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.

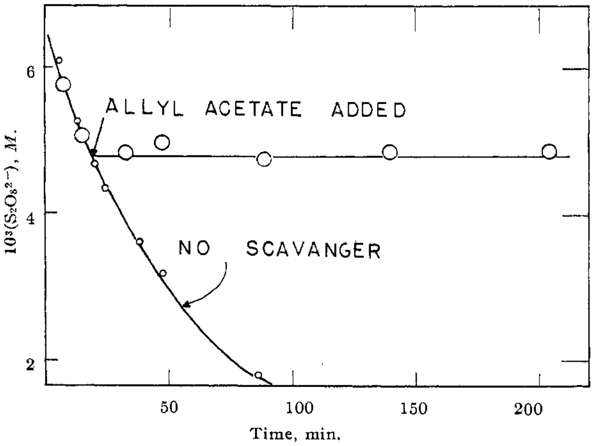

Figure 5.—Effect of added allyl acetate at 0.0064 M $K_2S_2O_8$, 0.0497 M H_3PO_2, 0.031 M H_2SO_4, pH 1.3, and 50.82°. Allyl acetate (5 ml) was added to 140 ml of the reacting solutions 21 min after the start of the reaction.

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).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
GEORGETOWN UNIVERSITY, WASHINGTON, D. C. 20007

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

BY MICHAEL T. POPE AND ELIAS PAPACONSTANTINOU

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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.

$O_{40}]^{3-}$. Since the 2:18 compounds are structurally related[2] to the 12-tungstates discussed previously,[1] a comparison of their reduction behavior is of interest. Moreover, a direct comparison of the reduction of isostructural molybdates and tungstates can also be made.[3] This article and the one following report the reduction stoichiometries of these anions together with a preliminary study of the stabilities of the reduced species.

The first quantitative measurements of the reduction of the 18-tungstodiphosphate anion were made by Wu,[4] who was able to isolate two forms of the ammonium salt of the oxidized anion by fractional crystallization. He observed that the less soluble salt ("*A*") was more easily reduced than the other ("*B*").[5] In alkaline solutions both compounds appeared to undergo a two-electron reduction, but since the oxidized anions are decomposed above pH 5–6, such results must be considered doubtful. Later polarographic studies of this anion have been inconclusive,[6,7] and those authors who were aware of the isomerism could not distinguish polarographically between the two forms. On the basis of bulk electrolyses, Souchay[6] concluded, however, that no more than six electrons could be added to the anion before decomposition occurred.

Other work on the reduction of this anion and the corresponding arsenate, for which no isomerism has been definitely established, has not been concerned with the identification of the reduction products.[8]

Experimental Section

Preparation and Analysis of the Compounds.—Literature methods were used for the preparation of ammonium salts of 18-tungstodiarsenate[9] and both *A* and *B* forms of 18-tungstodiphosphate.[4,10] Following Tsigdinos,[11] the salts were purified with dioxane. The resulting materials crystallized with several molecules of dioxane; typical analyses follow. *Anal.* Calcd for $(NH_4)_6[P_2W_{18}O_{62}]\cdot 4.2C_4H_8O_2\cdot 15H_2O$ (*A* form): N, 1.64; P, 1.21; W, 64.74; C, 3.94. Found: N, 1.63; P, 1.23; W, 64.80; C, 3.98. Calcd for $(NH_4)_6[P_2W_{18}O_{62}]\cdot 4.0C_4H_8O_2\cdot 15H_2O$ (*B* form): N, 1.64; P, 1.22; W, 64.96; C, 3.77. Found: N, 1.57; P, 1.24; W, 64.86; C, 3.79. Calcd for $(NH_4)_6[As_2W_{18}O_{62}]\cdot 3.5C_4H_8O_2\cdot 17H_2O$: N, 1.62; As, 2.90; W, 63.96; C, 3.25. Found: N, 1.54; As, 2.91; W, 64.38; C, 3.26. The dioxane and water contents of the crystals varied slightly from preparation to preparation. Such a variation is not unusual since some heteropoly salts are known to contain zeolytic water. The dioxane was shown not to interfere with the various measurements by repeating some of the experiments with materials crystallized from water.

