Slow Metastable Decay Process of $(C_3H_7{}^+)(C_3H_8)_n$ Cluster Ions Induced by Isomerization of the Propyl Ion

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Besides the usual single-monomer evaporation, the $(C_3H_8)_n(C_3H_7{}^+)$ cluster ions produced by electron-impact ionization of neutral propane clusters have been observed to decay by an additional channel leading to evaporation of up to four C_3H_8 monomers. It is shown that this additional fragmentation channel is initiated by a new decay mechanism, i.e., the isomerization of an *n*-propyl ion to a more stable *sec*-propyl ion within the cluster.

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Studies of the fragmentation processes following electron-impact ionization of van der Waals (vdW) clusters of small molecules (e.g., nitrogen [1]) have provided valuable information on the dynamics of energized cluster ions (energy flow, mechanisms of dissociation, rearrangement processes within ionized clusters, etc.). In particular, slow fragmentation processes, usually referred to as the metastable decompositions of cluster ions, provide an important source of information [2]. Although there exist many studies of neat or mixed clusters of atoms and/or small molecules [2,3], much less is known about the metastable fragmentation of ionized clusters of polyatomic molecules (e.g., see [4]). Because prompt and metastable fragmentations of the ionized single molecules have been thoroughly studied and are well understood [5], simple hydrocarbons such as ethane and propane are especially suitable systems for dissociation studies.

In this communication we report the results of our studies of metastable fragmentation of ionized clusters of propane and ethane. The dominant metastable dissociation process observed for stoichiometric and nonstoichiometric cluster ions is single-monomer evaporation, a well known and characterized (by the quasiequilibrium theory) process in the case of ionized vdW cluster ions [2]. None of the metastable decay reactions which occur for monomer ions (e.g., $C_3H_8{}^+ \rightarrow C_3H_7{}^+$, etc. [5]) occurs in the cluster environment, apparently due to the fast energy transfer from intramolecular modes to intermolecular vibrations of cluster constituents. Moreover, besides the usual monomer evaporation, however, an additional metastable decay reaction involving the loss of up to four monomers from the $(C_3H_7{}^+)(C_3H_8)_n$ ion has been observed. Taking into account the various features (temporal evolution, energetics, fragmentation pattern) of this novel metastable decay process we have concluded that this decay reaction is driven by the isomerization reaction within the cluster of *n*-propyl ions to isopropyl ions in the μs time regime. This reaction sequence constitutes a new mechanism for metastable dissociation of cluster ions (i.e., isolated-state-driven reactions), thereby adding a new variety to the two previously known metastable decay mechanisms of this kind, i.e., excimer-induced dissociation of rare-gas cluster ions [6] and the release of intramolecular vibrational quanta from N_2 molecules within an ionized nitrogen cluster [1].

The supersonic-beam–electron-impact ionization source and double-focusing mass spectrometer system has been described in detail earlier [7]. Ethane or propane neutral clusters are formed by expanding approximately 500 mbar of ethane or 250 mbar of propane seeded with 2.2 bars of Ar at $-90\,^\circ$C or $-64\,^\circ$C, respectively, through a 20-μm nozzle. Cluster ions formed by electron-impact ionization are mass analyzed in a double-focusing sector field mass spectrometer. Metastable decays of these ions may be detected (and distinguished from collision-induced dissociations; for details see Ref. [7]) if they occur either in the first field-free region or in the second field-free region of the mass spectrometer system.

The mass spectrum of both propane and ethane clusters shows, besides stoichiometric parent ions, groups of ions which correspond to nonstoichiometric fragment ions known from the fragmentation patterns of the monomer molecular ions [5]. The abundances of clustered fragment ions are, however, different from the abundances of monomer fragment ions that are known from the mass spectra of propane and ethane molecules. In particular, in propane the relative abundance of $(C_3H_7{}^+)(C_3H_8)_n$ is higher than that of other clustered fragment ions (e.g., clustered $C_2H_5{}^+$, $C_2H_4{}^+$, and $CH_3{}^+$ ions), a situation which is completely different from the monomer molecule mass spectrum.

