

$$C_5(\text{sixth carbon}) : \frac{1}{T_1} = 20K \sum_{a,b,c,d,e} (d_{ab})^2 (d_{bc})^2 (d_{cd})^2 (d_{de})^2 (d_{e0})^2$$

$$\times \frac{1}{6D_0 + a^2 D_1 + b^2 D_2 + c^2 D_3 + d^2 D_4 + e^2 D_5}$$

where $K = (N_H/10)(2\pi R)^2 = 2.15 \times 10^9 \text{ N}_H$

Appendix II

$$A_{00} = (1+2\sigma)^2/\sigma$$

$$A_{20} = A_{10} = A_{02} = A_{01}$$

$$= A_{-20} = A_{-10} = A_{0-2} = A_{0-1}$$

$$= (1/\sigma) - 2\sigma + 1$$

$$A_{11} = A_{-1-1} = A_{22} = A_{-2-2}$$

$$= A_{-12} = A_{2-1} = A_{-21} = A_{1-2}$$

$$= (1/\sigma) + \sigma - 2 + (9/2) \exp(-\tau/\tau_g)$$

$$+ (3/2)(1+2\sigma) \exp(-\tau/\tau_g)$$

$$A_{1-1} = A_{-11} = A_{12} = A_{21}$$

$$= A_{2-2} = A_{-22} = A_{-1-2} = A_{-2-1}$$

$$= (1/\sigma) + \sigma - 2 + (9/2) \exp(-\tau/\tau_g)$$

$$- (3/2)(1+2\sigma) \exp(-\tau/\tau_g)$$

where $1/\tau_g = 1/\tau_i + 1/\tau_e$

Appendix III

$$G_0(\tau_g) = \exp(-6D_0\tau)$$

$$G_1(\tau_g) = [\sigma/(1+2\sigma)^2] \exp(-6D_0\tau) \sum_{a=-2}^2 d_{a0} d_{a0} A_{aa}$$

$$G_2(\tau_g) = [\sigma/(1+2\sigma)^2]^2 \exp(-6D_0\tau)$$

$$\times \sum_a \sum_{bb'} d_{ab} d_{ab'} d_{b0} d_{b'0} A_{aa} A_{bb'} \cos[(2\pi/3)(b-b')]$$

$$G_3(\tau_g) = [\sigma/(1+2\sigma)^2]^3 \exp(-6D_0\tau)$$

$$\times \sum_a \sum_{bb'} \sum_{cc'} d_{ab} d_{ab'} d_{bc} d_{b'c'} d_{c0} d_{c'0} A_{aa} A_{bb'} A_{cc'}$$

$$\times \cos[(2\pi/3)(c-c')]$$

$$G_4(\tau_g) = [\sigma/(1+\sigma)^2]^4 \exp(-6D_0\tau)$$

$$\times \sum_a \sum_{bb'} \sum_{cc'} \sum_{dd'} d_{ab} d_{ab'} d_{bc} d_{b'c'} d_{cd} d_{c'd'}$$

$$\times d_{d0} d_{d'0} A_{aa} A_{bb'} A_{cc'} A_{dd'} \cos[(2\pi/3)(d-d')]$$

$$G_5(\tau_g) = [\sigma/(1+2\sigma)^2]^5 \exp(-6D_0\tau)$$

$$\times \sum_a \sum_{bb'} \sum_{cc'} \sum_{dd'} \sum_{ee'} d_{ab} d_{ab'} d_{bc} d_{b'c'} d_{cd} d_{c'd'}$$

$$\times d_{de} d_{d'e'} d_{e0} d_{e'0} A_{aa} A_{bb'} A_{cc'} A_{dd'} A_{ee'}$$

$$\times \cos[(2\pi/3)(e-e')]$$

Influence of Ammonia Solvation on the Structural Stability of Ethylene Cluster Ions

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The stable structures of pure ethylene and mixed ethylene-ammonia cluster ions are studied using an electron impact ionization time-of-flight mass spectrometer. Investigations on the relative cluster ion distributions of $(C_2H_4)_n(NH_3)_m^+$ under various experimental conditions suggest that $(C_2H_4)_2(NH_3)_3^+$ and $(C_2H_4)_3(NH_3)_2^+$ ions have the enhanced structural stabilities, which give insight into the feasible structure of solvated ions. For the stable configurations of these ionic species, we report an experimental evidence that both $(C_2H_4)_2^+$ $(C_2H_4)_3^+$ clusters as the central cations provide three and two hydrogen-bonding sites, respectively, for the surrounding NH_3 molecules. This interpretation is based on the structural stability for ethylene clusters and the intracuster ion-molecular rearrangement of the complex ion under the presence of ammonia solvent molecules.

