



THREE OXYACIDS OF PHOSPHORUS: TAUTOMERISM AND OXIDATION MECHANISMS

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A review of the chemistry of H_2PO_2 (**P1**), H_3PO_3 (**P3**) and phenylphosphonic acid (**PPA**), and their oxidations by metal and non-metal oxidants is presented.

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The tribasic orthophosphoric acid, $\text{PO}(\text{OH})_3$, is popularly known as phosphoric acid. It is manufactured by treating the rock phosphate, $\text{Ca}_3(\text{PO}_4)_2$, either in nitric or sulfuric acid. Its main use is in the production of superphosphate fertilizer, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ by treating phosphate rock with concentrated phosphoric acid. It is also used in the soft drinks and to produce phosphate compounds. Calcium phosphate is used in tooth paste. Trisodium phosphate (Na_3PO_4) is used as a water softener and cleaning agent. The sodium polyphosphate is used in the production of synthetic detergents. Some condensed phosphates are used in industrial water treatment.

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.

The dibasic phosphorous acid also known as phosphonic acid, $\text{HPO}(\text{OH})_2$, is used in water treatment, and as pesticide in controlling variety of microbial plant diseases. The acid and the phosphite salts are used in the pharmaceutical industry as antioxidant, stabilizer and chelating agent in plastic system, as solvent in paint and as flame retardant on fibres, optical brighteners and in lubricant additives and adhesives. It is also used as corrosion resistant and a review on its inhibitory action has been recently published.¹

The monobasic hypophosphorous acid, $\text{H}_2\text{PO}(\text{OH})$, also named as phosphinic acid, is mainly used in the electro less plating; i.e. deposition of select metal films from solution on a sensitized surface and in pharmaceutical industry.

Name of the oxy acid	Formula	Structural formula	Basicity	Oxidation state of P
Hypophosphorous acid or Phosphinic acid	H_3PO_2 (P1)	$\text{H}_2\text{PO}(\text{OH})$	monobasic	+1
Phosphorous acid or Phosphonic acid	H_3PO_3 (P3)	$\text{HPO}(\text{OH})_2$	dibasic	+3
Phenylphosphinic acid	$\text{C}_6\text{H}_5\text{H}_2\text{PO}_2$ (PPA)	$\text{C}_6\text{H}_5\text{HPO}(\text{OH})$	monobasic	+1
Orthophosphoric acid	H_3PO_4	$\text{PO}(\text{OH})_3$	tribasic acid	+5
Metaphosphoric acid	HPO_3	$\text{O} \leftarrow \text{PO}(\text{OH})$	monobasic	+5
Hypophosphoric acid	$\text{H}_4\text{P}_2\text{O}_6$	$(\text{HO})_2\text{OP}-\text{PO}(\text{OH})_2$	tetrabasic	+5
Pyrophosphoric acid	$\text{H}_4\text{P}_2\text{O}_7$	$(\text{HO})_2\text{OP}-\text{O}-\text{PO}(\text{OH})_2$	tetrabasic	+5

The absence of such tautomeric forms $\text{H}_2\text{P}(\text{O})\text{O}^-$ 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' $\text{H}_2\text{P}(\text{O})\text{OH}$ acid.¹¹

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

$$k_{\text{exch}} = k_{\text{H}}[\text{D}^+] + k_{\text{w}} \quad (3)$$

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.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.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 negative charges on the O atoms present in the anions have greater effect in this respect. The H_2O -addition mechanism of O exchange is applicable only to those atoms that are capable of octet expansion. It is for this reason that periodates in which I is capable of shell expansion undergo rapid exchange compared to no exchange in perchlorates.¹⁴

Specific studies

Hypophosphorous acid

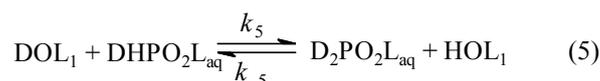
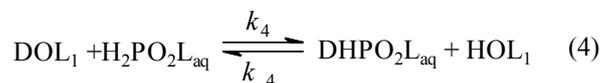
The exchange of tritium between **P1** and H_2O had the rate law: $R = (k_{\text{H}}[\text{H}^+] + k_{\text{P1}}[\text{P1}]) [\text{P1}]$ with $k_{\text{H}} = 0.055 \pm 0.0025$ and $k_{\text{P1}} = 0.0483 \pm 0.0024 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ at 30 °C. R is the rate at which one "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.¹⁵

The tritium (T, radioactive hydrogen) is reported to exchange as T^+ or T_2O with two P-H bonds of **P1**. The reaction $\text{H}_2\text{P}(\text{O})\text{OH} + \text{HTO} \leftrightarrow \text{HTP}(\text{O})\text{OH} + \text{H}_2\text{O}$, and the rate law for the rate limiting P-H fission was $k = k_1[\text{P1}] + k_2([\text{H}^+] + [\text{D}^+])$. The rate coefficients k_1 and k_2 equaled to $0.038 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$. 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.¹⁶

A parallel study of the exchange between D_2O and P-Hs of **P1** was studied using NMR spectroscopy. The rate expression, $k = k_1[\text{P1}] + k_2([\text{H}^+] + [\text{D}^+])$, was similar to that observed by Jenkins and Yost,¹⁶ and referred to the P-H

fission in the rate determining step of the reaction $\text{H}_2\text{POOH} + \text{D}_2\text{O} \rightarrow \text{HDPOOH} + \text{HDO}$. 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 °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.¹⁷

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.



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 °C. The rate constants $10^3 k_4 = 4.09$, $10^3 k_{-4} = 1.19$, $10^3 k_5 = 1.87$ and $10^3 k_{-5} = 1.01 \text{ mol dm}^{-3} \text{ s}$ at 25 °C. For the acid-catalyzed, rate-determining tautomerization of 'inactive' $\text{H}_2\text{P}(\text{O})\text{OH}$ to 'active' $\text{HP}(\text{OH})_2$, primary kinetic isotope effects $k_{\text{D}}/k_{\text{H}} = 0.36$ 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 tautomerization = 62 kJ was determined using the bond order (0.2) along with the Marcus theory of proton transfer.¹⁸

Phosphorous acid

The exchange reaction $\text{P-H} + \text{D} \leftrightarrow \text{P-D} + \text{H}$ (k_1, k_{-1}) in **P3** was studied in $\text{D}_2\text{O}/\text{H}_2\text{O}$ 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). The k_1 and k_{-1} had values of 3.42×10^{-3} and $1.67 \times 10^{-3} \text{ min}^{-1}$ respectively at 23 °C. The rate of exchange increased with increasing acidity (addition of HCl in H_2O , or DCl in D_2O). The exchange rate in $\text{HP}(\text{O})\text{OHO}^-$ and $\text{HP}(\text{O})\text{O}_2^{2-}$ ions was very slow. An isotope effect $k_{\text{H}}/k_{\text{D}} = 5.1$, 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.¹⁹

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 $1.97 \times 10^{-3} \text{ min}^{-1}$ at 1.49 mol dm^{-3} and 22 °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.

Phenylphosphinic acid

Phenylphosphinic acid, $\text{C}_6\text{H}_5\text{H-P}(\text{O})\text{OH}$, is also named as phenylphosphonous acid. Tautomerism in $\text{C}_6\text{H}_5\text{H-P}(\text{O})\text{OH}$ 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 C₆H₅H-P(O)OH resembles more with phosphinic acid H₂P(O)OH, rather more closely with that of dialkyl phosphonates (discussed below) than that of phosphorous acid HP(O)(OH)₂.²⁰

The exchange of P-H bond in C₆H₅H-P(O)OH in D₂O to P-D, studied in acidified EtOH-H₂O 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 H⁺ and OH⁻ ions and C₆H₅H-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 H₂O¹⁸ 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 OH⁻ ion catalyzed exchange presumably proceeded by direct proton abstraction. The rate law for the acid catalyzed reaction was $k = k_H[H^+] + k_w$ where k_w is the rate coefficient for the acid independent reaction.

Ester of Phosphonic acid

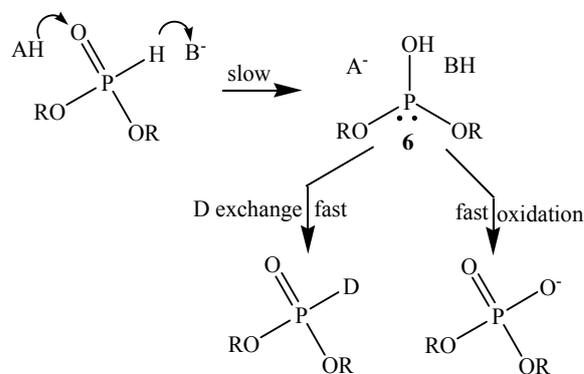
The reactions between dialkyl esters and cuprous halide,²² phenylazide,²³ and diazomethane²⁴ had been suggestive of equilibrium between the pentavalent 'inactive' and trivalent 'active' tautomeric form of the dialkyl esters of phosphorous acid. However, the existence of normal keto or 'inactive' form 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 D₂O, followed by the decreasing intensity of the P-H doublet in NMR spectrometer. The exchange reaction was first order in phosphonates and the rate law was: $k = k_H[H^+] + k_w$ where k is the specific rate constant and k_w is the catalytic constant for the spontaneous acid-independent exchange. $10^2 k_H$ ($\pm 10\%$) and $10^3 k_w$ ($\pm 30\%$) 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 Silver³¹ re-investigated the exchange of the P bonded H with D in D₂O 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 $k = k_{AcO^-}[AcO^-] + k_{AcOH}[AcOH] + k_w$. The hydrolysis of dialkyl phosphonates under the experimental conditions was negligible.³² The $10^2 k_{AcO^-}$ ($\pm 10\%$) = 52 and 7.5 dm³ mol⁻¹

min⁻¹ for dimethyl and diethyl phosphonate at 21.5 \pm 0.5 °C was much greater than the values of k_H^+ and k_w for the similar phosphonates,³¹ the 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.³³

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



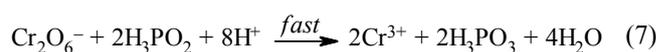
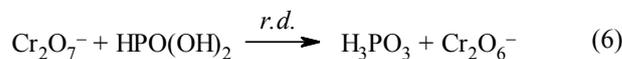
Scheme 2

Oxidation Studies

In this section the kinetics of oxidation of **P1**, **P3** and PhH₂PO₂ (hereafter abbreviated to **P1**, **P3** and **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 oxyacids and negative tests for the free radicals are not mentioned. No mention is made if the oxy-acid reacted in its 'inactive' form.

