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Catalysis by Heteropoly Compounds

V. The Reduction Mechanism of $H_3PMo_{12}O_{40}$[1]

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The reduction mechanism of heteropoly compounds of molybdenum and tungsten as well as the behavior of water contained in them was investigated. Stoichiometry of reduction by H_2 and reoxidation by O_2, together with the variation of ir and ESR spectra upon reduction, confirmed that the reduction of $H_3PMo_{12}O_{40}$ proceeded in two steps. In the first step, a hydrogen molecule dissociates into protons and electrons, the latter being trapped by molybdenum atoms. Both protons and electrons migrate rapidly throughout the whole bulk. In the second step, protons react with bridging oxygen atoms of heteropoly anion and are evolved as water. The anion structure is maintained in the first step, while it is partially destroyed in the second step.

INTRODUCTION

Since A-type heteropoly compounds are acids and at the same time oxidizing agents, they have been used as acid catalysts (hydration of propene in homogeneous systems is a commercialized process) and also as oxidation catalysts (methacrylic acid is industrially produced by the oxidation of methacrolein). Although several studies have already been reported on the reduction process and the structure of reduced products of heteropoly acids in solution (*1*), little is known about the mechanism of reduction–oxidation cycle in the solid state, which must be closely related to the function as oxidation catalyst (*2–4*). We have previously proposed a two-step redox mechanism of heteropoly compounds (*2, 4, 5*). However, different mechanisms have also been proposed (*6–9*) and the redox mechanism seems still controversial. In this study we examined in more detail the reduction mechanism mainly of 12-molybdophosphoric acid by ir and ESR spectroscopy.

EXPERIMENTAL

Materials. $H_3PMo_{12}O_{40} \cdot nH_2O$ (abbreviated hereafter as PMo_{12}) and $H_3PW_{12}O_{40} \cdot nH_2O$ (PW_{12}) were obtained commercially from Kanto Chemical Company, Inc. and Nippon Inorganic Colour and Chemical Company Ltd., respectively. PW_{12} was used after purification by extraction with ether and recrystallization. The stoichiometric salts of alkali were prepared by adding slowly the aqueous solutions of their carbonates to the aqueous solutions of heteropoly acids as described previously (*10*). Water contents of the starting materials were carefully measured. These salts will be abbreviated, for example, as $KPMo_{12}$ and $CsPMo_{12}$.

Infrared spectra. Samples (3–5 mg) were dispersed on a thin silicon plate and their ir spectra were recorded in an *in situ* ir cell, which was connected to a closed circulation system, by means of a FT-IR spectrometer (JEOL, JIR-10), as has been described previously (*11, 12*). In some cases, ir spectra were taken after the samples were pressed into KBr disks.

^{18}O exchange between $H_2{}^{18}O$ and heteropoly compounds. Standard procedure was as follows. Samples on silicon plates were

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first evacuated in the ir cell at room temperature for 1 h. They were heated at 300°C for 1 h in the presence of O_2 (50 Torr), kept at 200°C for 3 h in the presence of $H_2{}^{16}O$ (17–18 Torr), and then evacuated at room temperature for 10–20 min. ^{18}O-Enriched water (99%), $H_2{}^{18}O$, was introduced, kept for 8 min, and evacuated. This cycle was repeated 2 or 3 times in order to eliminate $H_2{}^{16}O$ adsorbed on glass wall. During the cycles, the ir spectra characteristic of the Keggin anion remained unchanged. After the pretreatment, 16–18 Torr of $H_2{}^{18}O$ was introduced and the sample was transferred to the heating zone of the ir cell, which was kept at 200°C. Infrared spectra were measured at room temperature after the sample was returned into the optical path, as described before (*2*, *10*). The color of the sample during the experiments remained yellow for Mo-containing samples and white for PW_{12} when the contamination from grease was carefully avoided.

ESR spectra. X-Band ESR spectra were recorded on a JES-PE-1X spectrometer usually at room temperature. About a 200-mg portion of samples was placed in an ESR tube connected to a closed circulation system. For the quantitative measurements, the signal of Mo^{5+} was doubly integrated and compared with a doubly integrated signal of $CuSO_4 \cdot 5H_2O$ powder (standard). Very similar results were obtained when DPPH was used as a standard.

Reduction by H_2. The samples were reduced by H_2 in a closed circulation system. The degree of reduction was followed by the pressure decrease. The H_2 reduction of PMo_{12} at room temperature was carried out after PMo_{12} was mechanically premixed in an agate pestle with Pd/C (palladium supported on carbon, Pd:5 wt%, Nippon Engelhald Inc.) as described previously (*5*). The Pd/C content in the mixture was 10 wt%. The mixture will be denoted by PMo_{12}–Pd/C.

