Reactions of Chromium(VI) with Phosphorus(III)[1] and Phosphorus(I). II. Ethyl-Substituted Phosphorus(III) Compounds

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Abstract: The reduction of $HCrO_4^-$ by $(C_2H_5O)_2(P{=}O)H$ and $(C_2H_5O)_2P({=}O)D$ is essentially brought about by C_2H_5OH following hydrolysis of the phosphite ester. With $(C_2H_5O)_2P({=}O)C_2H_5$ no hydrolysis occurs. Initial oxidation gives hydrolyzable ethyl phosphates such that initial rates are governed by direct reduction of $HCrO_4^-$ by ethyl diethyl phosphinate while final rates are due primarily to reduction of $HCrO_4^-$ by ethyl alcohol. From the study the following conclusions can be drawn. Oxidation of HO—P(=O)(H)– groups by $HCrO_4^-$ occurs *via* ester formation, O_3CrO—P(=O)(H)–, and concerted proton displacement by another proton *via* O_3CrO—P(H)($\ddot{O}:H^+$)–.[1] Use of phosphite esters and/or $ClCrO_3^-$ [1] blocks ester formation and inhibits P(III) oxidation. High pH (acetate buffer) prevents proton displacement and oxidation does not occur.[1] Oxidation of P(III) in which neither hydrolysis nor ester formation can occur, $(C_2H_5O)_2P(O)C_2H_5$, is about two orders of magnitude slower in 1 *M* $HClO_4$ than with H_3PO_3. Because reduction of $HCrO_4^-$ by ethanol and methanol contributes to the pertinent data, the kinetics of these reactions in 1 *M* $HClO_4$ have been studied independently. The equilibrium constant for chromate ester formation with alcohol in this medium is too small to detect. Ethanol is oxidized about 20 times as fast as methanol. $(C_2H_5O)_3P$: is oxidized rapidly by $HCrO_4^-$ in glacial acetic acid.

The oxidation of H_3PO_3 by Cr(VI) reported in paper I[1] of this series indicated quite clearly that ester formation (>Cr–O–P<) and P–H bond dissociation play a role either in the formation of the activated complex or in the rate-determining step. Formation of CrO_3Cl^- blocks ester formation inhibiting oxidation, and P–D bonds dissociate more slowly than P–H bonds. However, ester formation ($HPCrO_6^{2-}$) does occur at pH 5 without oxidation of P(III). Therefore, it became interesting to perform studies in which the various protons in H_3PO_3 are replaced by alkyl groups to see what effects blocking of ester formation and hydrolysis might have on Cr(VI) oxidation of P(III).

Experimental Section

Inorganic reagent grade chemicals, absolute ethanol, and methanol were used without further purification. $(C_2H_5O)_2P(O)H$, $(C_2H_5O)_3P$, and $(C_2H_5O)_2P(O)C_2H_5$ were kindly furnished by Professor A. F. Isbell and purified by distillation. Only Cr(VI) among reactants and products absorbs light significantly at 350 mμ. The disappearance of Cr(VI) was followed by measuring decreasing absorbance with time at 350 mμ using Beckman DU and Bausch and Lomb Spectronic 20 spectrophotometers with cell compartments kept at 25°. All runs contained $[Cr(VI)]_0 \leq 5 \times 10^{-4}$ *M* and a large excess of P(III) compounds or C_2H_5OH. $(C_2H_5O)_3P$ is insoluble in water but reacts hydrolytically to produce $(C_2H_5O)_2P(O)H + C_2H_5OH$. This reaction was used to make deuterated diethyl phosphinate.[3] All reactions were studied in 1 *M* ($HClO_4$ + $NaClO_4$).

Results

Oxidation of Ethanol by Cr(VI) in 1 *M* $HClO_4$. All reactions showed first-order disappearance of Cr(VI). The first-order rate constant (k_{obsd}) is directly proportional to [EtOH] over the range 0.01–1.0 *M*.

$$-d[Cr(VI)]/dt = k_a[Cr(VI)][EtOH]$$

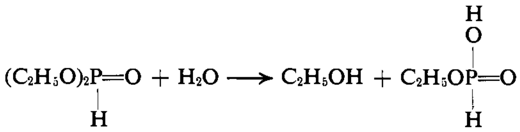
$$k_a = (6.3 \pm 1.0) \times 10^{-3} \qquad (1)$$