Introduction

The most remarkable progress in the cluster ion chemistry is the recent finding of the intracuster ion-molecule reactions.¹⁻⁴ As a large number of neutral molecules attach to

the central ion, the gas phase becomes to resemble that pertaining in solution in the vicinity of ions. The careful study of this system, thus, makes it possible to bridge the gap between gas-phase and solution chemistry. This in turn permits a more precise understanding of the nature of solution of ions by solvent molecules.⁵

Numerous experimental attentions^{6,7} have been also paid

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to cluster systems in which small number of solvent molecules are bound to a solute molecule. The investigation of solvation phenomena then provides the knowledge of mechanisms of "internal ion-molecule reaction" in clusters, giving direct information on the influence of solvation and insight into the structure of solvated ions. Although mass spectroscopic studies of mixed clusters do not provide direct information on quantitative thermodynamic properties, they do render an information on the cluster ion stability from the appearance of relatively significant intensities in the cluster ion distributions.^{7,8} In the case of cluster systems this stability is typically correlated to a stable and closed solvent shell, hydrogen bonded directly to a central cation.⁹ In recent years the study of magic numbers, *i.e.*, the occurrence of intensity anomalies in an otherwise smooth cluster ion distribution, has also been used to help uncover new ion-molecule chemistry within van der Waals clusters.¹⁰

The experimental and theoretical efforts have been directed towards understanding the dynamics involved in the intracuster ion-molecule reaction of ethylene clusters.^{11,12} The common conclusion from these studies is that the primary reaction proceeds through some long-lived intermediate which can be collisionally stabilized to yield a butene structure.¹³ The first experimental evidence for the existence of magic number of ethylene clusters was reported by Garvey and co-workers¹⁴ recently. The experiment has not fully covered the details of ionic structure in ethylene clusters and whether "stable structures" exist in the binary system containing polar solvent molecules. The study of the appearance of especially stable ions rearranged from some van der Waals cluster ions is also of extreme interest and importance.

In this paper, we present a study of stable structures of mixed ethylene-ammonia cluster ions, $(C_2H_4)_n(NH_3)_m^+$. The identification process of the heterocluster ions used in this study is based on mass assignment of the particular sequence of peaks and also on the observation of magic numbers in heterocluster mass spectra. The results provide insight into solvation phenomena from microscopic standpoints and hopefully shed new light on the structure of the ethylene cluster ions.

Experimental

The apparatus and experimental techniques used in the present work are essentially the same as those previously used.¹⁵ Briefly, cluster beams are generated in a supersonic expansion through a 800 μ m diameter pulsed nozzle at total pressure up to 64 psi with He as a carrier gas. The free jet is skimmed by a conical skimmer of 1 mm diameter placed 5 mm downstream of the nozzle. The resulting pulsed beam with a duration of about 500 μ s is introduced into the ionization region of a time-of-flight mass spectrometer (TOFMS) where a pulsed electron beam intersects it at orthogonal direction. Ions formed by the electron impact are accelerated in a double electrostatic field to about 1.1 KeV and directed through a 1 m long flight tube, which is differentially pumped by a 200 L/s turbomolecular pump. The ions are then detected by a channel electron multiplier (Murata, EMS-2082B) in connection with a fast preamplifier (ORTEC, Model 579). The mass spectrum is recorded by a digital storage oscilloscope (LeCory 9400A) coupled with IBM PC

