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Hydrogen-Atom and Charge Transfer Reactions within Acetylene/Methanol and Ethylene/Methanol Heteroclusters

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Reactions that proceed within mixed acetylene-methanol and ethylene-methanol cluster ions were studied using an electron-impact time-of-flight mass spectrometer. When acetylene and methanol seeded in helium are expanded and ionized by electron impact, the ion abundance ratio, $[CH_3OH^+]/[CH_2OH^+]$, shows a propensity to increase as the acetylene/methanol mixing ratio increases, indicating that the initially ionized acetylene ion transfers its charge to adjacent methanol molecules within the clusters. Investigations on the relative cluster ion intensity distributions of $[CH_3OH_2^+]/[CH_3OH^+]$ and $[(CH_3OH)_2H^+]/[CH_3OH \cdot CH_2OH^+]$ under various experimental conditions suggest that hydrogen-atom abstraction reaction of acetylene molecule with CH_3OH ion is responsible for the effective formation of CH_2OH ion. In ethylene/methanol clusters, the intensity ratio of $[CH_3OH_2^+]/[CH_3OH]$ increases linearly as the relative concentration of methanol decreases. The prominent ion intensities of $(CH_3OH)_mH$ over $(CH_3OH)_m \cdot CH_2OH$ ions ($m=1, 2, \text{ and } 3$) at all mixing ratios are also interpreted as a consequence of hydrogen atom transfer reaction between C_2H_4 and CH_3OH to produce the protonated methanol cluster ions.

Introduction

Recent studies on the properties, structures, and reactivities of molecular clusters contribute to an understanding of the chemical dynamics and bonding in systems lying between the gaseous and condensed phases.¹⁻⁴ Although the characteristics of the detected ion cluster distribution have often been attributed to the properties and even structural features of the neutral precursors, much less is known about the detailed microscopic processes governed by pairwise molecular interactions and local dynamics.^{5,6}

The study of specific chemical reactions within methanol cluster ions has received a great deal of attention since it is possible to observe directly how chemical reactivity changes as a function of stepwise solvation by monitoring the changes in reaction channel versus the cluster size.⁷⁻¹² These extensive studies show that the dissociation accompanied by the proton transfer occurring in cluster ions results in efficient production of the protonated ion. Apart from the numerous investigations of the ion-molecule reactions, fragmentations and molecular rearrangements, there are few reported cases of hydrogen transfer mechanisms taking place within the ionized methanol cluster itself.

Our recent investigations of the ion-molecule reactions with

thin methanol containing homo- and heteroclusters¹³⁻¹⁵ show that the intracuster proton transfer reactions strongly depend on their relative composition within clusters. In CH_3OH homoclusters, the predominant observation of protonated species, $(CH_3OH)_nH^+$ in the mass spectrum is attributed to the effective formation of ion-neutral complexes, $(CH_3OH)_n \cdot [CH_3OH_2^+ \cdots O(H)CH_2]$ and $(CH_3OH)_n \cdot [CH_3OH_2^+ \cdots OCH_3]$. The formation of protonated species in the mixed ethylene-methanol heterocluster systems, however, is found to be responsible for ethylene molecules within the clusters. In this respect, quantitative investigations on reaction mechanism will be helpful for understanding the proton and hydrogen-atom transfer processes in the gas-phase hydrogen-bonded cluster ions, since no detailed theoretical and experimental studies have been published so far on the mechanisms and energetics of these processes.

In this work, we investigated internal ion-molecule reactions in acetylene-methanol and ethylene-methanol heterocluster systems,^{13,14} in which we performed pressure-dependence studies to develop a quantitative interpretation of the reaction mechanisms behind our observations. The observed ion-molecule chemistry of methanol-containing heteroclusters is dramatically affected by the relative concentration of methanol molecules within the clusters. The present results provide further details of intracuster proton and hydrogen-atom transfer reactions, *i.e.*, the roles of ethylene and acety-

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lene molecules, following electron impact ionization of heteroclusters.

