Reactions of Chromium(VI) with Phosphorus(III) and Phosphorus(I). I. Dihydrogen Phosphite, Phosphorous Acid, and Hypophosphorous Acid[1]

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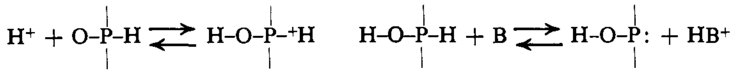
Abstract: Dihydrogen phosphite ion, $H_2PO_3^-$, is not oxidized by $HCrO_4^-$ at pH 4 but does form an anhydride, $HO_2POCrO_3^{2-}$. At pH 0, H_3PO_3 is slowly oxidized by $HCrO_4^-$, yielding H_3PO_4 and Cr(III).[3] Kinetic studies indicate that the oxidation involves anhydride formation ($H_2PCrO_6^-$ or H_3PCrO_6) and general acid catalysis



$$H^+ + O\text{–}\overset{|}{\underset{|}{P}}\text{–}H \rightleftharpoons H\text{–}O\text{–}\overset{|}{\underset{|}{P}}\text{–}{}^+H \qquad H\text{–}O\text{–}\overset{|}{\underset{|}{P}}\text{–}H + B \rightleftharpoons H\text{–}O\text{–}\overset{|}{\underset{|}{P}}: + HB^+$$

wherein the attacking proton can come from any acid in the system. In our system B may be H_2O or $H_2PO_3^-$. The presence and strength of the H–P bond inhibits oxidation of P(III). Deuterated phosphorous acid $DP(=O)(OH)_2$ is oxidized more slowly than the protonated form by a factor of 4. Chloride ion inhibits the oxidation in 1 *M* H^+ by forming CrO_3Cl^- which is less reactive than $HCrO_4^-$. Dihydrogen hypophosphite ion, $H_2PO_2^-$, forms no anhydride with $HCrO_4^-$ at pH 4 nor is it oxidized by $HCrO_4^-$. Hypophosphorous acid, H_3PO_2, is oxidized like H_3PO_3 at pH 0 with similar kinetic patterns.

When oxyions containing lower oxidation states of nonmetals are oxidized by $HCrO_4^-$, the reactions appear to fall into two groups: (a) slow reactions, *e.g.*, AsO_3^{3-}, and (b) rapid reactions, *e.g.*, HSO_3^-. Two equivalent oxidations ($AsO_3^{3-} \rightarrow AsO_4^{3-}$)[4] which have mechanisms analogous to the Westheimer mechanism[5] for the oxidation of alcohols are slow with bimolecular rate constants of about 10^{-4} sec^{-1} mole^{-1}. Probably the high energies of unstable intermediates Cr(IV) and Cr(V) constitute a barrier to reaction. In contrast are combined one- and two-equivalent oxidations ($2HSO_3^- \rightarrow {}^1/_2\, S_2O_6^{2-} + SO_4^{2-}$)[6] in which Cr(VI) is reduced in one step to Cr(III), by-passing the unstable intermediates. These reactions are very fast, having bimolecular rate constants (allowing for preequilibria) of about 10^4 sec^{-1} mole^{-1}. Hydroxylammonium ion, NH_3OH^+, appears to be oxidized rapidly to NO by a one-step three-equivalent change.[7]

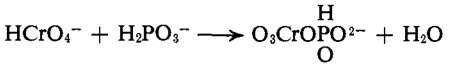
This paper discusses the oxidation of H_3PO_3 and H_3PO_2 which contain an additional barrier to reaction in the form of a stable –P–H bond.

Experimental Section

Reactions were studied by observing absorbance changes at 350 mμ in a Beckman DU spectrophotometer with a thermostated cell compartment.[6] Some work was done with a Bausch and Lomb Spectronic 20 spectrophotometer on which temperature control was difficult. Reagent grade chemicals were used without further purification. Standardizations of Cr(VI) and P(III) solutions were performed iodometrically. Generally, Cr(VI) concentrations were held below 10^{-3} *M* to avoid appreciable concentrations of $Cr_2O_7^{2-}$. The P–H bond in H_3PO_3 was deuterated by repeatedly dissolving crystalline H_3PO_3 in 99+% D_2O and evaporating excess D_2O (and H_2O) under vacuum for 48 hr. D_3PO_3 was dissolved in H_2O just prior to the start of the reaction with Cr(VI). Stoichiometry of oxidation of H_3PO_3 by Cr(VI) was measured by allowing the reaction to proceed completely with an excess of one reagent. The excess reagent was determined iodometrically.

Results

$HCrO_4^- + H_2PO_3^-$. At pH 4.0 in an acetic acid–acetate buffer containing 1.2 *M* acetic acid, the absorbance initially observed at 350 mμ did not change over a period of 2 to 4 weeks at 25°. The absorbance, however, was less than that for $HCrO_4^-$ alone and decreased with increasing $H_2PO_3^-$ concentration. Solutions 5×10^{-4} *M* in $HCrO_4^-$ containing 0.01 to 1.0 *M* $H_2PO_3^-$ were studied. A decrease in absorbance at 350 mμ of $HCrO_4^-$ solutions is also observed with HCl, HSO_4^-, H_3PO_4, etc.[8] The change in absorbance is assumed to be caused by anhydride formation according to the equation



$$HCrO_4^- + H_2PO_3^- \longrightarrow O_3CrO\overset{H}{\underset{O}{P}}O^{2-} + H_2O \qquad (1)$$

No such effect is observed with $H_2PO_3^-$ where both protons are bonded to phosphorus.

