Kinetics of Oxygen-Atom Transfer Reactions of α-$[PMo_{12}O_{40}]^{3-}$ and of A-β-$[PMo_3W_9O_{40}]^{3-}$ Anion Salts with PPh_3 in Non-Aqueous Solution

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The kinetics of the oxygen-atom transfer reactions of α-$[NBu^n{}_4]_3[PMo_{12}O_{40}]$ (abbreviated PMo_{12}) and of A-β-$[NBu^n{}_4]_3[PMo_3W_9O_{40}]$ (abbreviated PMo_3W_9) with PPh_3 were investigated in acetonitrile at 23—82 °C. Each reaction is first order in both the heteropolyanion salt and PPh_3. The second-order rate constants at 23 °C are $k_2=6.53\times10^{-4}$ and 4.58×10^{-5} ($dm^3\,mol^{-1}\,s^{-1}$) for the reduction of PMo_{12} and PMo_3W_9, respectively. The difference in the k_2 values is attributed to the number of active sites for oxygen transfer; PMo_3W_9 has only three corner-sharing oxygen atoms in the Mo(VI)–O–Mo (VI) bonds, whereas there are twelve corner-sharing and twelve edge-sharing oxygen atoms in PMo_{12}. The activation parameters are, however, almost identical for both reactions: $\Delta H^{\ddagger}=43.6$ and 43.4 ($kJ\,mol^{-1}$) and $\Delta S^{\ddagger}=-158$ and -181 ($J\,K^{-1}\,mol^{-1}$) for the reduction of PMo_{12} and PMo_3W_9, respectively. These results suggest a similar transition state in the oxygen-atom transfer reactions via the Mo–O–Mo sites of PMo_{12} and PMo_3W_9.

The redox mechanisms of the 12-molybdophosphate ($[PMo_{12}O_{40}]^{3-}$) anion have been systematically studied in relation to its catalytic functions.[1—4] It has been well clarified that a heterogeneous (vapor/solid phase) reduction of the polyanion is accompanied by an elimination of the bridging oxygen atom in the Mo–O–Mo bond. The behavior of the lattice oxygen atoms of the polyanion has therefore attracted much attention concerning its redox processes. Since the polyanion salts can be characterized as structurally well-defined oxomolybdenum complexes,[1] we have investigated the stoichiometric reduction of the Keggin-type polyanion salts with triphenylphosphine (PPh_3) in homogeneous systems, followed by a transfer of the bridging oxygen atoms of the polyanions to PPh_3.[5,6]

On the other hand, as model systems for molybdoenzymes, oxygen-atom transfer reactions of oxomolybdenum complexes have been well-established with regard to the mechanisms and kinetics.[7,8] In these systems it was demonstrated that substrates abstract the terminal oxygen atom of an Mo=O bond in the dioxomolybdenum complexes, whereas the bridging oxygen atom of an Mo–O–Mo bond in the μ-oxo dinuclear complex is unreactive. In contrast to these findings, our previous study[5,6] concerning oxygen-atom transfer reactions of α-$[PMo_{12}O_{40}]^{3-}$ and A-β-$[PMo_3W_9O_{40}]^{3-}$ polyanions (Fig. 1) revealed that PPh_3 does not abstract the terminal oxygen atom, but, rather, the bridging one in the polyanion according to reactions 1 and 2. Elimination of the bridging oxygen atom in an Mo–O–Mo bond upon reduction was also confirmed by the X-ray photoelectron spectra and the X-ray diffraction patterns of the isolated reduced polyanion salts.[5,6] We report here on kinetic studies of these oxygen-atom transfer reactions.

