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An Infrared Study on the Reduction Processes of Dodecamolybdophosphates

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The reduction processes of dodecamolybdophosphoric acid and its potassium salt were investigated by infrared (ir) spectroscopy. The changes of ir bands were analyzed in detail as a function of the degree of reduction x (electron/anion) for the vapor phase reduction of the potassium salt with H_2 (A) and of the acid with cyclohexane and methacrolein (B) as well as for the liquid phase reduction of the acid with $SnCl_2$ solution (C) and with an electrochemical method (D). It was shown that reduction was initiated with the formation of 4 electron reduced polyanions in A and D while $2e$ reduction preceded the $4e$ state in B and C. It was commonly observed in all cases that, of the three bonding types of oxygen of polyanions, the bridging oxygen (O_b) had exclusive reactivity until $x = 4$ and the terminal oxygen (O_t) was consumed at $x > 4$. However, the actual reduction scheme was somewhat different between the vapor phase reduction (A and B) and the liquid phase reduction. Polyanions were deprived of oxygen in the former case while protons were introduced to them in the latter case. The introduced protons were bonded rather strongly and eliminated as water molecules at 200–420°C on heating. In connection with the difference of reduction processes in A and B, X-ray photoelectron spectroscopy measurements of the surface Mo^{5+} fraction revealed that in A the reduction took place almost homogeneously within each grain of the sample while in B the surface region was reduced in preference to the bulk. It is suggested that H_2 enters the pore of the crystal lattice reducing the whole grain homogeneously, but cyclohexane and methacrolein with larger molecular sizes reduce the grains by a surface reaction.

INTRODUCTION

Dodecamolybdophosphates have been known to be effective catalysts for many heterogeneous and homogeneous oxidation reactions (*1–5*). One of the remarkable features of the catalysts is their high selectivity in the oxidation of unsaturated aldehydes to corresponding acids, such as that of methacrolein to methacrylic acid (*1, 2, 6,*). There have been several reports on the catalytic activity and mechanism of the catalysts in the oxidation reactions (*7, 8,*). It has been accepted almost unanimously that the catalytic mechanism involves the redox cycles of the catalysts. However, little progress has been achieved in the understanding of actual redox process at a molecular level. Dodecamolybdophosphates contain large cluster anions called Keggin units (*9*). In its fully oxidized form, a Keggin unit possesses 40 oxygen atoms which are classified into three bonding types (*10*), i.e., 4 oxygen atoms which are bonded to central P^{5+} (O_p), 24 to 2 Mo^{6+} (O_b), and 12 to only 1 Mo^{6+} (O_t). How the chemical reactivity of oxygen depends on such a bonding type is of great importance in connection with the catalytic mechanism, as has already discussed with other Mo-containing catalysts (*11*). As for the investigation of 12-molybdophosphates, ir spectroscopy seems to be one of the most useful techniques. Tsuneki *et al.* (*12*) for the first time have applied this technique to the reduction of $Ag_3PMo_{12}O_{40}$ with H_2. They observed that characteristic ir bands involving O_b, unlike one for O_t, decreased with reduction and proposed that the O_b species should be consumed in the reduction. No quantitative analyses were presented, however, to ensure that the spectral change was ascribable to the actual

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removal of O_b. As is well known, ir band intensity does not always reflect the concentration of local sites. In a symmetry sensitive mode of vibration, for example, its intensity can disappear simply by deterioration of the symmetry even if the local sites are preserved. In order to pursue the reaction by ir spectroscopy it is very necessary to analyze the spectral changes quantitatively as far as possible. In this report, we have tried to reveal the reduction processes of 12-molybdophosphoric acid and its potassium salt under various conditions by mainly using ir spectroscopy.

EXPERIMENTAL

Dodecamolybdophosphoric acid ($H_3PMo_{12}O_{40}$) was prepared from MoO_3 and H_3PO_4, and its potassium salt was from $H_3PMo_{12}O_{40}$ and K_2CO_3 (*13*). These samples were reduced by various methods as follows. Vapor phase reduction of the potassium salt with H_2 (30 Torr) was carried out in a closed system in the temperature range 350–400°C for 3–50 h. The degree of reduction was monitored with an electrobalance (Cahn, Type RG) connected to the apparatus. The water formed during the reduction was condensed with a dry ice–EtOH trap and further completely removed by evacuation after reduction. The reduced sample showed no weight decreases on heating up to ca. 500°C *in vacuo* and was scarcely reoxidized in dry air at room temperature. The reduction of $H_3PMo_{12}O_{40}$ with cyclohexane (C_6H_{12}) and methacrolein (C_4H_6O) was carried out in a flow system at 360°C. A gaseous mixture of 3.0% C_6H_{12} (or C_4H_6O) and balance (helium) was fed at $W/F = 0.5\ g \cdot s/cm^{-3}$. The degree of reduction was determined by analyzing gaseous products by gas chromatography.