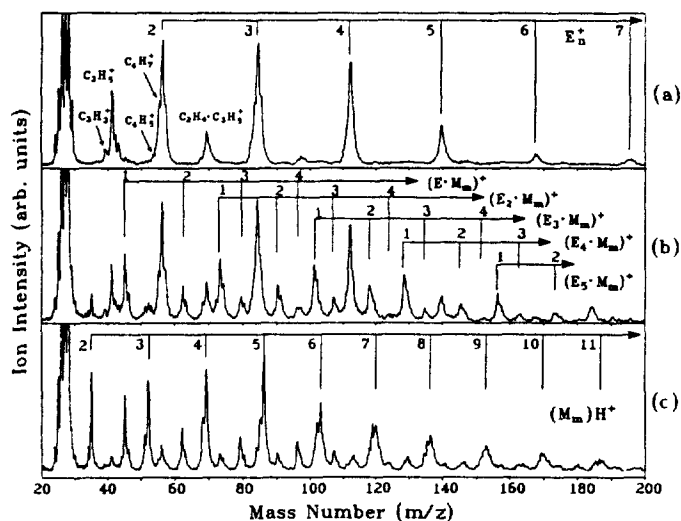


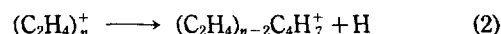
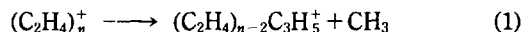
Figure 1. Comparison of electron impact (50 eV) TOF mass spectra of pure ethylene and mixed ethylene-ammonia clusters: (a) pure C_2H_4 (6%); (b) C_2H_4 (6%) + NH_3 (0.06%); (c) C_2H_4 (6%) + NH_3 (0.3%). The total stagnation pressure is 64 psi He. Integers above the peaks denote n and m , the numbers of C_2H_4 and NH_3 molecules in an individual cluster ion, respectively. E and M designate C_2H_4 and NH_3 molecules.

/AT computer. The experiments operate at 2 Hz and TOF spectra typically are accumulated for 500 pulses.

Ethylene and ammonia were obtained from Matheson with quoted purities of 99.5 and 99.99%, respectively, and were used without further purification.

Results and Discussion

Figure 1a shows the TOF mass spectrum of a pulsed molecular beam expanded from 64 psi He containing 6% ethylene at 50 eV impact energy. In addition to the fragment peaks, it exhibits a major sequence of cluster ions with the formula $(C_2H_4)_n^+$, which one could attribute to the unreacted parent cluster ions, *i.e.*, no protonation reaction. Similar results have been also recently reported in the electron impact ionization¹⁶ and the near-threshold vacuum UV photoionization¹² mass spectrometries. The minor peaks are due to the fragmented ions such as $C_3H_5^+$ and $C_4H_7^+$, which is consistent with the ethylene ion-molecule reactions.¹¹ It should be noted here that the fragmented cluster ions, $(C_2H_4)_n C_3H_5^+$ and $(C_2H_4)_n C_4H_7^+$, are also observed as a result of the intracuster ion-molecule reactions.^{13,17}



which correspond to the conventional ion molecule reactions of ethylene.

It has been known the component ratio of the gas mixture is a crucial factor in producing the mixed cluster ions.^{8,18} The effect of the gas mixing ratios on the abundance distribution of mixed cluster is demonstrated in Figure 1b and 1c which display the same portion of TOF mass spectra taken at different mixing ratios of ethylene/ammonia = 100/1 and 20/1. Now with an 6% ethylene-0.06% ammonia

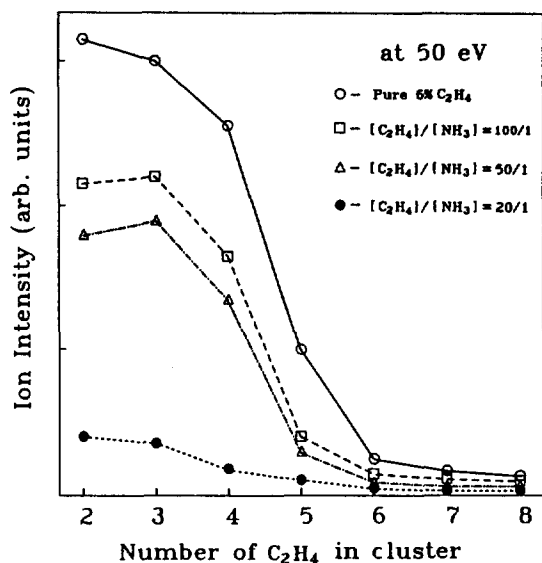


Figure 2. Intensity distribution of $(C_2H_4)_n^+$ ions at different mixing ratios: $P_0=64$ psi, electron impact energy=50 eV.

coexpansion we produce neutral clusters of the type $(C_2H_4)_n(NH_3)_m$. A large number of new homo- and heterocluster ion species become observable when an ethylene/ammonia coexpansion is ionized at 50 eV (Figure 1b). A major sequence of ion peaks, $(C_2H_4)_n^+$, is observed which closely resembles a pure ethylene in helium expansion. This is consistent with the view that very low concentrations of ammonia do not significantly alter the overall beam expansion conditions.