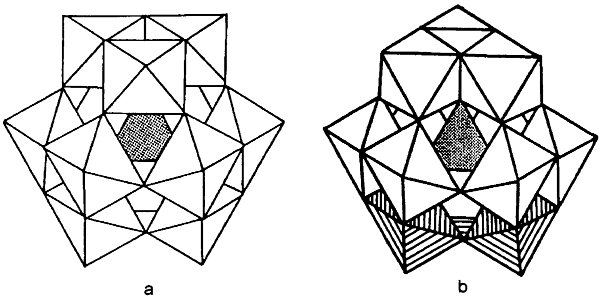

Fig. 1. Polyhedral representations of α-$[PMo_{12}O_{40}]^{3-}$ (**a**) and A-β-$[PMo_3W_9O_{40}]^{3-}$ anions (**b**). (Plain parts indicate MoO_6 octahedra in **a** and WO_6 octahedra in **b**. Hatched parts in **b** indicate MoO_6 octahedra.)

$$\alpha\text{-}[PMo_{12}O_{40}]^{3-} + PPh_3 \rightarrow \alpha\text{-}[PMo_{12}O_{39}]^{3-} + OPPh_3 \quad (1)$$

$$\text{A-}\beta\text{-}[PMo_3W_9O_{40}]^{3-} + PPh_3 \rightarrow \text{A-}\beta\text{-}[PMo_3W_9O_{39}]^{3-} + OPPh_3 \quad (2)$$

Experimental

Materials. Tetrabutylammonium 12-molybdophosphate (3−),[5] α-$[NBu^n{}_4]_3[PMo_{12}O_{40}]$ (abbreviated PMo_{12}), tetrabutylammonium 3-molybdo-9-tungstophosphate (3−),[6] A-β-$[NBu^n{}_4]_3[PMo_3W_9O_{40}]$ (abbreviated PMo_3W_9), and tetrabutylammonium 12-tungstophosphate (3−),[6] α-$[NBu^n{}_4]_3[PW_{12}O_{40}]$ (abbreviated PW_{12}) were prepared as previously described. Acetonitrile was distilled from calcium hydride and deoxygenated by bubbling nitrogen before use.

Reactions and Kinetics. The reactions of PMo_{12} and of PMo_3W_9 with PPh_3 were carried out in acetonitrile at different temperatures using a thermostated bath under a nitrogen atmosphere. The progress of the reaction was followed by the amount of triphenylphosphine oxide ($OPPh_3$) formed in the solution, which was determined based on the intensity of the Fourier-transform infrared (FT-IR) band of $OPPh_3$ according to a previously reported method.[5]

Electrochemical Measurements. The cyclic voltammetry and controlled-potential electrolysis of PMo_{12}, PMo_3W_9, and PW_{12}, (1.0×10^{-3} mol dm^{-3}) in acetonitrile were conducted with a BAS CV-50W in the presence of tetrabutylammonium perchlorate (1.0×10^{-1} mol dm^{-3}) as a supporting electrolyte, using a glassy carbon working electrode for cyclic voltammetry, a platinum working electrode for controlled-potential electrolysis, a platinum counter electrode, and a saturated calomel reference electrode.

Results and Discussion

Reactions of PMo_{12} and of PMo_3W_9 with PPh_3 in Acetonitrile. The reduction of PMo_{12} with PPh_3 in acetonitrile was followed by FT-IR spectral changes of the solution. In the region of 1100—700 cm^{-1} four major bands characteristic of the Keggin anion structure appeared; they were assigned to P–O, Mo=O (terminal oxygen), and two Mo–O–Mo (corner-sharing (O_{bc}) and edge-sharing oxygen (O_{be})) stretching vibrational modes.[9] The spectral changes of these bands under the reaction suggest that the bridging oxygen atom (O_{bc} and/or O_{be}) in the Mo–O–Mo bond is eliminated during the reduction of the polyanion, as previously described.[5] Concomitantly, the absorption band ascribed to PPh_3 representatively at 505 cm^{-1} decreases in intensity with time, and new bands ascribed to $OPPh_3$ arise representatively at 1194 (ν(P=O))[10] and 544 cm^{-1}, as shown in Fig. 2. The progress of the reaction was followed by the amount of $OPPh_3$ formed in the solution. The concentration of $OPPh_3$ could be determined by the intensities of the bands at 1194 and 544 cm^{-1}, since linear relationships between them were obtained independently of the coexistence of the other species in the solution.[5,11]

