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Oxidation of Hypophosphorous Acid by Peroxydisulfate. Kinetics and Mechanism(1)

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The oxidation of hypophosphorous acid by peroxydisulfate was found to obey the rate law: $-\mathrm{d}(S_2O_8{}^{2-})/\mathrm{d}t = [A + B(H_3PO_2)]^{1/2}(S_2O_8{}^{2-})^{3/2}$. A free-radical chain mechanism was proposed for the reaction. The reaction was independent of acidity up to pH 8 but fell off rapidly with pH above 8 and reached a low plateau at pH 11. This was explained to represent a kinetic titration of the hypophosphite radical, whose p*K* was estimated to be 9.1. The reaction was inhibited by oxygen, and the extent of this effect increased with pH. Activation energies were estimated and compared with those observed in the oxidation of phosphorous acid by peroxydisulfate. The reaction appeared to be more complex in solutions below pH 2, but no contribution from the tautomeric mechanism, encountered in many other reactions of hypophosphorous acid, was detected.

Introduction

Hypophosphorous acid, H_3PO_2, and phosphorous acid, H_3PO_3, are similar to each other structurally and chemically. Both contain a central phosphorus atom bonded tetrahedrally to four other atoms. Hypophosphorous acid is a monobasic acid, and its structure is believed to be $H_2P(O)OH$. Phosphorous acid has only one P–H bond and is a dibasic acid with the structure $HP(O)(OH)_2$.(3)

The two acids are strong reducing agents, and their reactions with a host of oxidizing agents have been investigated.(4–7) In the majority of cases the reactions were found to be similar to each other kinetically and to obey the rate law

$$\frac{-\mathrm{d}(\text{acid})}{\mathrm{d}t} = \frac{k'(\text{acid})(\text{ox.})}{k'' + k'''(\text{acid})/(\text{ox.})} \qquad (1)$$

where (acid) represents the concentration of either H_3PO_2 or H_3PO_3, and (ox.) that of the oxidizing agent.

A mechanism, involving an equilibrium between the "normal" and "active" forms of the respective acid, followed by the oxidation of the latter, has been proposed for these reactions. The "active" form was never isolated but is believed to be a tautomer of the acid. A study of the exchange of tritium between H_3PO_2 and H_2O(8) supports the tautomeric mechanism.

It appears, however, that both acids can undergo oxidation also by means of a free-radical chain reaction, not involving the tautomeric equilibrium. This has been demonstrated in the reduction of diazonium salts(9) and, more recently, in the oxidation of H_3PO_3 by peroxydisulfate.(10)

The reaction between hypophosphorous acid and peroxydisulfate has now been investigated and found to be very similar to the reaction of the latter with H_3PO_3. The standard potential for the oxidation of H_3PO_2 is 0.50 v;(11) it is, thus, a better reducing agent than H_3PO_3 (E° = 0.28 v(11)). It is also a faster reducing agent.

Experimental Section

Materials.—Stock solutions of reagent grade chemicals were prepared in triply distilled water. Hypophosphorous acid was prepared by exchanging its sodium salt (J. T. Baker monohydrate) on a Dowex strongly acidic resin.

Procedure.—The experimental procedure was identical with that employed in the study of the oxidation of H_3PO_3.(10) Runs were carried out in an excess of the reducing agent, under nitrogen, and the temperature was controlled to better than 0.1°. Aliquots (20 ml) were withdrawn at intervals from the reacting mixture into an acidified Fe(II) solution containing NaBr. This quenched the oxidation of H_3PO_2, and the subsequent titration of the excess iron with Ce(IV) gave the unreacted peroxydisulfate.(12) Six to eight aliquots were, normally, withdrawn from a single run, distributed to allow a 75% or better completion. Rate constants were determined from plots of a suitable function of $(S_2O_8{}^{2-})$ *vs.* time. Duplicate runs were carried out on many occasions, and the reproducibility was quite good.

