# Catalysis by Heteropoly Compounds. XII.[1] Absorption Properties of 12-Tungstophosphoric Acid and Its Salts

Toshio OKUHARA,* Shin TATEMATSU,† Kwan Young LEE, and Makoto MISONO*
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
(Received September 19, 1988)

The absorption of organic molecules into the bulk of $H_3PW_{12}O_{40}$ and its salts was studied. Polar (or basic) molecules, such as alcohols and amines, were readily absorbed into $H_3PW_{12}O_{40}$, but nonpolar hydrocarbons were not absorbed. The absorption depended not only on the polarity but also on the molecular size. The diffusion coefficients of the absorption of $C_1$—$C_4$ alcohols were of similar magnitudes, and were much smaller than that of the intracrystalline diffusion of methanol in ZSM-5. The amounts of absorbed molecules in $H_3PW_{12}O_{40}$ tended to be in discrete values: that is, integral multiples of the number of protons (3, 6, etc.). This fact indicates that these polar molecules are protonated and form stable secondary structures throughout the bulk. It was confirmed in the case of methanol or ethanol that the transition between the states of 6 and 9 molecules/anion took place through the pressure changes. The absorptivity was greatly suppressed by the substitution of $Cs^+$ for more than two $H^+$, while the Na salts showed an absorptivity similar to that of $H_3PW_{12}O_{40}$.

We previously reported that the important characteristic of solid heteropoly acids, such as $H_3PW_{12}O_{40}$, is that these compounds absorb readily polar molecules, such as alcohols and amines, but not nonpolar hydrocarbons.[2-4] This property discriminates molecules by the difference in the polarity. This is different from zeolites which recognize molecular size.

Due to the absorptivity, some reactions proceed very rapidly in the bulk. This state has been called the "pseudoliquid phase".[3-6] The pseudoliquid phase brings about peculiar activity patterns[6,7] and selectivities in the reactions of alcohols and ethers.[8-11] We recently reported unusual pressure dependencies of the rate and selectivity of ethanol dehydration over $H_3PW_{12}O_{40}$, and explained the phenomenon in terms of changes in the number of ethanol molecules absorbed in the pseudoliquid phase.[12] Thus, the pseudoliquid phase behavior is essential for understanding the catalysis of heteropoly compounds.

The absorption of alcohols has already been studied by us,[2] Niiyama et al.,[13] and Moffat et al.[14] However, the factors determining the absorption rate, the amount, and the diffusion coefficient in the pseudoliquid phase have not been fully elucidated and the transition process between two pseudoliquid phases[15] has not been examined in detail. In this study, the rates of absorption as well as the amounts were systematically measured for various molecules over $H_3PW_{12}O_{40}$ under controlled conditions. It was also attempted to control the absorptivity of $H_3PW_{12}O_{40}$ by the substitution of $Na^+$ or $Cs^+$ for $H^+$.

## Experimental

**Catalysts and Materials.** $H_3PW_{12}O_{40}$ (Nippon Inorganic Colour and Chemical Co., Ltd.) was recrystallized from water after purification by extraction with diethyl ether.[6] The salts of Na and Cs were prepared from $Na_2CO_3$ and $Cs_2CO_3$ by a previously described method.[6,10] The amount of water of crystallization was measured with a thermogravimeter (Shimadzu TG-30) which was connected to a vacuum system. The surface area was measured by the BET method using $N_2$-gas adsorption after the samples were pretreated at 130 °C in He. Pyridine, alcohols ($C_1$—$C_4$), and amines ($C_3$—$C_4$) were degassed by a freeze-thaw cycle; water contained as an impurity was removed by Molecular Sieve 3A. Ethers ($C_2$—$C_6$) were used after being degassed by a freeze-thaw cycle.

**Apparatus and Procedure.** Absorption and desorption of molecules were followed by a quartz spring balance (sensitivity; 14 mg mm$^{-1}$) which was connected to a vacuum system. The heteropoly compounds (about 1.0 g) were exposed to the vapor of the molecules at 28 °C and at a desired pressure after being evacuated at 130 °C for 1 h. We call the saturated amount of absorption obtained in the presence of the vapor the "amount of saturated absorption". The number of molecules held in heteropoly compounds after evacuation at 28 °C is called the "amount of irreversible absorption".

If absorption occurs into a particle with a radius, $r$, Eq. 1 can be used for large $t$,[16,17] where $Q_t$ and $Q_\infty$ are the amounts of absorption at time $t$ and at equilibrium, respectively:

$$Q_t/Q_\infty = 1 - (6/\pi^2)\exp(-D\pi^2 t/r^2). \quad (1)$$

Here, $D$ is the diffusion coefficient in a particle of $H_3PW_{12}O_{40}$. The concentration of molecule at the surface of the $H_3PW_{12}O_{40}$ particle is assumed to be constant during the absorption. We estimated $r$ to be about 1000 Å from the surface area (5.0 m$^2\cdot$g$^{-1}$) and the density (5.8 g$\cdot$cm$^{-3}$) of $H_3PW_{12}O_{40}$.[18] From Eq. 1, the slope of a straight line in a plot of $\ln(1-Q_t/Q_\infty)$ against $t$ gives $D$. This plot was compared with another one, $Q_t/Q_\infty=6(D/\pi r^2)^{1/2}t^{1/2}$, which is suitable for small $t$.[17] As a result, the former was confirmed to be adequate for our data.