Experimental

The molecular beam/time-of-flight mass spectrometer (TOFMS) used in this work has been described in detail elsewhere.^{15,16} In brief, neutral heteroclusters are introduced through a 500 m diameter pulsed nozzle in the source chamber. The molecular beam is skimmed and passes through the main chamber. The resulting pulsed beam with a pulse duration of about 100 ns enters the ionization region of TOF mass spectrometer, placed 10 cm downstream from the nozzle, where a pulsed electron beam intersects it orthogonally. Ions formed by electron impact are accelerated in a double electrostatic field to about 1.1 keV and are directed through a 1 m long flight tube, which is differentially pumped by a 200 l/s turbomolecular pump. The base pressure in the drift region, typically 1×10^{-7} Torr rises to about 5×10^{-7} Torr during normal operation. The ions are then detected by a chevron microchannel plated (MCP) detector in connection with a fast preamplifier. Mass spectrum is recorded by a 175 MHz transient digitizer coupled with a microcomputer. The experiments operate at 10 Hz and TOF spectra typically are accumulated for 500 pulses.

In the heterocluster formation, experiments are typically made with a gas mixture consisting of 6% acetylene (or ethylene), 0.03-0.06% methanol, and helium which is expanded at a stagnation pressure of up to 4.5 atm. Acetylene obtained from Matheson Co. (stated purity of >99.6%) was used after passing through a dry ice/acetone trap to remove acetone, which was used as a stabilizer from the acetylene cylinder. Ethylene (99.99%, Matheson Co.) was used without further purification. Spectrophotometric grade CH_3OH (99.9%) was used after further purification in a series of freeze-pump thaw cycles to remove dissolved atmospheric gases and other impurities of high vapor pressure.

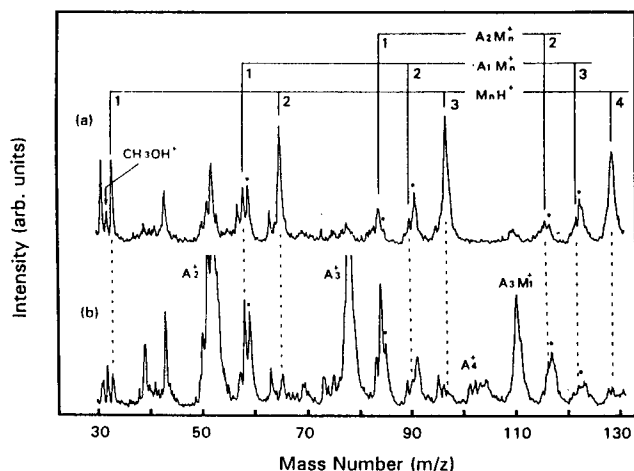


Figure 1. 70 eV TOF mass spectra of mixed acetylene-methanol clusters: (a) $\text{C}_2\text{H}_2(6\%) + \text{CH}_3\text{OH}(0.6\%)$; (b) $\text{C}_2\text{H}_2(6\%) + \text{CH}_3\text{OH}(0.06\%)$. The total stagnation pressure is 4.5 atm He. A and M designate acetylene and methanol molecules, respectively. *correspondings to the protonated heterocluster ions, $\text{A}_n\text{M}_m\text{H}^+$.

Results and Discussion

Figure 1 shows the TOF mass spectra of a pulsed molecular beam expanded from 4.5 atm He containing $\text{C}_2\text{H}_2(6\%) / \text{CH}_3\text{OH}(0.6\%)$ and $\text{C}_2\text{H}_2(6\%) / \text{CH}_3\text{OH}(0.06\%)$ at 70 eV impact energy. At 0.6% CH_3OH concentration the dominant cluster species consist of $(\text{CH}_3\text{OH})_m\text{H}^+$, which could be attribute to the protonation reaction, *i.e.*, all the parent cluster ions generated being consumed to form the protonated clusters. In addition to the homocluster ions, a new sequence of heterocluster ions of the type A_nM_m^+ , $\text{A}_n\text{M}_m\text{H}^+$, and $\text{A}_n\text{M}_m\text{CH}_3\text{O}^+$ also emerges throughout the observed mass spectrum, where acetylene and methanol molecules are designated as A and M.

