

# Intracuster Polymerization Reactions of Alkene Cluster Ions

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Received: November 25, 1996; In Final Form: March 19, 1997<sup>®</sup>

The unimolecular dissociation dynamics of selected alkene cluster ions (ethene, propene, 1-butene, *trans*-2-butene, and *cis*-2-butene) and their fast fragment ions has been investigated using a reflectron time-of-flight mass spectrometer. These ions were prepared by the supersonic expansion of a premixed sample gas containing 20% alkene in Ar, followed by multiphoton ionization (MPI) using a Ti:sapphire femtosecond laser. From the unimolecular decomposition patterns of all the ions investigated, we conclude that after photoionization a radical cation initiated intracuster polymerization takes place in these cluster ions. But, due to steric hindrance, it does not continue indefinitely as the cluster size increases. For ethene, pentamerization can be observed, and for propene, trimerization; while in the case of the three isomeric butenes, 1-butene is partially trimerized and only dimerization is observed in 2-butene.

## Introduction

Gas phase ion–molecule reactions involving systems of unsaturated hydrocarbons and their derivatives have been the subject of many investigations, spanning several decades. Many different experimental techniques have been utilized, including photolysis,<sup>1</sup> radiolysis,<sup>2,3</sup> high-pressure mass spectrometry,<sup>4–10</sup> tandem quadrupole MS/MS,<sup>11</sup> and ion cyclotron resonance.<sup>12–15</sup> In a high-pressure MS experiment in ethene,<sup>5,6</sup> Kebarle and co-workers observed that an increase in the concentration of ethene in the ion source led to large increases in the intensities of intermediate size  $C_{2n}H_{4n}^+$  with  $n = 4–5$  and the disappearance of smaller ions with  $n = 1–3$ . This effect was explained by invoking the occurrence of association reactions of ethene molecules. The reaction rate was found to fall off dramatically after the third and fourth additions, which was attributed to steric effects. Similar results obtained by various other experimental methods applied to the study of a number of different systems led the investigators to suggest that gas phase cationic polymerization is responsible for the occurrence of the high molecular weight ions.<sup>1–15</sup>

Meanwhile, considerable effort has been devoted to the investigation of these ion–molecule reactions in the cluster regime<sup>16–35</sup> as well. This has been prompted by the recognition that interrogating clusters provides a way of studying the energetics and dynamics of intermediate states of matter as cluster systems evolve from the gas toward the condensed state.<sup>36</sup> Photoionization and pressure dependence studies of the  $(C_2H_4)_2^+$ ,  $(C_2H_4)_3^+$ ,  $(C_3H_6)_2^+$ , and  $(c-C_3H_6)_2^+$  ions by Ng and co-workers<sup>18,19</sup> showed that these ions isomerize to stable molecular ions before fragmentation. Coolbaugh,<sup>22,23,25</sup> El-Shall,<sup>35</sup> and co-workers performed electron impact (EI) ionization experiments on ethene, 1,1-difluoroethene, propene, and isobutene clusters in which they found that the cluster mass spectra were all characterized by the appearance of an anomalous ion intensity distribution under certain experimental conditions. They attributed the anomalous intensity distribution to a radical cation initiated polymerization reaction that occurred in the clusters after ionization, and the size-dependent cluster chemistry was accounted for by kinetic bottlenecks in the ionic chain growth reactions that terminate with the formation of

stable cyclic ions.<sup>22,23,25</sup> Lykтей and co-workers performed a collision-induced dissociation (CID) study on ethene cluster ions from sizes 2 to 9, which indicated that the cluster ions with  $n \leq 5$  are covalently bonded ions; for  $n \geq 6$ , the ions were reported to consist of a  $C_{10}H_{20}^+$  core solvated by an appropriate number of loosely bound ethene monomers.<sup>27</sup> Unlike ethene and 1,1-difluoroethene which have one magic peak in the mass spectra in a relatively broad pressure range, propene<sup>23,25</sup> showed a magic peak at  $n = 3$  when the stagnation pressure,  $P_0$ , was low. However the magic number shifted to  $n = 4$  and then  $n = 6$  as  $P_0$  was increased. The appearance of a magic peak at  $n = 4$  and  $n = 6$  at high stagnation pressure was hard to explain, and the structural identities of large propene cluster ions remained an open question.

Belonging to the same alkene family as ethene, but having larger sizes and different carbon chain structures, propene and the butene group provide excellent experimental systems for investigating how the polymerization is influenced by the sizes and structures of cations as well as surrounding neutrals. To the best of our knowledge, the intracuster ion–molecule reactions in *n*-butene have not been studied, and there is a paucity of knowledge of the structural and chemical identities of propene and *n*-butene cluster ions. Even though various experimental techniques are available, multiphoton ionization (MPI) coupled with reflectron time-of-flight mass spectrometry (RTOF-MS) has been proven to be an especially useful method in the studies of formation, bonding, and structures of intracuster ion–molecule reactions.<sup>37</sup> Consequently, we carried out the studies of the metastable dissociation dynamics of ethene, propene, and three isomeric butenes using the RTOF-MS, and the results are presented herein.

