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Catalysis by Heteropoly Compounds. XIII.† An Infrared Study of Ethanol and Diethyl Ether in the Pseudoliquid Phase of 12-Tungstophosphoric Acid

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Ethanol, diethyl ether, and water absorbed in, and their thermal desorption from, the pseudoliquid phase of 12-tungstophosphoric acid have been studied by means of infrared spectroscopy. For all three molecules, the state of the absorption of 6 molecules per anion, $H_3PW_{12}O_{40}\cdot 6R_2O$ (R; C_2H_5 or H), was quite stable and the secondary structures were similar. The intensities of the C-H vibrations indicated that the methyl group of the ethanol molecules interacted with the anions and that its interaction became stronger as the amount of absorbed molecules decreased. In the thermal desorption of absorbed ethanol or diethyl ether, a protonated monomer and dimer as well as an ethoxy group were detected by means of infrared spectroscopy. These species are reaction intermediates of the dehydration of ethanol which were assumed previously (*J. Am. Chem. Soc.*, **109**, 5535 (1987)). It was also found that, upon the dehydration of $H_3PW_{12}O_{40}\cdot 6H_2O$, the proton which had been hydrogen-bonded to the oxygen atom of the water molecule ($(H_2O)_2H^+$) migrated onto the bridging oxygen of the heteropoly anion ($PW_{12}O_{40}^{3-}$).

Heteropoly acids such as $H_3PW_{12}O_{40}$ and their salts have been used as both heterogeneous solid catalysts[1-3] and homogeneous solution catalysts.[4] It has been reported that polar molecules are readily absorbed into the bulk of certain heteropoly acids[5] and that some catalytic reactions take place in the "pseudoliquid phase".[1,6] Since the whole protons in the bulk $H_3PW_{12}O_{40}$ can take part in the reactions, it shows a very high catalytic activity for the dehydration of alcohol or ether at low temperatures.[7,8] We recently demonstrated that the unusual pressure dependencies of the rate and selectivity of the dehydration of ethanol over $H_3PW_{12}O_{40}$ were closely correlated with the amount and the chemical state of the ethanol present in the bulk.[9] Thus, it is very important, for an understanding of the heterogeneous catalysis of heteropoly compounds, to elucidate at the molecular level the activated state of the molecules absorbed in the pseudoliquid phase.

In the case of heteropoly compounds, it is possible to investigate the reacting molecules and the polyanions simultaneously by means of spectroscopy. The primary structure of the heteropoly anion can be monitored by means of IR, as has been described by Rocchiccioli-Deltcheff et al.[10] and other groups.[11] The thermal desorption and transformation processes of acetone and ethanol in $H_3PW_{12}O_{40}$ have been studied with IR by Misono et al.[5] and Moffat et al.[12] Solid-state NMR is also useful for the study of heteropoly acid.[13] The present authors have previously investigated, by the use of solid-state NMR (^{31}P, ^{13}C, ^1H), the activated states of ethanol in the pseudoliquid phase of $H_3PW_{12}O_{40}$[14] and demonstrated the presence of protonated ethanols and the ethoxy group. Farneth et al. have observed a methoxy intermediate formed on the polyanion of $K_{3-x}H_xPW_{12}O_{40}$ by ^{13}C CP-MAS NMR.[13b]

In the present study, we have investigated the structure and the thermal transformation of activated ethanol and ether, mainly on the basis of the IR spectral changes brought about by heating. The local position of the protons of $H_3PW_{12}O_{40}$ during the dehydration process of $H_3PW_{12}O_{40}\cdot 6H_2O$ was also examined. These processes were then further discussed in relation to the catalytic dehydration.

Experimental

Materials. The $H_3PW_{12}O_{40}$ was purchased from the Nippon Inorganic Color and Chemical Co., Ltd., and was used after purification by ether extraction and recrystallization from water. The stoichiometric cesium salt ($Cs_3PW_{12}O_{40}$) was prepared using a Cs_2CO_3 aqueous solution as has been described previously.[15]

The C_2H_5OH (Amakasu Chemical Ind.; 99.5%), $(C_2H_5)_2O$ (Showa Ether Co. Inc., Research Grade), C_2H_5OD (Aldrich; 99.5%D), and D_2O (Aldrich; 99.8%D) were degassed by several freeze-pump-thaw cycles. The Al_2O_3 (Reference Catalyst of Catalysis Society of Japan, ALO-4, 170 $m^2\,g^{-1}$) and SiO_2 (Cabosil, 200 $m^2\,g^{-1}$) were pretreated in a vacuum at 400 °C for 2 h.

The deuterated 12-tungstophosphoric acid ($D_3PW_{12}O_{40}$) was obtained by exchange with D_2O as follows. After $H_3PW_{12}O_{40}\cdot nH_2O$ had been evacuated at room temperature (n=6), it was exposed to D_2O (15 Torr; 1 Torr≈133.322 Pa) and reevacuated. This procedure was repeated several times. After the complete change of ν(O-H) to ν(O-D) had been confirmed by IR, the sample was treated at 130 °C in a vacuum for 1 h to obtain $D_3PW_{12}O_{40}$.

Absorption and Desorption Measurements. The absorption amounts of water, ethanol, and diethyl ether into $H_3PW_{12}O_{40}$ were measured by the use of a thermal gravimeter (Shimadzu TG-30) connected directly to a vacuum system. After the evacuation of the $H_3PW_{12}O_{40}$ (ca. 40 mg) for 1 h at 130 °C, ethanol (20 Torr) or diethyl ether (50 Torr)

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† Part XII: T. Okuhara, S. Tatematsu, K. Y. Lee, and M. Misono, *Bull. Chem. Soc. Jpn.*, **62**, 717 (1989).

was introduced at room temperature. The thermal desorption, in which temperature was raised step-by-step, was carried out in the same system.