In order to follow rapid changes in the amounts of absorption by the pressure jump of methanol or ethanol, a

† Present address: Asahi Glass Co., Ltd., Hazawa-cho, Kanagawa-ku, Yokohama 221.

thermogravimeter connected to the vacuum system was used. About 50 mg of $H_3PW_{12}O_{40}$ was pretreated in vacuo at 130 °C for 1 h. Methanol and ethanol were introduced at 45 and 60 °C, respectively. The pressures were changed by controlling the temperature of the liquid of the alcohols in a Pyrex tube container connected to the system. It was confirmed that no reaction took place under these conditions.

## Results

**Rate of Absorption into $H_3PW_{12}O_{40}$.** Typical time courses of the absorption of methanol and diethyl ether are shown in Fig. 1. The ordinate is the amount of absorption in the unit of the number of molecules per polyanion, $PW_{12}O_{40}^{3-}$ (averaged over whole bulk). In the case of methanol, the initial rate of absorption, which is defined as the amount absorbed in the initial 10 min, appeared to be slightly dependent on the pressure; however, the amount of saturated absorption showed two discrete values: about 6 molecules/anion at the pressure of 15—30 Torr (1 Torr=133.3 Pa) and about 12 molecules/anion at 60—100 Torr. As discussed previously,[2] these amounts correspond to more than 50 surface layers. Therefore, it is obvious that the uptake is not the adsorption but the absorption. In accordance with this idea, the expansion of the sample volume was observed.

The absorption of diethyl ether was slow at a pressure lower than 70 Torr (Fig. 1b). However, at higher pressures (160—350 Torr), the absorption reached very rapidly about 6 molecules/anion. The presence of a similar critical pressure has previously been observed for acetone.[2]

In Table 1, the initial rates of absorption as well as the amounts of absorption are summarized. In spite of the great difference in the pressure introduced, the variation of the initial rates was within an order of magnitude for alcohols and amines. As for the alcohols, the rates in the pressure range of 20—30 Torr were in the following order: methanol≈ethanol >1-propanol>2-propanol.

Figure 2 shows a plot of $\ln(1-Q_t/Q_\infty)$ against $t$ for

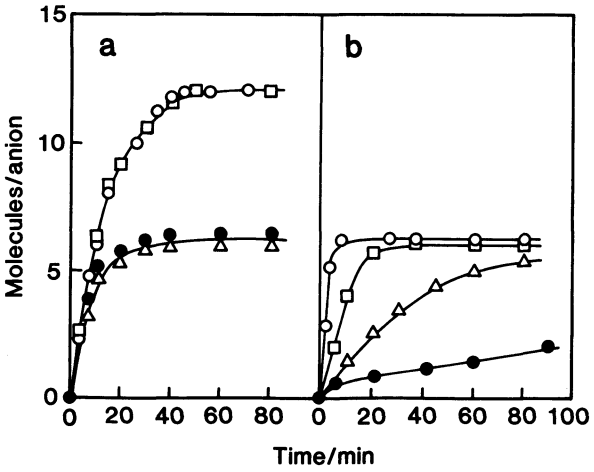


Fig. 1. Typical time course of absorption in $H_3PW_{12}O_{40}$ at 28 °C.
a) Methanol at 15 Torr (△), 30 Torr (●), 60 Torr (□), and 100 Torr (○). b) Diethyl ether at 70 Torr (●), 160 Torr (△), 200 Torr (□), and 350 Torr (○).