Results

Stoichiometry.—The two-electron oxidation of H_3PO_2 produces the phosphorous acid, H_3PO_3, which can undergo a further oxidation to H_3PO_4.(10) The hypophosphorous acid, however, is a much faster reducing agent than H_3PO_3, and its oxidation by peroxydisulfate followed the reaction

$$S_2O_8{}^{2-} + H_3PO_2 + H_2O \longrightarrow 2H^+ + 2SO_4{}^{2-} + H_3PO_3 \qquad (2)$$

without any significant concurrent oxidation to H_3PO_4. This is apparent from the data on experiments carried out to completion (no detectable peroxydisulfate), presented in Table I. H_3PO_3 was determined iodometrically(13) and H_3PO_2 cerimetrically.(14)

The Rate Law.—In solutions of pH 3 and above, the

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(1) Presented, in part, at the Western Regional Meeting of the American Chemical Society, Los Angeles, Calif., Nov 1965.

(2) A grant from the Petroleum Research Fund is gratefully acknowledged.

(3) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, pp 347, 348.

(4) A. D. Mitchell, *J. Chem. Soc.*, **117**, 1322 (1920); **120**, 1266 (1921); **121**, 1624 (1922); **123**, 629, 2241 (1923); **125**, 564, 1013 (1924).

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

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(11) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed, Prentice-Hall, Inc., New York, N. Y., 1952, p 78.

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(13) R. T. Jones and E. H. Swift, *ibid.*, **25**, 1272 (1953).

(14) D. N. Bernhart, *ibid.*, **26**, 1798 (1954).

Table I

Stoichiometry of Reaction 2[a]

	$(K_2S_2O_8)$, *M*		(H_3PO_2), *M*		(H_3PO_3), *M*	
	Initial	Final	Initial	Final	Initial	Final
Solution I	0.008	...	0.025	0.018	...	0.007
Solution II	0.016	...	0.075	0.060	...	0.0157

[a] Buffer of 0.150 *M* phosphate (pH about 6.8), 50.82°.

rate of the oxidation of hypophosphorous acid by peroxydisulfate was found to obey the equation

$$-d(S_2O_8^{2-})/dt = k_{obsd}(S_2O_8^{2-})^{3/2} \qquad (3)$$

Linear plots were obtained when $(S_2O_8^{2-})^{-1/2}$ was plotted *vs.* time, and the observed rate constants did not vary with the initial concentration of the oxidizing agent. In the presence of 0.150 *M* NaH_2PO_2, 0.6 *M* total ionic strength, and a pH of 6, at 47.09°, the experimental rate constants (10^3k_{obsd}, $M^{-1/2}$ sec^{-1}) were 3.70, 3.76, 3.81, and 3.92 for the original $K_2S_2O_8$ concentrations of 0.004, 0.010, 0.020, and 0.032 *M*, respectively.

k_{obsd} was a function of $(H_2PO_2^-)$, and its dependence on the concentration of the latter was represented by the equation

$$k_{obsd} = [A + B(H_2PO_2^-)]^{1/2} \qquad (4)$$

The constants A and B were obtained from the linear plots of k_{obsd}^2 *vs.* $(H_2PO_2^-)$. A plot obtained at 50.82° is represented in Figure 1.

pH Dependence.—The reaction was independent of acidity up to pH 8, but the rate fell off rapidly with pH above 8 and reached a low plateau at about pH 11. This is shown in Figure 2, where the rate constant is plotted *vs.* pH.

Effect of Other Substances.—The rate of the reaction varied very little with the ionic strength. Increasing the latter 12-fold, from 0.13 to 1.62 *M*, by the addition of phosphate buffers and Na_2SO_4, increased the rate by a factor of 1.6 only.

The reaction was strongly catalyzed by Cu(II) salts and inhibited by Br^-, NO_3^-, and allyl acetate. Oxygen had a less pronounced effect on the rate. In air-saturated solutions, in the absence of nitrogen, the reaction exhibited an "induction period," believed to represent the inhibition by molecular oxygen. The extent of this effect was a function of pH and is shown in Figure 3.

Reaction at a Low pH.—In solutions more acidic than pH 2 the kinetics of the reaction seemed to be a function of the concentration of peroxydisulfate. Three-halves-order plots curved toward the first-order dependence on $(S_2O_8^{2-})$ when its concentration was below 0.01 *M*. Experiments with the initial concentration of $S_2O_8^{2-}$ below 0.01 *M* gave linear first-order plots.