Figure 1(b) displays the same portion of TOF mass spectrum taken at an acetylene/methanol mixing ratio of 100 : 1. The overall spectral pattern is different from that of the 10 : 1 ratio shown in Figure 1(a). Besides the expected acetylene homocluster peaks, A_n^+ , a large number of heterocluster ions of A_nM_m^+ appear along with a minor contribution from M_mH^+ homocluster ions. It should be noted that, whereas the protonated heteroclusters show only small contributions compared with the corresponding unprotonated species at the acetylene/methanol mixing ratio of 100 : 1, the same ions are now substantially increased in abundance when they are formed at the 10 : 1 ratio. This observation implies that the relative composition of acetylene/methanol coexpansion plays an important role on the abundance distribution of heterocluster ions.

In order to compare the role of ethylene molecule with that of acetylene on the ion-molecule reaction of methanol-containing heteroclusters, the mass spectra were taken at different ethylene/methanol mixing ratio of 10 : 1 and 200 : 1 (see Figure 2). Contrary to the acetylene/methanol system, $\text{E}_n\text{M}_m\text{H}^+$ ions are now substantially increased in intensity compared to the corresponding unprotonated species in the 200 : 1 ratio, whereas the same ions show only small contri-

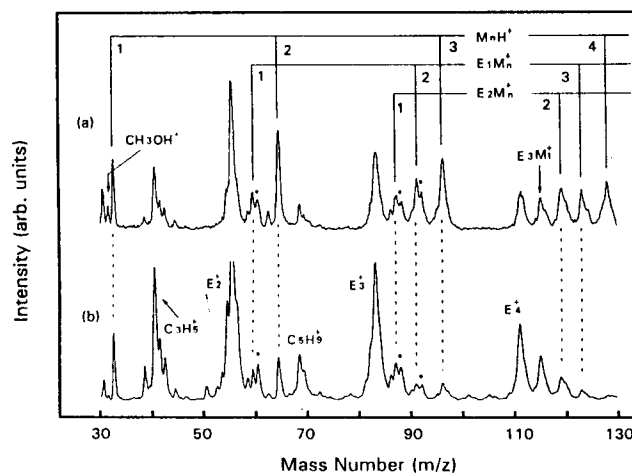


Figure 2. 70 eV TOF mass spectra of mixed ethylene-methanol clusters: (a) $\text{C}_2\text{H}_4(6\%) + \text{CH}_3\text{OH}(0.6\%)$; (b) $\text{C}_2\text{H}_4(6\%) + \text{CH}_3\text{OH}(0.03\%)$. The total stagnation pressure is 4.5 atm He. E and M designate ethylene and methanol molecules, respectively. *correspondings to the protonated heterocluster ions, $\text{E}_n\text{M}_m\text{H}^+$.

Table 1. Summary of thermochemical information for ion-molecule reactions of methanol, acetylene, and ethylene molecules

Reactions	ΔH_{rxn} , kcal/mol
CH ₃ OH ⁺ + CH ₃ OH → CH ₃ OH ₂ ⁺ + CH ₃ O	-14.60
C ₂ H ₂ ⁺ + CH ₃ OH → C ₂ H + CH ₃ OH ₂ ⁺	-12.24
C ₂ H ₂ ⁺ + CH ₃ OH → C ₂ H ₂ + CH ₃ OH ⁺	-13.13
C ₂ H ₂ + CH ₃ OH ⁺ → C ₂ H ₃ + CH ₂ OH ⁺	-18.07
C ₂ H ₂ + CH ₃ OH ⁺ → C ₂ H + CH ₃ OH ₂ ⁺	0.89
C ₂ H ₄ ⁺ + CH ₃ OH → C ₂ H ₃ + CH ₃ OH ₂ ⁺	-0.96
C ₂ H ₄ ⁺ + CH ₃ OH → C ₂ H ₄ + CH ₃ OH ⁺	7.52
C ₂ H ₄ + CH ₃ OH ⁺ → C ₂ H ₅ + CH ₂ OH ⁺	-4.95
C ₂ H ₄ + CH ₃ OH ⁺ → C ₂ H ₃ + CH ₃ OH ₂ ⁺	-8.52
C ₂ H ₅ ⁺ + CH ₃ OH → C ₂ H ₄ + CH ₃ OH ₂ ⁺	-19.30

^aThe enthalpies of formation of all neutral and ionic species are taken from Ref. 17.