In addition to the ethylene cluster ions, a new sequence of heterocluster ions of the type $(C_2H_4)_n(NH_3)_m^+$ ($n=1$ to 8 and $m=1$ to 10) also emerges throughout the observed mass spectrum. It is quite surprising that heterocluster ion is effectively formed under the condition of the trace amount of ammonia molecules. The unprecedented detection of these heterocluster ions is primarily attributed to the solvation of ammonia molecules around the ethylene cluster ion through hydrogen bonding. A very similar result has been observed in our recent study on acetylene-ammonia heterocluster ions.⁷ Although the $(C_2H_4)_n(NH_3)_mH^+$ cluster ion is also observed in the mass spectra, its contributions are minor due to the weak van der Waals force between the ethylene molecule and the hydrogen atoms bonded to protonated ammonia cluster ion.

As the ammonia concentration is increased further the ethylene/ammonia coexpansion exhibits number of marked changes in the relative intensities of the heterocluster ions (Figure 1c). One may immediately notice that the overall spectral pattern looks quite different from that of pure ethylene clusters in helium as shown in Figure 1a. At the relatively high concentration of ammonia (6% ethylene-0.3% ammonia), the mass spectrum is dominated by intense peak series originating from protonated ammonia cluster ions, and ethylene cluster ions as well as heterocluster ions are much less intense. It is inferred that the formation of ethylene homocluster ion is now quenched within the heterocluster system at relatively high NH_3 concentration. This is consistent with the view that ammonia clusters of various sizes are easily formed in a supersonic expansions as compared

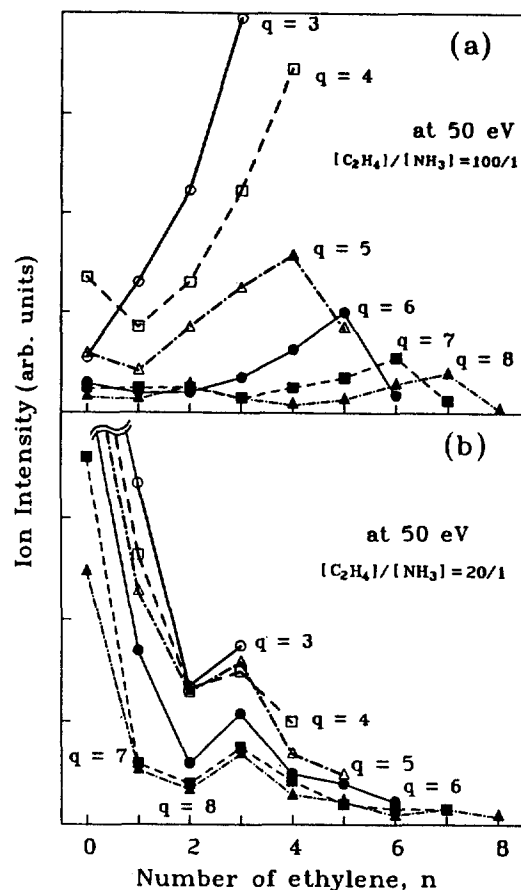


Figure 3. Intensity distributions of $(C_2H_4)_n(NH_3)_m^+$ ions as a function of number of ethylene molecules, n : (a) C_2H_4 (6%)+ NH_3 (0.06%); (b) C_2H_4 (6%)+ NH_3 (0.3%). q represents the total number of molecules involved in the clusters, $q=n+m$.

with van der Waals clusters such as ethylene due to its feasible hydrogen bonding. The formation of heterocluster ions also appears less favorable as a result of the intracuster excess energy dissipation in which some portions of the excess energies are liberated as a translational energy of the evaporating ethylene molecules *via* the excitation of van der Waals modes of the clusters.



