Intracluster electron transfer from a metal atom/cluster followed by anionic oligomerization of vinyl molecules

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Abstract. Intracluster electron transfer and oligomerization reaction were investigated by mass spectrometry of clusters of alkali metal atom (M) with acrylonitrile (AN; $CH_2=CHCN$). In the photoionization mass spectra of $M(AN)_n$, magic numbers were clearly observed at $n = 3k$ (k = 1-4 for M = Na and K, $k = 1$ for M = Li). The results of photodissociation of neutral $K(AN)_n$ indicate that the $n = 3$ cluster has an anomalous stability relative to other sizes of clusters. The C=C bond in vinyl molecules is also found to be necessary to form the magic numbers by measuring the photoionization mass spectrum of K atom with propionitrile. These results strongly support the intracluster anionic oligomerization reaction initiated by electron transfer from the alkali atom. The quantum chemical calculations have revealed that the evaporation induced by excess energy generated by intracluster oligomerization is important to form the magic numbers in the present clusters.

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1 Introduction

Ionic polymerization of vinyl molecules in the condensed phase is an important reaction as a method to obtain various useful materials. In recent years, ionic oligomerization in the gas phase has also been studied to some extent in order to elucidate the elementary reaction processes [1–17]. For this purpose, gas phase studies should have some advantages from the following features; (1) it is possible to discuss reactivity which is free from the solvent effect, and (2) assignment of the sequentially polymerized products are directly obtained by the mass spectrometric method. As one of the gas phase studies, a flowing ion-molecule reaction was investigated to elucidate the reaction mechanism of anionic oligomerization [1,2]. In these studies, negative ions such as F_3C^-, $NCCH_2^-$ and $C_3H_5^-$ were applied as the reaction initiator in the gas phase flowing afterglow apparatus. As for methyl acrylate, termination of the oligomerization was found at the trimer by mass spectrometric method. The structure of the initiator anion is found to be much related to this termination mechanism and several side-reactions were also observed. Studies on gas-phase clusters were also performed as a microscopic model for the initial step of anionic oligomerization. The cluster anions of vinyl compounds produced by electron transfer from high-Rydberg rare gas atoms were extensively investigated by Tsukuda and Kondow [3–5]. Photodissociation, collision-induced dissociation and pho-

toelectron spectroscopy of the cluster anions were also performed in their studies [6–8]. Trimeric terminations were also observed for cluster anions of acrylonitrile (AN; $CH_2=CHCN$) and its derivatives [3]. Through these studies, they concluded that the intracluster oligomerization is initiated by electron attachment to $(AN)_3$ and forms a stable anion radical that has a ring structure. On the other hand, as for methyl acrylate cluster anions, no pronounced signal (magic number) was observed at trimer, and the pentamer was found to have the most enhanced signal in the mass spectrum [4].

In the authors' group, intracluster reactions have been investigated for clusters containing vinyl molecules (VM) and an alkali metal (M) by means of a time-of-flight mass spectrometer (TOF-MS) with a cluster beam source [9,10]. In these studies, the magic numbers at $M(VM)_3$ (M = Li, Na and K) were observed in their photoionization mass spectra. It is concluded that these magic numbers are due to the trimeric unit with a cyclohexane derivative which is produced by anionic oligomerization initiated by the electron transfer from an alkali atom.

In this study, we have further investigated the clusters of M with AN and related systems in order to confirm the above conclusion. By the modification of experimental setup, magic-number behavior was much more clearly observed than in the previous study [9]. In order to study the stability of neutral clusters, photodissociation experiment of $K(AN)_n$ neutrals was performed. This result suggests that the $n = 3$ neutral has an anomalous stability relative to other sizes of clusters. We also measured the

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photoionization mass spectrum of K atom with propionitrile (PN; CH_3CH_2CN), which has a similar structure with AN except for the absence of C=C bond. As a result, the C=C bond in vinyl molecules is found to be necessary to form the magic numbers. These results strongly support our previous interpretation of the intracluster anionic oligomerization initiated by electron transfer from alkali metal. The quantum chemical calculations have also been performed to estimate the excess energy generated by intracluster oligomerization and to discuss the evaporation process after oligomerization.

