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Photoionization mass spectroscopy of clusters of alkali metal atoms with methyl vinyl ketone and acrolein: intracluster oligomerization initiated by electron transfer from a metal atom

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Abstract

We have investigated the photoionization mass spectrometry of clusters of an alkali metal atom (M: Na and K) and methyl vinyl ketone (MVK) or acrolein (AC) to discuss the intracluster oligomerization. In the mass spectra of $M(MVK)_n$, strong ion signals at $n = 3$ are observed. This magic number is explained by the cyclohexane derivative formation in the intracluster oligomerization of MVK initiated by electron transfer from an alkali metal atom. The results of the calculation for Na(MVK) based on density functional theory also show the presence of intracluster electron transfer. On the other hand, in $M(AC)_n$, intensity enhancement is observed at $n = 4$. These intensity enhancements may be due to intracluster reaction in $M(AC)_n$, which is different from the case of $M(MVK)_n$. (Int J Mass Spectrom 216 (2002) 29–40) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Oligomerization; Intracluster reaction; Photoionization

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1. Introduction

In recent years, the anionic polymerization of vinyl compounds in the condensed phase received much attention as a method to obtain various useful materials [1,2]. It has been established that strong bases, such as alkali metals and alkyllithium compounds, initiate anionic polymerization of vinyl compounds that bear electron-withdrawing groups. An electron transfer from these strong bases causes cleavage of the C=C double bond of the vinyl monomer to yield a carbanion. This carbanion reacts with another monomer to produce a propagated oligomer chain, which sequentially reacts with other monomer. Thus, the formation of the contact ion pair between the vinyl molecular anion and its counter-ion is important in the initial step of the polymerization. The anionic polymerization of α,β-unsaturated ketone and aldehyde, such as methyl vinyl ketone (MVK: CH_2=$CHCOCH_3$) and acrolein (AC: CH_2=CHCHO) is well studied in various reaction conditions (initiator, solvent and temperature) to identify the structures of polymerized products [2]. In the review article for works of polymerization of AC [3], it was pointed out that acrolein is one of the few monomers which contain two polymerizable groups (C=C double bond and carbonyl group) of different reactivities.

In recent years, ionic oligomerization in the gas phase has also been studied to some extent in order

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to elucidate the elementary reaction processes [4–23]. For this purpose, gas phase studies should have some advantages with following features: (1) it is possible to discuss reactivity which is free from the solvent effect, and (2) assignments of the polymerized products are directly obtained by mass spectrometric method. Especially, studies on gas-phase clusters were performed as a microscopic model for the initial step of anionic polymerization. Anionic clusters of vinyl compounds were extensively investigated by Kondow and coworkers [6–12]. In their studies, trimeric terminations were observed for cluster anions of acrylonitrile and its derivatives, and they concluded that the intracluster oligomerization is initiated by electron attachment to acrylonitrile trimer and forms a stable anion radical that has a ring structure.

The contact ion pair consisting of a vinyl molecular anion and its counter-ion is also expected to be another model for the initial step of anionic oligomerization. Clusters of an initiator and vinyl molecules (VM) are the models of such contact ion pairs to discuss the mechanism of the propagation reaction of the ion pair with another monomer. In the authors' group, intracluster reactions have been investigated for clusters containing VM and an alkali metal atom (M) by means of a time-of-flight mass spectrometer (TOF-MS) with a cluster beam source [20–23]. In these studies, the magic numbers at $M(VM)_3$ ($M = Li$, Na and K) were observed in their photoionization mass spectra, and it was concluded that these magic numbers are due to the trimeric unit with a cyclohexane derivative which is produced by intracluster anionic oligomerization. Thus, the evidence of anionic oligomerization was found for the neutral clusters and the electron transfer from metal to VM initiates the intracluster oligomerization. In addition, for alkali metal–methyl acrylate clusters, the mechanism of anionic oligomerization is found to be different from the methyl acrylate cluster anions [21]. From these studies, it has been found that the existence of the alkali metal atom in these clusters has a critical effect on the reactions in the initial step of the anionic oligomerization.

In this study, we have investigated clusters containing the alkali metal atom (Na, K) and MVK or AC by photoionization mass spectrometry in order to discuss the initial steps of the oligomerization of these molecules. The possibilities of the intracluster reactions are discussed from the size distributions observed in the photoionization mass spectra. We have compared the present results with those in the previous studies of $M(VM)_n$ and have discussed the intracluster anionic oligomerization initiated by electron transfer from the alkali metal atom. The quantum chemical calculations have also been performed to obtain the information about intracluster electron transfer in Na(MVK) and Na(AC).

2. Experimental section

Present experiments were performed by using an apparatus reported previously [20–23]. We used two-stage differentially pumped chambers consisting of a cluster source and a Wiley—McLaren type TOF-MS [24]. The clusters of metal atoms with molecules were produced by a pickup source [25–27] consisting of a combination of laser vaporization [28] and pulsed supersonic expansion. A mixture gas of helium and sample (MVK, AC) 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 helium 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 ∼3.0 keV by static electric fields and 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.

