Extensive Combinations of Clustering Sets of Sulfuric Acid and Various Solvents

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The FAB mass spectra of the mixtures of the sulfuric acid and 14 solvent molecules (acetone, methyl alcohol, ethyl alcohol, 1-propyl alcohol, 2-propyl alcohol, 1-butyl alcohol, 2-butyl alcohol, *t*-butyl alcohol, 1-pentyl alcohol, 1-hexyl alcohol, ethylene glycol, acetic acid, dimethyl sulfoxide, and water) were measured and CAD spectra of the cluster ions were also measured.

The FAB mass spectra showed the extensive cluster ions of H_2SO_4 with the solvent, $(a\text{H}_2\text{SO}_4 + b\text{Solv} + \text{H})^+$, a and b are positive integers or zero. We also tried to investigate CAD spectra of unsymmetrical protonated ions of sulfuric acid and water molecules, $(\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+$, precisely.

The mass spectra were found to be dehydrated ions, $(a\text{H}_2\text{SO}_4 + b\text{Solv} - \text{H}_2\text{O} + \text{H})^+$. In some cases, we determined which dehydration occurred from H_2SO_4 site or from solvent site. For that problem to be solved, the CAD spectra by means of MS/MS (mass spectrometry/mass spectrometry, tandem mass spectrometry) of $(a\text{H}_2\text{SO}_4 + b\text{Solv} + \text{H})^+$ and $(a\text{H}_2\text{SO}_4 + b\text{Solv} - \text{H}_2\text{O} + \text{H})^+$, were needed to measure. Further the special cluster ions $(\text{C}_n\text{H}_{2n+1}\text{OH} - \text{H}_2\text{O} + \text{H})^+$, if proton resides on the larger PA site, the dehydration occurs on the protonated site. We can decide the dehydration site by the present methods.

1. Introduction

Acid rain is a major problem in atmospheric chemistry, and moreover in the gas phase chemistry of aerosol particles. We are much interested in the original material of acid rain, *i.e.*, one of which is sulfuric acid, (H_2SO_4) .^{1)–6)} The sulfuric acid is well known as a strong acid and an oxidation agent.^{4), 5)} There were some reports concerning the fast atom bombardment mass spectrometry (FABMS) of sulfuric acid, and the metastable ion (MI) spectra and the collisionally activated dissociation (CAD) spectra of protonated sulfuric acid cluster ions.^{6)–9)} The sulfuric acid has become a new matrix of FABMS because some molecules are insoluble in the usual matrices. Instead of the popular matrix, (*i.e.*, glycerol) for measuring FABMS for some metal phthalocyanines, the sulfuric acid has been used as a new matrix.^{10)–12)} Here we also examine whether the sulfuric acid is versatile as a new matrix for metal phthalocyanines. Before studying the usage of sulfuric acid for the new matrix, we studied FABMS and CAD spectra by examining ions containing H_2SO_4 .

The FAB mass spectra showed the extensive cluster ions containing H_2SO_4 and

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water molecule, $(a\text{H}_2\text{SO}_4 + b\text{H}_2\text{O} + \text{H})^+$, a and b are integers or zero. We also tried to investigate CAD spectra of unsymmetrical protonated ions of sulfuric acid and water molecule, $(\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+$, and CAD spectra of protonated cluster ions, $(a\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+$. At first acetone instead of water molecule was used in FABMS measurements with sulfuric acid. The typical cluster ions were found to be $(a\text{H}_2\text{SO}_4 + \text{Ac} + \text{H})^+$ ($a = 1-7$, $\text{Ac} = \text{acetone}$). The mixtures of sulfuric acid and other solvents (totally 14 samples prepared) were measured for comparison with the results of mixtures of water or acetone by FABMS spectra.

Cluster ions of H_2SO_4 were investigated by Futrell partly.⁶⁾ We also tried to measure sulfuric acid with water by changing the concentration of sulfuric acid. And the mixtures of sulfuric acid with other solvents (*e.g.*, acetone, *etc.*) were also measured by FABMS and CAD methods. Many types of cluster ions (containing dimer ions) bounded with a proton are appeared and summarized. In the present paper, we measured CAD spectra and discussed the results obtained quantitatively.