## Experimental Methods

As shown in Figure 1, a reflectron time-of-flight mass spectrometer equipped with a supersonic molecular beam and laser ionization technique is used in this experiment. It employs a three-chamber differentially pumped vacuum system. Details can be found in previous papers.<sup>37e,38,39</sup> Briefly, neutral alkene clusters are generated by expanding the sample gas of 20% alkene in Ar through a 150  $\mu$ m diameter pulsed nozzle at a total stagnation pressure typically between 3 and 4 atm. Clusters are ionized by a focused ( $f = 50$  cm) 400 nm femtosecond laser

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, May 1, 1997.

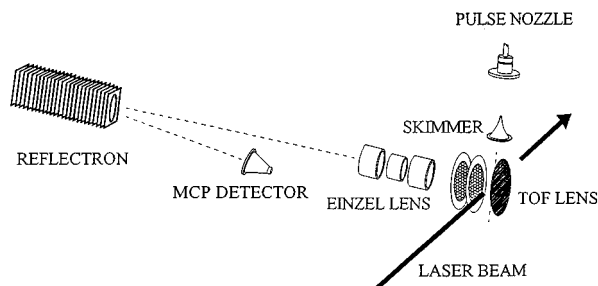


Figure 1. Reflectron time-of-flight mass spectrometer.

beam. The laser system consists of a mode-locked Ti:sapphire laser pumped by a CW argon ion laser which generates a 82 MHz pulse train, centered at 800 nm, with a pulse duration of about 73 fs and a pulse energy of 7 nJ. The pulses are amplified by a regenerative Ti:sapphire amplifier pumped by the second harmonic output of a 10 Hz Nd:YAG laser. After amplification, the laser beam is frequency doubled with a KDP crystal. Typically, the final output has a pulse of approximately 100 fs duration and 0.8 mJ energy. Ions formed by MPI are accelerated in a double-stage electrostatic field to several thousand electronvolts and directed through a 145 cm long field-free region. Thereafter, they are reflected by a reflectron at an angle of about  $3^\circ$  and travel 100 cm back through the field-free region toward a chevron microchannel plate detector (MCP). The signals are recorded by a transient recorder. Mass spectra are generally averaged over 500–1000 laser shots to improve the signal-to-noise ratio. The pressures in the field-free region and the reflectron region are typically about  $2 \times 10^{-6}$  Torr under working conditions.

TOF mass spectra of alkene cluster ions are obtained when the voltage setting applied on the reflectron is higher than the birth potential of the parent ions  $U_0$ , where  $U_0$  is defined as the voltage on the reflectron at which half of the parent ions penetrate through the reflectron (so-called cutoff) instead of being reflected toward the MCP. The reflectron is used as an energy analyzer to study the dissociation processes of the cluster ions during their passage through the field-free region. This is accomplished using a cutoff method,<sup>37d</sup> which involves observing the presence/absence of the daughter ion signals. The daughter mass is determined by  $U_0/U_d = M_p/M_d$ , where  $U_d$  is the cutoff potential of the daughter ion, also defined as the potential of a half intensity drop for the daughter ion signal, and  $M_p$  and  $M_d$  are the masses of parent and daughter ions. These dissociation pathways also have been confirmed by a time overlap experiment in which the daughter ion is made to follow the parent trajectory under the condition  $U_p^R/U_d^R = M_p/M_d$ , where  $U_p^R$  and  $U_d^R$  are reflectron voltages for the parent and daughter ions, respectively.

Propene and argon used in our experiment were obtained from MG Industries, ethene, 1-butene, *trans*-2-butene, and *cis*-2-butene were from Matheson Gas Products. The purity of all these gases is greater than 99%, and they were used without further purification.

## Results and Discussion

**1. General Observations.** Because of the femtosecond laser utilized in our experiment, with a flux of  $10^{28}$  photons/s during the 100 fs laser pulse, the ionization involves coherent absorption of a large number of photons leading to the population of high-lying excited states; autoionization to various excited ionic states takes place in competition with fragmentation. Normally, a much higher ionization efficiency and considerably less fragmentation can be obtained with femtosecond pulses compared