Mass spectra of the cluster ions nascently formed in the source were also measured along with the measurements. Cluster ions were generated by ion–molecule reactions between alkali metal ions formed by laser vaporization and neutral vinyl-molecule clusters in the expansion region of the free jet. The product cations were introduced to the acceleration region of the TOF-MS and accelerated to ∼1.0 keV by pulsed electric fields generated by a high-voltage pulse generator.

The sample rods of sodium (Rare Metallic, 99.9% pure) and potassium (Aldrich, 99.5% pure) were made under a nitrogen atmosphere in a vacuum dry-box to avoid reaction with water in the air. Chemicals were purchased at the following minimum percent impurities and used without further purification: MVK (Aldrich, 99% pure) and AC (Tokyo Kasei, 90% pure). The mixing ratio of MVK and AC in helium gas was estimated to be 3.8 and 6.5, respectively.

3. Calculation

The quantum chemical calculations for free molecules (MVK and AC) and 1:1 complexes (Na(MVK) and Na(AC)) were performed to examine the possibility of intracluster electron transfer. These calculations were carried out by using a density functional theory program of the Gaussian 94 package [29]. The 6-31+G* basis set and B3LYP functional [30] were utilized in these calculations. There are two conformers, *s-trans* and *s-cis*, for both MVK and AC. We calculated the optimized structures of these conformers and the 1:1 complexes between Na atom and these conformers. We made a natural population analysis [31] for the optimized structures to estimate the charge distributions within clusters. Optimized structures were calculated with no constraint of the structural parameters.

4. Results and discussion

4.1. Photoionization mass spectra of M(MVK)$_n$ and M(AC)$_n$ (M = Na and K)

Fig. 1a shows a typical mass spectrum obtained by one-photon ionization of Na(MVK)$_n$ by irradiation with a laser beam of 5.99 eV. A series of cluster ions of Na$^+$(MVK)$_n$ is mainly observed up to $n = 16$. The intensity of Na$^+$(MVK)$_3$ is observed intensely with respect to adjacent n ions. This intensity-anomaly (magic number) behavior at $n = 3$ is independent of the energy of the ionization laser in the region between 4.15 and 5.99 eV. We also measured the

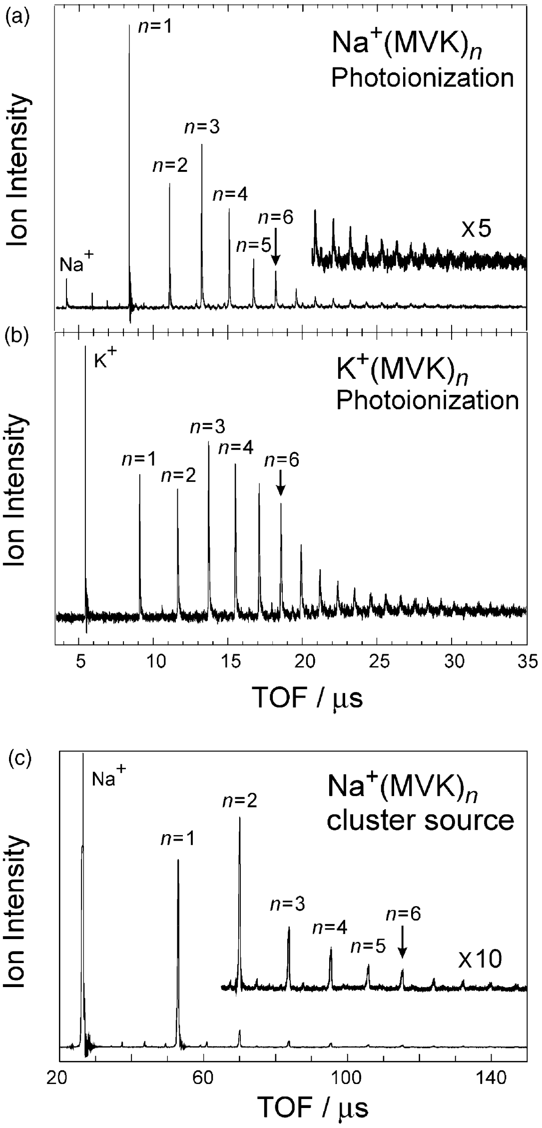

Fig. 1. Photoionization mass spectra of (a) Na(MVK)$_n$ and (b) K(MVK)$_n$. Ionization energy is 5.99 eV. (c) Mass spectrum of Na$^+$(MVK)$_n$ produced by ion–molecule reaction in the cluster source.

photoionization mass spectrum of clusters containing other alkali metal atoms, K(MVK)$_n$ (Fig. 1b). The series of K$^+$(MVK)$_n$ ions is also observed up to $n = 16$, and the magic number behavior at $n = 3$ is again observed as in Na(MVK)$_n$. These clusters were ionized by absorption of a single photon, because ionization energies of Na and K atoms are 5.14 and 4.34 eV, respectively [32], and in general these clusters have lower ionization threshold energies than alkali metal atoms. We also measured the mass spectrum of the Na$^+$(MVK)$_n$ ions nascently formed by ion–molecule reaction in the cluster source as shown in Fig. 1c. In the source, the cluster ions are produced by collision between the preformed molecular clusters and the metal ions generated by laser vaporization. In this mass spectrum, it is expected that the observed size distributions depend on the stability of ions produced by ion–molecule (cluster) reactions. In Fig. 1c, the intensities of Na$^+$(MVK)$_n$ decrease monotonically with increasing n, and the magic number behavior at $n = 3$ in Fig. 1a and b is not observed. Therefore, it is expected that the stability of Na$^+$(MVK)$_n$ produced by ion–molecule reactions does not depend sensitively on n, and that the magic number is related to the nature of neutral Na(MVK)$_n$ clusters.