The FAB mass spectra of the mixtures of the sulfuric acid and one of the 14 solvent molecules (acetone, methyl alcohol, ethyl alcohol, 1-propyl alcohol, 2-propyl alcohol, 1-butyl alcohol, 2-butyl alcohol, *t*-butyl alcohol, 1-pentyl alcohol, 1-hexyl alcohol, ethylene glycol, acetic acid, dimethyl sulfoxide, and water) were measured and CAD spectra of these cluster ions were also measured. The mass spectra were found to be protonated mixed cluster ions, $(a\text{H}_2\text{SO}_4 + b\text{Solv} + \text{H})^+$, ($\text{Solv} = \text{solvent}$) and dehydrated ions, $(a\text{H}_2\text{SO}_4 + b\text{Solv} - \text{H}_2\text{O} + \text{H})^+$. In some cases, we determined which dehydration occurred from H_2SO_4 site or solvent site. For that problem to be solved, the CAD spectra by means of MS/MS (mass spectrometry/mass spectrometry, tandem mass spectrometry) of $(a\text{H}_2\text{SO}_4 + b\text{Solv} + \text{H})^+$ and $(a\text{H}_2\text{SO}_4 + b\text{Solv} - \text{H}_2\text{O} + \text{H})^+$, were needed to measure.

Further the cluster ions $(\text{H}_2\text{SO}_4 + \text{Solv} + \text{H})^+$ were analyzed by the kinetic method.¹³⁾⁻¹⁵⁾ The order of proton affinity (PA) could be determined by this method. Relative proton affinity can also be measured by using kinetic method. In this method, a proton-bound dimer $\{(M_1 + \text{H} + M_2)^+\}$ is formed between two species (M_1 and M_2) and is then selectively isolated. Upon collision activated dissociation or metastable ion dissociation, the dimer fragments competitively to give either or both of the two protonated monomers $\{(M_1 + \text{H})^+$ and $(M_2 + \text{H})^+\}$. The logarithm of the ratio of the two rate constants of the ions, which are represented by abundances of product ion, is proportional to the difference in proton affinity. The kinetic method has been used to estimate proton affinities, electron affinities, and silver ion affinities. This method has also been used to examine gas-phase basicities and gas-phase acidities of alkylcarboxylic acids, alcohols, alkylamines, pyridines, and anilines. The difference of proton affinities has been measured using BE type, EBE type (present report described), and triple quadrupole mass spectrometers, where E and B represent electrostatic and magnetic fields, respectively. The kinetic method is said to be employed cautious because its accuracy is only confirmed in cases where the two species comprising the dimer have very similar structures. Therefore in this report similar structure molecules were examined precisely.

2. Experimental

The measurements of FABMS and CAD spectra were made with a JEOL DX 303 double focusing mass spectrometer (EBE type with a cylindrical electrostatic analyzer) using a JEOL DA 5000 data system described before.¹⁵⁾ The following conditions were adopted: mass spectrometer; resolution 1,000 and mass range m/z 0–1,000; FAB ion source, FAB gun argon and accelerating voltage of fast atom beam 3 kV; and CAD gas argon at a pressure of 2×10^{-6} Torr (1 Torr = 133.3 Pa) at the Penning gauge (to attenuate intensity of the precursor ion beam to $\sim 30\%$)¹⁵⁾ (variation in the gas pressure did not have a significant effect on the CAD spectra).

Sulfuric acid was obtained from Kanto Chemical Co., Ltd., for the atomic absorption analytical grade. Acetone, methyl alcohol, ethyl alcohol, 1-propyl alcohol, 2-propyl alcohol, 1-butyl alcohol, 2-butyl alcohol, 1-pentyl alcohol, 1-hexyl alcohol, and ethylene glycol were obtained from Nacalai Tesque Co., Ltd. Acetic acid, methyl alcohol, and dimethyl sulfoxide, were obtained from Wako Pure Chemical Co., Ltd. Chemical *t*-butyl alcohol was obtained from Kanto Chemical Co., Ltd. Each sample was used for measurements without further purification. The RMMs were checked by means of FABMS.

Sometimes vacuum valves were corroded severely by sulfuric acid vapour and/or mixtures of sulfuric acids and other solvents described.

