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Comparative Study of the Electrode Reactions of 12-Molybdosilicate and 12-Molybdophosphate

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It is well-known that 12-molybdosilicate (12-MSA) and 12-molybdophosphate (12-MPA) undergo three reversible electrode reactions in a mixed solvent such as 50% dioxane–water containing a strong acid.[2–4] The number of electrons involved in the three processes of both 12-MSA and 12-MPA is 2.

Generally speaking, the electrode reactions of 12-MSA and 12-MPA are very simple and very similar to each other. Therefore, it was thought that the role of central atoms such as P, Si, and As in the electrode reactions of 12-heteropolymolybdates is not so significant.[2,3]

In this paper, we present an interesting observation that indicates that the influence of a central atom on the electrode reactions of 12-MSA and 12-MPA cannot be ignored.

Experimental Section

The glassy-carbon electrode used in this study was obtained from Tokai Carbon Co. (Model GC-20). The gold-minigrid used for the thin-layer voltammetric experiment was obtained from Buckbee-Mears Co. (500 lines/in.). Sodium 12-molybdosilicate was obtained from Molybdenum Climax Co., and sodium 12-molybdophosphate, from Wako Pure Chemicals. Other chemicals were Wako Pure Chemicals reagent grade. All chemicals were used without further purification, and all solutions were deaerated with purified nitrogen before use.

Voltammetric experiments were performed by using a potentiostat (Fuso Model 311), a function generator (Fuso Model 348), and a wave memory (Riken Densh TCD-1000). A coulometer (Fuso Model 343) was used for coulometric experiments.

The construction of a gold-minigrid optically transparent thin-layer electrode (OTTLE) and standard procedures used for thin-layer voltammetric and spectroelectrochemical experiments were described elsewhere.[5,6]

Results and Discussion

Cyclic Voltammetry at a Glassy-Carbon Electrode (GCE). Typical voltammograms of 12-MPA and 12-MSA, which were obtained at a rather large sweep rate in 50% (w/w) dioxane–water solutions containing 1.0 N H_2SO_4 are shown in Figure 1. Both the 12-MPA and the 12-MSA give five reversible peaks on both cathodic and anodic scans, respectively. The number of electrons involved in each of the first three processes of 12-MPA and 12-MSA is 2, which was ascertained by thin-layer coulometry. The number of electrons involved in each of the fourth and fifth processes of both 12-MPA and 12-MSA was estimated to be 2 from peak separations and peak heights. The voltammetric results are summarized in Table I.

The rate constants of a heterogeneous electron-transfer process were estimated by using Nicholson's method.[7] The rate constants of the first four processes of both 12-MPA and 12-MSA are relatively large (around 10^{-1} cm s^{-1}) and not so different from each other. At a large sweep rate, therefore, the influence of the central atom on the electrochemical behavior of 12-heteropolymolybdates seems to be ignored.

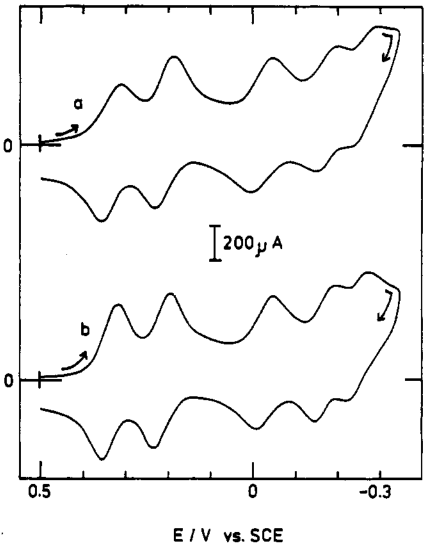

Figure 1. Cyclic voltammograms of 12-heteropolymolybdates at a glassy-carbon electrode in 50% (w/w) dioxane–water solutions containing 1.0 N H_2SO_4 (scan rate 8 V s^{-1}; initial potential 0.500 V vs. SCE; initial scan direction cathodic): (a) 10^{-3} M $Na_4SiMo_{12}O_{40}$; (b) 10^{-3} M $Na_3PMo_{12}O_{40}$.

