Kinetic Energy Release and Metastable Transitions

II. The Decomposition of Doubly-Charged Ions of Aliphatic and Alicyclic Hydrocarbons

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The decompositions of doubly-charged ions given by a number of C_3-C_8 aliphatic and alicyclic hydrocarbons have been investigated in a double-focusing mass spectrometer. Many processes were found in which high kinetic energy CH_3^+ and $C_2H_3^+$ ions are formed. Doubly-charged ions fragment by more than one route and in many cases, high kinetic energy fragment ions are formed in at least two different ways. Metastable transitions common to several compounds were observed, the intensities rising as the degree of unsaturation increased.

Many fragment ions in the mass spectra of organic compounds are formed with kinetic energies considerably in excess of thermal energies. Observations on satellite peaks given by CH_3^+ ions have shown that these ions carry approximately 2 eV excess energy in many cases and have led to the suggestion that these ions are formed by the decomposition of doubly-charged species [1, 2]. This has recently been shown to be the case for many aromatic compounds by observing the width of peaks given by metastable transitions [3]. This technique allows one both to identify the decomposition reaction and to evaluate the kinetic energy released in the process [4]. In many cases, it was found that the doubly-charged molecular ion lost one or more neutral species before decomposing into two singly-charged ions. A disadvantage of this method is that many peaks due to metastable transitions may be masked by normal peaks in the mass spectrum, but this can be overcome by observing the products of metastable transitions which occur in the first field-free region of a double-focusing mass spectrometer [5–7]. In this way, many more metastable transitions can be observed and the kinetic energy released can be evaluated in favorable cases [8]. The decompositions of doubly-charged ions given by a number of C_3-C_8 aliphatic and alicyclic hydrocarbons have been studied using this technique and the results are discussed in this paper.

Experimental Method

All observations were made using an MS9 double-focusing spectrometer (Associated Electrical Industries, Ltd.) which has been modified to allow independent variation of the accelerating voltage V and electrostatic analyser voltage E. If $m_1^{++} \rightarrow m_2^+$ with the release of T eV of kinetic energy in the region between the source and the electrostatic analyser, the m_2^+ ions are transmitted by the electrostatic analyser when the normal accelerating voltage V_0 is altered to V such that

$$\frac{V}{V_0} = \frac{m_1}{2\,m_2}\left[\frac{1}{(1 \pm (\mu\,T/2\,V\,e)^{\frac{1}{2}})^2}\right] \qquad (1)$$

where $\mu = (m_1 - m_2)/m_2$ and e is the electronic charge [8]. If V' is defined as $(m_1/2\,m_2)\,V_0$, Eq. (1) can be rearranged to give

$$T = \frac{(V-V')^2}{2\,\mu\,V}\,. \qquad (2)$$

It was shown in Part I that T evaluated in this way is less than the true value because of approximations

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made in deriving Eqs. (1) and (2) [8]. The correct value is found by calculating T at different accelerating voltages using Eq. (2) and extrapolating to the value which would be found at zero accelerating voltage.

In this work, the maximum value of V_0 was 8 kV; 70-volt electrons were used and the trap current was 90 μA or 300 μA, depending on the intensity of the signal, giving a source temperature of 230 – 270 °C. The pressures in the source and analyser tube were estimated to be 2×10^{-5} mm Hg and 9×10^{-7} mm Hg respectively.

The acetylenes were N.B.S. certified samples and other C_3 and C_4 hydrocarbons were obtained from Matheson Co. and Phillips Petroleum Co. The C_5-C_8 hydrocarbons were obtained from Koch-Light Ltd.

Results

1. C_3 *Hydrocarbons*

Only one metastable transition of a doubly-charged ion could be observed in the mass spectra of propylene and cyclopropane:

$$C_3H_5^{++} \rightarrow C_2H_2^{+} + CH_3^{+}. \qquad (1)$$

Both ions were observed but the intensities were too low to obtain an accurate value of the kinetic energy release by the extrapolation method. When $V_0 = 4$ kV, observations on the CH_3^+ ions led to an approximate value of 4.1 eV which is probably rather less than the true value.

