STUDY OF ORGANIC CATIONS IN THE GAS PHASE
BY TANDEM MASS SPECTROMETRY

by Yan An

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ABSTRACT

The structure elucidation of gas-phase isomeric species C₂H₄X⁺ (X = F, Cl, Br and I), C₃H₆X⁺ (X = Cl, and Br), (C₂H₅)₂O*C₂H₄X (X = Cl and Br), and C₂H₆O₂⁺ has been accomplished by employing tandem mass spectrometric techniques, i.e. metastable ion (MI) mass spectrometry, collision induced dissociation (CID) mass spectrometry, collision induced dissociative ionization (CIDDI) mass spectrometry and neutralization reionization (NR) mass spectrometry.

For C₂H₄X⁺ cations, apart from the α-isomer, CH₃CHX⁺, the cyclic ethylenehalonium \[ \begin{array}{c}
    \text{CH}_2 \\
    \text{CH}_2
\end{array} 
\] ions, CH₂CH₂ are also stable for X = Cl, Br and I (Chapter 3). The two isomers have readily been characterized by CID mass spectrometry and their neutral counterparts have been produced and studied by NR mass spectrometry. It was found that based on an analysis of the heat of formation values of these ions and the electronegativity and polarizibility data of the X atoms, the relative stability of the two isomers is essentially controlled by the C–X bond strength. The relative stability of the cyclic species, however, is also controlled by the polarizibility of the X atom, which indicated that its polarization by the charge-centered carbon involved the outer-electrons in the X atom to form a back-donating bond with the charge-centered carbon.

The isomeric halogen substituted triethylxonium ions (C₂H₅)₂O*C₂H₄X, (X = Cl and Br) were generated by appropriate gas phase ion molecular reactions between diethylether and appropriate C₂H₄XBr⁺ via Br⁺ loss (Chapter 4). The α-substituted isomer, (C₂H₅)₂O*CHXCH₃, and the β-substituted isomer, (C₂H₅)₂O*CH₂CH₂X, are both
stable in the gas-phase and do not interconvert on a time scale of $10^{-5}$ s.

Three $C_3H_6X^+$ isomers (at least) were found to be stable in the gas-phase (Chapter 5). They are $CH_3^-\cdot CX\cdot CH_3$, $CH_3\cdot CH\cdot CH_2$, and $CH_2\cdot CH_2$. These ions were characterized by their CID mass spectra and their different behavior in forming oxonium ions — $(C_2H_5)_2O^+\cdot C_2H_5X$ — with diethyl ether.

The distonic radical cations $^1CH_2CH_2O^+CHOH$ and $^1CH_2CH_2^+C(OH)_2$. have been directly generated and characterized by their MI and CID mass spectra (Chapter 7). Comparing the dissociative process of $^1CH_2CH_2O^+CHOH$ to that of $HCOOCH_2CH_3^+$ led to the conclusion that this distonic ion is the key intermediate in the dissociation of the latter. Thus the previous proposal, based only on the dissociation of $HCOOCH_2CH_3^+$, was confirmed. The heat of formation of $^1CH_2CH_2O^+CHOH$ was estimated from an appearance energy measurement to be $137 \pm 4$ kcal mol$^{-1}$; this is 16 kcal mol$^{-1}$ lower in energy than $HCOOCH_2CH_3^+$.  

A detailed study of distonic ions is presented in Chapter 6, including a survey of the common methods to generate and characterize these ions. Properties of such ions which were considered were: stability, isomerization, bond cleavage and ring-strain. The results showed that the characteristics of distonic ions which distinguish them from their conventional counterparts result from the specific interaction of charge and radical sites.
Acknowledgement

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Chapter 1

Introduction

For more than 30 years tandem mass spectrometry, (mass spectrometry / mass spectrometry, MS/MS) has been a valuable physical tool to study gas-phase organic ions, in particular to gain structural information and to elucidate fragmentation mechanisms.

The study of unimolecular or collision induced dissociations of ions is performed by using the first mass spectrometer to select ions with a certain mass. The fragmentation products of these ions are mass analyzed by a second mass spectrometer. In the triple scan technique, using three mass analysers (MS/MS/MS), further structural assignments can be made for individual fragment ions of the originally mass selected species.

The study of the fragmentation behaviour of gas-phase ions has recently led to the recognition of non-classical ion structures, such as DISTONIC IONS;\(^1\) ION-NEUTRAL COMPLEXES;\(^2\) and HYDROGEN-BRIDGED COMPLEXES.\(^3\) The first category refers to radical cations having the formal charge and radical sites separated; The second refers to those ions which consist of an incipient ion co-ordinated to a putative neutral, the two species being bound by ionic forces, rather than a covalent bond; The last type has two partners, a radical and a cation, bonded by a hydrogen atom.

This thesis is mainly concerned with exploring and expanding the use of tandem mass spectrometry to investigate some specific ionic families. They are ions of formula C\(_2\)H\(_2\)X\(^+\) (X = F, Cl, Br and I), C\(_3\)H\(_6\)X\(^+\) (X = Cl and Br), C\(_6\)H\(_{14}\)OX\(^+\) (X = Cl and Br) and C\(_3\)H\(_4\)O\(_2\)^{++}.
The aims of the thesis are:

1. To assign the structures for the above ion groups based on their unimolecular and collision induced dissociations and available thermochemical data;

2. To deepen our understanding of the factors which affect the stability of both classical and non-classical species.

References

1 Details will be discussed in Chapter 6


Chapter 2

Instrumentation and Experimentation

2.1 History

Although the first mass spectrometers of J. J. Thomson and F. W. Aston\textsuperscript{[1]} were built over 80 years ago, the major development leading to the technique of tandem mass spectrometry occurred in 1945 when Hipple and Condon observed and explained the presence of metastable ions in a mass spectrum.\textsuperscript{[2]} A metastable ion is one that is sufficiently stable to leave the ionization chamber, but that decomposes before reaching the collector. This requires a lifetime of $10^4 - 10^5$ sec. Investigation of metastable ions brought fundamental studies on the use of metastable ions as a source of chemical and physical information. This work was the driving force that has led to tandem mass spectrometry as it is practised today.

In the 1960s, the first experiments were performed in which instruments were used in unconventional modes to study the decompositions of metastable ions. These studies were made possible by developments in three different areas. The first development was the introduction of the accelerating-voltage scan on sector instruments by Barber and Elliott.\textsuperscript{[3]} The next major development was the discovery of the enhancement of magnitude and quantity of peaks in a "metastable ion" mass spectrum upon introduction of a collision gas into a localised region of the mass spectrometer.\textsuperscript{[4]} The fragmentation of a polyatomic ion following an energetic collision with a target gas is referred to as collision-induced dissociation (CID). At the time of the initial experiments using CID, the focus of the studies was very narrow and directed primarily toward exploration of the physical aspects
of the phenomenon. Not until a few years later, at the time of publication of the book *Metastable ions*,[5] did tandem mass spectrometry start to gather momentum. Publication of this book marked the beginning of the modern era of tandem mass spectrometry, a period in which instruments would be designed expressly for MS/MS and MS/MS/MS experiments.

More recently the development of the neutralization-reionization technique[6] has made tandem mass spectrometry a valuable tool to generate and study novel neutral species. In a tandem mass spectrometer the neutrals were generated by charge exchange of the fast ions with a permanent gas and further downstream the neutrals (and their fragmentation products) were collisionally ionized. Next, the ions were detected and if a species was observable which had the same m/z ratio as the mass-selected ion, it was concluded that the neutral counterpart was stable. The mass spectrometer used by Tomlinson et al[7] contained a furnace, which made neutralization by metal vapours possible. In the eighties the technique was extended for the investigation of the stability of the neutral counterparts of (well-characterised) poly-atomic, mostly organic ions.[8] Both metal vapours and permanent gases were successfully used for neutralization.

The first MS/MS/MS instrument was constructed in the late seventies.[9] The principal reason for developing triple sector mass spectrometers is to provide high mass resolution mainly for analytical purposes. The advantage of these instruments when used to study gas-phase organic ions is the ability to examine consecutive reactions taking place in sequential field-free regions of the instrument.
2.2 Instrument description

There are a number of instrumental components common to all mass spectrometers. The basic design requires an ion source, where ionization, and some fragmentation take place. The ions then must be separated according to their mass-to-charge ratio in the mass analyser. The detector detects the ions, measuring the relative abundance of each. Usually a data system records, processes, and stores the information. The vacuum system maintains a low pressure in the instrument; the low pressure minimises ion/molecule collisions so that the ions can move through the instrument in a well-defined path. To facilitate sample introduction, an inlet system provides a link between the outside world and the inside of the mass spectrometer.

The VG Analytical ZAB-3F mass spectrometer, a triple sector instrument, was used for the research presented in this thesis. Thus the instrument description will concentrate on the function of the various parts of the VG ZAB-3F mass spectrometer.

2.2.1 The ionization chamber

The ion source in the VG ZAB-3F is a typical electron impact ion source as shown in Figure 2.1.

Electrons are produced from an incandescent helical filament or ribbon usually made from tungsten or rhenium. The electrons are accelerated towards the ionization chamber and enter it through a system of collimating slits. The kinetic energy of the electrons can be varied simply by changing the potential difference between the filament and the ionization chamber.
The region within the ionization chamber is essentially free of electric fields and the electrons traverse it at constant velocity. Electrons which pass through a slit at the far end of the ionization chamber are accelerated towards an electrode at a potential higher than that of the ionization chamber and collected. This electrode is known as the "trap". One or two repeller electrodes are usually located within the ionization chamber. When a small positive voltage is applied to them, positive ions formed by the electrons will be repelled towards the slit A. The ions which leave the ionization chamber under the influence of the repeller electrodes do so with a very small kinetic energy corresponding to about one electron volt. Outside the ionization chamber, however, they come under the action of a strong electric field corresponding to a potential drop of several thousand volts over a distance of the order of a few mm and are accelerated towards a plate containing a slit, known as the source slit.

Figure 2.1 Ion source

![Diagram of ion source]

The kinetic energy of an ion of mass m and charge e accelerated through a
potential drop $V_{\text{acc}}$ is given by $\frac{1}{2} mv^2$ where $v$ is the terminal velocity and

$$\frac{1}{2} mv^2 = eV_{\text{acc}}$$ (1)

The beam of ions that has a kinetic energy equal to the full accelerating energy is known as the "main ion beam".