3. Results and Discussion

3.1 MS and CAD spectra in the cases of various mixtures of H_2SO_4 and H_2O

FABMS spectra of concentrated sulfuric acid are shown in Fig. 1. FABMS spectra of concentrated H_2SO_4 were identified as shown in Table 1. Major peaks were identified to be $(n\text{H}_2\text{SO}_4 + \text{H})^+$ and $(n\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+$, where n is the cluster number. The fact of presence of two types cluster ions is forced to remeasure the FABMS spectra of changing the concentration of sulfuric acid with H_2O . The results are shown in Figs. 2 and 3, the intensity of $(n\text{H}_2\text{SO}_4 + \text{H})^+$ versus cluster number n and that of $(n\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$

Fig. 1. Typical FABMS spectra of concentrated sulfuric acid.

Table 1. FABMS Spectra of Concentrated H_2SO_4 and Identification

m/z		
19 ($\text{H}_2\text{O} + \text{H}$) ⁺	99 ($\text{H}_2\text{SO}_4 + \text{H}$) ⁺	117 ($\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H}$) ⁺
48 SO^+	197 ($2\text{H}_2\text{SO}_4 + \text{H}$) ⁺	215 ($2\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H}$) ⁺
65 SO_2H^+	295 ($3\text{H}_2\text{SO}_4 + \text{H}$) ⁺	313 ($3\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H}$) ⁺
81 ($\text{H}_2\text{SO}_4 - \text{H}_2\text{O} + \text{H}$) ⁺	393 ($4\text{H}_2\text{SO}_4 + \text{H}$) ⁺	411 ($4\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H}$) ⁺
83 ($\text{H}_2\text{SO}_4 - \text{O} + \text{H}$) ⁺	491 ($5\text{H}_2\text{SO}_4 + \text{H}$) ⁺	509 ($5\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H}$) ⁺
	589 ($6\text{H}_2\text{SO}_4 + \text{H}$) ⁺	607 ($6\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H}$) ⁺
135 ($\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{H}$) ⁺	687 ($7\text{H}_2\text{SO}_4 + \text{H}$) ⁺	705 ($7\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H}$) ⁺
233 ($2\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{H}$) ⁺	785 ($8\text{H}_2\text{SO}_4 + \text{H}$) ⁺

Fig. 2. The intensity dependence of the $(n\text{H}_2\text{SO}_4 + \text{H})^+$ ions *versus* cluster number, n . The intensity of $(\text{H}_2\text{SO}_4 + \text{H})^+$ is normalized as 10. $\square$, conc H_2SO_4 ; +, 80%; $\diamond$, 60%; $\triangle$, 40%; $\times$, 20%.

Fig. 3. The intensity dependence of the $(n\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+$ ions *versus* cluster number, n . The intensity of $(\text{H}_2\text{SO}_4 + \text{H})^+$ is normalized as 10 (not shown in Fig. 3). $\square$, conc H_2SO_4 ; +, 80%; $\diamond$, 60%; $\triangle$, 40%; $\times$, 20%.

$+ \text{H})^+$ *versus* n , respectively, containing only neat H_2SO_4 and both H_2SO_4 and H_2O , changing molar ratios $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ from 1 : 0 to 1 : 11.84 (*i.e.*, volume ratios of H_2SO_4 with H_2O were from concentrated, 80%, 60%, 40%, to 20%). Figure 2 almost shows the same

behavior with changing the concentration of H_2SO_4 , but Fig. 3 shows the behavior of concentrated H_2SO_4 is different from those of other concentrations of H_2SO_4 . The conclusion of this result in the case of concentrated H_2SO_4 is shown below, intensities of dehydrated cluster ions $(n\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+$ were lower than in those of other cases. In other cases except for concentrated H_2SO_4 , m/z 135, $(\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{H})^+$ was also detected as the concentration of H_2O increased in almost all cases. The difference of results shows that concentrated H_2SO_4 haven't much H_2O than the other cases of concentration. Figures 4 and 5 show FABMS spectra of both conc- (freshly opened) and dil-sulfuric acids. From two spectra mass number, m/z , 135 was absent and present in Figs. 4 and 5, respectively. The mass number was identified to be $(\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{H})^+$.

Next, CAD spectra of both cluster ions, $(n\text{H}_2\text{SO}_4 + \text{H})^+$ and $(n\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+$ were investigated. Figures 6 and 7 indicate the CAD spectra of $(\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+$ and

Fig. 4. FABMS spectra of conc-sulfuric acid.

Fig. 5. FABMS spectra of dil-sulfuric acid (volume %, H_2SO_4 : H_2O =20:80).

