# Voltammetric Characterization of α- and β-Dodecamolybdophosphates in Aqueous Organic Solutions

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**Synopsis.** The electrochemical properties of α- and β-dodecamolybdophosphates were characterized at the glassy carbon (GC) electrode. It was found that the β-isomer was only stable in neat organic solvents. When molybdophosphate was prepared in aqueous organic solutions, a mixture of α- and β-isomers formed.

It has been known that heteropolymolybdates known as Keggin anions exist in α- and β-modifications.[1,2] According to Halasz and Pungor,[3] the β-modification converts spontaneously into the α-modification for silico- and germanomolybdic acids while α-arsenomolybdic acid changes into the β-modification.

As for phosphomolybdic acid, the increase of the absorbance by the presence of water-miscible organic solvents has been accounted for in terms of the formation of the β-form.[4] It has been assumed that both α- and β-forms are stable and no isomerization occurs. Recently Hori and Fujinaga have obtained spectrophotometric evidence that the irreversible change of β-molybdophosphate into the α-form occurs in aqueous organic solvents.[5] However, the solution chemistry of the β-form is still obscure.

Electrochemical measurements have proved to be suitable for distinguishing clearly between both forms of molybdophosphate. The purpose of the present study is to characterize both isomers in aqueous organic solutions.

## Experimental

The electrochemical measurements were made with a PAR (Princeton Applied Research) Model 174-A polarographic analyzer and a computer-controlled voltammetry system.[6] The voltammograms were recorded on a Riken Denshi Model D-8CP X-Y recorder. Working electrodes were GC rods of 3 mm diameter (GC-30S, Tokai Carbon) which were mounted in a Teflon tube by means of silicone rubber tubing. A saturated calomel electrode (SCE) was used as a reference and a platinum wire as a counter electrode.

Ultraviolet(UV)-visible spectra were obtained with a Hitachi Model 220-A spectrophotometer equipped with a constant temperature housing for the cell. Electrochemical and spectrophotometric measurements were carried out at 25±0.1 °C.

β-$[(n\text{-}C_4H_9)_4N]_3PMo_{12}O_{40}$ was prepared by the method of Rocchiccioli-Deltcheff et al.[7] Phosphomolybdic acid, $H_3PMo_{12}O_{40}\,xH_2O$ was purchased from E. Merck. This acid is referred to as the stable α-compound. The anhydrous acid obtained by heating at 150 °C was used. For the sake of brevity, Keggin anions, $XMo_{12}O_{40}^{m-}$ will be designated as $XMo_{12}$ in the following, where X=P, Si, Ge, and As. All other reagents were of analytical grade and were used as received.

## Results and Discussion

**Electrochemistry of α- and β-$PMo_{12}$.** Figure 1(a) shows a cyclic voltammogram of $1.60\times10^{-4}$ M (M= mol dm$^{-3}$) α-$PMo_{12}$ in 80% (v/v) $CH_3CN$ containing 0.1 M HCl. Reduction waves were observed with peak potentials ($E_p$'s) of +0.25, +0.14, −0.10, and −0.29 V. The anodic peaks occurred at +0.27, +0.16, −0.08, and −0.25 V in the reverse scan.[8-11]

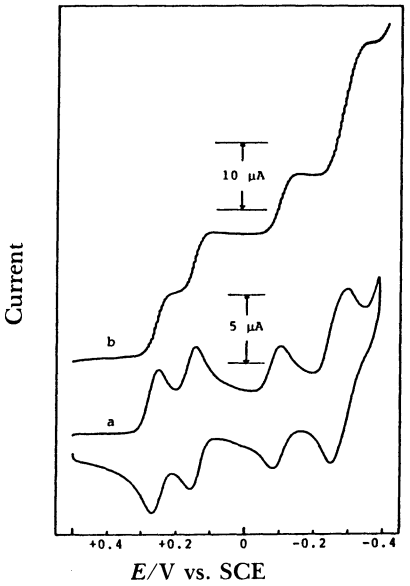


Fig. 1. A cyclic voltammogram (a) and a normal pulse polarogram (b) of $1.60\times10^{-4}$ M α-$PMo_{12}$ in 80% (v/v) $CH_3CN$ containing 0.1 M HCl. Scan rate, (a) 100 mV s$^{-1}$; (b) 10 mV s$^{-1}$.