In the case of *in situ* ir measurements of the H_2 reduction of the samples at room temperature, 220 mg of the sample was loaded in a glass basket for the measurement of H_2 absorption and 3–5 mg of the sample was on a silicon plate for the ir measurement. During the heat treatment the two samples were placed close with each other near the center of the heating zone of the ir cell. Infrared spectra were similarly measured for PMo_{12} reduced at 280–320°C. Infrared spectra were recorded at room temperature.

RESULTS

Infrared spectra of water contained in heteropoly compounds. In Fig. 1, ir spectra of PMo_{12} and $KPMo_{12}$ in the region of $\nu(OH)$ and $\delta(H_2O)$ are shown. The ir spectrum of PMo_{12} which contained about 28 water molecules (spectrum a) exhibited a broad band at 3650–2800 cm^{-1} with a peak at 3552 cm^{-1}. After the evacuation at room temperature (the sample contained about 5–6 water molecules after the evacuation (*10*)), a broad band with a peak at 3263 cm^{-1} remained (spectrum b). In the $\delta(H_2O)$ region there were two bands at 1724 and 1612 cm^{-1}. Introduction of D_2O vapor in large excess produced spectrum a′. The same spectrum as a′ was obtained by the deuteration at room temperature after evacuation at 300°C. The deuterated sample showed a broad band at about 2600 cm^{-1} (spectrum a′) and 2426 cm^{-1} (after evacuation at room temperature; spectrum b′), corresponding to the 3552- and 3263-cm^{-1} bands of undeuterated sample (spectra a and b). In the $\delta(D_2O)$ region there were two bands at 1412 and 1188 cm^{-1}. The evacuation at room temperature decreased the intensity of these two bands and produced a new weak band at ca. 1260 cm^{-1}.

In the case of $KPMo_{12}$, weak bands were observed in the $\nu(OH)$ and $\delta(H_2O)$ regions (3622 and 1604 cm^{-1}), as in the case of $CsPMo_{12}$ (*11*). These ir bands of K and Cs salts completely disappeared by the evacuation at room temperature. Upon deuteration these two bands shifted to about 2600 and 1188 cm^{-1}, respectively, as expected from the change in the reduced mass.

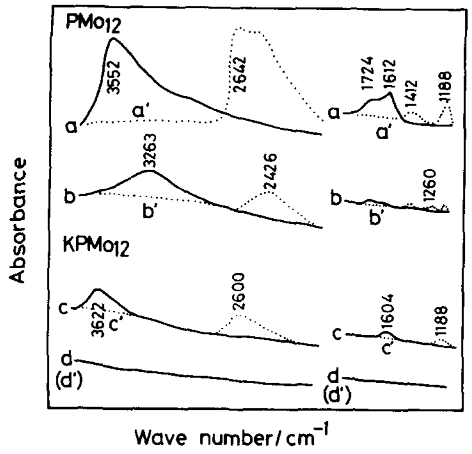


FIG. 1. Infrared spectra of PMo_{12} and $KPMo_{12}$. PMo_{12}; (a) In the presence of H_2O(17 Torr), (b) after the evacuation of (a). (a') Deuterated by D_2O (17 Torr), see text. (b') After the evacuation of (a'), all at 21°C. $KPMo_{12}$. (c) In the presence of H_2O (17 Torr), (d) after the evacuation of c. (c') Deuterated by D_2O (17 Torr), see text. (d) After the evacuation, all at 21°C. (Absorption due to water vapor was subtracted for (a), (a'), (c), and (c').)

PW_{12} containing about 5–6 H_2O exhibited broad bands at 3224 cm^{-1} in the ν(OH) region and at 1712 cm^{-1} in the $\delta(H_2O)$ region. The contact with D_2O at room temperature for 6 h, produced two broad ν(OD) bands at ca. 2600 and 2400 cm^{-1}. The former disappeared after the evacuation at 75°C for 1 h, but the latter remained. In the $\delta(D_2O)$ region there were two bands at 1450 and 1192 cm^{-1}. Evacuation at room temperature produced a band at 1265 cm^{-1} and the band at 1192 cm^{-1} became a shoulder.

^{18}O exchange between $H_2{}^{18}O$ and heteropoly compounds. Infrared spectra of PMo_{12}, $CsPMo_{12}$, and PW_{12} varied as shown in Fig. 2, when they were kept in contact with $H_2{}^{18}O$ (16–18 Torr) at 200°C for 2 h. Each band can be assigned as indicated in the figure according to the literature (*13*). In the case of PMo_{12} the bands assigned to ν(Mo=O), terminal oxygen, and ν(Mo—O—Mo), bridging oxygen, shifted to lower frequencies, demonstrating that the isotopic exchange of oxygen proceeded. The shifts were 39–46 cm^{-1}. The relative intensities of the shifted and unshifted bands indicate that after 2 h 60–70% of the oxygen was exchanged with ^{18}O of water. There was little difference in the rates of exchange between Mo=O and Mo—O—Mo. The magnitude of the isotope shift is close to those reported by Tsuneki *et al.* (*6*), Rawat *et al.* (*14*), and Hewett *et al.* (*15*). After 1 h at 300°C the ^{18}O exchange of both Mo=O and Mo—O—Mo was almost completed. The ν(P—O) band also shifted as the exchange of Mo=O or Mo—O—Mo proceeded, as reported before (*16*). However, the shift was very small for this band (~10 cm^{-1}).