Fig. 6. The CAD spectra of m/z 117: $(H_2SO_4 + H_2O + H)^+$, m/z 99: $(H_2SO_4 + H)^+$, m/z 81: $(H_2SO_4 - H_2O + H)^+$ or $(SO_3 + H)^+$, m/z 19: $(H_2O + H)^+$.

Fig. 7. The CAD spectra of m/z 215: $(2H_2SO_4 + H_2O + H)^+$, m/z 197: $(2H_2SO_4 + H)^+$, m/z 117: $(H_2SO_4 + H_2O + H)^+$, m/z 99: $(H_2SO_4 + H)^+$, m/z 19: $(H_2O + H)^+$.

$(nH_2SO_4 + H_2O + H)^+$ ($n=2$). Summarizing both CAD spectra of cluster ions, two types of reaction schemes were proposed.

- ① $[nH_2SO_4 + H]^+ \rightarrow [pH_2SO_4 + H]^+ + (n-p)H_2SO_4$
- ② $[nH_2SO_4 + H]^+ \rightarrow [pH_2SO_4 + H_2O + H]^+ + (n-p-1)H_2SO_4 + SO_3$

and

- ③ $[nH_2SO_4 + H_2O + H]^+ \rightarrow [pH_2SO_4 + H_2O + H]^+ + (n-p)H_2SO_4$
- ④ $[nH_2SO_4 + H_2O + H]^+ \rightarrow [pH_2SO_4 + H]^+ + (n-p)H_2SO_4 + H_2O$

The dissociation of these cluster ions without water (shown in ① and ②) produces both hydrated cluster ions and cluster ions without water. The dissociation of hydrated cluster ions (shown in ③ and ④) produces both hydrated cluster ions and cluster ions without water. CAD spectra of the protonated cluster ions of sulfuric acid, $(n\text{H}_2\text{SO}_4 + \text{H})^+$, showed the tendency of appearance of protonated small cluster size sulfuric acid with water.

Figure 8 shows in the cases of types ① and ② reactions, intensity ratios of $[(p\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+ / (p\text{H}_2\text{SO}_4 + \text{H})^+]$ from CAD spectra of $(n\text{H}_2\text{SO}_4 + \text{H})^+$ versus p decreases, intensity ratios become flat in almost all n values and the minimum appeared and after that minimum begins increasing. Figure 9 shows in the cases of types ③ and ④ reactions, intensity ratios of $[(p\text{H}_2\text{SO}_4 + \text{H})^+ / (p\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+]$ from CAD spectra of $(n\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+$

Fig. 8. In the cases of types ① and ② reactions, intensity ratios of $[(p\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+ / (p\text{H}_2\text{SO}_4 + \text{H})^+]$ from CAD spectra of $(n\text{H}_2\text{SO}_4 + \text{H})^+$ versus p decreases, intensity ratios become flat to increase in almost all n values.

Fig. 9. In the cases of types ③ and ④ reactions, intensity ratios of $[(p\text{H}_2\text{SO}_4 + \text{H})^+ / (p\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+]$ from CAD spectra of $(n\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+$ versus p decreases, intensity ratios is increasing in almost all n values. Both indicate that cluster ions are apt that intensity ratios become flat to increase in almost all n values.

The above two reactions behave opposite types of behavior.

$\text{H}_2\text{O} + \text{H})^+$ versus p decreases, intensity ratio become increasing in almost all n values. Both indicate that cluster ions are apt to be flat in intensity ratios and to increase in almost all n values

It becomes contrary behavior.

From CAD spectra the proton-bound cluster ions with sulfuric acids and water molecule, $(n\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+$ showed the strong tendency of appearing protonated smaller sizes of cluster ions of sulfuric acid. This means that water was dissociated from the sulfuric acid cluster molecules. The four reaction schemes (①, ②, ③, and ④) suggest that the equilibrium among H_2SO_4 , SO_3 , and H_2O was attained easily.

3.2 The proton affinity order of H_2SO_4 and many solvents

The CAD spectra of the unsymmetrical protonated dimer ion, $(\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H})^+$, produce both the $(\text{H}_2\text{SO}_4 + \text{H})^+$ and $(\text{H}_2\text{O} + \text{H})^+$ ions. In these cases, the former signal is stronger than the latter. The proton affinity (PA) of H_2SO_4 is also considered to be larger than that of H_2O . The CAD spectra of $(\text{H}_2\text{SO}_4 + \text{Solv} + \text{H})^+$ can sometimes give PA orders of H_2SO_4 and the solvent. Reported PA values in the literature of Lias *et al.*,¹⁶⁾ are shown in Table 2, where the PA's of H_2O and H_2SO_4 were reported to be 696 and 707 kJ/mol, respectively. The order of PA of solvent molecules by the present experiment and the published data are in good agreement with each other. As it was appeared to be the clustering number of H_2SO_4 is much bigger than that of H_2O .