No metastable transition leading to high kinetic energy CH_3^+ ions could be found in the mass spectra of methylacetylene and allene. In the case of allene, however, the loss of H and H_2 by the doubly-charged molecular ion was observed, but a much stronger signal was observed arising from the process

$$C_3H_4^{++} \rightarrow C_3H_3^{+} + H^{+}. \qquad (2)$$

Since the $C_3H_3^+$ ion carries only 2.5% of the energy released, no estimate of this could be obtained.

2. C_4 *Hydrocarbons*

Metastable transitions of doubly-charged ions in the mass spectra of n-butane, cis-butene-2, butene-1, 1,3-butadiene, dimethylacetylene and ethylacetylene were investigated and in all cases, the most intense signal was that due to the decomposition

$$C_4H_4^{++} \rightarrow C_3H^{+} + CH_3^{+}. \qquad (3)$$

Observations on both ions lead to a value of 2.85 ±0.3 eV for the kinetic energy release. Much weaker signals indicate that $C_3H_2^+$, $C_3H_3^+$, $C_3H_4^+$ and $C_3H_5^+$ ions can also be formed by the loss of CH_3^+ by doubly-charged C_4 species in appropriate cases. Loss of H^+ by several doubly-charged C_4 species is also observed, the strongest signal again arising from the decomposition of the $C_4H_4^{++}$ ion.

Within experimental error, the kinetic energy released in the decomposition of a given ion does not appear to depend on the molecule from which it is formed. No evidence could be found to suggest that any single-charged C_2 species are formed directly from doubly-charged C_4 species, but a very low intensity signal was observed due to the occurrence of reaction (1).

3. C_5 *Hydrocarbons*

In the mass spectra of 1,4-pentadiene, n-pentane and cyclopentene, the strongest signals arising from reactions which lead to high kinetic energy CH_3^+ ions were those due to

$$C_5H_8^{++} \rightarrow C_4H_5^{+} + CH_3^{+}, \qquad (4)$$

$$C_5H_6^{++} \rightarrow C_4H_3^{+} + CH_3^{+} \qquad (5)$$

together with weaker signals arising from similar decompositions of $C_5H_7^{++}$ and $C_5H_5^{++}$ ions, and from reaction (3). In addition, a weak signal was given by the reaction

$$C_5H^{++} \rightarrow C_4H^{+} + C^{+}. \qquad (6)$$

Several weak signals were observed which arise from reactions in which $C_2H_3^+$ ions were formed from doubly-charged C_5 species, the strongest signal being given by the reaction

$$C_5H_5^{++} \rightarrow C_3H_2^{+} + C_2H_3^{+} \qquad (7)$$

in which the kinetic energy release is estimated to be 2.4±0.25 eV using the extrapolation method.

4. C_6 *Hydrocarbons*

The mass spectra of n-hexane, 1,5-hexadiene, cyclohexane and cyclohexene were examined for metastable transitions of doubly-charged ions. In each case, the loss of CH_3^+ ions by $C_6H_4^{++}$, $C_6H_6^{++}$, $C_6H_7^{++}$, $C_6H_8^{++}$, $C_6H_9^{++}$ and $C_6H_{10}^{++}$ ions was observed, together with weak signals from $C_6H_{11}^{++}$ in the cases of n-hexane and cyclohexane. The strongest signal was given by the reaction

$$C_6H_6^{++} \rightarrow C_5H_3^{+} + CH_3^{+} \qquad (8)$$

but signals due to the decomposition of $C_6H_8^{++}$ and $C_6H_{10}^{++}$ ions were also moderately strong. The loss of CH_3^{+} ions by several doubly-charged C_5 species was also observed, the strongest signals again arising from the even-mass ions $C_5H_6^{++}$ and $C_5H_8^{++}$.

