁, however, does not match with the rate law (ix) that had been derived without considering the total [P3].44

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} & \rightleftharpoons \text{ fast } 2\text{HCrO}_4^- & (i) \\
\text{HCrO}_4^- + \text{H}^+ + \text{HX} & \rightleftharpoons \text{ fast } \text{HOCrO}_2\text{O}_2\text{X} + \text{H}_2\text{O} & (ii) \\
\text{HOCrO}_2\text{O}_2\text{X} + \text{H}_3\text{PO}_3 & \rightleftharpoons \text{ fast } \text{HPO}_3\text{X}\text{HOCrO}_2\text{O}_2\text{X} + \text{H}_2\text{O} & (iii) \\
\text{M} + \text{H}_3\text{PO}_3 + \text{HX} & \rightleftharpoons \text{ fast } \text{Cr}^{IV} + 2\text{H}_3\text{PO}_4 & (iv) \\
\text{M} + \text{H}_3\text{PO}_3 & \rightleftharpoons \text{ fast } \text{Cr}^{IV} + \text{H}_2\text{PO}_3 & (v) \\
\text{Cr}^{IV} + \text{H}_2\text{PO}_3 & \rightleftharpoons \text{ fast } \text{Cr}^{III} + \text{HO}_2\text{P}^\ast \text{(O)} & (vi) \\
2(\text{HO}_2\text{P}^\ast \text{(O)}) & \rightleftharpoons \text{ fast } \text{H}_3\text{P}_2\text{O}_6 & (vii) \\
k_{\text{obs}} = \frac{(k_1[HX] + k_2)[K_k][H_3\text{PO}_3]^2}{1 + [K_k][H_3\text{PO}_3]} & (viii) \\
or, k_{\text{obs}} = (k_1[HX] + k_2)[K_k][H_3\text{PO}_3][H\text{CrO}_4^-][H_3\text{PO}_3]^2 & (ix)
\end{align*}
\]

Scheme 5

A single electron transfer was proposed, Scheme 6, in the oxidations of P1 (Z = H) and P3 (Z = OH). The formation of the protonated anhydride, equation 15, involved an unlikely tri-body collision of HCrO₄⁻, H⁺ and ZP(=OH)₂ (‘active form’ of the acid). The rate determining step (1), the unaided decomposition of anhydride by a base to ZP(O)OH ion and CrIV, was followed by several fast steps giving the products. The values ΔH(kcal) = 15 ± 1 and 5 ± 0.6 and ΔS(eu) = 50.6 ± 1.5 and 16.9 ± 0.8, indicated that the intermediate with P1 is stronger than that formed with P3. The respective activation energy was 10.4 ± 0.8 and 5.8 ± 0.5 kcal mol⁻¹. The reactions were catalyzed by H⁺ ion, the catalytic effect of pyridine was observed only in P1 oxidation.45

\[
\begin{align*}
\text{ZP(O)OH} + \text{HCrO}_4^- + \text{H}^+ & \rightleftharpoons \text{ZP(=OH)CrO}_4\text{H} + \text{H}_2\text{O} & (15) \\
\text{ZP(O)OHCrO}_3\text{H} & \rightleftharpoons \text{ZP(=O)OH} + \text{Cr}^{IV} & (1) \\
\text{Cr}^{IV} + \text{ZHP(=O)OH} + \text{H}_2\text{O} & \rightleftharpoons \text{ZP(=O)OH}_2 + \text{H}_2\text{O} & (2) \\
\text{ZP(=O)OH}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{ZP(=O)OH}_3 + \text{H}_2\text{O} & (3) \\
2\text{Cr}^{IV} & \rightleftharpoons \text{Cr}^{IV} + \text{Cr}^{III} & (4)
\end{align*}
\]

Scheme 6

The oxidation of PPA in HClO₄ showed Michaelis-Menten kinetics.46 The mechanism was similar to that of Scheme 5 (Z = C₆H₅). The activation energy was 7.4 kcal.47 Surprisingly, the reaction was reported again by one of the authors with similar results and favoring the same mechanism from amongst few others that were discussed this time. However, the activation energy reported this time was 10.3 ± 1.2 kcal mol⁻¹.48

Another investigation substantiated the formation of the anhydride by the rapid scan of the reaction mixture beside the Michaelis-Menten kinetics. The spectrum in Figure 1 is recorded between 302 and 398 nm, selecting the middle wavelength at 350 nm, and on an arbitrary scale of 0-1 for the absorbance.

Figure 1. Rapid scan spectra of HCrO₄⁻ (O) and HCrO₄⁻ + PPA(Δ) between the λ, 302-398 nm taken between 4.352 and 4.402s after mixing at 25 °C (10⁻⁴[HCrO₄⁻] = 4.0, 10⁻⁴[PPA] = 4.0, [H⁺] = 1.5 mol dm⁻³).

The HCrO₄⁻ + PPA mixture has a higher absorbance over that HCrO₄⁻ alone suggesting the formation of some new
species which in this case is the anhydride. The study further concluded that PPA is not the reactive species because the deduced rate law conflicted with the observed results. Furthermore, the linear plot between log \( k_{\text{obs}} \) and \(-H_0\), the Hammett acidity function, with a slope of 1.02 ± 0.02 confirmed that the anhydride is protonated prior to its rate-limiting disproportionation. Because of this it becomes difficult to be specific about the reactive tautomer of PPA because the protonation of the anhydride formed by either of the tautomer results in the same intermediate that undergoes the redox reaction. The formation constant for the anhydride formed between PPA and HCrO\(_4^−\) was almost independent of temperature and had a value ca. 19 ± 4 dm\(^3\) mol\(^{-1}\) and 6.4 in the oxidation of P1 and P3 respectively. The effect of several organic solvents on the rate of the oxidation of PPA was analyzed with Kamlet-Taft’s and Swain’s equations, which indicated that the cation-solvating power of the solvents had a predominant role. The bimolecular reactions of pcc and pceH\(^+\) with oxy-acids constituted the parallel rate-determining reactions involving the transfer of a H\(^+\) ion from the P-H bond of the ‘inactive’ species to pce and pceH\(^+\) giving RP\(^+\)O2H (R = H, OH, Ph) and Cr\(^{III}\) species. RP\(^+\)O2H and Cr\(^{IV}\) reacted rapidly to give Cr\(^{III}\) and the higher oxy-acids.\(^{50}\)

Chromium(VI) complexes

The oxidations of P1, P3 and PPA (hereafter POA would represent the combination of three phosphorus oxy-acids) by pyridiniumchlorochromate (pcc) were first order both in pcc and the substrates. The H\(^+\) dependence was expressed by \( k_{\text{obs}} = a + b[H^+]\). The reaction showed \( k_{ij}/k_{ip} = 5.3\) and 6.4 in the oxidation of P1 and P3 respectively. The effect of several organic solvents on the rate of the oxidation of PPA was analyzed with Kamlet-Taft’s and Swain’s equations, which indicated that the cation-solvating power of the solvents had a predominant role. The bimolecular reactions of pcc and pceH\(^+\) with oxy-acids constituted the parallel rate-determining reactions involving the transfer of a H\(^+\) ion from the P-H bond of the ‘inactive’ species to pce and pceH\(^+\) giving RP\(^+\)O2H (R = H, OH, Ph) and Cr\(^{III}\) species. RP\(^+\)O2H and Cr\(^{IV}\) reacted rapidly to give Cr\(^{III}\) and the higher oxy-acids.\(^{50}\)

The reinvestigated oxidation of P1 by pcc, however, reported Michaelis-Menten kinetics and a different rate law \(\dot{k}_{\text{obs}} = k_i[A][P1][[H^+]]/(1 + K_c(1 + K_i[P1]))\) with \(K_c = 1.61\) dm\(^3\) mol\(^{-1}\) and \(k_i = 6.4 \times 10^{-4}\) s\(^{-1}\). The rate determining disintegration of the complex to P3 and Cr\(^{III}\) was followed simultaneously by the rapid reaction similar to reaction (4) in Scheme 6 and the oxidation of P1 by Cr\(^{IV}\) to P3 and Cr\(^{III}\), which was the final reduction product as Cr(II) could not be detected.\(^{51}\)

The Jodhpur group has repeated the oxidation of POA using very similar Cr\(^{IV}\)-complexes and nitrogenous oxidizing compounds with almost similar results. The results of these studies would not be repeated unless a different result had been reported.