Oxidation of Methanol. Only a few runs were attempted. The rate law is approximately

$$d[Cr(VI)]/dt = k_2[Cr(VI)][MeOH]$$

$$k_2 = (3 \pm 0.5) \times 10^{-4} \qquad (2)$$

Hydrolysis of Diethyl Phosphite, $(C_2H_5O)_2P(O)H$. The reaction



$$\underset{\displaystyle H}{(C_2H_5O)_2\overset{}{P}}{=}O + H_2O \longrightarrow C_2H_5OH + C_2H_5O\underset{\displaystyle H}{\overset{\displaystyle \overset{\displaystyle H}{O}}{P}}{=}O \qquad (3)$$

was followed for 1 and 0.1 *M* ester by noting the increase in acid titer with time. Hydrolysis of the diester was over 90% complete before a second end point indicated formation of some H_3PO_3 from the monoester. For reaction 3

$$\text{rate} = k_h[\text{diester}] \qquad k_h = (5.5 \pm 0.5) \times 10^{-5} \qquad (4)$$

First-order kinetics is observed throughout each run.

Hydrolysis of Triethyl Phosphite, $(C_2H_5O)_3P$. Triethyl phosphite is rather insoluble in water but reacts fairly rapidly to give a solution of diethyl phosphite and ethanol.

Reduction of Cr(VI) with Triethyl Phosphite. In glacial acetic acid triethyl phosphite reduces Cr(VI) at rates too fast to measure using equipment available to us at the time of this study. A solution 0.1 *M* in triethyl phosphite and 1 *M* in perchloric acid reduced Cr(VI) initially at a rate twice that of 0.1 *M* ethanol, but after 0.5 hr the rate was the same as if ethanol, equivalent to the hydrolysis of triethyl phosphite to diethyl phosphite, were the only reducing agent present. The faster initial rate could be caused by traces of unhydrolyzed triethyl phosphite.

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[1] Paper I: G. P. Haight, Jr., M. Rose, and J. Preer, *J. Am. Chem. Soc.*, **90**, 4809 (1968).

[2] University of Illinois; to whom correspondence should be directed.

[3] G. Aksnes and O. Grahl-Nielsen, *Acta Chem. Scand.*, **19**, 2373 (1965).

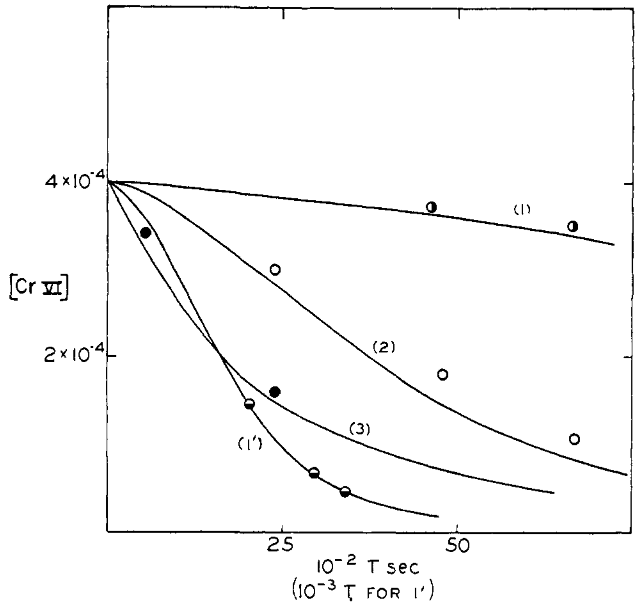


Figure 1. Cr(VI) *vs.* time for runs with $(C_2H_5O)_2P(=O)H$. Curves represent observed data for the protonated diester. Points are for the deuterated diester: 1, 1', P(III) = 0.01 *M;* 2, P(III) = 0.1 *M;* 3, P(III) = 1.00 *M*.