Liquid phase reduction of 12-molybdophosphoric acid was carried out either by using a reducing agent ($SnCl_2$) or by an electrochemical method. All the reduction procedure in the liquid phase was carried out in an N_2 atmosphere. In the former case, an aqueous solution of the acid (0.018 *M*) was mixed with calculated amounts of a $SnCl_2$ solution at 70°C. The pH of solution was controlled at 2 by addition of an HCl solution in order to precipitate tin(IV) hydroxide (*14*). The tin(IV) hydroxide was then removed off by centrifuge and filtration. The filtrate was crystallized by addition of 3 mol of KCl per mol of polyanion followed by evaporation at room temperature. In this method, the sample could be reduced up to an extent of 4 electron/anion at maximum. The electrolytic reduction of a 12-molybdophosphoric acid solution (0.34 *M*) was carried out in an H-type cell using cation-exchange membrane as a diaphragm. The potentials of a carbon cathode were controlled by a potentiostat (Hokuto Denko, HA-303) at 0.27 V for $0 < x < 2$, 0.10 V for $2 < x < 4$, −0.11 V for $4 < x < 6$, and −0.30 V for $6 < x$ vs an Ag/AgCl reference electrode. Here x stands for the degree of reduction in electron unit (*e*/anion) and it was determined from the passed electricity. The solution was then evaporated to dryness to crystallize the reduced product by evacuation at room temperature.

Infrared spectra of the reduced samples were recorded at room temperature using the KBr method. XPS spectra were recorded with Al$K\alpha$ radiation. Binding energies were referenced to the $Au_{4f\ 7/2}$ (83.8 eV) level of evaporated gold.

RESULTS

Vapor Phase Reduction of $(PMo_{12}O_{40})^{3-}$

Figure 1 shows ir spectra of the tripotassium 12-molybdophosphate samples reduced with H_2 to various extents (*15*). The degree of reduction (x) is defined as the number of introduced electrons or two times the number of removed oxygen atoms per Keggin unit. The unreduced sample (a) showed the ir bands corresponding to three bonding types of oxygen (*16, 17*), i.e., P–O_p (1065 cm^{-1}), Mo–O_t (960 cm^{-1}), and Mo–O_b–Mo (800 and 870 cm^{-1}). These bands are called O_p, O_t, and O_b band, respectively. With a progress of reduction,

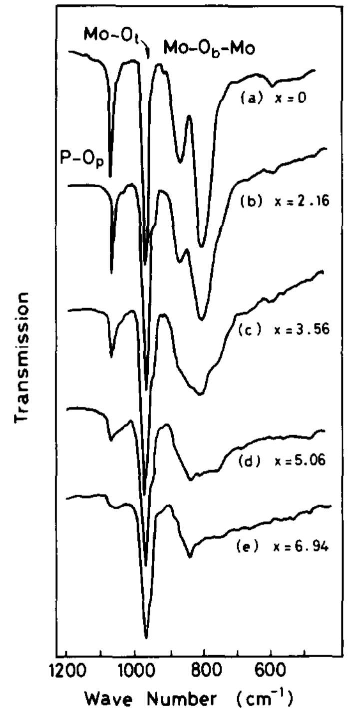


FIG. 1. Infrared spectra of tripotassium dodecamolybdophosphate reduced with H_2. x: Degree of reduction (e/anion).

the O_p and O_b bands were decreased and disappeared at $x > 4$. At $x > 4$, the O_b bands region was covered by new bands which were of totally different shape from the O_b bands. In contrast, the O_t band decreased with x only gradually being accompanied by band broadening.

The absorbance at each characteristic wave number is plotted as a function of x in Fig. 2. The absorbance at 1065, 870, or 800 cm^{-1} is denoted hereafter as A_p, A_{b1}, or A_{b2}, respectively, where the subscripts indicate the type of oxygen. As shown in the figure A_p decreased quite linearly with increasing x, to reach a ca. 10% level of the original value at $x = 4.2$. Linear decreases were also observed for A_{b1} and A_{b2}, where no corrections were made for overlapping with the new bands stated before: the true absorbances should be much smaller than the plots when x approaches to 4. On the other hand, the absorbance for the O_t band showed a contrasting reduction behavior. It decreased only gradually with increasing x. As the decrease was coupled with the band broadening, it would be more adequate to use the integrated absorbance (denoted as A_t) instead of the conventional absorbance for quantitative discussion. A_t was kept constant in the early stage of reduction, while a gradual decrease was observed at $x > 3$.