Table 1. Rate and Amount of Absorption of Molecule into $H_3PW_{12}O_{40}$

| Molecule | ($pK_a$) | Size[a] | $\mu$[b] | $P$[c] | Rate[d] | Absorption amount[e] | |
|---|---|---|---|---|---|---|---|
| | | | | | | $S$[f] | I[g] |
| $CH_3OH$ | (−2.0) | 20 | 1.71 | 30(20) | 5.2 | 6.0 | 3.1 (26) |
| | | | | 100(68) | 6.5 | 12.0 | 3.1 (26) |
| $C_2H_5OH$ | (−3.0) | 25 | 1.73 | 30(43) | 5.5 | 14.1 | 6.1 (64) |
| | | | | 50(71) | 6.5 | 14.5 | 6.2 (65) |
| $n$-$C_3H_7OH$ | (−3.0) | 30 | 1.73 | 20(80) | 3.8 | 14.0 | 6.2 (78) |
| $i$-$C_3H_7OH$ | (−3.2) | 31 | 1.67 | 30(57) | 3.1 | 12.1 | 6.1 (76) |
| $n$-$C_4H_9OH$ | (−3.8) | 35 | 1.81 | 4(50) | 2.0 | 5.4 | 2.8 (41) |
| $(CH_3)_2O$ | (−3.8) | 30 | 1.30 | 760(15) | 1.6 | 4.0 | 2.6 (33) |
| $(C_2H_5)_2O$ | (−3.6) | 37 | 1.17 | 350(59) | 6.2 | 6.3 | 5.8 (89) |
| $(n$-$C_3H_7)_2O$ | (−4.3) | 45 | 1.20 | 30(52) | 1.1 | 4.9 | 4.6 (86) |
| 1,4-Dioxane | (−2.9) | 33 | 1.40 | 30(76) | 2.2 | 8.3 | 4.8 (66) |
| $n$-$C_3H_7NH_2$ | (10.7) | 32 | 1.34 | 30(9) | 3.1 | 12.0 | 7.0 (89) |
| | | | | 150(43) | 9.6 | 17.5 | 8.4 (105) |
| $i$-$C_3H_7NH_2$ | (10.6) | 33 | — | 30(5) | 4.1 | 9.5 | 6.9 (86) |
| | | | | 300(46) | 7.5 | 14.8 | 7.9 (97) |
| $n$-$C_4H_9NH_2$ | (10.8) | 35 | 1.32 | 30(28) | 6.0 | 15.2 | 8.6 (125) |
| | | | | 50(47) | 8.0 | 17.7 | 8.8 (137) |
| $C_5H_5N$ | (5.2) | 31 | 2.32 | 15(62) | 4.0 | 8.5 | 6.0 (78) |
| $C_6H_6$[h] | | 34 | 0 | 65(43) | — | 0.50 | 0.10(1.4) |
| $C_2H_4$[h] | | 16 | 0 | 60(0.13) | — | 0.04 | 0.03(0.2) |

a) Cross section/Å$^2$. b) Dipole moment, Debye. c) Introduced at 28 °C; Torr. The figures in parentheses are the relative pressure/%. d) The initial absorption rate; number of molecules (anion·10 min)$^{-1}$. e) Number of molecule anion$^{-1}$. f) Saturated amount. g) Irreversible amount. The figures in parentheses are the number of surface layer (see text). h) Ref. 2.

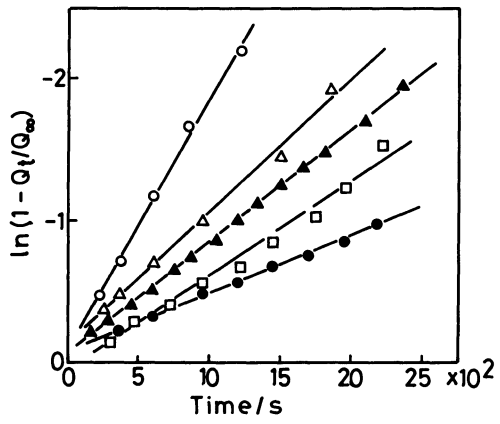


Fig. 2. Plots of $\ln(1-Q_t/Q_\infty)$ vs. $t$ for various polar molecules into $H_3PW_{12}O_{40}$ at 28°C.
(○) Methanol at 30 Torr, (△) ethanol at 30 Torr, (□) 1-propanol at 20 Torr, (●) 2-propanol at 30 Torr, and (▲) 1-propanamine at 30 Torr.

Table 2. Diffusion Coefficients of Molecules into $H_3PW_{12}O_{40}$ at 28°C

| Molecule | Pressure / Torr | $Q_\infty$[a] | Diffusion coefficient, $D$ / $10^{-14}$ cm²·s⁻¹ |
|---|---|---|---|
| $CH_3OH$ | 15 | 6.0 | 1.75 |
| | 30 | 6.0 | 1.80 |
| | 100 | 12.0 | 1.20 |
| $C_2H_5OH$ | 5 | 6.0 | 1.38 |
| | 10 | 6.0 | 1.60 |
| | 30 | 14.1 | 1.03 |
| | 50 | 14.5 | 1.00 |
| $n$-$C_3H_7OH$ | 20 | 14.0 | 0.63 |
| $i$-$C_3H_7OH$ | 30 | 12.1 | 0.42 |
| $n$-$C_4H_9OH$ | 4 | 5.4 | 0.86 |
| $(C_2H_5)_2O$ | 160 | 6.0 | 0.43 |
| | 200 | 6.0 | 2.00 |
| 1,4-Dioxane | 30 | 8.3 | 1.12 |
| $n$-$C_3H_7NH_2$ | 30 | 12.0 | 0.88 |
| | 150 | 17.5 | 0.68 |
| $i$-$C_3H_7NH_2$ | 30 | 9.5 | 0.48 |
| | 300 | 14.8 | 0.42 |
| $n$-$C_4H_9NH_2$ | 30 | 15.2 | 0.96 |
| | 50 | 17.7 | 0.83 |
| Pyridine | 15 | 8.5 | 0.66 |

a) Amount of saturated absorption; number of molecule·anion⁻¹.