The content of the crystallization water was measured by the TG. After evacuation at room temperature, the amount of water which remained was 6 molecules per anion; by further evacuation at 100 °C and 200 °C, it became 1 and 0.5 molecules per anion respectively.

Thermal Desorption. The thermal desorption of ethanol and diethyl ether absorbed in $H_3PW_{12}O_{40}$ was carried out in a closed circulation system connected to a gas chromatograph. After about 0.5 g of the catalyst was evacuated at 130 °C for 1 h, the gas was added at 25 °C. Then, the temperature of the catalyst was raised step-by-step. Gases desorbed at each temperature were collected in a trap kept at the temperature of liquid nitrogen and analyzed with a gas chromatograph (Shimadzu GC 8A, TCD, Porapak Q and/or Yanaco G 2800, FID, VZ-10).

IR Measurements. The heteropoly compounds (2—7 mg) were dispersed on a thin silicon plate and were pretreated by the same method as in the thermal desorption. Their IR spectra were recorded in an in situ IR cell,[16)] connected to a closed circulation system, by means of an FT-IR spectrometer (JEOL, JIR-10, MCT detector, 4 cm^{-1} resolution).

NMR Measurements. The samples for the NMR measurements were prepared using the closed circulation system or a quartz spring balance connected to the vacuum system. The amount of ethanol absorbed into $H_3PW_{12}O_{40}$ (ca. 0.5—1 g) was determined by measuring the pressure decrease or the change in weight.

High-resolution solid-state MAS NMR spectra were obtained on a Fourier Transform pulsed NMR spectrometer (JEOL JNM-GX270) equipped with a CP-MAS unit (JEOL NM-GSH27MU). The instrumental conditions were the same as those previously described.[14)]

Results

IR Spectra of $H_3PW_{12}O_{40}\cdot nH_2O$ ($n\leq 6$). The infrared spectra of $H_3PW_{12}O_{40}\cdot nH_2O$ and $D_3PW_{12}O_{40}\cdot nD_2O$, evacuated at various temperatures, are shown in Figs. 1 and 2 respectively. The spectrum of $H_3PW_{12}O_{40}\cdot 6H_2O$ after evacuation at room temperature was quite similar to that in the literature (Fig. 1a).[10)] The bands were assigned as follows, with reference to the structure in Fig. 3a. The band at 1080 cm^{-1} is attributed to the asymmetric stretching vibration of the central PO_4 tetrahedron (ν_{as}(P–O)), and the band at 976 cm^{-1}, to a stretching vibration of W=Ot, where Ot is the terminal oxygen. The other two bands, 887 and 795 cm^{-1}, are assigned to the stretching of the W–Oc–W bridges between corner-shared WO_6 octahedra (ν_{as}(W–Oc–W)), and to the stretching of the W–Oe–W bridges between edge-shared WO_6 octahedra (ν_{as}(W–Oe–W)), respectively.

As is shown in Fig. 1, the IR spectrum changed remarkably upon evacuation above 100 °C (Fig. 1b—d). The intensity of the ν(W=Ot) band at 976 cm^{-1} decreased, and a new band at 1007 cm^{-1} appeared. After the evacuation at 300 °C, the band at 1007 cm^{-1} remained, while the band at 976 cm^{-1} disappeared. In the ν_{as}(W–Oe–W) region, the band at 795 cm^{-1} split into two bands (798 and 768 cm^{-1}) after the 100 °C-evacuation. It was confirmed that the addition of

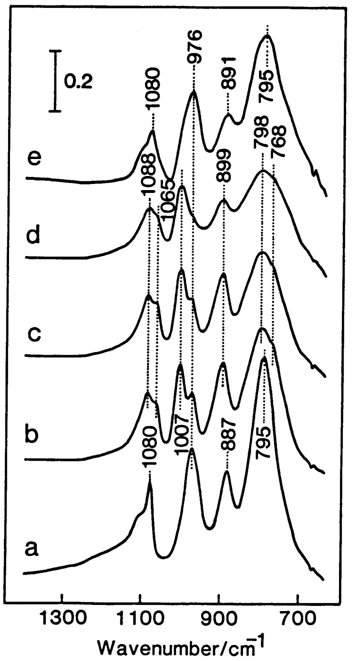


Fig. 1. Infrared spectra of $H_3PW_{12}O_{40}\cdot nH_2O$ during dehydration process; evacuated at (a) room temperature (n=6), (b) 100 °C, (c) 200 °C, (d) 300 °C, and (e) after (d), the sample was exposed to H_2O (15 Torr) and was evacuated at room temperature.

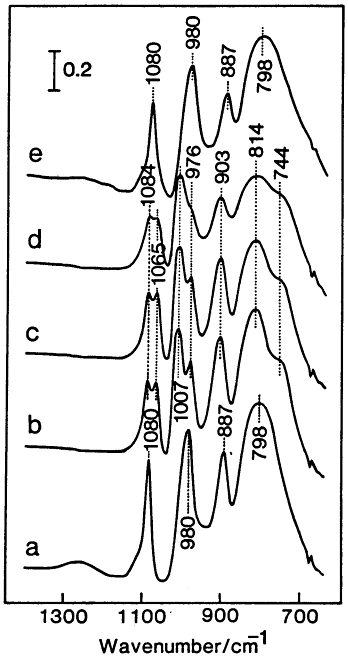


Fig. 2. Infrared spectra of $D_3PW_{12}O_{40}\cdot nD_2O$ during dehydration process; evacuated at (a) room temperature (n=6), (b) 100 °C, (c) 200 °C, (d) 300 °C, and (e) after (d), the sample was exposed to D_2O (15 Torr) and was evacuated at room temperature.