Figure 2 summarizes the intensity distributions of the major sequence of cluster ions, $(C_2H_4)_n^+$, as a function of cluster size n which are obtained with pure ethylene and three different ethylene/ammonia mixtures while maintaining other nozzle conditions unchanged. For mixing ratios above $[C_2H_4]/[NH_3]=20/1$, a clear intensity drop from $(C_2H_4)_4^+$ to $(C_2H_4)_5^+$ is readily discerned from the plot, which has also been observed by several other research groups.^{12,19} Garvey and co-workers¹⁴ have proposed that the observed ethylene cluster ions are produced as a result of the successive intracuster condensation reactions. The observation of the anomaly of the magic number at $n=4$ is then due to the formation of $C_8H_{16}^+$ molecular ion generated *via* a series of successive ion-molecule reactions within the cluster. They therefore attributed the origin of this magic number not to the stability of a solvate central cation but rather to the generation of

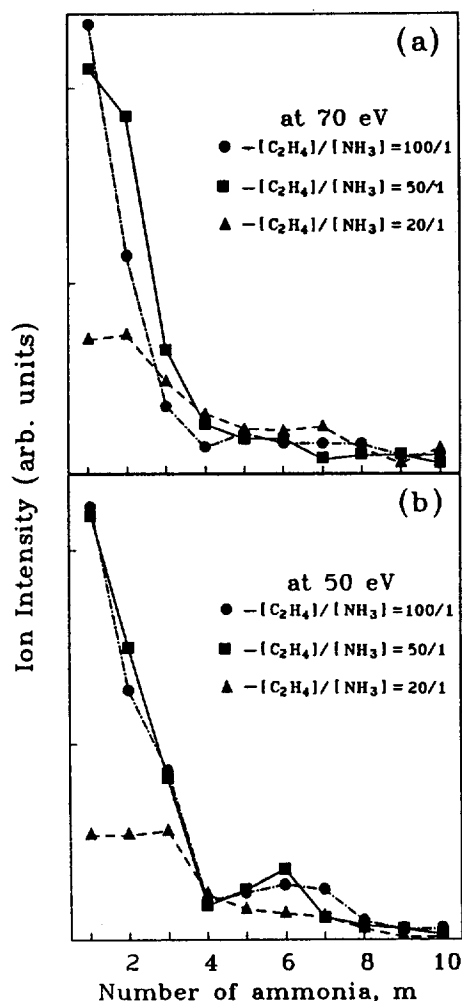


Figure 4. Plot of (a) $(\text{C}_2\text{H}_4)_3(\text{NH}_3)_m^+$ and (b) $(\text{C}_2\text{H}_4)_2(\text{NH}_3)_m^+$ ion intensities as a function of ammonia cluster number m at different mixing ratios. It should be noted that the intensity anomaly is insensitive to the experimental conditions mentioned above at $m=0$.

a new molecular ion due to a balance between the decrease in rate constant for each successive addition reaction and the evaporative loss of the remaining monomers.

The discontinuity, which corresponds to the salient intensity break between $n=4$ and $n=5$, however, exhibits a propensity of decrease and instead the magic number shifts to $n=3$ as the concentration of ammonia in the mixture is increased. In order to confirm the magic number shift from $n=4$ to $n=3$, the intensity distribution of heterocluster ions, $(\text{C}_2\text{H}_4)_n(\text{NH}_3)_m^+$, is investigated in a different way. Figure 3 displays the intensity distributions of $(\text{C}_2\text{H}_4)_n(\text{NH}_3)_m^+$ ions as a function of number of ethylene molecules, n , based on the conditions leading to the data in Figures 1b and 1c. The total number of molecules in heteroclusters is represented as $q(=n+m)$. At high mixing ratio (6% $\text{C}_2\text{H}_4/0.06\%$ NH_3), a distinct feature is readily discerned (Figure 3a): in small clusters ($q \leq 4$) the most intense ions denote ethylene homocluster ions, $(\text{C}_2\text{H}_4)_n^+(n \leq 4)$, among the clusters having the same q value. Interestingly, the heterocluster ions containing an ammonia molecule $(\text{C}_2\text{H}_4)_n(\text{NH}_3)^+$ become predominant

over the pure $(\text{C}_2\text{H}_4)_n^+$ clusters above $q=5$ even though the mixing ratio $[\text{C}_2\text{H}_4]/[\text{NH}_3]$ in the system is very large.