2 Experimental setup

Present experiments were performed by using an apparatus reported previously [9,10] with some modifications. We used two-stage differentially pumped chambers consisting of a cluster source and a Wiley-McLaren type TOF-MS [18]. The clusters of metal atoms with molecules were produced by a pickup source [19–21] consisting of a combination of laser vaporization and pulsed supersonic expansion. A sample gas mixed with helium was expanded from a pulsed valve with a stagnation pressure of 4 atm. The second harmonic of a Nd:YAG laser was focused onto a metal rod placed at about 10 mm downstream from the nozzle. In this source, the metal atom-molecule clusters are produced by collision of the vaporized metal atoms with molecular clusters preformed by supersonic expansion, although subsequent collisional relaxation with buffer He gas cannot be ruled out. One-photon ionization of neutral clusters was performed by irradiation with a pulsed laser beam. The photoions were accelerated to about 3.0 keV by static electric fields applied to acceleration electrodes which were modified in this study. The electrodes consist of 9 rings (60 mm o.d., 15 mm i.d., thickness 0.5 mm) and are designed to form sufficiently flat equipotential surface in the electrodes. The accelerated ions were introduced to a field free tube of 590 mm length arranged collinearly with the cluster beam. The mass-separated ions were detected by a dual microchannel plate. In the photodissociation experiment of neutral clusters, the second harmonic of a Nd:YAG laser was irradiated 100 ns prior to photoionization. The fluence of the dissociation laser was kept about 10 mJ/cm^2 during the measurement.

3 Results and discussion

3.1 Photoionization mass spectra of $M_m(AN)_n$ (M = Li, Na and K)

Figs. 1a-1c show the typical mass spectra of $M_m(AN)_n$ (M = Li, Na and K) clusters obtained by one-photon ionization. The photon energies were 5.64 eV for $Li_m(AN)_n$ (Fig. 1a) and 4.66 eV for $Na_m(AN)_n$ and $K_m(AN)_n$ (Figs. 1b and 1c). In these figures, the series of cluster ions of $Li^+(AN)_n$, $Na^+(AN)_n$ and $K^+(AN)_n$ are predominantly observed up to $n = 21$, 22 and 18, respectively. Several intensity anomalies (magic numbers) in the
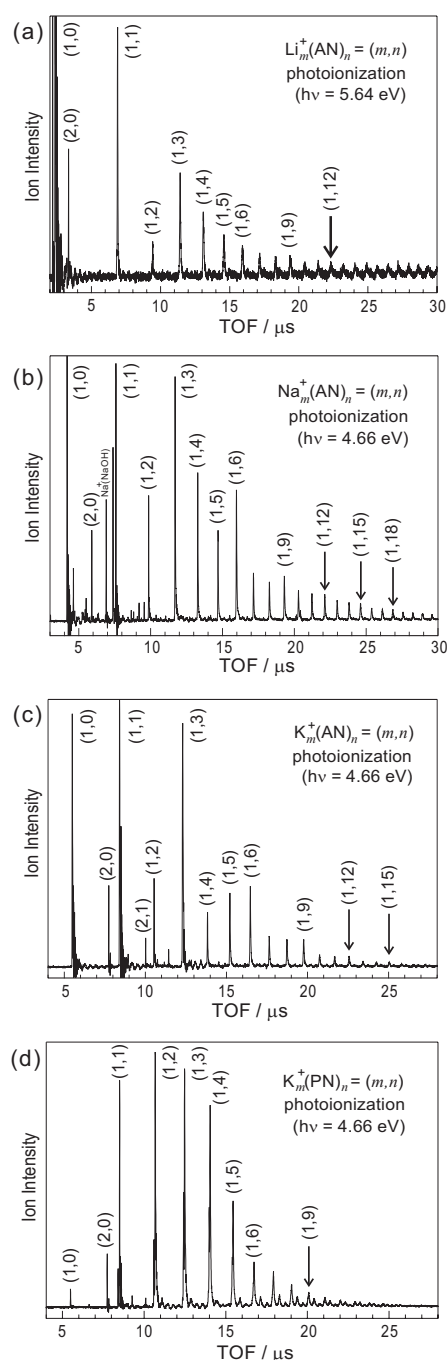
Fig. 1. Photoionization mass spectra of (a) $Li_m(AN)_n$, (b) $Na_m(AN)_n$, (c) $K_m(AN)_n$ and (d) $K_m(PN)_n$.

