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Electro-reduction of Phosphotungstic Acids

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Polarography of 3-, 9- and 12-phosphotungstic acids was studied in 0.1 *F* sulfuric acid in order to elucidate their kinetics of formation and to characterize their reduction products. The 12- acid gave three waves with limiting current ratios of 1:1:2 and half-wave potentials of −0.218, −0.448 and −0.695 v. *vs.* S.C.E. The 3- and 9- acids gave single waves at −0.55 and −0.596 v. *vs.* S.C.E., respectively. Controlled potential electrolyses showed that the first reduction of the 12- acid corresponded to two equivalents per mole but secondary reactions prevented analysis of the subsequent waves. Reactions are proposed to account for these results and are substantiated by observation of absorption spectra.

Reduction of phosphotungstic acid to heteropoly blues has been known since 1863 when Marignac observed the reduced complexes,[1] but a polarographic study of the reduction was not made until 1943 when a series of papers by Souchay and coworkers[1-8] was published. Their work was primarily concerned with *p*H of formation of the various complexes, and thus most of the studies were conducted in the *p*H range 2–7.

There are several phosphotungstic acids containing various W:P ratios, but the two most important are the 9- and 12-acids, *i.e.*, containing 9 and 12 atoms of tungsten to one atom of phosphorus. The 12-acid appears to be the more readily obtained form when solutions of sodium tungstate are acidified in the presence of phosphoric acid[9] but both the 9- and 12-acids exist in acid solution.

A study of the polarography of these two heteropoly acids was carried out in strong acid (>0.01 *M*) in the hope that it would be possible to distinguish between them in order to study the species which are present in strong acid-phosphate systems. In addition, a thorough study of the electrode reactions was made. Polarographic results were compared with the results from controlled potential electrolysis to identify the reduced species formed.

Experimental

A Sargent Model XXI Polarograph was used for all polarographic measurements. All runs were made at 25° with a drop time of 3.5 sec. (measured at an applied potential corresponding to a point on the plateau of the wave of interest) and a drop weight of 7.85 mg./drop.

An Analytical Instruments Controlled Potential Electrolysis instrument with coulometer was used for electrolyses of phosphotungstic acids. A mercury pool cathode was used with a platinum wire anode in a separate compartment. Due to the insolubility of the potassium salt of 12-phosphotungstic acid, a sulfuric acid bridge was used to connect the saturated calomel reference electrode to the sample solution. In most cases 100 ml. of 0.1 *M* tungsten was electrolyzed, except more dilute solutions were used when absorption spectra were to be taken.

Mallinckrodt 12-phosphotungstic acid (12-PTA) was used for preparing known solutions of the 12- acid. The solid was found to contain 69.7% tungsten. If one assumes 12 tungsten atoms per mole, this indicates a molecular weight of 3160 corresponding to the acid $H_3PW_{12}O_{40}\cdot 15H_2O$.

The 9-phosphotungstic acid was prepared by dissolving 112 g. of $Na_2WO_4\cdot 2H_2O$ in 350 ml. of hot water, adding 150 ml. of 85% phosphoric acid slowly and refluxing the mixture overnight. The ammonium salt was precipitated by adding 100 g. of ammonium chloride. After filtering, the salt was redissolved in 250 ml. of water and precipitated with 50 g. of ammonium chloride. Bromine water was added to oxidize the small amount of reduced tungsten. This recrystallization procedure was repeated four times. The ammonium salt then was dissolved in 300 ml. of 6 *F* hydrochloric acid and extracted with 100 ml. of ethyl ether. A yellow etherate formed the bottom layer which was drawn off and placed in a vacuum desiccator to dry. The yellow solid was found to contain 87.4% WO_3 and 3.01% P_2O_5, a mole ratio of 8.9:1.

Solutions containing 3-phosphotungstic acid were prepared by acidifying solutions of sodium tungstate in the presence of a large excess of potassium phosphate at room temperature. These solutions were stable for days at room temperature but the 3-acid was converted to the 12- acid form on boiling.

Tungsten analyses were performed by the cinchonine method while phosphate analyses were performed by precipitating magnesium ammonium phosphate and igniting to magnesium pyrophosphate.

All other reagents were of commercial analytical reagent grade.

The visible spectra of solutions of the reduced heteropoly acids were measured on a Beckman recording spectrophotometer. The 1 cm. cells were filled under nitrogen and the stoppers were sealed with silicone grease.