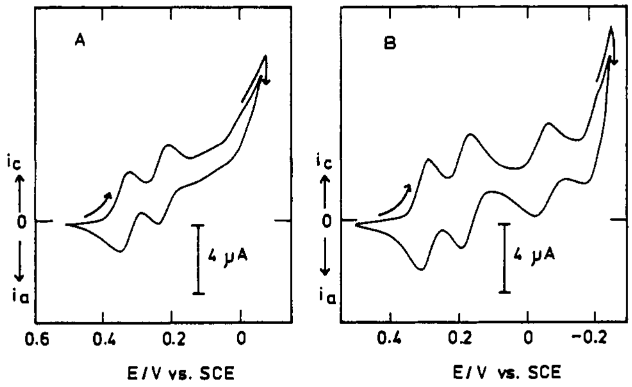

Figure 2. Cyclic voltammograms of 12-heteropolymolybdates at a glassy-carbon electrode in 50% (w/w) dioxane–water solutions containing 0.36 M H_2SO_4 (scan rate 2 mV s^{-1}; initial potential 0.500 V vs. SCE; initial scan direction cathodic): (A) 10^{-3} M $Na_3PMo_{12}O_{40}$; (B) 10^{-3} M $Na_4SiMo_{12}O_{40}$.

Table I. Voltammetric Results ($E^{\circ\prime}$, V) for the Five Two-Electron-Reduction Processes of 12-Molybdosilicate and 12-Molybdophosphate in 50% (w/w) Dioxane-Water Solutions Containing 1.0 N H_2SO_4

$SiMo_{12}O_{40}{}^{4-}$:	+0.336,	+0.212,	−0.016,	−0.164,	−0.260
$PMo_{12}O_{40}{}^{3-}$:	+0.328,	+0.203,	−0.036,	−0.181,	−0.262

Typical cyclic voltammograms of 12-MPA and 12-MSA obtained at a smaller scan rate are shown in Figure 2 and are clearly different. As seen in Figure 2A, the third cathodic peak of 12-MPA becomes a plateau and the corresponding anodic peak disappears. In the case of 12-MSA, on the other hand, the fourth cathodic peak becomes a plateau and the corresponding anodic peak almost disappears (Figure 2B).

The third cathodic wave of 12-MPA seems to be autocatalytic, which was observed at a small scan rate. The reaction mechanisms of this process seem to be explained as

$$R_2 + 2e^- \rightleftharpoons R_3 \qquad O + 2R_3 \rightarrow 3R_2$$

where O is the fully oxidized form of 12-MPA, R_2, the four-electron-reduction product of 12-MPA, and R_3 the six-

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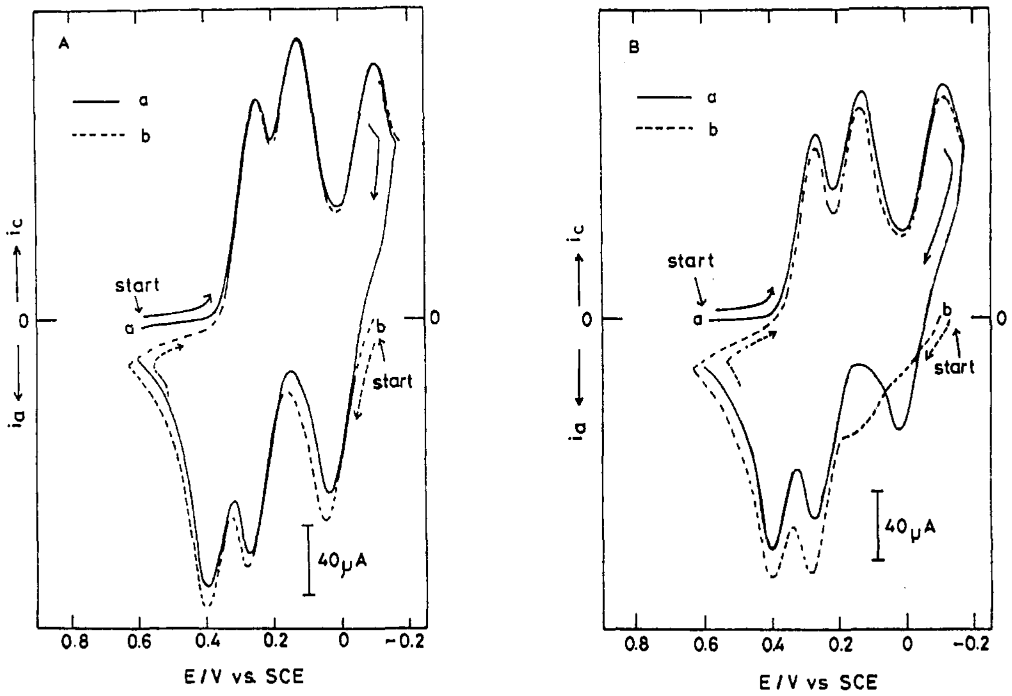