2.2.2 The magnetic analyser

The function of a magnetic analyser is shown in Figure 2.2. The use of an electromagnet as a mass analyser is based on the principle that charged particles which pass through a magnetic field, $B$, perpendicular to their motion, will follow a circular path of radius $r_m$. The $r_m$ is determined by $mv = Bzr_m$.

Figure 2.2 Focusing action of a sector magnetic analyser

Suppose that ions of mass $m$ and velocity $v$ emerge from the object point $O$ with a half-angular spread in the plane of the paper $\alpha$ ($\alpha << 1$). An ion with median direction, after traversing the distance $L$, enters the magnetic field, where it is constrained to follow a circular path of radius $r_m$. After deflection through the angle $\Phi$, it emerges from the field and proceeds to the image point $I$ at which there is a convergence of the ion beam which
diverged from O. For a certain magnetic analyser, the \( r_m \) is fixed. Ions of different \( m/z \) ratios are focused by varying the magnetic field strength \( B \), \( m/z = B r_m / v \). Since the translational energy of the source generated ions is equal to \( zV_{\text{acc}} \), it follows that:

\[
B^2 = m/z \cdot 2V_{\text{acc}} / r_m^2
\]  

(2)

2.2.3 The electrostatic analyser

An electrostatic analyser produces a radial electric field (E) if the outer plate is made positive with respect to the inner plate, and a beam of ions of various energies is injected midway between the plates and perpendicular to the direction of the electric field, there will be some ions which will describe a circular trajectory along the curve of radius \( r_e \) which is a line of equipotential. This condition is met when the translation energy (\( E_\sigma \)) of these ions, \( m v^2 / 2 \), is such that the electrostatic force on the ions is exactly balanced by the centrifugal force:

\[
\frac{m v^2}{r_e} = zE
\]  

(3)

Combining with that \( E_\sigma = m v^2 / 2 \),

\[
E = 2 \cdot E_\sigma / r_e \cdot z
\]  

(4)

Thus the ESA separates ions according to their translational energy-to-charge ratio. A fragment ion \( m_2^+ \) formed by dissociation of \( m_1^+ \) in the FFR-2 will have translational energy (\( E_{\sigma2} \)) equal to the ratio of the masses times \( E_\sigma \)

\[
E_{\sigma2} = m_2 / m_1 \cdot E_\sigma
\]  

(5)
By scanning $E$, all fragment ions of $m_1^-$ can be recorded. Alternatively by setting $E$ to match $E_{m_2}$, the fragment ion $m_2^-$ will be transmitted to FFR-3.

Figure 2.3  Focusing action of an electrostatic analyzer

2.2.4 The detector

The detectors in VG ZAB-3F mass spectrometer are off-axis Daly detectors, which employ a scintillator to detect secondary electrons emitted when ions strike a conversion dynode ($V_2$), as shown in Figure 2.4. The conversion dynode is at a high negative potential (~20 kV) and attracts the ions that emerge at ground potential from the exit slit of the mass analyzer. The high energy positive ions impinge on the central portion of the conversion dynode and secondary electrons are emitted (~about 6 electrons per ion over a wide mass range). The secondary electrons are accelerated by the electric field produced by the conversion dynode potential and strike CaF$_2$ scintillator. The scintillations produced are detected by an optically coupled photomultiplier.
2.2.5 Tandem mass spectrometers used for this thesis

The VG ZAB-3F triple sector mass spectrometer with BEE geometry is schematically shown in Figure 2.5.

Figure 2.4 Daly detector

Figure 2.5 VG ZAB-3F mass spectrometer
Where,  

IS:  Ion source  
B:  Magnetic analyzer  
ESA:  Electrostatic analyzer  
C:  Collision cell  
FFR:  Field-free region  
D:  Detector  

The GEC-AEI MS-902s is also a tandem mass spectrometer with an EB geometry, which was used to measure the appearance energy (AE) of metastably generated ions produced in the first field-free region. Ions were also detected by a Daly Photomultiplier, the advantage of which is that the metastable ion signals may be enhanced relative to source generated species.

2.3 Reactions in a tandem mass spectrometer

In general there are four types of reaction involving charged species that can be studied in a tandem mass spectrometer. First of all is ionization of an organic molecule in the ion source. There are quite a few ionization techniques applied to tandem mass spectrometry.\textsuperscript{[13]} However, in the region of this thesis only electron impact (EI) ionization will be discussed.

The most commonly observed reaction in a mass spectrometer is a unimolecular reaction, which includes unimolecular dissociation and isomerization. The unimolecular dissociation can occur either spontaneously from metastable ions or from initially stable ions rendered unstable by an activating process. The latter is also important, known as collision activation reactions, the third type reaction in a tandem mass spectrometer. Not only the collision process activates an ion to fragment, but also it results charge permutation, which facilities to study the chemistry of neutrals.
The last type of reaction is an ion-molecule reaction, which can be obtained in the VG ZAB-3F ion source at pressures greater than about 10^{-5} torr.

2.3.1 Ion formation by electron impact (EI) ionization

EI ionization of gaseous molecules is a widely practised ionization technique. Electrons accelerated through a potential of several electron volts have a wavelength of ~ 0.1 nm, which is similar to the molecular dimensions. This results in mutual quantum effects (distortions). The distorted electron wave can be considered to be composed of many different sine waves and some of these waves will be of the "correct" frequency (energy) to interact with a molecular electron, that is, to promote an electron from a lower to a higher orbital (excitation) or - if the electron energy is greater than a critical value (the ionization energy or appearance energy) - to eject an electron from the target, thus producing a positive ion (cation).

\[ m_i + e^- \rightarrow [m_i]^+ + 2e^- \quad (6) \]

The minimum energy required to remove an electron from the highest occupied orbital of a molecule is termed the ionization energy (IE). A vertical ionization energy (IEv) is determined when ionization process is not involved geometric change (Figure 2.6a), while an adiabatic ionization energy (IEa) is the energy difference between the ion and its precursor when both are at their round states (Figure 2.6b).

Because of the very short time for ionization (~10^{-16} s) compared to vibrational periods (~ 10^{-14} s) EI ionization can be considered largely to be a vertical process in the Franck-Condon sense, a process in which inter-nuclear distances remain essentially fixed.
at those appropriate for the neutral molecule. A stable ion can be formed by ionization without geometric change (Figure 2.6 a). An ionization process which involves a significant geometric change may produce no stable ion counterpart as shown in Figure 2.6 b.

Figure 2.6 Energy diagram for ionization process

The energy of the electrons is variable, but is usually set at ~ 70 eV at EI ionization, a value much larger than the ionization energy of molecules. Hence, the molecular ions are generated with a large amount of excess internal energy and may dissociate to fragment ions \((m_2^+)\) and neutrals \((m_a^-)\):

\[
[m_1]^+ \rightarrow [m_2]^+ + m_a^-
\]  

(7)
The minimum energy necessary to form a fragment ion from a given neutral precursor is termed the *appearance energy* (AE). IE and AE values can be measured with good accuracy, ± 0.05 eV, but only with the aid of specialized apparatus such as photoionization mass spectrometers[11] or mass analysers equipped with an energy-selected electron impact ion source.[12]

2.3.2 Unimolecular reactions

The EI mass spectrum is suited to determine the structure of an organic compound if the compound is sufficiently volatile. The molecular ion in such a spectrum contains information about the molecular weight and the elemental composition, while the numerous fragment ions in an ideal case reflect the structure directly. In practice, however, the elucidation of an unknown compound’s structure from its EI mass spectrum is complicated not only by the fact that the molecular ion decomposes via rearrangement reactions, but also by multistep dissociations. The unimolecular reaction of organic ions, thus, is crucial to establish a fragmentation map, which is helpful to elucidate the molecular structures. Unimolecular reactions of mass selected ions can readily be studied in a tandem mass spectrometer.

Metastable ions

Ions in a mass spectrometer can be classified rather arbitrarily as stable, unstable, or metastable (Figure 2.7), depending upon when, or if, they fragment during their passage through the instrument.
Figure 2.7  Energy distribution of ions

\[ E \]

Unstable ions

Metastable ions

Stable ions

*Stable ions* are those that have lifetimes longer than the time of passage through the instrument. *Unstable ions* are those that fragment within the ion source, and *metastable ions* dissociate spontaneously outside the ion source but before detection. Ions with high internal energies can fragment with rate constants greater than about $10^6 \text{ s}^{-1}$ and therefore do so before leaving the ion source. Metastable ions have intermediate internal energies and therefore dissociate with intermediate rate constants ($10^4 - 10^6 \text{ sec}^{-1}$).

The primary use of metastable ions in analysis is to elucidate fragmentation pathways. By using a tandem mass spectrometer with BE geometry, the magnet current is adjusted to select a precursor. A scan of the electrostatic analyzer then records all its fragment ions. The fragmentation pattern thus can be identified. The identification of a particular reaction pathway can provide valuable evidence as to the arrangement of atoms in a molecule. For example, in a hypothetical spectrum the presence of ions corresponding
in mass to AB and ABC could indicate either of the molecular structure possibilities A-B-C-B-A or A-B-B-C-A. However, a metastable decomposition of ABC → AB would be possible, barring rearrangements, only for the structure of A-B-C-B-A.

Detection of metastably generated fragment ions depends upon where, within the instrument, the fragmentation occurs. Fragment ions generated within the magnetic or electric analyzer cannot be detected, the equation of motion, eq. (2) and eq. (4) do not apply to mid-sector changes in mass. Fragmentations occurring after the electric analyzer will also go undetected, since no further energy or momentum analysis is made before detection. Only those fragments due to dissociations in the first or second field-free regions, between the source and magnet and the magnet and electrostatic analyzer respectively, can be independently detected.

By eq. (5) the fragment $m_2^+$, produced via fragmentation in the second field-free region, will be transmitted through the electric analyzer at an $E_r$ value corresponding to $m_2 / m_1 \cdot V_{acc}$. Thus the mass of a product ion may be calculated from its kinetic energy. This is not only applicable to fragments of metastable ions, but to all fragments produced (unimolecularly or by collision) in the second field-free region from mass selected precursors.