In the case of $CsPMo_{12}$ the extent of exchange reached about 25% after 0.5 h, but the rate was greatly reduced at this stage and the extent increased only to ca. 30% after 2 h. Even at 300°C, the extent of exchange was only 40–50%. No difference in the rate of exchange was observed between Mo=O and Mo—O—Mo of $CsPMo_{12}$.

Results of PW_{12} were quite similar to PMo_{12}. The rate of exchange for PW_{12} was comparable with or slightly slower than for PMo_{12}. The isotope shifts (ca. 40 cm^{-1}) were in agreement with those reported by Vilchez and Griffith (*17*). As the reaction temperature was lowered to 70 or 100°C,

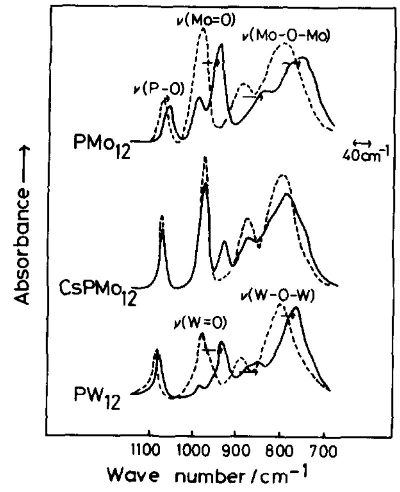


FIG. 2. Infrared spectra of 12-heteropoly compounds before and after the ^{18}O exchange with $H_2{}^{18}O$ vapor for 2 h at 200°C. Broken line: before the ^{18}O exchange. Solid line: after the ^{18}O exchange.

the rate of exchange was greatly reduced. At these temperatures, the exchange for PW_{12} was much slower than that for PMo_{12}.

Reduction by H_2 at room temperature. According to the temperature programmed reduction (TPR), the reduction of PMo_{12} by H_2 started at ca. 250–300°C. When Pd/C was added in order to promote the dissociation of hydrogen molecule, PMo_{12} was reduced at much lower temperatures (*5*). Figure 3 shows the results. PMo_{12}–Pd/C absorbed one hydrogen atom per anion in 1 min at room temperature and further uptake of hydrogen continued slowly. In contrast, the uptake was very small for PW_{12}. The H_2 uptake of Pd/C or PMo_{12} alone was less than one-tenth the uptake of PMo_{12}–Pd/C.

Figure 4 shows how the intensities of ir bands due to the Keggin structure of PMo_{12}– and $CsPMo_{12}$–Pd/C changed by H_2 reduction at room temperature. In the case of PMo_{12}, it was found that the intensity of the ν(P—O) band decreased by about 20% only by dehydration and reversibly restored upon rehydration. Since this change is presumably not directly related to the reduction process, the band intensities given in Fig. 4a were normalized to the intensity after the evacuation at room temperature. On the other hand, the band intensities of $CsPMo_{12}$ did not change upon dehydration or rehydration.

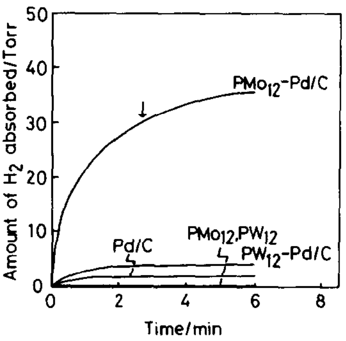


FIG. 3. Hydrogen uptake by PMo_{12} and PW_{12} mixed with Pd/C at 19°C. An arrow indicates the reduction level of 2 electrons/anion. Those without Pd/C and Pd/C itself are shown for comparison. PMo_{12}, PW_{12}: 225 mg with or without Pd/C (25 mg).