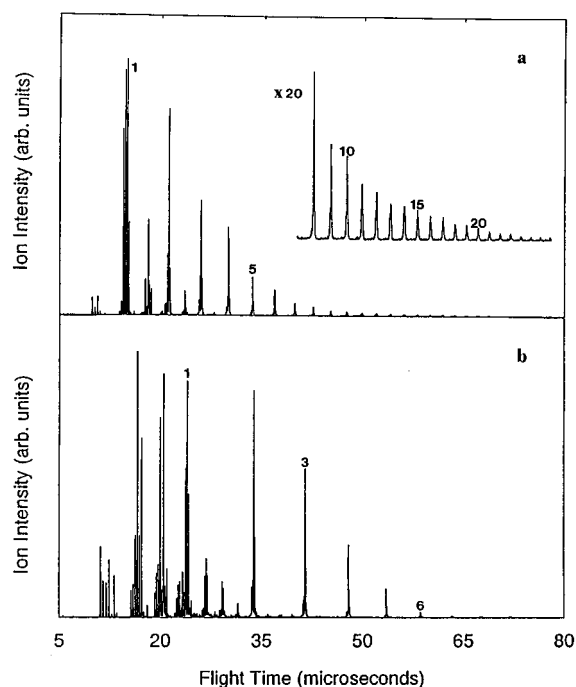


Figure 2. TOF mass spectra of (a) ethene ( $C_2H_4$ ) $_n^+$  and (b) 1-butene cluster ions ( $1-C_4H_8$ ) $_n^+$  obtained by femtosecond MPI at  $\lambda = 400$  nm.

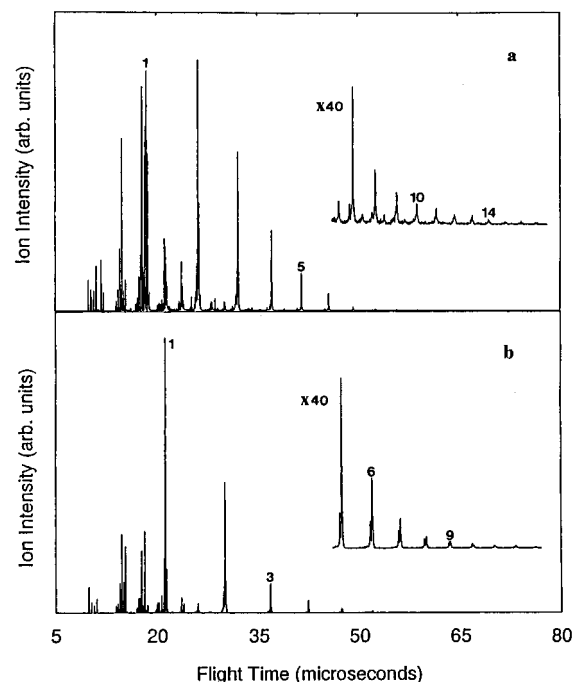


Figure 3. TOF mass spectra of (a) propene ( $C_3H_6$ ) $_n^+$  and (b) *cis*-2-butene cluster ions ( $2-C_4H_8$ ) $_n^+$  obtained by femtosecond MPI at  $\lambda = 400$  nm. The mass spectrum of *trans*-2-butene is very similar to *cis*-2-butene.

with the use of nanosecond nonresonant MPI.<sup>40</sup> Figure 2a,b and Figure 3a,b show the recorded mass spectra of ethene, propene, 1-butene, *trans*-2-butene, and *cis*-2-butene ions. The dominant peaks are the intact series with the stoichiometry of ( $C_nH_{2n}$ ) $_m^+$  ( $n = 2$  for ethene,  $n = 3$  for propene, and  $n = 4$  for the butenes), which can be observed up to  $m = 28$  for ethene,  $m = 17$  for propene, and  $m = 13$  for 1-butene and 2-butenes. Deprotonated series  $C_{nm}H_{2nm-1}^+$ , protonated series  $C_{nm}H_{2nm+1}^+$ , and other fragments like  $C_3H_5^+$ ,  $C_5H_9^+$ ,  $C_7H_{13}^+$  etc., which are called fast fragments in later sections, also can be observed.

**TABLE 1: Metastable Dissociation Channels of Ethene Cluster Ions and Their Fast Fragments<sup>a</sup>**

	parent ion mass (amu)								
	27	41	56	57	84	112	140	168	196
neutral	1	2	1	16	15	29	29	28	28
fragment	2 <sup>w</sup>		15 <sup>m</sup>		28 <sup>s</sup>	42 <sup>w</sup>	57 <sup>m</sup>	56 <sup>s</sup>	
mass (amu)			17 <sup>w</sup>			57 <sup>w</sup>			
			29 <sup>w</sup>						

<sup>a</sup> s, m, and w are used here to express the relative intensities of the second and third losses comparing with the first channel; s means relative intensity is greater than 50%, m for >25%, and w for <25%. The mass uncertainty for weak losses is  $\pm 1$ .

**TABLE 2: Metastable Dissociation Channels of Propene Cluster Ions and Their Fast Fragments<sup>a</sup>**

	parent ion mass (amu)							
	27	41	55	57	84	126	168	210
neutral	1	2	16	16	15	43	42	42
fragment	2 <sup>w</sup>	15 <sup>w</sup>			28 <sup>s</sup>	29 <sup>m</sup>	85 <sup>w</sup>	
mass (amu)					42 <sup>w</sup>	57 <sup>w</sup>		

<sup>a</sup> s, m, and w are used here to express the relative intensities of the second and third losses comparing with the first channel; s means relative intensity is greater than 50%, m for >25%, and w for <25%. The mass uncertainty for weak losses is  $\pm 1$ .