alcohols and amines (see Eq. 1). All of the curves could be fitted by straight lines. The diffusion coefficients, $D$, which were calculated from the slopes of the curves, are summarized in Table 2. In the case of the alcohols, the $D$ in the pressure range from 20 to 30 Torr was in the following order: methanol> ethanol>1-propanol>2-propanol. For a comparison, the data reported for the intracrystalline diffusion of various molecules for zeolites are given in Table 3.[19-24]

In Fig. 3, the pressure dependencies of the initial absorption rates and the diffusion coefficients are shown for methanol and 1-propanamine, where the abscissa is the relative pressure, which is the ratio of the pressure introduced to the saturated vapor pressure at 28°C multiplied by 100. It was found that the pressure dependence of the absorption rate was different in these molecules; when the relative pressure increased from 10 to 60%, the absorption rate of 1-propanamine increased by a factor of about 3. However, the increase in the rate for methanol was small. The initial absorption rate tended to be nearly constant for each molecule at higher relative pressures (>40%).

**Amounts of Absorption.** The influence of the pressure on the amounts of absorption is shown in

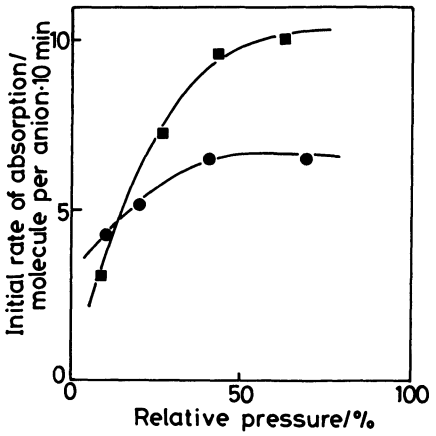


Fig. 3. Changes of the initial absorption rates as a function of the relative pressure.
●: Methanol, ■: 1-propanamine.

Table 3. Diffusion Coefficients of Molecules into Zeolites

| Molecules/Zeolite | Temperature / °C | $D$ / cm²·s⁻¹ | Ref. |
|---|---|---|---|
| $CH_3OH$/H-ZSM-5 | 30 | $2.6\times10^{-11}$ | 19 |
| $(CH_3)_2O$/H-ZSM-5 | 30 | $7.5\times10^{-11}$ | 19 |
| $C_2H_5OH$/Zeolite-T | 150 | $1.0\times10^{-11}$ | 20 |
| $C_2H_6$/H-ZSM-5 | 25 | $7.0\times10^{-11}$ | 21 |
| $C_3H_8$/H-ZSM-5 | 25 | $1.3\times10^{-11}$ | 22 |
| $n$-$C_4H_{10}$/Ca-A | 75 | $6.0\times10^{-14}$ | 22 |
| $C_6H_6$/H-ZSM-5 | 20 | $8.6\times10^{-11}$ | 19 |
| $C_6H_{12}$/H-ZSM-5 | 73 | $5.2\times10^{-14}$ | 23 |
| $C_6H_{12}$/H-ZSM-5 | 80 | $2.2\times10^{-14}$ | 24 |
| $p$-$C_8H_{10}$/H-ZSM-5 | 80 | $2.2\times10^{-12}$ | 24 |

Fig. 4. For methanol, the amounts of saturated absorption were about 6 and 12 molecules in the relative pressure of 10—80%. The amount of irreversible absorption was 3 molecules/anion in this pressure range. On the other hand, the amount of irreversible absorption of ethanol and diethyl ether was about 6 molecules/anion. As summarized in Table 1, the amounts of irreversible absorption of alcohols and ethers often showed values close to 3 and 6 molecules per anion, respectively. The ratios of the amount of irreversible absorption to that of monolayer adsorption are shown in parentheses in Table 1. Hereafter, this ratio is called the "number of surface layers".

The transition between the different absorption states can be seen in Figs. 5 and 6. The state of 6 molecules of methanol per anion, which was obtained at a pressure of 20 Torr, did not change upon the pressure increase to 55 Torr (Fig. 5). By a further increase to 70 Torr, the number of molecules increased to 9 molecules/anion. This state (9 molecules/anion) remained unchanged until the pressure was decreased to 20 Torr, inducing a change of the state to 6 molecules/anion. Figure 6 shows a similar behavior for ethanol. The transition between 6 and 9 molecules/anion took place reversibly through a pressure change from 45 to 3.5 Torr.