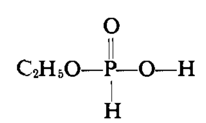
Reduction of Cr(VI) by Diethyl Phosphite in 1 *M* $HClO_4$. Absorbance due to Cr(VI) at 350 mμ decreases with time in the presence of diethyl phosphite. Typical runs shown in Figure 1 have the appearance of an autocatalytic reaction in early parts of the run. The induction period indicates that Cr(VI) does not oxidize diethyl phosphite directly but that hydrolysis products C_2H_5OH and monoethyl phosphite are the active reducing agents. If only alcohol were the reducing agent, the rate law would be described as

$$d[Cr(VI)]/dt = k_a[C_2H_5OH][Cr(VI)]$$

$$[C_2H_5OH] = P_0(1 - e^{-k_h t}) = [\text{monoester}]$$

$$d \ln [Cr(VI)]/dt = k_a P_0(1 - e^{-k_h t}) \qquad (5)$$

The value of k_a found by analysis of rate data using the integrated form of eq 5 is too high and decreases with time. This is consistent with an additional path for reduction of Cr(VI) by the monoester



$$C_2H_5O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}-O-H$$

The monoester can be postulated to form an anhydride with $HCrO_4^-$ [1] and can be expected to have a rate law similar to that for H_3PO_3 reduction of $HCrO_4^-$.[1] Using such an analogy, a complete rate law for the reduction of Cr(VI) by the hydrolysis products of the diester would be

$$-\frac{d \ln [Cr(VI)]}{dt} = \frac{(k_a + k_m)P_0(1 - e^{-k_h t})}{1 + KP_0(1 - e^{-k_h t})} \qquad (6)$$

where k_a is the rate constant for reduction of Cr(VI) by alcohol, k_h is the rate constant for hydrolysis of the diethyl phosphite, k_m is the rate constant for internal oxidation-reduction of $O_3CrOP(O)(OC_2H_5)H$, and K is the formation constant of the same species. P_0 is the initial concentration of diester.

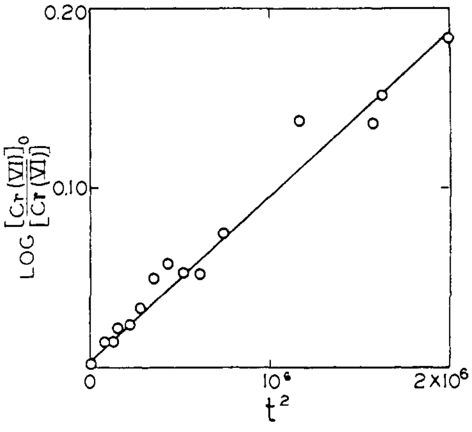


Figure 2. A plot of log $[Cr(VI)]_0/[Cr(VI)]$ *vs.* t^2 for run 2 in Figure 1. This should be a straight line if $1 - e^{-k_h t} \cong k_h t$.

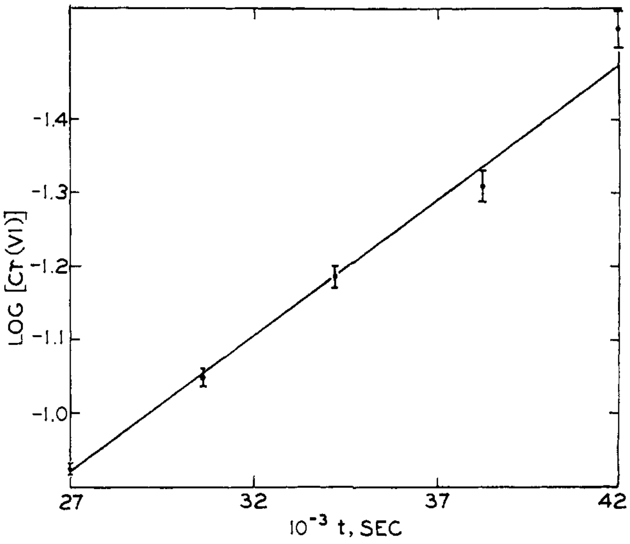


Figure 3. A first-order plot for [Cr(VI)] for the end of run 1, Figure 1.

Constants have been estimated as follows. For $k_h t$ very small, $1 + KP_0(1 - e^{-k_h t}) \cong 1$ and $1 - e^{-k_h t} \cong k_h t$. Then eq 6 may be integrated to give

$$\ln [Cr(VI)] = \frac{(k_a + k_m)P_0 k_h t^2}{2} + C \qquad (7)$$

Figure 2 shows a plot of ln [Cr(VI)] *vs.* t^2, giving a fair straight line, the slope of which gives $(k_a + k_m) = 0.033 \pm 0.012$. The value of k_a is 6.3×10^{-3}; therefore, $k_m = (2.6 \pm 0.8) \times 10^{-2}$.