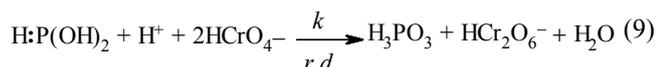
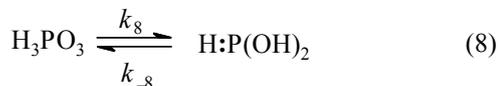
Chromium(VI)

Mitchell, while examining the effect of **P1** on titration of FeSO₄ by K₂Cr₂O₇, probably, for the first time postulated two reactions. The reaction between Cr₂O₇⁻ and HP(O)(OH)₂, the 'active' form, is unimolecular with respect to each and did not involve 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 H₂CrO₄.³⁵



The oxidation of **P3** in concentrated solutions of HClO₄, H₂SO₄ and HCl acids is reported without any formal rate law presuming Cr₂O₇²⁻ ion to be the reacting species because it was present in excess.³⁶

The intermediacy of the ‘active form’, H:P(OH)₂, equation (8), and HCr₂O₆⁻ ion, equation (9) was proposed assuming rapid reduction of HCr₂O₆⁻ to Cr(III) in the mechanism. The k_1k_3/k_{-1} had an estimated value of 466 at 25 °C.³⁷

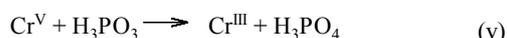
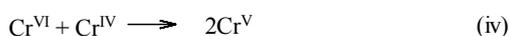
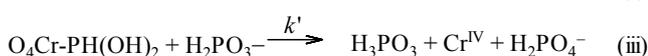
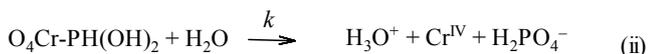
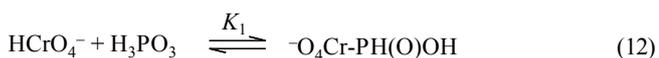


H₂PO₃⁻ was not oxidized in acetate buffer over several days at 25 °C, but it slowly oxidized at 100 °C to H₂PO₄⁻ ion. H-P bond of H₂PO₃⁻ inhibited the oxidation. However, **P3** oxidized fast in 1M H⁺ ion. The spectrometric equilibrium constant *K* for the equation (10) had a value 26. Although the rate law in equation (11) was given, yet the mechanism was not suggested. The values of k_1 and k_2 were ~10⁻⁴ mol dm⁻³ s⁻¹. Cl⁻ formed CrO₃Cl⁻ which inhibited the reaction.³⁸



$$\text{rate} = \frac{(k_1 + k_2[\text{H}_3\text{PO}_3])[\text{H}_3\text{PO}_3][\text{Cr(VI)}][\text{H}^+]}{1 + K[\text{H}_3\text{PO}_3]} \quad (11)$$

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 $k_2 = k'K_1K_a$ where *K_a* is the dissociation constant of the respective acid. A $k_H/k_D = 4$ suggested breaking of P-H bond in the rate determining step. H₂PO₂⁻ formed no anhydride at pH 4 nor was oxidized by HCrO₄⁻. The 10³ $k_1 = 1.7$, and $K_1 = 16$ were reported for **P3** at 25 °C. The corresponding values for **P1** were 6.0 and 11 respectively.⁴⁰



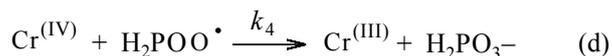
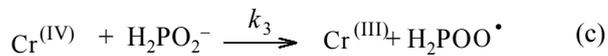
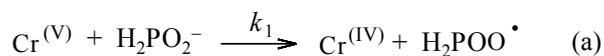
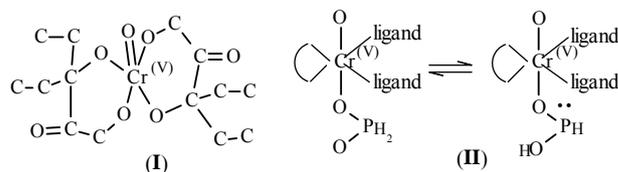
Scheme 3

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{(kK_1[\text{H}^+] + k'K_1K_a[\text{H}_3\text{PO}_3])[\text{Cr(VI)}][\text{H}_3\text{PO}_3]}{1 + K_1[\text{H}_3\text{PO}_3]} \quad (13)$$

Another study reported $K_1 = 13$ in addition to $K_a = 0.101$ in perchlorate media. Though the results agreed with the above mechanism, yet the rate equation (14) had two new terms, k_0 and $k_2[\text{H}^+]^2$, in addition to the terms appearing in equation (13). The k_0 may correspond either to the reaction of unprotonated complex having unknown number of solvent molecules or to abstraction of a phosphinic proton by OH⁻ ion from the neutral protonated complex. The $k_2[\text{H}^+]^2$ term is attributed to the formation of doubly protonated complex, H₄PCrO₆⁺, followed by proton abstraction by water.⁴¹

$$\text{rate} = (k_0 + k_1[\text{H}^+] + k_2[\text{H}^+]^2 + k_3[\text{H}_3\text{PO}_2])[\text{HCrO}_4^-][\text{H}_3\text{PO}_2] \quad (14)$$

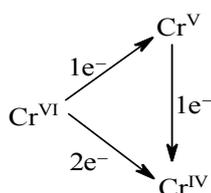
The oxidation of H₂PO₂⁻ by Cr^V chelate (**I**), formed with (C₂H₅)₂C(OH)CO₂H (**lig**), in buffered solution (**buff**) of the **lig** and its Na-salt, to H₂PO₃⁻ and Cr^{III} proceeded through bridged transition state (**II**) in which the mobilization of protons bound to P is favored by strongly acidic Cr^V or Cr^{IV}. The reaction towards the later stages becomes autocatalyzed, which was attributed to Cr^{IV} 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 Cr^{IV} starts getting accumulated when the reaction (c) becomes significant producing more free radical that reacts more rapidly with Cr^V compared to Cr^{IV} in reaction (d). This explains the catalysis of Cr^{IV} 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



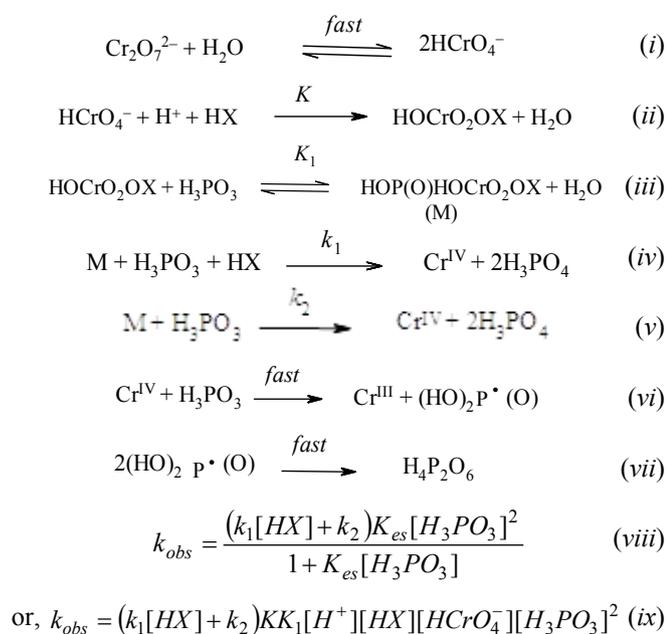
Scheme 4

The oxidation of H₂PO₂⁻ by Cr^{VI}, 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 Cr^V and Cr^{IV}, stabilized by the **lig**, by competing 1e⁻ and 2e⁻ paths (see below). The reduction of Cr^{VI} to Cr^{IV} and of Cr^{IV} to Cr^{II} involved hydride shifts from H₂PO₂⁻ to the Cr(=O), whereas formation of Cr^V and its reduction to Cr^{IV} involved preliminary coordination of H₂PO₂⁻ to the chromium center,

followed by P-H to O-H tautomerization (see **II**) within the binuclear complex and then transfer of a single-electron from P to the Cr center. The rates of formation of Cr^V and Cr^{IV} from Cr^{VI} were $(25.8 \pm 0.9) \times 10^{-8}$ and $(4.52 \pm 0.08) \times 10^{-8}$ mol dm⁻³ s⁻¹ respectively at 25 °C. The formation of Cr^{IV} had the rate law, $k_{\text{obs}} = (k_1 + k_2[\text{H}^+])[\text{H}_2\text{PO}_2^-][\text{H}^+][(\text{C}_2\text{H}_5)_2\text{C}(\text{OH})\text{CO}_2^-]^2$, with $k_1 = (15.3 \pm 0.2) \text{ M}^{-4} \text{ s}^{-1}$ and $k_2 = (2.5 \pm 0.2) \times 10^4 \text{ M}^{-5} \text{ s}^{-1}$. The $k_{\text{H}}/k_{\text{D}} = 3.9$ and 2.2 , $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 2.2$ and 1.7 were observed for generation of Cr^{IV} and Cr^V respectively. The formation of Cr^{II} indicated that the more usual state Cr^{III} was bypassed.⁴³



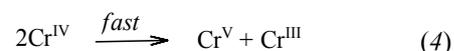
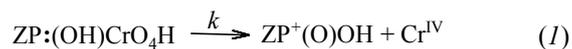
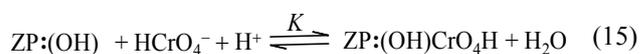
A very confusing paper on the oxidation of P3, which missed on the above mentioned references, mentions that Cr₂O₇²⁻ is the predominant Cr^{VI} species but considers HCrO₄⁻ as the reactive species in the mechanism consisting of reactions (i)-(vii), Scheme 5, where X = HSO₄⁻ or ClO₄⁻. The dimerization of the free radical (OH)₂P[•](O) to H₄P₂O₆ was not substantiated. The unsubstantiated formation of higher esters is stated to be more rapid than the rate-limiting formation of the 1:1 ester between HCrO₄⁻ and P3. However, their role in the mechanism was not explained. The reported rate law (viii), where K_{es} is perhaps equal to KK₁, however, does not match with the rate law (ix) that had been derived without considering the total [P3].⁴⁴



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 Cr^{IV}, was followed by several fast steps giving the products. The values ΔH(kcal) = 15 ± 1 and 5.2 ± 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



Scheme 6

The oxidation of **PPA** in HClO₄ showed Michaelis-Menten kinetics⁴⁶. 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 wave length at 350 nm, and on an arbitrary scale of 0-1 for the absorbance.