High kinetic energy $C_2H_3^{+}$ ions were also found to be formed by the decomposition of several doubly-charged C_6 species, the most intense signal arising from the process

$$C_6H_7^{++} \rightarrow C_4H_4^{+} + C_2H_3^{+}. \qquad (9)$$

It is also possible that $C_2H_4^{+}$ ions are formed in similar reactions since weak, overlapping signals were observed suggesting that $C_4H_2^{+}$ and $C_4H_3^{+}$ ions may be formed from $C_6H_5^{++}$ and $C_6H_6^{++}$ and from $C_6H_6^{++}$ and $C_6H_7^{++}$ ions respectively.

The relative intensities of the different metastable transitions varied very little from sample to sample, but in general, however, the intensities of the metastable transitions for a given sample pressure increased as the degree of unsaturation increased.

5. C_7 *Hydrocarbons*

A similar study was made of metastable transitions of doubly-charged ions in the mass spectra of n-heptane and n-heptene-1. Several fairly weak signals indicated the loss of CH_3^{+} ions by doubly-charged C_7 species, the strongest being given by the reaction

$$C_7H_{10}^{++} \rightarrow C_6H_7^{+} + CH_3^{+}. \qquad (10)$$

Most of the reactions found for C_6 hydrocarbons leading to CH_3^{+} ions were observed in the mass spectra of the two C_7 hydrocarbons, and again the strongest signals arise from the decomposition of the even-mass ions $C_5H_8^{++}$, $C_6H_6^{++}$, $C_6H_8^{++}$, together with moderately strong signals from $C_6H_9^{++}$ and $C_6H_{10}^{++}$.

Four metastable transitions were observed in which doubly-charged C_7 species gave high kinetic energy C_2 species, three different ions being formed:

$$C_7H_{14}^{++} \rightarrow C_5H_9^{+} + C_2H_5^{+}, \qquad (11)$$

$$C_7H_{12}^{++} \rightarrow C_5H_7^{+} + C_2H_5^{+}, \qquad (12)$$

$$C_7H_7^{++} \rightarrow C_5H_5^{+} + C_2H_2^{+}, \qquad (13)$$

$$C_7H_6^{++} \rightarrow C_5H_3^{+} + C_2H_3^{+}. \qquad (14)$$

Very weak signals also indicated that $C_5H_2^{+}$ and C_5H^{+} ions were formed from C_7 species but the decomposing ions could not be identified with certainty. C_5H^{+} ions were also formed in the decomposition of $C_6H_4^{++}$ and $C_5H_2^{++}$ ions. Other sources of high kinetic energy C_2 fragment ions were the processes

$$C_6H_{11}^{++} \rightarrow C_4H_7^{+} + C_2H_4^{+}, \qquad (15)$$

$$C_6H_7^{++} \rightarrow C_4H_4^{+} + C_2H_3^{+} \qquad (9)$$

and high kinetic energy C_3 fragment ions were formed in the two processes:

$$C_6H_{13}^{++} \rightarrow C_4H_7^{+} + C_3H_6^{+}, \qquad (16)$$

$$C_7H_7^{++} \rightarrow C_4H_4^{+} + C_3H_3^{+}. \qquad (17)$$

6. C_8 *Hydrocarbons*

Because of the increasing complexity of the systems, the only C_8 hydrocarbon to be investigated was cyclo-octa-1,3-diene. High kinetic energy CH_3^{+} ions were formed in a large number of decompositions, signals being observed for the decomposition of $C_8H_6^{++} - C_8H_{12}^{++}$, $C_7H_7^{++} - C_7H_{10}^{++}$ and $C_6H_9^{++}$, by far the most intense signal being given by the reaction