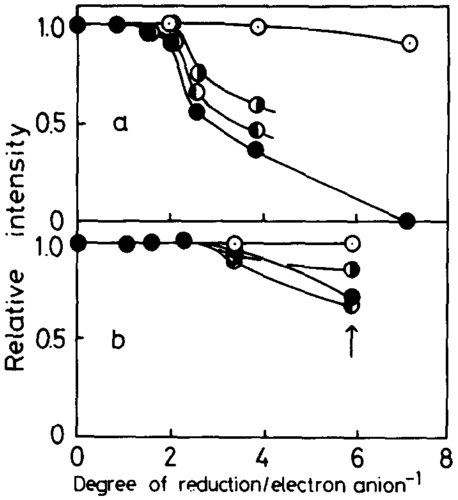


FIG. 4. Change in the infrared peak intensity by H_2 reduction of PMo_{12}– and $CsPMo_{12}$–Pd/C at room temperature. (a) PMo_{12}–Pd/C. (b) $CsPMo_{12}$–Pd/C. ●, ◑, ◐, and ○ correspond to the relative intensities of ν(P—O), ν(Mo—O—Mo, 883 cm^{-1}), ν(Mo—O—Mo, 791 cm^{-1}), and ν(Mo═O) bands. Plots of the peak areas against the degree of reduction gave very similar trends. Data indicated by an arrow are for $CsPMo_{12}$–Pd/C which was reduced at 100°C. Reduction beyond 3 electrons/anion was very slow at room temperature.

Until the degree of reduction reached ca. two electrons per anion, the ir spectrum little changed. As it exceeded two electrons per anion, the intensities of the ν(Mo—O—Mo) and ν(P—O) bands started to decrease, while that of the ν(Mo═O) band remained almost unchanged. At the later stage the lower frequency band of ν(Mo—O—Mo) changed in a complicated manner (791 → 810, 779 → 810, 725 cm^{-1}) and the ν(Mo═O) band shifted to 964 cm^{-1} from 980 cm^{-1}. But the bands due to ν(P—O) (1065 cm^{-1}) and ν(Mo—O—Mo) (883 cm^{-1}) did not shift. Ir spectra of PMo_{12}–Pd/C which was reduced to different extents at room temperature were also measured after quickly pressing them into KBr disks. The changes in intensities were in essential agreement with those in Fig. 4a, although the change in ir spectra tended to start at slightly lesser extent of reduction. Reoxidation of the prereduced sample took place in air at room temperature, but the extent was small (less than 20%). In the case of $CsPMo_{12}$–Pd/C (Fig. 4b), ir spectra did not change until the sample was reduced by about 3 electrons/anion, and changed similarly to the results shown in Fig. 4a by further reduction.

Figure 5 shows the change in the number of protons and the intensity of ν(OH) upon H_2 reduction of PMo_{12}–Pd/C at room temperature. The sample was reduced in the same manner as described above. The amount of Brønsted acid sites was estimated from the ir intensity of pyridinium ion (BPy) which was formed in the reduced sample. The sample (PMo_{12}–Pd/C) which had been reduced was contacted in the ir cell with pyridine vapor at room temperature and then evacuated at 100°C for 1 hr. The ir spectrum showed only BPy as characterized by the 1535-cm^{-1} band and no bands due to coordinated pyridine (e.g., 1440 cm^{-1}). As the reduction proceeded from 0 to 2 electrons/anion, the amount of BPy changed from 3 to almost 5 molecules/anion. With further reduction, it decreased. The intensity of the ν(OH) band little changed at the initial stage of reduction, but the intensity of the 3275-cm^{-1} band started to increase when the degree of reduction exceeded 2 electrons/anion. The ν(OH) band changed only slightly by the evacuation at room temperature, but disappeared by the evacuation at 200°C.

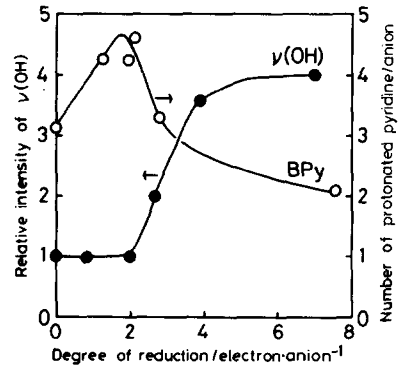


FIG. 5. Change in the integrated intensity of ν(OH) band and the amount of absorbed pyridine (protonated, BPy) for PMo_{12}–Pd/C reduced by H_2 at room temperature.

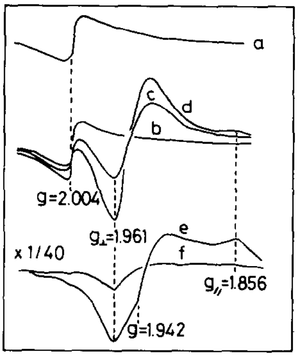


FIG. 6. ESR spectra of reduced PMo_{12}–Pd/C. (a) Pd/C only. (b) Before the reduction. (c) After the reduction at room temperature by 0.39 electrons/anion. (d) After the reduction at room temperature by 0.84 electrons/anion. (e) After the evacuation of sample (d) at 200°C. (f) After the evacuation of a sample similarly reduced as sample (d) at 300°C. Spectra (e) and (f) are presented in a reduced scale of 1/40.