Similar measurements were extended to the reduction of 12-molybdophosphoric acid with cyclohexane or methacrolein in a flow system. The main gaseous products were benzene (80 ~ 90%) and CO + CO_2 (10 ~ 20%) in the cyclohexane reduction while methacrylic acid (30 ~ 40%), CO + CO_2 (60 ~ 70%), and a small amount of acetic acid were produced in the methacrolein reduction. The results for the cyclohexane reduction are shown in Fig. 3. At the early stage of reduction ($x < 1$), A_p, A_{b1}, and A_{b2} decreased linearly with increasing x while A_t was kept constant. In this case, however, A_p, A_{b1}, and A_{b2} decreased with

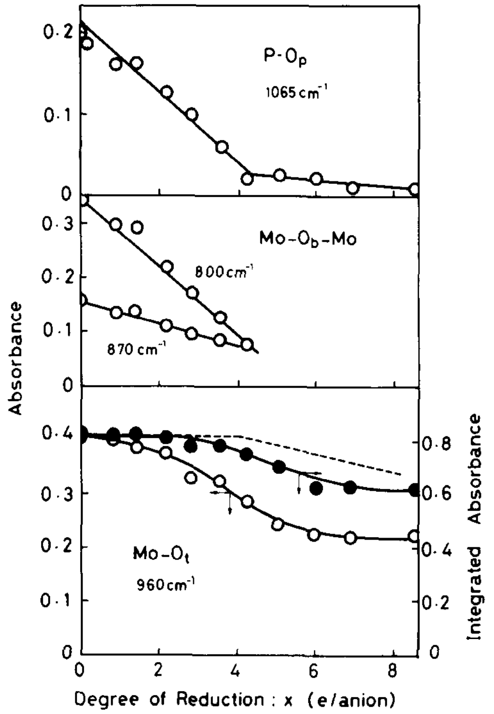


FIG. 2. Changes of the ir band intensities of heteropolyanion with the degree of reduction with H_2.

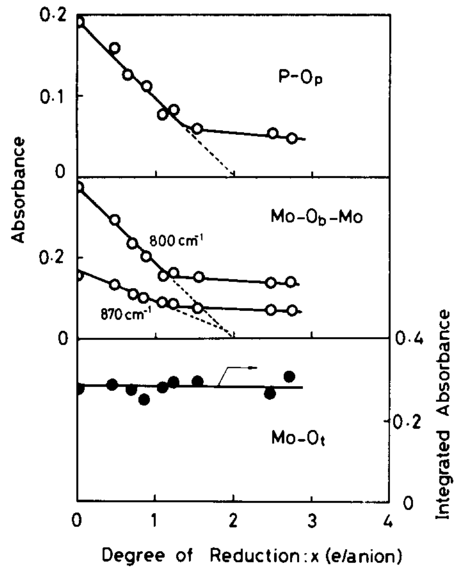


FIG. 3. Changes of the ir band intensities with the degree of reduction with cyclohexane.

slopes which were almost twice as steep as those in Fig. 2, their extrapolations intersecting the abscissa at ca. $x = 2$. Quite similar behavior was observed in the methacrolein reduction.

Liquid Phase Reduction of $(PMo_{12}O_{40})^{3-}$

In order to compare with the vapor phase reduction, heteropoly acid was reduced in liquid phase. The homogeneous reduction with $SnCl_2$ was first investigated. The degree of reduction was controlled by the amount of added $SnCl_2$. Figure 4 shows the absorbances of the characteristic ir bands for a series of reduced samples. The behavior of each band was basically the same as observed in the vapor phase reduction with cyclohexane (Fig. 3). At the early stage of reduction ($x < 2$), A_p, A_{b1}, and A_{b2} decreased linearly with increasing x, becoming weak or almost disappearing at $x = 2$. At $2 < x < 4$, the A_{b1} and A_{b2} decreased with far smaller slopes making inflection points at $x = 2$. In the O_p-band region, a weak band at 1055 cm^{-1}, which became apparent at $x = 2$ in place of the original O_p band, decreased gradually with increasing x. The integrated absorbance (A_t) of the O_t band remained constant at $0 < x < 4$.