The oxidation of POA by bipyridiniumchlorochromate, benzyltriethylammoniumchlorochromate, morpholiniumchlorochromate, tetraethylammonium chlorochromate, pyridinium bromochromate, ethyl-N-chlorocarbamate benzylimethylammoniumchlorobromate, and pyridiniumhydrobromideperbromide were identical and corresponded to the oxidation by pcc described above.\(^{50}\) However, in the last two studies, H\(^+\) ions had no effect on the rate.

The rates of oxidations of POA by pyridinium fluorotrioxochromate, and hexamethylenetetramine bromine in glacial acetic acid were independent of H\(^+\) ion. The oxidations by benzimidazoliumdichromate, butyltriphenylphosphoniumdichromate, chlorochromate, pyridiniumchlorochromate, quinoliniumdichromate, and quinoliniumfluorochromate was expressed by the expression \(k_{\text{obs}} = a + b[H^+]\). Michaelis-Menten kinetics was observed in all these studies, and other conclusions were identical to that described in the oxidation of POA by pcc above.\(^{50}\)

Manganese

The oxidations of PPA and those of P1 and P3, by Mn\(^{III}\) in H\(_2\)SO\(_4\) had inverse first order dependence in [H\(^+\)] which was explained by assuming MnHSO\(_4^{2+}\), formed from the reversible dissociation of Mn\(^{5+}\)H\(_2\)SO\(_4\) complex, as the reactive species. The mechanism is stated to be explainable by assuming bimerolecular reaction between MnH\(_2\)SO\(_4^{2+}\) and Ph(OH)\(_2\) or via the intervention of the complex MnPh\(_2\)O\(_4^{2+}\) formed by Mn\(^{5+}\) and PhHPO(O)OH. Formation of PhPO\(_2\)H is the rate determining step followed by rapid formation of PhPO\(_3\)H which is finally oxidized to PhO(P)OH\(_2\). The complex reacting with H\(_2\)O gives PhPO(O)OH\(_2\) and Mn\(^{3+}\), the latter reacts with Mn\(^{3+}\) giving Mn\(^{5+}\).

The oxidation of H\(_2\)PO\(_2^-\) by [Mn(pd)(H\(_2\)O)]\(^{3+}\) (Hpd = pentane-2,4-dione) in perchlorate medium was first order both in the Mn(III) and the substrate. The rate, however, decreased with increasing pH and Hpd. The proposed inner-sphere mechanism is in Scheme 7. The estimated values of \(K_{ii}\) and \(kK_{ii}\) were 1.44×10\(^{-4}\) and (4.3 ± 0.1)×10\(^{-4}\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) at 40 °C.\(^{59}\)

Oxidations of RHP(O)O\(_2^-\) (R = H, OH, Ph) by tris(pyridine-2-carboxylato)Mn\(^{III}\), Mn\(^{III}\)(C\(_5\)H\(_4\)NCO\(_2\))\(_3\) was studied in picoline-picolinic acid buffer in the pH 4.63-5.45 range. The oxidations had a common mechanistic pathway in which the substrates could be either six or seven coordinated with the Mn(III). The breaking of the coordinated complex to a free radical, which subsequently reacted with another Mn(III) molecule to give the product, was rate-determining. A \(k_i/k_{ip} = 4.26\) in the H\(_2\)PO\(_2^-\) oxidation indicated P-H fission in the rate-determining step.\(^{70}\)

Oxidation of P1 by [Mn\(^{IV}\)Mo\(_9\)O\(_{32}\)]\(^{6+}\) ion proceeds through an intermediate complex, supported spectrophotometrically,

formed prior to its rate determining decomposition. The H⁺ ion is supposed to have a role in an equilibrium marked (i) in the proposed mechanism based on a direct two electron transfer step (iii) shown in Scheme 8, and the rate law is given in (vi).\textsuperscript{71}

\[
\begin{align*}
H_2MnV_{\text{Mo}}O_{32} & \rightleftharpoons K_1 H_2MnV_{\text{Mo}}O_{32}^- + H^+ \\
H_2MnV_{\text{Mo}}O_{32} + H_2PO_2 & \rightleftharpoons K_2 \text{Complex} \\
\text{Complex} + 5H_2O & \overset{k_1}{\rightarrow} \text{Mn}^{\text{II}}\text{Mo}_{24}^{10-} + 3H\text{Mo}_{24}^{1-} + H_2\text{PO}_4 + 13H^+ \\
2Mn^{\text{VIII}} + 10H^+ + 6\text{MoO}_4^{1-} & \overset{\text{fast}}{\rightarrow} \text{Mn}^{\text{VII}} + 6\text{MoO}_4^{1-} \\
10H^+ + 6\text{MoO}_4^{1-} + H_2\text{PO}_4 & \overset{\text{fast}}{\rightarrow} H_2\text{HPo}_4\text{Mo}_{24} + H_2O \\
k_{\text{obs}} = \frac{k_1K_1[H^+][H_2\text{PO}_4]}{[H^+] + K_1[1 + K_2[H_2\text{PO}_4]]} 
\end{align*}
\]

Scheme 8

The H⁺ dependence in the MnO₄⁻ oxidation of P₃ had the form \(k_{\text{obs}} = a + b[H^+]\). The interference from Mn³⁺ oxidation was ruled out because F⁻ had no effect on the rate. The formation of Mn⁷⁺ in the reaction was indicated by the excellent agreement between the rates measured in terms of MnO₄⁻ (525 nm) and soluble Mn⁷⁺ (400 nm). The similar nature of the rate expression for the H⁺ dependence in the reaction and that in the exchange reaction suggests that the formation of species similar to the species 3(6) might be rate limiting in the oxidation. But, the fact that the reaction had no zero order dependence on MnO₄⁻ ion ruled out this possibility. Further, the ratio of \(3k_6[\text{MnO}_4^-]/k_{\text{obs}} = 265\), and \(3k_1K_2[\text{MnO}_4^-]/k_{\text{obs}} = 44\) or \(3k_6K_1[\text{MnO}_4^-]/k_{\text{obs}} = 3.9 \times 10^5\) supported that it is the ‘inactive’ P₃ which is oxidized. Yet another argument against the participation of the ‘active’ form in the oxidation is that \(\text{H}_2\text{AsO}_3\), \(\text{H}_2\text{SO}_3\) or HSO₄⁻, a pair of electron is available on As or S, can be titrated by MnO₄⁻ ion at room temperature compared to the slow oxidation of P₃. The rate acceleration by the H⁺ ion was explained by considering the two mechanisms shown in Schemes 9 and 10\textsuperscript{12}

\[
\begin{align*}
H^+ + \text{MnO}_4^- & \overset{K_1}{\rightarrow} \text{H MnO}_4 \quad (a) \\
\text{MnO}_4^- + H_2\text{PO}_3 + H_2O & \overset{k_2}{\rightarrow} H_2\text{PO}_4 + \text{Mn}^V + 2H^+ \quad (b) \\
\text{HMnO}_4 + H_2\text{PO}_3 + H_2O & \overset{k_3}{\rightarrow} H_2\text{PO}_4 + \text{Mn}^V + 3H^+ \quad (c) \\
\text{Mn}^VII + \text{Mn}^V & \overset{\text{fast}}{\rightarrow} 2\text{Mn}^\text{VI} \quad (d) \\
2\text{Mn}^{\text{VIII}} + 2H_2\text{PO}_3 + 2H_2O & \overset{\text{fast}}{\rightarrow} 2H_2\text{PO}_4 + 2\text{Mn}^V + 4H^+ \quad (e) \\
k_{\text{obs}} = 2\bigg(k_6 + k_1K_1[H^+]\bigg)[H_2\text{PO}_4] \quad (A) 
\end{align*}
\]