ESR spectra of Mo^{5+}. ESR spectra of PMo_{12}–Pd/C which was reduced to various extents and measured at room temperature are shown in Fig. 6. No essential differences were observed between the 180° out-of-phase signals and in-phase signals. The unreduced sample which was preevacuated for 2 h at room temperature showed only single signal ($g = 2.004$) due to Pd/C. The signal of Pd/C appeared at the same position with the same intensity (spectrum a), regardless of the mixing with PMo_{12} or the reduction of PMo_{12}. Figure 7 shows the change in the signal intensity with the reduction of PMo_{12}–Pd/C. No Mo^{5+} signal was detected by the reduction of 0.08 electrons/anion at room temperature. Upon further reduction, the intensity of Mo^{5+} signal increased linearly with the extent of reduction, as indicated in Fig. 7, curve a. However, the amount of Mo^{5+} detected by ESR corresponded only to 1/150 of the amount of hydrogen uptake.

The ESR signal of Mo^{5+} remarkably increased when the sample which had been reduced by 0.84 electrons/anion at room temperature was heated in vacuum as reported before by us (*3, 18, 19*) and by Eguchi *et al.* (*9*). The intensity became 15 times greater by the evacuation at 200°C and 60 times by the evacuation at 300°C,

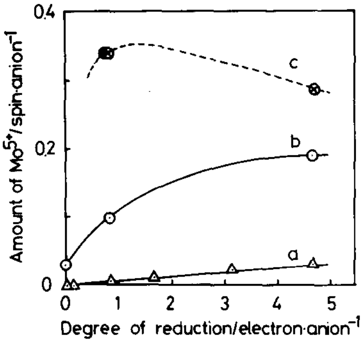


FIG. 7. Amount of Mo^{5+} detected by ESR at room temperature for PMo_{12}–Pd/C reduced by H_2. (a) After reduction at room temperature. (b) Samples were evacuated at 200°C after reduction at room temperature. (c) ⊗, Samples evacuated at 300°C after reduction at room temperature, and ●, PMo_{12} (without Pd/C) reduced at 300°C by 0.84 electrons/anion.

although the extent of reduction in average should not have changed.

In order to examine the influence of Pd/C on the mechanism of the reduction of PMo_{12}, PMo_{12} without Pd/C was reduced to the same extent at 300°C. The signal intensity of this sample agreed with the intensity of PMo_{12}–Pd/C which was reduced by 0.84 electrons/anion at room temperature and then heated in vacuum at 300°C, as shown in ● and ⊗ in Fig. 7. This fact indicates that Pd/C played a role only in the activation of H_2 molecules and the H_2-reduction mechanism of PMo_{12} was not interfered by the presence of Pd/C. ESR signal appeared when PMo_{12}–Pd/C was heated in vacuum in a grease-free system, although no ESR signal appeared when PMo_{12} alone was heated similarly. However, the intensity was not great (see Fig. 7, at 0 electron/anion).

Reduction of PMo_{12} by H_2 at 280–320°*C.* Figure 8 shows the changes in the ir band intensities of PMo_{12} (without Pd/C) upon the reduction by H_2 at 280–320°C. The reduction little changed the intensity of ν(Mo=O). On the other hand, the intensity changes of ν(Mo—O—Mo) and ν(P—O) bands exhibited an induction period in the initial stage of the reduction and the intensity decreased with further reduction. These results are very similar to those in Fig. 4a. The bands of ν(P—O) and ν(Mo—O—Mo) (H) (ν(Mo—O—Mo) at higher wavenumber) were at 1065 and 883 cm^{-1}, respectively, and did not shift by the reduction. In the region of the absorption band of 795 cm^{-1}, ν(Mo—O—Mo) (L) (ν(Mo—O—Mo) at lower wavenumber), a new band appeared at 760 cm^{-1} as the reduction proceeded. These results are in general agreement with those reported by Eguchi *et al.* (*7*), Tsuneki *et al.* (*6*), and Misono *et al.* (*2*). No bands appeared in the ν(OH) region. The ESR signal of Mo^{5+} increased with the reduction up to 1 electron/anion, but changed only slightly with further reduction, as in the previous results (*3*).