In the metastable decomposition (investigated in the first and the second field-free regions as a function of flight time) of propane and ethane cluster ions the strongest metastable fragmentation channel is the usual single-monomer evaporation from stoichiometric and nonstoichiometric ions. However, in addition to this usual decay mode, in propane there exists a metastable process involving the evaporation of up to four monomer molecules from the ions $(C_3H_7{}^+)(C_3H_8)_n$, i.e.,

$$(C_3H_7{}^+)(C_3H_8)_n \rightarrow (C_3H_7{}^+)(C_3H_8)_{n-p} + p(C_3H_8)\,, \tag{1}$$

where $p=4$ for $n \geq 8$ (measured up to $n=15$), $p=4$ (3)

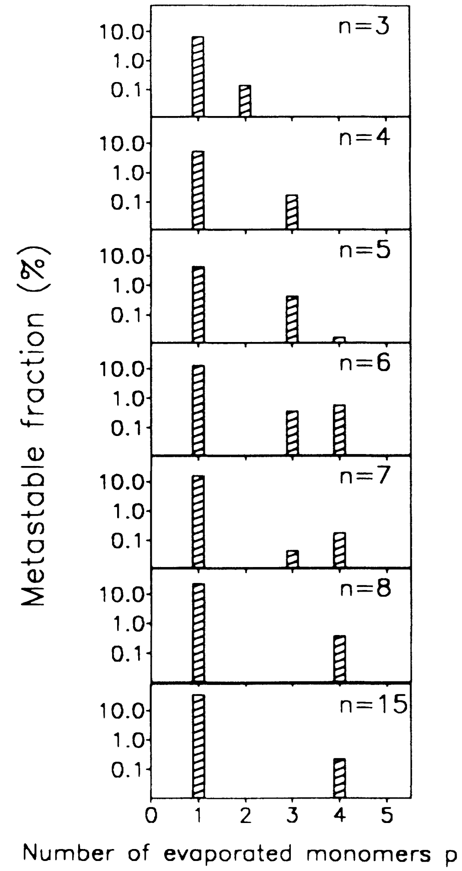

FIG. 1. The metastable fraction (fragment current produced in the first field-free region divided by parent current arriving at the detector) as a function of the number of desorbed monomers p for the reaction $(C_3H_7^+)(C_3H_8)_n \rightarrow (C_3H_7^+)(C_3H_8)_{n-p} + p(C_3H_8)$ for $n = 3$–8 and 15.

for $n=7$ and 6, $p=3$ (4) for $n=5$, $p=3$ for $n=4$, and $p=2$ for $n=3$ (the number in parentheses indicates the less abundant transition). The results are summarized in Figs. 1 and 2. The unusual metastable transition (1) can be explained only by an internal process of slow, delayed energy release within the cluster, occurring on the microsecond time scale. An analogous metastable decomposition of the evaporation of several monomer molecules could be detected neither for other propane cluster ions nor in ionized clusters of ethane.

The curves of the ion currents of the parent and fragment cluster ions for the above-mentioned transition (1) versus electron energy show long tails and nonlinear increases over a range of several eV (Fig. 3). The determination of the appearance energies (AE) of the produced ions is, therefore, rather difficult. Linear extrapolation leads to a value of the AE of the cluster ion of about 6 eV above the monomer AE (i.e., 11.6 ± 0.2 eV), but the curves of the cluster ions tail down and suggest a mixed contribution from various fragmentation processes in the ionization of the parent molecule.

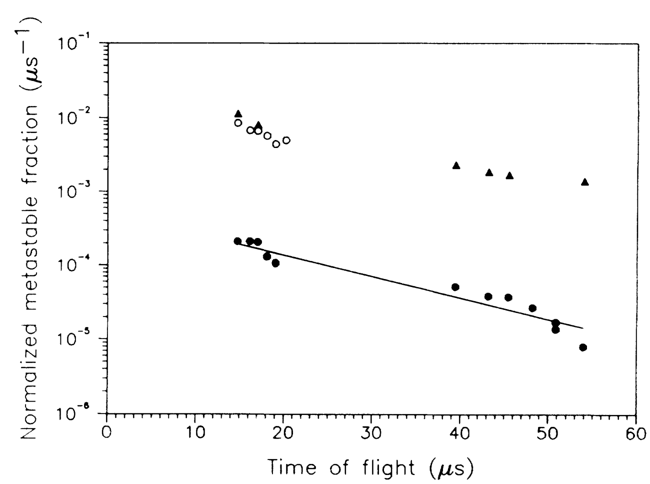

FIG. 2. Normalized metastable fraction (metastable fraction divided by the time window) vs flight time (from the region of ionization to the center of the first field-free region) for evaporation of one monomer from $(C_3H_8)_8^+$ (designated ▲), of one monomer from $(C_3H_8)_7(C_3H_7^+)$ (designated ○), and of four monomers from $(C_3H_8)_7(C_3H_7^+)$ (designated ●).