Sodium 12-tungstophosphate decahydrate was prepared and analyzed as described previously.[1]

Phosphorus and tungsten were determined gravimetrically as magnesium pyrophosphate and tungstic oxide. Ammonia was distilled from alkaline solutions into standard acid and the excess acid was titrated. Arsenic was separated by distillation as the trichloride which was titrated with standard iodine solution.[12]

Potentiometric Titrations and Polarography.—These procedures were carried out as described previously.[1] For the rotating platinum electrode polarograms, a synchronous motor operating at 600 rpm was used. Except where otherwise stated, the concentration of heteropoly anion was 5×10^{-4} *M* and the supporting electrolytes were mixtures of 1.0 *M* sulfuric acid and sodium sulfate or 1.0 *M* ammonium sulfate and ammonium hydroxide.[13] The capillary characteristics at 25° in 0.1 *M* sulfuric acid–0.9 *M* sodium sulfate were $t = 3.33$ sec/drop, $m = 1.91$ mg/sec at 0.000 v, and $t = 3.53$ sec/drop, $m = 1.85$ mg/sec at -0.270 v. All potentials are referred to the saturated calomel electrode.

Controlled-Potential Electrolysis.—This was carried out in an H cell with a mercury pool cathode using manual control or a McKee-Pederson potentiostat.

Results

Potentiometric Titrations.—Titrations of the three anions in 0.5 *M* sulfuric acid solution with chromium(II) sulfate using a mercury indicator electrode gave in each case two well-defined end points corresponding to the addition of two and four electrons per anion, together with a less well-defined one-electron end point; see Figure 1. Formal reduction potentials are given in Table I. These stoichiometries and potentials were confirmed by titration with europium(II) chloride in hydrochloric acid solution.

TABLE I

FORMAL REDUCTION POTENTIALS IN 0.5 *M* H_2SO_4

Anion	*E*, v *vs.* sce	No. of electrons
A-$[P_2W_{18}O_{62}]^{6-}$	+0.059	1
	−0.081	1
	−0.365	2
B-$[P_2W_{18}O_{62}]^{6-}$	+0.045	1
	−0.140	1
	−0.400	2
$[As_2W_{18}O_{62}]^{6-}$	+0.068	1
	−0.094	1
	−0.340	2

Polarography.—The polarograms presented in Figure 2 illustrate the behavior of *B*-$[P_2W_{18}O_{62}]^{6-}$ in 1.0 *M* sulfate supporting electrolyte.[14] The polarographic results for each of the three anions studied were very similar, differing only slightly in half-wave potentials, and are summarized in Table II. In acidic solutions

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(2) B. Dawson [*Acta Cryst.*, **6**, 113 (1953)] located the tungsten atoms in $K_6[P_2W_{18}O_{62}]\cdot 14H_2O$ and demonstrated that the anion could be constructed from two equivalent fragments of the Keggin structure found for $[PW_{12}O_{40}]^{3-}$.

(3) Comparison of the reduction of 12-tungstates with isostructural 12-molybdates is limited to those molybdates containing silicon, germanium, phosphorus, and arsenic as central atoms. None of these species is very stable toward hydrolytic degradation, a property which probably accounts for the conflicting results reported for the reduction of an ion such as $[SiMo_{12}O_{40}]^{4-}$. The 2:18-molybdates have a much broader pH range of stability.

(4) H. Wu, *J. Biol. Chem.*, **43**, 189 (1920).

(5) The two forms almost certainly contain different structural isomers of the heteropoly anion. Such isomerism has been observed for 12-tungstates. It is not known which form of the anion was examined by Dawson,[2] who appeared to be unaware of the existence of isomerism. Dawson's description of the color of his crystals suggests that they may have corresponded to Wu's *B* form.

(6) P. Souchay, *Ann. Chim.* (Paris), **19**, 102 (1944); **20**, 73 (1945).

(7) J. H. Kennedy, *J. Am. Chem. Soc.*, **82**, 2701 (1960).

(8) Since uric acid will reduce 18-tungstodiphosphate to a heteropoly blue, this heteropoly anion has been used for the colorimetric determination of uric acid [S. R. Benedict, *J. Biol. Chem.*, **51**, 187 (1922)]. Studies of the chemical reduction of the 2:18-tungstates appear to have been limited to this reducing agent [see for example E. van Dalen, Ph.D. Thesis, Purdue University, 1962].

(9) F. Kehrmann, *Z. Anorg. Allgem. Chem.*, **22**, 285 (1899).

(10) All attempts to isolate a second isomer of the arsenate anion were unsuccessful.

(11) G. A. Tsigdinos, Ph.D. Thesis, Boston University, 1962.

(12) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, "Applied Inorganic Analysis," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1962, pp 262, 269, and references therein.