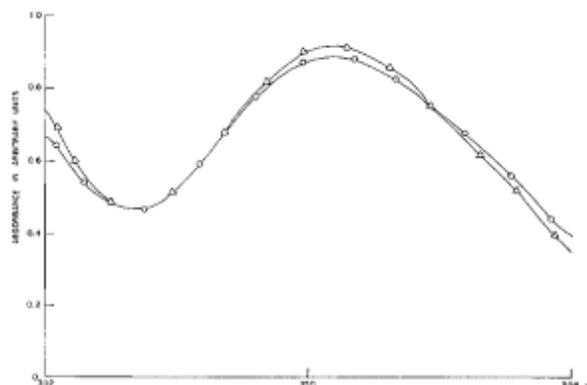


Figure 1. Rapid scan spectra of HCrO₄⁻ (O) and HCrO₄⁻ + PPA(Δ) between the λ 302-398 nm taken between 4.352 and 4.402s after mixing at 25 °C ($10^4[\text{HCrO}_4^-] = 4.0$, $10^3[\text{PPA}] = 4.0$, $[\text{H}^+] = 1.5 \text{ mol dm}^{-3}$).

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_{obs} and $-\text{H}_0$, 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. $19 \pm 4 \text{ dm}^3 \text{ mol}^{-1}$ and happened to be in agreement with the value $11 \pm 2 \text{ dm}^3 \text{ mol}^{-1}$ over the temperature range 26–46 °C as previously reported in ref. (48).⁴⁹

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 $k_{\text{obs}} = a + b[\text{H}^+]$. The reaction showed $k_{\text{H}}/k_{\text{D}} = 5.3$ 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 **pccH**⁺ with oxy-acids constituted the parallel rate-determining reactions involving the transfer of a H^- ion from the P-H bond of the 'inactive' specie to **pcc** and **pccH**⁺ giving $\text{RP}^+(\text{O})\text{OH}$ ($\text{R} = \text{H}, \text{OH}$ and Ph) and Cr^{IV} species. $\text{RP}^+(\text{O})\text{OH}$ 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 $k_{\text{obs}} = k_1 K_c [\text{P1}][\text{H}^+]/([\text{H}^+] + K_a)(1 + K_c [\text{P1}])$ with $K_c = 1.61 \text{ dm}^3 \text{ mol}^{-1}$ and $k_1 = 6.4 \times 10^{-4} \text{ s}^{-1}$. The rate determining disintegration of the complex to **P3** and Cr^{IV} was followed simultaneously by the rapid reaction similar to reaction (4) in Scheme 6 and the oxidation of **P1** by Cr^{V} to **P3** and Cr^{III} , which was the final reduction product as $\text{Cr}(\text{II})$ could not be detected.⁵¹

The Jodhpur group has repeated the oxidation of **POA** using very similar Cr^{VI} -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,⁵² benzyltriethylammoniumchlorochromate,⁵³ morpholiniumchlorochromate,⁵⁴ tetraethylammonium chlorochromate,⁵⁵ pyridiniumbromochromate,⁵⁶ ethyl-N-chlorocarbamate⁵⁷ benzyltrimethylammoniumchlorobromate,⁵⁸ and pyridiniumhydrobromideperbromide⁵⁹ 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.

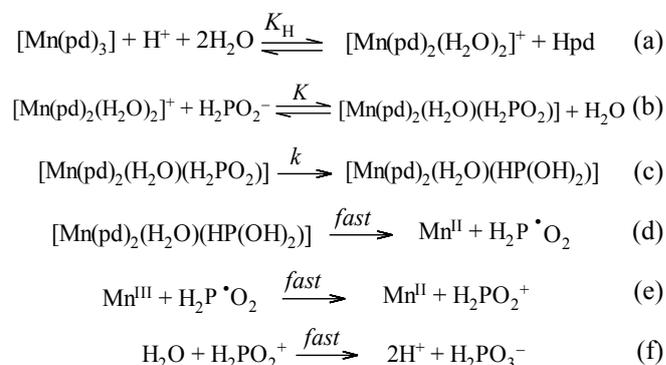
The rates of oxidations of **POA** by pyridinium fluorotrioxochromate,⁶⁰ and hexamethylenetetramine bromine in glacial acetic acid⁶¹ were independent of H^+ ion. The

oxidations by benzimidazoliumdichromate,⁶² butyltriphenylphosphoniumdichromate⁶³ ($k_{\text{H}}/k_{\text{D}} = 5.69$ for **P1**, $k_{\text{H}}/k_{\text{D}} = 5.30$ for **P3**), had first order dependence in H^+ ions varied using *p*-toluenesulphonic acid. The effect of H^+ ions in the oxidations by imidazoliumfluorochromate,⁶⁴ quinolinium-bromochromate,⁶⁵ and quinoliniumfluorochromate⁶⁶ was expressed by the expression $k_{\text{obs}} = a + b[\text{H}^+]$. 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**,⁶⁷ and those of **P1** and **P3**,⁶⁸ by Mn^{III} in H_2SO_4 had inverse first order dependence in $[\text{H}^+]$ which was explained by assuming MnHSO_4^{2+} , formed from the reversible dissociation of $\text{Mn}^{3+}\text{H}_2\text{SO}_4$ complex, as the reactive species. The mechanism is stated to be explainable by assuming bimolecular reaction between MnHSO_4^{2+} and $\text{Ph}_2(\text{OH})_2$ or via the intervention of the complex $\text{MnPhPO}_2\text{H}^{2+}$ formed by Mn^{3+} and $\text{PhHP}(\text{O})\text{OH}$. Formation of $\text{PhP}^+\text{O}_2\text{H}$ is the rate determining step followed by rapid formation of $\text{PhP}^+\text{O}_2\text{H}$ which is finally oxidized to $\text{PhP}(\text{O})(\text{OH})_2$. The complex reacting with H_2O gives $\text{PhP}(\text{O})(\text{OH})_2$ and Mn^{I} , the latter reacts with Mn^{III} giving Mn^{II} .

The oxidation of H_2PO_2^- by $[\text{Mn}(\text{pd})_2(\text{H}_2\text{O})_2]^+$ (Hpd = pentane-2,4-dione) in perchlorate medium was first order both in the $\text{Mn}(\text{III})$ 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_{H} , and kK were 1.44×10^5 and $(4.3 \pm 0.1) \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 40 °C.⁶⁹

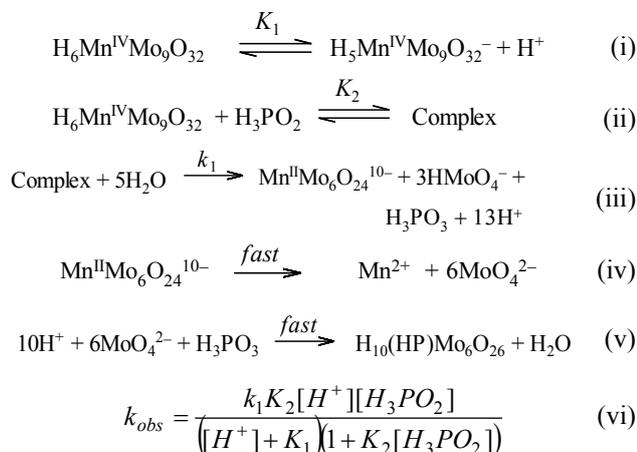


Scheme 7

Oxidations of $\text{RHP}(\text{O})\text{O}^-$ ($\text{R} = \text{H}, \text{OH}, \text{Ph}$) by tris(pyridine-2-carboxylato) Mn^{III} , $\text{Mn}^{\text{III}}(\text{C}_5\text{H}_4\text{NCO}_2)_3$, was studied in picolinate-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 $\text{Mn}(\text{III})$. The breaking of the coordinated complex to a free radical, which subsequently reacted with another $\text{Mn}(\text{III})$ molecule to give the product, was rate-determining. A $k_{\text{H}}/k_{\text{D}} = 4.26$ in the H_2PO_2^- oxidation indicated P-H fission in the rate-determining step.⁷⁰

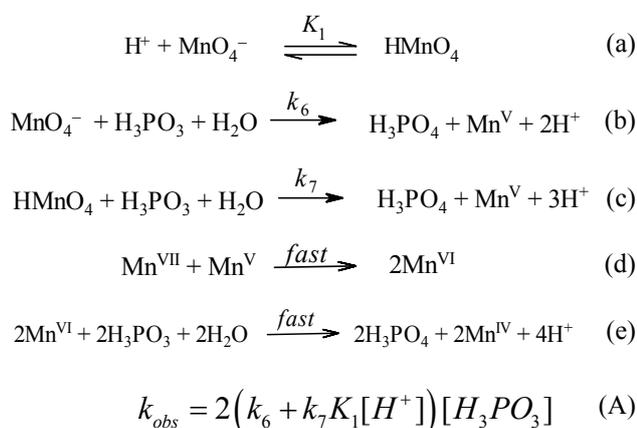
Oxidation of **P1** by $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ ion proceeds through an intermediate complex, supported spectrophotometrically,

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).

