CHEMISTRY LETTERS, pp. 185-188, 1989.

Isolation and Characterization of Some Oxygen-deficient Reduced Forms of Dodecamolybdophosphate Anion Salts

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By a reaction of $[n\text{-Bu}_4\text{N}]_3[\text{PMo(VI)}_{12}\text{O}_{40}]$ with PPh_3 in acetonitrile, reduced forms, $[n\text{-Bu}_4\text{N}]_3[\text{PMo(VI)}_{12-2x}\text{Mo(V)}_{2x}\text{O}_{40-x}]$ (x= 1, 2, 3), were isolated and characterized by X-ray diffractiometry, IR, and X-ray photoelectron spectroscopies. No decomposition took place on the anion structure of the reduced compounds, although three of the bridging oxygen atoms in the Mo-O-Mo bonds were eliminated.

Dodecamolybdophosphates are known to be practical oxidation catalysts and their reduced forms have systematically been studied in relation to their catalytic functions.[1)] Behavior of the lattice oxygen atoms of the polyanion has attracted much attention in its redox processes.[2-4)] Since the polyanion can be characterized as a structurally well-defined oxomolybdenum complex, it is of interest to investigate stoichiometric reduction of the dodecamolybdophosphate anion in a homogeneous system, which is accompanied by the elimination of the lattice oxygen atom from the polyanion. In the previous work,[5)] it was demonstrated that the dodecamolybdophosphate anion homogeneously undergoes two-electron reduction by PPh_3 in acetonitrile (MeCN), followed by the transfer of the bridging oxygen atom of the anion to PPh_3. The present study deals with the isolation and characterization of reduced forms of tetrabutylammonium dodecamolybdophosphate(3-), $[n\text{-Bu}_4\text{N}]_3[\text{PMo(VI)}_{12}\text{O}_{40}]$ (abbreviated as $\text{PMo}_{12}\text{O}_{40}$), obtained by the above-mentioned reaction.

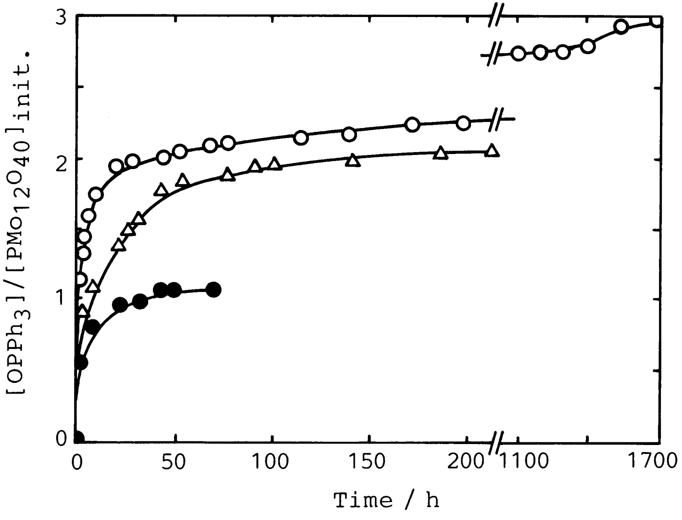

Fig. 1. Time course of the concentration of OPPh_3 formed in the reaction of $\text{PMo}_{12}\text{O}_{40}$ with PPh_3 in MeCN. ($[\text{PMo}_{12}\text{O}_{40}]_{\text{init.}}$; initial concentration of $\text{PMo}_{12}\text{O}_{40}$ (7.8×10^{-3} mol dm^{-3}), initial $[\text{PMo}_{12}\text{O}_{40}]/[\text{PPh}_3]$ molar ratio; 1:1(●), 1:2(△), and 1:3(○))