Scheme 9

\[
\begin{align*}
\text{H}^+ + \text{H}_2\text{PO}_4^- & \overset{K_1'}{\rightarrow} \text{H}_2\text{PO}_3 \quad (k) \\
\text{MnO}_4^- + H_2\text{PO}_3 + H_2O & \overset{k_4}{\rightarrow} H_2\text{PO}_4 + \text{Mn}^V + 2H^+ \quad (l) \\
\text{MnO}_4^- + H_2\text{PO}_3 + H_2O & \overset{k_5}{\rightarrow} H_2\text{PO}_4 + \text{Mn}^V + 2H^+ \quad (m) \\
k_{\text{obs}} = 2\bigg(k_8 + k_8K_1'[H^+]\bigg)[H_2\text{PO}_4] \quad (B) 
\end{align*}
\]

Scheme 10

The second order rate constant in the oxidation of monoethylphosphonate was ascribed to the deprotonation equilibrium of the single OH group in acidic media. The Mn⁷⁺ was reduced to Mn⁴⁺ in the oxidation of diethylphosphonate both in acidic and neutral solutions. The increasing rate with pH became unmeasurably fast at pH 12. The change over from a first order to a zero-order dependence in Mn⁷⁺ indicated the formation of an intermediate with a lone pair of electrons on the phosphorus atom, which reacted rapidly with MnO₄⁻ ion.\textsuperscript{73}

A similar oxidation of P₁ and H₂PO₄⁻ over pH 1-6, had \(k_9/k_{\text{D}} = 4.6\) at pH 5.42. The reaction involved a H⁺ abstraction, probably, via a bridged transition state \(\text{[O}_2\text{MnO}_3\text{H}..\text{PH(O)(OH)}]^+\), formed in the rate determining step, which undergoes a simultaneous ejection of a proton to form the intermediate \(\text{[O}_2\text{MnO}^0\text{P}^\text{III}H\text{O(OH)}]^+\). The X rapidly breaks down to Mn³⁺ and H₂PO₄ or reacting with another X gives Mn⁹⁺, H₂PO₄ and P₃. The similarity of \(k_9\) (80 dm³ mol⁻¹ s⁻¹, P₁) and \(k_1\) (48.5 dm³ mol⁻¹ s⁻¹, H₂PO₄⁻) at 24°C suggested that the OH group of P₁ was not involved in the rate-determining step.\textsuperscript{75}

Michaelis-Menten kinetics is reported in the above reinvestigated reaction in acid perchlorate solution suggesting formation of a weak 1:1 complex on the msec time scale, which enhanced the MnO₄⁻ spectrum monitored over 10-100 msec (Figure 2). No evidence was found for a radical intermediate or the participation of Mn⁷⁺ in the rate determining step. The kinetic isotope \(k_{\text{D}}/k_9 = 4.3\) was observed. The complex between MnO₄⁻ and H₂PO₄⁻ appeared stronger than that with P₁. The rate dependence on H⁺ indicated that the self-decomposition of [MnO₄⁻P₁]⁻ to the products in the rate determining step is also assisted by a proton in a simultaneous rate determining step. The mechanism is given in Scheme 11 and the observed rate law is given in equation 16.
The oxidation of POA by bis(2,2'-bipyridyl)copper(II) permanganate (BBCP) was catalyzed by H⁺. The rate was independent of 2,2'-bipyridine but increased with AcOH in the solvent mixture, and exhibited a substantial kinetic isotope effect. The ‘inactive’ form was the reactive species.†

The oxidation of PPA by MnH2SO4²⁺ (species in H2SO4) proceeds through the rate limiting bimolecular reaction between MnH2SO4²⁻ and PPA giving PhHP(O)2, which reacting rapidly with MnH2SO4 gives PhHPO2. The rapid reaction of the later with H2O gives the PhH3PO4. The retardation in the rate H⁺ ions was due to deprotonation of MnH2SO4³⁻, the MnIII species in H2SO4.⁷⁸

Silver

The reaction between P1 and AgNO3 showed limiting rates with increasing [H⁺] or [Ag(I)] depending on their ratios. The products Ag⁺ inhibited the rate whereas P3 increased the rate. Formation constants of Ag⁺ complexes with H2PO2⁻ (K₁ = 138 ± 19 dm³ mol⁻¹) and H2PO3⁻ (K₂ = 510 ± 30 dm³ mol⁻¹) were reported. The complex H2PO2Ag was considered unreactive in the proposed mechanism. Two mechanisms were considered. The mechanism involving P1 (inactive form) had a simple rate law whereas the one based on the reaction with H2P(OH)2 had a complicated rate law the quantitative verification of which was limited.⁷⁹

P3 reacted with Ag²⁺ in HClO4 through two parallel paths. In one path P3 is rapidly protonated to H2PO3⁺ which is dissociated to H⁺ from a P-H bond and P(OH)2 which is rapidly oxidized to H3PO4. The 10⁵/k₁ = (3.3 ± 0.3) sec⁻¹ at 3.0 M H⁺ and 22 °C was in good agreement with the D exchange rate constant 10⁵/k₁ = 5.2 sec⁻¹ under identical conditions. In the other path Ag⁺, formed through the reversible reaction 2Ag⁺ ↔ Ag⁺ + Ag⁺, reacted with P1 in the rate-determining step. However the possibility of the rate determining reaction of Ag⁺ with P4, formed by Ag⁶⁺ and P3 in a rapid reversible reaction, as an alternate to the second path was not ruled out.⁸⁰

The rate law from the mechanism of Ag⁺ oxidation of P1, Scheme 4, in HClO4 solution is given in equation 17, which under certain approximations is reduced to equation (18).

The oxidation of Ag⁺ by HClO4 catalyzed by AgII⁺ (BBCP) was characterized by the following rate equations:

\[
\text{Ag}^+ + \text{HClO}_4^- \rightarrow \text{AgClO}_4^+ + \text{H}^+ \quad \text{(I)}
\]

\[
\text{AgClO}_4^+ + \text{ClO}_4^- \rightarrow \text{Ag(ClO}_4)_2 \quad \text{(II)}
\]

\[
\text{Ag}^+ + \text{H}_2\text{O} \rightarrow \text{Ag(OH)} + \text{H}^+ \quad \text{(III)}
\]

\[
\text{Ag}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{AgH}_2\text{PO}_4^+ \quad \text{(IV)}
\]

\[
\text{Ag}^+ + \text{H}_2\text{PO}_2 \rightarrow \text{products} \quad \text{(V)}
\]

\[
\text{AgClO}_4^+ + \text{H}_2\text{PO}_2 \rightarrow \text{products} \quad \text{(VI)}
\]

\[
\text{Ag(ClO}_4)_2 + \text{H}_2\text{PO}_2 \rightarrow \text{products} \quad \text{(VII)}
\]
Three oxycarids of phosphorus

\[ k_2 = \frac{2k_2[H_3PO_2]^{+} + k_3K[H^+]^+} {1 + K[H^+]^{+} + K_2K_3[H^+]^{+}} \]  

(17)

\[ k_{obs} = \frac{2k_2[H_3PO_2]} {1 + K[H^+]^{+}} \]  