DISCUSSION

Behavior of water contained in heteropoly compounds upon heat treatment. There were two bands (1724 and 1612 cm^{-1}) in the $\delta(H_2O)$ region of PMo_{12} (Fig. 1). It has been reported that the hydrated proton (for example, $H^+(H_2O)$ or $H^+(H_2O)_2$) has a band at 1700 cm^{-1} (*20, 21*). Therefore, the band at 1724 cm^{-1} may be assigned to the hydrated proton as was previously suggested (*10, 11*). The absence of this band in the case of the salts of PMo_{12} supports this

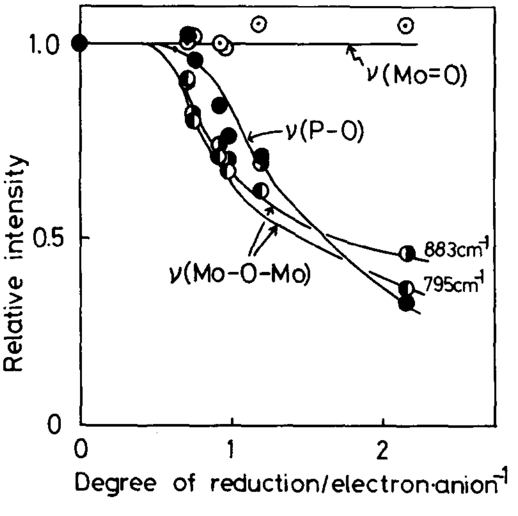


FIG. 8. Changes in the infrared peak intensity by H_2 reduction of PMo_{12} at 280–320°C.

assignment. The $\delta(D_2O)$ bands (1424 and 1260 cm^{-1}) are similarly assigned to $\delta(D^+(D_2O)_n)$ (n = 1,2), because $D^+(D_2O)_2$ shows ir bands at 1400 and 1250 cm^{-1} (*21*). The band at 3263 cm^{-1} (Fig. 1b) may be the ν(OH) band of protonated water, since hexahydrate of $PW_{12}[(H^+(H_2O)_2)_3 \cdot PW_{12}O_{40}]$, which is formed by the evacuation at room temperature has a band at 3224 cm^{-1}, and Kazanskii *et al.* (*22*) already assigned a broad band at 3100 cm^{-1} of PW_{12} to $(H^+(H_2O)_2)$. Further, it is known that $(H_3O)^+Br^-$ gives a band at 3250 cm^{-1} due to $\nu(H^+(H_2O))$ (*23*).

The bands at 3552 and 1612 cm^{-1} are assigned to unprotonated water, which are usually observed for water of crystallization and adsorbed water. Relatively small bands in the ν(OH) and $\delta(H_2O)$ regions for $KPMo_{12}$ and $CsPMo_{12}$ may be assigned to water of crystallization or physically absorbed water. Eguchi *et al.* (*24*) indicated that this is zeolitic water because the X-ray diffraction pattern did not change at higher temperatures. Niiyama *et al.* assigned this to physically adsorbed water (*25*). Considering the structural characteristics (*26*), the latter assignment seems more probable. Variations of the ir spectra upon heat treatment are consistent with the change in the water content (*10*).

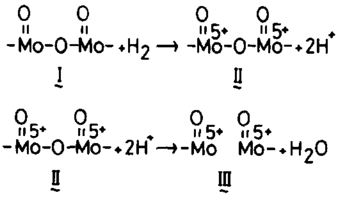
Rapid ^{18}O exchange between water and heteropoly compounds. As is shown in Fig. 2, the exchange proceeds throughout the bulk of PW_{12} and PMo_{12}. The rate was much more rapid than that observed for other oxide catalysts (*2*). This is due to the fact that water is easily absorbed into and desorbed from the bulk (*2*). The lattice oxygen rapidly exchanges with $H_2{}^{18}O$ which is absorbed in the bulk and the exchanged water comes out of the bulk. In contrast, in the case of $CsPMo_{12}$ only a part (20–30%) of the lattice oxygen exchanged rapidly and the remainder exchanged very slowly. If the high surface area of $CsPMo_{12}$ (170 m^2/g) is considered, the lattice oxygen of $CsPMo_{12}$ which exchanged rapidly at 200–300°C can be assigned to that on the surface monolayer. $CsPMo_{12}$ is insoluble in water and the secondary structure does not change easily, so that only the surface oxygen exchanges rapidly and the exchange of bulk oxygen would be very slow.

Though the ν(P—O) band shifts by isotopic oxygen exchange, the shift is much smaller than is expected by isotope effect. This oxygen is located inside the anion and it must be difficult to exchange with water. So the small shift of ν(P—O) is probably due to an indirect effect of isotopic exchange of oxygen located at outer part of the anion, as suggested before (*5, 6*). With hydration and dehydration the ν(Mo=O) band shifted owing to the change in hydrogen bonding, but no shift was observed for the ν(P—O) band. This is reasonable, since the Mo=O bond is located outside the anion and the P—O bond is inside the anion.

The rates of exchange for the terminal (M=O) and bridging oxygen (M—O—M, where M=Mo or W) are almost equal. It is probable that the exchange or rearrangement in the anion itself is rapid.