The ratio of metastable peak intensities was proposed to be related to the structure of a fragmenting ion. The “metastable peak abundance ratio test” was based on the premise that when two (or more) competing fragmentations from the same ion give reasonably intense metastable peaks, then the ratio of the abundances (measured under carefully controlled experimental conditions) may be used as a criterion for ion structure.
Simply, dissociation to give the same m/z peaks, with closely similar intensity ratios, is
good circumstantial evidence that the reacting configurations of the two precursor species
must be the same. Here we use term of reacting configuration, because all source
generated ions, under the EI condition (70 eV), may have enough energy to undergo
rearrangement to another structure prior to fragmentation.

Kinetic energy releases

In the dissociation of a singly charged polyatomic ion, represented by eq. (7) some
fraction of the internal energy in the reaction co-ordinate in excess of that of the ground-
state products is partitioned into the kinetic energy of separation of the fragments. This
so-called kinetic energy release (KER), symbolized by \( T \), leads to a spread in the kinetic
energy of the daughter ions \( (m_2^+) \), since the daughter ion is ejected isotropically in the
centre-of-mass frame of reference. The excess internal energy can be viewed as consisting
of two components, the reverse critical energy \( (T^r) \) and the nonfixed energy \( (T^\#) \). The
reverse critical energy is the energy difference between the ground state of the products
and the critical energy for the fragmentation. The nonfixed energy is the internal energy in
excess of the critical energy required to achieve a dissociation rate consonant with the
lifetime of the metastable ion. The observed kinetic energy release includes a fraction of
the reverse critical energy \( \varepsilon^r \) and a fraction of the nonfixed energy \( \varepsilon^\# \) such that:

\[
T = T^\# + T^r
\]  

(8)

where \( T^\# \) is the contribution from \( \varepsilon^\# \) and \( T^r \) is that from \( \varepsilon^r \). When \( \varepsilon^r \) is negligible, the value
of \( T \) is due to \( T^\# \).
When dissociation occurs in the second reaction region of a BE instrument, the ionic products can be analyzed for their kinetic energy by a scan of the electric sector plate voltage. The kinetic energy release, \( T \), will result in a broadening of the signal corresponding to the metastable generated ions. \( T \) values are commonly reported for the peak widths at their half-height, \( T_{0.5} \), irrespective of the shape of the peak.\(^5\)

\[
T_{0.5} = \frac{(m_1)^2}{16m_2m_n} \cdot \frac{(\Delta E_{0.5})^2}{V_{acc}} \quad (9)
\]

and

\[
(\Delta E_{0.5})^2 = \Delta E(m_2)^2 - \Delta E(m_1)^2
\]

where \( \Delta E(m_2) \) and \( \Delta E(m_1) \) are the peak widths at half-height for \( m_2^+ \) and \( m_1^+ \), respectively.

Metastable peak shapes, which are recorded under conditions of good energy resolution, fall into one of three categories (Figure 2.8).\(^{14}\)

**Figure 2.8** Metastable peak shapes

\[\text{a} \quad \text{b} \quad \text{c} \quad \text{d}\]

*Gaussian* type peaks (a) are generally associated with small kinetic energy releases, \( T_{0.5} \) typically no more than \( \approx 80 \text{ meV} \). *Flat-topped* (b) and *Dished* peaks (c) are associated with larger kinetic energy releases due to reverse activation energy, \( \varepsilon' \), although the inverse statement is not necessarily true. The observed dish is produced by Z-axial
discrimination against the ion beam and will be instrument dependent. Composite peaks (d) are the result of the combination of two or more metastable peaks. A composite metastable peak indicates the involvement of more than one transition state and/or the production of more than one isomeric fragment ion.

Isomerization

Metastable ions typically have lifetimes of several tens of microseconds and internal energies in excess of the critical energy for the lowest energy dissociation of several tenths of an electron volt. Metastable ions therefore typically produce few product ions in their dissociative reactions, and those product ions that do form result from the lowest energy dissociation mechanisms. These dissociations are characteristic of the so-called reacting configuration of the ion. This configuration may or may not also characterize the structure of stable ions in the mass-selected beam used in MS/MS experiments, because the energized ions are not limited to decomposition alone. A wide range of excess internal energies is transferred on ionization and so it is also possible for the molecular and fragment ions to rearrange to various isomeric structures, of classical or non-classical form. These isomerization reactions can greatly complicate the interpretation of mass spectra and thus some understanding of the parameters involved is necessary. The relative energy barriers for decomposition, $E_d$, and isomerization, $E_i$, are the parameters which principally determine whether and to what extent an ion $A^+$ rearranges to an isomeric ion $B^+$ at a given internal energy $E$. Figure 2.9 shows a two-dimensional energy diagram to illustrate this point.
If an isomerization reaction has a critical energy higher than that of energy for a dissociation reaction (Figure 2.9 a), the isomerization cannot occur and so the metastable dissociation may be characteristic of the ionic structure $A^+$. In the case of (b) where $E_i$ is less than both $E_d$ values, then isomerization is expected. At increased internal energies decomposition becomes possible, however having been preceded by a number of interconversions, the original placement of the atoms with respect to one another may have changed resulting in partial or full randomization of the initial structure. The observed metastable decomposition will depend on the dissociation energy and the density of states of these isomers. If both isomers have similar dissociation energies, the one with a higher density of states is expected predominantly to dissociate. Thus for (b) isomerization will not hide the structural elucidation of $A^+$ and $B^+$, whereas for (a) the investigation of the decompositions of these ions will give no information unique to one or the other structure. Situations between these limiting cases are also possible, such as (c)
must isomerize to B⁺ prior to fragmenting and thus both A⁺ and B⁺ will generate similar mass spectral observations.

2.3.3 Activation reactions

Increasing the pressure in a field-free region of a mass spectrometer causes ion-neutral collisions in which some of the ion’s kinetic energy is converted into internal energy. The resulting ion decomposition products can be studied using the same techniques developed for unimolecular metastable ion decompositions. The collision of a high-velocity ion with a target gas is the most widely used method to elucidate ionic structures.

The overall mechanism for collision-induced dissociation (CID) in generally accepted as proceeding in two steps.\textsuperscript{[10,16]} The sequence involves collisional activation of the selected ion in the first step and unimolecular dissociation in the second step, i.e.:

\[
\begin{align*}
N \\
m_1^+ \rightarrow m_1^{**} \rightarrow m_2^+ + m_a
\end{align*}
\] (10)

where \(m_1^{**}\) is the activated parent ion. The overall net equation of the CID process, including a mass and energy balance is:

\[
q + m_1^+ + N = m_2^+ + m_a + N' + T
\] (11)

where \(q\) is the endothermicity of the collision (i.e., the amount of energy converted from the translational energy of the collision partners into internal energy), \(N'\) is the target molecule in its postcollision state, and \(T\) is the kinetic energy liberated in the unimolecular
dissociation. Provided that no photoemission occurs, the internal energy of $m_1^{+\ast}$ appears as $T$ and the internal energies of $m_2^+$ and $m_n$.

The most frequently used collision gases are helium and oxygen. Although maximum yields of fragment ions are obtained at pressures corresponding to 40-80% beam reduction, collision gas pressures are usually maintained at a 10% reduction to avoid multi-collisions.$^{14,17}$

The second step of CID, namely unimolecular dissociation, differs from MI dissociation which involves only a narrow range of internal energy (Figure 2.7). The mass-selected ions which suffer collisional activation are ions, originating in the ion source, which have insufficient energy to fragment on the $\mu$s time-scale. These non-decomposing ions ($m_1^+$), as shown in Figure 2.7, possess a broad range of internal energies. If it is initially assumed that $m_1^+$ ions retain their structure irrespective of their internal energy within this range, then the CID mass spectrum for these ions can tentatively be taken as structure-specific. However, to substantiate this assumption it is necessary to inspect $m_1^+$ ions of low internal energy. This can be done in several ways: (i) by transmitting metastably generated $m_1^+$ ions with the second mass analyzer in the VG ZAB-3F mass spectrometer; (ii) by lowering the ionizing electron energy to the lowest value compatible with a reasonable signal-to-noise ratio and transmitting the resulting source-generated, low-energy $m_1^+$ ions. If the CID mass spectra of ions having broad and narrow internal energy ranges are the same, then it may provisionally be concluded that only a single ion structure is present.$^{14}$

2.3.4 Charge permutation

22
2.3.4 Charge permutation

Three types of charge permutation reactions can be studied by tandem mass spectrometry.

**Charge stripping (CS)**

Collisional excitation of fast mass-selected ions ($m_1^{++}$) may be sufficient to cause the loss of an electron, resulting in a doubly charged species ($m_1^{2+}$).

$$m_1^{++} + N \rightarrow m_1^{2+} + N + e^- \quad (12)$$

The signals resulting from CS may be easily differentiated from those of CID. They are greatly reduced in width, and appear at one half the electric sector voltage for transmission of their singly charged counterparts. Amplification of the CID mass spectrum is usually needed to detect charge stripping peaks because their intensity is in general far less than those from CID. The use of "soft" target gases, particularly O$_2$, resulting in less energized products, will increase the relative intensities of the CS peaks. As well, these target gases will yield more non-decomposing doubly charged parent ions relative to doubly charged fragments.$^{[14,18]}$

**Collision induced dissociative ionization**

The neutral fragment ($m_a$) from metastable or collision-induced dissociation of a parent ion may be reionized by charge permutation with target gas.

$$m_a + N \rightarrow m_a^+ + N + e^- \quad (13)$$
This can be done by applying an ion beam deflector set before the collision cell to deflect the ionic species or by applying to the collision cell a positive voltage which is greater than the ion acceleration voltage. Thus all ions were repelled and only neutral species resulting from the unimolecular dissociations of the mass-selected ions entered the cell. The neutral species suffered collisionally induced dissociative ionization in the collision cell and could be identified by the positive ions which were generated. The method proved to be of use in solving problems associated with the structure of the neutral fragment produced in certain ion fragmentations. For example, it was shown that $^1\text{CH}_2\text{OH}$ rather than $^2\text{OCH}_3$ is lost from ionized methyl acetate.$^{19}$

Neutralization-Reionization (NR)

NR mass spectrometry is used to generate and characterize various transient neutral species.$^{20}$ In its simplest form, NR mass spectrometry is carried out as a two-collision experiment in which precursor ions of kilovolt kinetic energies are neutralized by collisions with thermal gaseous atoms or molecules (14), and the neutral species formed are allowed 0.5-5μs to dissociate (15). The surviving neutral intermediates and their dissociation products are reionized by another collision (16) and the ions formed are analyzed and detected.

\[
\begin{align*}
\text{m}_1^+ & \to \text{m}_1 \quad \text{(14)} \\
\text{m}_1 & \to \text{m}_2 + \text{m}_3 \quad \text{(15)} \\
\text{m}_1 & \to \text{m}_1^+ \to \text{m}_2^+, \text{m}_3^+, \ldots \quad \text{(16)}
\end{align*}
\]
Characterization of the intermediate neutral is based on the NR mass spectrum in which the survivor and fragment ion relative abundances reflect the stabilities and dissociations of both the neutral and reionized species.