The sample $\text{PMo}_{12}\text{O}_{40}$ was prepared as described previously.[5)] A MeCN solution containing $\text{PMo}_{12}\text{O}_{40}$ and PPh_3 in the molar ratio of 1:1, 1:2, or 1:3 was refluxed under N_2 atmosphere. Each reaction was monitored by the amount of OPPh_3 formed in the solution. Figure 1 shows the time course of the concentration of $OPPh_3$ determined from the intensity of the ν(P=O) band,[6] which indicates that all PPh_3 is finally oxidized to $OPPh_3$ in each reaction. Therefore, $PMo_{12}O_{40}$ undergoes stoichiometric reduction by PPh_3, accompanied by the transfer of lattice oxygen atoms of the anion to PPh_3 as given in Eq. 1. When each reaction was completed, the solvent was evaporated to dryness under reduced pressure. A dark blue residue was washed with MeOH to remove $OPPh_3$, followed by recrystallization from MeCN to give microcrystals of the reduced compound. The isolated reduced compounds, $[n\text{-Bu}_4N]_3[PMo_{12}O_{40-x}]$ (x= 1, 2, and 3), are abbreviated as $PMo_{12}O_{39}$, $PMo_{12}O_{38}$, and $PMo_{12}O_{37}$, respectively. They were relatively stable on exposure to air. The analytical data for the reduced compounds are consistent with the calculated ones, as summarized in Table 1.

$$[n\text{-Bu}_4N]_3[PMo_{12}O_{40}] + x PPh_3 \longrightarrow [n\text{-Bu}_4N]_3[PMo_{12}O_{40-x}] + x OPPh_3 \quad (x = 1,\ 2,\ 3) \qquad (1)$$

Figure 2 shows the IR spectra of $PMo_{12}O_{40}$, the reduced compounds, and the reoxidized compound of $PMo_{12}O_{37}$.[7] The spectrum of $PMo_{12}O_{40}$ exhibits four major bands characteristic of the Keggin anion structure in the region between 1100 and 600 cm^{-1}; they are assigned to P-O (1063 cm^{-1}), Mo=O (956 cm^{-1}), and two Mo-O-Mo (880 and 804 cm^{-1}) stretching modes.[8] With a progress of reduction, the intensities of the P-O and two Mo-O-Mo bands decrease, while that of the Mo=O band remains almost unchanged. It was reported that the P-O and Mo-O-Mo bands are weakened as the symmetry of the anion is lowered upon reduction, and that the eliminated oxygen atoms are those of the bridging Mo-O-Mo bonds as long as

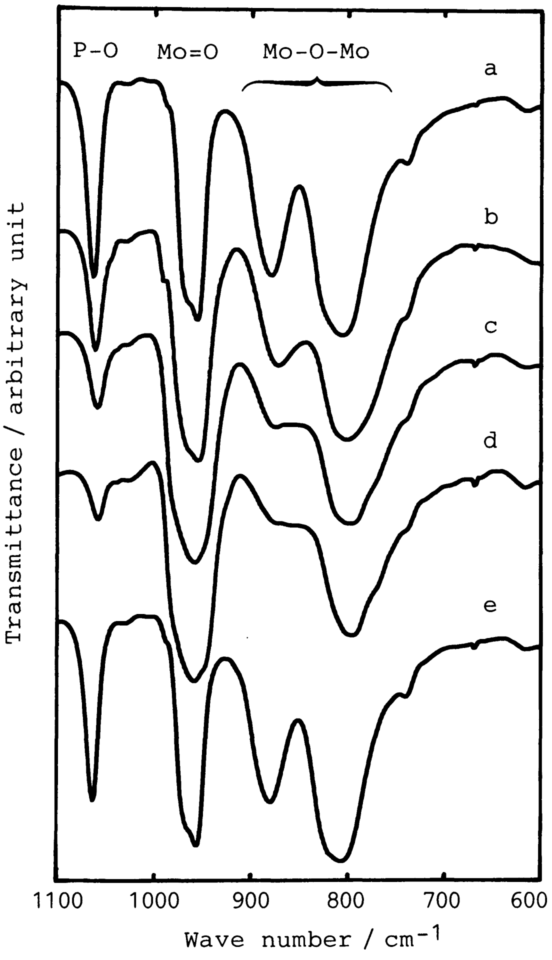

Fig. 2. IR spectra of $PMo_{12}O_{40}$ (a), $PMo_{12}O_{39}$ (b), $PMo_{12}O_{38}$ (c), $PMo_{12}O_{37}$ (d), and the reoxidized compound of $PMo_{12}O_{37}$ (e).(Measured in KBr disks)

