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A Voltammetric Study on the One-Electron Redox Processes of the Dawson-Type Heteropolymolybdate Complexes

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The electrochemical behaviors of the Dawson-type heteropolymolybdate anions, $[S_2Mo_{18}O_{62}]^{4-}$, $[P_2Mo_{18}O_{62}]^{6-}$, and $[As_2Mo_{18}O_{62}]^{6-}$ were investigated at the glassy carbon (GC) electrode. In CH_3CN where no protonation accompanies reduction, the voltammogram of the $[S_2Mo_{18}O_{62}]^{4-}$ anion consists of four one-electron redox waves followed by an ill-defined wave while the $[P_2Mo_{18}O_{62}]^{6-}$ and $[As_2Mo_{18}O_{62}]^{6-}$ anions exhibit two one-electron redox waves; the one-electron waves are reversible and diffusion-controlled. The Dawson anions undergo successive two-electron reductions under the conditions where protonation can accompany reduction. The effect of the presence of acid on the voltammetric behaviors has also been discussed.

The Dawson-type heteropoly complexes have been the subject of earlier electrochemical studies, especially with respect to electroanalysis and electrocatalysis. It is known that the 18-tungsto-2-phosphate anion, $[P_2W_{18}O_{62}]^{6-}$ is electroreduced successively by one-, one-, two-, and two-electrons in acidic solutions. In concentrated HCl solutions, the two one-electron waves merge into a single two-electron wave, leaving three two-electron waves.[1,2] This behavior has been accounted for in terms of the protonation of the reduced species.[3] On the other hand, the corresponding molybdate complex, $[P_2Mo_{18}O_{62}]^{6-}$ undergoes three successive two-electron reductions even in slightly acidic solutions.[4—7] No intermediate reduction steps of $[P_2Mo_{18}O_{62}]^{6-}$ have been reported so far even in neutral solutions where no protonation accompanies reduction. The difference of the electrochemical behavior between isostructural $[P_2Mo_{18}O_{62}]^{6-}$ and $[P_2W_{18}O_{62}]^{6-}$ has been rationalized on the basis of the chiral distortion of the former anion;[3,8,9] the former has the non-planar arrangement of the six Mo atoms in each equatorial position, while the latter has the planar arrangement.[10,11] It has been generally agreed that the one-electron reduction state is not attainable for the Dawson-type heteropolymolybdates, $[X_2Mo_{18}O_{62}]^{6-}$ (X=P, As).[3,4,9,12]

Recently, we have found that the 18-molybdo-2-sulfate anion, $[S_2Mo_{18}O_{62}]^{4-}$ exhibits four successive one-electron redox waves in CH_3CN.[13] In view of the results, previous explanations based on the chiral distortion of the Dawson anions are questionable, because the $[S_2Mo_{18}O_{62}]^{4-}$ anion has the same non-planar arrangement in the equatorial Mo ring as the $[P_2Mo_{18}O_{62}]^{6-}$ anion.[14] These considerations have prompted us to extend the voltammetric studies to the $[P_2Mo_{18}O_{62}]^{6-}$ and $[As_2Mo_{18}O_{62}]^{6-}$ anions with a view to elucidating the whole electrochemical properties of the Dawson anions. The present paper demonstrates the one-electron redox processes of all the Dawson-type heteropolymolybdate complexes studied.

Experimental

Voltammetric measurements were carried out with a microcomputer-controlled system.[15] A Tokai glassy carbon rod (GC-30S) with a surface area of 0.2 cm^2, being mounted in a Teflon® tube by means of silicone rubber tubing, was used as a working electrode. A platinum wire was used as the counter electrode and a Ag/Ag^+ (0.01 M; CH_3CN) electrode as the reference. The solutions were deoxygenated by bubbling nitrogen gas through them. Unless mentioned otherwise, the voltage scan rate was set at 100 mV s^{-1}. The measurements were made at 25±0.1°C. Controlled potential electrolysis was carried out with a Hokuto Denko Model HA-501 potentiostat equipped with a Model HF-202D coulometer. IR spectra were recorded with a Hitachi Model 270-30 spectrophotometer as KBr pellets.