Fig. 2a and b show photoionization mass spectra obtained by one-photon ionization of M(AC)$_n$ (M = Na and K) by irradiation with a laser beam of 5.99 eV. A series of cluster ions of M$^+$(AC)$_n$ is mainly observed as in Fig. 1, however the magic number at $n = 3$ observed in M(MVK)$_n$ is not observed. The most intense signal is found at $n = 4$. This behavior is observed when the photon energy of the ionizing laser is higher than 5.17 eV, while at 4.91 eV and below no intensity-anomaly is observed. Fig. 2c shows the mass spectrum of the Na$^+$(AC)$_n$ ions nascently formed by ion–molecule reaction in the cluster source. In this mass spectrum, the size distribution of Na$^+$(AC)$_n$ decreases monotonically with increasing n.

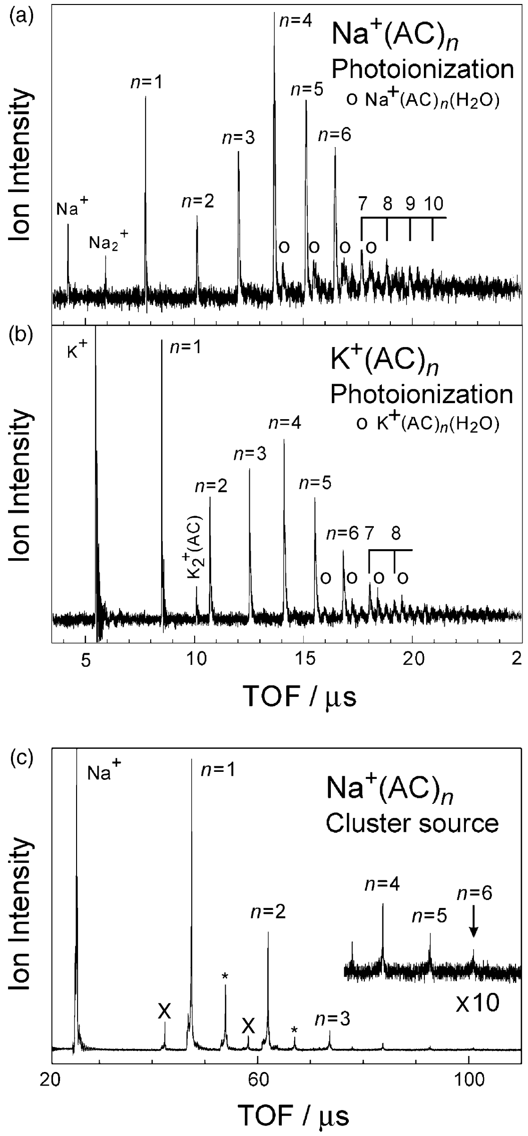

Fig. 2. Photoionization mass spectra of (a) Na(AC)$_n$ and (b) K(AC)$_n$. Ionization energy is 5.99 eV. In both mass spectra, peaks denoted by circles are assignable to M$^+$(AC)$_n$(H$_2$O) (M = Na, K). (c) Mass spectrum of Na$^+$(AC)$_n$ produced by ion–molecule reaction in the cluster source. Along with a series of Na$^+$(AC)$_n$ (n = 0–6), Na$_2{}^+$(AC)$_n$ (n = 1–3) and Na$^+$(NaOH)(AC)$_n$ (n = 0, 1) ions are denoted by $*$ and $\times$, respectively.

In the measurement of each photoion yield with scanning the ionization photon energy, we have determined the ionization thresholds (I_{th}) of Na(MVK)$_n$ and Na(AC)$_n$ (n = 1–6). These values are plotted in Fig. 3 along with the ionization energy of Na atom [32]. In Na(MVK)$_n$, I_{th} value decreases monotonically with n for n = 0–3, whereas those for $3 \leq n \leq 6$ are constant at 3.86 eV within experimental error.

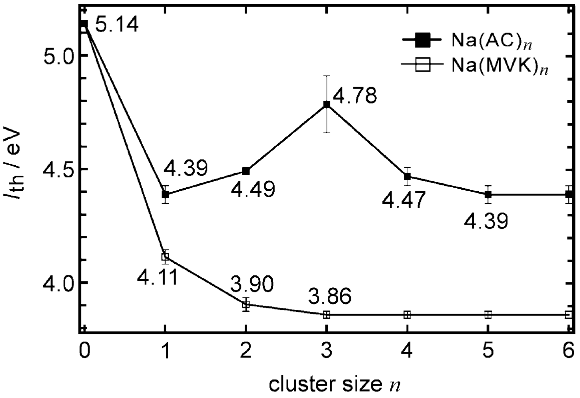

Fig. 3. Determined ionization thresholds (I_{th}) of Na(MVK)$_n$ and Na(AC)$_n$.