(13) In pH regions where these mixtures have no buffering capacity, polarograms run in acetate (pH 4.50) and phosphate (pH 6.90) buffers confirmed the results obtained.

(14) If the ionic strength of the supporting electrolyte was 0.5 *M* or less, the waves were so poorly resolved as to be virtually undetectable.

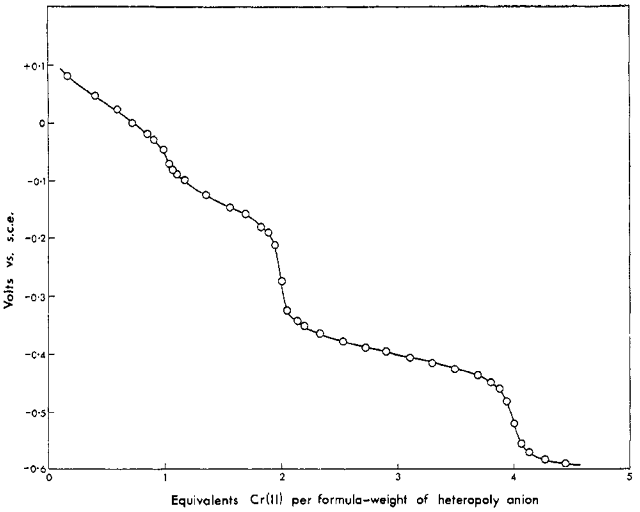

Figure 1.—Potentiometric titration of $(NH_4)_6[P_2W_{18}O_{62}]$ (*B* isomer) with 0.2 *M* $CrSO_4$ in 0.5 *M* H_2SO_4 at 30°. Concentration of heteropoly anion, ~4 × 10^{-3} *M*.

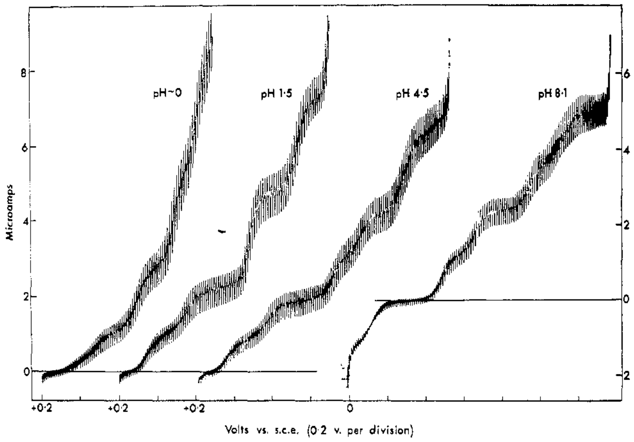

Figure 2.—Polarograms of *B*-$[P_2W_{18}O_{62}]^{6-}$ at 25°. The polarogram at pH 8.1 is of the two-electron blue and has been displaced upward to allow comparison with the others.

(pH <3) four waves with heights in the ratio 1:1:2:2 were observed. The first three waves corresponded to the three titrimetric end points and were assigned as one-, one-, and two-electron reductions. The fourth wave must correspond to a two-electron reduction at a potential which was not attainable with chromium(II). Slopes of plots of E *vs.* log $[i/(i_d - i)]$ indicated that the waves were reversible at low pH.[15] As the pH of the solution was increased, the third and fourth waves moved to more negative potentials and became less reversible in shape. By pH 6 the third wave had split into two reversible one-electron waves. Polarograms were not obtainable above pH 6 owing to the rapid decomposition of the heteropoly anions. However, as has been observed by Souchay[16] for reduced 12-molybdosilicate, the reduced compounds had a much broader pH range of stability. The fourth polarogram in Figure 2 was obtained from a solution of the heteropoly anion which had been reduced by controlled-potential electrolysis to the two-electron reduction product.[17] As can be seen in Figure 2, the first two one-electron waves were anodic as expected, although the first one was masked by the mercury dissolution wave which at pH 8.2 occurs at about 0.0 v. Also, by pH 8.2 the last wave had split into two one-electron waves, so that a total of six one-electron oxidation or reduction steps was observed. There was essentially no change in the form of the polarogram from pH 8 to 13. The two anodic waves which became increasingly obscured by the mercury wave as the pH of the solutions was increased could be clearly detected using a rotating platinum electrode, although with this electrode the hydrogen wave interfered with some of the waves at more negative potentials. Comparison of the polarograms at pH 13 shown in Figures 3 and 4 shows the limitations of both electrode systems. Figure 5 summarizes the half-wave potentials for *B*-$[P_2W_{18}O_{62}]^{6-}$. The results for the other two heteropoly anions were very similar and the limiting one-electron half-wave potentials are listed in Table II.