Results

Polarographic Reduction of Pure Heteropoly Acids.—Figure 1 shows the reduction of 12-phosphotungstic acid (12-PTA) over wide ranges of *p*H. The higher *p*H's have been studied by Souchay[1-8] and were not studied in this investigation. At *p*H 1, three distinct waves were observed. The heights of these waves were in the ratio of 1:1:2. The half-wave potentials of the three waves were −0.218, −0.448 and −0.695 v. *vs.* s.c.e. The diffusion currents for 0.0100 *M* tungsten (0.00083 *M* 12-PTA) were 2.14, 2.16 and 4.50 μamp. The height of the third wave was difficult to measure, see Fig. 1, because the current due to hydrogen reduction could not be corrected for by a blank measurement. This was due to an induced reduction of hydrogen ions by the 12-PTA, *i.e.*, it lowered the over-potential on mercury causing higher currents than the sum of tungsten reduction and a blank reading. Thus, 4.50 μamp. was probably somewhat high making the ratio very nearly 1:1:2.

The waves were shown to be diffusion controlled by observing the increase in current with increase in temperature and decrease in drop time. The current increased about 1%/degree and was proportional to (drop time)$^{-1/2}$, indicating that the waves were diffusion controlled. Assuming a diffusion coefficient equal to that found for ferric citrate ($i_d/Cm^{2/3}t^{1/6} = 0.9$),[10] one calculates for the first

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[1] P. Souchay, 1st International Polarographic Congress, Prague, 1951; Proceedings, **1**, 327 (1951).

[2] P. Souchay, *Ann. Chim.*, ser. 11, **20**, 73, 96 (1945).

[3] P. Souchay and J. Faucherre, *Bull. soc. chim., France*, **18**, 355 (1951).

[4] P. Souchay and A. Tchakirrian, *Ann. Chim.*, ser. 12, **1**, 249 (1946).

[5] A. Tchakirrian and P. Souchay, *ibid.*, ser. 12, **1**, 232 (1946).

[6] P. Souchay, *ibid.*, ser. 11, **18**, 73, 169 (1943).

[7] P. Souchay, *ibid.*, ser. 11, **19**, 102 (1944).

[8] P. Souchay, *ibid.*, ser. 12, **2**, 203 (1947).

[9] H. Wu, *J. Biol. Chem.*, **43**, 189 (1920).

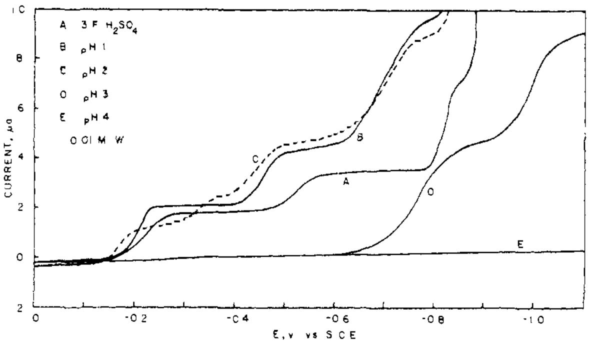

Fig. 1.—Polarography of 12-phosphotungstic acid.

reduction wave ($i_d/Cm^{2/3}t^{1/6} = 1.3$, where C was the 12-PTA concentration) between one and two tungstens per molecule reduced to tungsten (V). Since the diffusion coefficient of the larger heteropoly ion probably was smaller than that of the iron citrate complex, a reduction of at least two tungstens per molecule was indicated.

Plots of E *vs.* log $(i/i_d - i)$ showed the waves to be irreversible. The slope of the first reduction step was 70 mv. until near the end of the reduction when the slope increased markedly. The second wave had a slope of 67 mv. (except near the beginning where it, too, was much steeper), while the third wave had a slope of 35 mv.

9-PTA gave a single reduction wave, Fig. 2, with a half-wave potential of −0.596 v. *vs.* s.c.e. and a diffusion constant, $i_d/Cm^{2/3}t^{1/6}$ of 9.6 (where C was the concentration of the 9-PTA which was dimerized to give $H_6P_2W_{18}O_{62}$). This indicates the reduction of at least ten of the eighteen tungsten atoms per molecule if one compares with the iron citrate complex diffusion constant. Again the wave was irreversible (slope of 137 mv.) and appeared to be composed of more than one wave, because the curve was not smooth.

Thus, it should be possible to analyze a mixture of the 9- acid and the 12- acid by measuring the heights of the first and total waves. The first wave (at −0.218 v.) should determine the amount of 12- acid present while measurement of the total diffusion current (composed of the three waves of the 12- acid and the single reduction wave of the 9- acid, since the 9- acid half-wave potential was too close to the second 12- acid wave for good separation) should yield the sum of the 9- and the 12- acids.