As the composition of ammonia is increased, as shown in Figure 3b, NH_3 -containing cluster ions are increased. The most intriguing finding in Figure 3b is that there exists a local maximum at $n=3$, corresponding to the $(\text{C}_2\text{H}_4)_3(\text{NH}_3)_m^+$ cluster ions. The general tendency is that increasing the ammonia concentration in the neutral clusters causes shift of the intensity anomaly (magic number) to $n=3$. This information is suggestive of the fact that ethylene trimer ion exhibits a pronounced magic number, thereby having the stable geometry in the ammonia moiety.

To further investigate the structures of ionized ethylene clusters under the ammonia solvation, we concentrated on an examination of the general trends in the size distributions of cluster ions. In the present study, we are most interested in the relative stabilities of cluster ions, particularly the mixed cluster ions $(\text{C}_2\text{H}_4)_n(\text{NH}_3)_m^+$. Plotting the observed $(\text{C}_2\text{H}_4)_n(\text{NH}_3)_m^+$ ion intensities as a function of the number of ammonia molecules in the clusters, more clearly reveals the notable features.

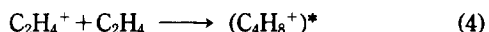
Figure 4a shows the intensity plot of the various $(\text{C}_2\text{H}_4)_3(\text{NH}_3)_m^+$ ions, normalized with respect to the most intense peak, as a function of m at three different mixing ratios. When the ethylene/ammonia mixing ratio is large (100/1) there is no intensity anomalies in the heterocluster ion distribution. As the NH_3 concentration is increased an interesting effect is seen in the intensity distribution of heteroclusters. The intensity break between $(\text{C}_2\text{H}_4)_3(\text{NH}_3)_2^+$ and $(\text{C}_2\text{H}_4)_3(\text{NH}_3)_3^+$ in the binary expansion is particularly pronounced as the mixing ratio is decreased. These findings were further confirmed under various experimental conditions, *e.g.*, gas component mixing ratios (ethylene/ammonia=50/1 to 10/1), nozzle stagnation pressures (44–64 psi), and electron impact energies (50–100 eV). The results show that the feature of intensity break in the cluster ion distribution is independent of experimental conditions mentioned above. The observation that an abrupt decrease in the intensity distribution of the $(\text{C}_2\text{H}_4)_3(\text{NH}_3)_m^+$ ions between $m=2$ and $m=3$ (Figure 4a) implies that the ethylene trimer does indeed afford a relatively stable structure.

In order to explain the sudden intensity break observed in the $(\text{C}_2\text{H}_4)_3(\text{NH}_3)_m^+$ clusters, a stable structure of certain ionic clusters produced *via* ionization should be considered since the magic number features usually entail the enhanced stability of certain cluster ions. After the neutral clusters are ionized by electron bombardment excess energies within the clusters are liberated by reorganization of the molecules accompanied by the intracuster ion-molecular rearrangements and by "boiling-off" of molecules, which leads to cooling down of the ionized clusters. From the result given above, we suggest that among the possible $\text{C}_6\text{H}_{12}^+$ isomers¹⁷ the stable geometry of ethylene trimer ion has a *trans*-3- $\text{C}_6\text{H}_{12}^+$ structure, where the available hydrogen-bonding sites will be two if there exist the solvent molecules such as ammonia.

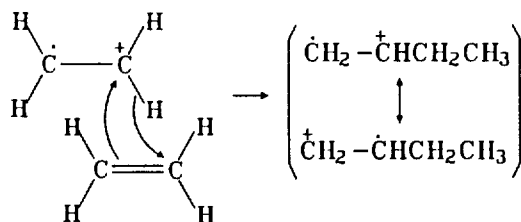
Figure 4b shows the intensity plot of the $(\text{C}_2\text{H}_4)_2(\text{NH}_3)_m^+$ ions as a function of m at three different mixing ratios. Most unexpected is the finding of drastic changes in the intensity distribution when NH_3 concentration is increased. That is, increasing ammonia concentration in the source causes the shift of intensity anomaly from $m=6$ to a small value of

