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

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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.

(2) Part II: M. T. Pope and E. Papaconstantinou, *Inorg. Chem.*, **6**, 1147 (1967).

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

(4) I. P. Alimarin, Z. F. Shakhova, and R. K. Motorkina, *Dokl. Akad. Nauk SSSR*, **106**, 61 (1956).

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(6) (a) P. Souchay and R. Massart, *Compt. Rend.*, **253**, 1699 (1961); (b) R. Massart and P. Souchay, *ibid.*, **256**, 4671 (1963).

(7) (a) H. Hahn and F. Hahn, *Naturwissenschaften*, **49**, 539 (1962); (b) H. Hahn and G. Schmidt, *ibid.*, **49**, 539 (1962); (c) H. Hahn and W. Becker, *ibid.*, **49**, 513 (1962); **50**, 402 (1963).

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

num indicator electrode. When the solution had been electrolyzed to the desired extent, the ammonium salt of the heteropoly blue was precipitated by addition of about 6 g of ammonium chloride. All subsequent operations were carried out in a nitrogen-filled glove box with deoxygenated solvents. The precipitated blues were purified by (twice) dissolving in water and reprecipitating with a three- to fourfold excess of dioxane. Finally, the crystalline materials were washed with 80% dioxane, pure dioxane, and ether, before storage in tightly stoppered bottles. All three blues gave the expected polarograms (see below) and the two- and four-electron compounds were further analyzed. *Anal.* Calcd for $(NH_4)_6H_2[P_2Mo_{18}O_{62}] \cdot 7.6C_4H_8O_2 \cdot 7H_2O$: N, 2.28; P, 1.69; Mo, 46.72; C, 9.91. Found: N, 2.35; P, 1.69; Mo, 46.69; C, 9.88. Calcd for $(NH_4)_6H_4[P_2Mo_{18}O_{62}] \cdot 4.4C_4H_8O_2 \cdot 6H_2O$: N, 2.48; P, 1.83; Mo, 50.94; C, 6.25. Found: N, 2.78; P, 1.88; Mo, 50.02; C, 6.05.

Nitrogen, phosphorus, and arsenic were determined as described previously.[2] Molybdenum was determined with a Jones reductor. In this analysis it was necessary to decompose the heteropoly anion with excess alkali prior to reacidification and reduction. Nitrogen and phosphorus in the heteropoly blues and all carbon analyses were determined commercially (Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.).

Potentiometric Titrations and Polarography.—The reduction titrations and polarography were carried out as described in previous papers.[2,9] The free acids of the heteropoly blues were prepared by ion exchange on a column of Dowex 50-X8 which had been thoroughly rinsed with deoxygenated water. About 0.8 g of heteropoly blue salt was dissolved in 20 ml of deoxygenated water and the solution passed through the column. The combined effluent and washings were diluted to 100 ml. To check that no oxidation had occurred during ion exchange, half of this solution was analyzed by adding excess 0.1 *N* potassium permanganate and back-titrating with iron(II) sulfate. Absence of ammonium ions in this oxidized solution was confirmed by addition of Nessler's reagent. The remainder of the effluent solution was titrated under nitrogen with 0.1 *N* sodium hydroxide, using a glass electrode.

Results

Reduction in Acidic Solution.—Figure 1 shows the results of a potentiometric titration of ammonium 18-molybdodiphosphate with chromium(II) sulfate in 0.5 *M* sulfuric acid. End points corresponding to two- and four-electron reductions are shown. The third end point was not well defined because it appeared at a potential where the platinum indicator electrode is unreliable in the presence of chromium(II) ions.[10] Titration of the corresponding heteropoly arsenate gave very similar results at 0°.[11] The reduction potentials were some 40–50 mv more positive than those of the phosphate.

Polarography with a rotating platinum electrode (rpe) more clearly showed the reduction behavior of these anions. In 1.0 *M* sulfuric acid supporting electrolyte each anion gave a polarogram with three waves of equal height.[12] The half-wave potentials of these waves corresponded closely with the titrimetric reduction potentials. According to plots of log $[i/(i_d - i)]$ *vs.* *E* the waves were essentially reversible in shape for two-electron reductions, but the anodic half-wave potentials measured from polarograms of the reduced species (see below) differed slightly from those of the cathodic waves as shown in Table I. Within the pH range in which the anions are stable (<3.5) the half-wave potentials of the three waves became more negative by about 60 mv/pH unit.