Known mixtures of 9-PTA and 12-PTA were prepared and analyzed polarographically. Although solutions of the pure acids were stable toward boiling and toward standing for weeks, the wave at −0.2 v. for a mixture of 9- and 12-PTA was much higher than predicted from 12-PTA reduction alone. If the current due to 12- acid reduction was subtracted, the remaining current was directly proportional to the 9- acid content but the proportionality constant varied with the 12- acid concentration. Thus, the current due to 9- acid was catalytic, depending on both the 12- and 9- acid concentrations. For example, in a solution containing 0.01 M tungsten as 9-PTA plus 0.01 M tungsten as 12-PTA the current at −0.3 v. was 1.34 μamp. (compared to 2.14 μamp. expected for 12-PTA reduction alone), while if the 12-PTA concentration was decreased to 0.001M, the current due to reduction of 9-PTA dropped to 0.87 μamp. Thus, mixtures of 9- and 12-PTA cannot be analyzed polarographically by this seemingly simple method.

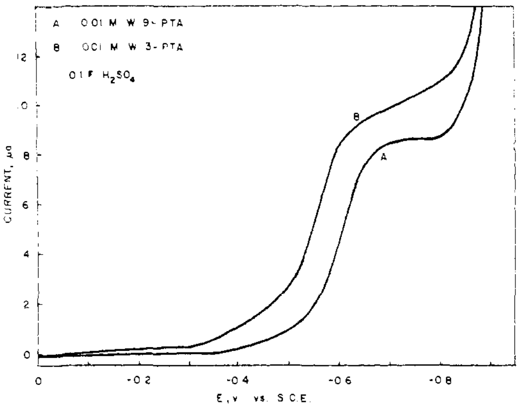

Fig. 2.—Polarography of 9- and 3-phosphotungstic acid.

Polarograhic Reduction of Acidified Phosphate–Tungstate Systems.—When solutions containing phosphate and tungstate ions were acidified, heteropoly complexes were formed. It was hoped that the complexes could be identified by observing their polarographic reduction.

A polarogram of a solution containing 0.01 M sodium tungstate, 0.001 M sodium phosphate and acidified to *p*H 1 showed three distinct waves. The half-wave potentials were −0.22, −0.49 and −0.69 v. *vs.* s.c.e.; the first and third corresponding very closely with those of 12-PTA. The second wave was higher than the first and had a half-wave potential about 40 mv. more negative than 12-PTA. The limiting current of the first wave varied with the order and rate of addition of reagents and as it decreased the limiting current of the second wave increased. Also, the half-wave potential of the second wave became more positive when the second wave decreased. Boiling the solution for 15 minutes converted all of the tungsten to the 12- acid form, *i.e.*, the potential of the second wave became −0.45 v. and its height equaled that of the first wave. Since 9-PTA solutions were stable toward boiling, these results indicate the existence of a third heteropoly acid giving a wave near −0.5 v.

Acidification of solutions containing 0.3 F sodium phosphate and 0.01 M sodium tungstate converted nearly all (85–100%) of the tungsten to this third heteropoly complex giving a single wave at −0.55 v. If sulfuric acid was added to a solution containing 0.03 M sodium tungstate and 0.9 F sodium phosphate and then diluted three-fold, only the third heteropoly complex was observed.

The reduction behavior of this heteropoly acid seemed to be similar to 9-PTA, but the half-wave potential was 50 mv. more positive, the diffusion current was somewhat higher (12.2 μamp. *vs.* 8.8 μamp. for 0.01 M W), and no catalytic reduction by 12-PTA at −0.23 v. was apparent. It was found that at room temperature this heteropoly complex was stable for days but boiling for 1 hr. converted it completely to the 12- acid form.

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(10) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishing Co., New York, N. Y., 1952, p. 288.

The composition of the unknown acid was determined by precipitating its cesium salt from a solution known to contain no 12-PTA and the mixture was kept in ice to prevent any conversion to the 12-acid form. It was found that a large amount of cesium had to be added to 0.5 *F* W in order to form the cesium salt which, similar to the 9- acid salt, was fairly soluble. The 12- acid salt, on the other hand, was insoluble. Tungsten and phosphorus analyses gave values of 49.2 and 2.83%, respectively corresponding to a mole ratio of 2.97:1, and indicating that this was 3-PTA.

Thus, solutions containing little excess phosphate ion under weakly acid conditions formed predominantly 12-PTA, while strongly acid solutions containing large excesses of phosphate ion favored formation of 3-PTA. Quantitative results were not obtained because the percentage of 12- acid varied with the rate and order of addition of reagents.