All reagents were of analytical grade and were used as received.

Preparation of the Dawson Complexes. The tetrabutylammonium (n-Bu_4N^+) salts of the Dawson-type heteropolymolybdate complexes, $(n\text{-}Bu_4N)_4S_2Mo_{18}O_{62}$,[16,17] $(n\text{-}Bu_4N)_{5.5}H_{0.5}P_2Mo_{18}O_{62}$,[18] and $(n\text{-}Bu_4N)_5HAs_2Mo_{18}O_{62}$[18] were prepared and purified according to the previous methods. The Dawson complexes were referred to as the α-isomer. Figure 1 shows their IR spectra to characterize them.

Results and Discussion

One-Electron Redox Voltammetric Waves. $[S_2Mo_{18}O_{62}]^{4-}$: Figure 2 shows cyclic voltammograms of 0.5 mM ($M=\mathrm{mol\,dm^{-3}}$) $[S_2Mo_{18}O_{62}]^{4-}$ in CH_3CN containing 0.05 M Bu_4NClO_4. When the potential scan was made to a negative limit of −1.8 V, ill-defined oxidation waves were obtained on the reverse anodic scan (Fig. 2A). As shown in Fig. 2B, therefore, the present study was restricted to the first four redox waves with midpoint potentials (E_{mid}'s) of +0.172, −0.066, −0.718, and −0.986 V, where $E_{\mathrm{mid}}=(E_{\mathrm{pc}}+E_{\mathrm{pa}})/2$ (E_{pc} and E_{pa} are cathodic and anodic peak-potentials, respectively.). As reported recently, each wave corresponded to a reversible one-electron transfer.[13] For the sake of simplicity, the redox processes were ex-

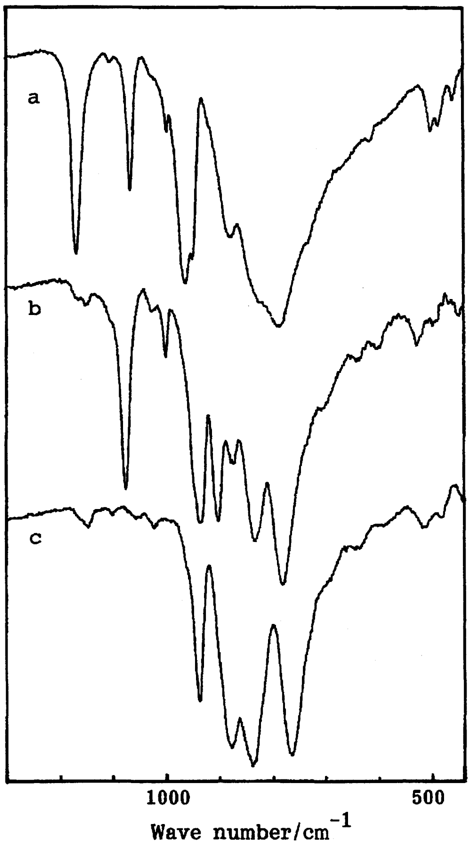

Fig. 1. IR spectra of (a) $(n\text{-}Bu_4N)_4S_2Mo_{18}O_{62}$, (b) $(n\text{-}Bu_4N)_{5.5}H_{0.5}P_2Mo_{18}O_{62}$, and (c) $(n\text{-}Bu_4N)_5HAs_2Mo_{18}O_{62}$ in the KBr pellets.

