

3-몰리브도-9-텅스토인산, 6-몰리브도-6-텅스토인산 및 이들의 환원 생성물

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3-Molybdo-9-tungstophosphoric Acid, 6-Molybdo-6-tungstophosphoric Acid and Their Reduction Products

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요 약. 3-몰리브도-9-텅스토인산, 6-몰리브도-6-텅스토인산과 이들의 1電子 및 2電子 환원 생성물을 합성하였다. 적외선 스펙트럼들로부터 이들이 모두 케긴 구조를 가짐을 확인하였다. 환원 생성물의 폴라로그래프와 전자흡수 스펙트럼들을 보고하였으며, 이들은 첨가된 각 전자가 한 몰리브덴 원자에 국소화되어 있는 모형과 일치한다.

Abstract. 3-Molybdo-9-tungstophosphoric acid, 6-molybdo-6-tungstophosphoric acid and their one-electron and two-electron reduction products have been synthesized. Infrared spectra show that all of them have Keggin structure. Polarograms and optical spectra of the reduced species are reported. Both data indicate that each additional electron is localized on a molybdenum atom.

Introduction

The 12-tungstophosphate and 12-molybdophosphate anions, $PW_{12}O_{40}^{3-}$ and $PMo_{12}O_{40}^{3-}$ are known to have the so-called Keggin structure.^{1,2} Since tungsten and molybdenum are quite similar chemically, it is expected that syntheses of Keggin-structure anions containing both tungsten and molybdenum atoms are possible. In fact, it has been claimed that a series of anions corresponding to the compositions $PMo_nW_{12-n}O_{40}^{3-}$ ($n=0\sim 12$) can be synthesized.³

As part of our study on heteropoly anions, we have synthesized $H_3PMo_3W_9O_{40}$, $H_3PMo_6W_6O_{40}$

(these two compounds are designated as (A) and (B), respectively below), and their reduction products and studied spectroscopic and electrochemical properties of these compounds.

Experimental Section

3-Molybdo-9-tungstophosphoric Acid. To a solution of 0.30 mole of $Na_2WO_4 \cdot 2H_2O$ and 0.10 mole of $Na_2MoO_4 \cdot 2H_2O$ in 700 ml of water were added 50 ml of 85% H_3PO_4 and slowly 100 ml of concentrated HCl. The mixture was kept at room temperature for a day, and then the heteropoly acid was extracted with ethyl ether. After separation, a stream of air was passed

through the etherate to free it of ether. The yellow solid that remained was recrystallized in 1 N HCl or 1 N H₂SO₄. Large yellow crystals in the form of hexagonal plates were obtained. Sometimes thin needles were also obtained from the same solution. Only the hexagonal crystals were used for this study.

Hydrogen was determined by titration with NaOH in methanol. Phosphorus was determined as Mg₂P₂O₇. Molybdenum was determined by a colorimetric method based on the colored complex which molybdate and hydrogen peroxide form in the alkaline medium.^{4,5} Water was determined by heating to 200 °C. Calcd. for H₃PMo₃W₆O₄₀·10H₂O: P, 1.1; Mo, 10.3; H₂O, 6.4. Found: P, 1.1; Mo, 10.6; H₂O, 6.4.

6-Molybdo-6-tungstophosphoric Acid. This was synthesized and analyzed according to similar methods as the above. Calcd. for H₃PMo₆W₆O₄₀·10H₂O: P 1.24; Mo 22.7; H₂O 7.1. Found: P 1.27; Mo 22; H₂O 7.2.

Reduction of the Heteropoly. Acids Solutions of heteropoly acids in 1 N H₂SO₄ or 1 N HCl were shaken with mercury metal. When the resulting violet solutions were evaporated, dark violet crystals were obtained. The heteropoly acids were also reduced by hydrazine in 1 N HCl, and dark violet or blue crystals were isolated by evaporation. Some reduction products were also produced by means of controlled-potential electrolysis.

Potentiometric Titrations. Potentiometric titrations were performed with a Corning Model 12 pH meter equipped with a saturated calomel electrode(SCE) and a glass electrode.