Definitions for the following terms are given. *A* is the measured absorbance of solutions. *C* is the concentration of Cr(VI) = 5×10^{-4} *M*. A_1 is the measured absorbance of 5×10^{-4} *M* $HCrO_4^-$. A_2 is the absorbance of 5×10^{-4} *M* $HO_2POCrO_3^{2-}$ but is not directly measurable. $A_1 - A$ is the change in absorbance observed when $H_2PO_3^-$ is added to $HCrO_4^-$.

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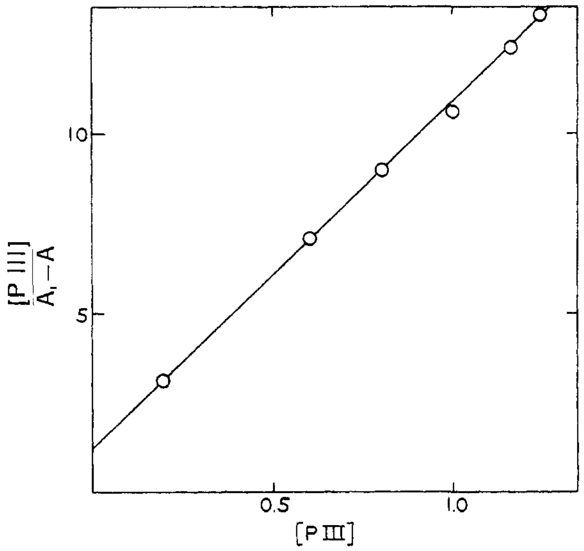

Figure 1. A plot of eq 2 to obtain K_f for $HPCrO_6^{2-}$. [Cr(VI)] = 3.56×10^{-4} *M*. Solution buffered at pH 4 with 1.2 *M* acetic acid and 0.29 *M* sodium acetate. Intercept/slope = $1/K_f = 0.14$. $K_f = 7.0$.

Since $H_2PO_3^-$ is in large excess, its equilibrium concentration is virtually what is added.

$$\frac{[HO_2POCrO_3^{2-}]}{[HCrO_4^-]} = \frac{A_1 - A}{A - A_2}$$

$$K_f = \frac{A_1 - A}{(A - A_2)[H_2PO_3^-]}$$

Rearranging

$$\frac{[H_2PO_3^-]}{A_1 - A} = \frac{1 + [H_2PO_3^-]K_f}{K_f(A_1 - A_2)} \qquad (2)$$

From the plot of $[H_2PO_3^-]/(A_1 - A)$ *vs.* $[H_2PO_3^-]$ given in Figure 1, *K* and $1/(A_1 - A_2)$ may be evaluated from the slope and intercept. From this plot *K* is found to be about 7 ± 1 M^{-1}. This value is reasonable compared with values of 4 and 9 for the formation constants of $CrSO_7^{2-}$ and $HPCrO_7^{2-}$, respectively.[8]

$HCrO_4^- + H_3PO_3$. At pH 0 oxidation of H_3PO_3 to H_3PO_4 occurs. No deviation from stoichiometry 3[P(III)]/2[Cr(VI)] was observed. All reactions with excess H_3PO_3 exhibit a first-order decrease in absorbance which is proportional to the total [Cr(VI)] with rapid equilibrium between all forms.

[H_3PO_3] Dependence. Referring to the data in Table I the rate at low concentrations deviates from first order in H_3PO_3 in a manner similar to that of As(III) when it is oxidized by $HCrO_4^-$.[4] In the latter case k_{obsd} is given by

$$k_{\text{obsd}} = k'[\text{As(III)}]/\{1 + Q[\text{As(III)}]\} \qquad (3)$$

In the present case the deviation from first order in H_3PO_3 does not fit a law analogous to eq 3 analytically. The order is less than 1, in fact, very close to 0.5 for 0.01 $M \leq [H_3PO_3] \leq 0.1$ *M*. However, at high concentrations, 0.1 $M \leq [H_3PO_3] \leq 1.0$ *M*, virtual first-order dependence on [H_3PO_3] is observed (Figure 2). These combined observations are consistent with the following expression for k_{obsd}

$$k_{\text{obsd}} = \frac{[H_3PO_3](k' + k_2[H_3PO_3])}{1 + K_f[H_3PO_3]} \qquad (4)$$

at constant [H^+].

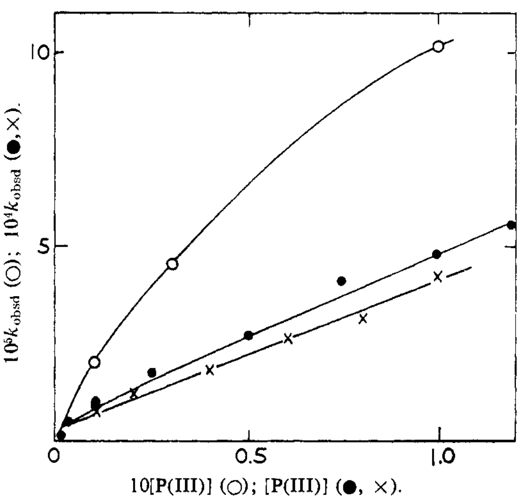

Figure 2. Variation of k_{obsd} with [H_3PO_3], showing the effect of preequilibrium at low [H_3PO_3] and approach to first order again at high concentrations: ●, [H^+] = 1.0 *M*; ×, [H^+] = 0.1 *M*.