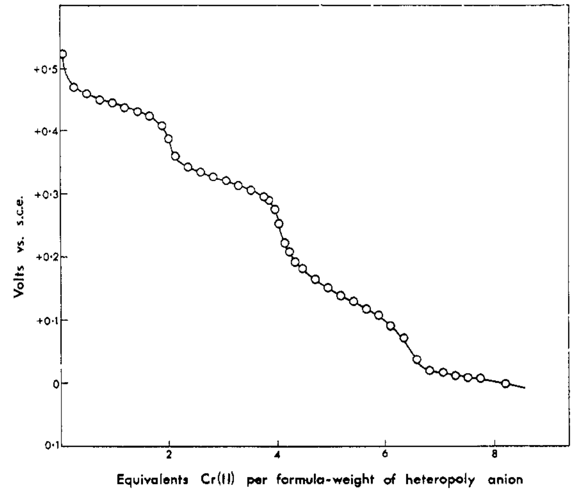

Figure 1.—Potentiometric titration of $(NH_4)_6[P_2Mo_{18}O_{62}]$ with 0.2 *M* $CrSO_4$ in 0.5 *M* H_2SO_4 at 25°. Concentration of heteropoly anion, ~4 × 10^{-3} *M*.

TABLE I

HALF-WAVE POTENTIALS[a] IN 1 *M* SULFURIC ACID AT 25°

$[P_2Mo_{18}O_{62}]^{6-}$		$[As_2Mo_{18}O_{62}]^{6-}$
Cathodic	Anodic	Cathodic
+0.460	+0.480	+0.510
0.350	0.363	0.395
0.183	0.180	0.228

[a] *Vs.* sce.

Isolation of the Reduced Salts.—Crystalline samples of the two-, four-, and six-electron heteropoly phosphate blues were prepared as described above. The extent of reduction of each compound was confirmed polarographically. Analysis of the two- and four-electron blues indicated that they were acid salts, and this was confirmed by potentiometric titrations showing two and four replaceable protons, respectively. Titration of the free acids of the blues, prepared by ion exchange, showed the expected basicities for $H_8[P_2Mo_{18}O_{62}]$ and $H_{10}[P_2Mo_{18}O_{62}]$ but demonstrated that the last two protons in $H_{12}[P_2Mo_{18}O_{62}]$ were not replaced before the anion began to decompose; see Figure 2. Typically, the titration curve of a heteropoly acid shows two end points, the second of which corresponds to the complete degradation of the anion to MoO_4^{2-} or WO_4^{2-}. The pH of the plateau between the first and second end points is a measure of the stability of the anion.[2] The second end point in the titration of oxidized $H_6[P_2Mo_{18}O_{62}]$ occurs after a further 34 equiv of alkali has been added to the neutralized acid,[8] according to the equation

$$[P_2Mo_{18}O_{62}]^{6-} + 34OH^- \longrightarrow 2HPO_4^{2-} + 18MoO_4^{2-} + 16H_2O$$

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(9) M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, **5**, 1249 (1966).

(10) J. J. Lingane, *Anal. Chem.*, **20**, 797 (1948).

(11) The arsenate titrations gave variable results at 25°, presumably because of partial decomposition.[8] Satisfactory polarograms at 25° could be obtained, however.

(12) A fourth wave, twice the height of the first three, appeared just prior to the hydrogen wave. This reduction step has not been investigated further.

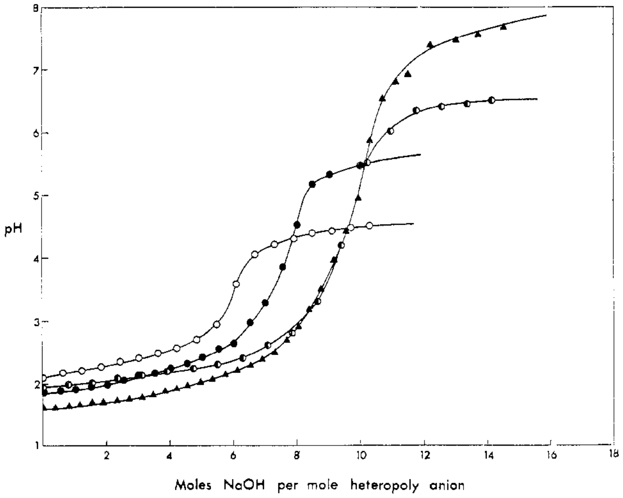

Figure 2.—Titration of oxidized and reduced 18-molybdodiphosphoric acids with 0.1 *N* NaOH at 40°: ○, $H_6[P_2Mo_{18}O_{62}]$; ●, two-electron blue, $H_8[P_2Mo_{18}O_{62}]$; ◐, four-electron blue, $H_{10}[P_2Mo_{18}O_{62}]$; ▲, six-electron blue, $H_{12}[P_2Mo_{18}O_{62}]$. (Similar results were obtained at 0°.)