The absorption properties of acidic salts of Na and Cs were measured by using ethanol as a probe molecule; they are summarized in Table 4. The uptakes of ethanol for Na and Cs salts are shown in Fig. 7 in units of "number of surface layer" as a function of the cation content. The "number of surface layer" was estimated from the cross section of ethanol (25 Å$^2$) and the surface area of these salts.[25] As can be seen in Fig. 7, the numbers of surface layers for Na salts were about 60

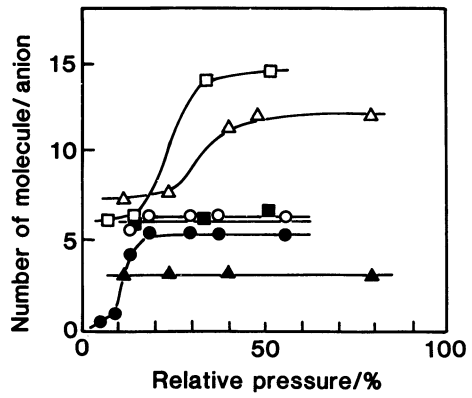


Fig. 4. Pressure dependence of the amounts of absorption into $H_3PW_{12}O_{40}$ at 28 °C.
Saturated amount: (□) ethanol, (△) methanol, (○) diethyl ether.
Irreversible amount: (■) ethanol, (▲) methanol, (●) diethyl ether.

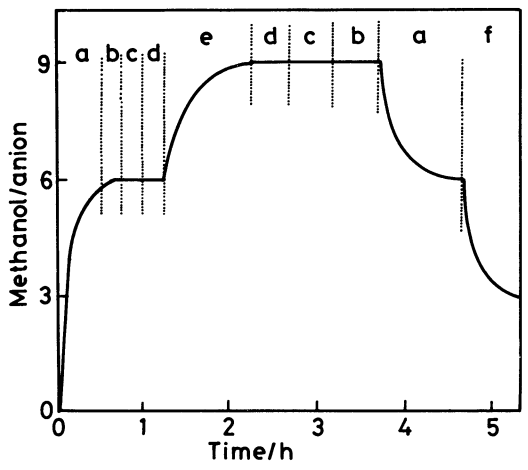


Fig. 5. Changes of absorption amount in $H_3PW_{12}O_{40}$ by the pressure jump of methanol at 45 °C.
(a) 20 Torr, (b) 30 Torr, (c) 40 Torr, (d) 55 Torr, (e) 70 Torr, (f) 0 Torr.

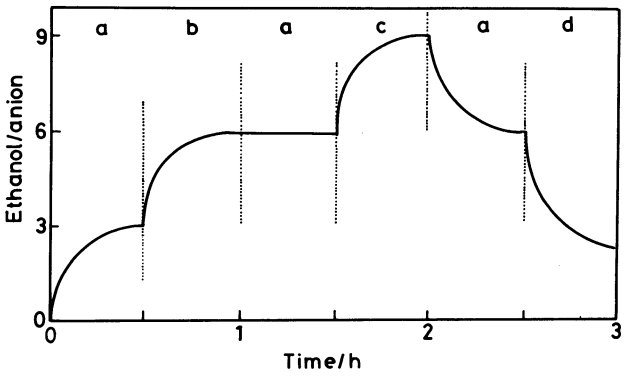


Fig. 6. Changes of absorption amount in $H_3PW_{12}O_{40}$ by the pressure jump of ethanol at 60 °C.
(a) 3.5 Torr, (b) 13 Torr, (c) 45 Torr, (d) 0 Torr.

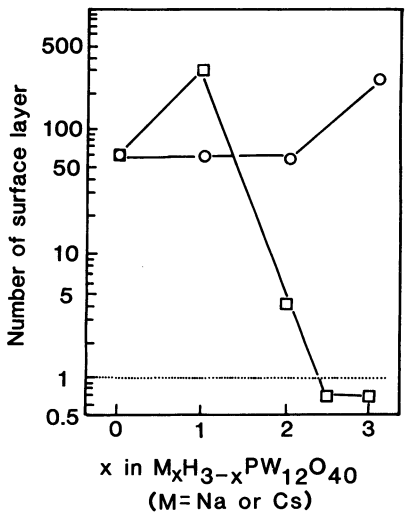


Fig. 7. Uptakes of ethanol into Na and Cs salts of $H_3PW_{12}O_{40}$ at 28 °C. (○) Na, (□) Cs.
The samples were pretreated at 150 °C. The pressure of ethanol was 30 Torr.