Because of the very short time-scale for electron transfer neutralization (10^{-16} s), it must be considered as a vertical Franck-Condon transition, i.e. the neutral is formed initially in the nuclear configuration of the ion. If the geometries of the ion and corresponding (stable) neutral are closely similar, stable neutrals will be generated upon neutralization of the ion. However if the geometries are markedly different then transition to an unstable part of the potential energy surface of the neutral may take place. If the neutral counterpart of the mass-selected ion is intrinsically unstable, or is stable but is generated with a large amount of internal energy due to exothermic neutralization, the generated neutral will fragment and/or rearrange to a more stable species (m_1').

\[
    m_1^+ \rightarrow m_1^* \rightarrow m_1'
\]  

(17)

It is also possible that upon neutralization, stable electronic excited states of the neutral are populated. These can undergo spontaneous radiative or radiationless transitions to lower electronic states, which could be stable or dissociative. Thus the absence of a recovery signal, i.e. ions which survive the neutralization-reionization process intact, does not necessarily indicate that the corresponding neutrals are unstable.

The natures of both the neutralization and reionization agent influence the internal energy of the ion obtained after neutralization-reionization. Since collision induced ionization is also vertical, it is possible that, although the corresponding ion is stable,
excitation to a repulsive part of the potential energy surface of the ion takes place. Consequently no recovery signal will be present. The convolution of these energies is shown in Scheme 2.1. The excitation energy deposited in the neutral (ΔE) can be passed on to the reionized survivor ion and fragment ions and augmented by reionization (ε) to promote their dissociations. The net result of neutral excitation thus depends on the critical energies for the neutral and ion dissociations.

\[
\begin{align*}
\text{Scheme 2.1} \\
E_i \text{ is the internal energy of } m_1^+ \text{ and } E_{\text{diss}} \text{ is the dissociation energy.}
\end{align*}
\]

Excitation of neutral intermediates that have one or more low-energy dissociation channels will induce neutral dissociation, while excitation of stable neutral species will be passed on the reionized ions and promote their dissociations. Likewise, stable neutral fragments formed by neutral dissociations will pass their internal energy on the reionized species to promote their fragmentations. Collisional energy transfer at kiloelectronvolt kinetic energies is non-specific, resulting in a broad range of internal energies, convolution of neutral and ion fragmentations is an inevitable feature of NR mass spectrometry.
2.3.5 Ion-molecule reactions in the ion source

Most mass spectra are a result of a series of competitive and consecutive unimolecular reactions. However, when a high-pressure ion source is used, such as a chemical ionization source, bimolecular ion/molecule reactions can occur. The most commonly observed ion/molecule reaction is proton transfer, but the formation of molecular ion/molecule adducts and fragment ion/molecule adducts has also been confirmed with conventional tandem mass spectrometry.\(^{(22)}\) Although ion cyclotron resonance (ICR) spectrometers are ideally suited to study many bimolecular reactions, high-pressure ion sources have the advantage of allowing collisional stabilization of the ion-molecule complexes. Thus the intermediates in exothermic reactions may be observed in many cases, while only the ionic products will be detected in an ICR spectrometer.\(^{(23)}\)

2.4 Ion thermochemistry

The IE and AE measurements are fundamental to ionic thermochemistry because the heats of formation of organic ions, which are often correlated with ion structure, can be obtained from these values provided that the heats of formation of the corresponding neutrals are known.

\[
\Delta_f H^0 (m_2^+) = IE (m_2) + \Delta_f H^0 (m_2)
\]

(18)

and

\[
\Delta_f H^0 (m_2^+) = AE (m_2^+) + \Delta_f H^0 (m_1) - \Delta_f H^0 (m_2)
\]

(19)

The ionic heat of formation gained from the IE value will be specific for the ion having at least initially the same structure as the neutral molecule. The ion enthalpy
derived from eq. (19) will be the same as that from eq. 18 on the conditions that (i) the
fragmentation of \( m_{i}^{+} \) has no significant kinetic shift and (ii) the reverse reaction has no
energy barrier.\(^{[14]} \)

Thousands of \( \Delta H^0 \) values of organic ions have been measured through IE and
AE measurements,\(^{[24]} \) facilitating ion structure assignment and the understanding of ionic
thermochemistry. With these values an empirical relationship between \( \Delta H^0 \) (Ion) and ion
size (as represented by the number of atoms, \( n \)) in homologous series of organic
compounds has been confirmed.\(^{[25]} \)

\[
\Delta H^0 \text{ (Ion)} = A - Bn + C/n
\]

(20)

Where, \( A, B \) and \( C \) are constant for a given homologous series and \( n \) is the number of
atoms in the molecule. An alternative approach is to evaluate the effect of stepwise
substitution on a substituted methyl cation\(^{[26]} \):

\[
\Delta \Delta H^0 \left[ \text{XCH}_3^+ / \text{XC(CH}_3)_m \text{H}_{3-m} \right] = \Delta H^0 \text{ (XCH}_3^+ \) - \Delta H^0 \left[ \text{XC(CH}_3)_m \text{H}_{3-m} \right] = A + Bm
\]

(21)

Where, \( m \) represents the number of methyl groups and \( A \) and \( B \) are the intercept
and slope, respectively.

By analyzing the values of \( A \) and \( B \), one can not only evaluate the heats of
formation of these substituted cations, but also evaluate the capacity of an ionic species to
accept the substitution. The latter results from the analysis of \( B \) values. A large \( B \) value
indicates a localized charge and a small \( B \) value indicates a delocalized charge.
The discovery of Equation 21 follows the point of view that the stability of a cation is related to the electronegativity of the heteroatom (X) in the cation. The scale of electronegativity suitable for evaluating the stability of organic ions is \( V_x \),\(^{[27]}\) which is obtained from the ratio of the number of covalent electrons \( (n_c) \) of atom \( X \) to the covalent radius \( (r_c) \):

\[
V_x = \frac{n_c}{r_c}
\]  \hspace{1cm} (22)

2.5 Ion structure assignment

With tandem mass spectrometry the ion structure is assigned specifically as to how the atoms are joined together and the probable (formal) locations of radical and/or charge sites. Details of geometry, such as bond lengths, bond angles and charge distribution are not yet accessible to experiment for polyatomic ions. Considerable progress has, however, been made in these areas by means of \textit{ab initio} molecular orbital calculations, performed at a sufficiently high level of theory.\(^{[28]}\)

The two chief experimental methods involving conventional tandem mass spectrometers currently available are: (i) Ion thermochemistry, i.e. IE and AE measurements; (ii) Ion dissociation characteristics, including MI, CID, CS and NR mass spectrometries.\(^{[14,29]}\) Each of these now is commonly assisted by employing isotopic labelling experiments. High level \textit{ab initio} calculations have also contributed greatly to the solution of the ion structure problem especially for those with unusual structures.\(^{[30]}\)

A good example to illustrate the combination of these technique to assign ionic structures in the gas phase is the study of isomeric \([\text{C}, \text{H}_3, \text{N}, \text{O}]^+\) ions.\(^{[31]}\)
[H₂NC(H)O]⁺⁺ (1) was generated by electron ionization of neutral H₂NC(H)O;

[H₂NCOH]⁺⁺ (2) was generated by fragmentation of [H₂NC(O)CH₂CH₃]⁺⁺ via C₂H₄ loss;

[H₃CNO]⁺⁺ (3) was generated by fragmentation of [H₃CNO₂]⁺⁺ via O loss; and

[H₂CNOH]⁺⁺ (4) was generated by thermolysis of trimetric formaldoxime hydrochloride.

The heats of formation of the four isomers were either experimentally measured or calculated by ab initio MO theory. The values were 189.0, 190.7, 231.1 and 230.9 kcal mol⁻¹ for ions 1, 2, 3, 4, respectively.

The four isomers were identified by MI mass spectrometry, as shown in the following.

\[
\begin{align*}
[H₂NC(H)O]⁺⁺ (1) & \rightarrow [H₂NCO]⁺ + H⁺ & T_{0.5}\ (meV) & 33 \\
[H₂NCOH]⁺⁺ (2) & \rightarrow [H₂NCO]⁺ + H⁺ & & 10 \\
& & \rightarrow [H₃N]⁺⁺ + CO & 43 \\
[H₃CNO]⁺⁺ (3) & \rightarrow [NO]⁺ + CH₃⁺ & 0.5 \\
[H₂CNOH]⁺⁺ (4) & \rightarrow [NO]⁺ + CH₃⁺ & 35 \\
& & \rightarrow [H₂NCO]⁺⁺ + H⁺ & 63
\end{align*}
\]

The CID mass spectra of these isomers provided further evidence. The signals at m/z 14 (CH₂)⁺⁺, 18 (H₂O)⁺⁺, and 31 (NOH)⁺⁺ in the CID mass spectrum of ion (4) confirmed its structure with a terminal CH₂ group. Moreover, some identical dissociation channels for ions 1 and 2, i.e. CO loss and NH₂⁺ loss, indicated that the isomerization energy barrier for 1 ↔ 2 is lower than these dissociation barriers. The calculated isomerization energy value supported this proposal.
2.6 References


3. M. Barber and R. M. Elliot, Presented at the ASTM E-14 Conference on Mass Spectrometry, Montreal, June 1964


Chapter 3

C$_2$H$_4$X cations and neutrals

3.1 Introduction

The structure and energetics of halogen substituted cations have generated widespread interest since their involvement in the bromination of alkenes was first proposed by Roberts and Kimball\textsuperscript{[1]}. Several decades later, the direct observation of an isolated cyclic halonium ion in the condensed phase came from Olah and Bolinger\textsuperscript{[2]} by proton magnetic resonance spectroscopy of the tetramethylethylene halonium ions, formed via ionization of 2,3-dihalo-2,3-dimethylbutanes in superacidic media [(CH$_3$)$_2$CXCX(CH$_3$)$_2$, with X = Cl, Br and I].