**TABLE 3: Metastable Dissociation Channels of 1-Butene Cluster Ions and Their Fast Fragments<sup>a</sup>**

	parent ion mass (amu)								
	27	41	55	56	57	112	168	224	280
neutral	1	2	16	1	16	29	56	56	56
fragment				15 <sup>s</sup>		42 <sup>m</sup>	29 <sup>m</sup>		
mass (amu)				17 <sup>m</sup>		56 <sup>w</sup>			

<sup>a</sup> s, m, and w are used here to express the relative intensities of the second and third losses comparing with the first channel; s means relative intensity is greater than 50%, m for >25%, and w for <25%. The mass uncertainty for weak losses is  $\pm 1$ .

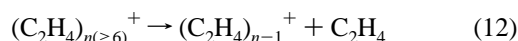
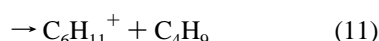
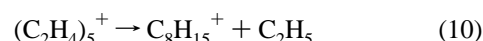
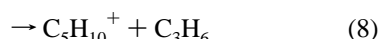
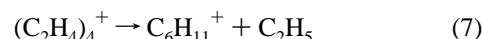
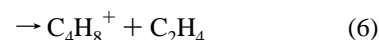
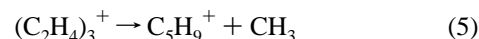
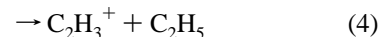
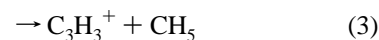
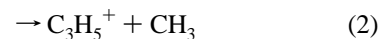
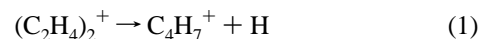
**TABLE 4: Metastable Dissociation Channels of 2-Butene Cluster Ions and Their Fast Fragments<sup>a</sup>**

	parent ion mass (amu)								
	27	41	55	56	57	112	168	224	280
neutral	1	2		1	16	29	56	56	56
fragment	2 <sup>w</sup>			15 <sup>s</sup>		56 <sup>s</sup>	112 <sup>w</sup>		
mass (amu)				17 <sup>m</sup>		85 <sup>w</sup>			
				29 <sup>m</sup>					

<sup>a</sup> s, m, and w are used here to express the relative intensities of the second and third losses comparing with the first channel; s means relative intensity is greater than 50%, m for >25%, and w for <25%. The mass uncertainty for weak losses is  $\pm 1$ .

Because of the extensive heating by the laser pulse during the ionization process, the ionized clusters are left with a significant amount of excess energy. Consequently, they experience fast fragmentation during their residence time in the ionization spot, evaporating one or successively several neutral monomers and/or fragments. After the excess energy in the cluster ions is dissipated by evaporation, and the remaining energy becomes partitioned among the internal cluster modes, the cluster ions gain long time (microseconds) stability. Thus, the product ions can survive long enough to enter the field-free region where their ensuing metastable fragmentation can be observed. Due to the vacuum pressure in the field-free region in our apparatus, the ions are able to pass through the field-free region with mostly collision-free ion trajectories, although small contributions of collision-induced dissociation to the decay channels cannot be completely excluded. The cutoff results of all the cluster ions investigated are summarized in Tables 1–4.

**2. Ethene Cluster Ions.** The unimolecular dissociation channels observed for ethene cluster ions are depicted in the following equations:



Ethene dimer has three loss channels, namely H, CH<sub>3</sub>, CH<sub>5</sub>, and C<sub>2</sub>H<sub>5</sub>. Assuming there is a weakly bound C<sub>2</sub>H<sub>4</sub> unit in the cluster, dominant C<sub>2</sub>H<sub>4</sub> loss would be observed. The absence of C<sub>2</sub>H<sub>4</sub> loss reveals that after ionization a possible ion–molecule reaction, which is called dimerization in the dimer case, takes place. It leads to the formation of a molecular C<sub>4</sub>H<sub>8</sub><sup>+</sup> ion. The existence of four competing dissociation processes with different decay fractions reflects the fact that the activation energies of these reactions differ, with larger decay fractions indicating processes with lower activation energies.

As shown in eqs 5 and 6, ethene trimer loses a monomer unit as well as a methyl group which could indicate that trimerization is not fully accomplished. This could result in the production of two structural isomers, the one that shows a monomer loss might have a loosely bonded C<sub>2</sub>H<sub>4</sub> unit in the cluster. As discussed later in the propene section, comparison of the fragmentation channels of the propene dimer and the ethene trimer suggests that polymerization occurred in both ions and that prior to dissociation they rearranged to similar structures.