The results of the electrochemical reduction of $H_3PMo_{12}O_{40}$ are shown in Fig. 5. The reduction behavior of the ir bands was clearly different from that in the $SnCl_2$ reduction just mentioned (Fig. 4), and resembled that in the H_2 reduction of the potassium salt (Fig. 2). It is noted that, in spite of the variation of the applied electrode potential with x, the spectral changes are quite sharp and well defined. A_p, A_{b1}, and A_{b2} linearly decreased to disappear at $x = 4$, while A_t began to decrease at $x = 4$ with a slope of $-A_t^0/12$ per introduced electron where A_t^0 denotes the integrated absorbance at $x = 0$.

Dehydration of Reduced Dodecamolybdophosphoric Acid

It is well known that the reduction of oxides at low temperature often proceeds not by eliminating the oxidic oxygen but by adding protons and electrons to the oxides. In order to examine whether the liquid phase reduction just mentioned follows this scheme, the dehydration behavior of electrochemically reduced samples was investi-

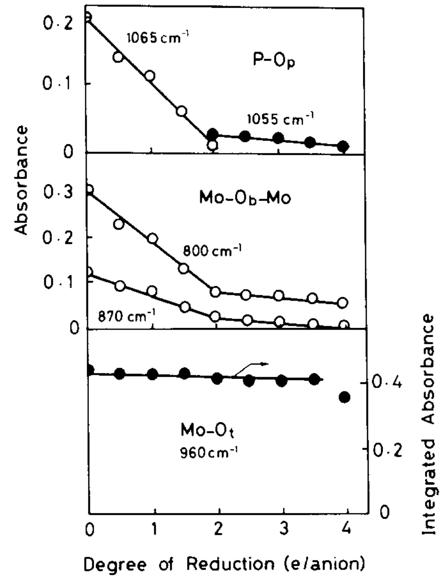


FIG. 4. Changes of the ir band intensities with the degree of reduction with $SnCl_2$.

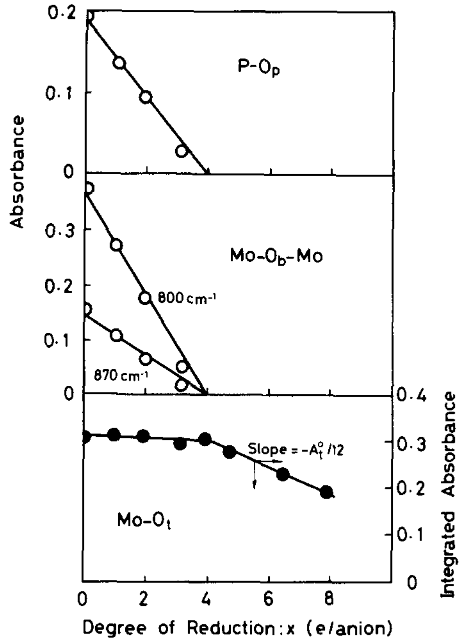


FIG. 5. Changes of the ir band intensities with electrochemical reduction.

gated by thermal gravimetry (TG). Figure 6 shows the TG curves of an unreduced and a reduced one ($x = 6.4$). The samples were heated at 6°C/min *in vacuo* after evacuation at room temperature. Both samples were dehydrated roughly in two steps. The first step, which corresponds to the elimination of water of crystallization as we reported previously (*18*), terminated below 150°C. The second step was observed in the temperature range 200–420°C, above which the samples were completely dehydrated. In differential thermal analyses each sample showed an exothermic peak at 420°C which was ascribable to the decomposition of the polyanion structure.

The amount of water desorbed in the second step was found to change with the degree of reduction as plotted in Fig. 7. The unreduced sample ($x = 0$) released 1.5 H_2O molecules per polyanion as estimated from the formula $H_3PMo_{12}O_{40}$. The desorbed water increased linearly with increasing x going through maximum 3.5 H_2O molecules/anion at $x = 4$. This behavior indicates not only that protons and electrons are introduced to $H_3PMo_{12}O_{40}$ but also that the introduced protons behave very much like the protons possessed by the unreduced sample, as will be discussed later.