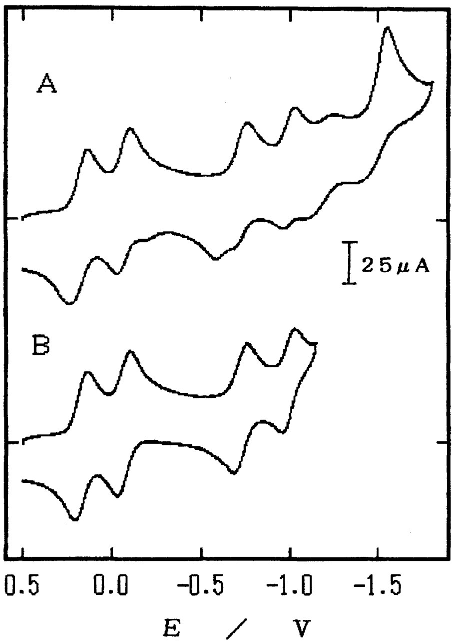

Fig. 2. Cyclic voltammograms of 0.5 mM $[S_2Mo_{18}O_{62}]^{4-}$ in CH_3CN containing 0.05 M Bu_4NClO_4. (A) the whole voltammogram; (B) the voltammogram restricted to the first four waves.

pressed as A(0/I), B(I/II), C(II/III), and D(III/IV), where the Roman numerals designate the number of electrons added to the oxidized anion(0).

The addition of water caused waves B, C, and D to shift in the positive direction while wave A did not change its potential location. It was found that the shift of E_{pc}'s was greater in the order $D \gg C > B$, indicating that the reduced anions with greater ionic charges are more strongly influenced by the presence of water. As the water content was raised, waves C and D became closer to each other; however, both waves were not merged in the presence of water in concentrations up to 10% (v/v).

$[X_2Mo_{18}O_{62}]^{6-}$ (X=P, As): It should be noted that the Dawson anions with P and As as the central heteroatoms bear greater negative charges, which give rise to the formation of the protonated salts such as $(n\text{-}Bu_4N)_{5.5}H_{0.5}P_2Mo_{18}O_{62}$ and $(n\text{-}Bu_4N)_5HAs_2Mo_{18}O_{62}$. It appears likely that the voltammetric behavior may be affected by the acidic proton in the salts of the Dawson anions. To confirm this, Fig. 3 illustrates cyclic voltammograms of 0.5 mM $[P_2Mo_{18}O_{62}]^{6-}$ in CH_3CN containing 0.05 M Bu_4NClO_4. Without addition of Bu_4NOH, as shown in curve (a), ill-defined distorted

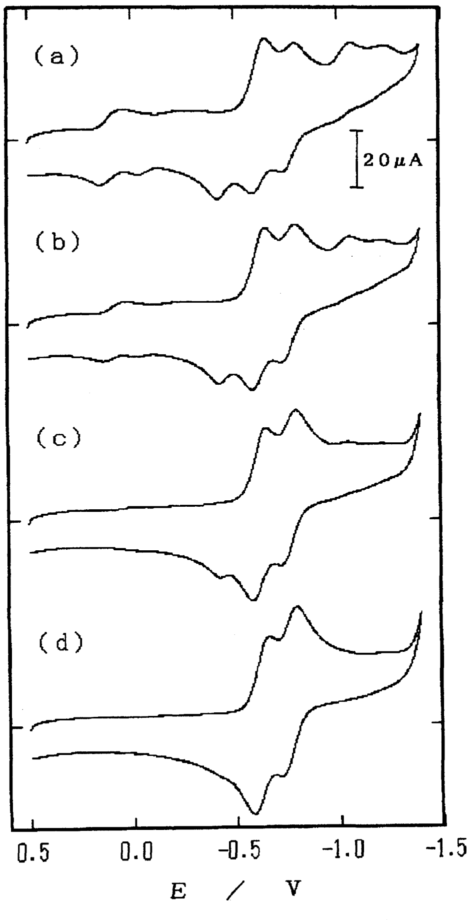

Fig. 3. Cyclic voltammograms of 0.5 mM $[P_2Mo_{18}O_{62}]^{6-}$ in CH_3CN containing 0.05 M Bu_4NClO_4. $[Bu_4NOH]$/mM: (a) none; (b) 0.1; (c) 0.2; (d) 0.25.

waves were observed. The increase of the Bu_4NOH concentration caused the voltammetric behavior to change gradually. In the presence of 0.25 mM Bu_4NOH, two well-defined redox waves were reproduced with E_{mid}'s of −0.60 and −0.73 V (curve (d)). Each current depended on the square root of the voltage scan rate (20—200 mV s^{-1}), indicating that the electrode process is diffusion-controlled. Coulometric studies showed that each reduction wave corresponded to a one-electron transfer. The E_{pc}'s and E_{pa}'s were independent of the voltage scan rate, indicating the reversible nature of each redox wave. With further addition of Bu_4NOH, however, the voltammogram became distorted again with a current decrease, suggesting the decomposition of the heteropolyanion.