Table 4. Rate and Amount of Uptake of Ethanol for Na and Cs Salts

| | $Na_xH_{3-x}PW_{12}O_{40}$ | | | | $Cs_xH_{3-x}PW_{12}O_{40}$ | | | |
|---|---|---|---|---|---|---|---|---|
| | $x=0$ | 1 | 2 | 3 | 1 | 2 | 2.5 | 3 |
| Rate[a] | 6.5 | 5.5 | 4.5 | 2.5 | 5.5 | 3.0 | 4.0 | 4.0 |
| Uptakes[b] | 6.2 | 4.3 | 2.9 | 2.2 | 3.1 | 1.9 | 1.8 | 1.7 |
| Surface area[c] | 5.0 | 3.7 | 2.5 | 0.8 | 0.5 | 21 | 114 | 176 |

a) Initial rate for absorption, molecules (anion·10 min)$^{-1}$. b) Irreversible amount. c) $m^2\ g^{-1}$ (after pretreatment at 130 °C). Ethanol (30 Torr) was added at 28 °C.

and 143 in $0 \leq x \leq 2$ and at $x=3$, respectively. On the other hand, this number changed greatly from 322 to 0.5 as $x$ varied from 1 to 3 for Cs salts.

## Discussion

**Factors Determining the Absorption.** The uptakes of benzene, ethylene (Table 1), and other hydrocarbons were nearly equal to or less than the amount of monolayer;[2] the numbers of surface layers were less than 1. This shows that these hydrocarbons are not absorbed. On the other hand, the numbers of surface layers for alcohols, ethers, and amines were greater than 26, indicating that these polar molecules are absorbed into the bulk of $H_3PW_{12}O_{40}$. Due to a large uptake, an increase in the sample temperature was always observed. Since $H_3PW_{12}O_{40}$ is a strong acid, an acid-base interaction must be the driving force of the absorption of basic (or polar) molecules.

The basicity may be expressed by $pK_a$ of the protonated molecules (conjugate acid), where $K_a$ is the dissociation constant of protonated molecules; $BH^+ + H_2O \rightleftarrows B + H_3^+O$ (B; base). Then, the molecules can be classified into three groups by their $pK_a$ values. The first group consists of alcohols and ethers, of which the $pK_a$ values are between $-2.0$ and $-4.3$. The molecules in the second group are amines having $pK_a$'s of about 10, which are much more strongly basic. The third is the group of hydrocarbons. While the values of $pK_a$ of hydrocarbons are not clear, these molecules must be much less basic than alcohols and ethers. In the gas phase, oxygenated compounds like alcohol and ether are generally more basic than olefins.[26]

The polarity of molecule also appears to be relevant to the absorption. The polarity may be represented by the dipole moment. As shown in Table 1, alcohol, ether, and amine have large dipole moments (e.g., about 1.7 (alcohols), 1.2 (ethers), 1.3 (amines), and 2.2 ($C_5H_5N$) in the unit of Debye),[27] but it is zero for ethylene and benzene. Generally, hydrocarbons have very small dipole moments. Therefore, it is concluded that either the basicity or polarity of molecules is important regarding absorption. Since these molecules tend to form hydrogen bonding, whether the hydrogen bonding is formed with $H_3PW_{12}O_{40}$ or not may be a key factor for absorption.

**Rate of Absorption.** As shown in Fig. 3, the initial absorption rate had a nearly constant value at the relative pressure higher than about 40%. When the initial rates measured at the relative pressure higher than 40% were plotted against the molecular size, correlations for polar molecules were obtained as shown in Fig. 8. The initial rates of alcohols greatly decreased as the molecular size increased (20 Å$^2$ (methanol)—35 Å$^2$ (1-butanol)). However, the initial rates for propanamines and 1-butanamine were distinctly higher than those of alcohols in spite of their greater molecular size. This difference is probably due to the large difference in the $pK_a$ values of alcohols ($-2 \leq pK_a \leq -3.8$) and amines ($pK_a \approx 10$). It may therefore be stated that the rate is primarily determined by the basicity (or polarity) and secondarily by the molecular size.

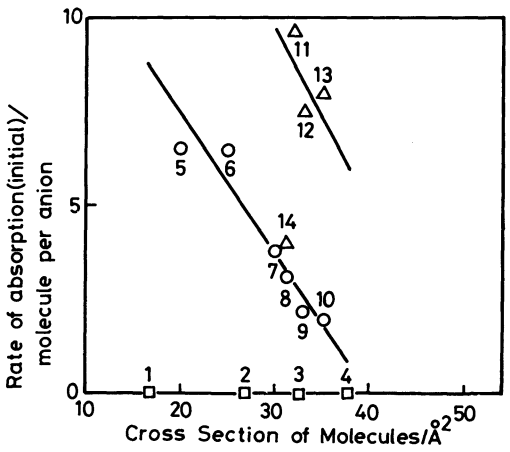


Fig. 8. Initial rates of absorption of various molecules by $H_3PW_{12}O_{40}$ vs. molecular size.
1. Ethylene (0.13), 2. dichloromethane (27), 3. benzene (43), 4. toluene (91), 5. methanol (68), 6. ethanol (71), 7. 1-propanol (80), 8. 2-propanol (57), 9. 1,4-dioxane (76), 10. 1-butanol (50), 11. 1-propanamine (43), 12. 2-propanamine (46), 13. 1-butanamine (47), 14. pyridine (62).
The figures in parentheses are the relative pressure.

