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NMR Evidence for Ethyl Cation and Protonated Ethanol in the Pseudoliquid Phase of $H_3PW_{12}O_{40}$

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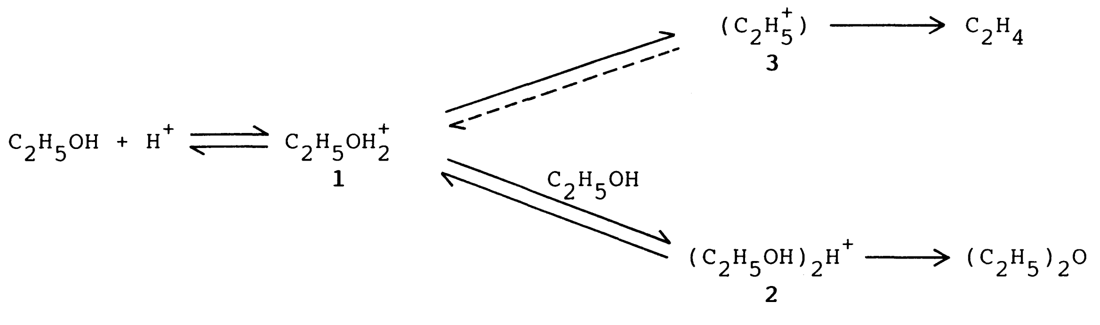
In the pseudoliquid phase of $H_3PW_{12}O_{40}$, an ethyl cation and two protonated ethanol species (monomer and dimer) have been detected by solid-state MAS NMR of ^1H, ^{13}C, and ^{31}P; these species are most probable reaction intermediates of dehydration of ethanol.

Heteropoly compounds in the solid state often exhibit very high catalytic activities and unique selectivities.[1)] It has been pointed out that their "pseudoliquid" behavior is very important for the catalysis of these compounds.[1,2)] We recently found unusual pressure dependencies of the rate and selectivity for dehydration of ethanol which proceeded in the bulk of $H_3PW_{12}O_{40}$ and explained this behavior by the following scheme.[3)] As the partial pressure of ethanol increases, the predominant species varied from **1** to **2** and then to $(C_2H_5OH)_nH^+$ $(n \geq 3)$; ethylene is favorably formed from **1** and diethyl ether from **2**, the $(C_2H_5OH)_nH^+ (n \geq 3)$ species being much less reactive.



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Here, we report that an ethyl cation, **3**, which may be a reaction intermediate from **1** to ethylene, as well as the monomer species, **1**, and the dimer species, **2**, has directly been observed by solid-state NMR of ^{1}H, ^{13}C, and ^{31}P. The dimer species has preliminarily been reported.[4] The ethyl cation or the like might also be involved in the formation of ether, although the detailed mechanism is not known yet.

Moffat et al.[5] have proposed a mechanism for dehydration of methanol or ethanol, in which protonated alcohol is converted to product via alkoxyl group. Farneth et al.[6] recently observed a methyl group adsorbed on $K_xH_{3-x}PW_{12}O_{40}$ by solid-state NMR. NMR study has been shown very useful also for the elucidation of the structure of these heteropoly compounds.[7,8]

Samples containing different amounts of ethanol were prepared in a vacuum system referring to the previous studies,[9] in which it was shown that $H_3PW_{12}O_{40}$ containing 3 and 6 molecules of ethanol per anion became stable under certain temperatures and pressures. After $H_3PW_{12}O_{40}\cdot 17H_2O$ was evacuated at 473 K (ca. 0.5 hydrates), it was treated in various ethanol pressures (≤ 6 kPa) at 298-333 K. The amount of ethanol absorbed was measured with the aid of a quartz spring balance. The amount after NMR measurement was also determined by gas chromatographic analysis.

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). ^{31}P-MAS NMR spectra were obtained at 109.2 MHz both with and without cross polarization (CP) and with high-power proton decoupling, while ^{13}C-MAS NMR spectra were obtained at 67.8 MHz with CP and proton decoupling. During the measurement of ^{13}C MAS NMR, it was observed that the temperature of the sample increased slightly. ^{1}H-MAS NMR spectra were obtained at 270 MHz with single pulse and without CP and proton decoupling. ^{31}P chemical shifts were referenced indirectly to 15 mol·dm^{-3} of H_3PO_4, and those for ^{13}C and ^{1}H to $(CH_3)_4Si$.

Table 1 shows the chemical shifts for $H_3PW_{12}O_{40}$ having various amounts of ethanol absorbed. As was preliminarily reported,[4] the sample **A**, which has 6-7 molecules of ethanol, gave well-resolved ^{1}H NMR spectra, indicating that ethanol in this state of the pseudoliquid phase is mobile and uniform. The signal of the ^{1}H NMR was assigned to the protonated ethanol dimer, **2**, from the chemical shift[10] and the relative peak intensity.[4]

What is the most remarkable is that, in the cases of **B** and **C**, two sets of signals different from the dimer, **2**, appeared. The signals for **C** are shown in Fig. 1. It was found that the relative intensities of the ^{13}C and ^{31}P peaks of the two sets (indicated as **i** and **ii** in Fig. 1) varied correspondingly from sample to sample. This indicates that there are two species, the relative ratio of them changing by the experimental conditions. ^{13}C chemical shifts of ethoxy in $(CO)_5WC(OC_2H_5)CH_3$ were reported to be 80.4 ppm for CH_2 and 14.6 ppm for CH_3.[11] Furthermore, Farneth et al.[6] have reported that methoxy group of $[(n\text{-}C_6H_{13})_4N]_2(OCH_3)PMo_{12}O_{39}$ shows a downfield shift to 74.7 ppm of ^{13}C NMR from 49.5 ppm of neat methanol. Therefore, it is very probable that the