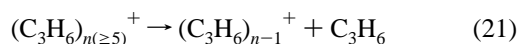
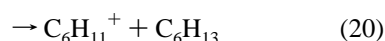
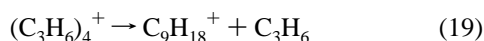
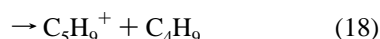
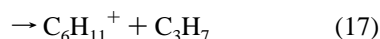
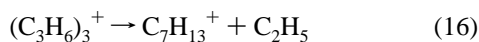
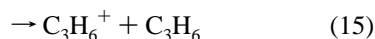
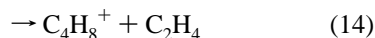
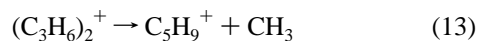
For ethene tetramer, three decay channels were found which are shown in eqs 7–9. For ethene pentamer, two losses were observed, namely C<sub>2</sub>H<sub>5</sub> and C<sub>4</sub>H<sub>9</sub>. The predominant C<sub>2</sub>H<sub>5</sub> loss in both the tetramer and the pentamer suggests that both are chemically bonded molecular ions.

For the hexamer and larger cluster ions, monomer loss is dominant, indicating a weakly bound ethene unit in the structure.

In general, the above-discussed dissociation patterns of ethene cluster ions reveal that intracluster polymerization occurred in these ions, leading to the observation of chemically bonded molecular core ions as large as C<sub>10</sub>H<sub>20</sub><sup>+</sup>. The results indicate that cluster ions up to the pentamer have a covalent binding nature, while the hexamer and larger cluster ions have an oligomerized ion core, possibly C<sub>10</sub>H<sub>20</sub><sup>+</sup>, solvated by loosely bound monomer units. The limitation of the polymerization could be explained by the increasing steric hindrance caused

by the increasing size of the cation, thus weakening the interactions between the charge center and the  $\pi$  electrons in the neutral, resulting in a much slower reaction rate as the cation size increases.

**3. Propene Cluster Ions.** The unimolecular dissociation channels of propene cluster ions are shown in the following equations:



Propene dimer has predominant losses of  $\text{CH}_3$  and  $\text{C}_2\text{H}_4$  as well as a weak loss of  $\text{C}_3\text{H}_6$ , which is the same as the decay channels of the ethene trimer ion except that the ethene trimer ion does not have the weak  $\text{C}_3\text{H}_6$  loss. It appears that the monomer loss observed in the ethene trimer and the propene dimer could originate from weakly bound complexes. However, as shown in the previous study of Smith and Williams,<sup>41</sup>  $\text{CH}_3$  and  $\text{C}_2\text{H}_4$  are major metastable fragments, and  $\text{C}_3\text{H}_6$  is a minor one arising from molecular  $\text{C}_6\text{H}_{12}^+$  ions generated from various neutral sources. Also, cluster studies<sup>17,18,26</sup> on  $(\text{C}_2\text{H}_4)_3^+$ ,  $(\text{C}_3\text{H}_6)_2^+$ , and  $(\text{c-C}_3\text{H}_6)_2^+$  ions have shown evidence that they indeed rearrange to similar structure prior to dissociation. Our observation on the metastable decay patterns of the ethene trimer, and our results for the propene dimer support the previous interpretation that these species decompose through common intermediate states. The slight difference observed in their decay channels could be caused by the differences in their internal energy distributions.

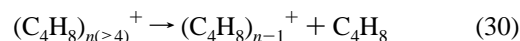
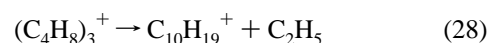
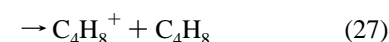
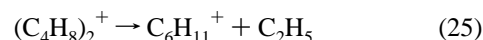
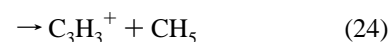
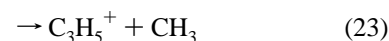
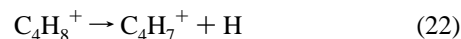
The observed fragments of the propene trimer ion are an ethyl group, a propyl group, and a butyl group. The lack of monomer loss reveals that the trimer is also a chemically bound ion.

Propene tetramer predominantly loses a monomer unit as well as a weak  $\text{C}_6\text{H}_{13}$  loss. The predominant monomer loss indicates a loosely bound  $\text{C}_3\text{H}_6$  unit in the cluster. Assuming the tetramer has a structure of the trimer ion core with a loosely attached monomer unit, its secondary decay channel should resemble the primary decay channels of the trimer ion. That is indeed the case. The secondary  $\text{C}_6\text{H}_{13}$  loss of the tetramer is a monomer loss plus a  $\text{C}_3\text{H}_7$  loss, which is shown to be a primary loss of the trimer ion. Hence, it is concluded that the tetramer probably has a structure comprised of a polymerized trimer ion core  $\text{C}_9\text{H}_{18}^+$ , with a loosely bonded  $\text{C}_3\text{H}_6$  unit. For pentamer and larger cluster ions, monomer loss is dominant, indicating their solvated structures.