However, in Na(AC)$_n$, the n dependence of I_{th} is more complicated. The I_{th} of $n = 3$ is about 0.3 eV higher than those of other sizes.

4.2. Intracluster electron transfer in M(MVK)$_n$ and M(AC)$_n$ (M = Na and K)

It is well known that the electron transfer from an alkali metal initiates the anionic polymerization reaction of MVK and AC in the condensed phase. Also in M(MVK)$_n$ and M(AC)$_n$ (M = Na and K), the alkali metal atom is expected to act as an electron donor to the MVK and AC clusters. In order to get further insight into the possibility of intracluster electron transfer, we have optimized the structures of Na(MVK) and Na(AC) based on DFT (B3LYP/6-31+G*) calculations.

The structures obtained for *s-cis* and *s-trans* MVK molecules are shown in Fig. 4a. For a free MVK molecule, the two conformational isomers are in an equilibrium, and relative abundance of *s-cis*:*s-trans* is determined to be 20:80 at room temperature by electron diffraction and spectroscopic studies [33]. In the present work, the *s-trans* conformer is calculated to be more stable than *s-cis* by 0.17 kcal/mol, and as a result, the relative abundance is estimated to be *s-cis*:*s-trans* = 43:57. Three isomers are found in the calculation for Na(MVK) as shown in Fig. 5a. In the isomer **1**, the Na atom binds to *s-cis* MVK. The binding energy (ΔE) with respect to free Na and MVK is evaluated to be 20.4 kcal/mol.[1] On the other hand, two stable structures are found for the complexes of Na–MVK (*s-trans*), as shown in **2** and **3**. The ΔE are evaluated to be 12.4 and 1.8 kcal/mol for **2** and **3**, respectively. The barrier in the internal rotation of the vinyl group (from *s-trans* to *s-cis* barrier) in free MVK was estimated to be 2.4 kcal/mol from the far-infrared spectrum of MVK [34]. In the formation of Na(MVK)$_n$ using the present pickup source, an alkali metal atom with a high kinetic energy collides with a MVK cluster formed by the pulsed jet under the collisional cooling condition, so that Na(MVK)$_n$ clusters are initially formed at high-temperature condition. Because of small rotational barrier of MVK, there is a possibility for formation of the most stable isomer **1** (Na(MVK) (*s-cis*)) in the collision between metal atom with the abundant *s-trans* MVK. The natural charges on the Na atom are +0.88, +0.55 and +0.37 for **1**, **2** and **3**, respectively, and thus the electron of the Na atom is partly transferred to MVK. The structures of MVK in these Na(MVK) isomers also reveal that the intracluster electron transfer partly takes place. In these isomers, the lengths of $C^1{=}C^2$ and $C^3{=}O$ bonds are about 1–6% longer than those of free MVK. In contrast, the length of $C^2{-}C^3$ bond is about 2–5% shorter. These changes in bond lengths can be explained clearly by consideration of the electron distribution in the singly occupied molecular orbital (SOMO) of Na(MVK), as shown in Fig. 5b. The electron density distributions in the SOMO of these isomers resemble that of the lowest unoccupied molecular orbital (LUMO) of free MVK (Fig. 4b), which has the antibonding nature of $C^1{=}C^2$ and $C^3{=}O$ bonds and the bonding nature of $C^2{-}C^3$ bond. Therefore, bond length changes in Na(MVK) are related to the electron

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[1] The binding energies ΔE of these isomers can be evaluated by

$$-\Delta E = E[\mathrm{Na(VM)}] - E[\mathrm{Na}] - E[\mathrm{VM}]$$

where E[Na(VM)] is the total energy of Na(VM); E[Na] and E[VM] are the total energies of Na atom and vinyl molecule, respectively.