$m=3$. During the course of this study, a large number of mass spectra were taken at a variety of stagnation pressure, mixing ratio, and ionization conditions. The results generally show the intensity anomalies at $(C_2H_4)_2(NH_3)_3^+$ or $(C_2H_4)_2(NH_3)_6^+$. This finding suggests that they stem originally from an intrinsic structural stability of the heteroclusters. The enhanced stability of $(C_2H_4)_2(NH_3)_6^+$ ion can be pictured as a situation in which the central $(C_2H_4)_2^+$ ion partially shares its charge with six surrounding NH_3 molecules through the six H atoms in the central $(C_2H_4)_2^+$ ion. The skewed parallel structure has been suggested for the neutral ethylene dimer¹⁶ from a theoretical study. This is hardly supported for the ethylene dimer ion by our experimental observation as well as a structural energy minimization by a molecular modeling software, MM2. The calculations reveal that the T-shaped structure is more favorable than the parallel one with a small energy difference. Although this simple picture requires an extensive computation to draw solid conclusion, it is qualitatively consistent both with the available structural information and with the experimental observation. As a logical extension, we suggest that the stability of $(C_2H_4)_2(NH_3)_6^+$ is due to six ammonia molecules equivalently solvating the T-shaped ethylene dimer ion.

The structural stability of $(C_2H_4)_2(NH_3)_3^+$ ion at high concentration of ammonia solvent can be interpreted as follows: when neutral heteroclusters are vertically excited through electron bombardment process, an internally excited intermediate complex $(C_4H_8^+)^*$ is generated^{11,20} by reaction (4). If the excess energy could be accommodated rapidly



enough to compete with the other channel the $(C_4H_8^+)^*$ ion might rearrange to form a stable isomer 1- $C_4H_8^+$ (1-butene), where the available hydrogen-bonding site will be three. This process can be expressed by the structure I.



STRUCTURE I

Previous investigations^{11,21} have shown that the rearrangement of the positive charge and the remaining electron from the p orbital leads very probably to a 1-butene ion structure, $[H_3C-CH_2-CH-CH_2]^+$. It is also noted that the contributions which appear at 39 amu ($C_3H_3^+$) and 53 amu ($C_4H_5^+$) are typical fragments of 1-butene parent ion.²² The present results indicate that the pathways leading to the formation of stable 1- $C_4H_8^+$ structure are facile in a heterocluster system where ethylene cluster ions are solvated in polar solvent molecules such as ammonia.

The variation of ion intensities with $[C_2H_4]/[NH_3]$ mixing ratios presented in Figure 4 may also be rationalized on the ground that as ammonia concentration increases, the evaporative processes following ionization may not be as efficient as stabilizing the intermediate ion due to the sticky

van der Waals bonding of the polar solvent molecules. It might also be expected that this less efficient stabilization may lead to the production of more $C_4H_8^+$ and $C_6H_{12}^+$ ions with sufficient excess energy to rearrange into the stable ions hence the increased prominence of the ions at $(C_2H_4)_2(NH_3)_3^+$ and $(C_2H_4)_3(NH_3)_2^+$. In a different set of experiments, we have also measured the $(C_2H_4)_n(NH_3)_m^+$ ($n \geq 4$) ion intensities as a function of m . Certainly, there is no clear intensity anomaly, i.e., monotonic decrease, in the ion distribution, indicating that ethylene tetramer and higher cluster ions do not definitely afford the rearrangements to the corresponding stable ion structures. As the size of the loose cluster ion increases, the interactions between moieties of the cluster ion should be less effective.

In conclusion, it becomes increasingly important that the study of intensity anomalies in heterocluster ions reveals the presence of enhanced stable structures. The present results provide direct evidence for the formation of stable ionic structures at particular cluster sizes under the presence of polar solvent molecules. The appearance of such cluster ions is discussed in terms of the intracuster ion-molecular rearrangement: an important process of intracuster energy redistribution which determines the stabilities and energetics of various van der Waals cluster ions.