For the reduction of $SiMo_{12}$, $GeMo_{12}$, and $AsMo_{12}$, the polarographic half-wave potentials ($E_{1/2}$'s) of the β-isomers are more positive than those of the corresponding α-isomers.[2] According to Fruchart and Souchay,[12] a four-electron reduction species of β-$PMo_{12}$ showed two oxidation waves with $E_{1/2}$'s of +0.55 and +0.37 V and a reduction wave with an $E_{1/2}$ of −0.07 V in 1 M $HClO_4$, while the oxidized form of α-$PMo_{12}$ showed four reduction waves with $E_{1/2}$'s of +0.36, +0.22, −0.01, and −0.15 V vs. SCE in 1 M $HClO_4$ containing 50% dioxane at a rotating platinum electrode. On the basis of their findings, it has been assumed that β-$PMo_{12}$ is electroreduced at more positive potentials than α-$PMo_{12}$. However, there have been no previous studies on the voltammetric behavior of the oxidized form of β-$PMo_{12}$.

Figure 2(a) shows a typical cyclic voltammogram of $1.68\times10^{-4}$ M β-$PMo_{12}$ in 80% (v/v) $CH_3CN$ containing 0.1 M HCl. The peak potentials for the cathodic waves are: +0.35, +0.25, −0.15, and −0.34 V while those for the anodic waves are: +0.38, +0.28, −0.12, and −0.27 V. Each wave is diffusion-controlled. Coulometric analysis showed that the first three waves corresponded to a

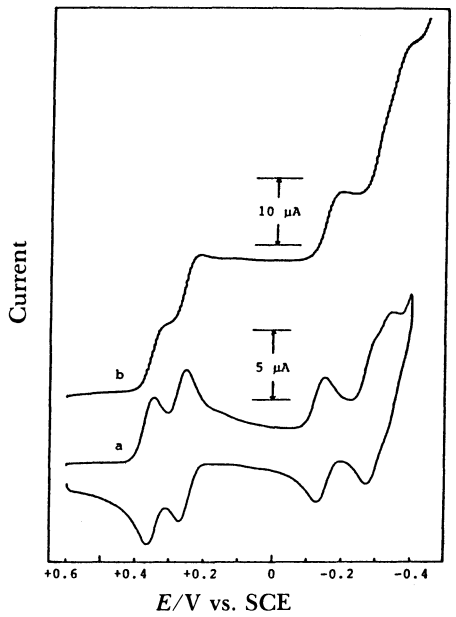


Fig. 2. A cyclic voltammogram (a) and a mormal pulse polarogram (b) of $1.68\times10^{-4}$ M $\beta$-$PMo_{12}$ in 80% (v/v) $CH_3CN$ containing 0.1 M HCl. Scan rate, (a) 100 mV $s^{-1}$; (b) 10 mV $s^{-1}$.

two-electron reduction and the fourth to a four-electron reduction. Curve (a) was obtained immediately after the addition of $\beta$-$PMo_{12}$ in the solution. When the solution was allowed to stand, a reduction wave with an $E_p$ of +0.14 V appeared. From a comparison with curve (a) of Fig. 1 it follows that $\beta$-$PMo_{12}$ changes gradually into the $\alpha$-form. It should be noted that the $E_p$ for the 1st wave of $\alpha$-$PMo_{12}$ is identical with that for the 2nd wave of $\beta$-$PMo_{12}$. Curves (b) in Figs. 1 and 2 show the corresponding normal pulse polarograms of $\alpha$- and $\beta$-$PMo_{12}$ in 80% (v/v) $CH_3CN$ containing 0.1 M HCl. Both polarograms resemble in shape and their limiting current ratios are 1 : 1 : 1 : 2, fitting the 2 : 2 : 2 : 4 electron ratios.