Oxygen-atom transfer reactions of dioxomolybdenum complexes ($Mo^{VI}O_2L_n$) (L = S_2CNR_2, S_2PR_2, cysteinato, 8-quinolinolato, acetylacetonato, etc., $n=2$; L = tetradentate S_4 or N_2S_2 donor ligand, $n=1$) with PR_3 (R = aryl or alkyl) are known to produce monooxomolybdenum complexes ($Mo^{IV}OL_n$) at first, followed by dimerization of $Mo^{IV}OL_n$ with unreacted $Mo^{VI}O_2L_n$ to afford μ-oxo dinuclear complexes ($Mo^V_2O_3L_{2n}$), which complicate the kinetics of the reaction.[7,8] However, under the conditions of the absence of a dinuclear $Mo^V_2O_3L_{2n}$ complex, the oxygen-atom transfer reaction of a dioxomolybdenum complex containing a bulky ligand[12,13] or a Shiff base ligand[14] shows fairly simple kinetics of the reaction, being of first order in both the $Mo^{VI}O_2L_n$ complex and the substrate.[8] For the present study, although the one oxygen-deficient reduced species, α-$[PMo_{12}O_{39}]^{3-}$, formed by reaction 1 could be further reduced by an excess of PPh_3, the secondary reduction is considerably slow compared with the primary one.[5] Furthermore, from reaction 1 with equimolar amounts of PMo_{12} and PPh_3, another polyanion species different from α-$[PMo_{12}O_{39}]^{3-}$ was not obtained, even under the refluxing conditions.[5] Thus, the second-order rate law (Eq. 3) was applicable to the kinetics of reaction 1; its integrated form is given in Eq. 4, where $[PMo_{12}]_0$ is the initial concentration of PMo_{12}:

$$-d[PMo_{12}]/dt = k_2[PMo_{12}][PPh_3] \qquad (3)$$

$$1/[PMo_{12}] = k_2t + 1/[PMo_{12}]_0 \qquad (4)$$

Plots of $1/[PMo_{12}]$ vs. time for the reaction of PMo_{12} (6.00×10^{-3} mol dm^{-3}) with an equimolar amount of PPh_3 at 23 °C are shown in Fig. 3. A linear correlation between them is observed up to 65% completion of the reaction. From the slope of these plots the second-order rate constant k_2 (23 °C) was evaluated to be 6.53×10^{-4} (dm^3 mol^{-1} s^{-1}). Reactions of PMo_{12} and PPh_3 in the molar ratio of 1:2, 1:3, and 1:0.5 were also carried out at 23 °C. Based on the kinetic data treated in second-order forms, the resulting rate constants were calculated to be 6.50×10^{-4}—6.61×10^{-4} (dm^3 mol^{-1} s^{-1}). As shown in Fig. 3, linear relationships between $1/[PMo_{12}]$ and reaction time were also observed for the reactions of PMo_{12} (7.85×10^{-3} mol dm^{-3}) with an equimolar amount of PPh_3 at 40, 60, and 82 °C.

The FT-IR spectral changes of the reaction of PMo_3W_9 with PPh_3 were essentially similar to those observed for the reaction of PMo_{12} with PPh_3, as previously reported.[6] The kinetic data for reaction 2 were treated in second-order forms. Linear correlations between $1/[PMo_3W_9]$ and the reaction time were observed for the reactions of PMo_3W_9 (5.30×10^{-3} mol dm^{-3}) with an equimolar amount of PPh_3 at various temperatures, as shown in Fig. 4.

The rate constants determined from the slopes of these plots for reactions 1 and 2 are summarized in Table 1. Figure 5 shows Eyring plots for the rate constants of both reactions obtained at various temperatures. The activation parameters were calculated using the Eyring equation: $\Delta H^\ddagger = 43.6$ and 43.4 (kJ mol^{-1}) and $\Delta S^\ddagger = -158$ and -181 (J K^{-1} mol^{-1}) for reactions 1 and 2, respectively (Table 1). These values in each