TABLE II

LIMITING ONE-ELECTRON HALF-WAVE POTENTIALS[a] AT 25°

$[As_2W_{18}O_{62}]^{6-}$	*A*-$[P_2W_{18}O_{62}]^{6-}$	*B*-$[P_2W_{18}O_{62}]^{6-}$
+0.101	+0.098	+0.064
−0.100	−0.104	−0.150
−0.422	−0.440	−0.474
−0.635	−0.640	−0.675
−0.890	−0.895	−0.950
−1.05	−1.06	−1.105

[a] *Vs.* sce.

Stabilities of the Oxidized Heteropoly Anions.—The fact that polarograms of the oxidized anions could be observed up to pH 6 indicated that these compounds were essentially undecomposed in such solutions. This observation is apparently not in agreement with some early polarographic work of Souchay[18] which indicated that the 2:18-tungstates were decomposed within the pH range 4.0–4.6. In order to confirm the conclusions of the present work, a solution of the free acid of *B*-$[P_2W_{18}O_{62}]^{6-}$, prepared by ion exchange on Dowex-50 resin, was titrated with standard sodium hydroxide solution. The results of this titration are presented in Figure 6. The first end point corresponds to the neutralization of the six acidic protons, and the second end point to the reaction

$$[P_2W_{18}O_{62}]^{6-} + 34OH^- \longrightarrow 2HPO_4^{2-} + 18WO_4^{2-} + 16H_2O$$

The plateau between the two end points, which represents the region where degradation of the anion is taking place, appears at about pH 7 and is in accord with the present polarographic results.[19]

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[15] Significantly, the waves in the polarograms of $[As_2W_{18}O_{62}]^{6-}$ appeared as reversible as those for the two isomers of $[P_2W_{18}O_{62}]^{6-}$. If the preparation of $(NH_4)_6[As_2W_{18}O_{62}]$ had contained a mixture of two isomers (which would be expected to differ slightly in reduction potential), the waves would have appeared to be less reversible in shape.

[16] P. Souchay, *Talanta*, **12**, 1187 (1965).

[17] The heteropoly salt was dissolved in water, the pH of which had been adjusted to 2.5 with sulfuric acid, and the solution electrolyzed at a potential corresponding to the midpoint of the plateau between the second and third waves. An aliquot of the reduced solution was added to deoxygenated buffer solution in the polarographic cell.

[18] P. Souchay, *Ann. Chim.* (Paris), **20**, 80 (1945).

[19] The position of this plateau is governed to a large extent by kinetic factors. Most workers who have studied polymerization reactions of tungstates have observed that equilibrium can take several weeks to be established at ambient temperatures. [See, for example, O. Glemser, W. Holznagel, W. Holtje, and E. Schwarzmann, *Z. Naturforsch.*, **20b**, 725 (1965).]

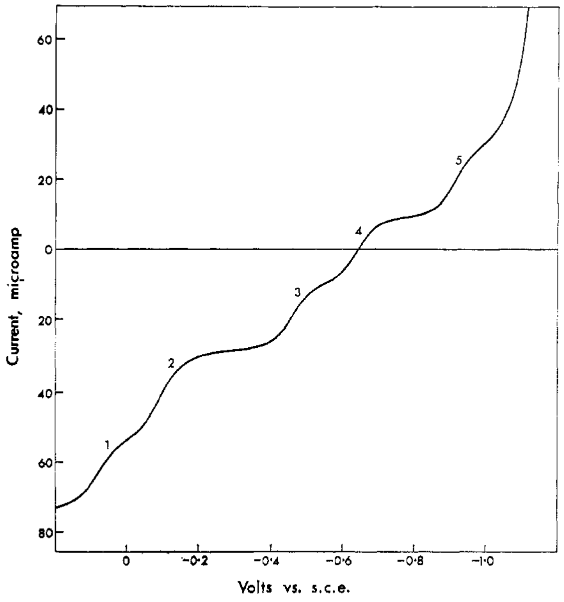

Figure 3.—Rotating platinum electrode (rpe) polarogram of reduced $[As_2W_{18}O_{62}]^{6-}$ in 1.0 *M* NaOH at 25°.