Table I. Experiments with H_3PO_3[a]

[P(III)], *M*	[H^+], *M*	10^5k_{obsd}, sec^{-1} Obsd	Calcd	μ
0.01	1.0	2.0	1.8	1.0
0.03	1.0	4.6	4.7	1.0
0.10	1.0	9.6	10.3	1.0
0.10	1.0	8.9	10.3	1.0
0.10	0.5	6.0	6.4	1.0
1.19	1.0	55	56	1.2
1.00	1.0	48	48	1.0
1.00	0.75	45.0	45	1.0
1.00	0.65	42.0	44	2.7
1.00	0.50	37.0	38	1.0
0.75	1.00	41.0	38	1.0
0.50	1.00	26.0	28	1.0
0.25	1.00	18	18	1.0
0.90	0.65	38	37	2.7
0.80	0.65	32	33	2.7
0.70	0.65	27	29	2.7
0.60	0.65	25	27	2.7
0.50	0.65	22	22	2.7
0.40	0.65	18	19	2.7
0.30	0.65	15	15	2.7
0.20	0.65	12	12	2.7
0.10	0.65	6.9	6.9	2.7

[a] $k_1 = 2.0 \times 10^{-3}$, $k_2 = 6.0 \times 10^{-3}$, $K_f = 16$.

Dependence on [H^+] (Figure 3). At high [H_3PO_3] and [H^+] > 0.5 *M*, a plot of k_{obsd} *vs.* [H^+] is linear with an intercept corresponding to a term zero order in [H^+]. This fact combined with eq 4 leads to the general rate law

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{[\text{Cr(VI)}][H_3PO_3](k_1[H^+] + k_2[H_3PO_3])}{1 + K_f[H_3PO_3]} \qquad (5)$$

The direct proportion between k_{obsd} and [H^+] at low [P(III)] and low [H^+] is thought to be fortuitous. H_3PO_3 dissociates significantly at [H^+] < 0.5 *M* and $H_2PO_3^-$ is inert to oxidation. All runs fit eq 5 within experimental error when allowance was made for dissociation of H_3PO_3 (see Table I).

Runs with [H_3PO_3] varying from 0.01 to 0.1 *M* were used to estimate k_1 and K_f assuming

$$k_{\text{obsd}} \approx \frac{k_1[H^+][H_3PO_3]}{1 + K_f[H_3PO_3]}$$

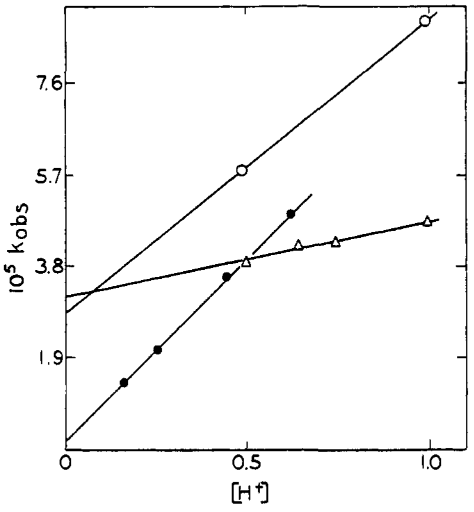

Figure 3. Hydrogen-ion effect. A zero-order term in H^+ is evident at high $[H_3PO_3]$. The apparent first-order dependence at low $[H^+]$ and low $[H_3PO_3]$ is fortuitous. Dissociation of H_3PO_3 to inert $H_2PO_3^-$ is significant especially when $[H^+] < 0.5$ *M*. ●, [P(III)] = 0.095 *M*, 24°; ○, [P(III)] = 0.10 *M*, 25°; △, [P(III)] = 1.0 *M*, 25°.

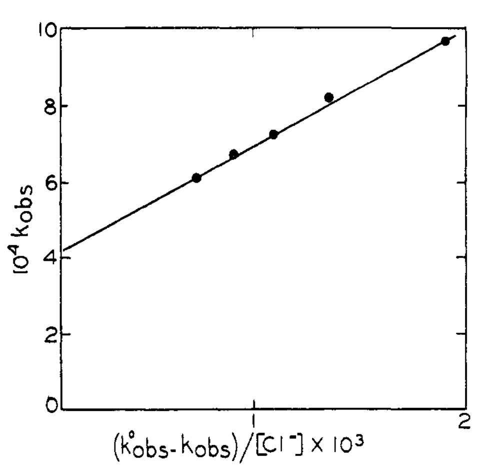

Figure 4. Chloride effect. A plot of eq 4. [P(III)] = 0.095 *M*, $[H^+]$ = 0.76 *M*, 24°.

Runs with $[H_3PO_3]$ varying from 0.3 to 1.0 *M* were used to estimate k_2/K_f assuming

$$k_{\text{obsd}} \approx (k_2/K_f)[H_3PO_3]$$

Initial estimates were improved by successive approximations until a general fit of data for all runs made at 25° was obtained. Final values and the fit to data are shown in Table I.