The amount of energy needed to dissociate four propane monomers from $(C_3H_8)_{n>8}$ may be estimated from the enthalpy of vaporization of liquid propane (19.04 kJ mol^{-1} at the boiling point [8]). This estimation leads to a lower limit value for the energy needed to evaporate the four monomers of 0.78 eV.

It is improbable that such an amount of energy could be stored for a relatively long time (several μs; see Fig. 2) in the cluster ion as electronic excitation energy (which would require an isolated electronic state) or as vibration-

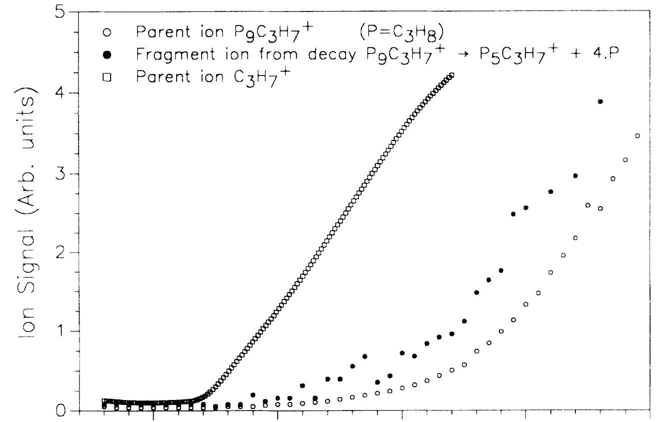

FIG. 3. Ion current vs electron energy for $C_3H_7^+$ (produced via electron-impact ionization of propane gas) designated □, $(C_3H_8)_8(C_3H_7^+)$ (produced via electron-impact ionization of propane clusters) designated ○, and $(C_3H_8)_5(C_3H_7^+)$ [produced by the metastable decay reaction $(C_3H_8)_9(C_3H_7^+) \rightarrow (C_3H_8)_5(C_3H_7^+) + 4(C_3H_8)$] designated ●.

al energy in specific vibrational modes of the central ion (which would require the storage of several vibrational quanta). The propane ion is a prime example of the successful application of the quasiequilibrium theory of mass spectra, and the rapid (and complete) degradation of electronic excitation energy into vibrational energy of the molecular propane ion has been proven in many experiments and supported by theory [5,9]. On the other hand, storage of vibrational energy of the required amount (0.78 eV) in the ion, i.e., of about 2-3 vibrational quanta at least, also seems quite improbable: One would have to ask why exactly that amount of energy which leads to the evaporation of four monomers is released, and why several vibrational quanta operate in such a specific manner and after a time delay long in comparison with usual dissociation processes.

There are several points which should be taken into consideration when trying to explain the metastable process (1).

(i) The process concerns $C_3H_7^+$ ions clustered by propane molecules. $C_3H_7^+$ can exist in several isomeric forms, i.e., *n*-propyl, isopropyl (*sec*-propyl), corner-protonated cyclopropane (*c*-propyl) [10].

(ii) An analogous process of metastable decomposition with the release of several monomers was not detected in ionized ethane cluster decomposition (isomeric structures of $C_2H_5^+$ ions do not occur).

(iii) On the other hand, an analogous process was observed in ionized butane clusters for $(C_4H_7^+)(C_4H_{10})_{n>7}$ ions, involving metastable decomposition with the ejection of 2-4 and 4-7 monomers [11] (note that $C_4H_7^+$ can exist in several isomeric forms).

This leads us to the suggestion that the metastable decomposition process (1) in propane results from energy release due to the isomerization of a more energetic form to a more stable form of the propyl ion in the cluster. The energies of the propyl isomers are well known [8]: The energy difference between the *n*-propyl ion ($\Delta H_f = 209$ kcal/mol) and the isopropyl ion ($\Delta H_f = 190$ kcal/mol) is 0.82 eV; the corner-protonated cyclopropane ion has $\Delta H_f = 199$ kcal/mol and thus lies 0.39 eV above the energy of the isopropyl ion, the most stable of all of the isomers (see also theoretical results [12]). The energy difference between the *n*-propyl and isopropyl isomers thus accounts well for the energy necessary to cause the evaporation of four propane molecules from the $(C_3H_7^+)(C_3H_8)_{n\geq 8}$ cluster ions. The fact that fewer than 4 molecules are evaporated for clusters smaller than $n=8$ can be explained if one takes into account the fact that the binding energy of the first monomer to the central ion is expected to increase with decreasing size of the cluster from the limiting value of 0.78 eV for larger clusters. The gradually decreasing number of dissociated molecules (see Fig. 1) is consistent with this view.