For a run with $P_0 = 0.01$, after two half-times for hydrolysis, [Cr(VI)] was still significant. We assume that $[C_2H_5OH]$ = [monoester] = 0.0075 *M*. If this is so

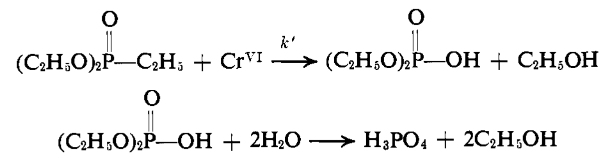
$$\frac{d[Cr(VI)]}{dt} = \frac{(k_a + k_m)(0.0075)}{1 + K(0.0075)}[Cr(VI)] \qquad (8)$$

If eq 8 holds true, a plot of log [Cr(VI)] *vs.* time should be a straight line. Figure 3 shows such a plot for the end of the run. $[C_2H_5OH]$ = 0.0075 at 36,000 sec. From Figure 3 we deduce that $k_{obsd} = 8.5 \times 10^{-5}$. If $(k_a + k_m)$ is 0.033, the K is calculated to be ~250. Since k_m and K are both unusually high (Table III), we hope a thorough study of the direct oxidation of monoester can be made in the future.

For our purposes, the significant result here is the failure of the diester to be oxidized significantly before undergoing hydrolysis. The oxidation of ethanol and monoester, the hydrolysis products, can best be studied directly. Therefore complete analysis of the complicated runs with diester has not been undertaken.

Runs were also carried out with diester containing deuterium substituted for hydrogen on the P–D bond. Figure 1 shows points for these runs as they appear relative to those for diesters containing a P–H bond. There is very little isotope effect, although a diester containing P–D bonds does reduce Cr(VI) somewhat more slowly than the P–H form. This is consistent with the analysis above. There is a small (10%) increase in hydrolysis rate when the diester is deuterated.[3] The oxidation of monoester should be slower if it is deuterated by a factor of about 4.[1] Considerable exchange of P–D for P–H should occur during a run.

Reduction of Cr(VI) by Ethyl Diethyl Phosphinate, $(C_2H_5O)_2P({=}O)C_2H_5$. Runs shown in Figure 4 are complex. Ethyl diethyl phosphinate does not hydrolyze detectably in the time required to reduce all the Cr(VI) used in these runs. In each case, there is a 5000-sec induction period with no detectable loss of Cr(VI). This is followed by an apparent first-order initial reaction for 0.01 M ester and a faster final first-order reaction for the same solution (solid dots in Figure 4). This is consistent with initial oxidation of the ester by Cr(VI) giving a hydrolyzable phosphate ester. At the end of the run, enough C_2H_5OH has been produced to become the dominant reducing agent.



$$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}{-}C_2H_5 + Cr^{VI} \xrightarrow{k'} (C_2H_5O)_2\overset{O}{\overset{\|}{P}}{-}OH + C_2H_5OH$$

$$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}{-}OH + 2H_2O \longrightarrow H_3PO_4 + 2C_2H_5OH$$

$$Cr^{VI} + C_2H_5OH \xrightarrow{k_a} \text{products}$$

$$\text{rate} = (k'[(C_2H_5O)_2POC_2H_5] + k_a[C_2H_5OH])[Cr(VI)]$$

$$k' = 3 \times 10^{-4}\,\text{sec}^{-1}\,M^{-1} \qquad (9)$$

In the run with 0.1 M ester (open dots in Figure 4), there is initial curvature indicating that the induction period is real, not just a period of undetectable change in the previous run. A good first-order plot consistent with the first term in eq 9 is obtained for most of the run.

Discussion

Oxidations by $HCrO_4^-$ have been characterized by[4,5] (1) preequilibria involving anhydride formation

$$MOH + HOCrO_3^- \rightleftarrows MOCrO_3^- + H_2O$$

(2) reduction of Cr(VI) to Cr(IV) in the rate-determining step; (3) capture of Cr(IV) by (a) one-electron reducing agent (I^-, SO_3^{2-}, Mn^{2+}) or (b) Cr(VI) to give 2Cr(V).