Chloride Inhibition. At pH 0, chloride ion inhibits the oxidation of H_3PO_3 by forming CrO_3Cl^-. Data can be accounted for by the empirical rate law

$$\text{rate} = k_{\text{obsd}}^0[\text{Cr(VI)}]^0 + k'[\text{CrO}_3\text{Cl}^-] \qquad (6)$$

where $k_{\text{obsd}}^0 = k_{\text{obsd}}$ in the absence of Cl^-, and $[\text{Cr(VI)}]^0$ is the concentration of all Cr(VI) species except CrO_3Cl^-.

$$[\text{Cr(VI)}]^0 + \text{Cl}^- \rightleftarrows \text{CrO}_3\text{Cl}^-$$

$$K' = \frac{[\text{CrO}_3\text{Cl}^-]}{[\text{Cl}^-][\text{Cr(VI)}]^0}$$

$$[\text{Cr(VI)}]_{\text{total}} = [\text{Cr(VI)}]^0 + [\text{CrO}_3\text{Cl}^-]$$

Rearranging

$$\text{rate} = \frac{k_{\text{obsd}}^0 + k'K'[\text{Cl}^-]}{1 + K'[\text{Cl}^-]}[\text{Cr(VI)}]_{\text{total}}$$

$$k_{\text{obsd}} = \frac{k_{\text{obsd}}^0 + k'K'[\text{Cl}^-]}{1 + K'[\text{Cl}^-]}$$

$$\frac{k_{\text{obsd}}^0 - k_{\text{obsd}}}{[\text{Cl}^-]} = k_{\text{obsd}}K' - k'K'$$

$$k_{\text{obsd}} = k' + \frac{1}{K'}\left(\frac{k_{\text{obsd}}^0 - k_{\text{obsd}}}{[\text{Cl}^-]}\right)$$

$$\text{intercept} = k' \qquad \text{slope} = 1/K' \qquad (7)$$

A plot of k_{obsd} *vs.* $(k_{\text{obsd}}^0 - k_{\text{obsd}})/[\text{Cl}^-]$ (shown in Figure 4) is linear with a slope of 0.28 or $K' = 3.5$ and an intercept of $4.2 \times 10^{-4} = k'$. If inhibition is caused by a shift in preequilibrium on addition of chloride ion, and CrO_3Cl^- did not directly oxidize H_3PO_3, the following equations would hold.

$$\text{rate} = k_{\text{obsd}}^0[\text{Cr(VI)}]^0$$

$$[\text{Cr(VI)}] = [\text{Cr(VI)}]^0 + [\text{CrO}_3\text{Cl}^-]$$

$$= [\text{Cr(VI)}]^0(1 + K'[\text{Cl}^-])$$

$$\text{rate} = \frac{k_{\text{obsd}}^0[\text{Cr(VI)}]}{1 + K'[\text{Cl}^-]}$$

$$k_{\text{obsd}} = \frac{k_{\text{obsd}}^0}{(1 + K'[\text{Cl}^-])} \qquad (8)$$

However, a plot of $1/k_{\text{obsd}}$ *vs.* Cl^- is distinctly curved. Therefore, a separate reaction path involving CrO_3Cl^- is involved in the oxidation of H_3PO_3.

The value of K_f for formation of $H_2O_2POCrO_3^-$ has been estimated from the dependence of the rate on $[H_3PO_3]$. Since the value of $[\text{CrO}_3\text{Cl}^-]/\{[\text{Cl}^-][\text{Cr(VI)}]^0\}$ in the absence of H_3PO_3 can be estimated from the literature,[9] a means is available for checking K_f. Let $[\text{Cr(VI)}]^0 = [\text{HCrO}_4^-] + [\text{H}_2\text{O}_2\text{POCrO}_3^-]$. At $[H^+] = 0.76$ *M*

$$\frac{[\text{CrO}_3\text{Cl}^-]}{[\text{Cl}^-][\text{HCrO}_4^- + \text{H}_2\text{O}_2\text{POCrO}_3^-]} = 3.4$$

$$\frac{[\text{CrO}_3\text{Cl}^-]}{[\text{Cl}^-][\text{HCrO}_4^-]} = 7.1 \quad \text{(calcd from ref 9)}$$

$$\frac{[\text{HCrO}_4^-]}{[\text{HCrO}_4^-] + [\text{H}_2\text{O}_2\text{POCrO}_3^-]} = 0.48$$

$$\frac{[\text{H}_2\text{O}_2\text{POCrO}_3^-]}{[\text{HCrO}_4^-]} = 1.09$$

$$[\text{H}_3\text{PO}_3] = 0.0945$$

$$K_f = 11.6$$

K_f from the Cl^- inhibition is found to be 12 *vs.* a value of 16 obtained from kinetics at low $[H_3PO_3]$.

$HCrO_4^-$ + H_2DPO_3 (P–D Bond). The value of k_{obsd} for reduction of $HCrO_4^-$ by 0.4 *M* H_3PO_3 in 1 *M* $HClO_4$ is 2.1×10^{-4} sec^{-1} while with a P–D bond present k_{obsd} is initially 5×10^{-5}, increasing over a 12-hr period in a single run to 7×10^{-5} as D was slowly re-

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[9] S. Y. Tong and R. L. Johnson, *Inorg. Chem.*, **5**, 1902 (1966).

placed by H. Thus, a deuterium isotope effect with $k_H/k_D \cong 4$ is observed.