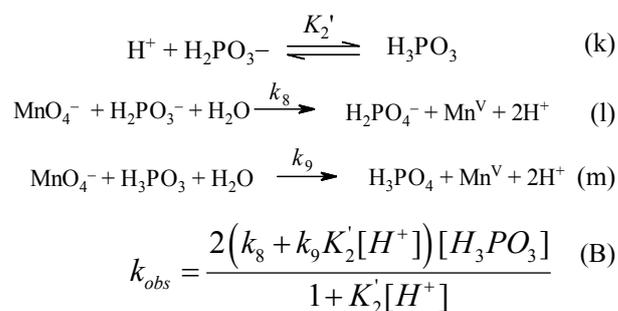


Scheme 8

The H^+ dependence in the MnO_4^- oxidation of P3 had the form $k_{\text{obs}} = a + b[\text{H}^+]$. The interference from Mn^{3+} oxidation was ruled out because F^- had no effect on the rate. The formation of Mn^{IV} in the reaction was indicated by the excellent agreement between the rates measured in terms of MnO_4^- (525 nm) and soluble Mn^{IV} (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 MnO_4^- ion ruled out this possibility. Further, the ratio of $3k_6[\text{MnO}_4^-]/k_w = 265$, and $3k_7K_1[\text{MnO}_4^-]/k_H = 44$ or $3k_9K_2[\text{MnO}_4^-]/k_H = 3.9 \times 10^3$ 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 H_3AsO_3 , H_2SO_3 or HSO_3^- , a pair of electron is available on As or S, can be titrated by MnO_4^- 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 10.⁷²



Scheme 9



Scheme 10

The reaction of MnO_4^- with **P3** and its anions, in presence of $\text{P}_2\text{O}_7^{4-}$ over pH 0-7.2, resulted in Mn^{V} and P^{V} in the rate limiting step. The rate expression is given in equation C. The reaction had a $k_H/k_D = 4.3 \pm 0.2$ at pH 2.2, 7.1 and 12.3. k_1 , k_2 and k_3 are the specific rate constants for **P3**, H_2PO_3^- and HPO_3^{2-} respectively, and K_1 and K_2 are the first and second dissociation constants of **P3**.

$$k = \frac{k_1[\text{H}^+]^2 + k_2K_1[\text{H}^+] + k_3K_1K_2}{K_1K_2 + K_1[\text{H}^+] + [\text{H}^+]^2} \quad \text{(C)}$$

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 Mn^{VII} was reduced to Mn^{IV} 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 Mn^{VII} indicated the formation of an intermediate with a lone pair of electrons on the phosphorus atom, which reacted rapidly with MnO_4^- ion.⁷³

A similar oxidation of **P1** and H_2PO_2^- over pH 1-6, had $k_H/k_D = 4.6$ at pH 5.42. The reaction involved a H^+ abstraction, probably, *via* a bridged transition state $[\text{O}_3\text{MnO} \cdot \text{H} \cdot \text{PH}(\text{O})\text{OH}]^\ddagger$, formed in the rate determining step, which undergoes a simultaneous ejection of a proton to form the intermediate $[\text{O}_3\text{Mn}^{\text{V}}\text{O} \cdot \text{P}^{\text{III}}\text{H}(\text{O})\text{OH}]^{2-}$ (X). The X rapidly breaks down to Mn^{V} and H_3PO_4 or reacting with another X gives Mn^{IV} , H_3PO_4 and **P3**. The similarity of k_1 ($80 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, **P1**) and k_2 ($48.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, H_2PO_2^-) at 24 °C suggested that the OH group of **P1** was not involved in the rate-determining step.⁷⁴

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 MnO_4^- spectrum monitored over 10-100 msec (Figure 2). No evidence was found for a radical intermediate or the participation of Mn^{3+} in the rate determining step. The kinetic isotope $k_H/k_D = 4.3$ was observed. The complex between MnO_4^- and H_2PO_2^- appeared stronger than that with **P1**. The rate dependence on H^+ indicated that the self-decomposition of $[\text{MnO}_4\text{P1}]^-$ to the products in the rate determining step is also assisted by a proton in a simultaneous rate determining step (r). The mechanism is given in Scheme 11 and the observed rate law is given in equation 16.

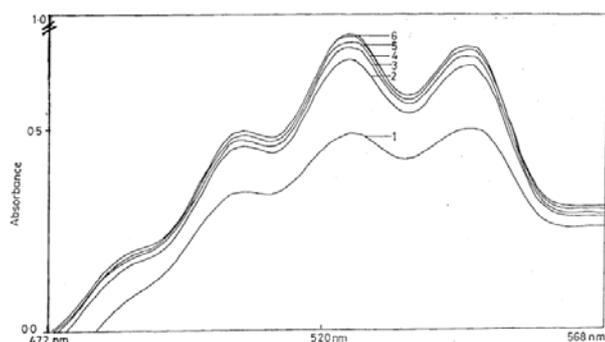
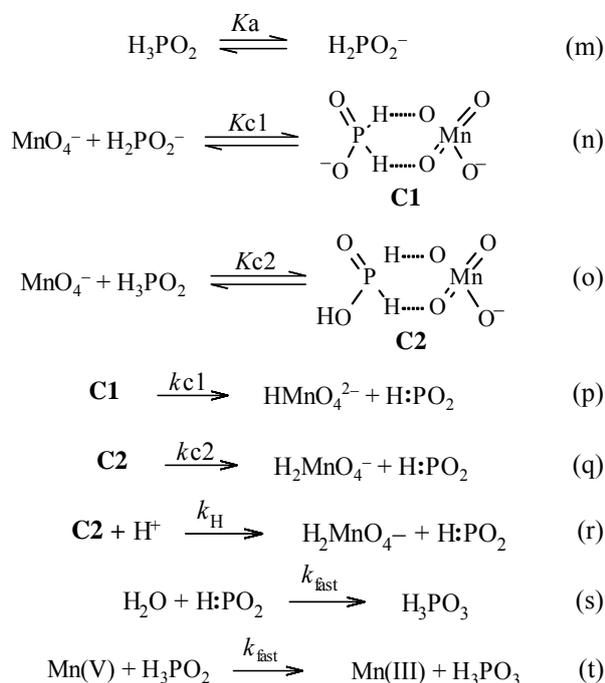


Figure 2. The rapid scans of the reaction mixture, 10^4 $[\text{MnO}_4^-] = 5.0$, $10^3[\text{P1}] = 5.0$, $[\text{H}^+] = 0.1$ mol dm^{-3} at 20 °C, recorded at 520 nm. The absorbance is on an arbitrary scale. The lowest spectrum was recorded 2 ms after mixing and the subsequent spectrum were recorded at the same interval. The saturation in the top most spectrum occurred in about 14 ms after mixing.



Scheme 11

$$k_{1\text{obs}} = \frac{(k_{C1}K_{C1}K_a + k_{C2}K_{C2}[\text{H}^+] + k_H k_{C2}[\text{H}^+]^2)[\text{H}_3\text{PO}_2]_0}{K_a + [\text{H}^+] + (K_{C1}K_a + K_{C2}[\text{H}^+])[\text{H}_3\text{PO}_2]_0} \quad (16)$$

An alternate mechanism in which reactions (n)-(r) are replaced by the rate determining reactions of $\text{MnO}_4^- + \text{H}_2\text{PO}_2^-$, $\text{MnO}_4^- + \text{P1}$ and $\text{MnO}_4^- + \text{P1} + \text{H}^+$ on the consideration that the complexes **C1** and **C2** might be side reactions so that the reaction becomes outer-sphere. The rate law (16) would still hold good.⁷⁵

The oxidation of **PPA** in acid perchlorate solution was similar to the above described reaction of **P1**. However, the values of the specific rate constants, $kc1$, $kc2$ and k_H , were appreciably lower than the corresponding values in **P1**. The activation parameters also differed widely.⁷⁶

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 effects.⁷⁷ The 'inactive' form was the reactive species.

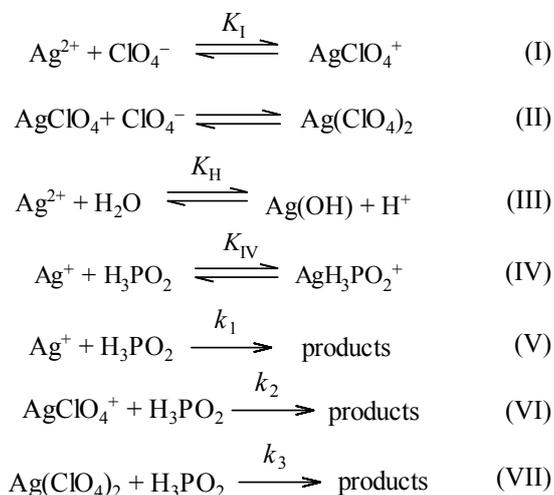
The oxidation of **PPA** by MnHSO_4^{2+} (species in H_2SO_4) proceeds through the rate limiting bimolecular reaction between MnHSO_4^{2+} and **PPA** giving PhHP^+O_2 , which reacting rapidly with MnHSO_4^{2+} gives PhHP^+O_2 . The rapid reaction of the later with H_2O gives the PhH_2PO_3 . The retardation in the rate H^+ ions was due to deprotonation of $\text{MnH}_2\text{SO}_4^{3+}$, the Mn^{III} species in H_2SO_4 .⁷⁸

Silver

The reaction between **P1** and AgNO_3 showed limiting rates with increasing $[\text{H}^+]$ or $[\text{Ag(I)}]$ depending on their ratios. The products Ag^0 inhibited the rate whereas **P3** increased the rate. Formation constants of Ag^+ complexes with H_2PO_2^- ($K_1 = 138 \pm 19$ dm^3 mol^{-1}) and H_2PO_3^- ($K_2 = 510 \pm 30$ dm^3 mol^{-1}) were reported. The complex $\text{H}_2\text{PO}_2\text{Ag}$ 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 H:P(OH)_2 had a complicated rate law the quantitative verification of which was limited.⁷⁹

P3 reacted with Ag^{2+} in HClO_4 through two parallel paths. In one path **P3** is rapidly protonated to H_4PO_3^+ which is dissociated to H^+ from a P-H bond and $:\text{P(OH)}_3$ in the rate determining step (k_1). $:\text{P(OH)}_3$ is rapidly oxidized to H_3PO_4 . The $10^5 k_1 = (3.3 \pm 0.3)$ sec^{-1} at 3.0 M H^+ and 22 °C was in good agreement with the D exchange rate constant $10^5 k = 5.2$ sec^{-1} under identical conditions. In the other path Ag^{III} , formed through the reversible reaction $2\text{Ag}^{\text{II}} \leftrightarrow \text{Ag}^{\text{III}} + \text{Ag}^{\text{I}}$, reacted with **P1** in the rate-determining step. However the possibility of the rate determining reaction of Ag^{II} with **P4**, formed by Ag^{II} 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^{II} oxidation of **P1**, Scheme 4, in HClO_4 solution is given in equation 17, which under certain approximations is reduced to equation (18).