The observation of trimerization in propene cluster ions leads to the conclusion that the propene dimer and trimer ions are covalently bound molecular ions, while larger cluster ions with  $n \geq 4$  probably all consist of a molecular  $\text{C}_9\text{H}_{18}^+$  ion core with

differing numbers of monomer units weakly bound to it. The switching of the binding nature from covalent to van der Waals at  $n = 3-4$  explains the special intensity anomaly of the trimer ion observed by Coolbaugh et al.<sup>23,25</sup> in the mass spectra of propene clusters. Still, further experiments are needed to explain the origins of the intensity abnormality at  $n = 4$  and 6 observed under high expansion pressures and low electron energies.

**4. 1-Butene Cluster Ions.** The unimolecular dissociation channels of 1-butene cluster ions are shown in eqs 22–30:



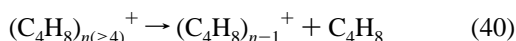
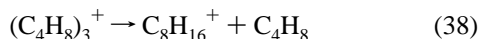
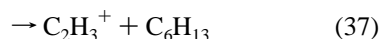
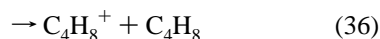
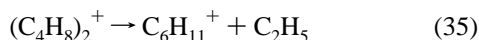
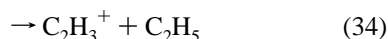
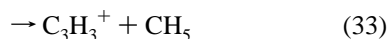
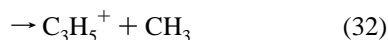
1-Butene monomer loses H,  $\text{CH}_3$ , and  $\text{CH}_5$  fragments, similar to the decay channels of the ethene dimer ion, indicating that either the ethene dimer ion rearranged to the 1-butene ion structure after dimerization or they both isomerized to a third structure.

1-Butene dimer loses  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_6$ , and  $\text{C}_4\text{H}_8$  fragments, which match very well with the dissociation channels of the ethene tetramer ion, leading to the conclusion that they share common ionic structure(s).

1-Butene trimer loses a monomer unit as well as an ethyl group which brings up two possible explanations: (i) the trimer has two isomers, with one being a molecular  $\text{C}_{12}\text{H}_{24}^+$  ion and the other a  $\text{C}_8\text{H}_{16}^+$  ion core solvated by a  $\text{C}_4\text{H}_8$  unit; (ii) the trimer is fully trimerized but has two competitive decay channels with comparable activation energies, one leading to a loss of  $\text{C}_4\text{H}_8$  and the other to a  $\text{C}_2\text{H}_5$ . As we know, in the ethene cluster ions, further association reaction of the  $\text{C}_{10}\text{H}_{20}^+$  ion core with the solvating  $\text{C}_2\text{H}_4$  units to form  $\text{C}_{12}\text{H}_{24}^+$  ion is not kinetically favored; neither is  $\text{C}_9\text{H}_{18}^+$  with  $\text{C}_3\text{H}_6$  in the propene case. Comparing the sizes of the ions and neutrals, it seems that an association reaction of  $\text{C}_8\text{H}_{16}^+$  with  $\text{C}_4\text{H}_8$  in the 1-butene cluster ions would not be much more favored than the other two cases. In other words, only a fraction of the 1-butene trimer has been able to rearrange to a molecular  $\text{C}_{12}\text{H}_{24}^+$  ion prior to dissociation, while others remain as a van der Waals  $(\text{C}_8\text{H}_{16}^+)(\text{C}_4\text{H}_8)$  complex.

Equation 30 shows that for tetramer and larger cluster ions monomer loss is dominant, indicating a weakly bound butene unit in the cluster. From the structural nature of the 1-butene trimer ion, it could be further concluded that larger cluster ions probably all have two structural isomers; one is a solvated  $(\text{C}_8\text{H}_{16}^+)(\text{C}_4\text{H}_8)_{n-2}$  complex and the other a  $(\text{C}_{12}\text{H}_{24}^+)(\text{C}_4\text{H}_8)_{n-3}$  complex.

**5. 2-Butene Cluster Ions.** The unimolecular dissociation channels of 2-butene cluster ions are shown in the following equations:



The ionization of 2-butenes involves the ejection of a  $\pi$  electron from the C=C bond, making C=C rotation less hindered; hence, the interconversion of *cis*-2-butene and *trans*-2-butene becomes facile. As a result, *cis*-2-butene and *trans*-2-butene ions should behave very similarly. So should the polymerized *trans*-2-butene and *cis*-2-butene cluster ions. As expected, the observed behavior of *trans*-2-butene and *cis*-2-butene cluster ions is quite similar, so they are discussed together for simplicity. As shown in Table 4, 2-butene monomer loses  $\text{CH}_5$  and  $\text{C}_2\text{H}_5$  with medium intensity, besides strong  $\text{CH}_3$  and H losses. Although the intensity ratios vary, the decay pattern is quite similar to that of the ethene dimer ion but differs slightly from that of the 1-butene monomer ion which does not display  $\text{C}_2\text{H}_5$  loss. Because radicals and charges migrate easily within molecular ions, often accompanied by simultaneous hydrogen rearrangements, the interconversion between isomers which only involves charge and hydrogen rearrangements usually requires a small activation barrier. From a molecular orbital theoretical calculation on butene ions by Jungwirth and Bally,<sup>42</sup> the 1-butene ion is estimated to be separated from the more stable 2-butene ion by a barrier of about 25 kcal/mol. H loss, the lowest dissociation path for the  $\text{C}_4\text{H}_8^+$  ions, involves an activation energy of more than 35 kcal/mol for the 1-butene ion and 46 kcal/mol for the 2-butene ion,<sup>42,43</sup> which are much larger than the isomerization barrier. It is obvious that the internal energies of these ions are more than sufficient to cause all the possible interconversions between the two  $\text{C}_4\text{H}_8^+$  isomers prior to fragmentation. The observed slight differences in their decay patterns could be caused by the differences in their internal energy distributions. From the rather similar decay patterns of the 1-butene monomer, the 2-butene monomer, and the ethene dimer ions, we conclude that the interconversions between these  $\text{C}_4\text{H}_8^+$  ions lead to a complete loss of their parent ion identities on the time scale involved in the metastable dissociation processes.

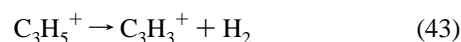
2-Butene dimer loses a dominant monomer unit as well as a dominant ethyl group and a minor hexyl group, which is obviously different from that of the 1-butene dimer; see Tables 3 and 4. The coexistence of a monomer loss and a molecular fragment loss in the 2-butene dimer brings up two possible explanations: (i) the 2-butene dimer has two isomers, one is a molecular  $\text{C}_8\text{H}_{16}^+$  ion and the other a  $\text{C}_4\text{H}_8^+$  ion core solvated by a  $\text{C}_4\text{H}_8$  unit; (ii) the 2-butene dimer is fully dimerized but has two competitive decay channels with comparable activation

barriers, one leading to a loss of  $\text{C}_4\text{H}_8$  and the other to a  $\text{C}_2\text{H}_5$ . From the collision-induced dissociation patterns of the molecular  $\text{C}_8\text{H}_{16}^+$  ions investigated by Lykтей<sup>27</sup> and Levensen,<sup>44</sup>  $\text{C}_4\text{H}_8$  loss is shown not to be a preferred channel for any of the  $\text{C}_8\text{H}_{16}^+$  ions. Therefore, it is highly probable that the strong  $\text{C}_4\text{H}_8$  loss in the 2-butene dimer ion originates from a loosely bound  $(\text{C}_4\text{H}_8)^+(\text{C}_4\text{H}_8)$  complex, indicating that the 2-butene dimer ion is only partially dimerized.

For 2-butene trimer and larger cluster ions, monomer loss is dominant, indicating that they all have solvated structures. From the structural identity of the dimer ion, it can be further inferred that two structural isomers also exist for larger clusters, one is  $(\text{C}_4\text{H}_8)^+(\text{C}_4\text{H}_8)_{n-1}$  and the other  $(\text{C}_8\text{H}_{16})^+(\text{C}_4\text{H}_8)_{n-2}$ .

## 6. Dissociation Patterns of Small Fast Fragment Ions.

Compared with other fast fragments born in the ionization process,  $\text{C}_2\text{H}_3^+$ ,  $\text{C}_3\text{H}_3^+$ ,  $\text{C}_3\text{H}_5^+$ ,  $\text{C}_4\text{H}_7^+$ , and  $\text{C}_4\text{H}_9^+$  are prominent peaks in the mass spectra of all the alkene cluster ions studied. They are also the major fragment ions for the metastable decay of the small alkene cluster ions, indicating their special stabilities. The following equations show the metastable decay channels for these ions:



$\text{C}_2\text{H}_3^+$  has two loss channels: one is a dominant H loss channel while the other corresponds to a minor  $\text{H}_2$  loss. The heat of reaction for reaction 41 is determined to be approximately 80 kcal/mol with no reverse activation barrier, based on an *ab initio* method with HF/6-31G\*\* level of theory using the classical  $\text{C}_{2v}$  structure for the  $\text{C}_2\text{H}_3^+$  ion. Assuming reaction 42 occurs as a 1,1-elimination reaction, the calculation shows that it has a heat of reaction of about 160 kcal/mol. With the activation energies in the same magnitude, reactions 41 and 42 are competing processes, but the difference of 80 kcal/mol determined that reaction 41 is more favored.