$M^+(AN)_n$ (M = Na and K) series are found in these mass spectra. The intensities of $n = 3$, 6 and 9 are observed strongly with respect to adjacent n ions, and the intensity gaps between $n = 12$ and 13 are also observed. In the present mass spectra, signal to noise ratio is much improved from these reported previously [9] by the modification of the ion-acceleration electrodes. Collinear arrangement of the neutral beam with TOF-MS is also effective for introducing heavy ions to the microchannel plate. As a result of these modifications,
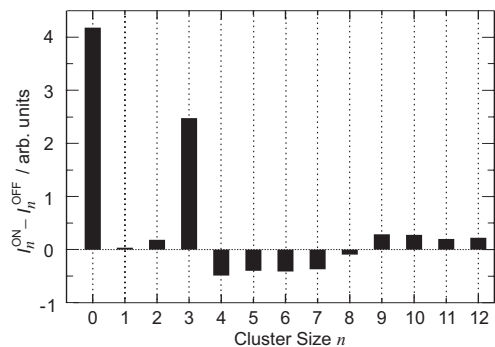
Fig. 2. The difference between ion intensities, I_n^{ON} (dissociation and ionization) and I_n^{OFF} (ionization only), $I_n^{ON} - I_n^{OFF}$, in $K^+(AN)_n$.

magic-number behavior at $n = 3k$ ($k = $ 1-4) in $M^+(AN)_n$ (M = Na and K) series is observed more clearly than in the previous mass spectra. However, in $Li^+(AN)_n$ series, the magic number is clearly found only at $n = 3$. We have also obtained the photoionization mass spectrum of clusters of a K atom with PN (Fig. 1d). In this figure, the size distribution of $K^+(PN)_n$ is found to be rather smooth with no features of magic numbers observed in $M(AN)_n$ clusters.

3.2 Stability of neutral clusters

The following factors which cause magic numbers were already discussed in the previous papers [9,10]; (1) the size-dependent stability of neutral clusters, (2) the ionization efficiency of neutral clusters at certain photon energy for ionization, and (3) the evaporation process after ionization. Among these, we can assume that the ionization efficiency (possibility (2)) is not sensitively dependent on n for all clusters in the present mass spectrum, because the photon energy is much higher than ionization thresholds of these clusters. In addition, in the ionization with a photon energy of 3.84 eV, which is only 0.21 eV above the ionization thresholds for $Na(AN)_n$ ($2 \leq n \leq 6$), the same magic-number behavior is found at $n = 3$ in the mass spectrum of $Na(AN)_n$ [9]. Therefore, the appearance of the magic number is little affected by the evaporation process after photoionization (possibility (3)). In order to discuss the possibility (1) further, we have also performed the photodissociation experiment of neutral $K(AN)_n$ clusters. In this experiment, we have obtained the difference of each ion intensity with the photodissociation laser (I_n^{ON}) and that without the laser (I_n^{OFF}). Photon absorption by the clusters induces the evaporation processes, and as a result, the population of the stable neutral species is expected to increase. The difference between I_n^{ON} and I_n^{OFF}, $I_n^{ON} - I_n^{OFF}$, is plotted *versus* n in Fig. 2. The ion intensities at K^+ and $K^+(AN)_3$ are found to be enhanced in the photoionization after photodissociation. This result indicates that the neutral $K(AN)_3$ has an anomalous stability relative to other sizes of clusters. The enhancement is also found at $n \geq 9$, although the decrease of the $K^+(AN)_6$ intensity is found. We will discuss this in Section 3.4. After

all, the magic numbers at $n = 3k$ observed in the photoionization mass spectra are concluded to be due to the relative stability of neutral clusters (possibility (1)).

3.3 Magic numbers formed by intracluster oligomerization initiated by electron transfer

In this section, we discuss the reason why the neutral $M(AN)_n$ (M = Li, Na and K) show magic numbers. As shown in Fig. 1, magic numbers at $n = 3k$ ($k = $ 1-4) are commonly observed for the three alkali atom systems. Therefore, it is expected that the ns valence electron of the alkali metal atom plays a crucial role in the formation of magic number clusters. In addition, the magic numbers are found to be observed only for the systems containing vinyl molecules. In fact, the magic numbers are not observed in the mass spectrum of $K(PN)_n$ as shown in Fig. 1d. If the size of a molecule is a key factor for magic numbers at $n = 3k$, the same periodical magic numbers will appear in the mass spectrum of $K(PN)_n$, as in $K(AN)_n$. This result indicates that the existence of the C=C bond is necessary to the formation of the magic numbers of $M(AN)_n$.