Both the high and the low $K_2S_2O_8$ reactions were pH independent. The data on the first-order rate constants are presented in Table II. It is apparent that varying the ratio $(H_3PO_2)/(H_2PO_2^-)$ from 0.6 to 5 had no effect on the rate. In the calculations of pH and ionic strength the dissociation constant of H_3PO_2 was estimated to be 8.67×10^{-2} at 50.82° and was assumed not to vary with the ionic strength.[15]

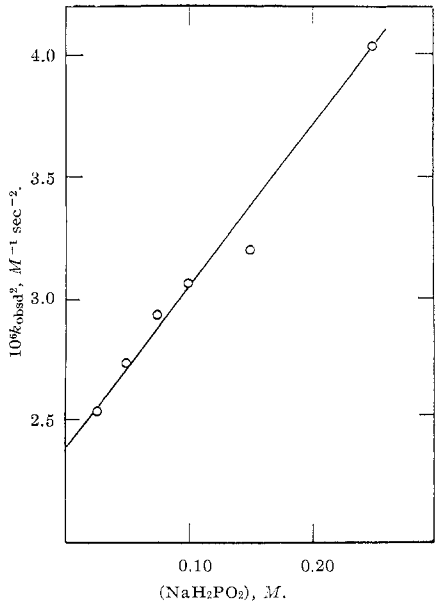

Figure 1.—Dependence of the observed rate constant on the concentration of NaH_2PO_2 at 50.82°, 0.0080 *M* $K_2S_2O_8$, 1.00 *M* ionic strength, and pH 6.6.

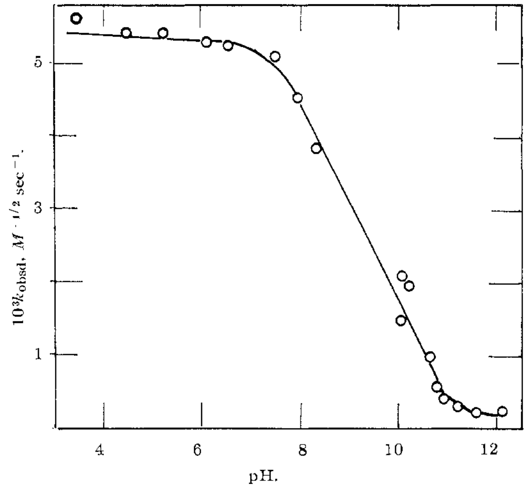

Figure 2.—pH dependence of the observed rate constant at 0.050 *M* NaH_2PO_2 and 50.82°.

Table II

pH Effect in Acidic Solutions[a]

$(HClO_4)$, *M*	$(LiClO_4)$, *M*	Calcd (H^+), *M*	10^4k_{obsd}, sec^{-1}
...	0.550	0.05	3.93
0.081	0.450	0.10	3.77
0.182	0.360	0.20	4.15
0.392	0.155	0.40	3.93

[a] 0.0080 *M* $K_2S_2O_8$, 0.051 *M* H_3PO_2, 0.58 *M* ionic strength, 50.82°.

Discussion

The following sequence is postulated for the oxidation of H_3PO_2 by peroxydisulfate in solutions of pH 3 and above: Initiation

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(15) The assumption was, probably, correct. Griffith and McKewon[5] determined the dissociation constants of H_3PO_2 at 30°. These were 0.075, 0.079, and 0.074 for 0.16, 0.57, and 1.31 *M* salt concentrations, respectively.