butions when they are formed at the 10 : 1 ratio. This observation is in good agreement with the previous results¹⁴ that the protonated heterocluster originates from the CH₃OH₂⁺ ion and not from the C₂H₅⁺ ion. Because of similar ionization potentials of C₂H₄ (10.51 eV) and CH₃OH (10.85 eV), either C₂H₄ or CH₃OH may be ionized within the heteroclusters. If by chance the methanol is initially ionized, the E_nM_{m-1}CH₃OH₂⁺ ions are expected to be produced through intracluster proton (or hydrogen atom) transfer reactions of (i) CH₃OH⁺ + CH₃OH ($\Delta H_{rxn} = -14.6$ kcal mol⁻¹) or (ii) CH₃OH⁺ + C₂H₄ ($\Delta H_{rxn} = -8.52$ kcal mol⁻¹). The enthalpies of the possible proton (or hydrogen atom) transfer reactions, estimated from the thermochemical data,¹⁷ are listed in Table 1.

In general, however, there are more ethylene than methanol molecules in the heterocluster and it is more likely that the electron will be ejected from the ethylene molecule. Therefore, the C₂H₅⁺ ion, produced from the ion-molecule reaction of C₂H₄⁺ + C₂H₄, and C₂H₄⁺ ion then readily undergo the proton transfer reactions with the methanol molecule, leading to CH₃OH₂⁺ formation. The large difference between the proton affinities¹⁸ of CH₃OH (8.03 eV) and C₂H₄ (7.10 eV) also supports the preferential bonding of a proton to a methanol molecule in E_nM_mH⁺ ions. A similar result has been found in a recent study of the unimolecular decomposition of mixed ammonia-acetone cluster ions.¹⁹

In the case of coexpanding a gas vapor with an ethylene/methanol ratio 10 : 1, protonated methanol in the heterocluster will now be preferentially solvated by the neutral methanol molecules, since hydrogen bonding is not available to the ethylene molecule. This situation, which occurs in the similar ion-molecule reactions in the methanol homoclusters, results in only a minor contribution from the protonated heteroclusters, E_nM_mH⁺. When the mixing ratio is increased to 200 : 1, however, the preferential solvation of protonated methanol by the neutral methanol molecules becomes unfavorable, owing to trace of methanol in the mixture. In this case, protonated methanol molecules have a greater chance of reacting with the ethylene molecules, increasing the prominence of E_nM_mH⁺ ions.

In order to shed more light on the intracluster ion-molecule reactions of methanol with acetylene or ethylene, we investigated the general trends in the ion abundance distri-

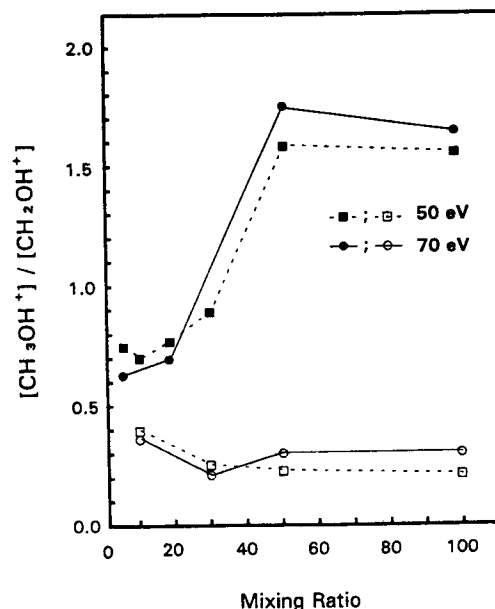


Figure 3. CH₃OH⁺/CH₂OH⁺ ion abundance ratio as a function of (closed circle and square) and C₂H₄/CH₃OH (open circle and square) mixing ratio at two different electron impact energies.