(18)

\[ k_2 \text{ is } (7.6 \pm 0.7) \times 10^2 \text{ M}^{-1} \text{ s}^{-1} \text{ at } 30 \degree \text{C and } K_{IV} \text{ is } 38 \pm 2.5 \text{ M}^{-1}. \]

Evidence for the complexes AgClO4+ and Ag(ClO4)2 in HClO4 is provided.81

The oxidation of H2PO2− by Ag(OH)4− in strong alkaline solution was explained by considering the mechanisms in Scheme 13, based on the fact that there was neither kinetic nor spectrophotometric evidence for the intermediate complex formation, and Scheme 14 which assumed the formation of an intermediate because such intermediates are common for square-planar Ag(III). The absence of an inverse [OH ] dependence indicated an axial Ag-O-P bridge in which phosphorus accepted an oxygen from the AgIII which then received a pair of electrons directly into the empty dx2−y2 orbital. The intermediate undergoes redox both by direct internal redox and also assisted by OH− ion. D2PO2− reacted considerably slower, (aH/aD = 2.46; bH/bD = 8.2), indicating that P-H bond is broken in the rate-determining step. The a and b are defined in the rate law

\[ k_{obs} = \frac{1}{2k_2[H_3PO_2]} \frac{1}{1 + K[H^+]^{+}} \]  

The ionic strength dependence of the rate reflected competition between the second and third-order paths.82

A coloured intermediate in the Ag+ catalyzed oxidation of P1 by [ethylene bis(biguanide)]Ag+ was formed by Ag+ complex, Ag+ and HP[Ag(OH)2−] which was tentatively ascribed to some kind of Ag→Ag3+ charge transfer. The mechanism, Scheme 15, (ionization of P1 ignored), involved a two-step electron transfer from P1 to Ag3+ via Ag+ within the intermediate. Free radical was not detected. The second-order rate constant = 6.73 dm−1 mol−1 s−1 was much larger than the second-order rate constant reported79 in the corresponding oxidation by Ag+ ion.83

An alternate mechanism for the above reaction was also proposed in which the order of coordination of Ag species had changed. Thus H2PO2− preferentially coordinated with Ag+ (d10) rather than to strongly coordinated [Ag(enbb)2]3− (d8) because the formation constant for the AgH2PO2 was 138 ± 19 dm−1 mol−1 (ref. 69). The mechanism would lead to the same rate law with plausible approximations.84
Three oxycids of phosphorus

Thallium

The reaction of Tl\(^{3+}\) with P1 in HClO\(_4\) solution proceeds through the formation of an intermediate. The intermediate can produce the products through three alternatives. In the first alternative (a) is followed by the rate limiting reaction involving a single-stage two-electron transfer to H\(_2\)O. In the second alternative (a) is followed by the rate determining H\(^+\) transfer from P1 to Tl\(^{3+}\) to produce P3 and Tl\(^+\)O\(_2\) which reacted rapidly with H\(_2\)O to give P3. In the third alternative (a) is followed by its possible rate determining disintegration to Tl\(^{2+}\) and H\(_2\)P\(_2\)O\(_3\) because Tl\(^{2+}\) had been postulated in several reactions. The H\(_2\)PO\(_3\) is rapidly oxidized by Tl\(^{2+}\) in presence of H\(_2\)O. Thus all these possibilities lead to the common rate law involving a single-stage two-electron transfer to H\(_2\)O. In the fourth mechanism, the rate determining reaction (V) followed the dissociation equilibrium of P3. All these lead to the common rate law with certain approximations.

\[ \text{Tl}^{3+} + \text{H}_3\text{PO}_2 \overset{K}{\longrightarrow}[\text{TlH}_3\text{PO}_2]^3+ \quad (a) \]

The investigation of the medium effects, (log \(k = \log k_0 + \beta + \alpha\text{[Cl}^\text{−}\])\text{[Cl}^\text{−}\] where \(k = k_0f_f/a\) and \(k_0 = \text{rate constant at zero} \)

ionic strength, \(f = \text{activity coefficient}, a \) and \(b \) are the reactants forming the intermediate complex (\(\beta\)), \(\beta = \log(f_f/a)/(f_f^0)\) where \(f_f^0 = \text{activity coefficients in the absence of acid in the solution, }\alpha = \text{a constant and } (x) = (\text{HClO}_4)/(\text{HClO}_4 + [\text{NaClO}_4])\text{ in the above reaction}^{98} \) indicated that log \(k \) did not equal to log \(k_0 + \beta + \alpha(x)\). This indicated that the reaction occurs in 1-step of a 2-electron change as described in the first alternative.

The rate in Cl\(^{−}\) ions catalyzed reaction of Tl\(^{3+}\)-P1 decreased initially reaching a minimum at [Cl]_0/[Tl\(^{3+}\)]_0 = 1, and then starts increasing to a limiting value when this ratio is ~ 50. The rate increased with H\(^+\) and levels off at about 0.5 M. H\(_2\)P(OH) is the reactive species and the proposed mechanism is in Scheme 16. Equation (w) is the rate law. The reactivity of various Tl\(^{3+}\) species increased in the order TlCl\(_3^−\) > TlCl\(_2^−\) > TlCl\(_2^+\) > Tl\(^{3+}\) > TlCl\(_2^+\). P1 was the reactive species.

\[ \frac{d[Tl(III)]}{dt} = \frac{k_3}{K_{d}} [\text{Cl}] [\text{TlCl}_3] + k_3 [\text{TlCl}_2] + k_3 [\text{TlCl}_2] + k_3 [\text{TlCl}_2] (P1[H] + [H]) + K_d) \]

Scheme 16

Four mechanisms were proposed in the oxidation of P3 in view of inverse rate dependence on [H\(^+\)] (Scheme 17), which could be caused either by the dissociation of P3 or by the hydrolytic equilibrium of Tl\(^{3+}\) ion. The complex [TlH\(_3\)PO\(_2\)]\(^3+\), involved in the rate determining reaction (IV), could be formed by either of the three equilibrium (I)-(III). In the fourth mechanism, the rate determining reaction (V) followed the dissociation equilibrium of P3. All these lead to the common rate law with certain approximations.

\[ \text{Tl}^{3+} + \text{H}_3\text{PO}_3 \overset{K}{\longrightarrow}[\text{TlH}_3\text{PO}_2]^3+ + \text{H}^+ \quad (I) \]

\[ \text{Tl(OH)}^{2+} + \text{H}_3\text{PO}_3 \overset{K}{\longrightarrow}[\text{TlH}_3\text{PO}_2]^3+ + \text{H}_2\text{O} \quad (II) \]

\[ \text{Tl}^{3+} + \text{H}_3\text{PO}_5 \overset{K}{\longrightarrow}[\text{TlH}_3\text{PO}_2]^3+ + \text{H}^+ \quad (III) \]

\[ \text{Tl}^{3+} + \text{H}_2\text{PO}_4^− + \text{H}_2\text{O} \overset{r.d.}{\longrightarrow}\text{Tl}^3 + \text{H}_3\text{PO}_4^− + \text{H}^+ \quad (IV) \]

\[ \text{Tl}^{3+} + \text{H}_2\text{PO}_4^− + \text{H}_2\text{O} \overset{r.d.}{\longrightarrow}\text{Tl}^3 + \text{H}_3\text{PO}_4^− + \text{H}^+ \quad (V) \]

Scheme 17

The reduction of chlorothallium(III) complexes, TlCl\(_n^−\) (n = 1-4), by P3 and H\(_2\)PO\(_5^−\) indicated that the rate first decreased to a minimum at [Cl]_1/[Tl(III)] = 4 and then increased with increasing [Cl\(^-\)]. The Cl\(^-\) ion catalysis was explained either by invoking a chloride bridge activated mechanism or by nucleophilic attack of the phosphorus nucleophile :P(OH)\(_3\) on chlorine. The preferred later mechanism is shown below.