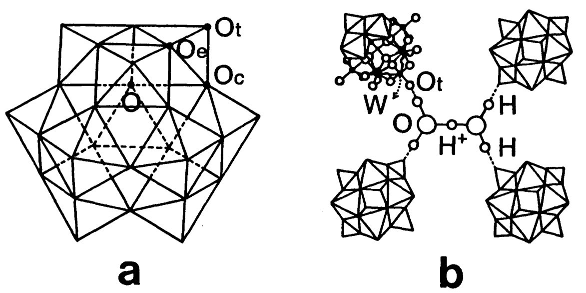


Fig. 3. Structure of (a) the primary structure of heteropoly anion ($PW_{12}O_{40}^{3-}$) and (b) the secondary structure of $H_3PW_{12}O_{40}\cdot 6H_2O$.

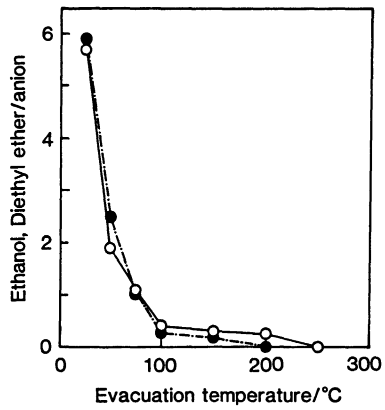


Fig. 4. The amount of ethanol (●) and diethyl ether (○) remained in the bulk of $H_3PW_{12}O_{40}$ during step-by-step thermal desorption.

water (15 Torr) to the 300 °C-evacuated sample and subsequent evacuation at room temperature completely recovered the original spectrum (Fig. 1e).

The infrared spectrum (Fig. 2a) of $D_3PW_{12}O_{40}\cdot 6D_2O$ was similar to that of $H_3PW_{12}O_{40}\cdot 6H_2O$ (Fig. 1a). During heating, the ν(W=Ot) band showed the same changes as that of $H_3PW_{12}O_{40}$. However, it was noted that the ν_{as}(W-Oe-W) band at 798 cm^{-1} split into two bands (814 and 744 cm^{-1}) which were distinctly different from the two bands observed for $H_3PW_{12}O_{40}$ (798 and 768 cm^{-1}). Also, in this case, the original IR spectrum (Fig. 2a) was recovered by the treatment with D_2O (Fig. 2e).

Amounts of Diethyl Ether and Ethanol Absorbed. Figure 4 shows the amounts of diethyl ether and ethanol which remained after the step-by-step thermal desorption. When diethyl ether vapor (150 Torr) was introduced at room temperature, the amount of diethyl ether absorbed became 6 molecules per anion after 30 min. This amount remained unchanged upon the evacuation at room temperature,[17] suggesting that the state of 6 molecules of diethyl ether per polyanion is stable, as in the case of water. The amounts of diethyl ether held were about 2 and 0 molecules per anion after 50 °C and 250 °C-evacuation respectively, as is shown in Fig. 4.

In the case of ethanol,[17] the absorption amount reached about 14 molecules per anion at 20 Torr. It decreased to 6, 2.5, and about 0 molecules per anion after evacuation at room temperature, 50 °C, and 200 °C respectively. At 45 °C, 9 and 6 molecules of ethanol per anion were absorbed when the pressures of ethanol were 40 and 5 Torr respectively. This value decreased to 3 molecules per anion upon the evacuation at 45 °C. In this way, the stable states of 3, 6, and 9 molecules of ethanol per anion could be obtained by controlling the pressure at 45 °C.

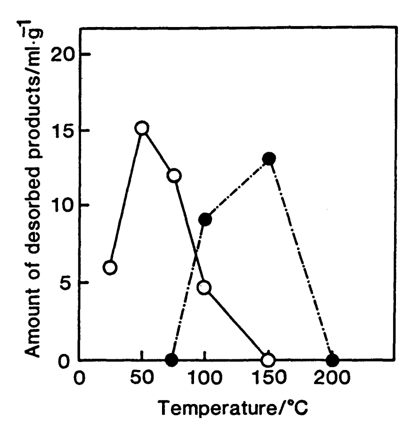


Fig. 5. Variation of products for thermal desorption of diethyl ether from $H_3PW_{12}O_{40}$. ○: $(C_2H_5)_2O$, ●: C_2H_4.

Figure 5 shows the products of the thermal desorption of diethyl ether from $H_3PW_{12}O_{40}$. Below 75 °C, only diethyl ether was desorbed. Ethylene was evolved in the range of 75—150 °C. Ethylene showed a maximum at 150 °C, but above 200 °C it was not detected. At 150—300 °C, small amounts of ethane, propane, and butane were detected in the gases desorbed. The total amount of these saturated hydrocarbons was about one-tenth that of the ethylene formed. The carbon balance in the absorption-desorption (up to 300 °C) was confirmed to be close to 100%.

As has been reported previously,[7b] ethanol was desorbed below 100 °C in the case of the thermal desorption of ethanol. The amount of ethylene desorbed reached a maximum at about 100 °C. Above 150 °C, ethane, propane, and methane were produced instead of ethylene.