**Formation of $\alpha$- and $\beta$-$PMo_{12}$ in Aqueous Organic Solutions.** The yellow color of $PMo_{12}$ is enhanced by the presence of water-miscible organic solvents such as acetonitrile and acetone. Since the color enhancement has been used for the spectrophotometric determination of the orthophosphate ion, it seems important to clarify the properties of $\alpha$- and $\beta$-$PMo_{12}$ in aqueous organic solutions. Figure 3(a) shows a UV-visible spectrum of $4.2\times10^{-5}$ M $\beta$-$PMo_{12}$ in neat $CH_3CN$. The spectrum was unchanged under these conditions. In 70% (v/v) $CH_3CN$ solutions, on the other hand, the yellow color faded with time. Simultaneously, the gradual change of the spectrum was observed. Curve (b) is the spectrum of $\alpha$-$PMo_{12}$ obtained after standing for 3 h; as discussed below, the complete transformation of $\beta$-$PMo_{12}$ to $\alpha$-$PMo_{12}$ was confirmed by the voltammetric measurements. The oxidized form of each isomer shows a common absorption maximum at 308 nm. The molar absorption coefficients of $\alpha$- and $\beta$-$PMo_{12}$ at 420 nm are calculated as 990 and 2120 $cm^{-1}M^{-1}$, respectively. Since UV-visible spectra of $\alpha$- and $\beta$-forms are very similar, it is difficult to identify

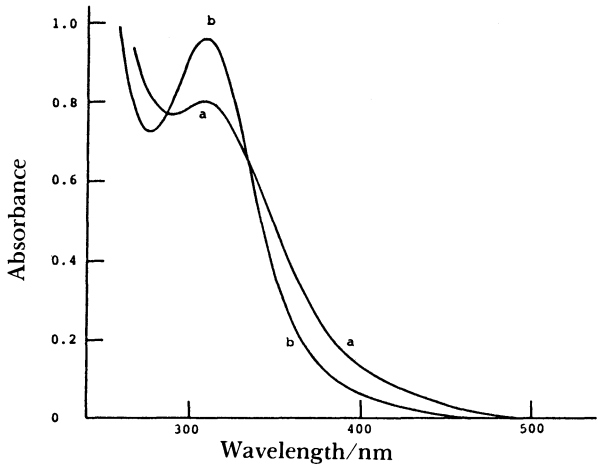


Fig. 3. UV-visible spectra of $4.2\times10^{-5}$ M $\alpha$- and $\beta$-$PMo_{12}$. (a) $\beta$-$PMo_{12}$ in neat $CH_3CN$; (b) $\alpha$-$PMo_{12}$ in 70% (v/v) $CH_3CN$. Path length, 1 cm.

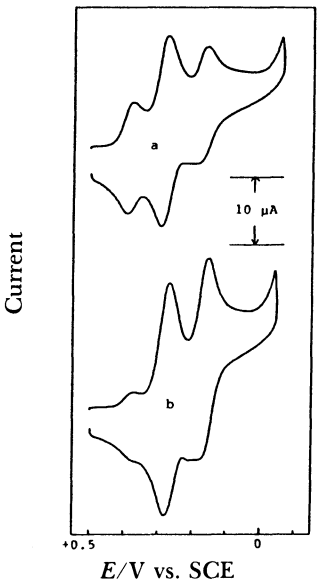


Fig. 4. Cyclic voltammograms of the 10.0 mM Mo(VI)/0.5 M HCl/40% (v/v) $CH_3CN$/0.5 mM phosphate system. (a) Immediately after the addition of phosphate; (b) 60 min after the addition of phosphate. Scan rate, 100 mV $s^{-1}$.

individual anions when both anions coexist in solution. As shown in Figs. 1 and 2, on the other hand, $\alpha$- and $\beta$-$PMo_{12}$ showed their characteristic reduction waves.