\[ \text{Cl}_{n−1}\text{TP}^3−\overset{\text{Cl}}{\longrightarrow}:\text{P(OH)}_3 \quad \text{products} \]

The complex formation between Ru\(^{3+}\) and P3 is envisaged in Ru\(^{3+}\)-catalyzed oxidation of P3 by Tl\(^{3+}\) ion in perchlorate solution. The rate law, \(k_{obs} = kKK[Ru{III}][P3]/([H]\text{[Cl]} + K)[P3]), \) based on the assumption that the decomposition of a termolecular complex [TlOH\(^2+\) · u\(^{III}\)PO\(_3^−\)] was rate determining. \(K \) and \(K_0 \) are respectively the formation constant for Ru\(^{3+}\)-P3 complex and hydrolytic constant for the hydrolysis of Tl\(^{3+}\) ion. The HP(O)(OH)\(_2\) was the reactive species.

\[ \text{RuCl}_3\overset{\text{Cl}}{\longrightarrow}\text{ClP(OH)}_3 \quad \text{products} \]

The catalysis by RuCl\(_3\) in the above reaction had the rate law: \(k_{obs} = kKK[Ru{III}][P3][\text{Cl}]/([H]\text{[Cl]} + K)[P3]), \) where \(K \) is the equilibrium constant (17.2 ± 1 dm\(^3\) mol\(^{−1}\) at (30 ± 0.1°C) for the envisaged complex formed by Ru\(^{3+}\) and P1 and \(K_0 \) is the hydrolytic constant for the hydrolysis of Tl\(^{3+}\) ion.

Cerium

The oxidation of P1 in HClO\(_4\), HNO\(_3\) and H\(_2\)SO\(_4\) solutions proceed through the complexes formed by P1 and Ce\(^{III}\) species, and acceleration of the rate with the acid. The oxidation of P1 was also studied in H\(_2\)SO\(_4\).
The mechanism in HClO4 solution is given in equations 19-21, that involved formation of various complexes (n = 1-6) as in equation (19). It was followed by another equilibrium (20) in which one of the coordinated H2PO2− was converted to HP(OH)O− in the presence of H+ ion. The complex containing the active form rapidly decomposed to the products as in equation (21). Complexes with n = 1 and 2 were stated to be formed in excess of CeIV. But at [P1] = 2[Ce(IV)], [Ce(H2PO2)2]+ dominated. However, it was partially converted to [Ce(H2PO2)3]− in excess of P1. The rate expression is in equation (22).

\[
\text{Ce}^{4+} + n\text{H}_2\text{PO}_2 \xrightarrow{K_n} [\text{Ce(H}_2\text{PO}_2)_{n-1}(\text{IV})^{(n-1)+} + n\text{H}^+] (19)
\]

\[
[\text{Ce(H}_2\text{PO}_2)_{n-1}(\text{IV})^{(n-1)+} + n\text{H}^+] \xrightarrow{k_{n}\text{H}} [\text{Ce(H}_2\text{PO}_2)_{n-2}(\text{IV})^{(n-2)+} + n\text{H}^+] \xrightarrow{k_{n}\text{H}} \cdots \xrightarrow{k_{n}\text{H}} [\text{Ce(H}^\text{II}(\text{OH})\text{O)(H}_2\text{PO}_2)_{(n-1)}](\text{IV})^{(n-1)+} + n\text{H}^+ (20)
\]

\[
[\text{Ce(H}^\text{II}(\text{OH})\text{O)(H}_2\text{PO}_2)_{(n-1)}](\text{IV})^{(n-1)+} \xrightarrow{k_n} \text{Ce}^{3+} + n\text{H}_3\text{PO}_3 (21)
\]

\[
-\frac{d[\text{Ce(IV)}]}{dt} = 2[H^+ \left( \frac{k_1\text{Ce(H}_2\text{PO}_2)^{3+} + k_2\text{Ce(H}_2\text{PO}_2)^{2+} + k_3\text{Ce(H}_2\text{PO}_2)^{3+}}{k_0\text{Ce(H}_2\text{PO}_2)^{3+}} \right)] (22)
\]

The reinvestigated reaction suggested that complexes with n = 1-6 were formed had similar H+ dependence but the formation of [Ce(H2PO2)4]14+ suggested. The neutral Ce(H2PO2)4 complex was stated to be most reactive because HP(O)O− had the highest probability for its existence, and its interaction with a water molecule in the coordination sphere. Thus the rate determining step is in equation (23).

\[
\text{Ce(H}_2\text{PO}_2)(\text{OH})_2 + n\text{H}_2\text{PO}_2 \xrightarrow{k_0} \text{Ce(H}_2\text{PO}_3)(\text{OH})_2 + n\text{H}_2\text{PO}_2 + n\text{H}^+ + n\text{H}^+ (23)
\]

The Ag+ catalysis in the above reaction was investigated. In the uncatalyzed reaction [Ce(P1)]4+ complexes with n = 1-6 were suggested to be initially formed, which was followed by the rapid equilibrium similar to (21). The complex containing HP(O)O− disintegrated to the products in the rate limiting step.

Two mechanisms were proposed to explain the Ag+ catalysis. In one mechanism, Ag+ oxidized P1 to P1+ in the initial rate determining step, which was followed by the rapid reaction of P1+ with another Ag+ ion and a water molecule to give P3 and Ag6+. The Ag6+ was rapidly reoxidized by Ce(IV) to Ag+ ion. In the other mechanism, the initially formed Ag+P1+ reacted rapidly with [Ce(P1)]1+ forming [AgP1Ce(P1)]1+, which reacted rapidly with H+ forming [AgP1Ce(OH)2Ce(P1)]1+. This complex disintegrated in the rate determining step to the products.

The redox in aqueous nitric acid decreased with increasing initial CeIV, an observation made earlier too but not explained.96 This study considered CeIV-CeIV dimers 99 which are unreactive to be responsible for the observation. Formation of a single complex rather than a number of complexes, suggested previously.100 The suggested mechanism is given in Scheme 5. Ag+ catalysis did not affect the order of reaction with respect to [Ce(IV)], and the kobs varied directly with [Ag(I)]. It seemed probable that the Ce(IV)-P1 complex was oxidised by Ag(I).101

\[
\text{H}_3\text{PO}_2 + \text{H}^+ \xrightarrow{K_1} \text{HP(OH)O}_2 + \text{H}^+ (I)
\]

\[
\text{Ce(IV)} + \text{HP(OH)O}_2 \xrightarrow{K_2} \text{Complex} (II)
\]

\[
\text{Complex + H}^+ \xrightarrow{k} \text{Ce(III)} + \text{H}_2\text{PO}_2 + \text{H}^+ (III)
\]

\[
\text{Ce(IV)} + \text{H}_2\text{PO}_2 + \text{H}_2\text{O} \xrightarrow{\text{fast}} \text{Ce(III)} + \text{H}_3\text{PO}_3 + \text{H}^+ (IV)
\]

Scheme 18

There have been few studies also. The P1 oxidation in H2SO4 involved [Ce(SO4)nP1]4− (n = 0-3) complexes. The disproportion of the complex with n = 2 was the rate determining step forming H2PO2 which reacted rapidly with CeIV in presence of water to give P3. HP(O)O− was not reactive. The reaction was stated to be catalyzed by Mn2+ and Ag+ without discussing the mechanism of catalyzed reaction.102

The RuCl3 catalyzed reaction of sulfato-cerium (IV) species with P1 reported complex dependence in P1.103

Ce(SO4)2 and HCe(SO4)3−, former being more reactive than the latter, reacted with P3 in parallel bimolecular reactions. No evidence either for the formation of an intermediate or the active form of P3 was obtained. The reaction was catalyzed by Ag(I) whereas Mn2+ and H+ ions had no effect on the rate.104

**Cobalt**

A reversible rate determining reaction between HP(O)O− and [CoW12O40]5− in Cl− resulted in the formation of H2PO2, which rapidly reacted with [CoW12O40]5− in presence of H2O to form P3. The probability of the formation of P1+ from the reaction of H2PO2 with [CoW12O40]5− was not excluded from the reaction that was independent of [H+]105

**Vanadium**

There have been quite a few studies on the oxidation of P1 and P3 by V5+ both in HClO4 and H2SO4 solution.