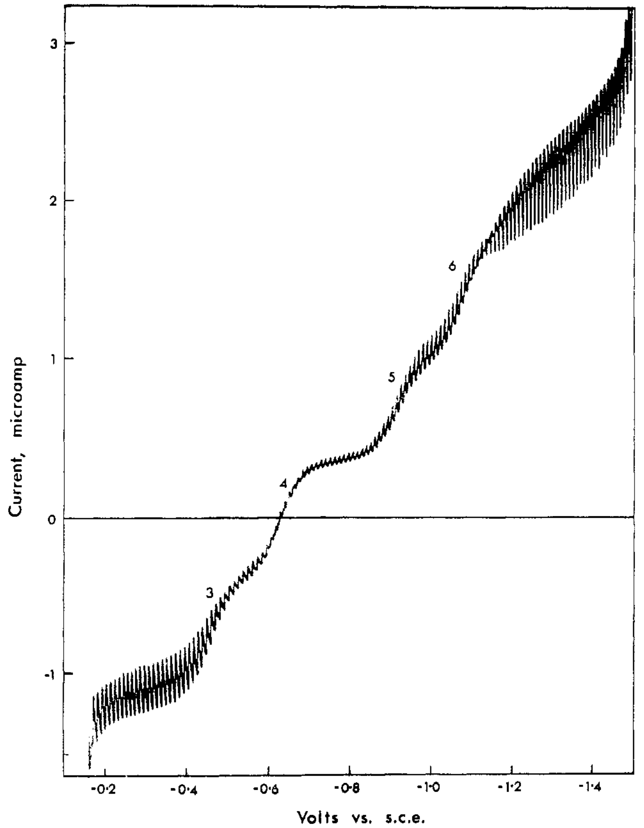

Figure 4.—Dropping mercury electrode (dme) polarograms of reduced $[As_2W_{18}O_{62}]^{6-}$ in 1.0 *M* NaOH at 25°.

Decomposition and Disproportionation of the Heteropoly Blues.—Although polarograms of the reduced species could be observed in alkaline solutions where the oxidized anions were completely degraded, at a sufficiently high pH even the reduced compounds were decomposed. The polarograms shown in Figures 3 and 4 were recorded 2 hr after preparation of the solution. The solute was originally the two-electron reduction product, but the position of zero current in the polarograms indicates that a disproportionation has occurred yielding a mixture of the three- and four-electron reduction products. The extent and the rate of disproportionation, as indicated from the observed decay of polarograms, depended upon the pH and the initial extent of reduction. Since neither the mechanism of decomposition of the oxidized form of these heteropoly anions[20] nor the stoichiometry of the reaction of heteropoly blues with hydroxide ion is well established, a detailed study and analysis of the decomposition–disproportionation reactions was not attempted. At any pH a particular reduced species underwent a series of disproportionation reactions yielding an apparent equilibrium mixture. The position

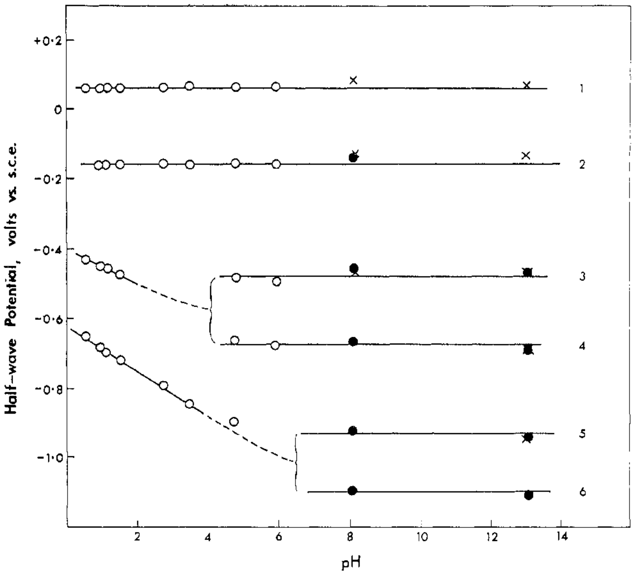

Figure 5.—Variation of half-wave potential with pH for the *B*-$[P_2W_{18}O_{62}]^{6-}$ structure. Measurements above pH 8 were made on the two-electron blue: ○, ●, dme; ×, rpe. The numbers 1–6 refer to the waves corresponding to those numbered in Figures 3 and 4.