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Total Synthesis of Sodium (3R, 4S)-3-[2-(2-Aminothiazol-4-yl)-(Z)-2-methoxyiminoacetamido]-4-methoxymethyl-2-azetidinone-1-sulfonate from L-Aspartic Acid

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A new monocyclic β -lactam analogue, sodium (3R, 4S)-3-[2-(2-aminothiazol-4-yl)-(Z)-2-methoxyiminoacetamido]-4-methoxymethyl-2-azetidinone-1-sulfonate (**3**) was synthesized from L-aspartic acid. Starting from L-aspartic acid, (S)-1-benzyl-4-benzyloxycarbonyl-2-azetidinone (**7**) was synthesized in four steps by following the established procedures and converted into (3R, 4S)-3-amino-1-*t*-butyldimethylsilyl-4-methoxymethyl-2-azetidinone (**13**) in six steps. Acylation of the amino group of **13** with 2-amino- α -(methoxyimino)-4-thiazoleacetic acid, desilylation, and sulfonation with sulfur trioxide-pyridine complex followed by ion exchange afforded sodium (3R, 4S)-3-[2-(2-aminothiazol-4-yl)-(Z)-2-methoxyiminoacetamido]-4-methoxymethyl-2-azetidinone-1-sulfonate (**3**). Antibacterial activities of this β -lactam compound **3** were, however, found to be quite low compared to cefotaxime.

Introduction

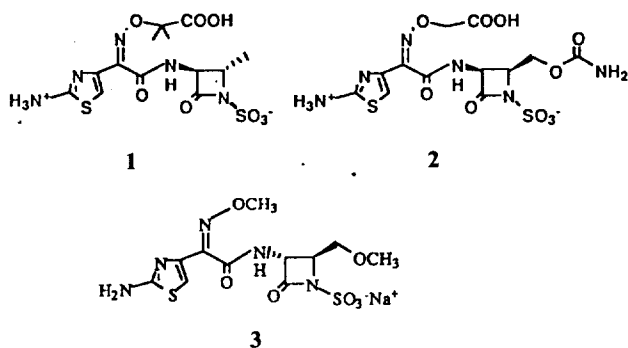
Since the discovery of penicillins in 1929¹ and cephalosporins in 1949², numerous classical β -lactam compounds have been introduced as antibiotics. After 1976, however, new types of β -lactam compounds, so-called nonclassical β -lactams, have been isolated from the natural sources. These are carbapenems,³ clavulanic acids,⁴ nocardicins,⁵ and monobactams.⁶ Of these, nocardicins contain characteristic oximino group and monobactams N-sulfonate functionality, which are very rare in nature.

tive bacteria, and high stability to β -lactamase.

In connection with our ongoing research on the β -lactam chemistry, we now wish to report the total synthesis and antibacterial activities of sodium (3R, 4S)-3-[2-(2-aminothiazol-4-yl)-(Z)-2-methoxyiminoacetamido]-4-methoxymethyl-2-azetidinone-1-sulfonate (**3**), a monocyclic β -lactam analogue structurally related to aztreonam and carumonam.

Results and Discussion

The (3R, 4S)-configuration of the title compound **3** can be derived from naturally occurring L-aspartic acid. We have already reported⁹ that the alcoholysis of L-aspartic anhydride hydrohalides produces α -esters regioselectively. Thus, treatment of L-aspartic acid with phosphorus trichloride afforded L-aspartic anhydride hydrochloride (**4**) and alcoholysis of this salt with benzyl alcohol produced α -benzyl L-aspartate (**5**) in high yield. N-Benzylation of the compound **5** with benzyl bromide and cyclization of the resulting α -benzyl N-benzyl-L-aspartate (**6**) with O-ethyl phosphorodichloridate¹⁰ and triethylamine in acetonitrile (0.01 M) at room temperature afforded (S)-1-benzyl-4-benzyloxycarbonyl-2-azetidinone (**7**) in 95% yield. The formation of the β -lactam **7** was confirmed by the lactam carbonyl absorption band appeared at $\nu=1750$ cm^{-1} in its IR spectrum. Reduction of the benzyloxycarbonyl group with excess sodium borohydride and methylation of the resulting hydroxymethyl group with methyl iodide in the presence of silver oxide produced (S)-1-benzyl-4-methoxymethyl-2-azetidinone (**9**) in 60% overall yield (see



Recently, new monocyclic β -lactam antibiotics such as aztreonam (**1**)⁷ and carumonam (**2**)⁸ which have characteristic structural features of nocardicins and monobactams, have been introduced. These new antibiotics are known to have strong antibacterial activities against gram-negative and posi-