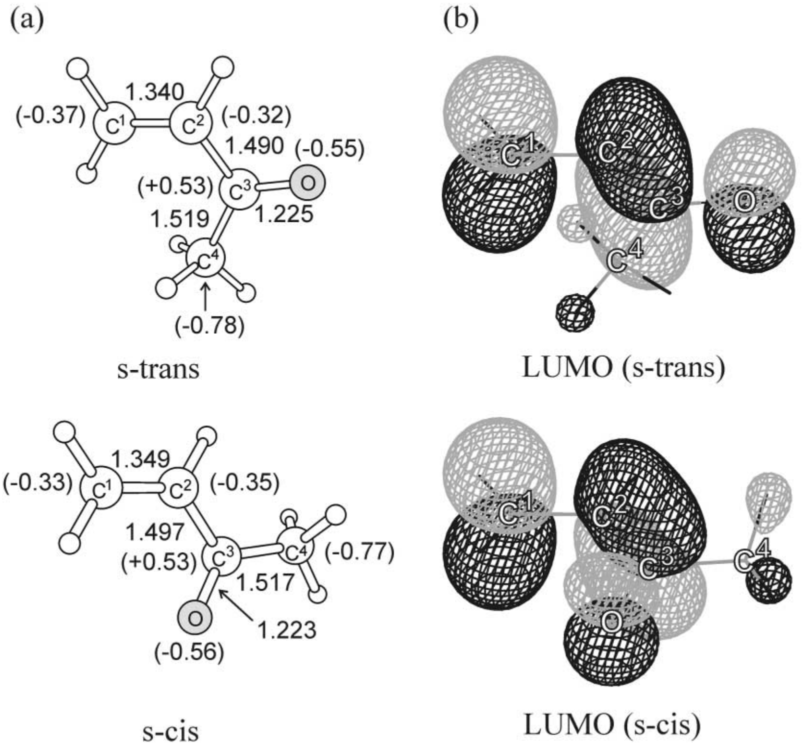


Fig. 4. (a) Optimized structures and natural charges (in parenthesis) of neutral *s-trans* MVK and *s-cis* MVK calculated at the B3LYP/6-31+G* level. Bond lengths and angles are shown in angstroms (Å) and degrees (°), respectively. (b) Contour surfaces of the square of atomic orbital coefficients of LUMOs of *s-trans* MVK and *s-cis* MVK.

transfer from the valence 3s orbital of the Na atom to the LUMO of MVK.

The structures obtained for *s-cis* and *s-trans* AC molecules and for three isomers of Na(AC) (designated as **4**–**6**) are shown in Figs. 6a and 7a, respectively. For a free AC molecule, two conformational isomers are in an equilibrium with a relative abundance of *s-cis*:*s-trans* $= 2{:}98$ at room temperature [35]. In the present calculation, total energy of *s-trans* isomer is estimated to be 2.16 kcal/mol more stable than *s-cis*, which is in good agreement with the previous study by MP3/6-311++G** calculation (2.15 kcal/mol) [36]. In Fig. 7a, the most stable isomer is **4** in which the Na atom binds to *s-cis* AC ($\Delta E = 23.2$ kcal/mol). In the isomers **5** and **6**, in which the Na atom binds to *s-trans* AC, ΔE are evaluated to be 13.6 and 2.0 kcal/mol for **5** and **6**, respectively. The *s-trans* to *s-cis* barrier in free AC was calculated to be 6.6 kcal/mol using MP3/6-311++G** [37]. Therefore, the formation of the most stable isomer **4** (NaAC (*s-cis*)) is possible in the collision between metal atom with *s-trans* AC, as discussed in Na(MVK). The natural charges on the Na atom are +0.89, +0.61 and +0.47 for **4**, **5** and **6**, respectively. In these isomers, the length of $C^1{=}C^2$ and $C^3{=}O$ bonds are about 2–6% longer than those of free AC and the length of $C^2{-}C^3$ bond is about 2–4% shorter. These structures of AC in these isomers is consistent with the natural population analysis, as discussed in Na(MVK).

In the mass spectrometric study of cluster anions of vinyl molecules, such as acrylonitrile and methyl acrylate, the trimer anions are produced more efficiently than monomer anions [7,8]. Although the