Mechanism of H_2 reduction of PMo_{12}. We previously proposed a reduction mechanism as shown in Fig. 9, mainly on the basis of the stoichiometry of H_2 reduction and O_2 reoxidation cycle including water evolution (*2*) and temperature programmed reduction (*5*). The reduction consists of two steps in this mechanism. Note that the degree of reduction is not apparently considered in this scheme (We do not mean that the second step begins when the anion is reduced exactly by two electrons.)

Present results confirmed this redox mechanism. At the initial stage of the re-



$$\underset{\text{I}}{-\overset{\overset{O}{\|}}{Mo}-O-\overset{\overset{O}{\|}}{Mo}-} + H_2 \longrightarrow \underset{\text{II}}{-\overset{\overset{O}{\|}\,5+}{Mo}-O-\overset{\overset{O}{\|}\,5+}{Mo}-} + 2H^+ \quad (1)$$

$$\underset{\text{II}}{-\overset{\overset{O}{\|}\,5+}{Mo}-O-\overset{\overset{O}{\|}\,5+}{Mo}-} + 2H^+ \longrightarrow \underset{\text{III}}{-\overset{\overset{O}{\|}\,5+}{Mo}\quad\overset{\overset{O}{\|}\,5+}{Mo}-} + H_2O \quad (2)$$

FIG. 9. Proposed mechanism for the reduction of PMo_{12} by H_2.

duction, ir spectra little changed (Fig. 4 and 8) and the increase of proton is almost equivalent with the uptake of hydrogen atom (Fig. 5). This is consistent with Eq. 1 of the scheme: H_2 molecule is dissociated, becoming electrons and protons, and the electrons are trapped by the anion keeping the anion structure (**I** and **II**) unchanged. In the second step the protons react with lattice oxygen of PMo_{12} to form H_2O. The increase of the band at 3275 cm^{-1} (Fig. 5) presumably reflects the formation of H_2O in the second step. Eguchi *et al.* (*7*) recently reported that the ν(Mo—O—Mo) and ν(P—O) bands decreased by the removal of bridging oxygen from the beginning of the reduction. Their reduction temperature was considerably higher than the present study, so that the second step to form the water (Eq. 2) should have proceeded very rapidly.

The interpretation of the changes in the ν(Mo—O—Mo) and ν(P—O) bands are still controversial. Some consider that the intensity of the ν(Mo—O—Mo) band decreases only by the removal of bridging oxygen (*6, 7*), but it was recently suggested that the ν(Mo—O—Mo) (and also ν(P—O)) bands were considerably reduced by the electrochemical reduction, where no structural changes probably took place (*8*). So further studies are required about the changes in the intensities of ν(P—O) and ν(Mo—O—Mo) bands caused by reduction.

ESR studies also support the two-step reduction mechanism. Pope *et al.* (*27*) reported the ESR signals of Mo^{5+} in PMo_{12} which was electrochemically reduced by 1 electron/anion. The original structure of PMo_{12} was retained by electrochemical reduction (*28, 29*). The Mo^{5+} signal which was isotropic at 9 K became much broader as the temperature of measurement increased. This change was attributed to the rapid hopping of electron among 12 equivalent Mo atoms in a Keggin anion. The temperature dependency of the line width demonstrates that the signal would hardly be detected at room temperature. In this connection, Pope *et al.* (*30*) also reported that the electron was localized on W atom in the case of non-Keggin-type polyacids. Therefore, it may be presumed that, when the anion structure is maintained, the electron can hop rapidly in an anion.

In the present work only a very small ESR signal was observed for PMo_{12}–Pd/C when it was reduced at room temperature. This result suggests that the electron is hopping rapidly and the Keggin structure is retained as was also indicated by the very small change in ir spectrum. That is, the reduction remains almost at the first stage (Fig. 9, Eq. 1).

Remarkable increase in the intensity of the ESR signal observed when the prereduced PMo_{12} was heated in vacuum is reasonably understood as the second stage of the reduction took place (Fig. 9, Eq. 2), as was suggested before (*19*).

When the temperature is raised, water is formed from oxygen atoms of anion and protons, producing coordinatively unsaturated Mo atoms. Unpaired electrons which are introduced by reduction will be localized at this coordinatively unsaturated Mo and then exhibit an anisotropic Mo^{5+} signal even at room temperature. Thus, the ESR measurement in the present study is consistently explained by the two-step mechanism for the H_2 reduction of PMo_{12}.

The oxidation of methacrolein over PMo_{12} proceeds by a redox mechanism, and the rate-determining step is probably the abstraction of hydrogen from an intermediate, which is accompanied by the reduction of PMo_{12} (*2, 3*). There was a fair correlation between oxidizing power or reducibility of heteropoly anion and the catalytic activity (*5, 31*). Therefore, the reduction mechanism as discussed in the present work could be closely related with the mechanism of the oxidation reaction of aldehydes. Further studies on this correlation are now in progress.