butions of CH₃OH⁺ and CH₂OH⁺ ions in the heterocluster mass spectrum. Figure 3 shows a plot of the CH₃OH⁺/CH₂OH⁺ ratio as a function of acetylene/methanol and ethylene/methanol heteroclusters at two different electron impact energies. A prominent feature is readily discerned from the plot; in the acetylene/methanol cluster CH₂OH⁺ ion decreases in intensity compared to the corresponding CH₃OH⁺ ion as the composition of acetylene is increased, whereas in the ethylene/methanol system CH₃OH⁺/CH₂OH⁺ ratio remains constant throughout the entire mixing ratio. This is consistent with the view that the hydrogen abstraction reaction pathways are greatly influenced by the acetylene concentration within the heteroclusters. This observation can be easily interpreted if it is assumed that the methanol molecule in the heterocluster acquires its charge in one of two ways, either by direct electron impact ionization of methanol molecule or by charge transfer from the initially ionized acetylene molecule. One can expect that the relative contribution of each ionization process is controlled by the mixing ratio of acetylene to methanol concentration. Because of similar ionization potentials of CH₃OH (10.85 eV) and C₂H₂ (11.42 eV), either CH₃OH or C₂H₂ within the heterocluster may be ionized by 50 and 70 eV ionization energies. At high acetylene/methanol ratio, there are more acetylene than methanol molecules in the heterocluster and it is more likely that the electron will be ejected from the acetylene molecule. Therefore, the charge transfer from initially ionized acetylene to the adjacent methanol molecule could result in the formation of stable CH₃OH⁺ ion, which does not decompose further to CH₂OH⁺ ion due to its endothermicity (18.17 kcal mol⁻¹) of fragmentation reaction, CH₃OH⁺ → CH₂OH⁺ + H. As the mixing ratio of acetylene/methanol decreases, however, methanol molecules have a greater chance of ionization by direct electron impact. The large excess energy imparted to the CH₃OH⁺ ion after direct electron impact ionization primarily induces the fragmentation reaction to produce CH₂OH⁺

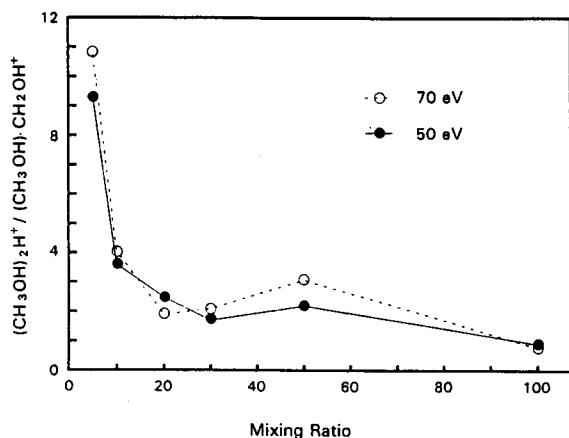


Figure 4. $(\text{CH}_3\text{OH})_2\text{H}^+ / (\text{CH}_3\text{OH})\text{CH}_2\text{OH}^+$ ion abundance ratio as a function of $\text{C}_2\text{H}_2 / \text{CH}_3\text{OH}$ mixing ratio at two different electron impact energies.

ion. In this regard, the present result strongly suggests that the directly ionized acetylene molecules make a major contribution to the formation of CH_3OH^+ ions by the non-dissociative charge transfer process.

In the case of ethylene/methanol system, the intensity ratio of $\text{CH}_3\text{OH}^+ / \text{CH}_2\text{OH}^+$ is independent of mixing conditions within the experimental error. Similar to the acetylene/methanol heteroclusters, the direct ionization of methanol molecules followed by the further fragmentation is attributable to the effective formation of CH_2OH^+ ions at relatively high methanol concentration, *i.e.*, low ethylene/methanol ratio. The low value of $\text{CH}_3\text{OH}^+ / \text{CH}_2\text{OH}^+$ ion intensity even for the increased ethylene composition, however, indicates that the formation of stable CH_3OH^+ ions by the charge transfer from C_2H_4^+ ions to methanol molecules is greatly reduced. One of the possible rationales of our result is that C_2H_4^+ ion or C_2H_5^+ ion, produced from the ion-molecule reaction of $\text{C}_2\text{H}_4^+ + \text{C}_2\text{H}_4$, can readily undergo the proton transfer reactions with the methanol molecule ($\Delta H_{\text{rxn}} = -0.96$ and -19.3 kcal mol⁻¹), leading to CH_3OH_2^+ ion formation. A similar result has also been found in a recent study of the ion-molecule reaction of mixed ethylene-methanol cluster ions.¹⁴