9-PTA could also be converted to a mixture of the 3- and 12- acids if a solution of 9-PTA was first made basic and then acidified. When this was done at room temperature, 59% of the tungsten was converted to 12- acid form (the remainder was 3-PTA) and boiling for five minutes after acidification increased this to 69% 12-PTA.

Controlled Potential Electrolysis.—Controlled potential electrolysis provides a direct method for determining the number of electrons involved in an electrode reaction. In order to determine the number of tungsten atoms reduced in the heteropoly complex at the various reduction steps observed polarographically, solutions of 12-PTA in 0.1 *F* sulfuric acid were electrolyzed at −0.30, −0.56 and −0.76 v. *vs.* s.c.e. (potentials corresponding to the diffusion plateaus of the three waves). At −0.30 v. electrolysis stopped when exactly two tungstens per heteropoly ion were reduced to tungsten (V). Both the coulometer readings and titration of the reduced solutions with potassium permanganate yielded the same results. At −0.56 v. electrolysis stopped shortly after the reduction of the first two tungsten atoms (2.2–2.5 electrons per mole) contrary to expectations from the polarographic results which predicted a 4 electron reduction. At 0.76 v. the electrolysis was never completed, and the current usually increased with time (after dropping to a minimum) indicating that hydrogen ion reduction was taking place. The electrolyses at −0.76 v. were stopped after 2 or 2.5 hr. and the reduced solutions were titrated with potassium permanganate. Approximately five tungsten atoms were reduced per heteropoly complex and no significant difference was observed between the titration figures, obtained after 2 hr. of electrolysis and those after 2.5 hr.

Reduction of 9-PTA at −0.75 v. *vs.* s.c.e. indicated a reduction of 13 tungsten atoms per molecule ($H_6P_2W_{18}O_{62}$). The coulometer readings (13.3) were slightly higher than the titration figures (13.1), indicating that little hydrogen reduction took place.

Known mixtures of 9- and 12-PTA were reduced at −0.30 v. The number of coulombs due to 12-PTA reduction (*i.e.*, two equivalents per mole) was subtracted, and the difference was attributed to 9-PTA reduction. The amount of reduction averaged one tungsten (V) per mole of $H_6P_2W_{18}O_{62}$ when solutions containing 0.1 *M* tungsten of 9-PTA and 0.01 *M* tungsten of 12-PTA were electrolyzed.

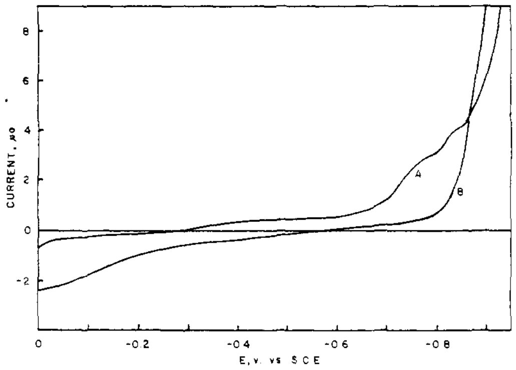

Fig. 3.—Polarography of reduced 12-PTA: A, 0.0083 *M* 12-PTA in 0.1 *M* H_2SO_4 reduced at −0.30 v.; B, 0.0083 *M* 12-PTA in 0.1 *M* H_2SO_4 reduced at −0.76 v.

Polarograms were run of samples of 12-PTA which had been reduced by controlled potential electrolysis at −0.3 v. *vs.* s.c.e. If this were a reversible reduction, the first wave should be anodic with a half-wave potential of −0.2 v. and the other two waves cathodic as before. However, as shown in Fig. 3 the reduced heteropoly acid was irreversibly oxidized at −0.2 v. and no further reduction took place at the potential expected for the second wave. An irreversible reduction (the wave never reached a diffusion plateau) did occur at −0.7 v., the potential expected for the third wave.

Thus, it was evident that reduction at −0.3 v. *vs.* s.c.e. yielded a stable species which was neither reduced nor oxidized readily, and this fact explains why little further reduction was observed at −0.56 v. using controlled potential electrolysis.

Polarograms of acidic 12-PTA solutions previously reduced by controlled potential electrolysis at −0.76 v. (see Fig. 3) showed only an irreversible oxidation at −0.2 v. and a cathodic hydrogen wave. Solutions reduced at −0.76 v. were greenish-black (due to suspended solids since the color intensity could be decreased by filtration) while those reduced at −0.3 v. had a deep blue color with an absorption peak at 760 mμ.