In the titrations of the heteropoly blues, further addition of alkali after the first end point resulted in an extremely slow reaction, even at 60°, giving a very poorly defined end point. As this second end point was approached, the blue color faded and a brown-green flocculent precipitate formed. In separate experiments, the oxidation state of the molybdenum in the precipitates was found to vary irreproducibly between +4 and +5. The pH of the plateau between the first and second end points increased with the degree of reduction of the heteropoly anion, demonstrating an enhanced stability of the reduced species. Increased stabilities of reduced heteropoly tungstates have already been noted.[2]

Reduction in Neutral and Alkaline Solutions.—Rpe polarograms showing the reduction behavior of the 2:18-molybdate structure up to pH 9 were measured by using solutions of the two-electron heteropoly blue which was more inert than the oxidized anion toward alkaline degradation. Where the potentials permitted, the polarographic behavior was reproduced using the dropping mercury electrode. Typical rpe polarograms are shown in Figure 3 and the variation of the half-wave potentials with pH is shown in Figure 4. Unlike those of the heteropoly tungstates,[2,9] the polarographic waves showed no signs of splitting into one-electron waves at high pH. All three waves moved to more negative potentials as the pH increased. The first wave became independent of pH at pH 4 and the second wave probably was pH independent by pH 8. As the pH increased the heteropoly anions underwent a series of disproportionation–decomposition reactions as was noted for the 2:18-tungstates.[2] These reactions were much more rapid and extensive than those for the tungstates under equivalent conditions.[2] The results at pH 12–13 in Figure 4 have greater uncertainty than the others because of the decomposition and disproportionation of the heteropoly structure in such solutions.

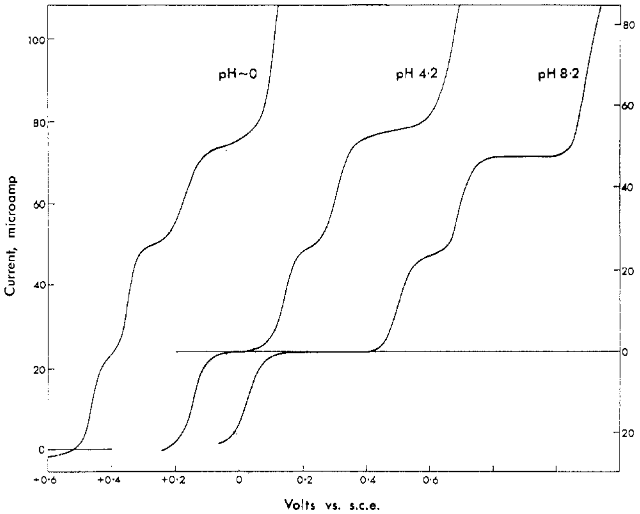

Figure 3.—Rpe polarograms of $(NH_4)_6[P_2Mo_{18}O_{62}]$ in 1.0 *M* H_2SO_4 and of $(NH_4)_6H_2[P_2Mo_{18}O_{62}]$ in acetate and ammonium sulfate buffers at 25°. Concentration of heteropoly anion, 2×10^{-4} *M*.

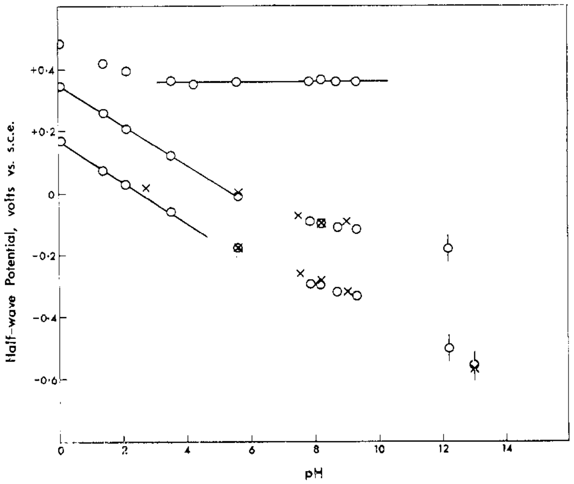

Figure 4.—Variation of half-wave potential with pH for the 18-molybdodiphosphate structure: ○, rpe; ×, dme.

Discussion

The isolation and analysis of reduced heteropoly salts and acids has confirmed polarographic interpretations of the nature of heteropoly blues. The polarographic and analytical data of the present work are in satisfactory agreement, and this study has also demonstrated several differences between isostructural heteropoly molybdates and tungstates.