In the condensed phase, it is well-known that the electron transfer from alkali metal initiates the anionic polymerization of AN. In this reaction, electron transfer causes a cleavage of the C=C bond of a vinyl molecule. Also in the present $M(AN)_n$ clusters, the observed magic numbers can be related with the intracluster electron transfer from alkali metal atom followed by oligomerization of AN. In fact, in the detailed studies of $(AN)_n^-$ ions by Kondow and co-workers [3,5–8], $n = 3$ and 6 are found to be magic numbers. These stable species are concluded to be produced by intracluster oligomerization after electron attachment to $(AN)_n$ [3,5–8]. The magic numbers observed in their studies coincide with those in the present photoionization experiments. After all, we conclude that the common magic numbers at $n = 3k$ in the photoionization mass spectra of $M(AN)_n$ (M = Li, Na and K) indicate the presence of intracluster electron transfer from alkali metal atom to AN, which is followed by anionic oligomerization. As for the magic numbers at $n = 3k$ ($k \geq 2$), plural trimer units are expected to be formed by the oligomerization. In such processes, the electron initially transferred from M to the first AN trimer should promote the oligomerization of other unreacted AN molecules further. In the condensed phase, the return of an electron to M^+ (neutralization of the cation) is suggested to be one of the termination reactions of anionic polymerization [23]. Therefore, it is suggested that the excess electron once returns to M and that it transfers again from the metal atom to unreacted AN molecules and initiates another oligomerization reaction.

In a previous paper [9], we proposed that oligomerized AN cluster in $M(AN)_3$ contains a ring geometry, which is assignable to 1,3,5-cyclohexanetricarbonitrile (CHTCN), as reported by Kondow and co-workers [3,5–8]. CHTCN is known as a stable species which is prepared from 1,3,5-cyclohexanetricarboxylic acid [22]. In the photodissociation experiment, ion intensities at K^+ and $K^+(AN)_3$ are enhanced by dissociation, as shown in Fig. 2. This result

also strongly suggests the existence of the trimer unit in $K(AN)_3$. Observed periodical magic numbers at $M(AN)_n$ (M = Na and K; $n = 3k$, $k \geq 2$) suggest that more than one CHTCN units are formed in these clusters by the mechanism noted above. In Fig. 2, the ion intensity at $n = 6$ is found to decrease by photodissociation. This reveals that $K(AN)_6$ photodissociates even if the stable $K(AN)_6$ is generated by dissociation of $K(AN)_n$ ($n \geq 7$). In other words, the elimination of CHTCN is suggestive from $K(AN)_6$. The dissociation pattern will depend on the wavelength of the dissociation laser. Thus the photodissociation experiments at different wavelength are now undergoing in the authors' group.

3.4 Evaporation process induced by intracluster oligomerization

We have estimated the excess energy generated by the formation of CHTCN (intracluster oligomerization of AN trimer) by theoretical calculation (RHF/6-31+G*). In this calculation, the total energy of CHTCN (E(CHTCN)) and that of an AN molecule (E(AN)) were used for estimation of the excess energy ($E_{ex}=E(\mathrm{AN})\times 3-E(\mathrm{CHTCN})$). E_{ex} was estimated to be 48.4-58.8 kcal mol^{-1} (2.10-2.55 eV) depending on the four different isomers in CHTCN owing to axial-equatorial conformation. Therefore, intracluster oligomerization which generates CHTCN is found to be a highly exothermic reaction. In the evaporation process, the efficiency of evaporation is presumed to depend on the binding energy (ΔE) between the metal atom and AN. In the calculations of optimized structures of Na(AN) 1:1 complex, two stable isomers were found and these ΔE were estimated to be 8.1 and 1.4 kcal mol^{-1} [9]. Therefore, for $M(AN)_n$ clusters with $n \geq 4$, this excess energy is expected to be dissipated by the evaporation of AN after oligomerization in addition to collisional relaxation in the cluster source, as noted in the experimental section. This evaporation process results in the intense peaks at $M^+(AN)_3$ in the photoionization mass spectra.

4 Conclusion

We have measured the photoionization mass spectra of clusters of alkali metal atom (M) with acrylonitrile (AN). Because of the improvement of the experimental setup, magic numbers are clearly observed at $n = 3k$ (k = 1-4 for $Na(AN)_n$ and $K(AN)_n$, k = 1 for $Li(AN)_n$). The experiments of photodissociation of $K(AN)_n$ reveals that the $n = 3$ neutral has an anomalous stability relative to other sizes of clusters. In the photoionization mass spectrum of $K(PN)_n$, the magic numbers at $n = 3k$ are not observed. From these results, C=C bond in the molecule is found to be necessary to the formation of the magic numbers. Based on the polymerization reaction in the condensed phase and the observations in the studies of $(AN)_n^-$ ions, it is concluded that the observed magic numbers at $n = 3k$ are generated by intracluster anionic oligomerization of AN

clusters induced by electron transfer from the alkali metal atom. By the quantum chemical calculations, the excess energy generated by intracluster oligomerization was estimated to be 48.4-58.8 kcal mol^{-1}. This result indicates that the efficient evaporation after oligomerization is essential to form the magic numbers.

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