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^- \quad (5a)$$

$$S_2O_8^{2-} + H_2PO_2^- \xrightarrow{k_2} SO_4^{2-} + SO_4^- + H_2PO_2 \quad (5b)$$

Propagation

$$SO_4^- + H_2O \xrightarrow{k_3} HSO_4^- + OH \quad (5c)$$

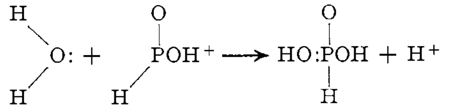
$$OH + H_2PO_2^- \xrightarrow{k_4} OH^- + H_2PO_2 \quad (5d)$$

$$H_2PO_2 + S_2O_8^{2-} \xrightarrow{k_5} H_2PO_2^+ + SO_4^{2-} + SO_4^- \quad (5e)$$

Termination

$$H_2PO_2 + H_2PO_2 \xrightarrow{k_6} H_2PO_2^+ + H_2PO_2^- \quad (5f)$$

followed by a rapid acid–base type reaction



$$H_2O: + H_2P(O)^+ \longrightarrow HO{:}P(O)(H)OH + H^+ \quad (5g)$$

This mechanism contains all the elementary processes necessary for the derivation of the experimental rate law, but is not all-exhaustive. The radicals OH, SO_4^-, and H_2PO_2 could participate in other reactions; for example, five additional bimolecular termination reactions are possible. Inclusion of these, however, in the mechanism leads to rate laws which have not been observed, and, consequently, these are considered to be unimportant.

The rate law is derived from eq 5 by means of the conventional steady-state treatment. Assuming

$$k_1 + k_2(H_2PO_2^-) \ll k_5(H_2PO_2) \quad (6)$$

i.e., postulating long chains, eq 7 is derived

$$-d(S_2O_8^{2-})/dt = [(k_5^2k_1/k_6) + (k_5^2k_2/k_6)(H_2PO_2^-)]^{1/2}(S_2O_8^{2-})^{3/2} \quad (7)$$

which is identical with the experimentally derived equation

$$-d(S_2O_8^{2-})/dt = [A + B(H_2PO_2^-)]^{1/2}(S_2O_8^{2-})^{3/2} \quad (8)$$

and establishes

$$A = k_5^2k_1/k_6 \text{ and } B = k_5^2k_2/k_6 \quad (9)$$

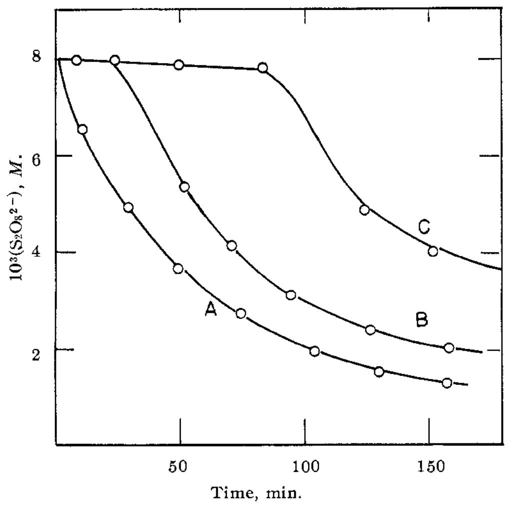


Figure 3.—Effect of O_2 at 0.050 *M* NaH_2PO_2 and 47.09°: run A, under N_2 (pH 3–8); runs B (pH 6.6) and C (pH 7.5), in air-saturated solutions.

Comparison of the rate of the oxidation of hypophosphorous acid with that of the thermal decomposition of aqueous peroxydisulfate, believed to proceed *via* reaction 5a as the rate-determining step,[16] indicates a chain length of about 300 in the oxidation of H_3PO_2 and justifies the assumption made in the derivation of the rate law (eq 6).

It was of interest to compare the activation energies in the reactions of H_3PO_3 and H_3PO_2 with peroxydisulfate.

The rate constants *A* and *B* were determined at three temperatures from the plots of k_{obsd}^2 *vs.* $(H_2PO_2^-)$. Temperature dependence of the square roots of the intercepts in these plots yields E_A, the activation energy of the hypophosphite-independent rate constant *A*, for at zero concentration of the reducing agent eq 4 becomes

$$k_{obsd} = A^{1/2} \quad (10)$$

From eq 9 one obtains the relationship

$$k_2 = k_1B/A \quad (11)$$

Thus, the experimental rate constants *A* and *B*, together with k_1, the rate constant of reaction 5a, calculated from the data of Kolthoff and Miller,[16] yield the rate constant k_2 of the competing (with 5a), chain-initiating reaction 5b. The experimental values *A* and *B*, together with the calculated k_1 and k_2, are presented in Table III.