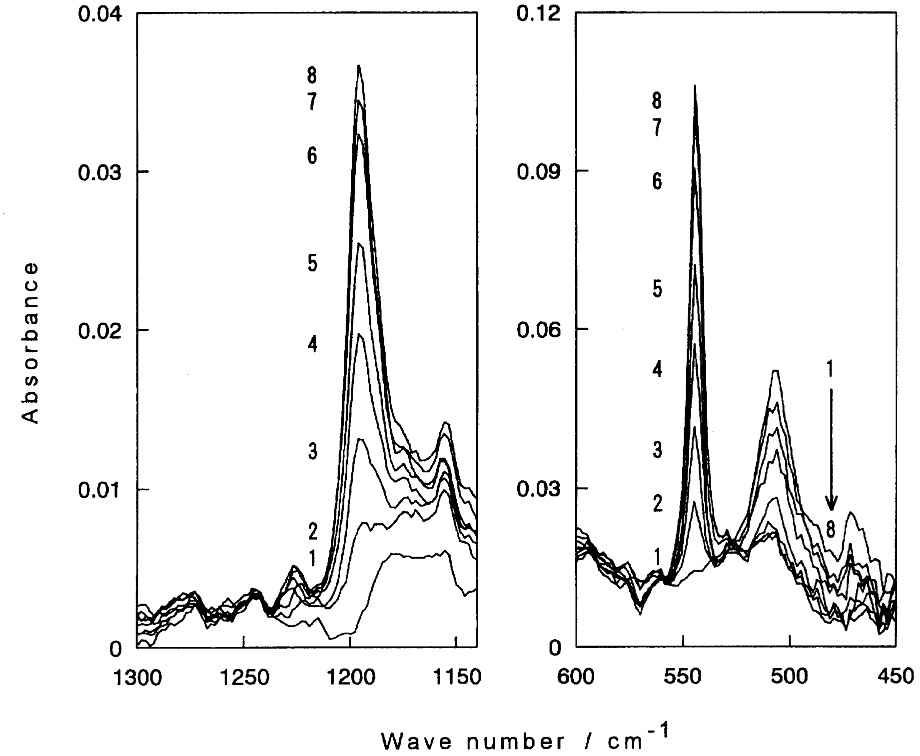

Fig. 2. FT-IR spectral changes of an acetonitrile solution containing PMo_{12} (6.00×10^{-3} mol dm^{-3}) and an equimolar amount of PPh_3. (reaction time at 23 °C; 0.1(1), 12(2), 29(3), 59(4), 123(5), 366(6), 1039(7), and 2526 h(8)).

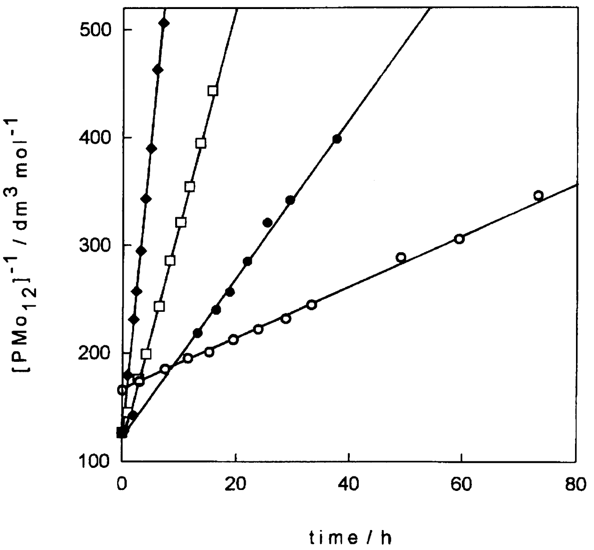

Fig. 3. Plots of $1/[PMo_{12}]$ vs. time for the reaction of PMo_{12} with an equimolar amount of PPh_3 in acetonitrile at 23 (○), 40 (●), 60 (□), and 82 °C (◆).