IR Spectra of $H_3PW_{12}O_{40}\cdot n(C_2H_5)_2O$ ($n\leq 6$) during Thermal Desorption. The changes in the IR spectra of diethyl ether present in $H_3PW_{12}O_{40}$ during step-by-step heating in a vacuum are shown in Fig. 6. After the evacuation at room temperature (6 molecules of diethyl ether per anion), four bands appeared, at 2985, 2939, 2900, and 2873 cm^{-1}, which corresponded to the ν(C-H) bands (Fig. 6a). The bands at 2985 and 2939 cm^{-1} are attributed to the degenerate stretching vibrations of CH_3, while the bands at 2900 and 2873 cm^{-1} are assigned to the symmetric stretching vibrations of CH_3 and CH_2 respectively.[18] After heating up to 75

°C, these bands became weaker, without any shifts in their positions. The evacuation at 100 °C broadened these bands and produced new, weak bands at 2954, 2924, 2897, and 2870 cm^{-1}. After 150 °C-evacuation, only the latter four bands remained. These bands completely disappeared after evacuation at 300 °C, however.

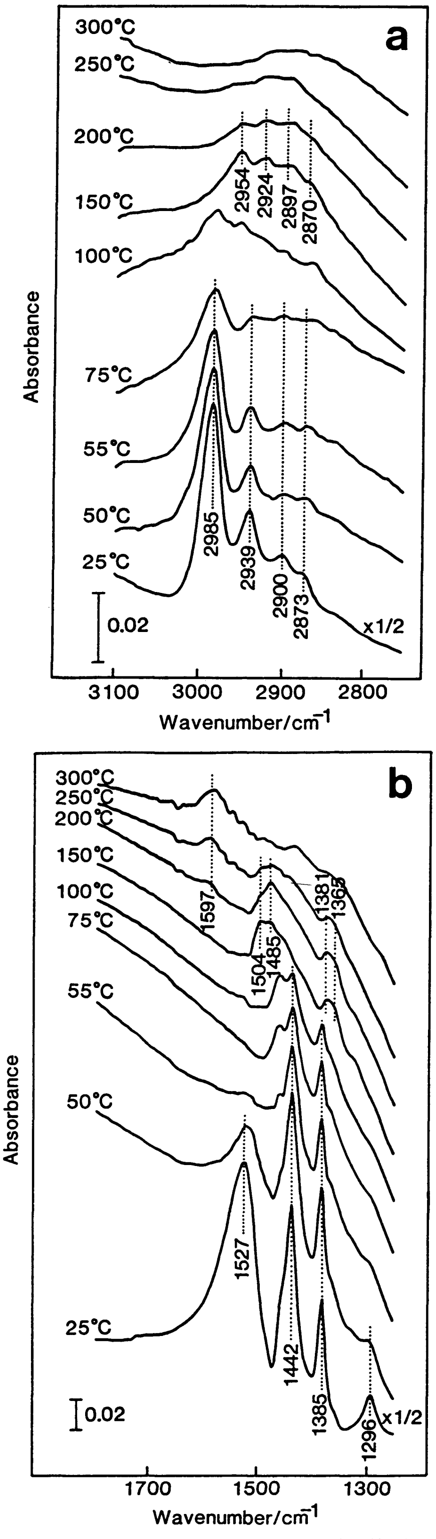


Fig. 6. Changes of IR spectra of diethyl ether absorbed in $H_3PW_{12}O_{40}$ during stepwise heating in vacuum; (a) in the ν(C-H) region; 3100—2750 cm^{-1}, (b) in the deformation region; 1800—1250 cm^{-1}.

The bands in the deformation region (1800—1250 cm^{-1}) are shown in Fig. 6b. The band at 1442 cm^{-1} is a characteristic band of the CH_3 degenerate deformation, and the shoulder at 1468 cm^{-1} is assignable to the CH_2 deformation band.[18] The 1385 cm^{-1} band is due to both the CH_3 symmetric deformation and the CH_2 wagging vibration.[18] It was notable that the band at 1527 cm^{-1} was present for $H_3PW_{12}O_{40}\cdot 6(C_2H_5)_2O$. This band was absent in the spectra of the gaseous and liquid diethyl ether[18] and for diethyl ether adsorbed on Al_2O_3 and SiO_2. In addition, when diethyl ether was introduced over $D_3PW_{12}O_{40}$, the 1527 cm^{-1} band was not observed. It probably shifted to about 1100 cm^{-1} (isotope shift), but this band was not obvious because of the presence of the strong IR bands of the heteropoly anion. As is shown in Fig. 6b, the intensity of the band at 1527 cm^{-1} decreased upon heating at 55 °C in a vacuum, in preference to the 1385 and 1442 cm^{-1} bands.

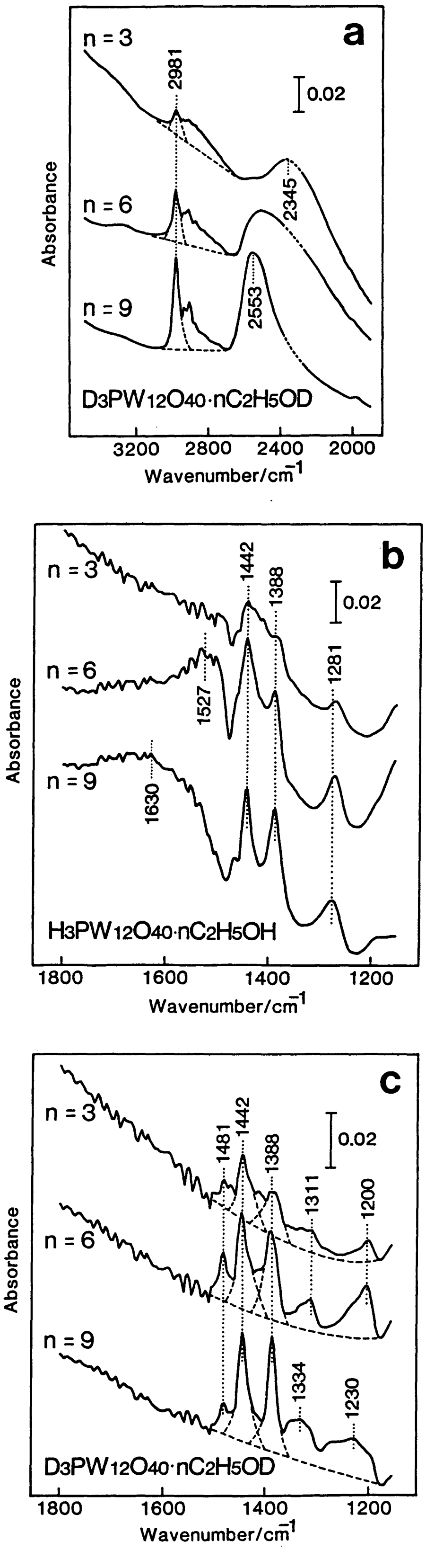
Upon heating at 150 °C, new bands at 1504, 1485, 1381, and 1365 cm^{-1} appeared, instead of the bands at 1442 and 1385 cm^{-1}. After the 200 °C-evacuation, a broad band at 1597 cm^{-1} appeared, and this band became intense at higher temperatures.