Polarography. Polarograms were recorded on a Heath-kit Model EUA-19-2. The number of electrons added was determined by the use of Ilkovic equation, $i_d = 607nCD^{\frac{1}{2}}m^{\frac{3}{2}}t^{\frac{1}{2}}$. The diffusion coefficient(D) used was 3.4×10^{-6} cm²/sec.⁶

Spectra. The uv-visible spectra were recorded

on a Beckman DK-2 spectrometer and the infrared spectra on a Beckman IR-8 and IR-33 spectrometers.

Results and Discussion

Oxidized Species. The first question is whether we have prepared Keggin-structure anions or Dawson-type⁷ anions (e.g. P₂W₁₈O₆₂⁶⁻). This could be answered by comparing the infrared spectra of our samples with those^{8,9} of PW₁₂O₄₀³⁻ and P₂W₁₈O₆₂⁶⁻ (See Fig. 1). The spectra of our samples lie between those of PW₁₂O₄₀³⁻ and PMo₁₂O₄₀³⁻ indicating that ours have Keggin structure.

Since Folin and Denis¹⁰ obtained Dawson-type heteropoly acids starting from the same reactants as ours, the temperature of the reaction mixture seems to be crucial in determining the products. Thus Dawson-type anions are major products

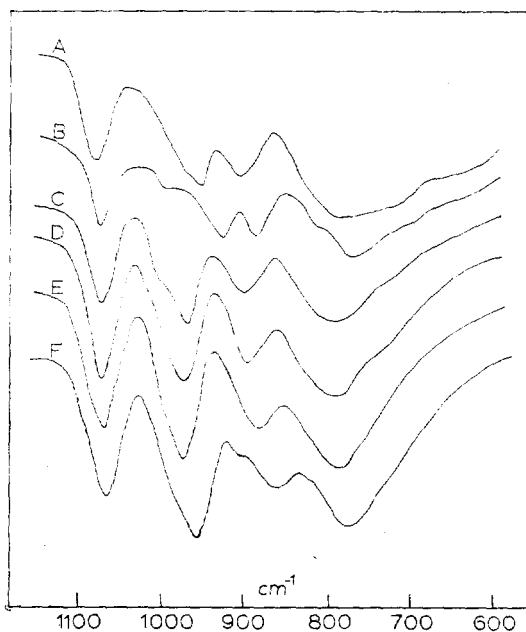
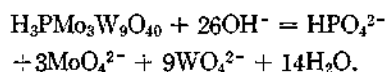


Fig. 1. Comparison of infrared spectra. (A) P₂W₁₈O₆₂⁶⁻, (B) P₂Mo₁₈O₆₂⁶⁻, (C) PW₁₂O₄₀³⁻, (D) PMo₃W₆O₄₀³⁻, (E) PMo₆W₆O₄₀³⁻, (F) PMo₁₂O₄₀³⁻.

when refluxed at a high temperature, while Keggin-type anions are formed at room temperature.

The potentiometric titration data for (A) are shown in Fig. 2. The first point of inflection observed for (A) in methanol corresponds to three equivalents of bases added, showing that the acid has three acidic protons. However, this point is not clearly defined in the aqueous solution probably due to partial degradation of the anion. The next point of inflection for (A) in water occurs at $\text{pH} \sim 8.5$ corresponding to 26 equivalents of bases added. This may be attributed to the complete degradation of the anion, which can be written



This point could not be observed in methanol because of precipitation in the alkaline medium. Similar results have been obtained for (B).

Reduced Species. Both (A) and (B) in 1 *N* H_2SO_4 are reduced by metallic mercury. Dark violet crystals obtained by evaporating the solutions showed the same infrared spectra as those

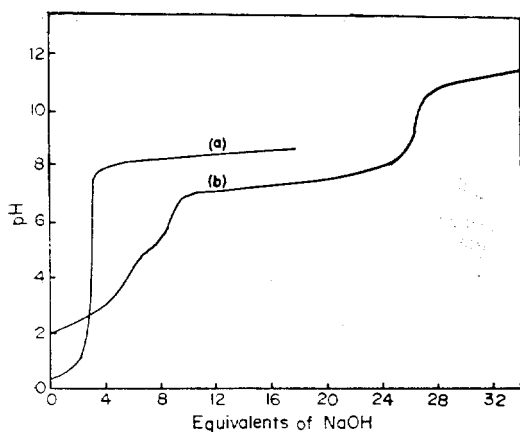


Fig. 2. Potentiometric titrations of $\text{H}_3\text{PMo}_3\text{W}_9\text{O}_{40}$ with NaOH in (a) methanol and (b) water. The absolute pH values for methanol solutions have no meaning, since the pH meter was standardized with aqueous buffer solutions.

for the oxidized species. This indicates that the anions are reduced without any significant structural changes. Photometric titrations with potassium permanganate revealed that both species had accepted one equivalent of electrons each. This reduction state was also checked by potentiometric titrations which showed that the products are tetraprotonic acids. (These one-electron reduction products are designated as (A1) and (B1), respectively.)