In the oxidation of P1, the rate in H2SO4 was faster than that in HClO4 solution. V(III)2+ was the reactive species in H2SO4 solution. P1 was oxidized in its reactive form,
The formation of VO$_2$H$_2$PO$_2$ and VO$_2$H$_2$PO$_2^+$ complexes were suggested in the reinvestigated oxidation of P1 in HClO$_4$. The respective formation constants were $16.6 \pm 2.2$ and $<1.4$ dm$^{-3}$ mol$^{-1}$. The mechanism suggested protonation of the complex VO$_2$H$_2$PO$_2$ by H$^+$ ($k_0$) followed by a tautomerization step in which water abstracts a phosphonic proton. The complexes VO$_2$(H$_2$PO$_2$)(H$_3$PO$_2$) ($k_1$) and VO$_3$(H$_3$PO$_2$)(H$_2$PO$_2$) ($k_2$) were similarly protonated followed by H$^+$ abstraction by water. Thus H$_2$P(OH)$_3$ intervened in the reaction attended by free radical formation. The $k_0$, $k_1$, and $k_2$ are the specific rate constants for the protonation steps. The Ag$^+$ catalyzed reaction had zero order dependence in V(V) indicating that P1 is oxidized to P3 primarily by Ag$^+$ through H$_2$PO$_2$. The catalysis operated through Ag$^+$/Ag$^0$ cycle.$^{109}$

The rate of oxidation of P3 by V$^V$ was faster in H$_2$SO$_4$ than in HClO$_4$. The reaction had second order dependence in the mineral acid concentration $\leq 5.5$M. The reactive species were VO$_2$2H$_2$SO$_4$ in H$_2$SO$_4$ and V(OH)$_2$ in HClO$_4$ solutions. These species reacted with Pr(OH)$_3$ in the slow step to form free radical P$^-$O(OH)$_2$. The course followed by the radical is described in the reaction of PPA in H$_2$SO$_4$ solution (see ref. 112).

The reinvestigated reaction confirmed second order dependence in HA (H$_2$SO$_4$ or HClO$_4$) and the faster rate in H$_2$SO$_4$. The intermediate V$^V$-P3 complex was formed prior to its decomposition to the free radical H$_2$P(OF)O$_3$ as a result of fission of P-H bond, supported by the $k_0$/$k_0^+$ > 1, and not that of H-O bond.$^{108,109}$ The catalysis by Ag$^+$ and the change of order from first to zero with respect to V$^V$ was explained by the rate controlling oxidation of P3 to H$_2$PO$_2$. The Ag$^+$ is rapidly oxidized to Ag$^+$ by V$^V$, and H$_2$P(OF)O$_3$ could be rapidly oxidized by both V(V) and Ag$^+$ in presence of water.$^{109}$ The oxidation of PPA by V(OH)$_2$HSO$_4$ in H$_2$SO$_4$ was faster than the oxidation by V(OH)$_2$ in HClO$_4$ solution. The formation of V$^V$-PPA was not detected in either of the acid. The acid catalysis was related to Hammett acidity function $-H_0$. V(OH)$_2$HSO$_4$ is stated to react with PPA in the rate limiting reaction to give the free radical PhP(OF)OH which was rapidly oxidized by V$^V$ to PhP(OF)OH ion in the following step. V(OH)$_2$ acting as a two-electron acceptor forming PhP(OF)OH in the slow step. The PhP(OF)OH ion reacted rapidly with water molecules giving C$_6$H$_5$P(O)(OH)$_2$. The rate limiting step happened to be the equilibrium between H$_2$P(OF)OH and HP(H$_2$)O$_2$ followed by rapid reaction between molecular HgCl$_2$ (not Hg$^{2+}$ or possible complexes) and two molecules of HP(H$_2$)O$_2$. The evidence for the rapid reaction is considered strong but not quite conclusive.$^{112}$

### Bismuth

The redox reaction of Bi$^V$ with P1, studied in aqueous mixture of HClO$_4$ and HF, was catalyzed by BiF$_5^-$ ion though the rate was independent of HF and F$^-$ ions. The proposed mechanism, Scheme 6, gives the rate law in equation (24).$^{113}$

\[
BiF_6^- + H^+ \xrightarrow{k_p} HBF_6
\]

\[
HBF_6 + H_3PO_2 \xrightarrow{k} \text{products}
\]

\[
HBF_6 + BiF_2^+ \xrightarrow{K} \text{complex}
\]

\[
\text{complex} + H_3PO_2 \xrightarrow{k_1} \text{products}
\]

\[k_{obs} = \left( K_p k + K_1 K_1 \left[ Bi^{III} \right] \right) \left[ P1 \right] \left[H^+ \right]^{(24)}
\]

### Iridium

In the oxidation of P1 by IrCl$_6^{2-}$ ions in HClO$_4$ solution the rate limiting step was the bimolecular reaction between the two reactants resulting in the formation of H$_2$PO$_2$ radical which was rapidly oxidized by another IrCl$_6^{2-}$ ion to P3. Cl$^-$ and SO$_4^{2-}$ ions accelerate the rate.$^{114}$

### Iron

The oxidation of P1 and PPA by FeL$_3^{3+}$ (L = 1,10-phenanthroline or 2,2'-bipyridine) in HClO$_4$ solution indicated that PPA was more reactive than P1, and these reacted in the ‘inactive’ form. An outer-sphere complex, Scheme 5, formed through paths (l) and (m), decomposed to free radical in the rate determining step. The paths are ambiguous because $\beta_2 = \beta_1 K_1 K_1$.$^{115}$

The alkaline oxidation of PPA by Fe(CN)$_6^{3-}$ in presence of OsO$_4$ indicated the formation of a complex between PPA and OsO$_4$ which then reacted with OH$^-$ in the rate determining step followed by a fast reaction between OsO$_4$ and Fe(CN)$_6^{3-}$.$^{116}$

### Nitrogen

The details of the mechanism of the oxidation of P1 by HNO$_3$ using Raman spectroscopy could not be accessed.$^{117}$
Three oxyacids of phosphorus

**Peroxodiphosphate**

The H₄P₂O₈ oxidation of P₁ in HClO₄ solution is in fact the oxidation by H₃PO₅, the hydrolytic product of the former because rate of hydrolysis happens to be larger than the rate of oxidation ($k$) of P₁ by H₂PO₅⁻. The $k_{obs}$ was given by equation (25) where $K_1$ and $K_2$ are related to the ionization of H₃PO₂ and H₃PO₅.¹¹⁸

$$k_{obs} = \frac{k[H₃PO₂][H⁺]}{[H⁺]^2 + K_1}$$  \hspace{1cm} (25)

**Peroxomon and disulfate**

Oxidation of P₃ by S₂O₈²⁻ in neutral solution was explained by a chain mechanism which was strongly suggested by the inhibition of the reaction by allyl acetate and fractional order dependence on P₃ and S₂O₈²⁻. The reactions in the chain mechanism are in Scheme 6, and the deduced rate law is in equation (26).¹¹⁹

$$-d[S₂O₈²⁻] \over dt = \frac{k₄[S₂O₈²⁻]^2}{kₖ₃ + k₄[H₂PO₂^-]^{1/2}} \left[ S₂O₈²⁻ \right]^{3/2}$$ \hspace{1cm} (26)

