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Reduction of the Dodecamolybdophosphate Anion with Triphenylphosphine in a Homogeneous System

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The reaction of $[n\text{-}Bu_4N]_3PMo_{12}O_{40}$ with PPh_3 in MeCN was investigated on the basis of FT-IR and electronic absorption spectra. It was found that two-electron reduction occurred on $[PMo_{12}O_{40}]^{3-}$, accompanied by the transfer of one bridging oxygen in Mo-O-Mo bonds to PPh_3.

Redox behaviors of heteropoly compounds have systematically been investigated on a molecular unit in relation to the catalytic mechanism of them. It has been shown that the reduction process of dodecamolybdophosphates, which are typical heteropoly compounds, varies with the experimental conditions and the nature of the reducing agent. The reduction of dodecamolybdophosphates by H_2,1-3) cyclohexane,2) or methacrolein2) in a heterogeneous system is accompanied by elimination of the bridging oxygen(s) of them, whereas the reduction of them by $SnCl_2$2) or electrolysis2,4) in a homogeneous one is accompanied by addition of protons to them without elimination of any oxygens. It is worth noting, therefore, to investigate the behavior of oxygens of dodecamolybdophosphate anion in its redox process. In this study, for the purpose of elimination of the oxygen from the anion in a homogeneous system, a reaction of tetrabutylammonium dodecamolybdophosphate(3-), $[n\text{-}Bu_4N]_3PMo_{12}O_{40}$ (abbreviated as PMo_{12}), with PPh_3 has been attempted. The reduction process of PMo_{12} is discussed on the basis of FT-IR and electronic absorption spectra.

The sample PMo_{12} was prepared by the cation-exchange reaction of $H_3PMo_{12}O_{40}\cdot xH_2O$ with $n\text{-}Bu_4NBr$ in MeOH. The precipitate was filtered and recrystallized from MeCN to give the yellow crystals. The reaction of PMo_{12} with an excess amount of PPh_3 was homogeneously carried out in MeCN at 23 °C under N_2 atmosphere. The yellow solution gradually turned green and finally dark blue, which was a characteristic color of reduced heteropoly anions.

Figure 1 shows the FT-IR spectral changes of a MeCN solution containing PMo_{12} and PPh_3. The bands ascribed to PPh_3 decrease in absorbance with the elapse of time, which is demonstrated by the representative band at 505 cm^{-1} in Fig. 1c. On the other hand, new bands ascribed to $OPPh_3$ arise; representatively at 1194 (ν(P=O))5) and 544 cm^{-1} as depicted in Figs. 1a and 1c. These spectral changes indicate that PPh_3 reduces PMo_{12} accompanying the oxygen transfer from the anion to PPh_3. In the region b, there are four major bands due to the Keggin anion structure, which are assinged to ν(P-O)(Op band), ν(Mo=O)(Ot band), and ν(Mo-O-Mo)(Ob bands), respectively.6) During the reaction, the Ob and Op bands are weakened, as previously reported for the reduction of the anion.1-4) The Ob bands drastically decrease in the intensity, whereas the Ot band rather increases; therefore the oxygen eliminated from the anion is attributed to the bridging oxygen.

The concentration of $OPPh_3$ formed in the reaction of PMo_{12} with an excess amount of PPh_3 was determined from the intensity of the ν(P=O) band shown in Fig. 1a. The concentration was also determined by gas chromatography: $n\text{-}C_{16}H_{33}Ph$ was added to the solution as an internal standard and $OPPh_3$ was separated from