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REFERENCES

1. Tsigdinos, G. A., *Top. Curr. Chem.* **76,** 1 (1978).
2. Misono, M., Sakata, K., Yoneda, Y., and Lee, W. Y., "Proceedings, 7th International Congress on Catalysis, 1980, Tokyo," p. 1047. Kodansha–Elsevier, 1981.
3. Konishi, Y., Sakata, K., Misono, M., and Yoneda, Y., *J. Catal.* **77,** 169 (1982).
4. Misono, M., "Proceedings, 4th International Conference on the Chemistry and the Uses of Molybdenum, Colorado, Aug. 1982." Climax Molybdenum, Ann Arbor.
5. Katamura, K., Nakamura, T., Sakata, K., Misono, M., and Yoneda, Y., *Chem. Lett.* **1981,** 89.
6. Tsuneki, H., Niiyama, H., and Echigoya, E., *Chem. Lett.* **1978,** 645; **1978,** 1183.
7. Eguchi, K., Toyozawa, Y., Furuta, K., Yamazoe, N., and Seiyama, T., *Chem. Lett.* **1981,** 1253.
8. Akimoto, M., and Echigoya, E., *Chem. Lett.* **1981,** 1759.
9. Eguchi, K., Yamazoe, N., and Seiyama, T., *Chem. Lett.* **1982,** 1341.
10. Misono, M., Mizuno, N., Katamura, K., Kasai, A., Konishi, Y., Sakata, K., Okuhara, T., and Yoneda, Y., *Bull. Chem. Soc. Jpn.* **55,** 400 (1982).
11. Furuta, M., Sakata, K., Misono, M., and Yoneda, Y., *Chem. Lett.* **1979,** 31.
12. Misono, M., Konishi, Y., Furuta, M., and Yoneda, Y., *Chem. Lett.* **1978,** 709.
13. Rocchiccioli-Deltsheff, C., Thouvenot, R., and Frank, R., *Spectrochim Acta A* **32,** 587 (1976).
14. Rawat, T. S., Dixit, L., Raizada, B. B., and Katiar, A. K., *Indian J. Phys. B* **52,** 193 (1978).
15. Hewett, W. P., Newton, J. H., and Weltner, W., *J. Phys. Chem.* **72,** 2640 (1975).
16. Sakata, K., Misono, M., and Yoneda, Y., *Chem. Lett.* **1980,** 151.
17. Vilchez, F. G., and Griffith, W. P., *J. Chem. Soc. Dalton* 1418 (1972).
18. Mizuno, N., Misono, M., and Yoneda, Y., "48th Symposium on Catalysis, Okayama," October, 1981, 1W20.
19. Mizuno, N., Misono, M., and Yoneda, Y.,"45th National Meeting of the Chemical Society of Japan, Tokyo," April, 1982.
20. Ferriso, C. C., and Horing, D. F., *J. Chem. Phys.* **23,** 1464 (1955).
21. Pavia, A. C., and Giguere, P. S., *J. Chem. Phys.* **52,** 3551 (1970).
22. Kazanskii, L. P., and Potapova, I. V., Spitsyn, A. V. I., *Dokl. Akad. Nauk SSSR* **235,** 387 (1977).
23. Rudolph, J., and Zimmermann, H., *Z. Phys. Chem. Neue Felge* **43,** 311 (1964).
24. Eguchi, K., Yamazoe, N., and Seiyama, T., *Nippon Kagaku Kaishi* **1981,** 336.
25. Niiyama, H., Saito, Y., Yoshida, S., and Echigoya, E., *Nippon Kagaku Kaishi* **1982,** 569.
26. Brown, G. M., Noe-Spirlet, M.-R., Busing, W. R., and Leug, H. A., *Acta Crystallogr. B* **33,** 1038 (1977).
27. Prados, R. A., and Pope, M. T., *Inorg. Chem.* **15,** 2547 (1976).
28. Kazansky, L. P., Potapova, I. V., and Spitsyn, V. I., *in* "Proceedings of Climax Third International Conference on the Chemistry and Uses of Molybdenum" (H. F. Barry, and P. C. H. Mitchell, Eds.), p. 67. Climax Molybdenum Co. Ltd., Ann Arbor, 1979.
29. Pope, M. T., *Inorg. Chem.* **11,** 1973 (1972).
30. Varga, G. M., Papaconstantinou, E., and Pope, M. T., *Inorg. Chem.* **9,** 662 (1970).
31. Misono, M., Komaya, T., Sekiguchi, H., and Yoneda, Y., *Chem. Lett.* **1982,** 53.