As shown in Table 2, the diffusion coefficients for alcohols tended to become lower as the molecular size increased (from methanol to 2-propanol). This trend is the same as the initial rates. Since the diffusion coefficient is regarded as being the rate constant of absorption, the rate of absorption would be proportional to the product of the diffusion coefficient and the concentration of the molecule at the surface. There-

fore, the difference in the initial rate for alcohols may mainly be ascribable to a difference in the diffusion coefficient. Although the diffusion coefficients of the amines were not so great (Table 2), the initial rates were high (Fig. 8). The higher initial rates for the amines are probably brought about by the higher concentrations of amines on the surface as compared with those of alcohols, while the concentration at the surface during the absorption is not yet known.

The diffusion coefficient for the hydrocarbons into the pore of ZSM-5 zeolite varied from $10^{-11}$ to $10^{-14}$ $cm^2 \cdot s^{-1}$ depending on the molecules (Table 3). This great difference in D is called the molecular sieve effect.[17] In the case of $H_3PW_{12}O_{40}$, the difference between hydrocarbons and polar molecules was very large. But, the diffusion coefficients of alcohols and amines into the bulk of $H_3PW_{12}O_{40}$ showed similar values, about $0.42—1.80\times10^{-14}$ $cm^2 \cdot s^{-1}$ (at 30 Torr). The uptake of $H_3PW_{12}O_{40}$ is not diffusion into pores,[3] but absorption into the bulk between the polyanions. Therefore, it may meet a much greater resistance than the diffusion of molecules into the micropores of zeolite.

It is clear that the absorptivity of $H_3PW_{12}O_{40}$ was greatly suppressed by the substitution of $Cs^+$ for $H^+$, while the absorptivity varied little upon substitution of $Na^+$ for $H^+$ (Fig. 7). Since the acidity decreased upon substitution of $Na^+$ for $H^+$,[6] the decrease in the rate of ethanol absorption as the content of $Na^+$ increased (Table 4) also suggests the importance of the acidity of heteropoly compounds (basicity of molecules).

**Transition between Pseudoliquid Phases.** As for the absorption of polar molecules, there are at least two states which differ in the number of absorbed molecules. The states of 6 and 9 molecules/anion existed (Figs. 5 and 6) and each state was stable within a certain range of pressure. We reported for the dehydration of 2-propanol over $H_3PW_{12}O_{40}$ that there were at least two pseudoliquid phases differing in the catalytic activity.[15] At 80 °C, the number of 2-propanol absorbed was 3 molecules/anion for the high-activity state and 8—9 molecules/anion for the low-activity states. Their transitions brought about unusual pressure dependencies of the activity.[15]

It is noted that the amounts of alcohol, ether, and pyridine were nearly integral multiples (1, 2, and 3) of the number of protons present in the bulk of $H_3PW_{12}O_{40}$. These numbers indicate that these molecules are homogeneously absorbed and that the stable forms are probably, e.g., $CH_3OH_2^+$, $(C_2H_5OH)_2H^+$, and $(Py)_2H^+$. IR and gravimetric measurements have previously suggested that pyridinium ion in dimer species, $(Py)_2H^+$ existed.[2] Recently, $^1H$ and $^{13}C$ solid-state NMR of ethanol absorbed on $H_3PW_{12}O_{40}$ have been measured.[28] $^1H$ NMR spectra of $H_3PW_{12}O_{40}\cdot6C_2H_5OH$ resembled those of protonated ethanol in superacid,[29] suggesting that this species is $(C_2H_5OH)_2H^+$.[28] Furthermore, the infrared spectra of $H_3PW_{12}O_{40}\cdot6C_2H_5OH$ also supported the presence of $(C_2H_5OH)_2H^+$ in the bulk.[30] Although the exact structure of a compound having 6 molecules/anion is unknown yet, for example, the structure of $H_3PW_{12}O_{40}\cdot6C_2H_5OH$ may be similar to that of $H_3PW_{12}O_{40}\cdot6H_2O$, of which the structure was determined by X-ray diffraction,[31] since the XRD patterns were similar.

## Summary

1. For absorption, the basicity or polarity of molecules was important. The rate of absorption depended on the molecular size as well as basicity.

2. In the absorption state (i.e., pseudoliquid phase), the numbers of molecules were integral multiples of the number of protons; the amount of irreversible absorption of methanol was equal to the number of $H^+$; those of ethanol, diethyl ether, and propanols were twice the number.

3. In the presence of gas-phase methanol or ethanol, the transition between different pseudoliquid phases takes place reversibly, depending on the pressure ranges.