XPS Analyses of Reduced Samples

In conjunction with above studies, valence states of metal cations in the reduced samples were investigated by XPS. Two series of samples were used, i.e., the potassium salt samples reduced with H_2 (series I) (*15*) and the heteropoly acid samples reduced with C_6H_{12} (series II). In both series the binding energy for P_{2p} level (133.4 eV) was unchanged irrespective of reduction, confirming that the valence state of P^{5+} was kept during the reduction. The Mo_{3d} region for the unreduced sample consisted of a

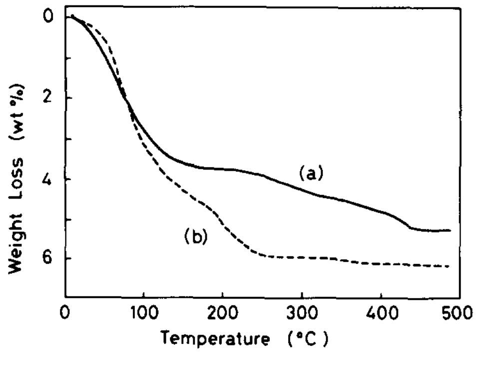


FIG. 6. TG curves of (a) unreduced and (b) reduced (6.40*e*/anion) 12-molybdophosphoric acid.

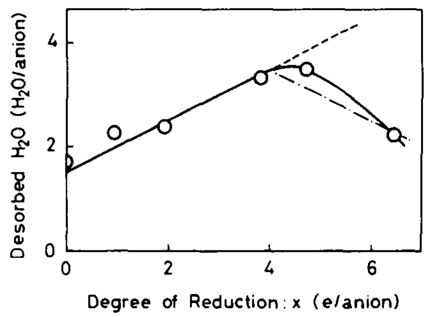


FIG. 7. The amounts of H_2O desorbed in the 2nd dehydration step for electrochemically reduced samples. Expected values from (---) Eq. (4), (–·–) Eq. (6).

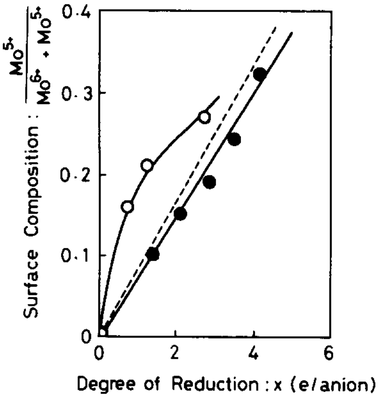


FIG. 8. XPS analyses of reduced samples. (---) Calculated, (●) reduced with H_2, (○) reduced with C_6H_{12}.

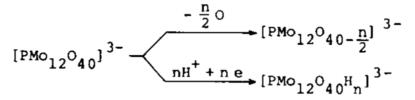
doublet, $Mo_{3d\ 5/2}$ (232.4 eV) and $Mo_{3d\ 3/2}$ (235.5 eV) in agreement with the reported values for Mo^{6+} (*19*). These signals were broadened on reduction because of an overlap of the signals from lower valent Mo ions. Spectral deconvolution revealed the overlapping of a doublet of $Mo^{5+}_{3d\ 5/2}$ (231.3 eV) and $Mo^{5+}_{3d\ 3/2}$ (234.4 eV) (*19*). The formation of Mo^{4+} was detected only when the samples were reduced extensively, e.g., to $x = 8.54$.

The fractions of Mo^{5+} in total Mo ions were estimated from the deconvoluted spectra. The surface fractions of Mo^{5+} thus obtained for both series are plotted as a function of x in Fig. 8. The broken line in the figure represents an ideal case where the reduction of Mo^{6+} to Mo^{5+} takes place statistically throughout the whole bulk of the samples. The Mo^{5+} fraction in series I increased linearly in fair agreement with the ideal case, while that in series II, deviated upward from the ideal case especially at lower degrees of reduction. It is thus indicated that, in series II, the surface region of $H_3PMo_{12}O_{40}$ particles was reduced in preference to the bulk.

DISCUSSION

Reduction Behavior of ir Bands

The ir spectral changes of heteropoly anions with reduction appear to be very informative. First we propose a schematic model for the heteropoly anion reduction (Fig. 9). It is assumed that each anion is reduced by n electrons in the initial step before it is further reduced in the subsequent steps.



$$[PMo_{12}O_{40}]^{3-} \begin{cases} \xrightarrow{-\frac{n}{2}O} [PMo_{12}O_{40-\frac{n}{2}}]^{3-} \\ \xrightarrow{nH^+ + ne} [PMo_{12}O_{40}H_n]^{3-} \end{cases} \quad (1)$$