This observation of the non-classical C$_2$H$_4$X$^+$ cation in the condensed phase sparked the theoretical calculations aimed to evaluate the relative energies of these cations and their isomers and related transition states. According to calculation there are two stable isomers of C$_2$H$_4$X$^+$ for X = Cl and Br. They are the $\alpha$-substituted haloethyl cation, CH$_3$CHX$^+$ (I), and the cyclic- ethylenehalonium cation, $\text{CH}_2\text{X}^+\text{CH}_2$ (II). For C$_2$H$_4$F$^+$, isomer II is about 30 kcal/mol$^1$ higher in energy than isomer I. The $\beta$-substituted structures, XCH$_2$CH$_2$ (III), were calculated to be transition states between isomers I and II, and do not exist as minima on the potential energy surfaces. No calculations on C$_2$H$_4$I$^+$ have been reported. The results of the calculations are summarized in Table 3.1. Although the calculated values are scattered, the differences between F-, Cl- and Br- substituted ethyl cations are clear from the average values. The cyclic-CH$_2$F$^+$CH$_2$ ion is ~ 30 kcal/mol$^1$ higher
in energy than CH₃CHF⁺ and about as high as FCH₂CH₂⁺. It is noteworthy that the energy of the transition state for hydrogen bridging, ⎿ H⁺ ⎝ CHF—CH₂, is about the same as that for fluorine bridging. Thus the CH₃CHF⁺ ion is unlikely to isomerize to the cyclic — CH₂F⁺CH₂. In the case of C₂H₅X⁺ (X = Cl and Br), the cyclic-CH₃X⁺CH₂ ion is similar in energy to CH₃CHX⁺. However, the acyclic ion XCH₂CH₂⁺ is much higher in energy. Thus isomers I and II have a similar stability but are separated by a high energy barrier.

The theoretical calculations strongly support experimental values for the heats of formation of C₂H₅X⁺. The measured heats of formation of C₂H₅X⁺, for X = F, Cl, Br and I, are shown in Table 3.2, along with a brief description of the experimental method. The experimentally derived values for ΔH⁰ C₂H₅X⁺ (X = Cl, Br) and CH₃CHF⁺ from different measurements are very close to each other. The heat of formation of cyclic- ⎞ CH₂F⁺CH₂ was only obtained by estimation using the method of equivalent cores, which assumes that "The energy of the process in which an electron is transferred from a core level of an atom to the nucleus of the atom is independent of the chemical environment of the atom".¹⁷⁶

In the gas phase, the unimolecular and bimolecular reactions of both CH₃CHX⁺ and cyclic-CH₃X⁺CH₂, for X = Cl and Br, have been reported by several groups using tandem mass spectrometry¹⁸-²⁰ and ion cyclotron resonance mass spectrometry²¹-²³. However for C₂H₄F⁺, the cyclic ethylenefluorinium ion has only been observed as a proposed intermediate species in the gas phase during the electron impact-induced decomposition of 2-phenoxyethyl fluoride.¹⁷,²⁴ The gas-phase reactions of C₂H₄I⁺ cations
have not been reported.

The results reported in this Chapter are from detailed studies of the gas-phase unimolecular reactions of the $\text{C}_2\text{H}_4\text{X}^+$ cations, the chief aim of which was to identify the isomers. The Neutralization-Reionization mass spectra of $\text{C}_2\text{H}_4\text{X}^+$ cations are reported here for the first time. Compared with $\text{C}_2\text{H}_4\text{X}^+$, fewer studies have been reported on the corresponding $\text{C}_2\text{H}_4\text{X}$ radicals.$^{[25-37]}$

The heats of formation of $\text{C}_2\text{H}_4\text{X}$ radicals ($X = \text{F, Cl and Br}$) have been measured$^{[25-29]}$ via kinetic studies and by appearance energy measurements. The values are summarized in Table 3.3.

Most of the theoretical studies of $\text{C}_2\text{H}_4\text{X}$ radicals were performed in regard to bridging in the $\beta$-haloethyl radical, $\text{CH}_2\text{XCH}_2^+$.$^{[30-34]}$ Engels and Peyrimhoff calculated the energy difference between the minimum asymmetric structure $\text{XCH}_2\text{CH}_2^+$ ($X = \text{F, Cl and Br}$) and the optimal symmetric structure $\text{CH}_2\text{X}^+\text{CH}_2$, using MRD-CI calculations.$^{[30-32]}$ The differences were 33, 8 and 1 kcal/mol$^1$ for $X = \text{F, Cl and Br}$, respectively. Thus $\text{C}_2\text{H}_4\text{F}^+$ is certainly expected to behave as a classical unbridged radical.$^{[31]}$ Guerra's calculation agreed that the symmetric bridged structure is less stable than the classical structure for $\text{C}_2\text{H}_4\text{X}^+$ ($X = \text{F and Cl}$). The energy differences between the two structures were 36.0 kcal/mol$^1$ for $X = \text{F}$ and 13.3 kcal/mol$^1$ for $X = \text{Cl}$, respectively.$^{[31]}$ The symmetric structure was found to be stable with respect to dissociation.$^{[31]}$ Robinson et al, calculated that the dissociation of $\text{C}_2\text{H}_4\text{F}^+$ to $\text{C}_2\text{H}_4 + \text{F}$ was endothermic by 46 kcal/mol$^1$ and the energy barrier to $\text{C}_2\text{H}_3\text{F} + \text{H}^+$ was about 44 kcal/mol$^1$. The C-F dissociation energy in $\text{C}_2\text{H}_4\text{F}^+$ was calculated to be 37 kcal/mol$^1$.$^{[30]}$ However, the C-Cl dissociation of
\( \text{C}_2\text{H}_4\text{Cl}^* \) was only 17 kca/mol.\(^{[36]} \) The lower stability of ClC\(_2\)H\(_4\) \(^*\) (with respect to Cl-C\(_2\)H\(_4\) separation) can be traced to the different strengths of the fluorine-carbon and chlorine-carbon bonds.\(^{[32]} \)

Barat et al, studied the reaction of hydrogen atoms with vinyl chloride.\(^{[37]} \) At low-pressure, room temperature conditions, the consumption of C\(_2\)H\(_3\)Cl by reaction with H\(^*\) occurs primarily by n-ipso attack by H on the =CH\(_2\) group to form (CH\(_3\)CHCl)\(^*\). This energized complex then undergoes a H-shift to form (CH\(_2\)CH\(_2\)Cl)\(^*\), which decomposes to form Cl + C\(_2\)H\(_4\).

The decomposition behaviour of C\(_3\)H\(_3\)X\(^*\) radicals may also be examined by NR mass spectrometry; results will be shown in this chapter.

3.2 Experimental

All metastable ion (MI), collision induced dissociation (CID) and neutralization reionization (NR) mass spectra were performed with a VG-ZAB-3F mass spectrometer. The ionization energy was 70 eV and the ion translational energy (accelerating voltage) 8 keV, unless, otherwise indicated. The correction of the CID mass spectra for MI contributions was done by setting a potential of -1000 V on the collision cell. The NR mass spectrum was performed using a potential of -1000 V on the ion beam deflector electrode between the neutralization and reionization cells. The distances between the two cells were 10 cm and 2 cm in the 2ffr and 3ffr, respectively. Appearance energy (AE) measurements were performed either using the MS-9 mass spectrometer or an electron monochromator. For greater detail of the experimental procedures, see Chapter 2.
3.3 Results

3.3.1 Formation of the C₂H₄X⁺ isomers

In general C-X (X = Br or I) bond dissociations in molecular ions proceed with a negligible reverse energy barrier. Thus a good way to produce a desired cation is to use an appropriate halogen containing precursor. To produce the C₂H₄X⁺ cation, the selected precursor was C₂H₄XY (X = F, Cl, Br and I; Y = Br and I).

\[ \text{CH}_3\text{CHX}^+ \text{ (I) is produced from CH}_3\text{CHXY}^{++} \text{ by Y loss.} \]

\[ \text{CH}_3\text{CHXY}^{++} \rightarrow \text{CH}_3\text{CHX}^+ \text{ (I) + Y} \]  \hspace{1cm} (1)

\[ \text{CH}_2\text{X}^+\text{CH}_2 \text{ (II) is produced from CH}_2\text{XCH}_2\text{Y}^{++} \text{ by loss of Y.} \]

\[ \text{CH}_2\text{XCH}_2\text{Y}^{++} \rightarrow \text{CH}_2\text{X}^+\text{CH}_2 \text{ (II) + Y} \]  \hspace{1cm} (2)

The C₂H₄X⁺ cations are numbered as shown below:

<table>
<thead>
<tr>
<th>X</th>
<th>CH₃CHX⁺</th>
<th>CH₂X⁺CH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>Ia</td>
<td>IIa</td>
</tr>
<tr>
<td>Cl</td>
<td>Ib</td>
<td>IIb</td>
</tr>
<tr>
<td>Br</td>
<td>Ic</td>
<td>IIc</td>
</tr>
<tr>
<td>I</td>
<td>Id</td>
<td>IIId</td>
</tr>
</tbody>
</table>

3.3.2 Unimolecular dissociation of C₂H₄X⁺ isomers

The metastable ion (MI) dissociations of C₂H₄X⁺ (X = F, Cl and Br) were dominated by HX loss with a large kinetic energy release (KER) for X = F and a very small kinetic energy release for X = Cl and Br. The KER values are shown in Table 3.4. No fragmentation was observed in the MI mass spectrum of C₂H₄I⁺.
In CID mass spectra, as shown in Table 3.5, the eight cations, Ia-d, IIa-d, show structure distinguishing dissociations. The dissociation energies of $\text{C}_2\text{H}_3\text{X}^+$ ions are summarized in Table 3.6. The comparison of CID mass spectra of $\text{CH}_3\text{CHF}^+$ at different translational energies is shown in Table 3.7.