Table 1. ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shifts for C_2H_5OH Absorbed in $H_3PW_{12}O_{40}$

Sample	Chemical Shifts/ppm					
	^{31}P a)	^{13}C b)		^{1}H b)		
		CH_3	CH_2	CH_3	CH_2	OH_x
A(6-7) c)	-15.0	17.2	61.9	1.6	4.2 4.0(sh)	9.5 9.2(sh)
B(4.2)	-14.3	16.8	65.0		____ d)	
C(2.2) **i**	-14.2	16.6	65.7		____ d)	
ii	-12.3	14.3	82.1			
neat C_2H_5OH		17.9	57.3			

a) Referred to H_3PO_4. b) Referred to TMS. sh indicates shoulder peak.
c) Ethanol to polyanion in molar ratio in parentheses.
d) Very weak and broad.

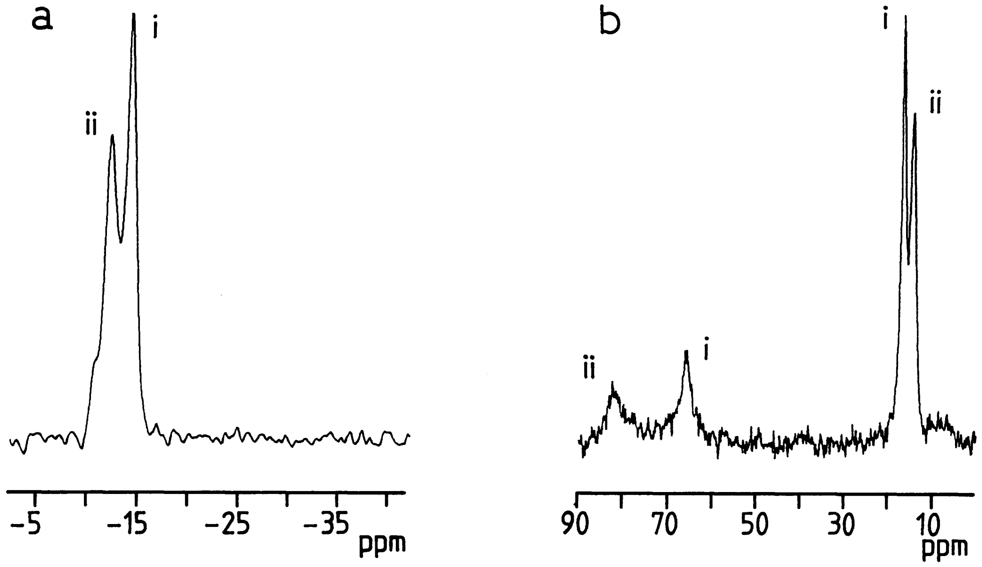

Fig. 1. (a)^{31}P and (b)^{13}C MAS NMR spectra of $(C_2H_5OH)_n \cdot H_3PW_{12}O_{40} (n \approx 2)$.

species **C-ii** is due to an ethoxy group directly bound to the heteropoly anion ($C_2H_5\text{-}O{<}^{W}_{W}$). It is interesting that the chemical shift of ^{31}P (-12.3 ppm) for the species **C-ii** is the same as that of the ^{31}P NMR for $(C_2H_5O)_3PW_{12}O_{37}$,[7)] supporting this assignment. Considering the long C-O bond distance (1.64 Å) of C_2H_5O in $(C_2H_5O)_3PW_{12}O_{37}$[7)] as compared with 1.43 Å for C_2H_5OH and 1.42 - 1.45 Å for $O\text{-}C_3H_7$ of $Mo_2(O\text{-}i\text{-}Pr)_6(Py)_2(\mu\text{-}C_2H_2)$,[12)] this species may be regarded as ethyl cation coordinated with polyanion rather than ethoxy species.

The NMR data together with the stoichiometry of H^+ and ethanol (0.7 <

$C_2H_5OH/H^+ < 1.4$) for the samples, **B** and **C**, suggest that the signal present in common for **B** and **C-i**, i.e., ^{13}C; 16.6, 65.7 ppm, and ^{31}P; -14.2 ppm is assignable to a monomer species, **1**. It is reasonable that the values of ^{31}P and ^{13}C chemical shifts for monomer species are between the dimer and the ethyl cation (closer to the dimer). It is likely that the ethyl cation was formed from the protonated ethanol monomer owing to the temperature rise of the sample caused by the irradiation for proton decoupling. The ethyl cation seems to be formed when the measurement is longer, the temperature is higher and the amount of ethanol absorbed is smaller. In the cases of both **B** and **C**, ^1H peaks were hardly detectable, indicating that those species in the pseudoliquid phase became less mobile and the signal became much broader than that for **A**.

Thus, we believe that the three reaction intermediates for ethanol dehydration, protonated monomer, dimer, and ethyl cation, were detected for the first time by the solid-state NMR.

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