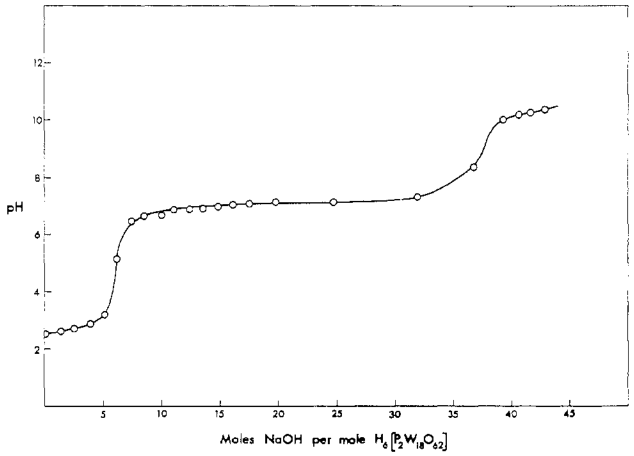

Figure 6.—Titration of $H_6[P_2W_{18}O_{62}]$ (*B* isomer) with 0.1 *N* NaOH at 60°. Concentration of heteropoly acid, $\sim 1.6 \times 10^{-3}$ *M*.

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(20) Souchay[18] has concluded that the initial step in the alkaline degradation of a 2:18-tungstate is the formation of a 2:17-anion of unknown structure.

of equilibrium and the rate of attaining the equilibrium depended upon the extent of reduction of the starting material. Besides the disproportionation reactions, all of the heteropoly anions, oxidized and reduced, underwent direct alkaline degradation, the extent and rate of degradation again depending upon the degree of reduction of the heteropoly anion. All rates and extents of decomposition and disproportionation increased with increasing pH. These results may be illustrated by the following schemes for the one-electron reduction product. At pH 8.2

$$\begin{tikzcd} {[P_2W_{18}O_{62}]^{7-}} \arrow[r, "\text{fast}"] \arrow[d] & {[P_2W_{18}O_{62}]^{6-}} \arrow[d] & + & {[P_2W_{18}O_{62}]^{8-}} \arrow[d] \\ \text{slow degradation} & \text{``instantaneous'' degradation} & & \text{very slow degradation} \end{tikzcd}$$

After 24 hr the "equilibrium" mixture contained equivalent amounts of $[P_2W_{18}O_{62}]^{7-}$ and $[P_2W_{18}O_{62}]^{8-}$. At pH 11.2

$$\begin{tikzcd} {[P_2W_{18}O_{62}]^{7-}} \arrow[r, "\text{``instantaneously''}"] & {[P_2W_{18}O_{62}]^{8-}} \arrow[dl, "\text{fast}"'] & + & {[P_2W_{18}O_{62}]^{6-}} \arrow[d] \\ {[P_2W_{18}O_{62}]^{9-}} \arrow[d] & + & {[P_2W_{18}O_{62}]^{7-}} \arrow[d] & \text{instantaneous degradation} \\ \text{very slow degradation} & & \text{instantaneous disproportionation, etc.} & \end{tikzcd}$$

After 24 hr the "equilibrium" mixture contained equivalent amounts of $[P_2W_{18}O_{62}]^{8-}$ and $[P_2W_{18}O_{62}]^{9-}$.

Reduction of 12-Tungstophosphate.—Solutions of the oxidized anion $[PW_{12}O_{40}]^{3-}$ are stable only below pH 1.5, so that only four electrons can be added to the anion before the solvent is reduced.[1] However, polarography of the reduced species should be extendable to solutions of higher pH, as has been found for the 2:18-anions. In fact the two electron reduction product of $[PW_{12}O_{40}]^{3-}$ was inert enough to enable polarograms to be observed in 1.0 *M* sodium hydroxide.[21] The results of a polarographic study are summarized in Figure 7. The reduction pattern closely resembles that of the 2:18-anions with a total possible addition of six electrons.

Discussion

The polarographic results summarized in Figure 5 show that the initial steps in the reduction of heteropoly 2:18-tungstates involve the addition of six electrons. The reduction potentials of the three anions were quite reproducible, and the differences between the two isomers of $[P_2W_{18}O_{62}]^{6-}$ showed in samples which had undergone repeated recrystallizations and precipitations. Unlike the two forms of 12-molybdosilicate,[22] interconversion of the isomers must be very slow at room temperature. Since the reduction potentials of the isomers are similar, it is probable that the anions have very similar structures[23] and that these structures remain intact as electrons are added. The pH dependence of some of the half-wave potentials indicates that protonation accompanies these reduction steps, as observed for the 12-tungstates.[1] It can be concluded from Figure 5 that the 2:18-tungstate structure can carry a charge of −8 without significant protonation in acidic solutions. The maximum unprotonated charge for the smaller 12-tungstates under similar conditions was found to be −6. At pH 13 the six-electron reduction products must have charges close to −12 (2:18) and −9 (1:12).