Table 1. Analytical data for the reduced compounds

Compound	Found (%)					Calcd (%)				
	C	H	N	Mo$^{a)}$	P$^{b)}$	C	H	N	Mo	P
$PMo_{12}O_{39}$	22.86	4.28	1.59	45.1	1.26	22.76	4.30	1.66	45.4	1.22
$PMo_{12}O_{38}$	22.71	4.20	1.62	45.5	1.26	22.90	4.32	1.67	45.7	1.23
$PMo_{12}O_{37}$	23.09	4.29	1.60	45.7	1.23	23.05	4.35	1.68	46.0	1.24

a) Determined by atomic absorption spectrophotometry.

b) Determined by the photometric method according to JIS K0102.

the intensity of the Mo=O band does not decrease upon reduction.[1-3] Therefore, the bridging oxygen atoms of the Mo-O-Mo bonds seem to be eliminated in the present reduced compounds. The spectrum of each reoxidized compound was identical with that of $PMo_{12}O_{40}$, as demonstrated in Fig. 2e. These observations indicate that the anion structure of the Keggin type is retained in the reduced compounds.

Figure 3 shows the X-ray diffraction patterns of $PMo_{12}O_{40}$, the reduced compounds, and the reoxidized compound of $PMo_{12}O_{37}$. The patterns of the reduced compounds are not identical with that of $PMo_{12}O_{40}$. The elimination of bridging oxygen atoms may cause any change of the crystal structure and an irregular arrangement of the reduced anions. On the other hand, the patterns of the reoxidized compounds were very close to that of $PMo_{12}O_{40}$, as demonstrated in Fig. 3e. These findings also suggest that no decomposition took place on the anion structure during the reduction.

Valence states of molybdenum atoms of the reduced compounds were examined by XPS spectra.[9] The spectra of Mo 3d electrons of $PMo_{12}O_{40}$ and the reduced compounds are shown in Fig. 4. The spectrum of $PMo_{12}O_{40}$ exhibits the characteristic Mo(VI) $3d_{5/2}$ (233.1 eV) and Mo(VI) $3d_{3/2}$ (236.3 eV) doublet caused by the spin-orbit coupling.[10] The doublet observed for $PMo_{12}O_{39}$ is broadened on the low binding energy side, and that for $PMo_{12}O_{38}$ develops a shoulder, and that for $PMo_{12}O_{37}$ is split into two signals. Deconvolution of these spectra reveals that a second doublet due to Mo(V) appears at 1.3±0.1 eV lower than that of Mo(VI) as depicted in Fig. 4. The separation between $3d_{5/2}$ and $3d_{3/2}$ bands (the spin-orbit split) is found to be 3.2 eV for all the deconvoluted curves. Both the binding energies and the spin-orbit split for each doublet are in good agreement with the values reported for molybdophosphates[3,11,12] and molybdenum oxides.[10,11] No signal due to Mo(IV) and further reduced molybdenum species were observed in the lower binding energy region.[10,11] The contents of Mo(VI) and Mo(V) in the reduced compounds were estimated from peak areas of the deconvoluted curves. The ratio of Mo(VI) against Mo(V) was obtained as to be 5.1 for $PMo_{12}O_{39}$, 2.0 for $PMo_{12}O_{38}$, and 0.94 for $PMo_{12}O_{37}$, respectively. This suggests that the elimination of one oxygen atom from the anion produces two Mo(V). On the other