3.3 MS and CAD spectra in the case of mixture of H_2SO_4 and acetone (Ac)

As a solvent, acetone (Ac) with H_2SO_4 , was also measured by FABMS method. In the case of acetone, we usually use it to rinse the electrodes in the ion source. Because of the high volatility of acetone, we believed that acetone would vaporize right after introducing into the vacuum apparatus before doing experiments. However we sometimes were able to get the mass spectra of m/z 59 by FABMS (*i.e.*, protonated acetone molecule ion). These results led us to measure the mixture of sulfuric acid and acetone by FABMS method.

The mixtures of acetone (Ac) and H_2SO_4 were measured on purpose by FAB mass spectrometry. Typical mass spectra were identified in Table 3. By this measurement, we concluded that the protonated cluster sulfuric acid ions, $(a\text{H}_2\text{SO}_4 + \text{H})^+$, were present

Table 2. Reported Proton Affinity of Various Solvents (kJ/mol)¹⁶⁾

*No data available.

	H_2O	CH_2	C_2H_4	C_3H_6	C_4H_8	H_2SO_4	Eg
Proton affinity	696	*	680	752	820	707	*

	Me	Et	Pr	Bu	Ac	Aa	DMSO
Proton affinity	761	787	798	799	823	796	884

Eg: ethylene glycol, Me: methyl alcohol, Et: ethyl alcohol, Pr: 1-propyl alcohol, Bu: 1-butyl, Ac: acetone, Aa: acetic acid.

Table 3. FABMS Spectra of Concentrated H_2SO_4 and Acetone Identified

m/z	157 ($\text{H}_2\text{SO}_4 + \text{Ac} + \text{H}$) ⁺	175 157 + H_2O
19 ($\text{H}_2\text{O} + \text{H}$) ⁺	255 ($2\text{H}_2\text{SO}_4 + \text{Ac} + \text{H}$) ⁺	273 255 + H_2O
31 H_3CO^+	353 ($3\text{H}_2\text{SO}_4 + \text{Ac} + \text{H}$) ⁺	371 353 + H_2O
43 CH_3CO^+	451 ($4\text{H}_2\text{SO}_4 + \text{Ac} + \text{H}$) ⁺	
58 Ac^+	549 ($5\text{H}_2\text{SO}_4 + \text{Ac} + \text{H}$) ⁺	
59 ($\text{Ac} + \text{H}$) ⁺	647 ($6\text{H}_2\text{SO}_4 + \text{Ac} + \text{H}$) ⁺	
	745 ($7\text{H}_2\text{SO}_4 + \text{Ac} + \text{H}$) ⁺

Fig. 10. The typical CAD spectra of m/z 157: ($\text{H}_2\text{SO}_4 + \text{Ac} + \text{H}$)⁺, precursor ion; m/z 157: ($\text{H}_2\text{SO}_4 + \text{Ac} + \text{H}$)⁺, product ions; m/z 99: ($\text{H}_2\text{SO}_4 + \text{H}$)⁺, m/z 81: ($\text{H}_2\text{SO}_4 - \text{H}_2\text{O} + \text{H}$)⁺, m/z 59: ($\text{Ac} + \text{H}$)⁺, m/z 43: ($\text{Ac} - \text{CH}_3 + \text{H}$)⁺.