Discussion

It was evident from the polarographic and controlled potential electrolysis results that the first reduction step of 12-PTA was the reduction of two tungsten atoms to tungsten(V). Polarographic results indicated that 12-PTA could also be directly reduced (at −0.56 v. *vs.* s.c.e.) to another species containing four tungsten(V), or (at −0.76 v. *vs.* s.c.e.) to a species containing eight tungsten (V). These reactions may be formulated (neglecting any charge neutralization by hydrogen ion)

$$PW_{12}O_{40}^{-3} + 2\,e^- \xrightarrow{-0.3\text{ v.}} PW_{12}O_{40}^{-5} \qquad (1)$$

$$PW_{12}O_{40}^{-3} + 4\,e^- \xrightarrow{-0.56\text{ v.}} PW_{12}O_{40}^{-7} \qquad (2)$$

$$PW_{12}O_{40}^{-3} + 8\,e^- \xrightarrow{-0.76\ \text{v.}} PW_{12}O_{40}^{-11} \quad (3)$$

The first reduction product, $PW_{12}O_{40}^{-5}$, was stable and was neither reduced nor oxidized easily polarographically or by controlled potential electrolysis and had a characteristic deep blue color. This first product could be reduced further at -0.76 v. although the reduction did not go to completion, and the final mixture may have been $PW_{12}O_{40}^{-5}$ and $PW_{12}O_{40}^{-11}$ or $PW_{12}O_{40}^{-7}$ and $PW_{12}O_{40}^{-11}$.

Polarographically, at *p*H 2 (see Fig. 1), the first two-electron reduction was split into two equal waves indicating the possibility of the reduction product $PW_{12}O_{40}^{-4}$ which corresponds to a one electron reduction. This ion may be an intermediate in the catalytic reduction of 9-PTA by 12-PTA (as shown by the controlled potential electrolysis results) according to the reaction

$$PW_{12}O_{40}^{-5} + P_2W_{18}O_{62}^{-6} \longrightarrow PW_{12}O_{40}^{-4} + P_2W_{18}O_{62}^{-7} \quad (4)$$

explaining why the 9- acid could be reduced one equivalent per mole at -0.23 v. in the presence of 12-PTA. $PW_{12}O_{40}^{-4}$ was immediately reduced at the electrode to the more stable $PW_{12}O_{40}^{-5}$ or oxidized by another $P_2W_{18}O_{62}^{-6}$ to $PW_{12}O_{40}^{-3}$.

The controlled potential electrolyses also confirmed the occurrence of reaction 1 at -0.3 v., but it was odd that little further reduction occurred at -0.56 v., since the polarographic results must correspond to the actual electrode reactions taking place at the mercury pool cathode. An explanation for the discrepancy in the results lies in the possible reactions

$$PW_{12}O_{40}^{-7}\ \text{(produced at } -0.56\ \text{v.)} + PW_{12}O_{40}^{-3} \longrightarrow 2PW_{12}O_{40}^{-5} \quad (5)$$

$$PW_{12}O_{40}^{-11}\ \text{(produced at } -0.76\ \text{v.)} + 3PW_{12}O_{40}^{-3} \longrightarrow 4PW_{12}O_{40}^{-5} \quad (6)$$

Thus, the first two faradays of electricity per mole produced $PW_{12}O_{40}^{-5}$ even though the products of the electrode reactions were the more reduced compounds. Only at -0.76 v. could $PW_{12}O_{40}^{-5}$ be reduced further. The electrode reactions, 2 and 3, were observed polarographically, since reactions 5 and 6 did not occur instantaneously and were slower than the drop time of the dropping mercury electrode.

This hypothesis was substantiated experimentally by reducing 12-PTA at -0.76 v. and then adding de-aerated 12-PTA to the reduced solution. The greenish solution turned blue in a few minutes, showing the formation of $PW_{12}O_{40}^{-5}$ according to reaction 6.

A situation similar to the reduction of two tungsten atoms to tungsten(V) occurs if two of the tungsten atoms in 12-PTA are replaced with two atoms of an element in the plus five oxidation state such as vanadium. Russian workers[11,12] have prepared such vanadium compounds, and were not able to isolate, even when using excess vanadium, compounds containing more than two vanadium atoms per mole. This supports our hypothesis that the most stable reduced 12-heteropoly acids contain only two "poly" atoms in the plus five oxidation state.

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(11) A. I. Kokorin, *J. Gen. Chem.* (*U.S.S.R.*), **27**, 615 (1957).

(12) Z. F. Shakhova and R. K. Motorkina, *ibid.*, **26**, 2969 (1956).