When (A) and (B) in 1 *N* HCl were reduced by hydrazine, more than one equivalent of electrons were added to the anions. The isolated crystals were found to be the two-electron reduction products on the basis of photometric titrations using potassium permanganate. (These two-electron reduction products are designated as (A2) and (B2), respectively.)

Other reduction states have been obtained by reducing with stannous chloride, but these states have not been characterized well.

Polarography. Polarograms of (A1) and (B1) in 1 *M* H_2SO_4 are shown in Fig. 3, and the data for the first waves summarized in Table 1. It is noticed that the number of added electrons for each species is the same as the number of molybdenum atoms minus one. This is explained

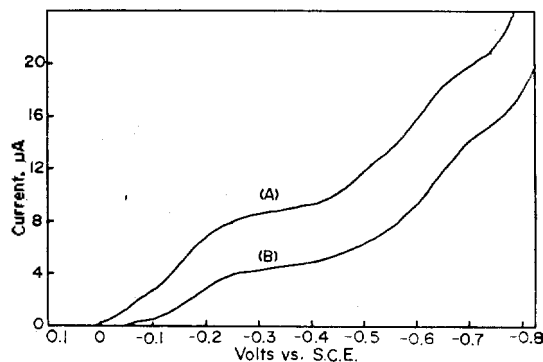


Fig. 3. Dropping mercury electrode polarograms of (A) $\text{H}_4\text{PMo(V)Mo}_5\text{W}_9\text{O}_{40}$ and (B) $\text{H}_4\text{PMo(V)Mo}_2\text{W}_9\text{O}_{40}$ in 1.0 *M* H_2SO_4 . Concentrations of heteropoly acids, 0.5 mM.

most easily by assuming that Mo(VI)'s are reduced to Mo(V)'s before the tungsten atoms. If the electrons entered multicenter molecular orbitals, this kind of behavior would not be expected. The second waves are attributed to the reduction of the tungsten atoms and further reduction of the molybdenum atoms.

Polarography of (B) at the rotating platinum electrode showed one-electron reduction wave at +0.55 V, which is assigned to the reduction of a molybdenum atom. This assignment was confirmed by a controlled potential electrolysis. It is interesting to note that this potential is quite similar to the corresponding value¹¹ of $\text{PMoW}_{11}\text{O}_{40}^{3-}$, +0.52 V, indicating that the reduction potential is not sensitive to the number of molybdenum atoms in the anion.

Optical Spectra. Both (A) and (B) show only one band at 36 kK in their optical spectra. But all reduced species absorb strongly in the visible region. Their spectra are shown in Fig. 4 and the spectral data summarized in Table 2. The spectrum of (A1) is quite similar to that¹¹ of $\text{PMo(V)W}_{11}\text{O}_{40}^{4-}$. Since there is clear esr evidence¹² that the additional electron is localized mainly on the molybdenum atom for this anion,

it is certain that the electron in (A1) is also localized on one of the molybdenum atoms. Then the band at 15 kK may be attributed to a charge transfer transition corresponding to $\text{Mo(V)} \rightarrow \text{W(VI)}$.¹² A similar transition corresponding to $\text{Mo(V)} \rightarrow \text{Mo(VI)}$ is expected to occur at $9 \pm 2 \text{ kK}$,¹² if Mo(V) has a neighboring Mo(VI). Absorption in this region is small for (A1), but comparatively large for (B1), the spectrum of which is otherwise quite similar to that of (A1). This is exactly what we expect, for Mo(V) has a better chance of having adjacent Mo's in (B1) than in (A1). But this cannot distinguish whether molybdenum atoms are distributed randomly