and ($n\text{H}_2\text{SO}_4 + \text{Ac} + \text{H}$)⁺ also appeared. This means that the protonated cluster sulfuric acid is likely to be bound to acetone strongly. These ions are classified into three types of ions, fragment ions and/or molecular ions of acetone molecule, acetone adduct of sulfuric cluster ions, ($n\text{H}_2\text{SO}_4 + \text{Ac} + \text{H}$)⁺, and (water/acetone/sulfuric acid) mixtures cluster ions, ($n\text{H}_2\text{SO}_4 + \text{Ac} + \text{H}_2\text{O} + \text{H}$)⁺ or $[(n+1)\text{H}_2\text{SO}_4 - \text{SO}_3 + \text{Ac} + \text{H}]^+$. These ions contained three types of molecules. In these MS and CAD spectra of these cluster ions, mass number m/z 59 was regarded as to be the protonated acetone molecule ion and these ions can be obtained easily. CAD spectra of the unsymmetrical protonated dimer ion, ($\text{H}_2\text{SO}_4 + \text{Ac} + \text{H}$)⁺ was shown in Fig. 10. They produce the both ($\text{H}_2\text{SO}_4 + \text{H}$)⁺ and ($\text{Ac} + \text{H}$)⁺ ions, in this case, the former is much smaller than the latter one. The PA of Ac is also larger than that of H_2SO_4 . The literature PA values of Lias *et al.*,¹⁶⁾ are shown in Table 2, where the PA's of Ac and H_2SO_4 were 823 and 707 kJ/mol, respectively. From sections of 3.2 and 3.3, PA order was confirmed to be,

The literature and experimental results were proved to be in good agreement.

3.4 MS and CAD spectra in the case of mixture of H_2SO_4 and many alcohols and other solvents

As solvents, the normal alcohols were chosen and these mixtures with sulfuric acid

Table 4. FABMS Spectra of Mixtures of H_2SO_4 and Various Solvents
 $(a\text{H}_2\text{SO}_4 + b\text{Solv} - c\text{H}_2\text{O} + \text{H})^+$, a, b, and c are positive integer or zero.
 ◎: very strong, ○: strong, △: weak, and *: no peak.

	a=1 b=1 c=0	a=1 b=1 c=1	a=1 b=2 c=0	a=2 b=2 c=1
Me	○	◎	△	○
Et	○	◎	△	◎
Pr	○	◎	△	○
Bu	△	○	△	○
Pe	△	○	*	△
He	△	○	△	○
Eg	△	○	*	*
Ac	○	△	△	*

Solv: solvent, Me: methyl alcohol, Et: ethyl alcohol, Pr: 1-propyl alcohol, Bu: 1-butyl alcohol, Eg: ethylene glycol, Ac: acetone.

Table 5. Intensity of CAD Spectra of $(\text{ROH} + \text{H})^+$
 100% indicates the intensity of the precursor ion.

	Me	Et	Pr	Bu	Pe	He
$(\text{ROH} - \text{H}_2\text{O} + \text{H})^+$	0.42	1.35	3.68	6.00	7.01	10.8

of FABMS spectra were measured from methyl alcohol ($\text{C}_n\text{H}_{2n+1}\text{OH}$, $n=1$) to hexyl alcohol ($\text{C}_n\text{H}_{2n+1}\text{OH}$, $n=6$). The relation between intensity of these fragmentations *versus* n was shown in Table 4, where $(a\text{H}_2\text{SO}_4 + b\text{Solv} - c\text{H}_2\text{O} + \text{H})^+$, a, b, and c are integers or zero.

FABMS spectra of mixtures with H_2SO_4 with 1-propyl alcohol or 2-propyl alcohol showed almost the same behavior, but the mass numbers, m/z 183 and m/z 281, $(\text{H}_2\text{SO}_4 + 2\text{C}_3\text{H}_7\text{OH} - 2\text{H}_2\text{O} + \text{H})^+$ and $(2\text{H}_2\text{SO}_4 + 2\text{C}_3\text{H}_7\text{OH} - 2\text{H}_2\text{O} + \text{H})^+$, respectively, showed different behaviors described below. The former ion for 2-propyl alcohol was much larger than that for 1-propyl alcohol, but the latter of 1-propyl alcohol was larger than that of 2-propyl alcohol.

Moreover, FABMS spectra of butyl alcohols (1-, 2-, and *t*-butyl alcohols) were different with each other. The interaction of H_2SO_4 with these alcohols was complex and the precise analysis remains to be elucidated.