As shown in Tables 1–4,  $\text{C}_3\text{H}_5^+$  ions generated from the four alkene cluster ions all decompose into  $\text{C}_3\text{H}_3^+$  ion by  $\text{H}_2$  elimination; thus, their chemical binding identity is obvious.  $\text{C}_3\text{H}_5^+$  could be generated from propene and butene by a direct monomer fragmentation channel. On the other hand, in the ethene case, it could be coming from two processes. One of these is a fragmentation of  $\text{C}_2\text{H}_4^+$  into  $\text{CH}^+$  followed by an ion–molecule reaction of the  $(\text{CH}^+)\text{C}_2\text{H}_4$  complex; another is a dimerization reaction followed by fragmentation. *Ab initio* MP2/6-311G\*\* calculations show that the fragmentation of  $\text{C}_2\text{H}_4^+$  into  $\text{CH}^+$  requires a minimum energy of 180 kcal/mol, whereas  $(\text{C}_2\text{H}_4)_2^+ \rightarrow \text{C}_4\text{H}_8^+ \rightarrow \text{C}_4\text{H}_7^+$  has a negligible activation barrier and heat of reaction. The signal intensity of  $\text{C}_3\text{H}_5^+$  compared with that of  $\text{CH}^+(I_{\text{C}_3\text{H}_5^+}/I_{\text{CH}^+} = 20)$  in the mass spectrum of  $(\text{C}_2\text{H}_4)_n^+$  confirms that  $(\text{C}_2\text{H}_4)_2^+ \rightarrow \text{C}_4\text{H}_8^+ \rightarrow \text{C}_4\text{H}_7^+$  is the preferred channel. The fact that  $\text{C}_3\text{H}_5^+$  is a fast fragment of the polymerized dimer ion indicates that the dimerization of ethene cluster ions must have occurred on a time scale shorter than that of the fast fragmentation.

$\text{C}_4\text{H}_7^+$  from propene and 1-butene, and  $\text{C}_4\text{H}_9^+$  from all four systems, lose only  $\text{CH}_4$  in the metastable decay, indicating their covalent binding nature. Unfortunately, in the ethene and

2-butene clusters, the daughter ion  $C_3H_3^+$  from  $C_4H_7^+$  ( $CH_4$  loss) and  $C_2H_3^+$  from  $C_4H_8^+$  ( $C_2H_5$  loss) are time-overlapped in the mass spectra, and  $C_3H_3^+$  is cut off at a higher voltage. This makes it impossible to identify the  $CH_4$  loss channel.

As shown in Tables 1–4, irrespective of their different origins, i.e., from ethene, propene, or butenes, the ions with the same stoichiometry always display surprisingly similar decay patterns, indicating their covalent binding nature. These observations confirm our conclusion about the intracuster polymerization that occurs within these cluster systems.

## Conclusions

The present study provides the first experimental evidence on the structural identities of propene, 1-butene, and 2-butene cluster ions. In this study, the metastable dissociations of intact alkene cluster ions and some of their fast fragments are investigated and found to exhibit different decay patterns for clusters of different sizes. The main metastable decay of small intact cluster ions is normally via molecular fragments, whereas for larger intact cluster ions, a neutral monomer loss is dominant. Fast fragment ions like  $C_2H_3^+$ ,  $C_3H_5^+$ ,  $C_4H_7^+$ , and  $C_4H_9^+$ , ions with the same stoichiometry always show the same dissociation pattern irrespective of their different origins, i.e., from ethene, propene, or butenes. From the unimolecular decomposition patterns of all the ions investigated, we conclude that a radical cation initiated intracuster polymerization takes place in all these alkene cluster ions, but due to the steric effects, only to a limited degree. Polymerization in ethene cluster ions can be observed up to the pentamerization, leading to the formation of molecular ions as large as  $C_{10}H_{20}^+$  ion. Consequently, cluster ions with  $n \leq 5$  are covalently bound molecular ions, while  $n \geq 6$  cluster ions have solvated structures; in the propene cluster ions, trimerization can be observed, resulting in the detection of molecular  $C_9H_{18}^+$  ion. It is determined that  $(C_3H_6)_n^+$  ions with  $n \leq 3$  are chemically bonded ions, whereas  $n \geq 4$  ions are loosely bound complexes with a  $C_9H_{18}^+$  core. In the case of 1-butene, it is partially trimerized. 1-Butene dimer is a molecular  $C_8H_{16}^+$  ion, while the trimer has two isomers, one is a chemically bonded  $C_{12}H_{24}^+$  ion and the other a dimer ion core with a loosely attached  $C_4H_8$  unit. From the tetramer on, the cluster ions possess solvated structures; 2-butene cluster ions are shown to be only partially dimerized, indicating that the polymerization in this case is the least efficient. 2-Butene dimer has two isomers, one is a  $C_8H_{16}^+$  ion and the other  $(C_4H_8)^+-(C_4H_8)$ . Trimer and larger cluster ions appear to have solvated structures.

**Acknowledgment.** Financial support by the U.S. National Science Foundation, Grant CHE-9632771, is gratefully acknowledged. L. Poth, Feodor Lynen-Fellow, acknowledges support by the Alexander von Humboldt Foundation, Germany.

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