IR Spectra of $H_3PW_{12}O_{40}\cdot nC_2H_5OH$ (n=3, 6, 9). Figure 7a—d shows the IR spectra of ethanol absorbed in $H_3PW_{12}O_{40}$ or $D_3PW_{12}O_{40}$. In the case of the C_2H_5OD-$D_3PW_{12}O_{40}$ system, the O-D stretching band shifted from 2553 to 2345 cm^{-1} as the amount of C_2H_5OD decreased from 9 to 3 molecules per anion. In the ν(C-H) region (Fig. 7a), the $\nu_{\mathrm{deg}}(CH_3)$ bands at 2981 and 2935 cm^{-1}, the $\nu_s(CH_3)$ band at 2904 cm^{-1}, and the $\nu_s(CH_2)$ band at 2870 cm^{-1} appeared. These bands were quite similar to those of absorbed diethyl ether. The integrated intensities of the 2981 cm^{-1} band ($\nu_{\mathrm{deg}}(CH_3)$) decreased from 1.00 to 0.53 and 0.30 as the amounts of C_2H_5OD absorbed decreased from 9 to 6 and 3 molecules per anion respectively.

The IR spectra of $H_3PW_{12}O_{40}\cdot nC_2H_5OH$ in the deformation region (1800—1150 cm^{-1}) are shown in Fig. 7b. There was a broad band around 1630 cm^{-1} for the state of 9 molecules per anion. This band shifted to 1527 cm^{-1} for 6 molecule per anion; this position was in good agreement with that for 6 molecules of diethyl ether per anion. This band disappeared at 3 molecules per anion, however. Those bands at 1700—1500 cm^{-1} (Fig. 7b) shifted to about 1200 cm^{-1} upon the substitution of D for H in the OH group of C_2H_5OH, as is shown in Fig. 7c ($D_3PW_{12}O_{40}\cdot nC_2H_5OD$). For the states of 9, 6, and 3 molecules of C_2H_5OD per anion, the relative integrated intensities of the bands at 1442 cm^{-1} were 1.00, 1.17, and 0.77, while those at 1388 cm^{-1} were 1.00, 1.23, and 0.70.

Figure 7d shows the IR bands of the heteropoly anion of $D_3PW_{12}O_{40}$ absorbing different amounts of

C_2H_5OD. There was little difference in the IR spectra of the anion between 6 and 9 molecules of C_2H_5OD per anion. For 3 molecules per anion, the ν(W-Oe-W) band tended to split into 814 and 764 cm^{-1} and the ν(W=Ot) band, into 991 and 980 cm^{-1}.



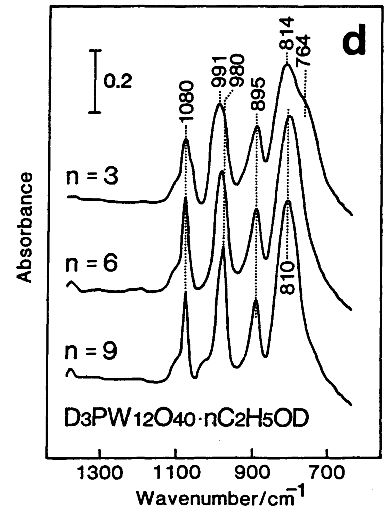


Fig. 7. IR spectra of ethanol absorbed in $H_3PW_{12}O_{40}$ or $D_3PW_{12}O_{40}$; (a) $D_3PW_{12}O_{40}\cdot nC_2H_5OD$, in the region of ν(C-H) and ν(O-D) (3500—1900 cm^{-1}), (b) $H_3PW_{12}O_{40}\cdot nC_2H_5OH$, in the region of δ(C-H), ν(O-H), and δ(O-H) (1800—1150 cm^{-1}), (c) $D_3PW_{12}O_{40}\cdot nC_2H_5OD$, in the region of δ(C-H), ν(O-D), and δ(O-D) (1800—1150 cm^{-1}), (d) $D_3PW_{12}O_{40}\cdot nC_2H_5OD$, in the region of characteristic bands of heteropoly anion (1400—633 cm^{-1}).

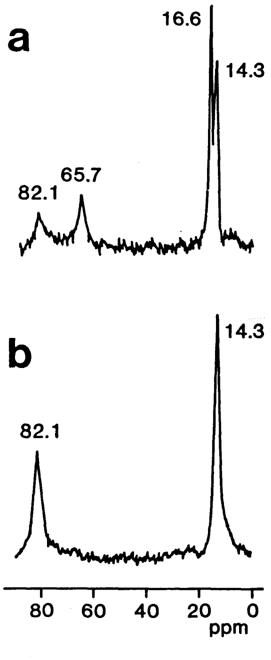


Fig. 8. The change of ^{13}C CP-MAS NMR spectra of $H_3PW_{12}O_{40}\cdot nC_2H_5OH$ by heating; (a) after evacuation at 45 °C (n=2.2), (b) after heating at 150 °C.