$$C_8H_{10}^{++} \rightarrow C_7H_7^{+} + CH_3^{+} \qquad (18)$$

together with a moderately strong signal due to

$$C_7H_9^{++} \rightarrow C_6H_6^{+} + CH_3^{+}. \qquad (19)$$

The loss of $C_2H_3^{+}$ ions by all the above-mentioned C_8 species was also observed, the strongest signals being due to the decompositions

$$C_8H_{10}^{++} \rightarrow C_6H_7^{+} + C_2H_3^{+}, \qquad (20)$$

$$C_8H_9^{++} \rightarrow C_6H_6^{+} + C_2H_3^{+}. \qquad (21)$$

Several weak signals indicated that $C_3H_3^{+}$ fragment ions were also lost by C_8 species, the most prominent being that due to

$$C_8H_6^{++} \rightarrow C_5H_3^{+} + C_3H_3^{+}. \qquad (22)$$

An idea of the complexity of the system may be gained from the fact that 33 metastable transitions were observed in which doubly-charged ions gave rise to $C_5 - C_7$ singly-charged species.

Discussion

A metastable transition is observed for a particular fragmentation only if the internal energies of some of the fragmenting ions are such that the specific rate constants for their decompositions are in the range $10^5 - 10^6$ sec^{-1}. If the minimum rate constant for a process exceeds 10^6 sec^{-1}, no metastable transition will be observed even though the process may be very important in the ion source. For similar reasons, the intensities of observed metastable transitions cannot be related simply to the relative importance of the different decomposition processes in the source. Nevertheless, in view of the large number of transitions which have been observed, several generalizations can be made.

Although doubly-charged molecular ions may fragment immediately into two singly-charged species with the release of kinetic energy, it is quite common for them to lose one or more neutral fragments before dissociating to give the two singly-charged fragment ions [3, 9]. In general, the more intense signals are observed for metastable transitions of doubly-charged fragment ions which possess four or six hydrogen atoms less than the number present in the fully-saturated hydrocarbon molecule, but for the reasons outlined above, this does not necessarily mean that these processes are the most important sources of high kinetic energy fragment ions within the ion source. It is interesting to note that with four exceptions, it is the *even* mass doubly-charged ions which give the stronger metastable transitions; these are all even-electron species and are analogous to the *odd* mass singly-charged even-electron species which are much more abundant than odd-electron species in most hydrocarbon mass spectra.

The same metastable transition can be observed in the mass spectra of a wide variety of compounds (e. g. those given by $C_4H_4^{++}$ and $C_6H_6^{++}$). Although the routes leading to the formation of the dissociating ion must differ from compound to compound, the kinetic energy released in the decomposition and calculated from the width of the peak does not appear to vary with the origin of the ion. This may be a real effect and be related to the potential energy surfaces involved in the decomposition or alternatively, it may be a consequence of the fact that the energy content of the dissociating ions which is necessary to produce a metastable transition will be the same in each case. If the latter explanation were correct, one would expect the kinetic energy released in the decomposition to decrease as the time between the formation and dissociation of the ion increased, but the close agreement in the values of the kinetic energy released in the process

$$C_6H_6^{++} \rightarrow C_5H_3^{+} + CH_3^{+}$$

obtained from measurements on satellite peaks [2] and metastable peak widths [3] suggests that such a variation is likely to be very small and that it may lie within experimental error.