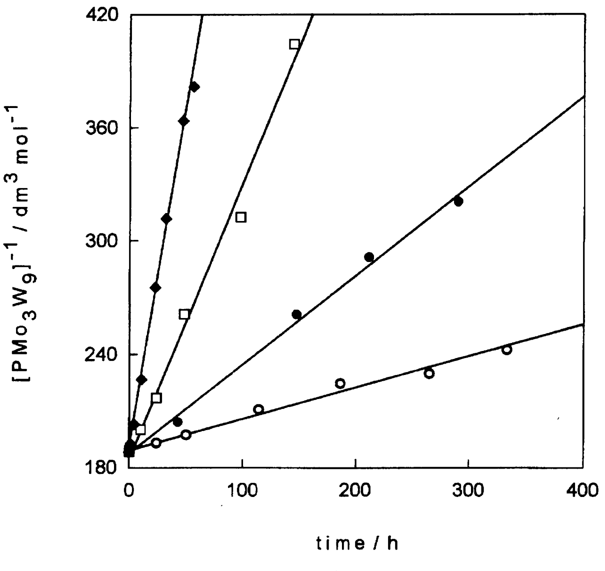

Fig. 4. Plots of $1/[PMo_3W_9]$ vs. time for the reaction of PMo_3W_9 with an equimolar amount of PPh_3 in acetonitrile at 23 (○), 40 (●), 60 (□), and 82 °C (◆).

parameter are almost identical for both reactions. Negative activation entropies indicate an associative mechanism for these reactions.

Reduction Mechanisms of PMo_{12} and PMo_3W_9. The redox behavior and oxidizing power of heteropoly compounds can be evaluated in connection with their redox potentials.[1,3,14—16] Cyclic voltammograms of PMo_{12} and PMo_3W_9 measured in acetonitrile are illustrated in Fig. 6. The first and second highest reversible couples observed for both heteropolyanion salts correspond to each one-electron reduction–oxidation transfer between Mo(VI) and Mo(V). The one-electron transfer for each couple was confirmed by controlled-potential electrolysis, which was consistent with the results of the Keggin-type polyanion in an aprotic

Table 1. Kinetic and Activation Parameters[a)] for the Oxygen-Atom Transfer Reactions of Heteropolyanion Salts with PPh_3

Salt	10^4k_2/dm^3 mol^{-1} s^{-1}				$\Delta H^\ddagger$	$\Delta S^\ddagger$
	23 °C	40 °C	60 °C	82 °C	kJ mol^{-1}	J K^{-1} mol^{-1}
PMo_{12}	6.53 (±0.05)	20.3 (±0.3)	56.1 (±0.7)	151 (±2)	43.6 (±2.7)	−158 (±8)
PMo_3W_9	0.458 (±0.005)	1.31 (±0.08)	4.06 (±0.23)	10.0 (±0.2)	43.4 (±3.0)	−181 (±9)

a) Errors estimated at the 95% confidence level in parentheses.

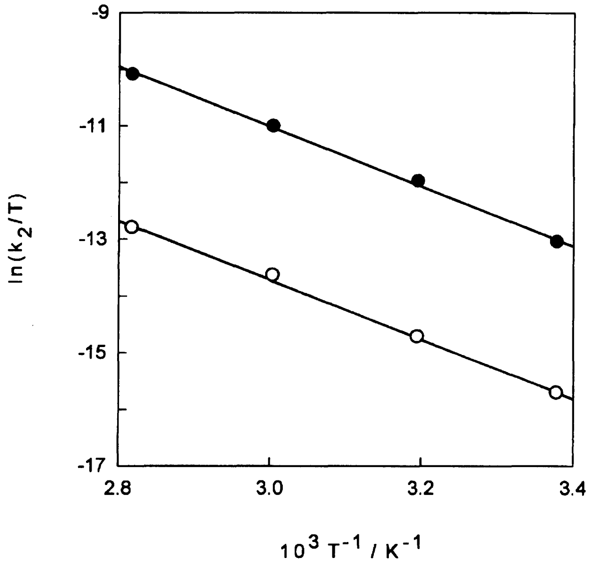

Fig. 5. Eyring plots of the rate constants for the reductions of PMo_{12} (●) and of PMo_3W_9 (○) with PPh_3.