TABLE III

RATE CONSTANTS AS A FUNCTION OF TEMPERATURE

Temp, °C	10^6A, M^{-1} sec^{-2}	10^6B, M^{-2} sec^{-2}	10^6k_1, sec^{-1}	10^6k_2, M^{-1} sec^{-1}
40.77	2.3	12.6	0.22	1.17
47.09	9.3	32.6	0.61	2.13
50.82	23.9	64.2	1.14	3.05

From the plot of log k_2 *vs.* $1/T$, E_2, the activation energy for the reaction between $S_2O_8^{2-}$ and the reducing agent (eq 5b), was determined.

Finally, it follows from eq 9 and 10 that

$$E_A = E_5 + {}^1/_2(E_1 - E_6) \quad (12)$$

Assuming zero activation energy for the chain-terminating reaction (E_6) and inserting E_1 from ref 16, one can estimate E_5, the activation energy of reaction 5e between peroxydisulfate and the radical derived from the reducing agent. These different activation energies are compared with the corresponding values in the H_3PO_3 reaction in Table IV.

TABLE IV

ACTIVATION ENERGIES (KCAL MOLE^{-1})

	H_3PO_3[10]	H_3PO_2
E_A	32.5	23.4
E_1	33.5	
E_2	14.0	19.2
E_5	15.7	6.6

Inspection of these values explains the greater reactivity of H_3PO_2 as compared with H_3PO_3. Even

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[16] I. M. Kolthoff and I. K. Miller, *J. Am. Chem. Soc.*, **73**, 3055 (1951).

though E_2 is slightly larger in the oxidation of H_3PO_2, its faster rate of oxidation results from the significantly lower E_5. Since both A and B depend on k_5^2, its relatively lower temperature coefficient in the H_3PO_2 reaction is responsible for the increased reactivity.

The dependence of the rate on pH, Figure 2, bears a close resemblance to a typical titration curve, where one plots pH *vs.* volume of base, except that the axes have been interchanged, the volume of base has been replaced by the observed rate constant, k_{obsd}, and the curve is viewed in a mirror perpendicular to the original volume axis. This close resemblance suggests a reaction

$$X + OH^- \rightleftharpoons Y \tag{13}$$

where X is a species participating in the reaction and Y is its conjugate base. If Y is less reactive than X, the rate will be independent of pH when the concentration of Y is insignificant, will fall off with pH as (Y) increases, and will level off when all X has been converted to Y. This is the observed behavior, and it implies that the rate law for the reaction is the same at the low plateau as in the region below pH 8; only the rate changes as Y increases, not the rate law. To verify this, the dependence of the rate on (H_3PO_2) was measured above pH 11. Since the reaction is very slow at this high pH, these experiments were carried out at a higher temperature and are presented in Table V and Figure 4. Table V indicates the falling off of k_{obsd} with pH at 63.7° and its leveling off at about pH 11, and Figure 4 shows that the dependence of k_{obsd} on (H_3PO_2), at pH 11.3, is represented by eq 4, obtained below pH 8. This establishes the validity of the rate law for the high-pH region.

In the conventional titration of a weak acid, pK is equal to pH when half of the acid has been neutalized. Similarly, in the present case, pH, where the rate is halfway between the two plateaus, yields pK of species X. From Figure 2, this pH is 9.1.

Species X cannot be identified with either the peroxydisulfate or hypophosphorous acid. Peroxydisulfate does not undergo neutralization, and hypophosphorous acid is known to be a monobasic acid with pK of about 1. Consequently, one has to associate reaction 13 with one of the radicals participating in the reaction. A similar explanation has been offered in other cases.[17] Of the three radicals involved in the reaction—SO_4^-, OH, and H_2PO_2—the latter is the most likely to be identified with species X. Neutralization of the hydroxyl radical has been reported[17] to take place above pH 11, and SO_4^- does not, probably, form a conjugate base. Had it been neutralized in the pH range 8–11, at least several other reactions of peroxydisulfate could have exhibited a change in rate in this pH range.[18]

TABLE V

MEASURED RATE CONSTANTS AT 63.7° [a]

pH	10^3k_{obsd}, $M^{-1/2}$ sec^{-1}
10.42	6.35
10.83	3.30
11.06	2.26
11.33	1.63
11.59	1.63
11.72	1.63
11.73	1.71
11.91	1.71

[a] 0.0080 M $K_2S_2O_8$, 0.050 M NaH_2PO_2, 0.2–0.3 M phosphate buffer.