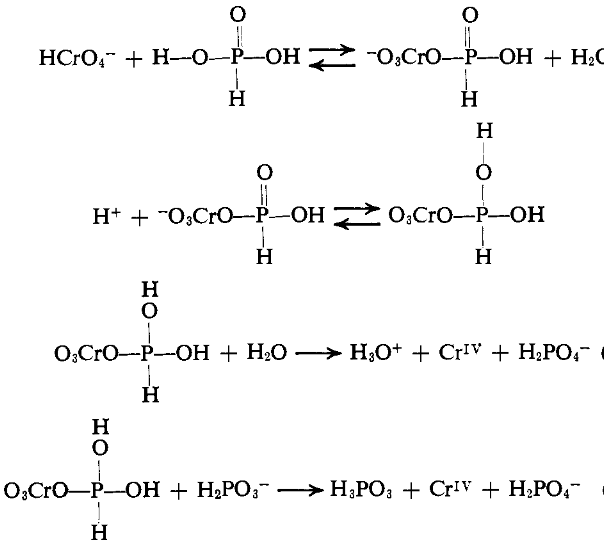
H_3PO_2 and $H_2PO_2^-$ + $HCrO_4^-$. No reaction, neither anhydride formation nor redox, occurs at pH 4-5. Preliminary studies in 1 *M* $HClO_4$ show a reaction first order in Cr(VI) with k_{obsd} varying between 5.92×10^{-5} and 1.91×10^{-3} as H_3PO_2 varies from 0.01 to 1.0 *M*. This is consistent with the rate law

$$\text{rate} = \frac{[\text{Cr(VI)}][H_3PO_2](k_1[H^+] + k_2[H_3PO_2])}{1 + K_f[H_3PO_2]} \qquad (9)$$

with $K_f = 11$, $k_1 = 6.5 \times 10^{-3}$, and $k_2 = 13.5 \times 10^{-3}$. K_f is probably the formation constant for the anhydride $O\text{-}PH_2\text{-}OCrO_3^-$.

Discussion

Mechanism of H_3PO_3 Oxidation. The rate law suggests formation of an intermediate anhydride $H_2PCrO_6^-$ followed by attack by a proton donor (H_3O^+ or H_3PO_3). The large deuterium isotope effect suggests that the H-P bond is broken in the rate-determining step.



$$HCrO_4^- + H{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}{-}OH \rightleftharpoons {}^-O_3CrO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}{-}OH + H_2O \qquad (I)$$

$$H^+ + {}^-O_3CrO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}{-}OH \rightleftharpoons O_3CrO{-}\overset{\overset{\displaystyle H}{|}}{\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle H}{|}}{P}}}{-}OH \qquad (II)$$

$$O_3CrO{-}\overset{\overset{\displaystyle H}{\displaystyle O}}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{P}}}{-}OH + H_2O \longrightarrow H_3O^+ + Cr^{IV} + H_2PO_4^- \qquad (III)$$

$$O_3CrO{-}\overset{\overset{\displaystyle H}{\displaystyle O}}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{P}}}{-}OH + H_2PO_3^- \longrightarrow H_3PO_3 + Cr^{IV} + H_2PO_4^- \qquad (IV)$$

$$Cr^{IV} + Cr^{VI} \longrightarrow 2Cr^{V} \qquad \text{(fast)} \quad (V)$$

$$Cr^{V} + H_3PO_3 \longrightarrow Cr^{III} + H_3PO_4 \qquad \text{(fast)} \quad (VI)$$

Base removal of H^+ from the P-H bond by H_2O and/or $H_2PO_3^-$ initiates internal oxidation-reduction of the Cr(VI)-P(III) ester. Thus, steps III and IV are rate determining. Steps V and VI are conjectural, based on analogy with Westheimer mechanisms[5] for alcohol oxidations.

Derivation of the Rate Law from the Mechanism.

$$\text{rate} = [H_3PCrO_6](k_{III} + k_{IV}[H_2PO_3^-])$$

where k_{III} includes $[H_2O]$ which is constant.

$$\text{rate} = [H_2PCrO_6^-][H^+]\left(k_{III} + k_{IV}K_i\frac{[H_3PO_3]}{[H^+]}\right)$$

$$= [H_2PCrO_6^-](k_{III}[H^+] + k_{IV}K_i[H_3PO_3])$$

$$[\text{Cr(VI)}]_{total} = [H_2PCrO_6^-] + [HCrO_4^-]$$

$$= [H_2PCrO_6^-]\frac{[K_f[H_3PO_3] + 1]}{K_f[H_3PO_3]}$$

$$[H_2PCrO_6^-] = \frac{K_f[H_3PO_3][\text{Cr(VI)}]}{1 + K_f[H_3PO_3]}$$

$$\text{rate} = \frac{[H_3PO_3][\text{Cr(VI)}](K_ik_{III}[H^+] + k_{IV}K_iK_f[H_3PO_3])}{1 + K_f[H_3PO_3]} \qquad (10)$$

Equation 10 is of the same form as the observed rate law. Many studies of oxidations of P(III) compounds[10] and of deuterium[11] and tritium[12] exchange at the P-H bond have been interpreted to mean that the formation of tautomeric -P-O-H from H-P-O is an important step in such reactions. Qualitative experiments[11] with triethyl phosphite, $(C_2H_5O)_3P$:, show that this material is oxidized so fast as to require rapid mixing techniques for study.