It was noted that there were little differences between the spectral changes of $H_3PW_{12}O_{40}\cdot nC_2H_5OH$ and $H_3PW_{12}O_{40}\cdot n(C_2H_5)_2O$ during thermal desorption.

^{13}C CP-MAS NMR of Ethanol Absorbed into $H_3PW_{12}O_{40}$. The ^{13}C CP-MAS NMR spectra of $H_3PW_{12}O_{40}\cdot 2.2C_2H_5OH$ are shown in Fig. 8a. As has been described previously,[14] the peaks at δ 16.6 (CH_3) and

65.7 (CH_2) were assigned to the protonated ethanol monomer ($C_2H_5OH_2^+$), and the signal at δ 14.3 and 82.1, to the ethoxy group on the heteropoly anion (C_2H_5O). In addition, a protonated dimer ($(C_2H_5OH)_2H^+$) has been detected with ^{13}C peaks at δ 17.2 and 61.9 for $H_3PW_{12}O_{40}\cdot 6C_2H_5OH$.14) After heating at 150 °C, the peaks at δ 16.6 and 65.7 disappeared, leaving only the peaks at δ 14.3 and 82.1.

Discussion

Location of H^+ in the Heteropoly Anion. The primary structure (Keggin structure)19) and the secondary structure20) of $H_3PW_{12}O_{40}\cdot 6H_2O$ are illustrated in Fig. 3. $H_3PW_{12}O_{40}\cdot 6H_2O$ has a stable structure, which has been established by X-ray and neutron diffraction.20) The polyanions are packed in a bcc structure, in which the protonated water dimer, $(H_2O)_2H^+$, is connected to four anions by hydrogen bonding at the terminal oxygen atoms (Ot) of the anions, as is shown in Fig. 3b. Therefore, the band at 976 cm^{-1} (Fig. 1a) can firmly be assigned to the stretching vibration of the W=Ot bond, the Ot atom of which is bonded to the protonated water molecules, as is shown in Fig. 3b, and the 887 and 795 cm^{-1} bands, to the asymmetric stretching vibrations of W-Oc-W and W-Oe-W, which are not connected to either water or proton.

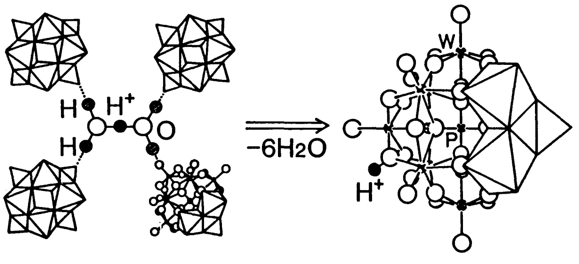
As the sample was dehydrated, the 976 cm^{-1} band decreased and the band at 1007 cm^{-1} grew correspondingly (Fig. 1a—d), as in the case of $H_3PMo_{12}O_{40}$.16) The 1007 cm^{-1} band observed for dehydrated $H_3PW_{12}O_{40}$ may reasonably be assigned to W=Ot, which is not coordinated with either a free proton, water, or $(H_2O)_2H^+$. The shift of the W=Ot band to a wavenumber higher by 31 cm^{-1} is consistent with the disappearance of hydrogen bonding.21)

The substitution of D for H caused no change in the wavenumber of the W=Ot band (compare $H_3PW_{12}O_{40}\cdot 6H_2O$ (Fig. 1a) and $D_3PW_{12}O_{40}\cdot 6D_2O$ (Fig. 2a)). The absence of the isotope shift for the W=Ot band indicates that the hydrogen bonding between the terminal oxygen and the hydrogen of the water molecules is weak. It is known that the O-H bond becomes longer as the hydrogen bonding becomes stronger.22) The O-H bond distance of the water molecule in $H_3PW_{12}O_{40}\cdot 6H_2O$ is 0.951 Å,20) which is close to the O-H bond length (0.958 Å) of the water molecule in the gas phase. Therefore, the hydrogen bonding between W=Ot and $(H_2O)_2H^+$ is considered to be weak.

As for the dehydration process (Figs. 1b—d and 2b—d), a significant difference was noted in the W-Oe-W band (795 cm^{-1}) between $H_3PW_{12}O_{40}$ and $D_3PW_{12}O_{40}$; the W-Oe-W band split into 798 and 768 cm^{-1} for $H_3PW_{12}O_{40}$, but it split into 814 and 744 cm^{-1} for $D_3PW_{12}O_{40}$. In contrast, there was no difference detected for the W=Ot band. This fact shows that, after dehydration, the proton interacts with the bridging oxygen (Oe), but not with the terminal oxygen (Ot). The above-mentioned shift of W=Ot to a higher wavenumber after dehydration is consistent with this idea. This is also in agreement with the fact that the bridging oxygen is more basic than the terminal oxygen.23—25) For example, Knoth et al. have reported that the methyl cation in $CH_3OPMo_{12}O_{39}^{2-}$ is located on the bridging oxygen atom,24) and Tonomura et al. observed a shift of the W-Oe-W band which was presumably due to the interaction with tetrahydrofuran through a proton located on the bridging oxygen atom.25)

Since there are twelve Oe's and three protons per $PW_{12}O_{40}^{3-}$, the band at 814 cm^{-1}, which was stronger (Fig. 2b—d), may be assigned to nine W-Oe-W (non-protonated) bonds, and the 744 cm^{-1} band, to three W-OeD$^+$-W (protonated) bonds. The shift to a lower wavenumber for the latter is consistent with the presence of hydrogen-bonding.21)

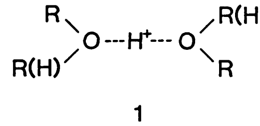
On the basis of these results, the following dehydration scheme for $H_3PW_{12}O_{40}\cdot 6H_2O$ is proposed. This process is reversible upon dehydration-hydration.