3.3.3 Neutralization-Reionization (NR) mass spectra of $\text{C}_2\text{H}_4\text{X}^+$

The NR mass spectra of $\text{C}_2\text{H}_4\text{X}^+$ ($X = \text{F, Cl Br and I}$) are shown in Figure 3.1 - 3.7. The neutralization target was dimethylamine (DMA). Xe was also used as neutralization target and it showed results similar to those with DMA. O$_2$ was used as the reionization target. The NR mass spectra of each $\text{C}_2\text{H}_4\text{X}^+$ were obtained both in the 2ffr (the distance between two cells is 10 cm) and in the 3frr (distance is 2 cm). No recovery signal was observed in the NR mass spectrum of $\text{C}_2\text{H}_4\text{I}^+$ (Figures 3.6 and 3.7). The NR mass spectrum of $\text{C}_2\text{H}_4\text{I}^+$ was dominated by I$^+$. The energy values related to the dissociations of $\text{C}_2\text{H}_4\text{X}^+$ radicals are shown in Table 3.8.

3.3.4 Deuterium-labelling of cyclic-CH$_2$XCD$_2$ ($X = \text{Cl, Br}$).

The MI mass spectra and CID mass spectra of XCD$_2$CH$_2^+$ (XCD$_2$CH$_2^+$ - Y, $X = \text{Cl, Br, Y = Br, Cl}$) and XCH$_3$CD$_2^+$ (XCH$_3$CD$_2^+$ - Y, $X = \text{Cl, Br, Y = Br, Cl}$) are identical. Both metastable $\text{C}_2\text{H}_2\text{D}_2\text{Cl}^+$ isomers showed the same ratio of DCl loss to HCl loss as 1:16. The ratio sharply increased to 1:1.6 in the CID mass spectra. Both metastable $\text{C}_2\text{H}_2\text{D}_2\text{Br}^+$ isomers showed the same ratio of DBr loss to HBr loss, namely 1:14. The ratio increased to 1:1.06 in the CID mass spectra. Table 3.9 shows the partial CID mass spectra of $\text{C}_2\text{H}_2\text{D}_2\text{X}^+$ ($X = \text{Cl, Br}$).
3.4 Discussion

3.4.1 C₂H₄F⁻ isomers

The C₂H₄F⁻ cations produced either from CH₃CHF₂ or from CH₂FCH₂Br showed similar dissociations in their CID mass spectra, as shown in Table 3.5. The appearance energy (AE) measured for the process of CH₂FCH₂Br → C₂H₄F⁻ + Br⁺ is 10.94±0.05 eV (252 kcal·mol⁻¹), corresponding to a heat of formation for C₂H₄F⁻ of 165.6 kcal·mol⁻¹ [taking ΔH° (CH₃CHF₂Br) = -60 kcal·mol⁻¹, ΔH° (Br) = 26.7 kcal·mol⁻¹]³¹⁸. This value is the same as the heat of formation of CH₃CHF⁺ (165 kcal·mol⁻¹)³¹⁵,³¹⁶. Thus the C₂H₄F⁻, produced from CH₂FCH₂Br⁻, appears to be CH₃CHF⁺ (Ia). Moreover, since the threshold for production of C₂H₄F⁻ is the same as the calculated enthalpy change of the reaction [AE = ΔH° (CH₃CHF⁺) + ΔH° (Br) - ΔH° (CH₂FCH₂Br)] and this dissociation has little reverse energy barrier (T₀ = 0.76 kcal·mol⁻¹), indicating the threshold product ion cannot be CH₂−CH₂ (ΔHr = 183 kcal·mol⁻¹). So the hydrogen shift may happen before the Br cleavage, i.e.

\[
\begin{align*}
\text{CHF-CH₂-Br}^- & \rightarrow [\text{CHF - CH₂...Br}]^- \rightarrow \text{CH₃CHF}^+ + \text{Br}^+ \\
\end{align*}
\]

(3)

Morton et al, showed that the cleavage of the O-C bond in PhO-CH₂CH₂F⁺ involves an ion-neutral complex, [PhO⁺ CH₂CH₂F]. In the complex, the cyclic-CH₂F⁻CH₂ (IIa) was proposed to be an intermediate in competition with H-bridged CH₂H⁺CHF. In contrast, the free C₂H₄F⁻ ions have the structure of CH₃CHF⁺. However, in the case of
the cleavage of the Br-C bond in CH$_2$FCH$_2$Br$^+$, the cyclic-CH$_2$F$^+$CH$_2$ cannot have been an intermediate, otherwise, the AE value should have been at least 17 kcal mol$^{-1}$ higher than that observed.

\[
\begin{align*}
\text{CH}_2\text{FCH}_2\text{Br} & \rightarrow \text{CH}_2\text{F}^+\text{CH}_2 + \text{Br}^- \\
\Delta H_i (\text{kcal mol}^{-1}) & = 269
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CHF}^+ + \text{Br}^+ & \rightarrow \text{CH}_3\text{CHF}^+ + \text{Br}^- \\
\Delta H_i (\text{kcal mol}^{-1}) & = 252
\end{align*}
\]

In the 2ffr CID mass spectrum the dissociation of C$_2$H$_4$F$^+$ was dominated by HF loss. However in 3ffr CID mass spectrum the major dissociations were H and H$_2$ losses, as shown in Table 3.7. The parent ions in the 3ffr have a slightly lower average internal energy than those in the 2ffr. The CID mass spectrum of C$_2$H$_4$F$^+$, generated from metastable BrCH$_2$CH$_2$F$^+$ ions also showed a more intense peak for C$_2$H$_3$F$^+$ (H loss) than for C$_2$H$_3$F$^+$ (HF loss). Thus the fragmentation of CH$_3$CHF$^+$ is very sensitive to its internal energy. The dissociation of C$_2$H$_4$F$^+$ ions having lower internal energy is dominated by H and H$_2$ losses and the dissociation at slightly higher internal energy is dominated by HF loss. It is proposed that the HF loss channel may involve an isomerization into a stable isomer, CH$_2$CHFH$^+$. The isomerization barrier for CH$_3$CHF$^+$ \(\rightarrow\) CH$_2$CHFH$^+$ is less than the energy required to dissociate the ion into C$_2$H$_3$F$^+$ (\(\Delta H^0 = 227\) kcal mol$^{-1}$) + H$_2$.

The absence of C$_2$H$_4$F$^+$ in the CID mass spectra of C$_2$H$_4$F$^+$, although it is less endothermic than some observed fragmentations (see Table 3.6), shows that the energy barrier for the F loss is at least as high as 63 kcal mol$^{-1}$ (compare with the energy required for dissociation to C$_2$HF$^{2+}$ + H$_2$ + H), as shown in Table 3.6.

In Figure 3.1, it can be seen that the NR mass spectra of C$_2$H$_4$F$^+$ are similar to the corresponding CID mass spectra, even though the total ion current after NR with
DMA/O₂ was judged to be approximately a factor of 10⁴ lower than the current of the mass selected ions entering the collision cells, indicative of a small overall cross-section for the process.⁶ The NR mass spectra performed in the 2ffr (Figure 3.1 b) showed the fragments F⁺, HF⁻ and C₂H₄⁺, which are not observed in the corresponding CID mass spectrum. These fragments must arise from decomposition of the neutral C₂H₄F⁻. In the NR mass spectrum of C₂H₄F⁺ performed in the 3ffr (Figure 3.1 c), the recovery signal increased and neutral fragments decreased. In the 3ffr the distance between the two collision cell is 2 cm, significantly shorter than that in the 2ffr (10 cm) where the neutral C₂H₄F spends a longer time before reionization, and so in the 3ffr the neutrals showed less dissociation. In the NR mass spectrum of C₂H₄F⁺ performed in the 2ffr (Figure 3.1 b), the more intense C₂H₂⁺, C₂H₃⁺ and CF⁺, CHF⁻, CH₂F⁺ ions compared to those in the 3ffr (Figure 3.1 c), indicated that the C₂H₄F radicals may have some dissociation channels similar to that of the ion. Note that C₂H₄F may dissociate to C₂H₃ + HF, the reaction of the lowest energy among its dissociations, see Table 3.8.

3.4.2 C₂H₄Cl⁺ isomers

The identical MI and CID mass spectra (see Table 3.9) of D-labelled C₂H₂D₂Cl⁺ ions (IIb) confirmed the cyclic structure of CH₂Cl⁻CH₂.

The CID mass spectra of the C₂H₄Cl⁺ isomers (Table 3.5) indicate that the two isomers, CH₃CHCl⁺ (Ib) and cyclic - CH₂Cl⁺CH₂ (IIIb) are readily distinguishable. Isomer Ib fragments to CH₃⁺ + CHCl and CHCl⁺ + CH₃; However, isomer IIb fragments to CH₂⁺ + CH₂Cl and CH₂Cl⁺ + CH₂. The small fragment at m/z 49 (CH₂Cl⁺) from Ib indicates some H shift from the CH₃ group to the CHCl group. Thus this H-shift is energetically
accessible by collision activation.

\[
\begin{align*}
\text{CH}_2\text{-CHCl}^+ & \rightarrow \text{CH}_2\text{-CHCl} \rightarrow \text{CH}_2\text{Cl}^+ + \text{CH}_2
\end{align*}
\] (5)

The CID mass spectra of D-labelled IIb showed neither a fragment at m/z 50 (CHDCl) nor one at m/z 17 (CHD$_2^+$), indicating the reactions in Scheme 3.1 did not occur. This reveals that the energy barrier for H-shift (reaction i) or cyclic-opening (reaction ii) is relatively high.

\[\text{Scheme 3.1}\]

In the MI mass spectra both isomers dissociated to C$_2$H$_5^+$ + HCl, with a very small KER value ($T_{0.5} = 1.4$ meV). The appearance energy (AE) values for this dissociation are 12.5±0.2 eV for IIb and 12.7±0.2 eV for IIIb. The results indicated no reverse energy barrier for the dissociation processes. The D-labelling experiments showed a strong isotope effect for HCl:DCl losses (MI, 16; CID, 1.6). Furthermore, the observation of H$_2$Cl$^+$ in the CID mass spectra of the two isomers and the presence of HDCl$^+$, D$_2$Cl$^+$ in the
CID mass spectrum of cyclic-CH₂Cl'CD₂ (see Table 3.9) confirms that the fragmentation may well involve another isomer, either CH₂CHClH⁺ (like CH₂CHFH⁺) or an ion-neutral complex [C₂H₃⁺ ClH], which will be discussed later. Theoretical calculations have set the complex 4.5 kcalmol⁻¹ below the product energies.¹¹¹

The NR mass spectra of both isomers Ib and IIb showed a small recovery signal (Figures 3.2 and 3.3). However the fragmentations of the two isomers were still distinguishable, indicating little or no interconversion between the two C₂H₄Cl⁺ radicals. It is noteworthy that as the distance between the neutralization cell and reionization cell is increased (in 2ffr, Figures 3.2 b and 3.3 b), the recovery intensity is lower due to the decomposition of the neutral C₂H₄Cl⁺. However the intensity of C₂H₅⁺, supposed to be produced from the reionized neutral, is not lower. This phenomenon reveals that the decomposition of the neutral may also produce C₂H₅⁺ + HCl, as in the case of C₂H₄F. The energy required for this dissociation is about the same as that of dissociation to C₂H₄ + Cl⁺, see Table 3.8.