The fact that HSO_3^- is oxidized by $HCrO_4^-$ at pH 5 with a rate constant of the order of 10^8 times those observed in this study together with the rapid oxidation of $(C_2H_5O)_3P$ suggests that the presence of an unprotonated pair of electrons on P or S greatly facilitates oxidation.

Tables I, II, and III summarize values of rate and equilibrium constants obtained in this study and compare them with values found in similar systems. K_f is very similar to constants for preequilibria observed in the oxidations of As(III) and S(IV). However, very low values for k_{III} and k_{IV} attest to the inertia of the P-H bond.

Table II. Experiments with H_3PO_2 in 1 *M* $HClO_4$

$[H_3PO_2]$, *M*	$[H^+]$, *M*	k_{obsd}	k_{obsd} (calcd)
1.0	1.0	1.91×10^{-3}	1.92×10^{-3}
0.10	1.0	3.74×10^{-4}	3.74×10^{-4}
0.010	1.0	5.92×10^{-5}	5.92×10^{-5}
0.010	1.0	5.61×10^{-5}	5.92×10^{-5}
0.027^a	0.97^a	1.3×10^{-5}	$1.34 \times 10^{-4\,b}$
0.090^a	0.91^a	2.9×10^{-4}	3.2×10^{-4}
0.23^a	0.31^a	5.1×10^{-4}	5.3×10^{-4}
0.57^a	0.38^a	7.3×10^{-4}	$6.6 \times 10^{-4\,b}$

[a] Calculated using pK_i for H_3PO_2 = 1.0. [b] 1 *M* H_2SO_4.

Table III. Formation Constants for Cr(VI) Anhydrides and k_1

Anhydride	K_f (from $HCrO_4^-$)	10^3 k_1	pH	Ref	Measurement[a]
$O_3CrO\overset{H}{P}O_2^{2-}$	7	0	4	This work	Sp, Eq
$O_3CrO\overset{H^-}{P}(=O)OH$	16	1.7	0	This work	Kinetics, P
$O_3CrO\overset{H^-}{P}(=O)H$	11	6	0	This work	Kinetics, P
$O_3CrOP(=O)(OH)_2^-$	9.4	...	1	*b*	Sp, Eq
$O_3CrOP(=O)OH^{2-}$	2.9	...	5	*b*	Sp, Eq
O_3CrCl^-	11	...	0	9	Sp, Eq
$O_3CrOSO_2^{2-}$	36	10^7	4	6	Kinetics, P
$O_3CrOSO_3^{2-}$	4	...	0	6	Sp, Eq
$O_3CrOAsO_2H^{2-}$	22	16.8	4.6	3	Kinetics, P

[a] Sp, spectrophotometry; Eq, equilibrium; P, preequilibrium. [b] F. Holloway, *J. Am. Chem. Soc.*, **74**, 225 (1952).

Dihydrogen phosphite ion, $H_2PO_3^-$, does not undergo D-H exchange at the P-H bond nor is it oxidized by

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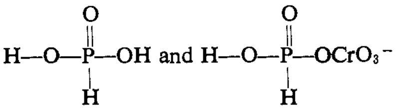
(10) P. Nylen, *Z. Anorg. Allgem. Chem.*, **235**, 161 (1938).

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

(12) W. A. Jenkins and D. M. Yost, *J. Inorg. Nucl. Chem.*, **11**, 297 (1959).

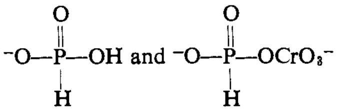
$HCrO_4^-$ despite the fact that it forms $HPCrO_6^{2-}$ typical of anhydride intermediates formed during Cr(VI) oxidations.

Phosphorous acid, H_3PO_3, forms $H_2CrPO_6^-$ with $HCrO_4^-$, exhibits H–D exchange at the P–H bond, and is oxidized to H_3PO_4 by $HCrO_4^-$. Evidently, in



$$H{-}O{-}\overset{O}{\underset{H}{\overset{\|}{P}}}{-}OH \text{ and } H{-}O{-}\overset{O}{\underset{H}{\overset{\|}{P}}}{-}OCrO_3^-$$

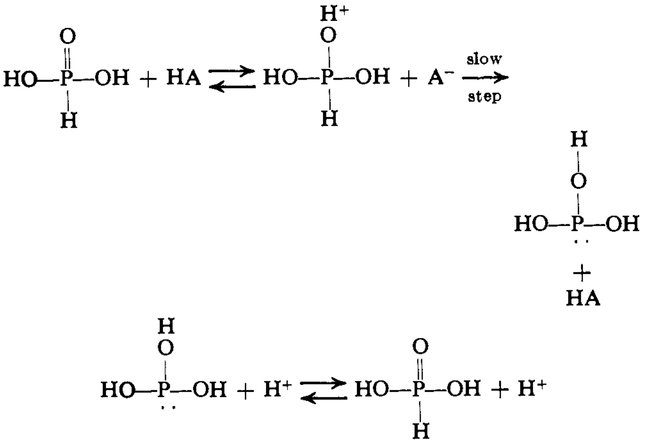
proton attack on the lone oxygen atom attached to phosphorus labilizes the P–H bond yielding proton exchange with the medium and, in the latter case, internal oxidation–reduction as well. In