The oxidation of P₁ by S₂O₈²⁻ also followed a free-radical chain mechanism in which the steps (a)-(c), Scheme 20 for the oxidation of P₃, were common but the steps (d)-(g) were different as given in Scheme 9, and a different rate law as given in equation (27). The reaction was independent of acidity up to pH 8 but fell off rapidly with pH > 8 and reached a low plateau at pH 11. O₂ inhibited the reaction, and the effect increased with pH. The reaction was more complex in solutions < pH 2, and had no contribution from HP₃(OH)₂.¹²⁰

$$-d[S₂O₈²⁻] \over dt = \frac{k₅[S₂O₈²⁻]^2}{k₆ + k₅[H₂PO₂^-]^{1/2}} \left[ S₂O₈²⁻ \right]^{3/2}$$ \hspace{1cm} (27)

**Chlorine and its compounds**

The Chloramine T oxidation of P₁ was catalyzed by Cl⁻ and the rate increased with H⁺ and tended to have a limiting value at high concentrations.¹²¹
MeC₆H₄SO₂NCl₂ was the suggested reactive species in the chloramine oxidation of P₃, studied in acetate buffers, and the equation 29, where k is the observed third order rate constant, represented the rate law.²¹²

\[
k = \frac{k_{1}K_{d}[H^{+}] + k_{2}K_{d} + k_{3}K_{d}[H^{+}]^{-1}}{(4K_{d}[RNHCl] - RNH}_{2}[H^{+}] + [K_{1}]) (29)
\]

The oxidation of P₁, P₃ and PPA by N-chlorosuccinimide was similar to the oxidation by butyltriphenyl phosphonium dichromate.⁶³ The (CC=O)₂NH⁺Cl was the considered reactive species.¹²⁶

**Bromine and its compounds**

The earliest report on the reactions of P₃ with Br₂ in the presence of HBr (or H₂SO₄) and neutral bromides, and with Cl₂ in the presence of HCl and neutral chlorides. The reaction of both H₂PO₃⁻ and HPO₃²⁻ ions either with Br₂ or Cl₂ was bimolecular in nature, and retarded by H⁺ ion and the resulting halide ion. The rate law was given by equation (30) where k₁ and k₂ are the rate coefficients for the bimolecular reaction of X₂ (X = Cl or Br) with H₂PO₃⁻ and HPO₃²⁻ ions respectively, K₁ and K₂ are respectively the first and second dissociation constants of P₃, K₃ is the association constant for Br₂ from Br₂ and Br⁻, and kₗ₉obs is the second order rate constant. The dependence on H⁺ ruled out the reaction of X₂ with H₂PO₃⁻.²¹⁷

\[
k_{obs} = \frac{k_{1}K_{3}K_{3}}{K_{1}[H^{+}] + K_{2}K_{2}[H^{+}] + [K_{1}]) (30)
\]

The investigation of the corresponding reduct with P₁ and H₂PO₃⁻ reported that the oxidation of P₁ by Br₂ and Cl₂ occurs through the intermediacy of HP(OH)₂⁻, and the latter reacted with X₃ and probably with X₃, but not with HOX. However, H₂PO₃⁻ was oxidized by Br₂ only and not by Br⁻ or HOBr. The H⁺ in the range where P₁ mostly existed as H₂PO₃⁻ had no effect on the rate of the reaction. The mechanism in Scheme 23 was probable for the oxidation by Cl₂ also though the treatment for Br₂ oxidation tended to be more accurate than that by Cl₂. The k₁/kₗ₁ ≈ 10⁻¹² was reported.¹²⁴

\[
\begin{align*}
H₃P(O)O^{-} + H^{+} &\rightleftharpoons H₂P(O)OH \quad k_{1} \quad k_{-1} \\
&\stackrel{Br_{2}}{\rightleftharpoons} HP(O)OH \quad k_{2} \quad k_{-2} \\
&\stackrel{Br_{2}}{\rightleftharpoons} H₂PO₃ \quad k_{3} \quad k_{-3}
\end{align*}
\]

Scheme 23

In the oxidation of P₁, P₃ and PPA by aqueous Br₂ at [H⁺] = 0.001-5.0 M, the Br₂ was the reactive species. The H⁺-dependence indicated that the oxy-anion was oxidized more rapidly than the parent acid. The substantial k₂/kₗ₂ in the oxidations of P₁ and P₃ indicated cleavage of the P-H bond as the rate determining step. A study of [H⁺] variation showed the.²⁹

The oxidation of [Co(NH₃)₅{OP(H)(OH)O}]²⁺ and phosphite ions by Br₂ was studied over extended pH ranges. The oxidation of [Co(NH₃)₅{OP(H)(O)₂}]²⁺ was much faster than the oxidation of [Co(NH₃)₅{OP(H)(OH)(O)²}]²⁻. The reaction oxidant specie was Br₂, and not Br⁻ or HOBr, and the k₂/kₗ₂ = 2.4 indicated that the redox involved the rate determining fission of P-H bond. The rate law for the reaction was given by equation (31) where k is the specific rate constant for the oxidation, K₁ and K₂ are the first and second dissociation constants of H₂PO₃⁻ and K₃ is the acid dissociation constant of [Co(NH₃)₅{OP(H)(OH)O}]²⁻ ion, and [Phos] = [Co(NH₃)₅{OP(H)(O)₂}]²⁻ + [Co(NH₃)₅{OP(H)(OH)(O)²}]²⁻.

\[
k_{obs} = \frac{kK_{d}[Phos]}{[H^{+}] + [K_{1} + K_{2}Br_{2}]} (31)
\]

The Br₂ oxidation of free phosphate ions indicated that H₂PO₃⁻ was extraordinarily reactive than H₂PO₄⁻, which was the suggested reactive entity in an earlier study.¹²⁹ The k₂/kₗ₂ = 1.7 supported the fission of P-H bond in the rate determining step. The rate law for H₂PO₃⁻ oxidation is given in equation (32), where k is the specific rate constant for the oxidation, K₁ and K₂ are the first and second dissociation constants of H₂PO₃⁻ and K₃ is same as defined above. The redox occurred without oxygen exchange, the additional oxygen in the product H₃PO₄ comes from water.¹³⁰

\[
k_{obs} = kK_{d}[Phos] (32)
\]

Different rate laws i.e. equations (33) and (34) were respectively proposed for the oxidation of [NH₃)₅CoOP(H)(OH)O]²⁻ (I) and H₂PO₄⁻ by Br₂ along with a cyclic transition state. The oxidation of (I) was independent of H⁺ ion. [NH₃)₅CoOP(H)(OH)O]²⁻ was not detected during the oxidation. In equation (33), kₗ₉ and k₃ are the second order rate constants for the reactions effected by Br₂ and Br⁻ respectively and k₃ is the same meaning as defined in the above reaction.¹³⁰ The reaction with Br⁻ proceeded via a weak [Co(NH₃)₅OP(H)O]²⁻Br⁻ ion-pair.

\[
k_{obs} = \frac{k_{Br_{2}} + k_{Br_{3}}[Br_{2}^{-}]}{K_{Br_{2}}(Br_{2}^{-})}[\left(\frac{[NH_{3})_{5}CoOP(H)(O)_{3}^{2+}}{1 + K_{Br_{3}}[Br_{2}^{-}]})\right] (33)
\]

\[
k_{obs} = \frac{kK_{d}[Phos]}{[H^{+}] + [K_{1} + K_{2}Br_{2}]} (34)
\]

