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Catalytic Effects of Chlorate Ions on the Electrode Reaction Processes of 12-Molybdophosphate and 12-Molybdosilicate

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Synopsis. The third cathodic waves corresponding to the reduction processes from the four-electron to the six-electron reduction products of both 12-molybdophosphate and 12-molybdosilicate are catalytic in nature in the presence of chlorate ions. The six-electron reduction product of 12-molybdophosphate is oxidized by chlorate ions more rapidly than that of 12-molybdosilicate.

It is well known that the reduction products of 12-heteropoly molybdates show a deep blue color, which are often called heteropoly molybdenum blue compounds, and that many workers applied the formation of heteropoly molybdenum blue compounds to the determination of traces of P^V, As^V, or Si^{IV} without the clarification of the properties of the heteropoly molybdenum blue compounds in detail.

The physicochemical properties of the heteropoly molybdenum blue compounds have been recently clarified by several workers by using various techniques.[1–4] On the other hand, the informations about the chemical reactivities of the heteropoly molybdenum blue compounds are still in scarcity, although such informations seem to be important to the application of the compounds as catalysis.

The authors, therefore, studied recently the electrochemical behaviors of 12-molybdophosphate and 12-molybdosilicate in water–dioxane mixed solutions, and found that the six-electron reduction product of the 12-molybdophosphate is more reactive for a homogeneous electron transfer reaction than that of 12-molybdosilicate.[5,6]

In the present paper are presented the results of a study of the effects of some inorganic anions on the electrode reaction processes of 12-molybdophosphate and 12-molybdosilicate at a thin-layer electrode cell.

Experimental

Materials. Sodium salts of 12-molybdosilicate and 12-molybdophosphate were obtained from Climax Molybdenum Co. and Wako Pure Chemical Ind., respectively. Other chemicals used were of analytical reagent grade. All solutions were prepared with twice-distilled water and deaerated with high-purity nitrogen.

Measurement. Voltammetric experiments were performed with a potentiostat (Hokuto Denko Co., HA 501) in connection with a function generator (Hokuto Denko Co., HB 104).

The thin-layer electrode was constructed by sandwiching a gold-minigrid (500 mesh; Buckbee-Mears Co.) between two glass slides. The electrochemical cell volume was 41.4 μl.

Standard procedures were used for a thin-layer voltammetric experiment.[7]

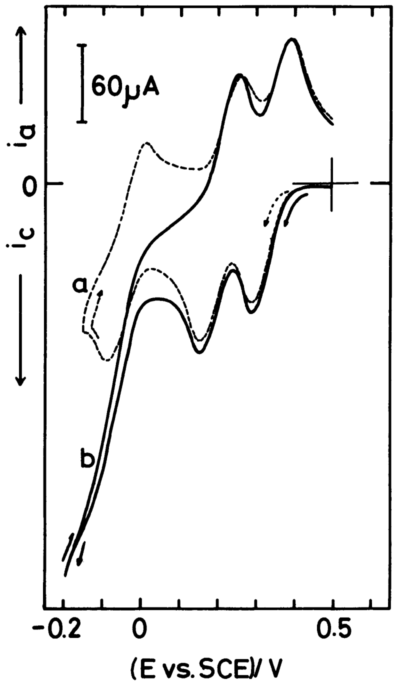

Fig. 1. Thin-layer cyclic voltammograms of 1.0×10^{-3} M 12-molybdophosphate in 50%(v/v) dioxane–water solutions containing 0.5 M H_2SO_4 at 22 °C. [$NaClO_3$]: (a) 0, (b) 0.05 M. Scan rate 2 mV s^{-1}; initial potential +0.500 V *vs.* SCE.

Results and Discussion

Typical thin-layer cyclic voltammograms of 12-molybdophosphate are given in Fig. 1. In the absence of chlorate ions, 12-molybdophosphate in 50% (v/v) dioxane-water solutions containing sulfuric acid exhibits three consecutive two-electron reversible waves in agreement with the results of the voltammetric studies at a platinum electrode.[8]

Most of the previous electrochemical investigations of heteropoly molybdates were carried out with sulfuric acid or hydrochloric acid as a supporting electrolyte. Nitrate and perchlorate were little used as a supporting electrolyte. This might be resulted from the consideration of the fact that nitrate and perchlorate oxidized the reduction products of some molybdenum(VI) complexes.[9,10] However, this study has shown that neither nitrate nor perchlorate ions do exhibit a catalytic effect on the electrode reaction processes of 12-molybdophosphate; the cathodic waves of 12-molybdophosphate was found to be little affected by the addition of nitrate or perchlorate ions.