The *n*-propyl ion may be formed by electron ionization and subsequent fragmentation of the propane molecular ion in the cluster. Also, the *n*-propyl ion can be formed by hydride-ion transfer reactions of various propane fragment ions within the cluster. The following processes are known to occur with large rate constants in the gaseous phase [13]:

$$C_2H_5^+ + C_3H_8 \rightarrow C_2H_6 + C_3H_7^+ , \qquad (2)$$

$$C_2H_4^+ + C_3H_8 \rightarrow C_2H_5 + C_3H_7^+ , \qquad (3)$$

$$C_2H_3^+ + C_3H_8 \rightarrow C_2H_4 + C_3H_7^+ , \qquad (4)$$

$$CH_3^+ + C_3H_8 \rightarrow CH_4 + C_3H_7^+ , \qquad (5)$$

$$C_3H_5^+ + C_3H_8 \rightarrow \text{products} . \qquad (6)$$

Reactions (2)-(5) are exoergic both for the formation of isopropyl and *n*-propyl ions; reaction (6) is exoergic for the formation of the isopropyl ion, but endoergic (by 10.7 kcal/mol), if the *n*-propyl ion is formed. Interestingly, the rate constant for reaction (6) is about $\frac{1}{3}$ of that for reactions (2)-(5) [13], indicating that the channel opened in the other cases (evidently formation of *n*-propyl ion) is closed. This suggests that in reactions (2)-(5) both *n*-propyl and isopropyl ions are likely to be formed. Formation of propyl ions by chemical hydride-ion transfer reactions within the cluster presumably accounts for the increased relative intensities of clustered $C_3H_7^+$ ions in the mass spectra of ionized clusters in comparison with the abundances of other fragment ions [removed by the reactions (2)-(6)]. Also, the participation of highly fragmented ions (involving higher appearance energies) may at least qualitatively explain the tailing of the ionization efficiency curves for clustered propyl ions shown in Fig. 3.

Our model implies that the rate of isomerization of the *n*-propyl to the isopropyl ion and the resulting release of 0.8 eV energy is such as to influence processes on the microsecond time scale. Conflicting postulations have been made with respect to the isomerization rates of the various propyl isomers. According to Mc Ewen and Rudat [14], a large number of available gas phase data suggest that conversion of the *c*-propyl to the *sec*-propyl isomer is fast ($\sim 10^{-7}$ s [15]) but isomerization of *n*-propyl to *sec*-propyl is relatively much slower [16]. It should be mentioned, however, that recent gas phase radiolytic results on alkylation of benzene by propyl ions are consistent with the requirement of a fast rate for the rearrangement of *n*-propyl ions and a much slower (10^{-7}-10^{-5} s) rate for the rearrangement of *c*-propyl to isopropyl ions [17]. However, it seems improbable that the slow isomerization rate of *c*-propyl to isopropyl could be responsible for process (1), as the energy released (0.39 eV) is too small to account for the dissociation of four monomer molecules. We propose instead that the process responsible for the observed fragmentation is indeed the *n*-propyl to isopropyl isomerization whose rate in the ion cluster has been determined from the slope of the fitted line shown in Fig. 2 to be approximately (15 μs)$^{-1}$ in accordance with a number of isomerization studies of gas phase hydrocarbon ions [14-16].

In conclusion, we have reported a novel process for the metastable decomposition of $(C_3H_7^+)(C_3H_8)_n$ ions occurring in ionized propane clusters which results in the ejection of up to four propane monomers. We suggest that the driving force for this slow process is the isomerization of n-propyl ions to isopropyl ions within the cluster; this rearrangement isomerization process occurs with the release of 0.82 eV of energy—an amount just sufficient to lead to the evaporation of four monomer molecules in the nonstoichiometric cluster ions of $n \geq 8$ mentioned above.

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