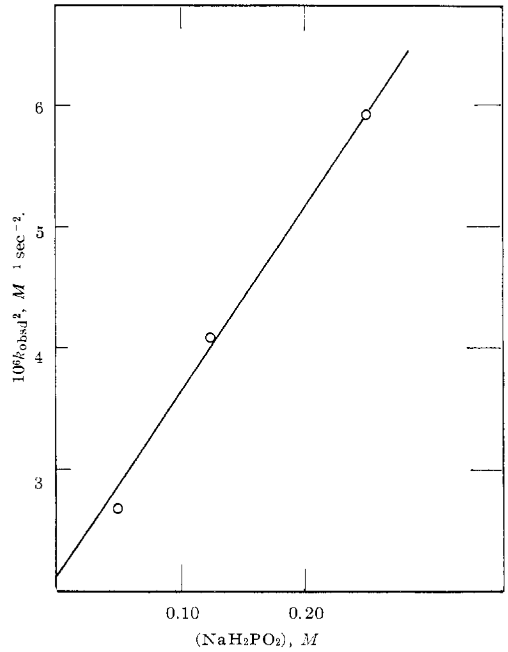

Figure 4.—Dependence of the high-pH rate constant on (NaH_2PO_2) at 0.0080 M $K_2S_2O_8$, 63.7°, and pH 11.3.

On the basis of this argument, one can represent reaction 13 by

$$H_2PO_2 + OH^- \rightleftharpoons HPO_2^- + H_2O \tag{14}$$

Figure 2 represents, then, a kinetic titration curve of the hypophosphite radical.

It should be noted that a similar pattern has been observed in the oxidation of phosphorous acid. Table I of ref 10 indicates a rapid decrease of the rate above pH 9.3. This was not understood at the time the article was written, and the falling off of the rate was attributed to impurities present, or effective, in alkaline solutions (the decline of the rate was not followed all the way to the low plateau). The phosphite radical appears to be a weaker acid than H_2PO_2. Whereas pK of the hypophosphite radical is about 9.1, that of the phosphite radical is, probably, above 10.

Inhibition of the reaction by oxygen was not investigated quantitatively. It is apparent from Figure 3 that it is strongly pH dependent. A plausible explanation would involve a reaction of O_2 with the conjugate base of the hyphosphite radical. Removal of HPO_2^- would shift equilibrium 14 to the right, and, thus,

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[17] C. R. Giuliano, N. Schwartz, and W. K. Wilmarth, *J. Phys. Chem.*, **63**, 353 (1959); M.-S. Tsao and W. K. Wilmarth, "Free Radicals in Inorganic Chemistry," Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, pp 113–122.

[18] The lack of pH dependence of the rate is not a definite proof for the absence of a neutralization reaction. It is quite possible for both X and Y to exhibit identical reactivities toward a particular substrate. It is, however, unlikely that this should happen in all known reactions of peroxydisulfate.

oxygen inhibition would become important several pH units below the pK of H_2PO_2.

Low pH Reaction.—No satisfactory interpretation can be offered for the change of the three-halves-order kinetics to first-order dependence on $(S_2O_8^{2-})$ when its concentration was below 0.01 M in solutions more acidic than pH 2.

Wilmarth and Haim presented[19] a helpful tabulation of the various rate laws one may encounter in the reactions of peroxydisulfate and their mechanistic interpretations. Examination of this table and introduction of additional reactions to the mechanism, eq 5, made it possible to assemble a sequence of reactions which led to the first-order dependence on peroxydisulfate concentration and the dependence on (H_3PO_2) in accord with eq 4, which was the observed behavior at low $(S_2O_8^{2-})$ in acidic solutions. Actually, at least two different sequences gave the experimental rate law; but the approximations and assumptions, employed in these derivations, were quite drastic and not satisfactorily justified. Furthermore, none of these explained the change to three-halves-order kinetics at higher concentrations of peroxydisulfate.