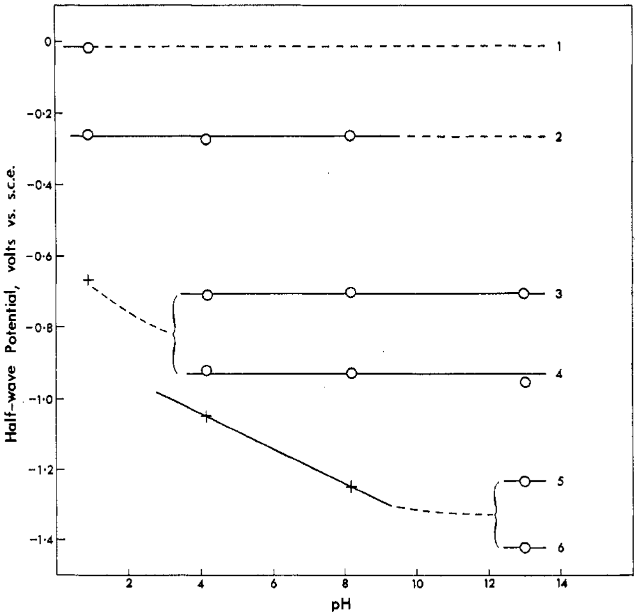

Figure 7.—Variation of dme half-wave potential with pH for $[PW_{12}O_{40}]^{3-}$ structure. Except for those[1] at pH 1, measurements were made on the two-electron blue: +, two-electron waves; ○, one-electron waves. The numbers 1–6 show the correspondence with Figure 5.

The heights of the polarographic waves are in accordance with one-electron reductions for such large electroactive species. Thus the diffusion coefficient of *A*-$[P_2W_{18}O_{62}]^{6-}$, calculated from the limiting current of the first wave in 0.1 *M* sulfuric acid–0.9 *M* sodium sulfate, is $(1.46 \pm 0.15) \times 10^{-6}$ cm² sec⁻¹. Application of the Stokes–Einstein equation, $D = kT/6\pi\eta r$, yields an effective hydrodynamic radius of 10 ± 1 A for this anion. Similar values of D and r are found for the other two anions, and the magnitude of r is in keeping with the crystallographic dimensions.[24] The value of D should be compared with that found for $[SiW_{12}O_{40}]^{4-}$ under similar conditions,[1] $(2.56 \pm 0.15) \times 10^{-6}$ cm² sec⁻¹. These values provided further independent evidence for the invalidity of Riecke's law.[25,26]

It has been noted previously[1] that the reduction potential of a heteropoly anion–heteropoly blue couple

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(21) Disproportionation took place in these solutions, but this did not affect the half-wave potentials. See Figure 3.

(22) T. D. H. Strickland, *J. Am. Chem. Soc.*, **74**, 868 (1952).

(23) Plausible structures for the isomers can be constructed from Dawson's[2] by rotating W_3O_{13} groups, or even, with some strain, by forming the centrosymmetric structure postulated by Wells prior to Dawson's work: A. F. Wells, "Structural Inorganic Chemistry," 1st ed, Oxford University Press, London, 1945, p 344.

(24) Dawson's structure approximates to an ellipsoid with axes of ∼17 and ∼12 A.

(25) D = constant × $M^{-1/2}$ where M is the ionic weight of the diffusing species. In this case the ratio of D's is 1.72 ± 0.13 whereas $(M_{\text{tungstophosphate}}/M_{\text{tungstosilicate}})^{1/2} = 1.23$.

(26) L. C. W. Baker and M. T. Pope, *J. Am. Chem. Soc.*, **82**, 4176 (1960).

is essentially independent of the nature of the central atom, so that the similar potentials for the three anions studied here are not unexpected. The charge dependence of the reduction potentials of the 12-tungstates was rationalized on a simple electrostatic "conducting-sphere" model.[1] In the absence of any further structural or bonding information, such a model can also be used to rationalize the more positive potential of the larger $[P_2W_{18}O_{62}]^{6-}$ *vs.* $[PW_{12}O_{40}]^{3-}$. A more sophisticated model for the bonding in heteropoly blues (and for heteropoly anions in general) must await the results of a thorough investigation of their magnetic and spectral properties. Such a study is in progress.