Comparing the NR mass spectra of CH₃CHCl⁺ (Figure 3.2) and CH₂Cl⁺CH₂ (Figure 3.3) the former showed the more intense recovery signal. The latter showed more intense peaks for Cl⁺ and HCl⁺⁺. These results indicate that neutral CH₃CHCl⁺ is more stable than CH₂Cl CH₂⁺; \( \Delta H^0(CH₃CHCl⁺) \approx 18 \text{ kcalmol}^{-1} \) whereas \( \Delta H^0(CH₂ClCH₂⁺) \) is ca 22 kcalmol⁻¹.²²,²³

[\( \text{Cl⁺} \) ]

[\( \text{Cl⁺} \) ]

The CH₂ CH₂ produced from neutralization of CH₂-CH₂ (IIb) would be the transition state between ClCH₂CH₂⁺ and CH₂CH₂Cl⁺. This transition state has been
calculated to be 6 - 13 kcalmol\(^{-1}\) higher in energy than ClCH\(_2\)CH\(_2\)\(^+\).\(^{31-33}\) It is therefore possible that CH\(_2\)-CH\(_2\) may isomerize to ClCH\(_2\)CH\(_2\)\(^+\) before reionization. The different peak ratio of CCl\(^+\) to CH\(_2\)Cl\(^+\) in the NR mass spectrum of IIb compared to that in the CID mass spectrum of IIb indicates that the reionized C\(_2\)H\(_4\)Cl\(^+\) ions are not pure IIb ions.

3.4.3 C\(_2\)H\(_4\)Br\(^+\) isomers

The identical MI and CID mass spectra of D-labelled IIc ions confirm the structure as cyclic-CH\(_2\)Br\(^+\)-CH\(_2\). The CID mass spectra (Table 3.5), indicated that the two isomers, CH\(_3\)CHBr\(^+\) (Ic) and cyclic-CH\(_2\)Br\(^+\)-CH\(_2\) (IIc) are distinguishable. Isomer Ic fragmented to CHBr\(^+\) + CH\(_3\), whereas, isomer IIc fragmented to CH\(_2\)Br\(^+\) + CH\(_2\). The CID mass spectra of D-labelled IIc showed no fragment at m/z 92 (CH\(_2\)DBr\(^+\)), indicating no H-shift between the two carbons, as in the case of C\(_2\)H\(_3\)D\(_2\)Cl\(^+\).

In the MI mass spectra both isomers showed the fragment C\(_2\)H\(_3\)\(^+\), with the same extremely small KER value (T\(_{0.5}\) = 0.1-0.2 meV). The D-labelling experiments again showed a strong isotope effect (MI, 14; CID, 1.06). Furthermore, the observation of H\(_2\)Br\(^+\) in the CID mass spectra of the two isomers confirmed the proposal that the fragmentation may involve another isomer, either CH\(_2\)CHBrH\(^+\) or an ion-neutral complex [C\(_2\)H\(_3\)\(^+\) : BrH] which also will be discussed later. The binding energy in this complex is probably less than that in the complex [C\(_2\)H\(_3\)\(^+\) : ClH] (4.5 kcalmol\(^{-1}\))\(^{111}\).

The NR mass spectra of both isomers Ic and IIc (Figures 3.4 and 3.5) showed a small recovery signal. However, the fragmentation of the two isomers was still distinguishable in the region CBr\(^+\), CHBr\(^+\) and CH\(_2\)Br\(^+\), indicating no interconversion.
between the two C₂H₄Br radicals. In Figure 3.4, a large recovery signal was observed in
the 3ffr NR mass spectrum of CH₃CHBr⁺, indicating less dissociation of neutral
CH₃CHBr⁺. The very small recovery signal in Figure 3.5 indicates CH₂BrCH₂⁺ is less
stable than CH₃CHBr⁺ under these experimental conditions.

3.4.4 C₂H₃I⁺ isomers

In the MI mass spectra of C₂H₄I⁺, no dissociation by HI loss was observed,
indicating presumably that C₂H₃IH⁺ ions are not formed. Unlike the other C₂H₃X⁺ cations,
the CID mass spectra of C₂H₄I⁺ ions are not dominated by HI loss, but by C₂H₄ loss
instead, see Table 3.5 and Figures 3.6 and 3.7, even though the energy for C₂H₃⁺ + HI is
about 6 kealmol⁻¹ lower than that of I⁺ + C₂H₄, see Table 3.6. Thus the HI loss process
must have a higher activation energy than that for C₂H₄ loss. The CID mass spectra of
CH₃CHI⁺ (IId) and cyclic-CH₂ I⁺CH₂ (IIId) are distinguishable via the diagnostic CHI⁺⁺
and CH₂I⁺ peaks, see Table 3.5. The complete absence of CH₂I⁺ in the CID mass spectrum
of CH₃CHI⁺ shows that any H-shift is inaccessible by collision activation.

The NR mass spectra of the C₂H₄I⁺ isomers were dominated by I⁺ (~90%, Figures
3.6 and 3.7). No recovery signals were observed. If I⁺ was produced by the reionization of
I⁺ which may result from the dissociation of neutral C₂H₄I⁺, the C₂H₄⁺ ion should be also
observed, as the ionization energy of C₂H₄ (10.51 eV) is close to that of I (10.45 eV).
Thus the I⁺ is most likely produced from the dissociation of the reionized C₂H₄I⁺, which
may be formed in an excited state during neutralization-reionization process. This excited
C₂H₄⁺ ion dissociates completely to I⁺ + C₂H₄.
3.4.5 Some features of \( \text{C}_2\text{H}_4\text{X}^+ \) ions

3.4.5.1 \( \text{C}_2\text{H}_4\text{X}^+ \) and \([\text{C}_2\text{H}_3^+ \text{XH}]\) species

The very small KER values in the MI dissociations of \( \text{C}_2\text{H}_4\text{X}^+ \) (\( X = \text{Cl}, \text{Br} \)) indicate the possible existence of an ion-neutral complex \([\text{C}_2\text{H}_3^+ \text{XH}]\)\(^{[40]}\).

\[
\text{C}_2\text{H}_4\text{X}^+ \rightarrow \text{C}_2\text{H}_3\text{XH}^+ \rightarrow [\text{C}_2\text{H}_3^+ \text{XH}] \tag{7}
\]

The observed \( \text{H}_2\text{X}^+ \) in the CID mass spectra of \( \text{C}_2\text{H}_4\text{X}^+ \) (\( X = \text{Cl}, \text{Br} \)) supports this proposal. In such complexes, proton (or hydrogen) transfer is common\(^{[40]}\). Furthermore, the formation of \([\text{C}_2\text{H}_3^+ \text{XH}]\) involves an H-shift from carbon to halogen (reaction 7) and so there should be a strong isotope effect. This was indeed observed for the D-labelled \( \text{CD}_2\text{X}^+\text{CH}_2 \) (\( X = \text{Cl}, \text{Br} \)) ions which showed very strong isotope effects of 1:16, for \( X = \text{Cl} \), and 1:14, for \( X = \text{Br} \) in favour of \( \text{HX} \) loss.

The strong isotope effect was also observed in the \( \text{HCl} \) loss from \( \text{C}_2\text{H}_5\text{Cl}^+ \) ions.\(^{[41]}\) According to ab initio calculations this dissociation involves an ion-neutral complex \([\text{C}_2\text{H}_4^+ \text{HCl}]\).\(^{[42]}\) Thus the \( \text{HX} \) losses in the dissociations of \( \text{C}_2\text{H}_4\text{X}^+ \) and \( \text{C}_2\text{H}_5\text{X}^+ \) ions show similar features.

In the case of \( \text{C}_2\text{H}_4\text{F}^+ \), the HF loss was the chief high energy dissociation, but lost its importance among low energy ions. Thus a stable isomer may be produced if the precursor ion contains enough energy to pass over the isomerization barrier. This isomer is proposed to be \( \text{C}_2\text{H}_3\text{FH}^+ \). The difficulty in the formation of \( \text{C}_2\text{H}_3\text{FH}^+ \) (compared to \( \text{C}_2\text{H}_3\text{ClH}^+ \) and \( \text{C}_2\text{H}_3\text{BrH}^+ \)) could be explained by the lower proton affinity (PA) of fluorine,
compared to the PA of other small halogenated molecules, see Table 3.10.

However the PA of RI is the highest among RX (R = H, CH₂, CH₃, C₂H₃, C₂H₄, C₂H₅), and HI loss was not observed in the MI dissociation of C₂H₄I⁺. In the CID mass spectra of C₂H₄I⁺, the HI loss was overwhelmed by the C₂H₄ loss channel. The geometry of C₂H₄I⁺ has not been calculated. The C-I bond in C₂H₄I⁺ is expected to be longer than the C-X bond in C₂H₄X⁺ (X = F, Cl, Br) and so the energy barrier for the H-shift in C₂H₄I⁺ should be higher than that for the direct C-I bond cleavage.