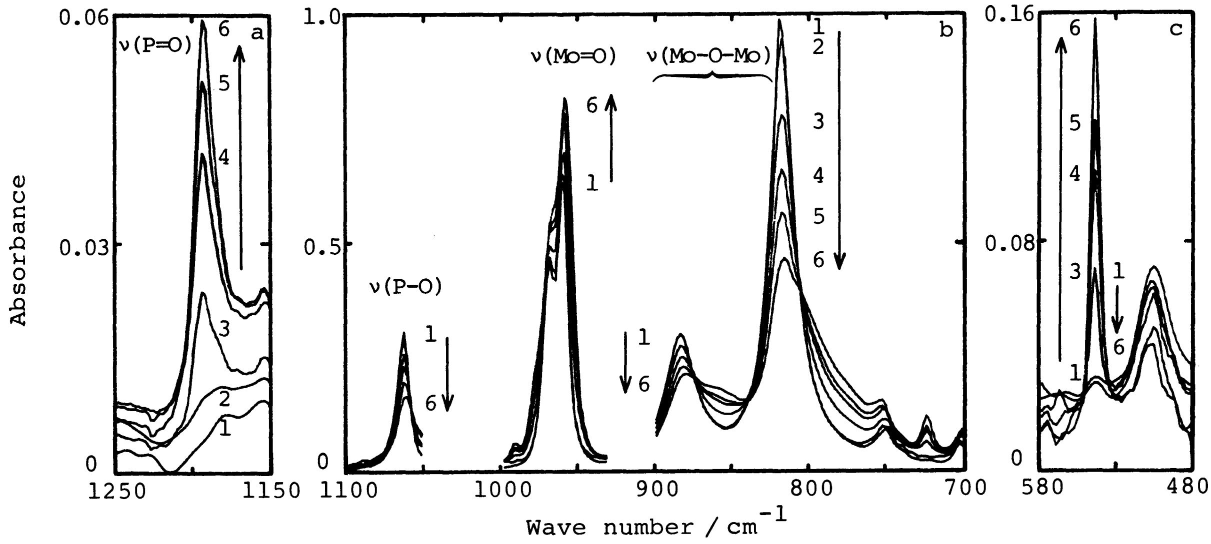

Fig. 1. FT-IR spectral change of a MeCN solution containing PMo_{12} (4.96×10^{-3} mol dm^{-3}) and PPh_3 (9.92×10^{-3} mol dm^{-3}). (reaction time: 0.072(1), 2.7(2), 21(3), 45(4), 68(5), and ≥116 h(6), cell length: 0.1 mm)

other species by using a capillary column at 230 °C. The results are summarized in Table 1, indicating that PMo_{12} reacts with an equimolar amount of PPh_3 accompanying elimination of one oxygen from the anion.

Table 1. Determination of $OPPh_3$ formed in the reaction of PMo_{12} with PPh_3 in MeCN

$[PPh_3]/[PMo_{12}]$	$[OPPh_3]/[PMo_{12}]$	
	FT-IR[a)]	GC[b)]
2	0.9	1.0
5	0.9	1.1

a) $[PMo_{12}]= 2.1 \times 10^{-2}$ mol dm^{-3}.
b) $[PMo_{12}]= 4.0$ mol dm^{-3}.

Figure 2 shows the electronic absorption spectra of the reacting solution. Two bands appear at 730 and 970 nm. The spectral changes for the electrolytic reduction of PMo_{12} in MeCN are shown in Fig. 3. At the applied potential, -0.30 V *vs.* SCE, PMo_{12} was progressively reduced and finally the two-electron reduced anion, $[PMo_{12}O_{40}]^{5-}$, was produced.[7)] The number of electrons (n) injected per PMo_{12} was determined by a coulometer. The spectra for

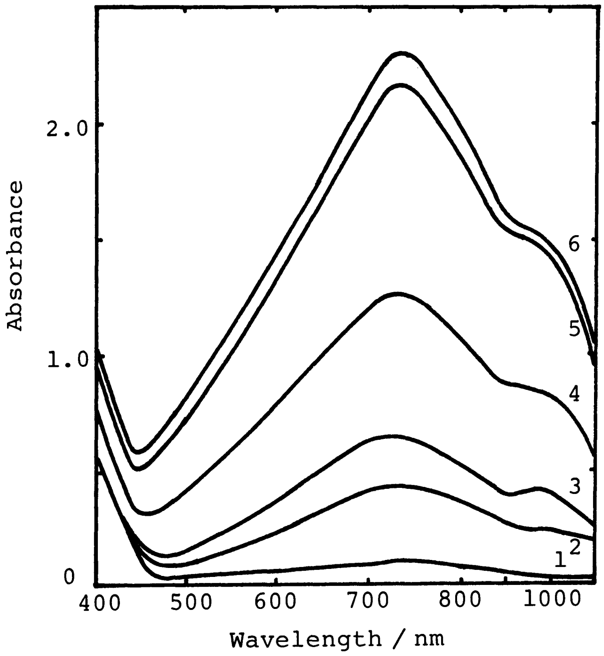

Fig. 2. Electronic absorption spectral change of a MeCN solution containing PMo_{12} (4.13×10^{-3} mol dm^{-3}) and PPh_3 (1.24×10^{-2} mol dm^{-3}). (reaction time: 0.18(1), 1.3(2), 4.5(3), 20(4), 93(5), and ≥150 h(6), cell length: 1 mm)