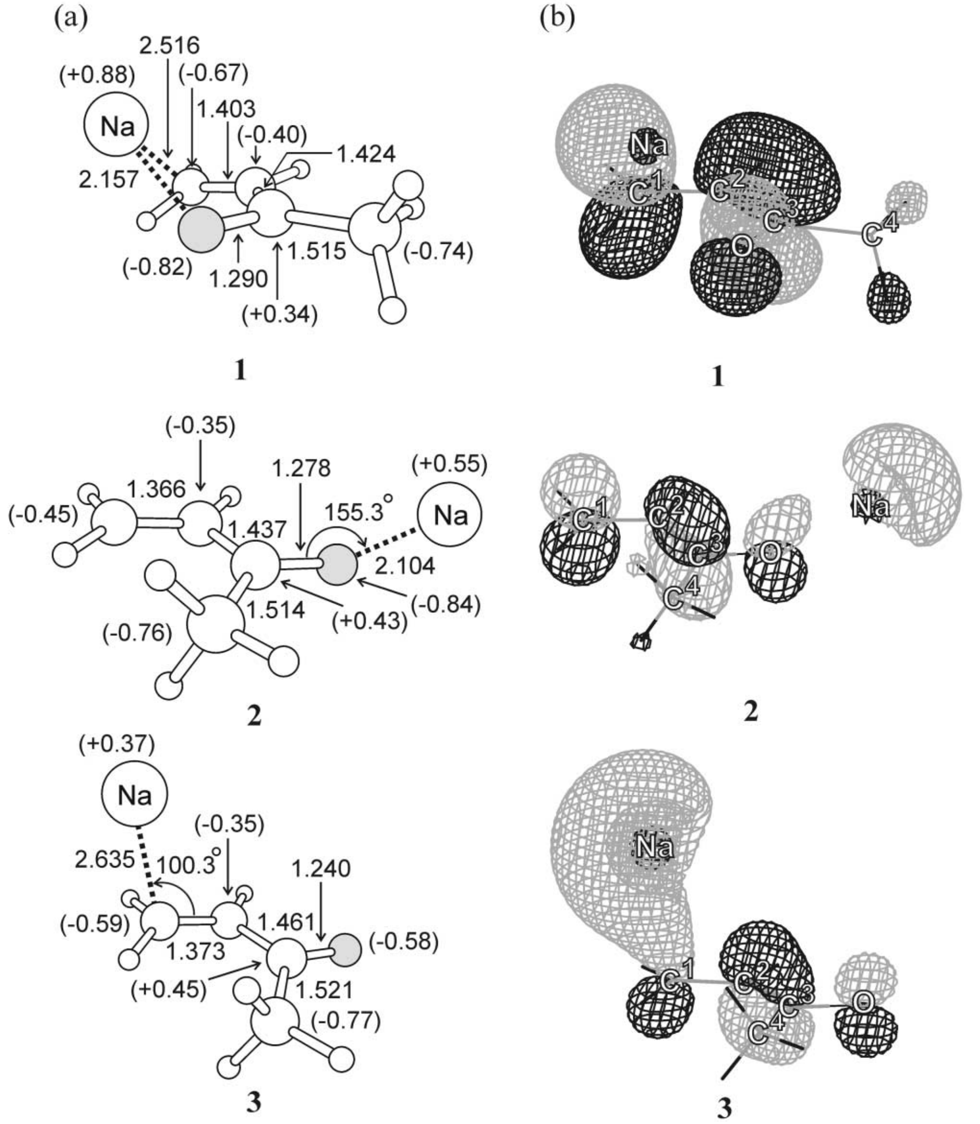


Fig. 5. (a) Optimized structures and natural charges (in parenthesis) of Na(MVK) isomers (**1**–**3**) calculated at the B3LYP/6-31+G* level. Bond lengths and angles are shown in angstroms (Å) and degrees (°), respectively. (b) Contour surfaces of the square of atomic orbital coefficients of SOMOs for three isomers are also shown.

electron affinity of MVK has not been determined and the study of $(MVK)_n^-$ is not reported so far, it is expected that $(MVK)_3$ can accept the excess electron more efficiently than the MVK molecule. Therefore, it is anticipated that in $Na(MVK)_3$, a much larger part of the valence electron of the Na atom is transferred to $(MVK)_3$ than in Na(MVK). Almost the same discussion can be applicable to $Na(AC)_3$. In addition, the electron affinity of AC is estimated to be a positive value from electron transmission spectroscopy [38], although the exact value has not been determined so far.

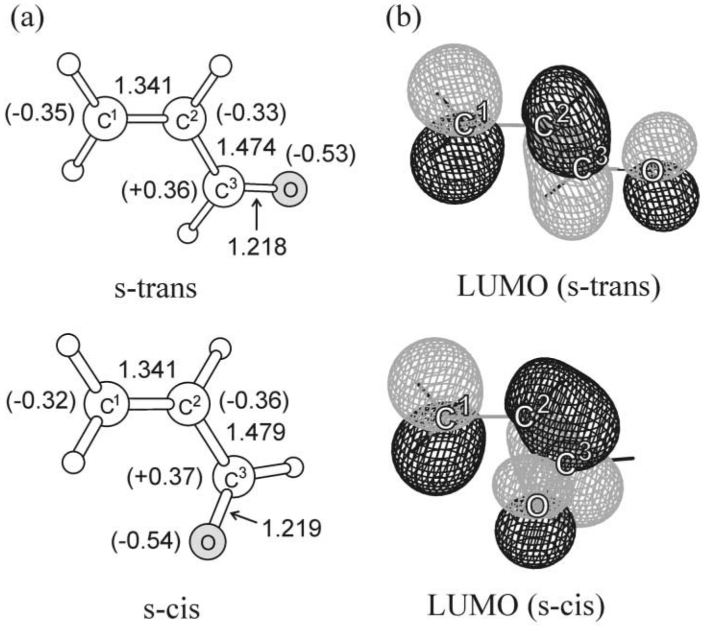


Fig. 6. (a) Optimized structures and natural charges (in parenthesis) of neutral *s-trans* AC and *s-cis* AC calculated at the B3LYP/6-31+G* level. Bond lengths and angles are shown in angstroms (Å) and degrees (°), respectively. (b) Contour surfaces of the square of atomic orbital coefficients of LUMOs of *s-trans* AC and *s-cis* AC.

4.3. Magic number in M(MVK)$_n$ and its structure

The magic number at $n = 3$ observed in the photoionization of M(MVK)$_n$ (M = Na and K) possibly originates from the following two processes [20–23]: (1) collisional complex formation between the neutral alkali metal atom with MVK clusters and (2) photoionization of M(MVK)$_n$. In process 1, magic numbers are related to the relative stability of neutral M(MVK)$_n$ clusters. On the other hand, two factors should be considered in generating magic numbers for process 2: (2-1) the n-dependent photoionization efficiency of M(MVK)$_n$ and (2-2) the evaporation after ionization that depend on the stability of M$^+$(MVK)$_n$. For (2-2), ions formed by photoionization may have enough energy to dissociate intermolecular bonds in the cluster ions. If the evaporation takes place efficiently after photoionization, relatively stable ions will tend to be populated by evaporation from less stable ions, and as a result, the n-dependent stability of photoions is expected to be reflected by the size distribution in the photoionization mass spectrum. To discuss the possibilities of (2-1) and (2-2), it is important to know the ionization thresholds (I_{th}) of M(MVK)$_n$ clusters. As shown in Fig. 3, the I_{th} value of M(MVK)$_n$ is found to decrease monotonically with n for $n = 0$–3, whereas those for $3 \leq n \leq 6$ are found to be constant at 3.86 eV. The magic number behavior is observed at a photon energy that is high enough with respect to these I_{th} values, and therefore, it is expected that the ionization efficiency is not a major factor of forming magic number at $n = 3$ in the present mass spectrum. Therefore, possibility (2-1) can be ruled out. On the other hand, the possibility of evaporation process (2-2) is also not expected to be serious, because the magic number is also observed at the photon energy of 4.15 eV, which is only about 0.3 eV above the ionization thresholds. Calculated dissociation energy for Na$^+$(MVK) is estimated to be more than 1.5 eV [39], so that the evaporation is insignificant at this photon energy. Therefore, the appearance of the magic number is little affected by the evaporation after photoionization. After all, the