4. The absorptivity of $H_3PW_{12}O_{40}$ can be controlled by the formation of acidic salts of Cs.

The present work was supported in part by a Grant-in-Aid for Scientific Research No. 62470070 from the Ministry of Education, Science and Culture and by Asahi Glass Foundation.

## References

1) Part XI: N. Mizuno and M. Misono, *J. Phys. Chem.*, in press.

2) M. Misono, N. Mizuno, K. Katamura, A. Kasai, Y. Konishi, K. Sakata, T. Okuhara, and Y. Yoneda, *Bull. Chem. Soc. Jpn.*, **55**, 400 (1982).

3) M. Misono, K. Sakata, Y. Yoneda, and W. Y. Lee, Proc. 7th Intern. Congr. Catal., Tokyo, 1980, Kodansha (Tokyo)-Elsevier (Amsterdam), 1981, p. 1047.

4) M. Misono, *Catal. Rev.*, **29**, 269 (1987).

5) T. Okuhara, T. Hashimoto, M. Misono, Y. Yoneda, H. Niiyama, Y. Saito, and E. Echigoya, *Chem. Lett.*, **1983**, 573.

6) T. Okuhara, A. Kasai, N. Hayakawa, Y. Yoneda, and M. Misono, *J. Catal.*, **83**, 121 (1983).

7) Y. Saito and H. Niiyama, *J. Catal.*, **106**, 329 (1987).

8) T. Okuhara, A. Kasai, N. Hayakawa, M. Misono, and Y. Yoneda, *Chem. Lett.*, **1981**, 391.

9) T. Okuhara, T. Hibi, K. Takahashi, S. Tatematsu, and M. Misono, *J. Chem. Soc., Chem. Commun.*, **1984**, 697.

10) T. Hibi, K. Takahashi, T. Okuhara, M. Misono, and Y. Yoneda, *Appl. Catal.*, **24**, 69 (1986).

11) T. Baba, J. Sakai, H. Watanabe, and Y. Ono, *Bull. Chem. Soc. Jpn.*, **55**, 2555 (1982).

12) M. Misono, T. Okuhara, T. Ichiki, T. Arai, and Y. Kanda, *J. Am. Chem. Soc.*, **109**, 5535 (1987).

13) Y. Saito, H. Niiyama, and E. Echigoya, *Nippon Kagaku Kaishi*, **1984**, 391.
14) J. G. Highfield and J. B. Moffat, *J. Catal.*, **95**, 108 (1985).
15) K. Takahashi, T. Okuhara, and M. Misono, *Chem. Lett.*, **1985**, 841.
16) J. Crank, "The Mathematics of Diffusion," Clarendon Press, Oxford (1957), p. 89.
17) R. M. Barrer, "Zeolite-Science and Technology," ed. by F. R. Ribeiro et al., Martinus Nijhoff Publishers (1984), p. 261.
18) W. Pier and A. Weiss, Landolt-Bornstein Neue Series III/7f (1977).
19) P. Wu and Y. H. Ma, Proc. 6th Intern. Zeolite Conf., Reno, 1984, Butterworths, p. 251.
20) R. L. Gorring, *J. Catal.*, **31**, 13 (1973).
21) M. Bulow, H. Schlodder, L. V. C. Rees, and R. E. Richards, Proc. 7th Intern. Zeolite Conf., Tokyo, 1986, Kodansha, Elsevier, p. 579.
22) R. M. Barrer and D. J. Clarke, *J. Chem. Soc., Faraday Trans. 1*, **70**, 535 (1974).
23) H. Chon, B. J. Ahn, and S. E. Park, Proc. 8th Intern. Congr. Catal., Berlin, 1984, Verlag Chemie, Weinheim, IV-555.
24) C. Wu, G. Qin, and Y. Xie, Proc. 7th Intern. Zeolite Conf., Tokyo, 1986, Kodansha, Elsevier, p. 481.
25) N. Hayakawa, T. Okuhara, M. Misono, and Y. Yoneda, *Nippon Kagaku Kaishi*, **1982**, 356.
26) D. H. Ave and M. T. Bowers, "Gas Phase Ion Chemistry," ed. by M. T. Bowers, Academic Press, New York (1979), Vol. 2, Chap. 9.
27) B. Starch, "Landolt-Bornstein Tables," New Series, II/4 Springer (1967); A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Company, San Francisco and London (1963).
28) Y. Kanda, K. Y. Lee, S. Nakata, S. Asaoka, and M. Misono, *Chem. Lett.*, **1988**, 139.
29) G. A. Olah, J. Sommer, and E. Namanworth, *J. Am. Chem. Soc.*, **89**, 3576 (1967).
30) K. Y. Lee, N. Mizuno, T. Okuhara, and M. Misono, *Bull. Chem. Soc. Jpn.*, in press.
31) G. M. Brown, M. R. Neo-Spiret, W. R. Busing, and H. A. Levy, *Acta Crystallogr., Sect. B*, **33**, 1038 (1977).