Therefore voltammetric measurements were made to elucidate the formation and conversion reactions of $\alpha$-and $\beta$-$PMo_{12}$ in aqueous organic solutions. Similar experiments were carried out with coulopotentiography.[13] An aliquot of 0.1 M phosphate solution was added to a 20 ml solution consisting of 10 mM Mo(VI)/0.5 M HCl/40% (v/v) $CH_3CN$, and the cyclic voltammogram was taken immediately after the addition of phosphate. As shown in Fig. 4(a), three reduction waves appeared with $E_p$'s of +0.37, +0.27, and +0.15 V until the final current rise due to the reduction

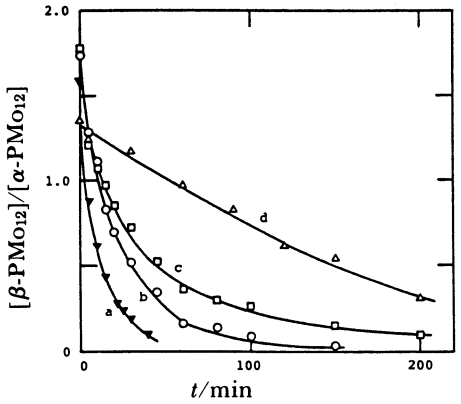


Fig. 5. Dependence of the ratio of [$\beta$-$PMo_{12}$] to [$\alpha$-$PMo_{12}$] on time for 50 mM Mo(VI)/0.5 M HCl/0.5 mM phosphate systems containing 40% (v/v) organic solvents; (a) ethanol, (b) acetonitrile, (c) 1,4-dioxane, (d) acetone.

of Mo(VI). The 1st and 2nd waves correspond to the reduction of $\beta$-$PMo_{12}$, and the 2nd and 3rd waves to the reduction of $\alpha$-$PMo_{12}$. When the solution was allowed to stand, as shown in curve (b) of Fig. 4, the 1st wave decreased with a simultaneous increase of the 3rd wave, which indicates the spontaneous conversion of $\beta$-$PMo_{12}$ to $\alpha$-$PMo_{12}$.

Normal pulse polarographic measurements were carried out in order to study the kinetics of the transformation of $\beta$-$PMo_{12}$ to $\alpha$-$PMo_{12}$ in aqueous organic solutions. Figure 5 shows the change of the ratio of [$\beta$-$PMo_{12}$] to [$\alpha$-$PMo_{12}$] with time for 50 mM Mo(VI)/0.5 M HCl/0.5 mM phosphate systems containing 40% (v/v) ethanol, acetonitrile, 1,4-dioxane, and acetone. The ratio of [$\beta$-$PMo_{12}$] to [$\alpha$-$PMo_{12}$] in solution was determined by measuring the limiting currents of the 1st and 2nd waves.[9] It was found that the transformation rate was the slowest in the acetone-containing solution. Kinetic analysis for the curves showed that the conversion reaction was of the first-order, and the rate constants were calculated as $7.6\times10^{-4}$, $3.3\times10^{-4}$, $1.9\times10^{-4}$, and $0.6\times10^{-4}$ $s^{-1}$ in solutions containing ethanol, acetonitrile, 1,4-dioxane, and acetone, respectively. As the concentrations of organic solvents were increased, the transformation rates became slower. However, the ratio of [$\beta$-$PMo_{12}$] to [$\alpha$-$PMo_{12}$] did not exceed 2 in solutions containing the organic solvents examined here. It should be emphasized that a mixture of $\alpha$- and $\beta$-$PMo_{12}$ is always obtained in aqueous organic solvents.

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