For comparison, Fig. 4 shows the corresponding cyclic voltammograms of $[As_2Mo_{18}O_{62}]^{6-}$ in CH_3CN. As can be seen, $[As_2Mo_{18}O_{62}]^{6-}$ behaves in the same way as $[P_2Mo_{18}O_{62}]^{6-}$, exhibiting two reversible one-electron redox waves in the presence of 0.55 mM Bu_4NOH. Only differences are that the two redox waves are somewhat ill-separated. The E_{mid}'s of the one-electron redox waves were estimated to be −0.56 and −0.68 V. As shown in Figs. 3 and 4, the one-electron voltammetric waves of $[X_2Mo_{18}O_{62}]^{6-}$ (X=P, As) are very sensitive to the presence of traces of acid.

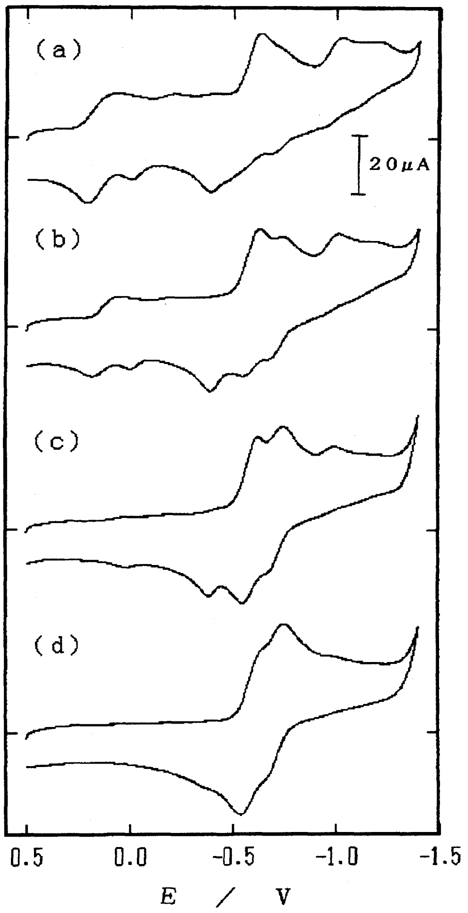

Fig. 4. Cyclic voltammograms of 0.5 mM $[As_2Mo_{18}O_{62}]^{6-}$ in CH_3CN containing 0.05 M Bu_4NClO_4. $[Bu_4NOH]$/mM: (a) none; (b) 0.2; (c) 0.4: (d) 0.55.

By controlled potential electrolysis at the one-electron reduction steps under the conditions of curves (d) in Figs. 3 and 4, both $[P_2Mo_{18}O_{62}]^{6-}$ and $[As_2Mo_{18}O_{62}]^{6-}$ produced mixed-valence blue species, in which the heteropoly skeletons were retained because the original yellow heteropolyanions were restored by the reoxidation at 0 V.

In the presence of water, the one-electron waves for $[X_2Mo_{18}O_{62}]^{6-}$ (X=P, As) tend to merge into a single wave, eventually giving rise to an apparent two-electron wave at the water content >5% (v/v). The one-electron waves were obtainable at the water content <3% (v/v).