The condition of dehydration behavior was considered to be linear increase as the n increases linearly shown in Table 5, and adduct proton is added to OH and dehydration is occurred at first from the O-H bonding. Table 6 shows CAD spectra of $(\text{H}_2\text{SO}_4 + \text{ROH} + \text{H})^+$, five characteristic fragment ions, $(\text{ROH} + \text{H})^+$, $(\text{ROH} - \text{H}_2\text{O} + \text{H})^+$, $(\text{H}_2\text{SO}_4 + \text{ROH} - \text{H}_2\text{O} + \text{H})^+$, $(\text{H}_2\text{SO}_4 + \text{H})^+$, $(\text{H}_2\text{SO}_4 - \text{H}_2\text{O} + \text{H})^+$ are present. From these results, CAD spectra of $(\text{ROH} + \text{H}_2\text{SO}_4 + \text{H})^+$ shows the dehydration of $(\text{ROH} + \text{H}_2\text{SO}_4 - \text{H}_2\text{O} + \text{H})^+$ ion strongly, because the ROH and H_2SO_4 combine strongly and tight bonding was made. In the cases of mixtures of normal chain alcohols, $\text{C}_n\text{H}_{2n+1}\text{OH}$, ($n=1-4$) and H_2SO_4 , the FAB

Extensive Combinations of Clustering Sets of Sulfuric Acid and Various Solvents

Table 6. Intensity of CAD Spectra of $(\text{H}_2\text{SO}_4 + \text{Solv} + \text{H})^+$

100% indicates the intensity of the precursor ion. — indicates no detection.

	Me	Et	Pr	Bu	Eg	Aa	Ac
$(\text{H}_2\text{SO}_4 + \text{Solv} - \text{H}_2\text{O} + \text{H})^+$	0.47	1.39	4.80	1.55	1.98	—	—
$(\text{H}_2\text{SO}_4 + \text{H})^+$	0.04	0.61	0.95	0.68	1.27	0.72	0.40
$(\text{H}_2\text{SO}_4 - \text{H}_2\text{O} + \text{H})^+$	0.03	—	—	—	0.35	0.21	0.10
$(\text{Solv} + \text{H})^+$	0.09	1.12	2.49	1.10	2.40	5.51	4.80
$(\text{Solv} - \text{H}_2\text{O} + \text{H})^+$	—	—	2.83	1.45	1.31	0.32	—

Solv: solvent, Me: methyl alcohol, Et: ethyl alcohol, Pr: 1-propyl alcohol, Bu: 1-butyl alcohol, Eg: ethylene glycol, Aa: acetic acid, Ac: acetone.

Table 7. Intensity of CAD Spectra of $(\text{H}_2\text{SO}_4 + \text{Solv} - \text{H}_2\text{O} + \text{H})^+$

100% indicates the intensity of the precursor ion. — indicates no detection.

	Me	Et	Pr	Bu	Eg
$(\text{H}_2\text{SO}_4 + \text{Solv} - 2\text{H}_2\text{O} + \text{H})^+$	0.38	—	—	—	—
$(\text{H}_2\text{SO}_4 + \text{H})^+$	0.04	1.71	0.20	0.15	0.11
$(\text{H}_2\text{SO}_4 - \text{H}_2\text{O} + \text{H})^+$	0.28	0.10	0.11	0.10	0.03
$(\text{Solv} + \text{H})^+$	0.38	—	—	—	0.38
$(\text{Solv} - \text{H}_2\text{O} + \text{H})^+$	0.06	0.11	3.20	5.27	2.55

Solv: solvent, Me: methyl alcohol, Et: ethyl alcohol, Pr: 1-propyl alcohol, Bu: 1-butyl alcohol, Eg: ethylene glycol.

spectra are mainly composed of $(\text{H}_2\text{SO}_4 + \text{C}_n\text{H}_{2n+1}\text{OH} + \text{H})^+$, and $(\text{H}_2\text{SO}_4 + \text{C}_n\text{H}_{2n+1}\text{OH} - \text{H}_2\text{O} + \text{H})^+$.

The CAD spectra of $(\text{H}_2\text{SO}_4 + \text{Solv} - \text{H}_2\text{O} + \text{H})^+$ were measured in the cases of solvents of methyl, ethyl, 1-propyl, and 1-butyl alcohols, and ethylene glycol. These results are shown in Table 7, where the intensity of the $(\text{ROH} - \text{H}_2\text{O} + \text{H})^+$ expresses the CAD spectra from $(\text{ROH} + \text{H})^+$. So that in the case of normal alcohols, we can decide quantitatively the site of dehydration occurred.