Dehydration scheme

States of Molecules in $H_3PW_{12}O_{40}\cdot nC_2H_5OH$ and $H_3PW_{12}O_{40}\cdot n(C_2H_5)_2O$ (n=3, 6, and 9). The amounts of molecules absorbed in $H_3PW_{12}O_{40}$ showed discrete values—for example, 3, 6, and 9 molecules per anion for ethanol and 6 molecules per anion for diethyl ether.17)

First, we will discuss the absorption state of 6 molecules per anion for ethanol, diethyl ether, and water. The states of $H_3PW_{12}O_{40}\cdot 6C_2H_5OH$ and $H_3PW_{12}O_{40}\cdot 6(C_2H_5)_2O$ (Fig. 7b and 6b) exhibited a characteristic band at 1527 cm^{-1}. Klages et al. observed the same band for the 2 : 1 complex of diethyl ether and $HSbCl_6$.26) It is probably assignable to a ν(O-H) mode of $[(C_2H_5)_2O\cdots H\cdots O(C_2H_5)_2]^+SbCl_6^-$ by analogy with a protonated water dimer.27) This band was absent for the 1 : 1 complex ($[(C_2H_5)_2OH]^+SbCl_6^-$). Therefore, the band at 1527 cm^{-1} is considered to be a characteristic band of the protonated dimer species, **1**.

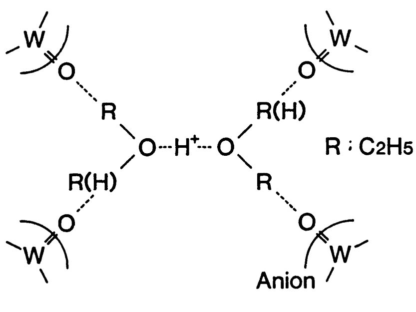


R : C_2H_5

1

The presence of the protonated dimer species, $(C_2H_5OH)_2H^+$, has previously been indicated by the solid-state MAS NMR study of the present authors.[14] Note that six ether or ethanol molecules per anion correspond to two molecules per proton. The fact that this band was not observed for ethanol adsorbed on $Cs_3PW_{12}O_{40}$ as for diethyl ether adsorbed on Al_2O_3 or SiO_2 is reasonable, since these oxides do not have Bronsted-acid sites. The absence (because of a shift to a lower wavenumber) of the 1527 cm^{-1} band for $D_3PW_{12}O_{40}\cdot 6C_2H_5OD$ and $D_3PW_{12}O_{40}\cdot 6(C_2H_5)_2O$ is also consistent with the above assignment.

The positions of the ν(C-H) bands (2985, 2939, 2900, and 2873 cm^{-1}) observed for $H_3PW_{12}O_{40}\cdot 6(C_2H_5)_2O$ were very similar to those of $(C_2H_5)_2O$ in CCl_4 (2980, 2935, 2897, and 2868 cm^{-1})[18] and in the $(C_2H_5)_2O$-$AlCl_3$ complex (2983, 2940, and 2877 cm^{-1}).[28] However, the relative intensities of these bands were quite different. The $\nu_s(CH_2)$ band (2868 cm^{-1}) is more intense than the $\nu_{deg}(CH_3)$ band (2980 cm^{-1}) for $(C_2H_5)_2O$ in CCl_4, while the $\nu_{deg}(CH_3)$ band is stronger for $(C_2H_5)_2O$-$AlCl_3$. The suggested reason why $\nu_s(CH_2)$ in $(C_2H_5)_2O$-$AlCl_3$ is weak is a stronger electron-withdrawing effect of $AlCl_3$, which destabilizes the dipolar contribution to the C-H bond of the CH_2 group.[29] In the case of $H_3PW_{12}O_{40}\cdot 6(C_2H_5)_2O$, the relative intensity was similar to $(C_2H_5)_2O$-$AlCl_3$ (Fig. 6a). This supports the formation of $[(C_2H_5)_2O]_2H^+$. From these results, we can propose the following model.



Dimer model

Since the XRD pattern, which mainly reflects the secondary structure of the polyanion packing, was very similar for $H_3PW_{12}O_{40}\cdot 6C_2H_5OH$ and $H_3PW_{12}O_{40}\cdot 6H_2O$,[14] the structure of $H_3PW_{12}O_{40}\cdot 6C_2H_5OH$ indicated above may be reasonable.

The δ(C-H), ν(O-D), and δ(O-D) region of $D_3PW_{12}O_{40}\cdot nC_2H_5OD$ can be examined in more detail because there is no overlapping of the bands in this region. The intensities of the ν(C-H) band and the δ(C-H) bands were not proportional to the concentrations of ethanol (Fig. 7a, c). Moreover, the intensities of the bands at 1442 cm^{-1} ($\delta_{deg}(CH_3)$) and 1388 cm^{-1} ($\delta_s(CH_3)$ $+w(CH_2)$) relative to the 2981 cm^{-1} band ($\delta_{deg}(CH_3)$) changed significantly with the n, as is shown in Fig. 9. Higuchi et al. have reported that the intensities of ν(C-H) and δ(C-H) of the methyl group of CH_3I varied greatly depending on the polarities of the solvents.[30] The changes in Fig. 9, together with the nonproportionality (Fig. 7a, c), suggest that the CH_3 group interacts with heteropoly anions and that the interaction becomes stronger as the amount of the absorption of ethanol decreases.