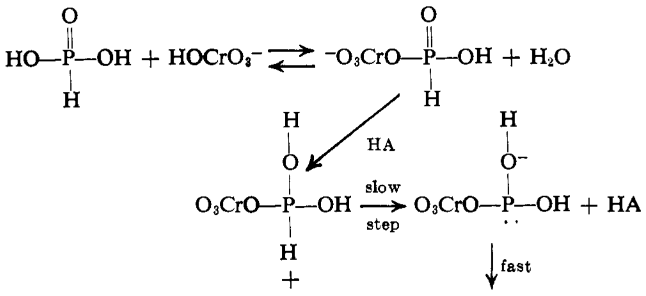
$$^-O{-}\overset{O}{\underset{H}{\overset{\|}{P}}}{-}OH \text{ and } ^-O{-}\overset{O}{\underset{H}{\overset{\|}{P}}}{-}OCrO_3^-$$

proton attack simply produces a stable species and the P–H bond is not labilized.

Exchange



Oxidation



HA may be any acid. In our case H_3O^+ and H_3PO_3 are both effective, hence the second-order term in H_3PO_3. A^- may be water or $H_2PO_3^-$ acting as bases to assist the proton away from the P–H bond.

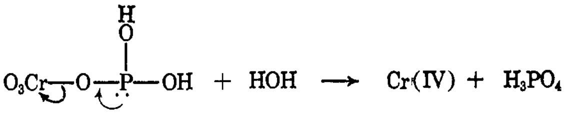
The mechanism is consistent with the insensitivity of data to changes in ionic strength. Two sets of data at $\mu = 1.0$ and $\mu = 2.7$ are explained with the same rate and equilibrium parameters. The mechanism involves three distinct steps.

(1) The formation of an anhydride by reaction of neutral H_3PO_3 with $HCrO_4^-$ should be insensitive to changes in ionic strength.

(2) The acid-catalyzed labilization of the P–H bond has been shown not to vary with ionic strength for hydrogen–tritium exchange involving H_3PO_2 by Jenkins and Yost[12] over twofold changes in ionic strength.

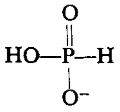
(3) The internal oxidation–reduction of P and Cr in the anhydride should not be affected by changes in ionic strength.

Proton attack on hydrogen phosphinate produces phosphorous acid with a lone pair of electrons. Proton attack on the lone pair produces exchange. A P(III) intermediate with a lone pair of electrons on phosphorus is apparently susceptible to oxidation since the oxidation of $(EtO)_3P$: is very fast. The presence in the activated complex of Cr(VI) attached by an oxygen bridge suggests that the electrons are transferred to Cr through the bridge accompanied by addition of H_2O from the solvent water to form phosphoric acid.



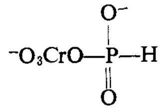
$$O_3Cr{-}O{-}\overset{\overset{H}{O}}{\overset{|}{P}}{-}OH + HOH \longrightarrow Cr(IV) + H_3PO_4$$

Dihydrogen phosphite ion



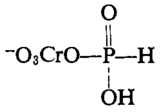
$$HO{-}\overset{O}{\underset{O^-}{\overset{\|}{P}}}{-}H$$

does not exchange because a proton attack on either oxygen simply forms neutral $(HO)_2P({=}O)H$. At pH 5 $[H^+]$ and $[H_3PO_3]$ are too low for a second, P–H labilizing, proton attack to occur. Similar arguments can be used to account for the inertia of i to oxidation *vs.*



$$^-O_3CrO{-}\overset{O^-}{\underset{O}{P}}{-}H$$

i



$$^-O_3CrO{-}\overset{O}{\underset{OH}{\overset{\|}{P}}}{-}H$$

ii

the lability of ii.

Hypophosphite ion, $H_2P({=}O)O^-$, is not oxidized nor does it form an anhydride. H_3PO_2 appears to do both. The combined evidence is that an –OH group must be present on P for anhydride formation. All but one oxygen must be bound to proton or metal before proton attack can labilize P–H bonds. Anhydride formation does not of itself labilize P–H bonds. Both anhydride formation and labilizing of P–H bonds by proton attack on oxygen are involved in the mechanism of oxidation of H_3PO_3 and H_3PO_2 by $HCrO_4^-$.

Phosphorus is less electronegative than hydrogen. This could suggest a view that only in $(HO)_3P$:, the rare tautomer, is P(III) present and susceptible to oxidation. Of course, the H in –P–H then becomes hydridic and susceptible to oxidation from -1 to $+1$. Nothing in our experiments suggests direct abstraction and oxidation of H^- from –P–H by $HCrO_4^-$. This is not to say it does not occur in 1 *M* H^+ but that, if it does, it is slow compared to other oxidation mechanisms. CrO_3Cl^- oxidizes H_3PO_3 by a path independent of that employed by $HCrO_4^-$. Cl^- probably blocks ester formation. Possibly hydride abstraction can occur in this case. Direct attack of O_3CrCl^- on P(III) to form an oxygen bridge with five-coordinate P is another distinct possibility. Our data give no basis for choice. Paper II[13] describes experiments involving the blocking of various preequilibria involving protons by substituting ethyl groups to form $(EtO)_3P:$, $(EtO)_2P(=O)H$, and $(EtO)_2P(=O)Et$, and studying their oxidation by $HCrO_4^-$.

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[13] G. P. Haight, Jr., F. Smentowski, M. Rose, and C. Heller, *J. Am. Chem. Soc.*, in press.