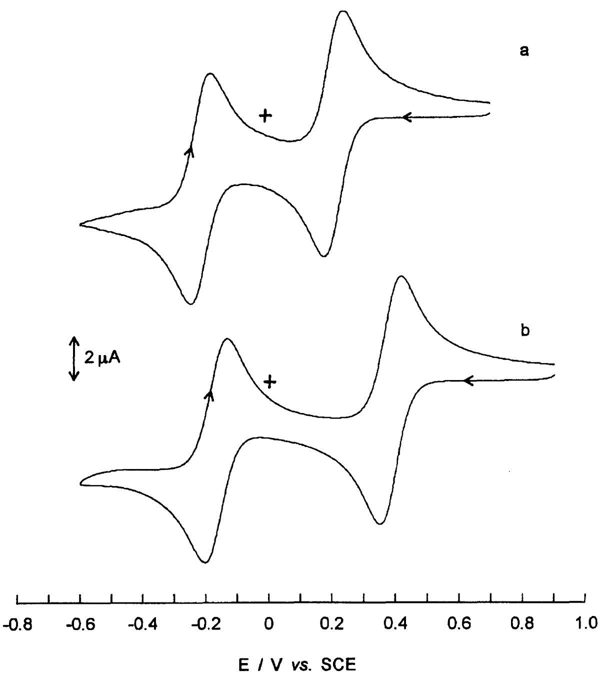

Fig. 6. Cyclic voltammograms of PMo_{12} (**a**) and PMo_3W_9 (**b**) (1.0×10^{-3} mol dm^{-3}) in acetonitrile containing $[NBu^n{}_4][ClO_4]$ (1.0×10^{-1} mol dm^{-3}). (scan rate 10 mV s^{-1}, initial potential +0.700 (**a**) and +0.900 V vs. SCE (**b**), initial scan direction cathodic)

solvent.[17)] The voltammtetric data are summarized in Table 2. The half-wave potentials ($E_{1/2}$) of PMo_3W_9 were observed to be higher than the corresponding potentials of PMo_{12}. The positive shifts of the Mo(VI)/Mo(V) redox potentials of mixed molybdotungstophosphate anions, compared with those of the molybdophosphate anion, were also observed.[1,15,16,18)] In addition, the reduction of a β-isomer polyanion is known to occur at a higher potential than the corresponding α-isomer polyanion.[19)] On the other hand, the W(VI)/W(V) redox couples of PW_{12} were observed at lower potential regions ($E_{1/2} = -0.224$ and -0.745 V vs. SCE) in acetonitrile. Accordingly, the reduction of the W(VI) atoms in PMo_3W_9 would occur at lower potentials than the reduction of Mo(VI) atoms. Such an electrochemical redox behavior is consistent with the findings that PW_{12} was not reduced by PPh_3 and that the reduction of PMo_3W_9 with PPh_3 did not occur on W atoms, but, rather, on Mo atoms; the bridging oxygen atoms in the W–O–W and Mo–O–W bonds were not transferred to PPh_3.[6)]

Although the electrochemical reduction of the Mo(VI) atom in PMo_3W_9 occurs at a higher potential compared with that in PMo_{12}, the k_2 value of reaction 2 is smaller than that of reaction 1 at the same temperature by more than one order of magnitude (Table 1). These findings indicate that the difference in the rates of the present reactions can be attributed to the number of active sites for the oxygen-atom transfer reaction of these two heteropolyanion salts, rather than the re-

Table 2. Voltammetric Data for Heteropolyanion Salts[a)]

Salt	$E_{1/2}$[b)]/V	ΔE[c)]/mV	i_{pc}/i_{pa}[d)]
PMo_{12}	+0.204	61	1.04
	−0.218	60	0.94
PMo_3W_9	+0.374	60	1.01
	−0.175	63	0.99

a) In acetonitrile containing $[NBu^n{}_4][ClO_4]$ (1.0×10^{-1} mol dm^{-3}), scan rate 10 mV s^{-1}. b) Half wave potential (V vs. SCE) for the Mo(VI)/M(V) redox couple. c) Separation of cathodic and anodic peaks. d) Ratio of cathodic and anodic peak currents.

duction potentials of the Mo(VI) atoms of these salts.

The reduction of PMo_3W_9 with PPh_3 does not occur on W(VI) atoms, but on Mo(VI) atoms, accompanied by the elimination of one of the O_{bc} atoms in the Mo(VI)–O–Mo(VI) bonds, as previously reported.⁶⁾ There are only three O_{bc} atoms in PMo_3W_9, whereas twelve O_{bc} and twelve O_{be} atoms exist in PMo_{12}. The activation enthalpies and entropies are, however, almost identical in each parameter for reactions 1 and 2 (Table 1). These results suggest that the transition state for the oxygen-atom transfer reaction via the Mo–O–Mo site of PMo_3W_9 is the same as that of PMo_{12}.

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