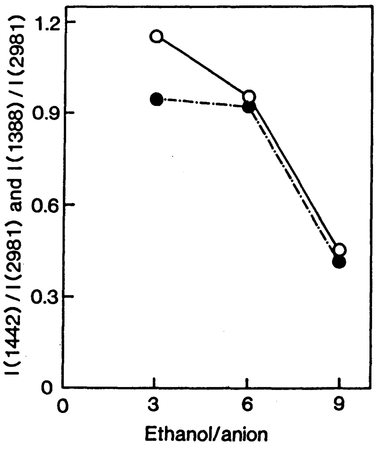


Fig. 9. Changes of the peak intensity of the 1442 (○) and 1388 (●) cm^{-1} relative to the 2981 cm^{-1} band as a funtion of the amount of C_2H_5OD absorbed into $D_3PW_{12}O_{40}$. I(1388), I(1442), and I(2981) are the integrated peak intensities of the bands at 1388, 1442, and 2981 cm^{-1}, respectively.

Transformations of Molecules during Thermal Desorption. When $H_3PW_{12}O_{40}\cdot 6(C_2H_5)_2O$ was heated at 55—75 °C in a vacuum, the characteristic band of $[(C_2H_5)_2O]_2H^+$ (at 1527 cm^{-1}) disappeared, while the frequencies of the δ(C-H) bands did not change (Fig. 6b). The species formed is probably a monomer of protonated diethyl ether, since the IR spectrum was very similar to that of $[(C_2H_5)_2OH]^+SbCl_6^-$.[26] Therefore, it is concluded that $[(C_2H_5)_2O]_2H^+$ (dimer) was transformed to $(C_2H_5)_2OH^+$ (monomer) upon the heat treatment at 55 °C.

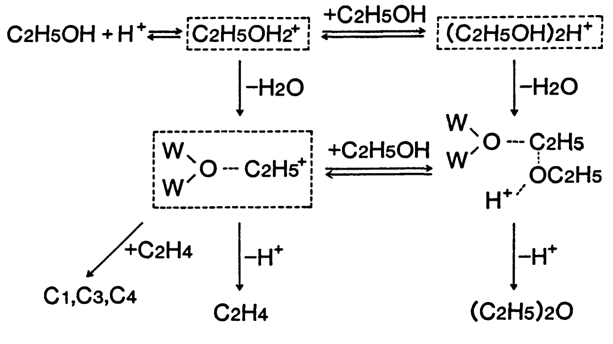
As is shown in Fig. 6b, the evacuation at 100—150 °C brought about significant changes in the δ(C-H) bands, indicating that the monomer of protonated ether was transformed to another species. Correspondingly, the $\nu_{deg}(CH_3)$ band distinctly shifted from 2985 cm^{-1} (75 °C) to 2954 cm^{-1} (Fig. 6a). These spectral changes are due to the formation of ethoxide formed on the polyanion (C_2H_5O), which was previously detected by NMR.[14] The large shift of the $\nu_{deg}(CH_3)$ band from 2980 cm^{-1} to a lower frequency is often observed upon the formation of alkoxide—for example, the shifts of C_2H_5O-Mg to 2950 cm^{-1},[31] of C_2H_5O-Al to 2959 cm^{-1},[32] and of C_2H_5O-Ca to 2945 cm^{-1}.[31]

This assignment is confirmed by ^{13}C NMR. As is shown in Fig. 8, only one species (14.3 and 82.1 ppm) remained after $H_3PW_{12}O_{40}\cdot nC_2H_5OH$ was heated at 150 °C, and the ^{13}C chemical shifts are close to those of

-OCH_2CH_3 in $(CO)_5WC(OCH_2CH_3)CH_3$: δ 80.4 for α-carbon (CH_2) and δ 14.6 for β-carbon (CH_3).[33] Moffat et al. have claimed, on the basis of the IR data, the formation of an isopropyl group during the thermal desorption of ethanol from $H_3PW_{12}O_{40}$.[12] The bands at 2954, 2924, and 2897 cm^{-1} (Fig. 6a) are also consistent with the isopropyl group (2950, 2936 cm^{-1})[34] and with tertiary CH (2890 cm^{-1}).[35] However, the species responsible for the spectrum b in Fig. 8 may not be an isopropyl group, for the following reasons. First, it is not probable that isopropyl group, which is a polymerization-decomposition product of ethanol, was formed as a single species. Secondly, the ^{13}C chemical shifts of CH_3 of ethanol and diethyl ether (δ 17.6 and 16.4, respectively) are much closer to that in Fig. 8b than are those of isopropyl alcohol and diisopropyl ether (δ 25.1 and 24.3, respectively).[36] It must be considered that the CH_3 group usually shows much smaller shifts than the CH_2 group.[36] Therefore, the species formed by heating at 150 °C is assignable to ethoxide on the heteropoly anion.

It should be noted that this species showed the peak of α-carbon (δ 82.1) downfield from tungsten ethoxide, $W(OC_2H_5)_6$ (δ 69.8).[37] Olah et al. reported that the isopropyl cation in a superacid solution showed a peak at δ 320.6,[38] while the peak of W(O-*i*-Pr)$_6$ appeared at δ 76.1.[37] This suggests that the ethyl cation should have a peak greatly downfield from the ethoxide, although it has not been detected by NMR. Thus, the species at δ 82.1 is considered to be the ethoxy group, the ethyl group of which has a more cationic character than does ordinary ethoxide.

On the basis of these results, we propose the following scheme for the thermal desorption of ethanol absorbed in $H_3PW_{12}O_{40}$.



Reaction scheme

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