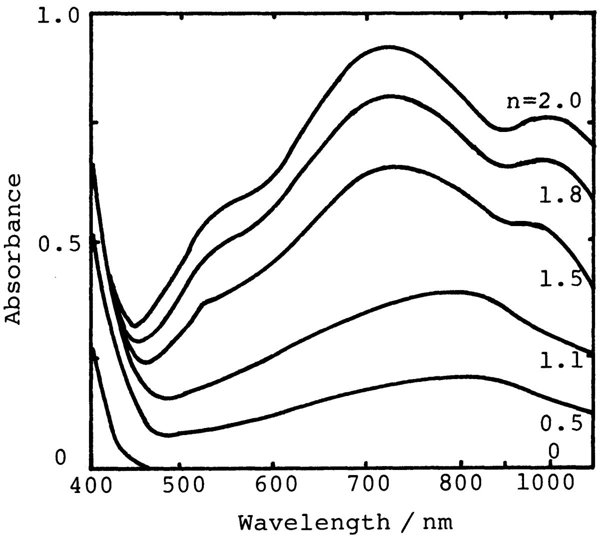

Fig. 3. Electronic absorption spectra of PMo_{12} (2.0×10^{-3} mol dm^{-3}) under the electrolytic reduction at -0.30 V *vs.* SCE in MeCN. (supporting electrolyte: *n*-Bu_4NBr (0.1 mol dm^{-3}), cell length: 1 mm, n: the number of electrons injected per PMo_{12})

n= 0.5 and 1.1 show a broad band around 800 nm and for n$\geqslant$ 1.5 two bands at 730 and 1000 nm, which are assigned to intervalence charge transfer (Mo(V)→Mo(VI)) bands.[8)] These two spectral features seem to be responsible for the one-electron and two-electron reduction of the anion, respectively. The spectral differences between one-electron and two-electron reduced anions were also reported for some "heteropoly blues".[9,10)] Since the spectral feature in Fig. 2 is essentially similar to that of the electrolytically two-electron reduced anion (Fig. 3), PMo_{12} undergoes two-electron reduction by PPh_3.

In conclusion, the two-electron reduction of PMo_{12} by PPh_3 in MeCN proceeds homogeneously, accompanied by the transfer of one bridging oxygen in the anion to PPh_3 as follows.

$$[n\text{-}Bu_4N]_3PMo(VI)_{12}O_{40} + PPh_3 \longrightarrow [n\text{-}Bu_4N]_3PMo(VI)_{10}Mo(V)_2O_{39} + OPPh_3$$

References

1) H. Tsuneki, H. Niiyama, and E. Echigoya, Chem. Lett., 1978, 645 and 1183.
2) K. Eguchi, Y. Toyozawa, N. Yamozoe, and T. Seiyama, J. Catal., 83, 32(1983).
3) K. Katamura, T. Nakamura, K. Sakata, M. Misono, and Y. Yoneda, Chem. Lett., 1981, 89.
4) M. Akimoto and E. Echigoya, Chem. Lett., 1981, 1759.
5) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London(1958), p.311.
6) C. Rocchiccioli-Deltcheff, R. Thouvenot, and R. Franck, Spectrochim. Acta, Part A, 32, 587(1976).
7) The applied potential was determined from cyclic voltammetry of the same solution as that for the electrolytic reduction, which showed two one-electron reversible reductions ($E_{1/2}$= +0.24 and -0.17 V *vs.* SCE, respectively) in the potential range from +0.40 V to -0.35 V.
8) M. T. Pope, "Heteropoly and Isopoly Oxometalates," Springer-Verlag, Berlin(1983), p.109.
9) G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, Inorg. Chem., 9, 662(1970).
10) J. M. Fruchart, G. Herve, J. P. Launay, and R. Massart, J. Inorg. Nucl. Chem., 38, 1627(1976).

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