The degree of reduction (x) obtained experimentally is a macroscopic average for the whole sample, and at $0 < x < n$ should be a mixture of the unreduced and the *ne* reduced polyanions. Available information on the reduction steps is limited for liquid phase reduction. Polarographic reduction of $(PMo_{12}O_{40})^{3-}$ proceeds stepwise by an introduction of 2 electrons because anions with $n = 1, 3, 5, \ldots$ are unstable (*20, 21*). As another example, the Keggin anion of tungsten, $(H_2W_{12}O_{40})^{7-}$, introduces electrons by a multiple of 6, i.e., $n = 6$, 12, and 24 (*22*). As shown in Eq. (1), the molybdophosphate anions are reduced either by releasing oxygen atoms or by accepting protons and electrons. Recently, Misono *et al.* (*7, 23*) reported that the oxygen vacancies are produced successively by dehydration of polyanions with the introduced pro-

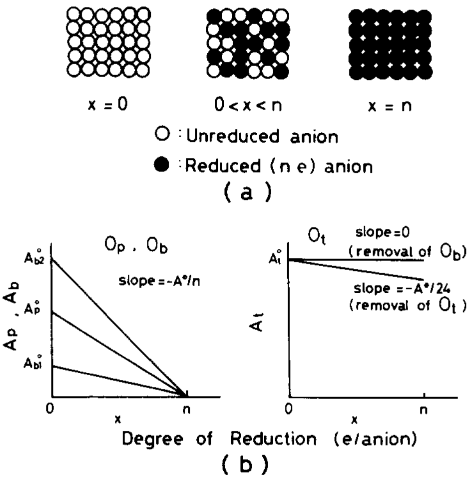


FIG. 9. A schematic model for the reduction of heteropolyanions via *ne* reduced intermediates (a) and the corresponding behavior of ir spectra on reduction (b).

tons during vapor phase reduction of 12-molybdophosphoric acid with H_2 even at 250°C.

In the unreduced polyanion, O_p and O_b atoms are coordinated to more than one metal cation, forming a highly symmetric Keggin unit. The ir bands characteristic of these oxygen atoms must be very sensitive to the changes of anion symmetry and will be extinguished when the anion symmetry is deteriorated with reduction. Lyhamn *et al.* (*17*) have reported that the O_p band (1065 cm^{-1}) and the O_b band (870 cm^{-1}) are ascribable to vibrational modes of a polyanion with T_d symmetry. This confirms that these bands are symmetry sensitive and appear only when the polyanion possesses the highest symmetry. Although the identification of the other O_b band (800 cm^{-1}) is ambiguous in their report, present observation strongly suggests that this band is also very symmetry sensitive. This means that A_p, A_{b1}, and A_{b2} should be proportional to the concentration of the unreduced anions, because reduction inevitably results in deterioration of the anion symmetry. When an *ne* reduction step takes place as assumed above, each absorbance will decrease linearly with increasing x up to $x = n$ at a slope of $-A°/n$, where $A°$ is the absorbance at $x = 0$ as illustrated in Fig. 9, and thus we can estimate n from the slope.

On the other hand, the terminal oxygen O_t is bonded to a single Mo ion. The O_t band at 960 cm^{-1}, which is ascribed to a stretching vibration of Mo–O_t, is not sensitive to deterioration of the anion symmetry except for possible band broadening or shifting. The integrated absorbance, A_t, should reflect the concentration of O_t, and decrease only when O_t consumed. As 12 O_t atoms are possessed by a heteropolyanion, the A_t vs x plots will decrease at a slope of either $-A_t^°/24$ or $-A_t^°/12$ depending on whether O_t atoms are removed or are attached with protons in reduction. Thus on the basis of reduction behavior of the O_t band, one can judge which oxygen, O_t or O_b, is actually reactive in the reduction.

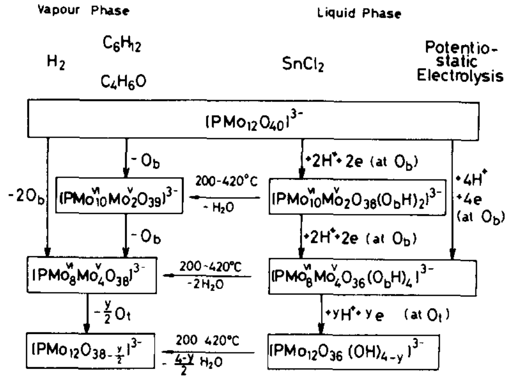


FIG. 10. Reduction processes of 12-molybdophosphate anion.

That is, if O_t is reactive A_t will decrease together with A_p, A_{b1}, and A_{b2}, whereas if O_b is reactive only A_t will remain unchanged. Consumption of O_p is ruled out because it is located deep inside the anion.