One of the most interesting features in the mass spectra of acetylene/methanol heteroclusters is that the intensities of methanol cluster ions, $(\text{CH}_3\text{OH})_m\text{CH}_2\text{OH}^+$, for $m = 1-3$ make substantial contributions as decreasing methanol concentration (see Figure 1). To investigate the hydrogen transfer reactions within heteroclusters, we concentrated on an examination of general trends in the intensities of methanol homocluster ions. Figure 4 gives a plot of the $(\text{CH}_3\text{OH})_2\text{H}^+ / (\text{CH}_3\text{OH})\text{CH}_2\text{OH}^+$ abundance ratio as a function of the acetylene/methanol ratio obtained at two different electron impact energies. A prominent feature can readily discerned. The abundance ratios are approximately 10.0 at acetylene/methanol = 5. These ratios then decrease exponentially with increasing C_2H_2 concentration. Therefore, the present results strongly suggest that the proton (and hydrogen atom) transfer reaction pathways are greatly influenced by the acetylene concentration within the clusters. The possible reactions can be summarized by reactions (1)-(4) within the heterocluster ions where A and M represent C_2H_2 and CH_3OH molecules,

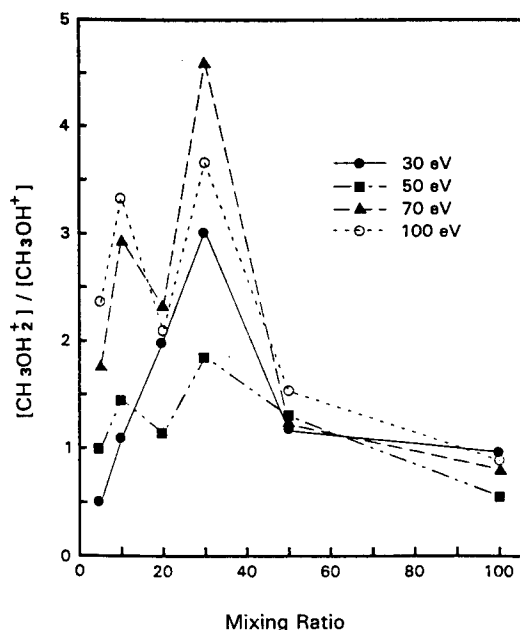
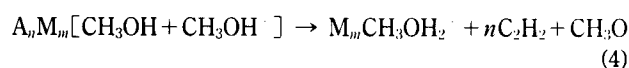
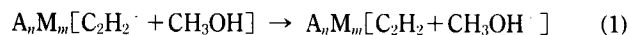


Figure 5. $\text{CH}_3\text{OH}_2^+ / \text{CH}_3\text{OH}^+$ ion abundance ratio as a function of $\text{C}_2\text{H}_2 / \text{CH}_3\text{OH}$ mixing ratio at four different electron impact energies.

respectively.



In the case of coexpanding a gas vapor with a low mixing ratio of acetylene/methanol, CH_3OH^+ ions in the heteroclusters will now be preferentially solvated by the neutral methanol molecules owing to the increased methanol concentration and thus feasible hydrogen bonding. This situation affords the well known ion-molecule reactions that occur in the methanol homoclusters, *i.e.*, reaction (4), resulting in a substantial increase in $(\text{CH}_3\text{OH})_m\text{H}^+$ ions. As increasing the mixing ratio, however, the reaction mechanisms involve charge transfer (reaction (1)) followed by the subsequent hydrogen atom transfer (reactions (2) and (3)) within the heterocluster ions. Table 1 summarizes the related ion-molecule reactions. From the thermodynamic point of view, CH_2OH^+ formation channel from $\text{C}_2\text{H}_2 + \text{CH}_3\text{OH}^+$ reaction is more exothermic (*ca.* 19 kcal mol⁻¹) than CH_3OH_2^+ formation channel. In a recent study on the reaction of C_2H_2^+ with CH_3OH , Iraqi *et al.*²⁰ reported that the branching ratio for proton transfer was observed to be 85% CH_2OH^+ and 15% CH_3OH^+ . In this regard, a substantial decrease in $(\text{CH}_3\text{OH})_2\text{H}^+ / (\text{CH}_3\text{OH})\text{CH}_2\text{OH}^+$ ratio can be interpreted as a result of an effective hydrogen atom transfer reaction (from CH_3OH^+ ion to C_2H_2 molecules) since the reaction (2) prevails over reaction (3).