Scheme 12

$$k_{1obs} = \frac{2[H_3PO_2] \left(k_1 + k_2 K_{II} [ClO_4^-] + k_3 K_2 K_3 [ClO_4^-]^2 \right)}{(1 + K_{IV} [Ag(I)]) \left(1 + K_H [H^+]^{-1} + K_2 [ClO_4^-] + K_2 K_3 [ClO_4^-]^2 \right)} \quad (17)$$

$$k_{obs} = \frac{2k_2 [H_3PO_2]}{1 + K_{IV} [Ag(I)]} \quad (18)$$

k_2 is $(7.6 \pm 0.7) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ at 30 °C and K_{IV} is $38 \pm 2.5 \text{ M}^{-1}$. Evidence for the complexes $AgClO_4^+$ and $Ag(ClO_4)_2$ in $HClO_4$ is provided.⁸¹

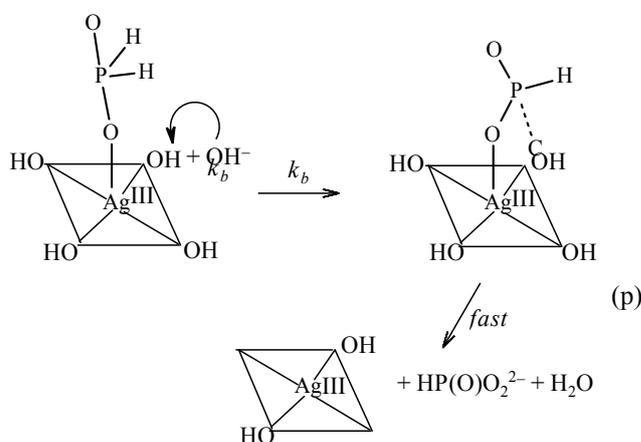
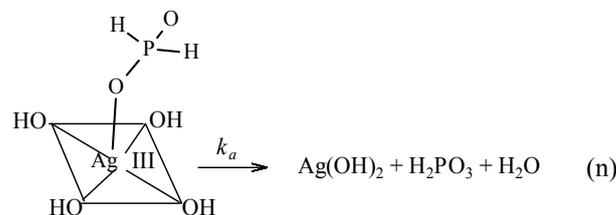
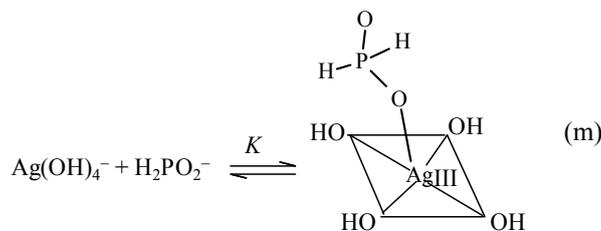
The oxidation of $H_2PO_2^-$ by $Ag(OH)_4^-$ in strong alkaline solution was explained by considering the mechanisms in Scheme 13, based on the fact that there was neither kinetic nor spectrophotometric evidence for the intermediate complex formation, and Scheme 14 which assumed the formation of an intermediate 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 Ag^{III} which then received a pair of electrons directly into the empty $d_{x^2-y^2}$ orbital. The intermediate undergoes redox both by direct internal redox and also assisted by OH^- ion. $D_2PO_2^-$ reacted considerably slower, ($a_H/a_D = 2.46$; $b_H/b_D = 8.2$), indicating that P-H bond is broken in the rate-determining step. The a and b are defined in the rate law $k_{obs} = (a + b[OH^-])$. The ionic strength dependence of the rate reflected competition between the second and third-order paths.⁸²



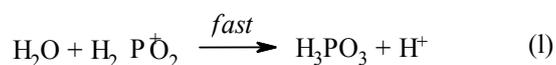
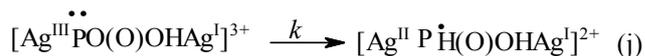
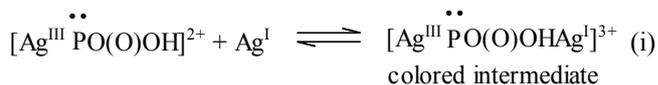
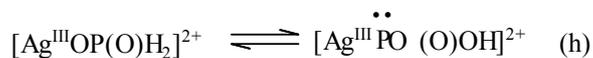
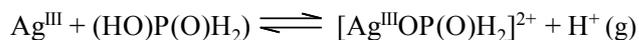
Scheme 13

A coloured intermediate in the Ag^+ catalyzed oxidation of **P1** by [ethylene bis(biguanide)] Ag^3 was formed by Ag^{3+} complex, Ag^+ and $HP:(OH)O^-$ which was tentatively ascribed to some kind of $Ag^+ \rightarrow Ag^{3+}$ charge transfer. The mechanism, Scheme 15, (ionization of **P1** ignored), involved a two-step electron transfer from **P1** to Ag^{3+} via Ag^+ within the intermediate. Free radical was not detected. The second-order rate constant = $6.73 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ 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 $H_2PO_2^-$ preferentially coordinated with Ag^+ (d^{10}) rather than to strongly coordinated $[Ag(enbbg)]^{3+}$ (d^8) because the formation constant for the AgH_2PO_2 was $138 \pm 19 \text{ dm}^3 \text{ mol}^{-1}$ (ref. 69). The mechanism would lead to the same rate law with plausible approximations.⁸⁴



Scheme 14



Scheme 15

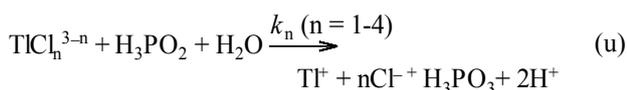
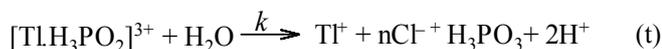
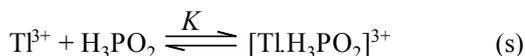
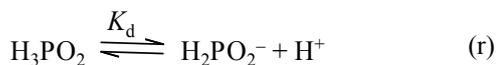
Thallium

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_2O . In the second alternative (a) is followed by the rate determining H^- transfer from **P1** to Tl^{3+} to produce $H_3P^+O_2$ which reacted rapidly with H_2O to give **P3**. In the third alternative (a) is followed by its possible rate determining disintegration to Tl^{2+} and $H_2P^+O_2$, because Tl^{2+} had been postulated in several reactions.^{85,86,87} The $H_2P^+O_2$ is rapidly oxidized by Tl^{2+} in presence of H_2O . Thus all these possibilities lead to the common rate law $k_{obs} = kK[P1]/(1 + K[P1])$ where K is the formation constant of $TlP1^{3+}$ formed in (a).



The investigation of the medium effects, ($\log k = \log k_0 + \beta + \alpha(x)$) where $k = k_0 f_a f_b / f_{\neq}$ and $k_0 =$ rate constant at zero ionic strength, $f =$ activity coefficient, a and b are the reactants forming the intermediate complex (\neq), $\beta = \log(f_a^0 f_b^0 / f_{\neq}^0)$ where $f^0 =$ activity coefficients in the absence of acid in the solution, $\alpha =$ a constant and $(x) = [HClO_4]/([HClO_4] + [NaClO_4])$,⁸⁹ in the above reaction⁸⁸ 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.⁹⁰

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. $H_2P(O)OH$ is the reactive species and the proposed mechanism is in Scheme 16. Equation (w) is the rate law. The reactivity of various Tl^{III} species increased in the order $TlCl_4^- > TlCl_3 > TlCl_2^+ > Tl^{3+} > TlCl^{2+}$. **P1** was the reactive species.⁹¹

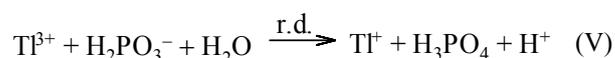


$$-d[Tl(III)]/dt = (kK[Tl^{3+}] + k_1[TlCl_2^+] + k_2[TlCl_2^+] + k_3[TlCl_3] + k_4[TlCl_4^-])([P1][H^+]/([H^+] + K_d)) \quad (w)$$

Scheme 16

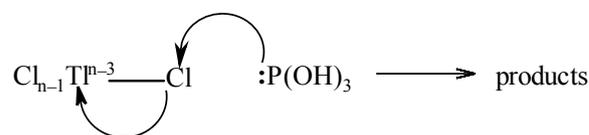
Four mechanisms were proposed in the oxidation of **P3** in view of inverse rate dependence on $[H^+]$ (Scheme 17),

which could be caused either by the dissociation of **P3** or by the hydrolytic equilibrium of Tl^{3+} ion. The complex $[TlH_2PO_3]^{2+}$, 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.⁹²



Scheme 17

The reduction of chlorothallium(III) complexes, $TlCl_n^{3-n}$ ($n = 1-4$), by **P3** and $H_2PO_3^-$ indicated that the rate first decreased to a minimum at $[Cl^-]/[Tl(III)] \approx 4$ 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.⁹³