From a comparison of the results in Figs. 2, 3, and 4, it follows that the one-electron reduction of the Dawson anions proceeds reversibly until the ionic charge on the reduced species becomes −8. In addition, the one-electron reduction of $[S_2Mo_{18}O_{62}]^{4-}$ occurs at more positive potentials than $[X_2Mo_{18}O_{62}]^{6-}$ (X=P, As), which is in line with the results that under conditions of no protonation, the first one-electron reduction potentials of $[XW_{12}O_{40}]^{n-}$ (n=3—7) become more positive as n decreases, showing a linear dependence on the ionic charge.[19] Under the conditions where protonation can accompany reduction, on the other hand, two one-electron waves merge into a single two-electron wave. Each two-electron reduction process causes no change of the ionic charge of the heteropolyanion owing to the protonation of the reduced form. In this case, the redox potentials are practically independent of the ionic charge on the heteropolyanions.[3,20]

Effect of Acid on the Voltammetric Behavior. $[S_2Mo_{18}O_{62}]^{4-}$: Upon stepwise addition of perchloric acid to the solution of Fig. 2B, new waves, denoted as E and F, appeared at the expense of waves B, C, and D. Simultaneously, additional waves K and K′ appeared and grew in height at more positive potentials than wave A. In the presence of 0.25 mM $HClO_4$, as discussed later, wave B disappeared completely while subsequent waves C and D remained (Fig. 5a). With further increase in the $HClO_4$ concentration, as shown in Fig. 5b, waves G and H developed with an increase in the height of waves K and F. At $HClO_4$ concentrations >0.6 mM, the original one-electron reduction waves, A—D disappeared completely, leaving five waves, K, E, F, G, and H. In the $HClO_4$ concentration range of 1.0—2.0 mM, another waves, L and M developed with disappearance of waves, E, F, G, and H (Figs. 5c and 5d). As shown in Fig. 5e, finally, the voltammogram exhibited four well-defined waves, K, L, M, and N of equal height at the $HClO_4$ concentration of 3.0 mM or more; the four waves were succeeded by ill-defined waves. Figure 6 shows the E_{pc}'s as a function of the $HClO_4$ concentration.

On the basis of our previous results,[17] each of the four reduction waves, K—N corresponded to a re-

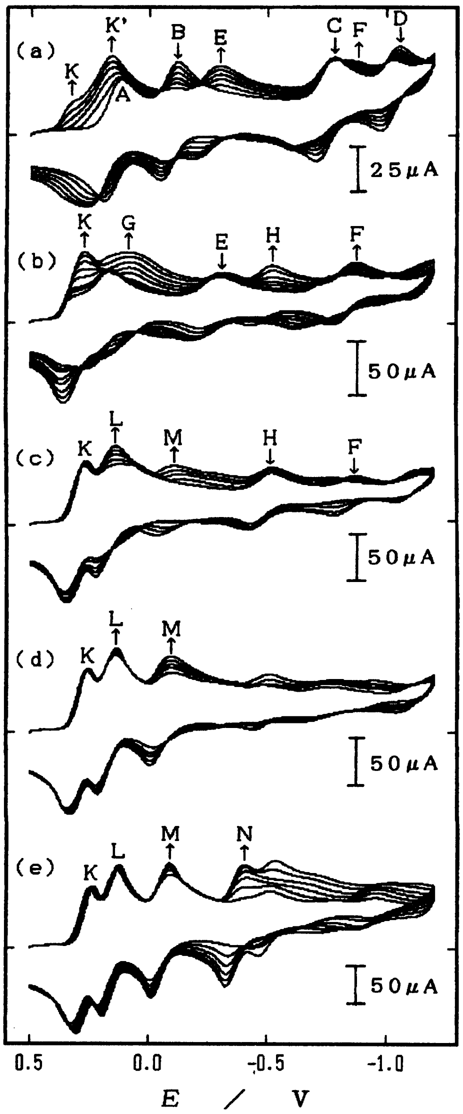

Fig. 5. Cyclic voltammograms of 0.5 mM $[S_2Mo_{18}O_{62}]^{4-}$ in CH_3CN containing 0.05 M Bu_4NClO_4. $[HClO_4]$/mM: (a) 0—0.25; (b) 0.3—0.9; (c) 1.0—1.4; (d) 1.5—1.9; (e) 2.0—3.0.