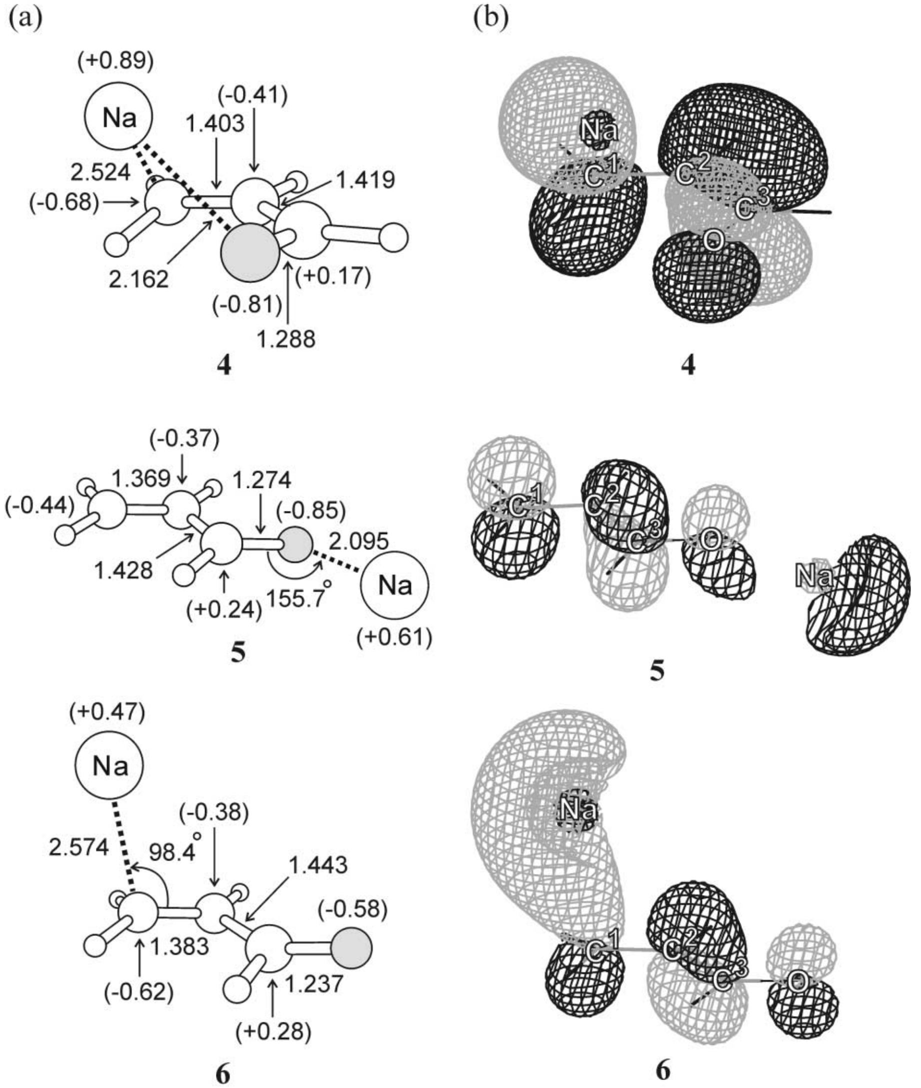
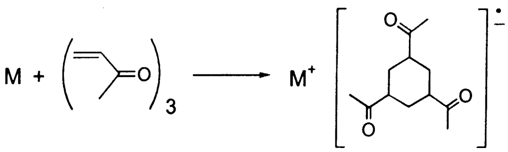


Fig. 7. (a) Optimized structures and natural charges (in parenthesis) of Na(AC) isomers (**4**–**6**) calculated at the B3LYP/6-31+G* level. Bond lengths and angles are shown in angstroms (Å) and degrees (°), respectively. (b) Contour surfaces of the square of atomic orbital coefficients of SOMOs for three isomers are also shown.

magic number at $n = 3$ observed in the photoionization mass spectrum is concluded to be due to the size distribution of neutral Na(MVK)$_n$ clusters (possibility (1)).

In the neutral clusters containing alkali metal atoms (M = Li, Na and K) and vinyl molecules (VM), such as acrylonitrile, acrylic ester and methacrylic ester, the same magic number at $M^+(VM)_3$ was observed in their photoionization mass spectra [20–23]. These results are explained by the intracluster electron transfer from M to VM followed by anionic oligomerization. This magic number is attributed to the formation of trimeric unit with a cyclohexane derivative produced by intracluster oligomerization of vinyl molecules. The nature of MVK is the same as those of acrylonitrile and acrylic ester in view of vinyl species that have



Scheme 1.

electron-withdrawing groups. Therefore, in the present system, the oligomerization reaction is also expected to proceed and produce an anion radical of a cyclohexane derivative with a six-membered ring (Scheme 1).