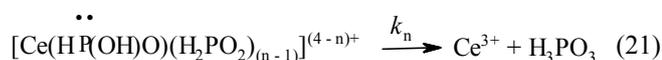
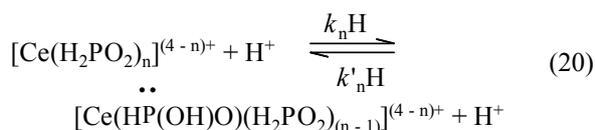
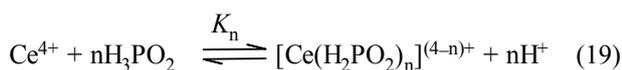
The complex formation between Ru^{3+} and **P3** is envisaged in Ru^{3+} -catalyzed oxidation of **P3** by Tl^{3+} ion in perchlorate solution. The rate law, $k_{obs} = kK_k[Ru^{3+}][P3]/([H^+] + K_h)(1 + K[P3])$, was based on the assumption that the decomposition of a termolecular complex $[TlOH^{2+} \cdot u^{III} \cdot {}_3PO_2]$ was rate determining. K and K_h 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.⁹⁴

The catalysis by $RuCl_3$ in the above reaction had the rate law: $k_{obs} = kK_k[Ru^{3+}][P1]/([H^+] + K_h)(1 + K[P1])$ where K is the equilibrium constant ($17.2 \pm 1 \text{ dm}^3 \text{ mol}^{-1}$ at $(30 \pm 0.1)^\circ\text{C}$) for the envisaged complex formed by Ru^{3+} and **P1** and K_h is the hydrolytic constant for the hydrolysis of Tl^{3+} ion.⁹⁵

Cerium

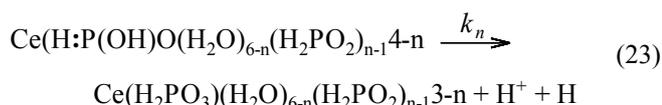
The oxidation of **P1** in $HClO_4$, HNO_3 and H_2SO_4 solutions proceed through the complexes formed by **P1** and Ce^{IV} species, and acceleration of the rate with the acid. The oxidation of **P3** was also studied in H_2SO_4 .

The mechanism in HClO₄ solution is given in equations 19-21, that involved formation of various complexes (n = 1-3) 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 Ce^{IV}. But at [P1] = 2[Ce(IV)], [Ce(H₂PO₂)₂]²⁺ dominated. However, it was partially converted to [Ce(H₂PO₂)₃]⁺ in excess of P1. The rate expression is in equation (22).⁹⁶



$$-\frac{d[\text{Ce}(\text{IV})]}{dt} = 2[\text{H}^+ \left(\begin{matrix} k_1^H [\text{Ce}(\text{H}_2\text{PO}_2)_3]^+ \\ k_2^H [\text{Ce}(\text{H}_2\text{PO}_2)_2]^{2+} \\ k_3^H [\text{Ce}(\text{H}_2\text{PO}_2)]^+ \end{matrix} \right)] \quad (22)$$

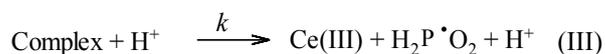
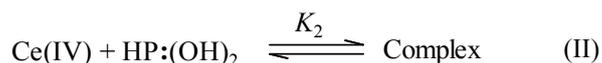
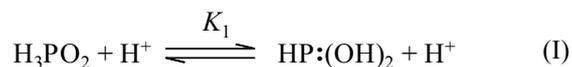
The reinvestigated reaction suggested that complexes with n = 1-6 were formed had similar H⁺ dependence but the formation of [Ce(H₂PO₂)_n]⁽⁴⁻ⁿ⁾⁺ suggested. The neutral Ce(H₂PO₂)₄ complex was stated to be most reactive because HP:(O)O⁻ had the highest probability for its existence, and its interaction with a water molecule in the coordination sphere. Thus the rate determining step is in equation (23).⁹⁷



The Ag⁺ catalysis in the above reaction was investigated. In the uncatalyzed reaction [Ce(P1)_n]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 Ag⁰. The Ag⁰ was rapidly reoxidized by Ce(IV) to Ag⁺ ion. In the other mechanism, the initially formed AgP1⁺ reacted rapidly with [Ce(P1)_n]⁴⁺ forming [AgP1Ce(P1)_n]⁵⁺, which reacted rapidly with H⁺ forming [AgP:(OH)₃Ce(P1)_n]⁵⁺. This complex⁹⁸ disintegrated in the rate determining step to the products.

The redox in aqueous nitric acid decreased with increasing initial Ce^{IV}, an observation made earlier too but not explained.⁹⁶ This study considered Ce^{IV}-Ce^{IV} dimers⁹⁹ which are unreactive¹⁰⁰ to be responsible for the observation. Formation of a single complex rather than a number of complexes, suggested previously.^{96,98} The suggested mechanism is given in Scheme 5. Ag⁺ catalysis did not affect the order of reaction with respect to [Ce(IV)], and the k_{obs} varied directly with [Ag(I)]. It seemed probable that the Ce(IV)-P1 complex was oxidised by Ag(I).¹⁰¹



Scheme 18

There have been few studies also. The P1 oxidation in H₂SO₄ involved [Ce(SO₄)_nP1]⁽⁴⁻²ⁿ⁾⁺ (n = 0-3) complexes. The disproportionation of the complex with n = 2 was the rate determining step forming H₂PO₂ which reacted rapidly with Ce^{IV} in presence of water to give P3. HP:(OH)₂ 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 later, 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:(OH)₂ and [CoW₁₂O₄₀]⁵⁻ in HCl resulted in the formation of H₂P^{*}O₂, which rapidly reacted with [CoW₁₂O₄₀]⁵⁻ in presence of H₂O to form P3. The probability of the formation of P1⁺ from the reaction of H₂P^{*}O₂ 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 V^V both in HClO₄ and H₂SO₄ solution.

In the oxidation of P1, the rate in H₂SO₄ was faster than that in HClO₄ solution. V(OH)₃²⁺ was the reactive species in H₂SO₄ solution. P1 was oxidized in its reactive form,

HP:(OH)₂ to HP*(O)OH which subsequently reacted with another V^V molecule in presence of H₂O to give **P3**.¹⁰⁶

The formation of VO₂.H₂PO₂ and VO₂.H₃PO₂⁺ complexes were suggested in the reinvestigated oxidation of **P1** in HClO₄. The respective formation constants were 16.6 ± 2.2 and < 1.4 dm³mol⁻¹. The mechanism suggested protonation of the complex VO₂.H₂PO₂ by H⁺ (k₀) followed by a tautomerization step in which water abstracts a phosphinic proton. The complexes VO₂(H₂PO₂)(H₃PO₂) (k₁) and VO₂(H₂PO₂)(H₃PO₂)₂ (k₂) were similarly protonated followed by H⁺ abstraction by water. Thus HP:(OH)₂ intervened in the reaction attended by free radical formation. The k₀, k₁ and k₂ 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 H₂PO₂. The catalysis operated through Ag⁺/Ag⁰ cycle.¹⁰⁷

The rate of oxidation of **P3** by V^V was faster in H₂SO₄ than in HClO₄. The reaction had second order dependence in the mineral acid concentration ≤ 5.5M. The reactive species were VO₂.2H₂SO₄⁺ in H₂SO₄ and V(OH)₂³⁺ in HClO₄ solutions. These species reacted with P:(OH)₃ in the slow step to form free radical P*(O)OH.¹⁰⁸ The course followed by the radical is described in the reaction of **PPA** in H₂SO₄ solution (see ref. 112).

The reinvestigated reaction confirmed second order dependence in HA (H₂SO₄ or HClO₄) and the faster rate in H₂SO₄. The intermediate V^V-**P3** complex was formed prior to its decomposition to the free radical H₂P*(O)O₃ as a result of fission of P-H bond, supported by the k_H/k_D > 1, and not that of H-O bond.^{108,108} 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 H₂P*(O)O₃. The Ag⁰ is rapidly oxidized to Ag⁺ by V(V), and H₂P*(O)O₃ could be rapidly oxidized by both V(V) and Ag⁺ in presence of water.¹⁰⁹ The oxidation of **PPA** by V(OH)₃HSO₄⁺ in H₂SO₄ was faster than the oxidation by V(OH)₃²⁺ in HClO₄ solution. The formation of V^V-**PPA** was not detected in either of the acid. The acid catalysis was related to Hammett acidity function -H₀. V(OH)₃HSO₄⁺ is stated to react with **PPA** in the rate limiting reaction to give the free radical PhP*(O)OH which was rapidly oxidized by V^V to PhP⁺(O)OH ion in the following step. V(OH)₃²⁺ acted as a two-electron acceptor forming PhP*(O)OH in the slow step. The PhP⁺(O)OH ion reacted rapidly with water molecules giving C₆H₅P(O)(OH)₂.¹¹⁰

Almost entirely different results were reported in the reinvestigated reaction of **PPA** in perchlorate solution. The k_{obs} = a + b[H⁺] prompted the suggestion that VO₂⁺ and V(OH)₃²⁺ ions were the reactive species for the paths that were independent and dependent on H⁺ ions. In the proposed mechanism, VO₂⁺ and V(OH)₃²⁺ reacted bimolecularly with PhP:(OH)₂ and PhHP(O)OH respectively to give a free radical¹¹¹ instead of phosphonium ion,¹¹⁰ thereby suggesting that V^V does not behave as a two-electron oxidant.¹¹⁰

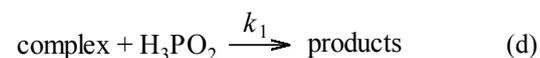
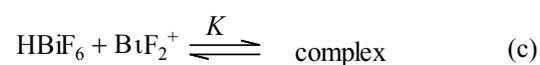
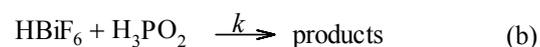
Mercury