It was of importance to detect any occurrence of a nonchain reaction at this low pH, as several other reactions of hypophosphorous acid, believed to involve its tautomer, were acid catalyzed.[4-8] The method chosen here was the addition of allyl acetate to the reacting solution. Allyl acetate is known to be an effective scavenger of sulfate radical ions and has been used previously to quench other chain reactions of peroxydisulfate.[10,20]

The effect of allyl acetate on the low $(S_2O_8^{2-})$ reaction is shown in Figure 5. A similar result was also observed at a high $(S_2O_8^{2-})$. Addition of scavenger completely arrested the reaction. This indicates that the oxidation of H_3PO_2 by $S_2O_8^{2-}$ is a chain reaction also at the low pH.

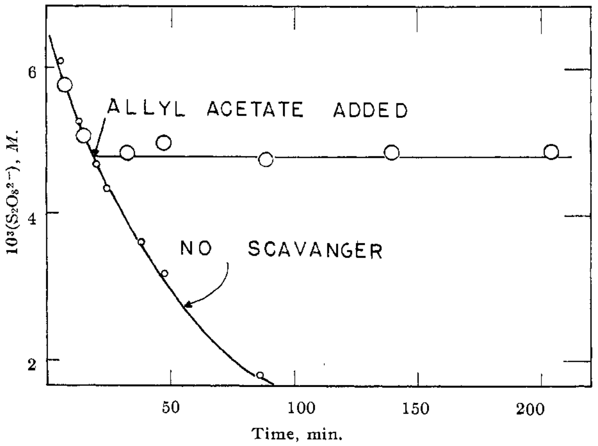

Figure 5.—Effect of added allyl acetate at 0.0064 M $K_2S_2O_8$, 0.0497 M H_3PO_2, 0.031 M H_2SO_4, pH 1.3, and 50.82°. Allyl acetate (5 ml) was added to 140 ml of the reacting solutions 21 min after the start of the reaction.

It is not improbable that other intermediates, generated in the acid-catalyzed decomposition of peroxydisulfate,[16,19] are involved in the reaction or that H_3PO_2 may react at a different rate than $H_2PO_2^-$. This interpretation, however, would require the rate of the acidic reaction to vary with pH, which was not observed (*cf.* Table II).

Acknowledgment.—The author is indebted to Professor W. K. Wilmarth for helpful discussions.

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(19) W. K. Wilmarth and A. Haim in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, pp 175-225.

(20) I. M. Kolthoff, E. J. Meehan, and E. M. Carr, *J. Am. Chem. Soc.*, **75**, 1439 (1953); E. Ben-Zvi and T. L. Allen, *ibid.*, **83**, 4352 (1961); A. J. Kalb and T. L. Allen, *ibid.*, **86**, 5107 (1964).

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Heteropoly Blues. II. Reduction of 2:18-Tungstates

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The three heteropoly anions A-$[P_2W_{18}O_{62}]^{6-}$, B-$[P_2W_{18}O_{62}]^{6-}$, and $[As_2W_{18}O_{62}]^{6-}$ are reduced in acidic and neutral solutions at the dropping mercury and rotating platinum electrodes. The initial reduction steps examined here correspond to the addition of up to six electrons per anion. The reduced species are quite inert to alkaline degradation, permitting an investigation of the redox behavior of the polytungstate structure in solutions of pH 0–13. By using the reduced anion $[PW_{12}O_{40}]^{5-}$ it was possible to show that the Keggin structure can also accept at least six electrons in neutral and alkaline solutions.

Introduction

The reduction of heteropoly tungstate and molybdate anions to heteropoly blues is not limited to those 1:12 species with the Keggin structure.[1] Most workers in the field have observed that the 18-molybdo- and 18-tungstodiphosphate anions, $[P_2Mo_{18}O_{62}]^{6-}$ and $[P_2W_{18}O_{62}]^{6-}$, are much more readily reduced than are the corresponding 12-anions, $[PMo_{12}O_{40}]^{3-}$ and $[PW_{12}$-

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(1) See M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, **5**, 1249 (1966), and references therein.