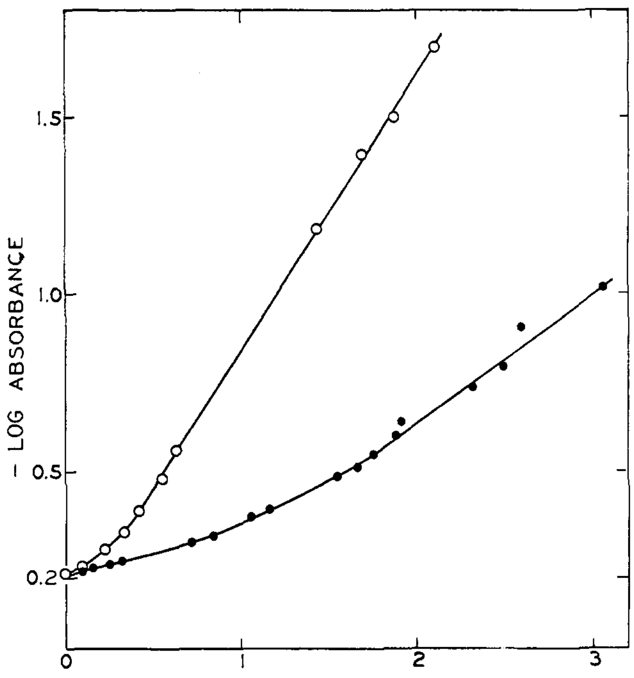


Figure 4. Oxidation of $(C_2H_5O)_2P({=}O)C_2H_5$ by $HCrO_4^-$: ○, 0.1 M $(EtO)_2EtPO$; ●, 0.01 M $(EtO)_2EtPO$. Ethanol in initial products becomes the dominant reducing agent late in the run.

Reductions by P(III) have been characterized by enolization of $H{-}\overset{|}{\underset{|}{P}}{=}O$ to $:\overset{|}{\underset{|}{P}}{-}OH$ followed by electrophilic attack on the electron pair of the enol form.[3]

In paper I[1] it was deduced that H_3PO_3 formed an anhydride with $HCrO_4^-$ which underwent oxidation–reduction to give H_3PO_4 and Cr(IV) as enolization took place. The present study was designed to determine the effect of substituting C_2H_5 for various H atoms in H_3PO_3.

In aqueous chromate solutions ethyl esters of phosphorous acid may be expected to exchange protons bonded to phosphorus with water protons and to hydrolyze to phosphorous acid and ethyl alcohol as well as form esters with $HCrO_4^-$ and undergo oxidation. Tables I–III summarize data on all these phenomena

Table I. Hydrogen Exchange in P(I) and P(III) Compounds

P(III) compd	Rate constant k, M^{-1} sec^{-1}	Ref
$(RO)_2P({=}O)H$ (D_2O)	1.3×10^{-4}	*a*
H_3PO_2 (HTO)	6.3×10^{-4}	*b*

[a] Z. Luz and B. Silver, *J. Am. Chem. Soc.*, **83**, 4518 (1961). [b] W. A. Jenkins and D. M. Yost, *J. Inorg. Nucl. Chem.*, **11**, 297 (1959).

Table II. Hydrolysis of P(III) Compounds

P(III) compd (0.1–1.0 M)	Hydrolysis rates (k, sec^{-1}) in 1 M $HClO_4$ (298°K)
$(C_2H_5O)_3P$	Very fast → $(C_2H_5O)_2P({=}O)H$
$(C_2H_5O)_2P({=}O)H$	5.5×10^{-5} M[a]
$(C_2H_5O)_2P({=}O)D$	6×10^{-5}
$C_2H_5OP({=}O)(OH)H$	1×10^{-3}
$(C_2H_5O)_2P({=}O)C_2H_5$	Immeasurably slow

[a] In 1 M H^+, acid catalyzed.

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(4) F. H. Westheimer, *Chem. Rev.*, 45, 419 (1949); R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, Chapter 4.

(5) G. P. Haight, Jr., E. Perchonock, F. Emmenegger, and G. Gordon, *J. Am. Chem. Soc.*, 87, 3835 (1965).