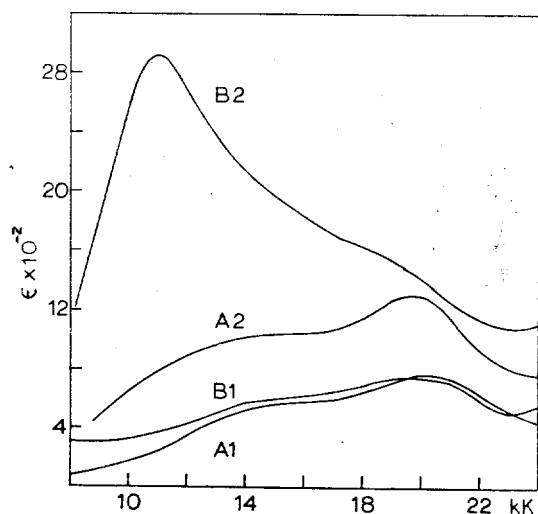


Fig. 4. Absorption spectra of (A1) $\text{H}_4\text{PMo(V)Mo}_2\text{W}_9\text{O}_{40}$ and (B1) $\text{H}_4\text{PMo(V)Mo}_5\text{W}_6\text{O}_{40}$ in 1 M H_2SO_4 and (A2) $\text{H}_5\text{PMo}_2(\text{V})\text{Mo}_5\text{W}_6\text{O}_{40}$ and (B2) $\text{H}_5\text{PMo}_2(\text{V})\text{Mo}_6\text{W}_6\text{O}_{40}$ in 1 M HCl.

Table 1. Formal reduction potentials in 1.0 M H_2SO_4

Anion	E , V vs. sce	No. of electrons
$\text{PMo}_3\text{W}_9\text{O}_{40}^{4-}$	-0.17	2
$\text{PMo}_6\text{W}_6\text{O}_{40}^{4-}$	-0.16	5

Table 2. Spectral data for reduced species^a

Compound	Position ^b (intensity ^c) of maxima
$\text{H}_4\text{PMo}_3\text{W}_9\text{O}_{40}$ (A1)	15(560) sh ^d , 20.1(760)
$\text{H}_5\text{PMo}_3\text{W}_9\text{O}_{40}$ (A2)	15(1,050) sh, 19.8(1,300)
$\text{H}_4\text{PMo}_6\text{W}_6\text{O}_{40}$ (B1)	15(600) sh, 20(740)
$\text{H}_5\text{PMo}_6\text{W}_6\text{O}_{40}$ (B2)	11.1(2,900), 18.5(1,600) sh

^a(A1) and (B1) in 1 M H_2SO_4 ; (A2) and (B2) in 1 M HCl.

^bkK; ^cMolar absorptivity; ^dshoulder

among the 12 sites or one particular distribution is preferred.

The spectrum of the two-electron species (A2) is approximately a superposition of two one-electron spectra, indicating that the interaction between the two Mo(V) sites is small. However, the spectrum of (B2) is quite different from the others, the most intense band occurring at 11 kK. Again this band may originate in the Mo(V) \rightarrow Mo(VI) charge transfer. If true, this implies that the first electron is trapped preferentially by the molybdenum atom with the maximum number of adjacent tungsten atoms and that the second electron occupies a molybdenum site with more adjacent molybdenum atoms. In this case the second electron is more probable than the first electron to undergo the Mo(V) \rightarrow Mo(VI) transition.

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References

1. J. F. Keggin, *Proc. Roy. Soc. (London)*, **A 144**, 75(1934).
2. A. J. Bradley and J. W. Illingworth, *ibid.*, **A 157**, 113(1936).
3. A. I. Kokorin and N. A. Polotebnova, *Zh. Obshch. Khim.*, **26**, 3(1956).
4. A. D. Funck, *Z. Anal. Chem.*, **68**, 283(1926).
5. W. P. Griffith, *J. Chem. Soc.*, 5345(1963).
6. M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, **5**, 1249(1966).
7. B. Dawson, *Acta Cryst.*, **6**, 113(1953).
8. G. Lange, H. Hahn and K. Dehnicke, *Z. Naturforsch.*, **24b**, 1498(1969).
9. E. Papaconstantinou, Ph. D. Thesis, Georgetown University, Washington, D. C., U. S. A., 1970.
10. O. Folin and W. Denis, *J. Biol. Chem.*, **43**, 189(1920).
11. J. J. Altenau, M. S. Thesis, Georgetown University, Washington, D. C., U. S. A. 1970.
12. H. So and M. T. Pope, *Inorg. Chem.*, **11**, 1441(1972).