The six-membered ring structure in $M(MVK)_3$ ($M = Na$ and K) is more stable than other sizes because of the lack of ring strain as discussed in the preceding papers [20–23]. The same magic number behavior was found in acetylene [18] and isobutene [19] cluster cations and was also explained by six-membered ring structures formed by cationic oligomerization. However, the magic number at $M(MVK)_3$ is less evident than those in the former studies of M-acrylonitrile [20,22] and M-acrylic ester [21]. The clusters for $n = 4$ and 5 are expected to contain one six-membered ring structure and one and two monomer(s), respectively. The involvement of a six-membered ring structure in $n > 3$ clusters is supported by photodissociation of neutral clusters [22] and also by negative-ion photoelectron spectroscopy [40] of metal–acrylonitrile clusters, although the ions for $n = 4$ and 5 were neither strongly observed in those systems [20,22] nor in metal–acrylate clusters [21]. As discussed in the previous papers [20–23], the appearance of the magic number behavior is expected to be a result of evaporation processes after intracluster reaction. Thus, the increased intensity at $n = 4$ and 5 in the present metal–MVK clusters indicates the suppression of evaporation of monomers. In other words, the binding energies of the unreacted MVK monomers in the present clusters are presumed to be larger than those in other metal–vinyl molecules systems, although no quantitative information is available at present. This enhancement at $n = 4$ and 5 is also observed in the metal–methacrylate clusters which contain the cyclohexane derivative for $n \geq 3$ clusters [23].

4.4. Intracluster reactions in $M(AC)_n$

As noted in Section 4.1, the most intense signal is found at $n = 4$ for $M(AC)_n$, while the magic number is observed at $n = 3$ for $M(MVK)_n$. We will discuss the possible reasons for this difference. At first, we consider the evaporation process after photoionization of $M(AC)_n$. As shown in Fig. 3, I_{th} of $Na(AC)_n$ ($n = 1$–6) is found to lie between 4.39 and 4.78 eV. Therefore, at the photon energy of 5.17 eV in which the intensity enhancement at $n = 4$ is observed, available excess energy caused by photoionization is smaller than 0.78 eV. Calculated dissociation energy for $Na^+(AC)$ is estimated to be 1.5 eV [39], so that the evaporation process is insignificant at this photon energy. Thus, the intensity distribution in $M(AC)_n$ is not related to the evaporation process after photoionization. Next, we consider the possibility of intracluster reaction. As shown in Figs. 5b and 7b, 3s electron of Na atom is partly transferred to the LUMO of molecules for both Na(MVK) and Na(AC). Therefore, the intracluster oligomerization of $(AC)_n$ will be initiated by electron transfer from the alkali metal atom, as in $M(MVK)_n$. In $M(MVK)_n$, the cyclization reaction at $M(MVK)_3$ leads to the formation of stable cyclohexane derivative, as discussed in Section 4.3. However, in $M(AC)_n$, the observed intensity enhancement ($n = 4$) is different from $M(MVK)_n$ ($n = 3$). The absence of the magic number at $n = 3$ in $M(AC)_n$ clearly indicates that three successive reaction at C=C double bonds in $M(AC)_3$ has small contribution in all possible reaction processes. Therefore, it can be considered that there is another mechanism of intracluster reaction in $M(AC)_4$. As mentioned in Section 1, AC has two reactive sites (C=C bond and carbonyl group) in anionic polymerization in the condensed phase [3]. It is known that the reactivity of C=C bond and carbonyl group in AC depends on the catalyst and the reaction conditions [3]. Therefore, one possible reason for the intensity enhancements at $M(AC)_4$ is the formation of stable products by the cleavage of both C=C and C=O bonds. The complicated n dependence of I_{th} in $Na(AC)_n$ (Fig. 3) may gives the information about this intensity enhancement. Although no clear picture on the structure of $M(AC)_4$ can be provided at present, the quantum chemical calculation of larger clusters, such as $M(AC)_4$, will provide useful suggestion on this stable structure.

5. Conclusion

We have measured the photoionization mass spectra of clusters of alkali metal atom (M) with methyl vinyl ketone (MVK) or acrolein (AC). Intense ion signals assignable to $M^+(MVK)_3$ ions are observed for $M = Na, K$. In comparison with the result of size distribution of $Na^+(MVK)_n$ ions formed by ion–molecule (cluster) reactions in the cluster source, the obtained magic numbers at $M^+(MVK)_3$ are found to be due to the stability of neutral clusters, $M(MVK)_3$. From the previous results of the studies of alkali metal atom–vinyl molecule clusters, the observed magic number at $n = 3$ can be attributed to the species produced by intracluster oligomerization reaction after electron transfer from the metal atom to the MVK clusters. The results of calculation for Na(MVK) based on DFT calculation also support this consideration. On the other hand, in $M(AC)_n$ ($M = Na, K$), intensity enhancements are observed at $n = 4$. One possible reason for this intensity enhancements at $M(AC)_4$ is the formation of stable products by the cleavage of both C=C and C=O bonds.

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