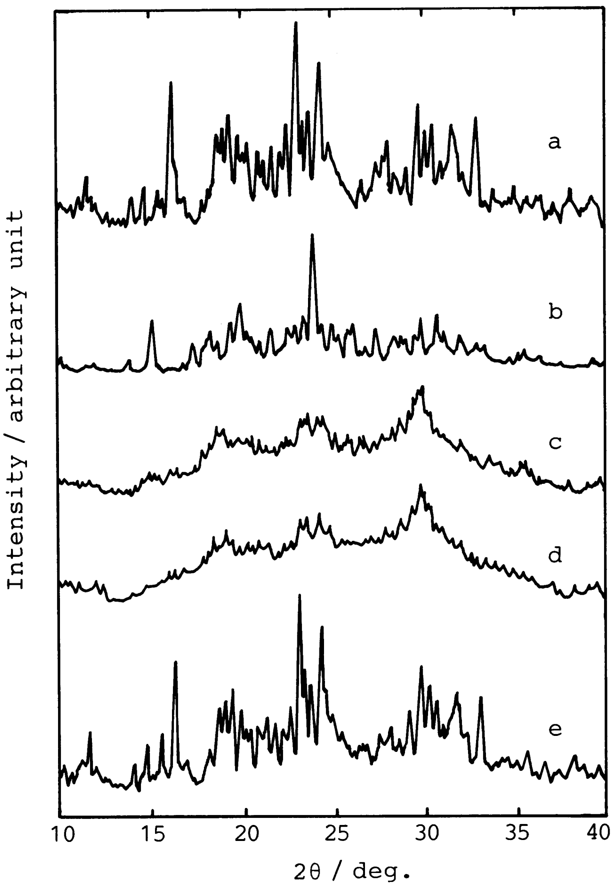

Fig. 3. X-Ray diffraction patterns of $PMo_{12}O_{40}$ (a), $PMo_{12}O_{39}$ (b), $PMo_{12}O_{38}$ (c), $PMo_{12}O_{37}$ (d), and the reoxidized compound of $PMo_{12}O_{37}$ (e).
(Measured with CuKα radiation)

hand, the binding energies of P 2p electrons were almost unchanged (134.5-134.7 eV) for both original and reduced compounds, as reported previously for some molybdophosphate anions.[3,12] This indicates that no internal oxygen atoms bonded P atom are eliminated during the reduction, the valence state of P(V) being preserved.

In conclusion, two-, four-, and six-electron reduced forms, $[n\text{-Bu}_4\text{N}]_3[\text{PMo(VI)}_{12-2x}\text{Mo(V)}_{2x}\text{O}_{40-x}]$ (x= 1, 2, and 3) were isolated, accompanied by the elimination of bridging oxygen atoms of the Mo-O-Mo bonds. The elimination of one oxygen atom produces two Mo(V) in the anion. No decomposition takes place on the anion structure of the reduced compound to the extent that half Mo(VI) atoms in $\text{PMo}_{12}\text{O}_{40}$ are reduced to Mo(V) atoms.

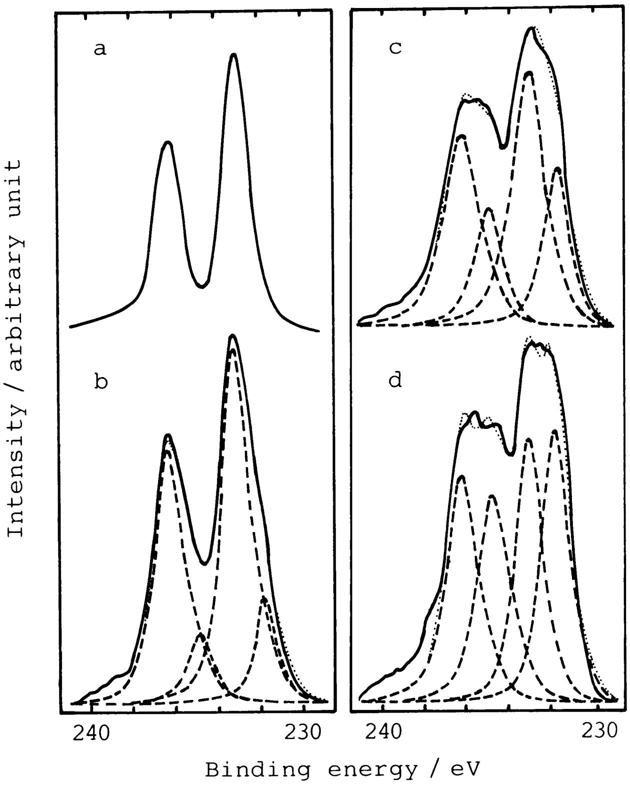

Fig. 4. XPS spectra of $\text{PMo}_{12}\text{O}_{40}$ (a), $\text{PMo}_{12}\text{O}_{39}$ (b), $\text{PMo}_{12}\text{O}_{38}$ (c), and $\text{PMo}_{12}\text{O}_{37}$ (d). Dashed and dotted lines represent deconvoluted and synthesized curves, respectively.

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(Received September 12, 1988)