The reaction between **P1** and HgCl₂ in HCl, in not too dilute solutions, was catalyzed by H⁺ but independent of HgCl₂. The rate limiting step happened to be the equilibrium

between H₂P(O)OH and HP:(OH)₂ followed by rapid reaction between molecular HgCl₂ (not Hg²⁺ or possible complexes) and two molecules of HP:(OH)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 HClO₄ and HF, was catalyzed by BiF₂⁺ ion though the rate was independent of HF and F⁻ ions. The proposed mechanism, Scheme 6, gives the rate law in equation (24).¹¹³



Scheme 19

$$k_{\text{obs}} = \left(K_p k + \frac{K_p K k_1 [\text{Bi}^{\text{III}}]}{1 + K [\text{Bi}^{\text{III}}]} \right) [\text{P1}][\text{H}^+] \quad (24)$$

Iridium

In the oxidation of **P1** by IrCl₆²⁻ ions in HClO₄ solution the rate limiting step was the bimolecular reaction between the two reactants resulting in the formation of H₂P*(O)O₂ radical which was rapidly oxidized by another IrCl₆²⁻ ion to **P3**. Cl⁻ and SO₄²⁻ ions accelerate the rate.¹¹⁴

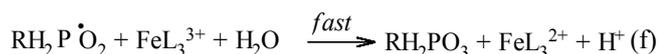
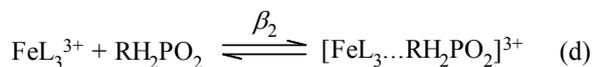
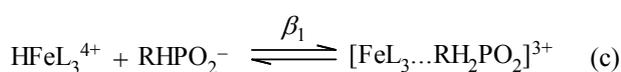
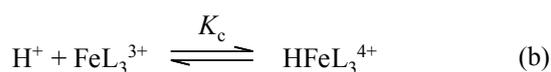
Iron

The oxidation of **P1** and **PPA** by FeL₃³⁺ (L = 1,10-phenanthroline or 2,2'-bipyridine) in HClO₄ 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 β₂ = β₁K_aK_c.¹¹⁵

The alkaline oxidation of **PPA** by Fe(CN)₆³⁻ in presence of OsO₄ indicated the formation of a complex between **PPA** and OsO₄ which then reacted with OH⁻ ion in the rate determining step followed by a fast reaction between OsO₄ and Fe(CN)₆³⁻.¹¹⁶

Nitrogen

The details of the mechanism of the oxidation of **P1** by HNO₃ using Raman spectroscopy could not be accessed.¹¹⁷



Scheme 20

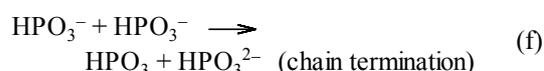
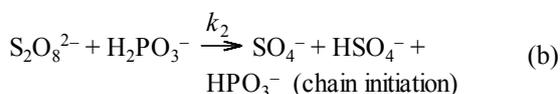
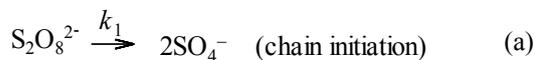
Peroxodiphosphate

The $\text{H}_4\text{P}_2\text{O}_8$ oxidation of **P1** in HClO_4 solution is in fact the oxidation by H_3PO_5 , the hydrolytic product of the former because rate of hydrolysis happens to be larger than the rate of oxidation (k) of **P1** by H_2PO_5^- . The k_{obs} was given by equation (25) where K_1 and K_2 are related to the ionization of H_3PO_2 and H_3PO_5 .¹¹⁸

$$k_{\text{obs}} = \frac{k[\text{H}_3\text{PO}_2][\text{H}^+]}{([\text{H}^+] + K_1)([\text{H}^+] + K_2)} \quad (25)$$

Peroxomon and disulfate

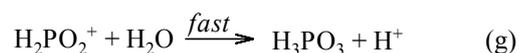
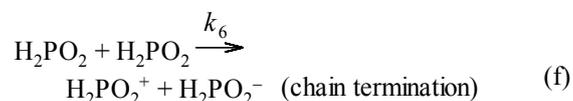
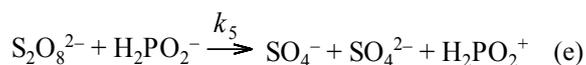
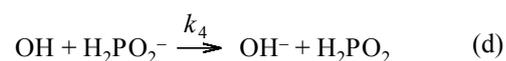
Oxidation of **P3** by $\text{S}_2\text{O}_8^{2-}$ in neutral solution was explained by a chain mechanism which was strongly suggested by the inhibition of the reaction by allyl acetate and fractional order dependence on **P3** and $\text{S}_2\text{O}_8^{2-}$. The reactions in the chain mechanism are in Scheme 6, and the deduced rate law is in equation (26).¹¹⁹



Scheme 21

$$\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = 0.5(k_1 + k_2[\Sigma \text{P3}]) \left[\text{S}_2\text{O}_8^{2-} \right]^{\frac{3}{2}} \quad (26)$$

The oxidation of **P1** by $\text{S}_2\text{O}_8^{2-}$ 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. O_2 inhibited the reaction, and the effect increased with pH. The reaction was more complex in solutions < pH 2, and had no contribution from $\text{HP}:(\text{OH})_2$.¹²⁰



Scheme 22

$$\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = \left(\frac{k_5^2 k_1}{k_6} + \frac{k_5^2 k_1 [\text{H}_2\text{PO}_2^-]^2}{k_6} \right) \left[\text{S}_2\text{O}_8^{2-} \right]^{\frac{3}{2}} \quad (27)$$

The $\text{S}_2\text{O}_8^{2-}$ oxidation of **P1**, induced by irradiation with visible light, in the presence of photocatalyst $\text{Ru}(\text{bipy})_3^{2+}$ followed the rate law in equation (28) where k_0 and k_q are respectively the excitation and quenching rate constants.¹²¹

$$-\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = \frac{k_q I_a [\text{S}_2\text{O}_8^{2-}]}{k_0 + k_q [\text{S}_2\text{O}_8^{2-}]} \quad (28)$$

The oxidation of **P1** by peroxomonosulphate ($\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$) in aqueous acidic solution proceeded through the formation of adduct by HSO_5^- and H_3PO_2 prior to its rate determining decomposition to **P3** and HSO_4^- . The possibility of OH^\cdot and $\text{SO}_4^{\cdot-}$ radicals intervening in the reaction was eliminated.¹²² The RuCl_3 -catalyzed oxidation of **P1** by HSO_5^- ion in acetate buffer had also been reported.¹²³

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.¹²⁴

$\text{MeC}_6\text{H}_4\text{SO}_2\text{NCl}_2$ 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.¹²⁵

$$k = \frac{k_1 K_d [H^+] + k_2 K_1 K_d + k_3 K_1 K_2 K_d [H^+]^{-1}}{(4 K_d [RNHCl] + RNH_2) ([H^+] + K_1)} \quad (29)$$

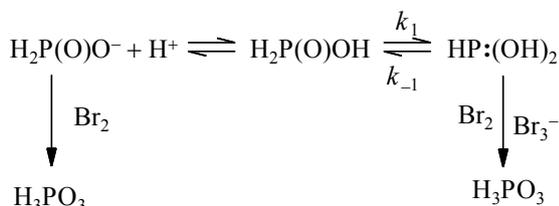
The oxidation of **P1**, **P3** and **PPA** by N-chlorosuccinimide was similar to the oxidation by butyltriphenyl phosphoniumdichromate.⁶³ The $(\text{CC}=\text{O})_2\text{NH}^+\text{Cl}$ was the considered reactive species.¹²⁶

Bromine and its compounds

The earliest report on the reactions of **P3** with Br_2 is in the presence of HBr (or H_2SO_4) and neutral bromides, and with Cl_2 in the presence of HCl and neutral chlorides. The reaction of both H_2PO_3^- and HPO_3^{2-} ions either with Br_2 or Cl_2 was bimolecular in nature, and retarded by H^+ ion and the resulting halide ion. The rate law was given by equation (30) where k_1 and k_2 are the rate coefficients for the bimolecular reaction of X_2 ($\text{X} = \text{Cl}$ or Br) with H_2PO_3^- and HPO_3^{2-} ions respectively, K_1 and K_2 are respectively the first and second dissociation constants of **P3**, K_3 is the association constant for Br_3^- from Br_2 and Br^- , and k_{obs} is the second order rate constant. The dependence on H^+ ruled out the reaction of X_2 with H_3PO_3 .¹²⁷

$$k_{\text{obs}} = \frac{k_1 K_1 K_3}{K_1 + [H^+]} + \frac{k_2 K_1 K_2 K_3}{[H^+] (K_1 + [H^+])} \quad (30)$$

The investigation of the corresponding redox with **P1** and H_2PO_2^- reported that the oxidation of **P1** by Br_2 and Cl_2 occurs through the intermediacy of $\text{HP}(\text{OH})_2$, and the latter reacted with X_3^- and probably with X_2 , but not with HOX . However, H_2PO_2^- was oxidized by Br_2 only and not by Br_3^- or HOBr . The H^+ in the range where **P1** mostly existed as H_2PO_2^- had no effect on the rate of the reaction. The mechanism in Scheme 23 was probable for the oxidation by Cl_2 also though the treatment for Br_2 oxidation tended to be more accurate than that by Cl_2 . The $k_1/k_{-1} \sim 10^{-12}$ was reported.¹²⁸



Scheme 23

In the oxidation of **P1**, **P3** and **PPA** by aqueous Br_2 at $[\text{H}^+] = 0.001\text{--}5.0 \text{ M}$, the Br_2 was the reactive species. The H^+ -dependence indicated that the oxy-anion was oxidized more rapidly than the parent acid. The substantial $k_{\text{H}}/k_{\text{D}}$ in the oxidations of **P1** and **P3** indicated cleavage of the P-H

bond as the rate determining step. A study of $[\text{H}^+]$ variation showed the.¹²⁹