Br₂ oxidized H₂P(O)O⁴⁻ whereas H₂PO₃ and Br⁻ were unreactive. A k₂/kₗ₂ = 2.7 was noted with the implication similar to that stated in the above reaction.¹³⁰ The mechanism envisaged that the attack by O-atom at one end of the polarized Br₂ molecule was synchronous with fission.
of P-H bond and substantial transfer of H atom to the other. The transition state is therefore cyclic.\textsuperscript{131}

\text{Br}\textsubscript{3} ion was the reactive species in the oxidations by tetrabutylammoniumtribromide (\texttt{tbabt} in AcOH-H\textsubscript{2}O),\textsuperscript{132} and benzytrimethylammoniumtribromide (\texttt{btmb} in 9:1(vol/vol) acetonitrile-acetic acid).\textsuperscript{133} The reactive species in the oxidation by benzytrimethylammonium dichloroiodate (\texttt{btaci}) in presence of ZnCl\textsubscript{2} was [Ph\text{CH}\textsubscript{2}Me\textsubscript{3}N\textsuperscript{+}][ZnCl\textsubscript{2}],\textsuperscript{134} 

The oxidation of POA by acidic N-bromoacetamide is second order in POA and inverse first order in H\textsuperscript{+} ions. The oxy-acids reacted in the ‘inactive’ form with for that indicated the transfer of H from the P-H bond to the iodate in the rate determining step.\textsuperscript{135}

In the parallel oxidations by sodium N-bromobenzenesulphonamide in HClO\textsubscript{4} solution, the oxy-acids reacted in the ‘inactive form and (PhSO\textsubscript{2}NH\textsubscript{2}Br\textsuperscript{+})’ was postulated as the reactive species. A substantive k\textsubscript{eq}/k\textsubscript{D} in the oxidation of P1 and P3 indicated a rate determining step similar to that described above.\textsuperscript{136}

\textbf{Iodine}

An earlier report on the reaction of P1 and P3 with I\textsubscript{2} in both acidic and alkaline solution reported an equilibrium between H\textsubscript{2}PO(OH)\textsubscript{2} and HP(OH)\textsubscript{2}. Alkaline solutions drove the system in the direction of H\textsubscript{2}PO(OH)\textsubscript{2} which did not react with I\textsubscript{2}, while acidic solution favored the formation of HP(OH)\textsubscript{2}. The latter reacts with excess of I\textsubscript{2} forming I\textsubscript{2}PO\textsubscript{3} and P\textsubscript{3}\textsuperscript{–}. The rapid reaction of HP(OH)\textsubscript{2} with I\textsubscript{2} in slightly acidic solution was studied in various buffer solutions. The appreciable increase in speed of reaction of P3 existed as HPO(OH)\textsubscript{2} and P\textsubscript{2}O(OH)\textsubscript{2} in solution. The latter reacts with I\textsubscript{2} and H\textsubscript{2}O forming H\textsubscript{3}PO\textsubscript{4}. The greater stability of HPO(OH)\textsubscript{2} prevents it from forming intermediary compounds with I\textsubscript{2}; the reaction does not go to completion even with an excess of I\textsubscript{2}.\textsuperscript{137}

Another report suggested that compounds in which a H\textsuperscript{+} ion is bound directly to P, and is in the same state of charge, reacted identically with I\textsubscript{2}. The acidic compounds reacted with I\textsubscript{2} in the neutral state while the univalent anion did not react with I\textsubscript{2} with noticeable speed. The rapid reaction of P3 with I\textsubscript{2} in slightly acidic solution was studied in various buffer solutions. The appreciable increase in speed of reaction with the pH of the solution was explained by the fact that only the secondary ion reacted with I\textsubscript{2} and considerably more slowly with I\textsubscript{3}– ion. The methyl, ethyl- and isopropyl esters exhibited an increased reactivity with I\textsubscript{2}.\textsuperscript{138}

The reaction of H\textsubscript{3}PO\textsubscript{2} with I\textsubscript{2} involved the general acid catalyzed transformation of H\textsubscript{3}P(O)O\textsubscript{2} to HP(O)O\textsubscript{2} and HP(O)O\textsubscript{2}H. The former had no detectable reaction with I\textsubscript{2} whereas the latter reacted with I\textsubscript{2} and I\textsubscript{3}–. The study of the reaction in phosphate, arsenate and phosphite buffers (pH 6-8) indicated that H\textsubscript{3}PO\textsubscript{2} also reacted directly with I\textsubscript{2}.\textsuperscript{139}

The corresponding reaction of P3, studied in the pH range 2-9 indicated that HP(O)O\textsubscript{2}– ions reacted directly with I\textsubscript{2}. The reaction of H\textsubscript{3}PO\textsubscript{3} at pH < 1 was subject to general acid-base catalysis, similar to that shown in Scheme 2, forming \text{P}\textsubscript{(OH)}\textsubscript{3} which was oxidized by both I\textsubscript{2} and I\textsubscript{3}–. The reaction H\textsubscript{2}PO\textsubscript{3}– + I\textsubscript{2} was negligibly small to be detectable.\textsuperscript{140}

The exchange rate of the P-H bond of P3 in D\textsubscript{2}O increased with DCI. The oxidation was acid catalyzed and tautomerism played a role in the oxidation only above ~1N HCl. The proposed mechanism had similarity with the Scheme 2. A k\textsubscript{eq}/k\textsubscript{D} ≈ 3.6 was observed in the oxidation. The oxidation at pH 8.6 (borate buffer) was consistent with a mechanism involving the attack of I\textsubscript{2} on HP(O)O\textsubscript{2}– ions. The oxidation of HP(O)OHO– was much slower than that of HP(O)O\textsubscript{2}– ion.\textsuperscript{141}

The oxidation of P1 involved an equilibrium between H\textsubscript{3}P(O)O\textsubscript{2} and HP(O)O\textsubscript{2} where the conversion to HP(O)O\textsubscript{2} is rate determining. HP(O)O\textsubscript{2} is rapidly oxidized by IO\textsubscript{3}– ion. It is probable that the reaction of IO\textsubscript{3}– with HP(O)O\textsubscript{2} might be at a much slower rate than do other substances conforming to this rate law.\textsuperscript{142}

The reactions of H\textsubscript{3}PO\textsubscript{3}– and P1 with ICl and ICl\textsubscript{3} in H\textsubscript{2}O solutions and with ICl\textsubscript{4}– in aqueous solution were in conformity with the existence of H\textsubscript{3}P(O)O\textsubscript{3} and HP(O)O\textsubscript{2}. The oxidation reaction of P1 with I\textsubscript{2} occurred with preliminary addition of I to the acid.\textsuperscript{143}

\textbf{Hydrogen peroxide}

The catalytic effect of Ti\textsuperscript{IV} in the oxidation of P1 by H\textsubscript{2}O\textsubscript{2} in H\textsubscript{2}SO\textsubscript{4} was ascribed to the formation of TiO\textsubscript{2}(SO\textsubscript{4})\textsubscript{2} as an intermediate formed through the reactions H\textsubscript{2}O\textsubscript{2} + TiO\textsubscript{2}(SO\textsubscript{4})\textsubscript{2}H– → H\textsuperscript{+} + O\textsubscript{2}(TiO\textsubscript{2}(SO\textsubscript{4})\textsubscript{2})\textsuperscript{3–}, or H\textsubscript{2}PO\textsubscript{3} + TiO\textsubscript{2}(SO\textsubscript{4})\textsubscript{2}H– → H\textsubscript{3}PO\textsubscript{4} + H\textsuperscript{+} + TiO\textsubscript{2}(SO\textsubscript{4})\textsubscript{2}–.\textsuperscript{144}

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Three oxyacids of phosphorus

Section A – Review

[List of references]

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