In order to gain an insight into the hydrogen atom and charge transfer reactions of acetylene/methanol system, the ion intensity ratios of $\text{CH}_3\text{OH}_2^+ / \text{CH}_3\text{OH}^+$ was plotted as a function of mixing ratio at four different ionization energies

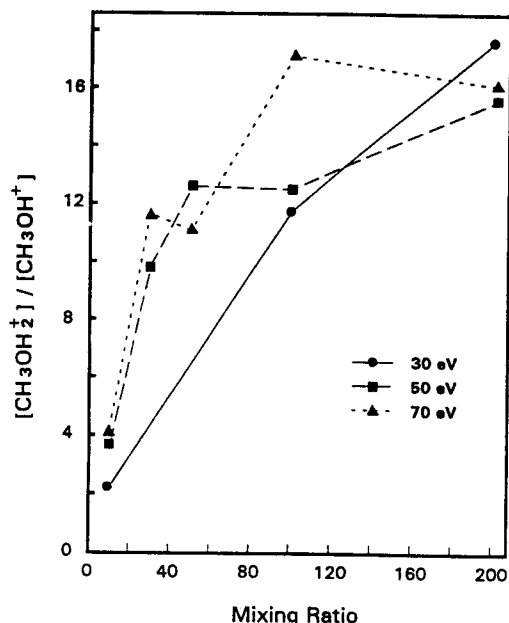


Figure 6. $CH_3OH_2^+/CH_3OH^+$ ion abundance ratio as a function of C_2H_4/CH_3OH mixing ratio at three different electron impact energies.

in Figure 5. It is interesting to note that there exists a local maximum at acetylene/methanol=30. The increasing tendency of $CH_3OH_2^+/CH_3OH^+$ intensity ratio at low mixing ratio is ascribed to the depletion of CH_3OH^+ ions due to the effective formation of CH_2OH^+ ions *via* hydrogen abstraction of C_2H_2 molecules from CH_3OH^+ ions (reaction (2)) as mentioned earlier. This result clearly demonstrates that hydrogen abstraction reaction of C_2H_2 molecule plays a profound effect for the CH_2OH^+ formation. Although the unimolecular decomposition of CH_3OH^+ formed directly by the electron impact is also expected to produce CH_2OH^+ ion, it gives the small contributions as increasing C_2H_2 concentration in the mixture. When the mixing ratio is increased further, the charge transfer from ionized ethylene (reaction (1)) now makes a major role to the formation of stable CH_3OH^+ ion, thus decreasing $CH_3OH_2^+/CH_3OH^+$ ratio.

Figure 6 shows a plot of the $CH_3OH_2^+/CH_3OH^+$ ratio as a function of the ethylene/methanol ratio obtained at three different electron impact energies. It is seen that the values of intensity ratio are greater than those for the acetylene/methanol system. In addition, the results show that the $CH_3OH_2^+$ ion abundance increases monotonically as the composition of ethylene is increased. This is consistent with the view that ethylene molecules in heteroclusters contribute to the overall protonation processes. Reaction energetics listed in Table 1 also support our conclusion that the intracluster ion-molecule reactions of $C_2H_4^+ + CH_3OH$ and $C_2H_2^+ + CH_3OH^+$ produce predominantly the protonated methanol ions, $CH_3OH_2^+$.

Conclusion

We have investigated hydrogen-atom and charge transfer reactions occurring within the acetylene/methanol and ethylene/methanol heterocluster ions. Observations on the rela-

tive intensities of CH_2OH^+ , CH_3OH^+ , and $CH_3OH_2^+$ ions in the acetylene/methanol heterocluster mass spectra suggest that the major intracluster ion-molecule reaction is the charge transfer process (from the ionized acetylene to methanol molecule). The subsequent hydrogen-atom transfer from CH_3OH^+ ion to the adjacent acetylene molecules produces CH_2OH^+ ions. In ethylene/methanol clusters, however, the intensity ratio of $CH_3OH_2^+/CH_3OH^+$ increases linearly as the relative concentration of methanol decreases, indicating that ethylene molecules in heteroclusters contribute to the overall protonation processes; the hydrogen-atom transfer reactions between C_2H_4 and CH_3OH^+ produce the protonated methanol cluster ions.

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