On the other hand, chlorate ions gave a remarkable influence on the third cathodic wave, although the first two cathodic waves remained almost unchanged upon the addition of chlorate ions. In the presence of chlorate ions, the third cathodic wave exhibited a plateau rather than a peak and increased in height with an increase of chlorate ion concentrations. Moreover, the third anodic peak corresponding to the reoxidation of the six-electron reduction product disappears completely. These indicate that the third reduction wave of 12-molybdophosphate is catalytic in nature in the presence of chlorate ions.

The mechanism of this catalytic wave involves apparently regeneration of the four-electron reduction product of 12-molybdophosphate, which is supported by the disappearance of the third anodic peak. The controlled potential electrolysis was performed at the potential at which the catalytic current was observed in the presence of chlorate ions. The solution subjected to the electrolysis reacted with silver nitrate to yield the precipitates of silver chloride. This indicates that chlorate ions are reduced to chloride ions by the six-electron reduction product of 12-molybdophosphate.

According to these results, this catalytic wave can be explained by the sequence of the following reactions:

$$\mathrm{PMo^{V}{}_4Mo^{VI}{}_8O_{40}{}^{7-} + 2e^- \underset{fast}{\rightleftharpoons} PMo^{V}{}_6Mo^{VI}{}_6O_{40}{}^{9-}} \qquad (1)$$

$$\mathrm{3PMo^{V}{}_6Mo^{VI}{}_6O_{40}{}^{9-} + ClO_3{}^- + 6H^+ \longrightarrow 3PMo^{V}{}_4Mo^{VI}{}_8O_{40}{}^{7-} + Cl^- + 3H_2O} \qquad (2)$$

The cyclic regeneration of the electroactive four-electron reduction product of 12-molybdophosphate accounts for the enchancement of the reduction current.

The third cathodic wave of the cyclic voltammogram of 12-molybdophosphate in the presence of chlorate ions at a glassy carbon electrode was found also catalytic in nature. At scan rates larger than 20 mV s^{-1}, however, the third cathodic wave depended on the scan rate and the anodic wave corresponding to the third cathodic wave appears on the anodic scan. This indicates that the chemical reaction (Eq. 2) is relatively slow.

The same set of experiments was performed for 12-molybdosilicate. Typical cyclic voltammograms of 12-molybdosilicate are shown in Fig. 2. In the absence of chlorate ions, 12-molybdosilicate in 50% (v/v) dioxane–water solutions containing sulfuric acid also gave three two-electron reversible waves. Neither nitrate nor perchlorate ions exhibited a catalytic activity for the electroreduced 12-molybdosilicate.

In the presence of chlorate ions, the third reduction wave of 12-molybdosilicate, as shown by curve b in Fig. 2, was found to be catalytic in nature. However, it still exhibits a peak rather than a plateau. This appearance of peak may be due to a slow chemical reaction of the six-electron reduction product of 12-molybdosilicate and chlorate ions; chlorate ions can oxidize the six-electron reduction product of 12-molybdosilicate, but more slowly than that of 12-molybdophosphate.

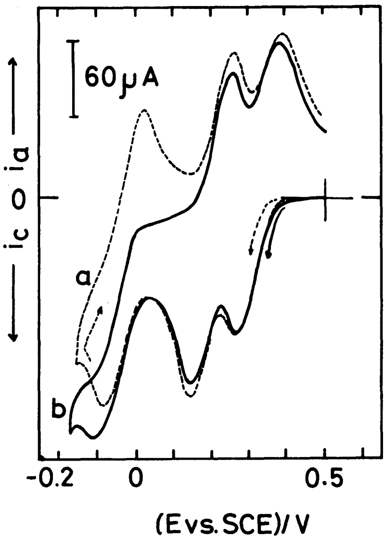

Fig. 2. Thin-layer cyclic voltammograms of 1.0×10^{-3} M 12-molybdosilicate in 50%(v/v) dioxane-water solutions containing 0.5 M H_2SO_4 at 22 °C. [$NaClO_3$]: (a) 0, (b) 0.05 M. Scan rate 2 mV s^{-1}; initial potential +0.500 V *vs.* SCE.

It is interesting to note that the reaction rate of the six-electron reduction product of 12-molybdosilicate for chlorate ions is slower than that of 12-molybdophosphate for chlorate ions. This could support the fact that the six-electron reduction product of 12-molybdophosphate is more reactive for a homogeneous electron transfer reaction than that of 12-molybdosilicate.$^{6)}$

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