Table III. Reaction with $HCrO_4^-$

Reducing agents	K_f (anhydride), M^{-1}	$10^{-3}k_1$ (oxidation), M^{-1} sec^{-1}	Ref
$(C_2H_5O)_3P$:	. . .	Very fast	*a*
$(C_2H_5O)_2P(=O)H$	. . .	<0.1	*a*
$(C_2H_5O)P(=O)$-(OH)H	200 $(C_2H_5OP(=O)(H)OCrO_3^-)$	26 (k_m)	*a*
$HOP(=O)(OH)H$	16 $(H(HO)P(=O)OCrO_3^-)$	1.7	1
$H_2P(=O)OH$	11 $(H_2P(=O)OCrO_3^-)$	6	1
$H_2AsO_3^-$	22	17	*b*

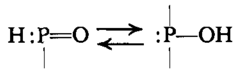
[a] This work. [b] J. G. Mason and A. D. Kawalak, *Inorg. Chem.*, **3**, 1248 (1964).

in a comparative way. It is possible, using these data, to draw certain conclusions concerning various pathways by which $HCrO_4^-$ and H_2CrO_4 can oxidize P(III) compounds.

From the results cited above, we conclude the following.

1. $HCrO_4^-$ will rapidly attack a lone pair of electrons on P(III) if it does not result from enolization. In triethyl phosphite, $(C_2H_5O)_3P$:, the lone pair is present and can presumably act as a Lewis base to accept O atoms or other Lewis acids from oxidants. Triethyl phosphite reacts very fast with $HCrO_4^-$.

2. $HCrO_4^-$ is ineffective in attacking a lone pair of electrons on P(III) if the lone pair is exposed only briefly as a result of a tautomeric equilibrium



$$H{:}\underset{|}{P}{=}O \rightleftarrows {:}\overset{|}{\underset{|}{P}}{-}OH$$

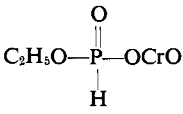
3. Hydrolysis of $(C_2H_5O)_2P(=O)H$ is fast compared with its oxidation by $HCrO_4^-$, and all reduction of $HCrO_4^-$ can be accounted for by the hydrolysis products. This indicates that oxidation of $(C_2H_5O)_2P(=O)H$, if it is possible, is at least an order of magnitude slower than oxidation of P(III) species containing P(OH)H groups.

4. The result of conclusion 3 implies that $HCrO_4^-$ usually forms an anhydride with P(III) containing a P–H bond in order to oxidize P(III).

5. It seems clear that the mechanism of oxidation of P(III) by Cr(VI) does not proceed by abstraction of hydride (H^-) by Cr(VI) even though the P–H bond is broken in the rate-determining step.[1]

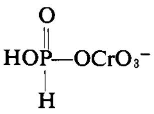
Blocking anhydride formation (P–O–Cr), tautomerization, and hydrolysis by using ethyl diethyl phosphinate, $(C_2H_5O)_2P(=O)C_2H_5$, yields a reduction of Cr(VI) which is an order of magnitude slower than any other studied with an induction period independent of the concentration of ethyl diethyl phosphinate. No explanation of the induction period has occurred to us. Beyond the induction period, all data are consistent with very slow direct oxidation of ethyl diethyl phosphinate accompanied by oxidation of ethanol produced by hydrolysis of the initial P(V) product.

Blocking only one -OH group on P(III) in monoethylphosphorous acid, $C_2H_5OP(=O)(OH)H$, increases the rate of reduction of Cr(VI) apparently because the formation constant for the anhydride (i) is roughly ten times as great as that for ii.



$$C_2H_5O{-}\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}{-}OCrO_3^-$$

i



$$HO\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}{-}OCrO_3^-$$

ii

Three distinct pathways for oxidation of P(III) compounds by Cr(VI) have been discovered, only one of which has been clearly elucidated.

1. If there is a -(H)P(O)OH group, oxidation by Cr(VI) involves chromate ester formation plus acid-assisted breaking of the P–H bonds.

2. $(C_2H_5O)_2P(O)C_2H_5$ is oxidized directly but very slowly by $HCrO_4^-$. Hydrolysis does not occur in the absence of $HCrO_4^-$. Since oxidizable products form, the rate law is very complex and no mechanistic interpretation is possible at this time.

3. $(C_2H_5O)_3P$: is oxidized very fast by $HCrO_4^-$ in glacial acetic acid. Initial rates in water where it hydrolyzes rapidly are also high. Here, too, ester formation appears unlikely. A kinetic study employing rapid mixing techniques is planned.

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