The kinetic inertness of the reduced anions, which has been observed by other workers,[16] is of interest since it suggests a way of investigating the mechanism of alkaline degradation of heteropoly structures. The increased inertness is not due solely to the increased negative charge, for the reduced 12-tungstophosphate $[PW_{12}O_{40}]^{5-}$ could be studied for a short period in 1.0 *M* sodium hydroxide, in which solvent the oxidized anion $[FeW_{12}O_{40}]^{5-}$ is very rapidly decomposed.

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Contribution from the Department of Chemistry,
Georgetown University, Washington, D. C. 20007

Heteropoly Blues. III. Preparation and Stabilities of Reduced 18-Molybdodiphosphates[1,2]

By ELIAS PAPACONSTANTINOU and MICHAEL T. POPE

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The heteropoly anions $[P_2Mo_{18}O_{62}]^{6-}$ and $[As_2Mo_{18}O_{62}]^{6-}$ each undergo three successive two-electron reductions in acidic solutions. No intermediate reduction steps have been observed. The reduced heteropoly molybdates are weaker acids than the corresponding tungstates and disproportionate more rapidly in neutral and alkaline solutions. Crystalline samples of ammonium salts and solutions of the free acids of the three reduced molybdophosphates have been characterized.

Introduction

The favorable reduction potentials of heteropoly molybdates have allowed several workers to isolate heteropoly molybdate blues without difficulties of rapid reoxidation,[3-7] but no complete analysis of such a blue has been reported. Moreover, most of the work has been restricted to reduction of the 12-molybdophosphate and -silicate anions which are very susceptible to hydrolytic degradation even in acid solutions. In the only published investigation of the reduction of heteropoly 2:18-molybdates, Wu treated acidic solutions of ammonium 18-molybdodiphosphate with various reducing agents and was able to isolate crystalline samples of three heteropoly blues.[3] These materials, characterized only by ignition and by titration with potassium permanganate, were formulated as $3(NH_4)_2O\cdot P_2O_5\cdot 17MoO_3\cdot MoO_2\cdot xH_2O$, $3(NH_4)_2O\cdot P_2O_5\cdot 16MoO_3\cdot 2MoO_2\cdot xH_2O$, and $3(NH_4)_2O\cdot P_2O_5\cdot 15MoO_3\cdot 3MoO_2\cdot xH_2O$. Such results suggest two-, four-, and six-electron reductions of the $[P_2Mo_{18}O_{62}]^{6-}$ anion and indicate an analogy with the tungstates for which six one-electron reductions have been observed.[2]

Experimental Section

Preparation and Analysis of Compounds.—Ammonium salts of the oxidized 18-molybdodiphosphate and -arsenate anions were prepared and purified as described by Tsigdinos.[8]

As found before,[2] the salts contained several molecules of dioxane. *Anal.* Calcd for $(NH_4)_6[P_2Mo_{18}O_{62}]\cdot 7.4C_4H_8O_2\cdot 9H_2O$: N, 2.27; P, 1.68; Mo, 46.54; C, 9.61. Found: N, 2.13; P, 1.72; Mo, 46.58; C, 9.56. Calcd for $(NH_4)_6[As_2Mo_{18}O_{62}]\cdot 8.0C_4H_8O_2\cdot 11H_2O$: N, 2.16; As, 3.86; Mo, 44.51; C, 9.91. Found: N, 2.10; As, 3.84; Mo, 44.34; C, 9.79.

The heteropoly blues were prepared by electrolytic reduction. A solution of about 20 g of ammonium 18-molybdodiphosphate in 50 ml of 0.5 *M* sulfuric acid was electrolyzed at a platinum gauze cathode in a conventional H cell. The catholyte was stirred by a current of purified nitrogen and was separated from the anolyte (0.5 *M* H_2SO_4) by a potassium chloride–agar plug which also served as a junction for the reference calomel electrode. Although the three heteropoly blues could be generated by controlled-potential electrolysis at +0.36, +0.24, and 0.0 v *vs.* sce, it was found that considerable time could be saved by applying a higher potential (10–15 v). Such a method of preparation is possible because the reduction steps are rapid and reversible and because, at a platinum electrode in 0.5 *M* sulfuric acid, hydrogen is evolved before the heteropoly anion is reduced to the stage where its structure is destroyed. The extent of reduction during electrolysis at high potential was followed by means of a plati-

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[1] Presented in part at a Meeting-in-Miniature of the Chemical Society of Washington, May 1965.

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