Figure 3. Thin-layer cyclic voltammograms of 12-heteropolymolybdates at a gold-minigrid OTTLE in 50% (w/w) dioxane–water solutions containing 0.36 M H_2SO_4 (scan rate 2 mV s^{-1}): (A) 10^{-3} M $Na_4SiMo_{12}O_{40}$ (a) for initial potential 0.600 V vs. SCE and initial scan direction cathodic and (b) after electrolysis for about 40 min at the potential where 12-molybdosilicate is reduced to the six-electron-reduction product of 12-molybdosilicate and the anodic scan was started; (B) 10^{-3} M $Na_3PMo_{12}O_{40}$ (a) for initial potential 0.600 V vs. SCE and initial scan direction cathodic and (b) after electrolysis for about 40 min at the potential where 12-molybdophosphate is reduced to the six-electron-reduction product of 12-molybdophosphate and the anodic scan was started.

electron-reduction product of 12-MPA. In the case of 12-MSA, the fourth cathodic process seems to be autocatalytic.

The six-electron-reduction product of 12-MPA is more reactive for a homogeneous electron-transfer reaction than that of 12-MSA.

Thin-Layer Voltammetry at a Gold-Minigrid OTTLE. Thin-layer cyclic voltammograms of 12-MSA obtained in 50% (w/w) dioxane–water solutions containing 0.36 M H_2SO_4 are shown in Figure 3A. Curve a in Figure 3A is an ordinary cyclic voltammogram (starting potential +0.600 V vs. SCE). On the other hand, curve b in Figure 3A was obtained by the following procedures. After electrolysis for about 40 min at the potential where the 12-MSA is reduced to the six-electron-reduction product of 12-MSA, the anodic scan was started and the scan was reversed at +0.600 V vs. SCE. Curves a and b in Figure 3A are almost the same. This indicates that the six-electron-reduction product of 12-MSA is very stable in this medium.

Thin-layer cyclic voltammograms of 12-MPA obtained in 50% (w/w) dioxane–water solutions containing 0.36 M H_2SO_4 are shown in Figure 3B. The relationship between curve a and curve b is the same as that in Figure 3A. As seen in curve b, the anodic peak corresponding to the reoxidation of the six-electron-reduction product of 12-MPA was less defined than that of curve a. Spectral changes in the six-electron-reduction product of 12-MPA with time observed by using a gold-minigrid OTTLE had no isosbestic points. These facts indicate that the six-electron-reduction product of 12-MPA is rather unstable even in this medium and that the transformation reaction of the six-electron-reduction product of 12-MPA is not a simple one.[6]

In conclusion, in the case that the electrode reaction processes of 12-heteropolymolybdates are accompanied by chemical reactions and that these chemical reactions cannot be ignored, the influence of a central atom on the electrode reactions of 12-heteropolymolybdates is very significant. The properties of high-reduction products of 12-MPA seem to be very different from those of 12-MSA.

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Metal Complexes of Fluorophosphines. 11. Further Observations on Iron Carbonyl Complexes of (Methylamino)bis(difluorophosphine)[1]

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Previous papers of this series[2-4] have described a variety of iron carbonyl derivatives of the small-bite bidentate strong π-acceptor ligand $CH_3N(PF_2)_2$ including the mononuclear complex $[CH_3N(PF_2)_2]_2FeCO$ and two series of binuclear complexes: yellow $[CH_3N(PF_2)_2]_nFe_2(CO)_{10-2n}$ ($n = 1$ and 2) without an iron–iron bond and yellow to orange $[CH_3N(PF_2)_2]_nFe_2(CO)_{9-2n}$ ($n = 1$, 2, and 4) with an iron–iron bond. Further work since the publication of these results has resulted in the isolation of two new iron carbonyl complexes of $CH_3N(PF_2)_2$: mononuclear $CH_3N(PF_2)_2Fe(CO)_4$ (I), con-

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