Several doubly-charged ions were found to fragment in more than one way to give different pairs of singly-charged fragment ions with the release of different amounts of kinetic energy in some cases. For example, the ion $C_8H_{10}^{++}$ may lose CH_3^+ or $C_2H_3^+$ with the release of approximately 2.7 eV and 3.3 eV of kinetic energy respectively, based on observations made on these metastable transitions in the samm spectrum of p-xylene at several different accelerating voltages. (The results obtained from cyclo-octa-1,3-diene with $V_0 = 8$ kV were identical to those obtained from p-xylene at this accelerating voltage.) On the other hand, when $C_5H_8^{++}$ loses CH_3^+ and $C_2H_3^+$, the kinetic energy released is 2.3 eV and 2.4 eV respectively, i. e. the same within experimental error. It is possible that there are two isomeric forms of the ion $C_8H_{10}^{++}$ which fragment in different ways with the release of different amounts of kinetic energy, whereas one need assume only one form of $C_5H_8^{++}$ to exist with the two types of fragmentation occurring in a statistical manner. The release of different amounts of kinetic energy in similar decompositions of isomeric singly-charged ions in the mass spectra of certain aromatic nitrocompounds has been reported previously: the loss of NO by the molecular ions of ortho- and para-nitroanilines is accompanied by the release of 0.81 eV, but the corresponding decomposition in the case of the meta-nitroaniline occurs without the release of kinetic energy [4]. A similar variation in kinetic energy release has also been observed for the $C_2H_5O^+ \rightarrow CHO^+ + CH_4$ in the mass spectra of aliphatic alcohols and ethers [10].

It has generally been assumed that the energy released in a fragmentation of a doubly-charged ion can be related to the coulombic repulsion between the two positive charges and on this basis, BEYNON

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and FONTAINE[11] have suggested that $C_6H_6^{++}$ is linear rather than cyclic. If it is assumed that all doubly-charged ions are linear and that the positive charges are localized on the terminal carbon atoms, the energy available from coulombic repulsion will decrease gradually as the length of the carbon chain increases. The results in Table 1 show that whereas there is a gradual decrease in the energy released in going from C_3 to C_5 compounds, there is a marked increase in energy associated with the decomposition of C_6, C_7 and C_8 doubly-charged species. This suggests that the simple model given above is inadequate and that the energy released depends in a much more complex manner on the structures of reactant and product ions and on their respective heats of formation.

	Metastable Peak Width	Satellite Peak
C_3H_6	$\geqq 2.64$	2.75
Butene-1	2.03	2.59
cis-Butene-2	2.03	2.65
iso-Butene	2.03	2.76
n-Butane	2.03	2.48
iso-Butane	2.03	2.66
Butadiene	2.03	2.59
n-Pentane	1.80	2.24
cyclopentene	1.80	2.54
n-hexane	2.16	1.95
1,5-hexadiene	2.16	2.20
cyclohexane	2.16	2.26
cyclohexene	2.16	2.37
benzene	2.16	2.27

Table 1. K.E. carried by CH_3^+ ions from different compounds (eV).

As the complexity of the molecule increases, light ions such as CH_3^+ and $C_2H_3^+$ are formed in many different fragmentation processes. If several of these processes contribute significantly to the yield of high kinetic energy CH_3^+ and $C_2H_3^+$ ions, it is unlikely that observations on satellite peaks given by these ions will be sufficiently detailed for one to be able to identify these processes with certainty. On the other hand, if one particular process is largely responsible for the production of these high kinetic energy ions, it should be possible to identify the reaction by comparing the results obtained from observations on satellite peaks and metastable peak widths if it is assumed that the same kinetic energy is released in a given decomposition whether it occurs in the source or the analyser tube. In Table 1, the results obtained for CH_3^+ ions are compared, the value being calculated from the most intense metastable transition. In the case of benzene, it is reasonably certain that the decomposiiton of $C_6H_6^{++}$ is the major source of high kinetic energy CH_3^+ ions so that the two techniques are being applied to the same reaction and consequently the agreement is quite good. In some of the other cases, however, the disagreement is well outside the estimated experimental error, and it must be concluded that the metastable transitions quoted in the table are not the major sources of high kinetic energy CH_3^+ ions in the source. It is possible that some doubly-charged molecular ions are formed in very short-lived electronic states so that they rapidly dissociate into two singly-charged fragment ions, whereas other doubly-charged molecular ions, possibly formed in different electronic states, can be stabilized for a few microseconds by the elimination of one or more neutral species before giving the two singly-charged species. In view of the agreement in the case of benzene and other C_6 hydrocarbons, it seems improbable that a systematic error can explain the discrepancy.

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