Dissociation Energies of Bismuth–Antimony Molecules[1a]

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Abstract: This article describes measurements of the dissociation energies of heteronuclear diatomic and tetratomic molecules in the equilibrium vapor of liquid solutions of bismuth and antimony. The experiments are based on the molecular beam sampling method using mass spectrometric detection. The following energies have been determined for dissociation of molecules to atoms at 0°K: $BiSb_3$ (8.27 ± 0.11 eV), Bi_2Sb_2 (7.52 ± 0.08 eV), Bi_3Sb (6.82 ± 0.06 eV), and BiSb (2.58 ± 0.04 eV). These values are shown to have quantitatively systematic trends in relation to the known homonuclear molecules Sb_4, Bi_4, Sb_2, and Bi_2 and others in the same family group. Some discussion of single bond energies of the group Va elements is given.

Recent experiments have shown that a large number of stable heteronuclear diatomic and tetratomic molecules are formed by intercombinations of atoms of the nitrogen family elements.[2a] These molecules are expected to be analogs of the well-known homonuclear species of these elements and, consequently, should have systematically related properties as members of the same group.[2b] This article describes measurements of dissociation energies which establish this systematic relationship for the homonuclear and heteronuclear molecules of Bi and Sb.

Experimental Methods

The experiments reported here involve the molecular beam sampling by mass spectrometric detection of vapors in equilibrium with liquid solutions of Bi–Sb over a temperature range of 225° in the region of 625°. The mass spectrometer, Knudsen cell, and other experimental equipment and devices used are well described elsewhere.[3,4] In general, the experimental methods were similar to those used previously for a study of the bismuth system.[3]

Measurements of the ion intensities of the gaseous Bi–Sb species at various temperatures were carried out with liquid solutions of composition 11, 21, 40, and 60 atom % Sb. Because these metals form a continuous series of solutions with no eutectic,[5] the measurements were straightforward, and in all cases the change in composition with vaporization was less than 1% over the duration of the experiments. Measurements of ion intensities of Bi_2^+ from pure Bi(l) and Sb_4^+ from pure Sb(s) were made under identical conditions following each set of experiments on the binary system to obtain scaling factors which convert ion intensities to absolute partial pressures.

Parent Molecules and Fragmentation Contributions

Appearance potentials of the ion species from the vapor of a 40 atom % Sb solution at 625° and the relative intensities of these species at electron-impact energies of 20 eV are given in Table I of ref 1. It is shown that all possible homonuclear and heteronuclear monatomic, diatomic, triatomic, and tetratomic ions are formed by 20-eV electrons with intensities ordered in agreement with the relative volatilities of the two pure metals. The appearance potentials confirm, however, that there are only nine parent molecules in detectable concentrations: Sb_4, $BiSb_3$, Bi_2Sb_2, Bi_3Sb, Bi_4; Sb_2, BiSb, Bi_2; and Bi. All other ions are formed by electron-impact fragmentation of these molecules.

Fragmentation also enhances the ion currents of the parent monatomic and diatomic ions, and this complicates the measurements of the heats of reaction. The table shows that Sb_4 and $BiSb_3$ to a smaller extent contribute the major current of Sb_2^+ while $BiSb_3$, Bi_2Sb_2, and Bi_3Sb contribute heavily to the current of $BiSb^+$. Furthermore, the ion current of Bi_2^+ is enhanced by fragmentation of Bi_2Sb_2 and Bi_3Sb. According to a detailed analysis of a similar problem discussed elsewhere,[3] the parent ion current may be obtained from expressions of the form

$$I(Bi_2^+) = I_t(Bi_2^+) - (\sigma_f/\sigma_d)I(Bi_2Sb_2^+) - (\sigma_f'/\sigma_d')I(Bi_3Sb^+) \quad (1)$$

which is applicable in this example to the Bi_2^+ ion current. The term $I(Bi_2^+)$ represents the unknown parent ion current, $I_t(Bi_2^+)$ represents the measured total current, and σ_f/σ_d and σ_f'/σ_d' represent the ratios of the fragmentation cross sections for the production of Bi_2^+ from parent Bi_2Sb_2 and Bi_3Sb to the direct ionization cross sections for the formation of $Bi_2Sb_2^+$ and Bi_3Sb^+. From a practical standpoint, these ratios also include the sensitivity and other instrument constants.

On the basis of the relative intensities of Sb_4^+ and Sb_2^+ from pure Sb vapor measured with 20-eV electrons and a knowledge of the concentrations of the

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[1] (a) Research sponsored by the U. S. Army Research Office—Durham, Department of the Army, Contract No. DA-31-124-ARO-D-304. (b) National Aeronautics and Space Administration Predoctoral Fellow.

[2] (a) F. J. Kohl, J. E. Prusaczyk, and K. D. Carlson, *J. Am. Chem. Soc.*, 89, 5501 (1967); (b) K. D. Carlson, F. J. Kohl, and O. M. Uy, "Inorganic Applications of Mass Spectrometry," Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press.

[3] F. J. Kohl, O. M. Uy, and K. D. Carlson, *J. Chem. Phys.*, 47, 2667 (1967).

[4] O. M. Uy, F. J. Kohl, and K. D. Carlson, *J. Phys. Chem.*, 72, 1611 (1968).

[5] M. Hansen and K. Anderko, "Constitution of Binary Alloys," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1958, p 333.