The oxidation of $[\text{Co}(\text{NH}_3)_5\{\text{OP}(\text{H})(\text{O})_2\}]^+$ and phosphite ions by Br_2 was studied over extended pH ranges. The oxidation of $[\text{Co}(\text{NH}_3)_5\{\text{OP}(\text{H})(\text{O})_2\}]^+$ was much faster than the oxidation of $[\text{Co}(\text{NH}_3)_5\{\text{OP}(\text{H})(\text{OH})\text{O}\}]^{2+}$. The reactive oxidant specie was Br_2 , and not Br_3^- or HOBr , and the $k_{\text{H}}/k_{\text{D}} = 2.4$ 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, $K_{\text{Br}_3} = [\text{Br}_3^-]/[\text{Br}_2][\text{Br}^-]$, K_a is the acid dissociation constant of $[\text{Co}(\text{NH}_3)_5\{\text{OP}(\text{H})(\text{OH})\text{O}\}]^{2+}$ ion, and $[\text{Phos}] = [\text{Co}(\text{NH}_3)_5\{\text{OP}(\text{H})(\text{O})_2\}]^+ + [\text{Co}(\text{NH}_3)_5\{\text{OP}(\text{H})(\text{OH})\text{O}\}]^{2+}$.

$$k_{\text{obs}} = \frac{k K_a [\text{Phos}]}{(K_a + [\text{H}^+]) (1 + K_{\text{Br}_3} [\text{Br}^-])} \quad (31)$$

The Br_2 oxidation of free phosphite ions indicated that HPO_3^{2-} was extraordinarily reactive than H_2PO_3^- , which was the suggested reactive entity in an earlier study.¹²⁹ The $k_{\text{H}}/k_{\text{D}} = 1.7$ supported the fission of P-H bond in the rate determining step. The rate law for HPO_3^{2-} oxidation is given in equation (32), where k is the specific rate constant for the oxidation, K_{a1} and K_{a2} are the first and second dissociation constants of H_3PO_3 and K_{Br_3} is same as defined above. The redox occurred without oxygen exchange, the additional oxygen in the product H_3PO_4 comes from water.¹³⁰

$$k_{\text{obs}} = \frac{k K_{a1} K_{a2} [\text{P3}]}{([\text{H}^+]^2 + K_{a1} [\text{H}^+] + K_{a1} K_{a2}) (1 + K_{\text{Br}_3} [\text{Br}^-])} \quad (32)$$

Different rate laws i.e. equations (33) and (34) were respectively proposed for the oxidation of $[(\text{NH}_3)_5\text{CoOP}(\text{H})_2\text{O}]^{2+}$ (**1**) and $\text{H}_2\text{P}(\text{O})\text{O}^-$ by Br_2 along with a cyclic transition state. The oxidation of (**1**) was independent of H^+ ion. $[(\text{NH}_3)_5\text{CoOP}(\text{H})_2\text{O}]^{2+}$ was not detected during the oxidation. In equation (33), k_{Br_2} and k_{Br_3} are the second order rate constants for the reactions effected by Br_2 and Br_3^- respectively and K_{Br_3} has the same meaning as defined in the above reaction.¹³⁰ The reaction with Br_3^- proceeded via a weak $[\text{Co}(\text{NH}_3)_5\text{OP}(\text{H})_2\text{O}]^{2+} \cdot \text{Br}_3^-$ ion-pair.

$$k_{\text{obs}} = \frac{(k_{\text{Br}_2} + k_{\text{Br}_3} K_{\text{Br}_3} [\text{Br}^-]) [(\text{NH}_3)_5\text{CoOP}(\text{H})_2\text{O}^{2+}]}{(1 + K_{\text{Br}_3} [\text{Br}^-])} \quad (33)$$

$$k_{\text{obs}} = \frac{k_{\text{Br}_2} K_a [\text{H}_3\text{PO}_2]_0}{(K_a + [\text{H}^+]) (1 + K_{\text{Br}_3} [\text{Br}^-])} \quad (34)$$

Br_2 oxidized $\text{H}_2\text{P}(\text{O})\text{O}^-$ whereas H_3PO_2 and Br_3^- were unreactive. A $k_{\text{H}}/k_{\text{D}} = 2.7$ 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 Br_2 molecule was synchronous with fission

of P-H bond and substantial transfer of H atom to the other. The transition state is therefore cyclic.¹³¹

Br_3^- ion was the reactive species in the oxidations by tetrabutylammoniumtribromide (**tbatb** in $\text{AcOH-H}_2\text{O}$),¹³² and benzyltrimethylammoniumtribromide (**btmab** in 9:1(vol/vol) acetonitrile-acetic acid.¹³³ The reactive species in the oxidation by benzyltrimethylammonium dichloroiodate (**btaci**) in presence of ZnCl_2 was $[\text{PhCH}_2\text{Me}_3\text{N}^+][\text{Zn}_2\text{Cl}_6^-]2\text{I}^+$.¹³⁴

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

In the parallel oxidations by sodium N-bromobenzenesulfonamide in HClO_4 solution, the oxy-acids reacted in the ‘inactive form and $(\text{PhSO}_2\text{NH}_2\text{Br})^+$ was postulated as the reactive species. A substantive $k_{\text{H}}/k_{\text{D}}$ in the oxidation of **P1** and **P3** indicated a rate determining step similar to that described above.¹³⁶

Iodine

An earlier report on the reaction of **P1** and **P3** with I_2 in both acidic and alkaline solution reported an equilibrium between $\text{H}_2\text{PO}(\text{OH})$ and $\text{HP}:(\text{OH})_2$. Alkaline solutions drove the system in the direction of $\text{H}_2\text{PO}(\text{OH})$ which did not react with I_2 , while acidic solution favored the formation of $\text{HP}:(\text{OH})_2$ which reacted with excess of I_2 forming $\text{HP}(\text{OH})_2\text{I}$ and $\text{P}:(\text{OH})_2\text{I}$ (with elimination of HI) when **P1** was in excess. The $\text{HP}(\text{OH})_2\text{I}_2$ is decomposed by H_2O first into $\text{HP}(\text{OH})_4$ and then into $\text{HPO}(\text{OH})_2$. Similarly **P3** existed as $\text{HPO}(\text{OH})_2$ and $\text{P}:(\text{OH})_3$ in solution. The latter reacts with I_2 and H_2O forming H_3PO_4 . The greater stability of $\text{HPO}(\text{OH})_2$ prevents it from forming intermediary compounds with I_2 , the reaction does not go to completion even with an excess of I_2 .¹³⁷

Another report suggested that compounds in which a H^+ ion is bound directly to P, and is in the same state of charge, reacted identically with I_2 . The acidic compounds reacted with I_2 in the neutral state while the univalent anion did not react with I_2 with noticeable speed. The rapid reaction of **P3** with I_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_2 and considerably more slowly with I_3^- ion. The methyl, ethyl- and iso-propyl esters exhibited an increased reactivity with I_2 .¹³⁸

The reaction of H_3PO_2 with I_2 involved the general acid catalyzed transformation of $\text{H}_2\text{P}(\text{O})\text{OH}$ to $\text{HP}:(\text{OH})_2$. The former had no detectable reaction with I_2 whereas the latter reacted with I_2 and I_3^- . The study of the reaction in phosphate, arsenate and phthalate buffers (pH 6-8) indicated that H_2PO_2^- also reacted directly with I_2 .¹³⁹

The corresponding reaction of **P3**, studied in the pH range 2-9 indicated that HPO_3^{2-} ions reacted directly with I_2 . The reaction of H_3PO_3 at pH < 1 was subject to general acid-base catalysis, similar to that shown in Scheme 2, forming

$\text{P}:(\text{OH})_3$ which was oxidized by both I_3^- and I_2 . The reaction $\text{H}_2\text{PO}_3^- + \text{I}_2$ was negligibly small to be detectable.¹⁴⁰

The exchange rate of the P-H bond of **P3** in D_2O increased with DCI . The oxidation was acid catalyzed and tautomerism played a role in the oxidation only above $\sim 1\text{N}$ HCl . The proposed mechanism had similarity with the Scheme 2. A $k_{\text{H}}/k_{\text{D}} \approx 3.6$ was observed in the oxidation. The oxidation at pH 8.6 (borate buffer) was consistent with a mechanism involving the attack of I_2 on $\text{HP}(\text{O})\text{O}_2^{2-}$ ions. The oxidation of $\text{HP}(\text{O})\text{OHO}^-$ was much slower than that of $\text{HP}(\text{O})\text{O}_2^{2-}$ ion.¹⁴¹

The oxidation of **P1** involved an equilibrium between $\text{H}_2\text{P}(\text{O})\text{OH}$ and $\text{HP}:(\text{OH})_2$ where the conversion to $\text{HP}:(\text{OH})_2$ is rate determining. $\text{HP}:(\text{OH})_2$ is rapidly oxidized by IO_3^- ion. It is probable that the reaction of IO_3^- with $\text{HP}:(\text{OH})_2$ might be at a much slower rate than do other substances conforming to this rate law.¹⁴²

The reactions of H_2PO_2^- and **P1** with ICl and ICl_3 in HCl solutions and with ICl_4^- in aqueous solution were in conformity with the existence of $\text{H}_2\text{P}(\text{O})\text{OH}$ and $\text{HP}:(\text{OH})_2$. The oxidation reaction of **P1** with I_2 occurred with preliminary addition of I to the acid.¹⁴³

Hydrogen peroxide

The catalytic effect of Ti^{IV} in the oxidation of **P1** by H_2O_2 in H_2SO_4 was ascribed to the formation of $\text{TiO}_2(\text{SO}_4)_2^{3-}$ as an intermediate formed through the reactions $\text{HO}_2 + \text{TiO}_2(\text{SO}_4)_2^{2-} \rightarrow \text{H}^+ + \text{O}_2(\text{TiO}_2(\text{SO}_4)_2)^{3-}$ or $\text{H}_2\text{PO}_3 + \text{TiO}_2(\text{SO}_4)_2^{2-} \rightarrow \text{H}_3\text{PO}_4 + \text{H}^+ + \text{TiO}_2(\text{SO}_4)_2^{3-}$.¹⁴⁴

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