Paths of Vapor Phase Reduction

On the basis of the above considerations, we tried to elucidate the reduction paths of heteropolyanions from the ir spectral changes. The reduction paths thus estimated are summarized in Fig. 10. The details are briefly described below. In the reduction of $K_3PMo_{12}O_{40}$ with H_2 (Fig. 2), A_p changed with x at a slope of $-A_p^°/4.2$. The behavior of A_{b1} and A_{b2} was less accurate because of the band overlapping. From such behavior, we conclude that each heteropolyanion is first converted to a 4*e* reduced state. Furthermore, the reduction proceeds by losing two O_b atoms per anion since A_t remains constant at $0 < x < 3$. A_t decreased at $x > 4$ with a slope roughly equal to $-A_t^°/24$. This suggests that the 4*e* reduced intermediate loses O_t atoms in further reduction. The slight deviation of the actual results from this scheme are probably due to partial heterogeneity in gas–solid reaction.

In the reduction of $H_3PMo_{12}O_{40}$ with C_6H_{12} (Fig. 3) or C_4H_6O, the initial decreases of A_p, A_{b1}, and A_{b2} with x are twice as steep as those in the foregoing case. This indicates that the reduction is initiated with the formation of $2e$ reduced polyanions. The appearance of inflections in the absorbance plots at $x < 2$, however, suggests that the heterogeneity of reduction is more significant in this case. The constancy of A_t assures the consumption of O_b atoms in this region. As mentioned above, the reduction of $K_3PMo_{12}O_{40}$ with H_2 produces $4e$ reduced intermediates while that of H_3P $Mo_{12}O_{40}$ with C_6H_{12} or C_4H_6O does $2e$ intermediates. The absence of $2e$ intermediates in the former case suggests that the $2e$ intermediates are not stable enough or they are reduced to $4e$ states very rapidly. This difference seems to be important from a catalytic point of view. Although the reason for it is not clear at present, it is felt that the difference is deeply associated with the kind of substrate. As evidenced by XPS, the surface Mo^{5+} fractions in the H_2 reduction of the potassium salt were in good agreement with the expected values. This confirms not only that two Mo^{5+} are produced per removed oxygen atom but also that the reaction takes place rather homogeneously inside each particle of the samples. In the C_6H_{12} reduction of the acid sample, however, the Mo^{5+} fractions are higher at the surface than in the bulk, indicating that the reduction proceeds heterogeneously from the surface to the bulk. The crystal lattice of potassium salt at elevated temperatures has micropores produced by dehydration (*18*). Such pores may also be produced in the acid sample, though the sample is no longer crystalline at elevated temperatures. We assume that H_2 molecules are small enough to come in the pores of the potassium salt, reducing the polyanions homogeneously. In contrast, C_6H_{12} or C_4H_6O molecules may be too large so that the reduction with them proceeds by surface reaction to which oxygen is supplied from the bulk by diffusion. Such a situation is considered to have some connection with the observed difference in reduced intermediate, but further investigation is needed to elucidate it.

Paths of Liquid Phase Reduction

The behavior of ir bands in the liquid phase reduction is basically the same as in the vapor phase reduction, but the changes are obviously sharper since the reduction apparently proceeds homogeneously. The formation of $2e$ reduced intermediate in the $SnCl_2$ reduction is clearly evidenced by the behavior of O_p and O_b bands (Fig. 4). It is noted that the O_p band is replaced by a new weak band, and again decreases with increasing x. It is tentatively ascribed to a vibration of PO_4 with lower symmetry. The preferential reactivity of O_b atoms at $x < 4$ is also obvious from the constancy of A_t.

The electrochemical reduction produces $4e$ reduced intermediates again by the reaction of O_b (Fig. 5). It is worth noting that the redox reaction

$$[PMo_{12}O_{40}]^{3-} + [PMo_{12}O_{36}(O_bH)_4]^{3-} \rightarrow 2[PMo_{12}O_{38}(O_bH)_2]^{3-} \quad (2)$$

is negligibly slow owing to its high activation energy. Only when x exceeds 4, O_t becomes reactive. In the hydrated forms, the reduction obviously proceeds by an introduction of protons and electrons as follows.

$$[PMo_{12}O_{36}(O_bH)_4]^{3-} + yH^+ + ye \rightarrow [PMo_{12}O_{36-y}(O_bH)_4(O_tH)_y]^{3-} \quad (y = x - 4) \quad (3)$$

This can be confirmed from the twice as steep decrease of O_t, $-A_t^0/12$, at $x > 4$ as that for the vapor phase reduction.