In the case of $n=1$ (CH_3OH), the dehydration occurred in the site of H_2SO_4 . In the case of $n=2$, ($\text{C}_2\text{H}_5\text{OH}$), the fragment ion of $(\text{H}_2\text{SO}_4 + \text{H})^+$ is most stable than other fragment ions, $(\text{H}_2\text{SO}_4 - \text{H}_2\text{O} + \text{H})^+$, $(\text{C}_2\text{H}_5\text{OH} + \text{H})^+$, $(\text{C}_2\text{H}_5\text{OH} - \text{H}_2\text{O} + \text{H})^+$. In the cases of $n=3$, ($1\text{-C}_3\text{H}_7\text{OH}$), and $n=4$, ($1\text{-C}_4\text{H}_9\text{OH}$), dehydration occurred in the sites of $\text{C}_n\text{H}_{2n+1}\text{OH}$ over thirty times than in the site of H_2SO_4 and fifty times than in the site of H_2SO_4 . In the case of ethylene glycol, from solvent site the dehydration occurred, but $(\text{Solv} + \text{H})^+$ ion was also appeared, unlike $\text{R}=\text{Et}$, Pr , and Bu .

The reason of these phenomena can be explained partly by the order of PA. The order of PA is described below.

But the PA of Eg (ethylene glycol) was not published until now, the PA of EG is supposed to be larger than that of sulfuric acid.

Both CH_3OH and acetone are thought to be more volatile than other solvents used in the present experiments, these solvents were used to rinse. Therefore in the case of methyl alcohol, dehydration of H_2SO_4 was caused by methyl alcohol which was directly confirmed.

Fig. 11. The typical FABMS spectra of the mixture of DMSO with H_2SO_4 . And DMSO is easily to be made into cluster ions than that of H_2SO_4 , $(a\text{H}_2\text{SO}_4 + b\text{DMSO} + \text{H})^+$, in this case $(2\text{H}_2\text{SO}_4 + 3\text{DMSO} + \text{H})^+$ was also identified.

Table 8. FABMS Spectra of Mixtures of Concentrated H_2SO_4 and DMSO Identified

m/z	
15 (CH_3) ⁺	177 ($\text{H}_2\text{SO}_4 + \text{DMSO} + \text{H}$) ⁺
47 (SCH) ⁺	255 ($\text{H}_2\text{SO}_4 + 2\text{DMSO} + \text{H}$) ⁺
64 ($\text{DMSO} - \text{CH}_2$) ⁺	333 ($\text{H}_2\text{SO}_4 + 3\text{DMSO} + \text{H}$) ⁺
79 ($\text{DMSO} + \text{H}$) ⁺	431 ($2\text{H}_2\text{SO}_4 + 3\text{DMSO} + \text{H}$) ⁺
157 ($2\text{DMSO} + \text{H}$) ⁺	

DMSO: dimethyl sulfoxide.

In the case of CAD spectra from $(\text{H}_2\text{SO}_4 + \text{C}_n\text{H}_{2n+1}\text{OH} - \text{H}_2\text{O} + \text{H})^+$, if protons reside on the larger PA site, the dehydration occurs on the protonated site. We can decide the dehydration site by the present methods.

3.5 MS and CAD spectra in the case of mixture of H_2SO_4 and DMSO

FABMS spectra of H_2SO_4 and dimethyl sulfoxide (DMSO) was shown in Fig. 11. The mass numbers were identified, m/z 157 and 431 as $(2\text{DMSO} + \text{H})^+$ and $(2\text{H}_2\text{SO}_4 + 3\text{DMSO} + \text{H})^+$, respectively, and cluster ions of sulfuric acid clusters can't be detected throughly in Fig. 11. The identification of the FABMS spectra was shown in Table 8. And DMSO is easily to be made into cluster ions than that of H_2SO_4 , $(a\text{H}_2\text{SO}_4 + b\text{DMSO} + \text{H})^+$, in this case $(2\text{H}_2\text{SO}_4 + 3\text{DMSO} + \text{H})^+$ was also identified. Therefore, $a < b$ is confirmed to be, but almost all solvents except DMSO, in the same methods, $(a\text{H}_2\text{SO}_4 + b\text{Sol} + \text{H})^+$, the condition of $b < a$ was confirmed.

4. Conclusion

In this report, we brought the conclusion of the total results of experiment and preliminary consideration was done below. There were three considerations, first, the interaction between H_2SO_4 and solvent molecules concerning acid rains problems must be considered more precisely. Secondary, CAD spectra and kinetic method gave much

information about the environmental science. Thirdly, dehydration problems from the protonated unsymmetrical dimer ions were discussed directly. The kinetic method was better usage because the two species comprising the dimer have very similar structures in the present report.

This paper is dedicated to the late Professor Toshio Sugiura.

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Keywords

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