versible two-electron transfer with consumption of two protons. Thus, the four reduction waves can be expressed as $K(0/IIH_2)$, $L(IIH_2/IVH_4)$, $M(IVH_4/VIH_6)$, and $N(VIH_6/VIIIH_8)$, respectively, where symbols such as IIH_2, IVH_4, etc. denote protonated reduced anions. The 8-electron reduction species ($VIIIH_8$) accepts further electrons with decomposition. These results indicate that the decomposition of the Dawson anion is not responsible for the appearance of new waves, K′, E, F, G, and H. The observed behavior can be accounted for in terms of protonation insufficient to obtain the two-electron waves K—N.

A tentative explanation can be given on the basis of the following assumptions:

1) The one-electron reduction potentials become more positive as the ionic charge of the heteropolyanion decreases by protonation.

2) Two-electron reduction occurs under the conditions where protonation accompanies the electrode processes.

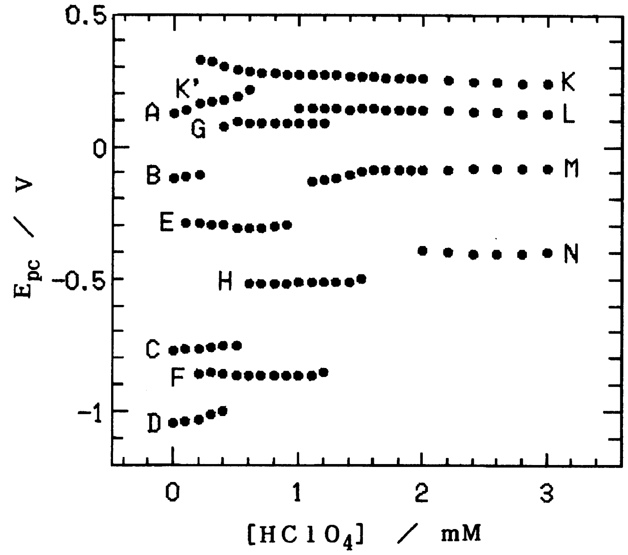

Fig. 6. E_{pc}'s for $[S_2Mo_{18}O_{62}]^{4-}$ as a function of the $HClO_4$ concentration.

It is difficult to ascertain the number of electrons corresponding to the reduction steps of waves E, F, G, and H. However, the cathodic-to-anodic peak separations for the waves averaged (70—90) mV, which suggests that each wave may correspond to irreversible one-electron reduction. In the presence of traces of acid, as shown in Fig. 5a, the reduction of the oxidized anion may proceed according to $K(0/IIH_2)$ and K′(0/IIH) instead of A(0/I), which explains the appearance of new waves at more positive potentials than wave A. As the results, wave B(I/II) disappears, leaving wave E(IIH/IIIH). In spite of the disappearance of wave B(I/II), however, succeeding waves C(II/III) and D(III/IV) are obtained. This observation can be accounted for by a disproportionation of species (IIIH) into species (II) and species (IVH_2); thus, wave F can be assigned as $F(IVH_2/VH_2)$. Under the conditions of Fig. 5b, wave $K(0/IIH_2)$ developed with appearance of

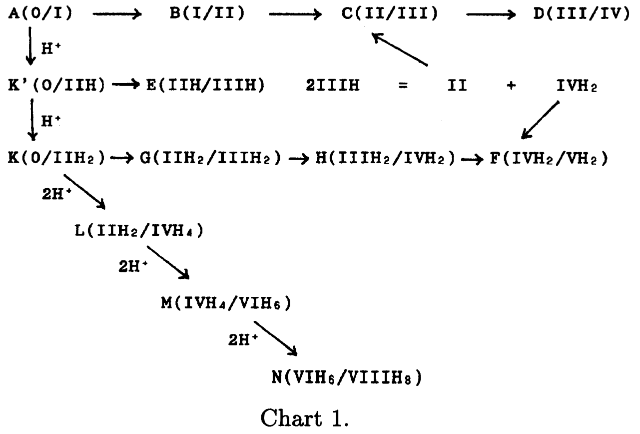

Chart 1.