Figure 4 summarizes the polarographic results and shows that the 2:18-molybdate structure is reduced, initially, in three two-electron steps. Unlike the corresponding tungstates, it has not been possible to discover conditions where intermediate (one-, three-, and five-electron) reduction products are stable. No satisfactory rationalization for this difference between molybdates and tungstates can be offered at present, but it may be noted that similar two-electron reductions have been reported for 12-molybdosilicate.[6]

The variation of the half-wave potentials with pH in solutions of pH <3.5–4 is interpreted, as before,[2,9] in terms of protonation accompanying reduction, *i.e.*

$$[P_2Mo_{18}O_{62}]^{6-} \longrightarrow [H_2P_2Mo_{18}O_{62}]^{6-} \longrightarrow [H_4P_2Mo_{18}O_{62}]^{6-} \longrightarrow [H_6P_2Mo_{18}O_{62}]^{6-}$$

Since direct reduction of the heteropoly anion must be carried out in such solutions to prevent hydrolytic degradation, it is not surprising that the heteropoly blues are isolated as acid salts, as found here and elsewhere.[3] The eventual pH independence of the first and second half-wave potentials at pH 4 and 8–9, respectively, indicates that, under these conditions, the two- and four-electron blues are unprotonated. The third half-wave potential never became pH independent, a result consistent with two nonreplaceable protons in the six-electron blue, $H_{12}P_2Mo_{18}O_{62}$ (see Figure 2).

Apart from the difference in stoichiometry noted above (two- as opposed to one-electron reductions), two other differences between isostructural molybdates and tungstates are apparent if Figure 4 is compared with the corresponding results for the 2:18-tungstates.[13] First, the molybdates are much more readily reduced than are the tungstates, the difference in reduction potential being some 0.4 v. Second, the molybdates are weaker acids than the tungstates; *e.g.*, $[P_2Mo_{.8}O_{62}]^{8-}$ is not unprotonated below pH 4 whereas $[P_2W_{18}O_{62}]^{8-}$ is essentially unprotonated at pH 1. A partial explanation for this difference in acid strengths may lie in the fact that heteropoly molybdates are slightly smaller than the corresponding tungstates,[14] resulting in an increased charge density on the surface of the molybdate anions. In this connection it may be noted that when the compounds were isolated by precipitation with dioxane, the molybdates consistently bound more molecules (seven or eight) of dioxane than did the tungstates (three or four).[15,16]

Like the heteropoly tungstates, the molybdate anions, upon reduction, became more stable toward alkaline degradation. This enhanced stability showed up both in the polarographic and titrimetric measurements. Polarograms of the reduced species in alkaline solutions showed that decomposition of the anions occurred mainly *via* disproportionations, *e.g.*

$$2[P_2Mo_{18}O_{62}]^{8-} \xrightarrow{OH^-} [P_2Mo_{18}O_{62}]^{10-} + MoO_4^{2-},\ HPO_4^{2-},\ \text{etc.}$$

The disproportionations were more rapid and occurred at a lower pH than the corresponding reactions of the tungstates,[2] in keeping with the generally observed greater lability and lower stability of isopoly and heteropoly molybdates. The end products of alkaline degradation of the heteropoly molybdate blues are phosphate and orthomolybdate ions together with an insoluble molybdenum "hydroxide." As noted above, the oxidation state of the molybdenum in the insoluble fraction was found to vary between +4 and +5. Direct titration with alkali could not satisfactorily define the stoichiometry of the over-all reaction because of its extreme slowness, with the resulting possibilities of partial oxidation. However, the results of such titrations suggested that the reaction could probably be described by a combination of

$$[P_2Mo_{18}O_{62}]^{(6+n)-} + (34 - 3n)OH^- \longrightarrow 2HPO_4^{2-} + (18 - n)MoO_4^{2-} + nMo(OH)_5 + (16 - 4n)H_2O$$

and

$$[P_2Mo_{18}O_{62}]^{(6+n)-} + (34 - 2n)OH^- \longrightarrow 2HPO_4^{2-} + [18 - (n/2)]MoO_4^{2-} + (n/2)Mo(OH)_4 + (16 - 2n)H_2O$$

Acknowledgment.—This research has been supported by the Army Research Office, Durham, N. C., through Grant No. DA-ARO(D)-31-124-G512.

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[13] Paper II, Figure 5.

[14] The unit cell dimensions for the molybdate isomorphs of $M_3[PW_{12}O_{40}]\cdot 4H_2O$ (M = Tl(I), K, NH_4) are 1–2.5% smaller than the corresponding tungstates: R. W. G. Wyckoff, "Crystal Structures," Vol. 3, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1965, p 887.

[15] The one exception to this observation, the four-electron molybdate blue with 4.4 molecules of dioxane, had been more severely dried prior to analysis (overnight in a current of nitrogen) than had the other salts.

[16] A referee has pointed out that, according to vibrational spectra, M–O bonds in WO_4^{2-} are stronger than those in MoO_4^{2-}. Such a difference may well be present in the bonding of external oxygen atoms in heteropoly anions and may also help account for the differences in acid strengths.