As mentioned above, the liquid phase reduction gave different intermediate depending on the reduction methods, i.e., $2e$ intermediates in the $SnCl_2$ reduction and $4e$ intermediates in the electrochemical reduction. According to the polarographic study of Tsigdinos (*20*), $H_3PMo_{12}O_{40}$ is consecutively reduced by 2 electron steps in 1 *M* H_2SO_4 (1 : 1 water-dioxane) solution at +0.31, +0.18, −0.065, −0.22 V vs SCE. Present condition for $SnCl_2$ reduction is well within the range to reduce $(PMo_{12}O_{40})^{3-}$ anion by $2e$ steps to $4e$ anion. As for the electrochemical reduction, the highest potential applied is also ranges to 4e reduction. Higher potential could not be used practically because the rate became too small. It is considered that each polyanion arriving at the electrode surface is reduced up to 4e reduced state before going back into the solution.

Dehydration from the Reduced $H_3PMo_{12}O_{40}$ Samples

In contrast to the vapor phase reduction at high temperatures, the liquid phase reduction is known to introduce protons and electrons to the polyanion (*21*) as stated before. The thermal behavior of reduced polyanions, i.e., the desorption of water and the successive formation of oxygen vacancies, has not been reported. The water desorption from the reduced samples occurred in two steps. The desorbed amount in the second step increased linearly with x in coincidence with the following reaction as shown in Fig. 7.

$$H_3PMo_{12}O_{40-x}(O_bH)_x \xrightarrow{\text{2nd step}} PMo_{12}O_{38.5-\frac{x}{2}} + \frac{3+x}{2} H_2O \qquad (x \leq 4) \quad (4)$$

This means that the introduced protons behave very much like the three acidic protons possessed by the polyanion from the beginning. At $x > 4$, the amount of desorbed water at the second step decreased with increasing x (Fig. 7). It seems that when protons are introduced in excess of 4 a part of them are desorbed as water molecules in the first step, only the remaining protons undergoing dehydration at the second step. The following scheme is conceived from the dehydration behavior at $x > 4$.

$$H_3PMo_{12}O_{36}(O_bH)_4(O_tH)_y \xrightarrow{\text{1st step}} H_3PMo_{12}O_{36}(OH)_{4-y} + yH_2O \quad (5)$$

$$H_3PMo_{12}O_{36}(OH)_{4-y} \xrightarrow{\text{2nd step}} PMo_{12}O_{38.5-\frac{4+y}{2}} + \frac{7-y}{2} H_2O \qquad (y = x - 4) \quad (6)$$

CONCLUSION

The present investigation has shown that ir spectroscopy is very effective to reveal the reduction processes of 12-molybdophosphates at a molecular level. It is emphasized that the reduction of polyanions in both vapor phase and liquid phase went through well-defined intermediate polyanions which were reduced by 2 or 4 electrons. That is, 2e intermediates were formed in the reduction of 12-molybdophosphoric acid with cyclohexane, methacrolein, and $SnCl_2$, while 4e intermediates were produced in those of the potassium salt with H_2 and of the acid with the electrochemical method. This assures that polyanions are reduced in regular manners.

The actual schemes of reduction were found to differ between vapor phase reduction and liquid phase reduction. The heteropolyanions were deprived of oxygen atoms in the former while it received protons and electrons in the latter. The introduced protons in the latter were found to behave very much like the acidic protons possessed by the unreduced sample of 12-molybdophosphoric acid. This suggests a possibility that the acidity of 12-molybdophosphates may change with the reduction.

As for how the reduction proceeds within individual grains of the solid samples in the vapor phase reduction, interesting information was obtained by XPS. That is, the surface and bulk of grains were reduced rather homogeneously in the H_2 reduction of the potassium salt, the surface part was preferentially reduced in the cyclohexane or methacrolein reduction of the acid. It is suspected that this difference may arise from whether the reductant molecules are small enough to enter the micropores of the grains. However, further study is needed to know the real reason for this phenomenon. In fact, there was a remarkable regularity in the reactivity of oxygen within a heteropolyanion, despite the differences of the actual reduction schemes under various conditions. It was shown in all cases that the bridging oxygen atoms (O_b) were exclusively reactive until the degree of reduction (x) reached the level of 4e/anion, while the terminal oxygen atoms were consumed at $x > 4$. This finding not only provides an interesting example where the reactivity of oxygen depends very sensitively upon the bonding types but also appears to be very important from a viewpoint of redox mechanism of this system.

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