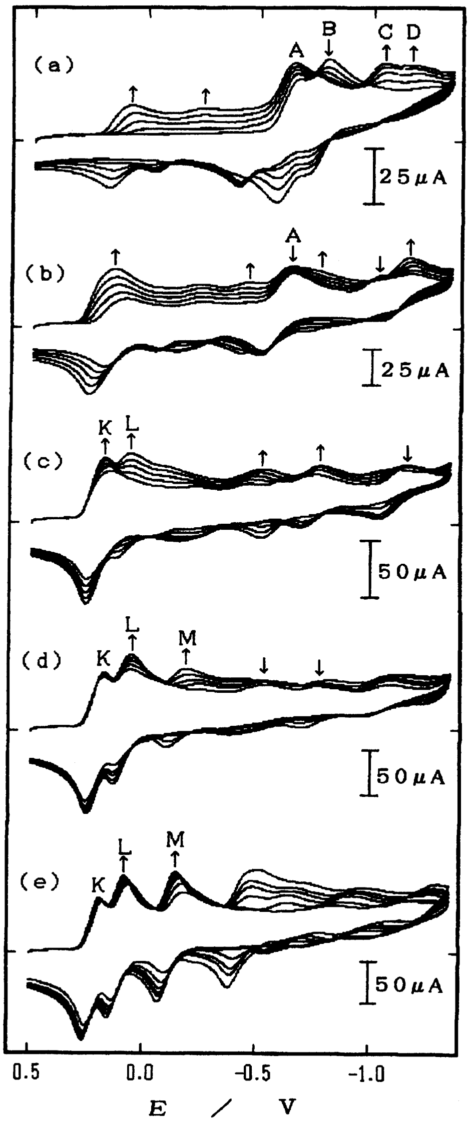

Fig. 7. Cyclic voltammograms of 0.5 mM $[P_2Mo_{18}O_{62}]^{6-}$ in CH_3CN containing 0.05 M Bu_4NClO_4+0.25 mM Bu_4NOH. $[HClO_4]$/mM: (a) 0—0.4; (b) 0.5—0.9: (c) 1.0—1.4; (d) 1.5—1.9; (e) 2.0—3.0.

waves G and H; wave F grew as well. In view of these observations, the electrode processes for waves G and H can be assigned as $G(IIH_2/IIIH_2)$ and $H(IIIH_2/IVH_2)$ followed by wave $F(IVH_2/VH_2)$.

A plausible reaction sequence is summarized in Chart 1.

$[X_2Mo_{18}O_{62}]^{6-}$ (X=P, As) : Figure 7 illustrates the effect of acid on cyclic voltammograms of 0.5 mM $[P_2Mo_{18}O_{62}]^{6-}$ in CH_3CN containing 0.05 M Bu_4NClO_4. Two one-electron reduction waves, which were obtained in the presence of 0.25 mM Bu_4NOH, were denoted as A(0/I) and B(I/II), respectively. With addition of $HClO_4$, the voltammogram was changed gradually, as shown in Figs. 7a, 7b, 7c, and 7d. However, the change was ill-defined compared to the behavior of $[S_2Mo_{18}O_{62}]^{4-}$. Therefore, no discussion was made on the electrode process of each wave. Finally, as shown in Fig. 7e, the voltammogram consisted of three well-defined waves, followed by a distorted wave. Each of the three waves corresponds to a reversible two-electron reduction with consumption of two protons; i.e., they can be denoted as $K(0/IIH_2)$, $L(IIH_2/IVH_4)$, and $M(IVH_4/VIH_6)$. It is known that the fourth distorted wave becomes a four-electron reduction wave in more strongly acidic solutions.[3—5)]

The characteristics of the voltammetric behavior of $[As_2Mo_{18}O_{62}]^{6-}$ are the same as those of $[P_2Mo_{18}O_{62}]^{6-}$ shown by the results in Fig. 7.

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