3.4.5.2 H-shift in CH₃CHX⁺

An H-shift in CH₃CHX⁺ is required to account for the observation of CH₂X⁺ in the CID mass spectra of CH₃CHX⁺ ions.

\[
\begin{array}{c}
\text{H} \\
\text{CH₂ - CHX⁺} \\
\text{I (I)} \\
\rightarrow \\
\text{CH₂ - CH₂X} \\
\text{(III)} \\
\rightarrow \\
\text{CH₂X⁺ + CH₂} \\
\text{III (7)}
\end{array}
\]

According to some high level theoretical calculations, see Table 3.1, the average energy difference between I and III is ~ 31 kcal/mol for X = F[8,9] and ~ 21 kcal/mol for X = Cl[11] and Br[14]. However the energy barrier for CH₃CHCl⁺ isomerizing to ClCH₂CH₂⁺ is ~ 32 kcal/mol[11] which is higher than that for CH₃CHBr⁺ (21.8 kcal/mol[14]). Thus the H-shift from the CH₃ group to the CHX group requires an energy ranging from 22 - 32 kcal/mol. Note that for the classical ethyl cation, the carbon to carbon H-shift requires no energy[45].
3.4.5.3 Relative stabilities of $\text{C}_2\text{H}_4\text{X}^+$

The heats of formation of $\text{CH}_3\text{CHX}^+$ increased in going from $X = F$ to $X = I$, (see Table 3.2) and they can be related to the electronegativity (EN) of the halogens. Indeed, the $\Delta H_f^0$ values for $\text{CH}_3\text{CHX}^+$, $X = F$, Cl, Br, showed a linear relationship with $V_x$, see line 1 in Figure 3.8. The $V_x$ is a new scale of EN,\textsuperscript{[44]} and has been shown quantitatively to relate to the bond dissociation energies (BDE) of many common organic compounds.\textsuperscript{[45]} The linear relationship between $\Delta H_f$ (CH$_3$CHX$^+$) and $V_x$ reveals that the BDE C-X in CH$_3$CHX$^+$ determines the stability of CH$_3$CHX$^+$. From the slope of line 1, the heat of formation of CH$_3$CHI$^+$ can be estimated to be $\sim$ 219 kcalmol$^{-1}$.

The heats of formation of the cyclic ions CH$_2$X$^+$CH$_2$ ($X = \text{Cl, Br, I}$) also showed a linear relationship with $V_x$, see line 2 in Figure 3.8. The slope of line 2 is smaller than that of line 1. This reveals that the stability of cyclic-CH$_2$X$^+$CH$_2$ is not only affected by the EN of the halogens. Another factor affecting the stability of these latter ions is the polarizability of the halogen atoms, as shown in Figure 3.9, where the $\Delta \Delta H_f^0 = \Delta H_f^0$ (CH$_3$CHX$^+$) - $\Delta H_f^0$ (CH$_2$X$^+$CH$_2$). The higher polarizable atom (such as I) is showing that the cyclic species is more stable ($\Delta \Delta H_f^0 > 0$), because the halogen atom in CH$_2$X$^+$CH$_2$ will be polarized by the charge on C$_2$H$_4^{+}$+. Thus, in the case of CH$_2$X$^+$CH$_2$ ($X = \text{Br, I}$), the polarizability of X stabilizes the cation by a back electron donation. In contrast, the polarizability of X ($X = F, \text{Cl}$) destabilizes the cation by decreasing the BDE of C-X.
3.5 References


Table 3.1  The theoretically calculated relative energies (kcalmol⁻¹) of the C₂H₄X⁺ cations

<table>
<thead>
<tr>
<th></th>
<th>XCH₃CHX⁺</th>
<th>CH₂X⁺CH₂</th>
<th>XCH₂CH₂⁺</th>
<th>TS¹</th>
<th>CH₂CHXH⁺</th>
<th>Methods</th>
<th>Ref.</th>
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<td></td>
<td></td>
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1. Transition state of either H-bridged for CH₃CHX⁺ → XCH₂CH₂⁺ or X-bridged for XCH₂CH₂⁺ → 'CH₂CH₂X.
2. Transition state of H-bridged for CH₃CHX⁺ → XCH₂CH₂⁺.
3. Transition state of X-bridged for XCH₂CH₂⁺ → 'CH₂CH₂X.
4. An ion-neutral complex [C₂H₃⁺ CI⁻].
<table>
<thead>
<tr>
<th>CH₃CHX'</th>
<th>CH₂X'CH₂</th>
<th>Methods</th>
<th>Ref.</th>
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<td>ICR-PA²</td>
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<td></td>
<td>164.9</td>
<td>181.6</td>
<td>Estimation³</td>
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1. PIMS-AE: Photoionization mass spectrometry-Appearance energy measurements
2. ICR-PA: Ion cyclotron resonance mass spectrometry-Proton affinity measurements
3. Estimation by the method of equivalent cores
4. EREEM-AE: Energy resolved electrostatic electron monochromator-Appearance energy measurements
Table 3.3  Heats of formation of C₂H₄X radicals (kcalmol⁻¹)

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<th>CH₃CHX</th>
<th>CH₂XCH₂</th>
<th>Methods</th>
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1. EREEM-AE: Energy resolved electrostatic electron monochromator-Appearance energy measurements

Table 3.4  Kinetic energy release values (T₀,5, meV) of C₂H₄X⁺ cations

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<th>Cl</th>
<th>Br</th>
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<tr>
<td>I → C₂H₃⁺ + HX</td>
<td>445</td>
<td>1.4</td>
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<tr>
<td>II → C₂H₅⁺ + HX</td>
<td>461</td>
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Structure I = CH₃CHX⁺,  II = CHₓX⁺CH₂
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<td>(100)</td>
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<td>(27)</td>
<td>(19)</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;X&lt;sup&gt;+&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>12</td>
<td>20</td>
<td>7.7</td>
<td>3.6</td>
<td>3.2</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;X&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>1.1</td>
<td>1.1</td>
<td>8.0</td>
<td>3.0</td>
<td>2.5</td>
<td>1.3</td>
</tr>
<tr>
<td>X&lt;sup&gt;+&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>7.6</td>
<td>9.6</td>
<td>10</td>
<td>6.0</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;X&lt;sup&gt;+&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>4.4</td>
<td>5.0</td>
<td>4.9</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;X&lt;sup&gt;+&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>1.1</td>
<td>0.8</td>
<td>1.7</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CX&lt;sup&gt;+&lt;/sup&gt;</td>
<td>31</td>
<td>22</td>
<td>14</td>
<td>9.0</td>
<td>6.2</td>
<td>3.4</td>
<td>11</td>
<td>9.3</td>
</tr>
<tr>
<td>CHX&lt;sup&gt;+&lt;/sup&gt;</td>
<td>17</td>
<td>15</td>
<td>18</td>
<td>8.4</td>
<td>8.0</td>
<td>3.0</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;X&lt;sup&gt;+&lt;/sup&gt;</td>
<td>4.2</td>
<td>5.4</td>
<td>2.2</td>
<td>18</td>
<td>0.9</td>
<td>4.3</td>
<td>4.2</td>
<td>19</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;X&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.7</td>
<td>0.6</td>
<td>1.6</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;X&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>14</td>
<td>10</td>
<td>7.6</td>
<td>2.0</td>
<td>1.2</td>
<td>0.8</td>
<td>0.9</td>
<td>1.0</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;X&lt;sup&gt;+&lt;/sup&gt;</td>
<td>33</td>
<td>25</td>
<td>21</td>
<td>3.1</td>
<td>4.6</td>
<td>1.0</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;X&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>21</td>
<td>24</td>
<td>27</td>
<td>8.4</td>
<td>10</td>
<td>3.7</td>
<td>9.0</td>
<td>7.7</td>
</tr>
</tbody>
</table>

* He, 90% transmission; Values in parenthesis have been corrected for contributions from the MI mass spectrum.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\text{C}_2\text{H}_4\text{F}^+$</th>
<th>$\text{C}_2\text{H}_4\text{Cl}^+$</th>
<th>$\text{C}_2\text{H}_4\text{Br}^+$</th>
<th>$\text{C}_2\text{H}_4\text{I}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_3^+\text{HX}$</td>
<td>201</td>
<td>244</td>
<td>257</td>
<td>272</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4^++\text{X}^+$</td>
<td>274&lt;sup&gt;2&lt;/sup&gt;</td>
<td>284</td>
<td>282</td>
<td>281&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>$\text{X}^+\text{C}_2\text{H}_4$</td>
<td>433&lt;sup&gt;2&lt;/sup&gt;</td>
<td>340</td>
<td>311</td>
<td>278</td>
</tr>
<tr>
<td>$\text{HX}^++\text{C}_2\text{H}_3^+$</td>
<td>368&lt;sup&gt;2&lt;/sup&gt;</td>
<td>335</td>
<td>323</td>
<td>309&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>$\text{H}_2\text{X}^+\text{C}_2\text{H}_2$</td>
<td>238&lt;sup&gt;2&lt;/sup&gt;</td>
<td>261</td>
<td>272</td>
<td>279&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>$\text{CX}^+\text{CH}_4$</td>
<td>253</td>
<td>279</td>
<td>344</td>
<td>-</td>
</tr>
<tr>
<td>$\text{CHX}^++\text{CH}_3^+$</td>
<td>303</td>
<td>333</td>
<td>320</td>
<td>-</td>
</tr>
<tr>
<td>$\text{CH}_2\text{X}^+\text{CH}_2$</td>
<td>292</td>
<td>322</td>
<td>317</td>
<td>-</td>
</tr>
<tr>
<td>$\text{C}_2\text{HX}^++\text{H}_2+\text{H}^+$</td>
<td>337</td>
<td>357</td>
<td>349</td>
<td>-</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_3\text{X}^+\text{H}_2$</td>
<td>227</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_3\text{X}^+\text{H}^+$</td>
<td>258</td>
<td>288</td>
<td>297</td>
<td>298</td>
</tr>
</tbody>
</table>

1. All values from reference 38 in kcal mol<sup>-1</sup>. Some heats of formation of the cations are not available.

2. The fragment is not observed in CID mass spectrum of $\text{C}_2\text{H}_4\text{X}^+$. 

58
<table>
<thead>
<tr>
<th></th>
<th>Second field-free region</th>
<th>Third field-free region</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8 kV²</td>
<td>5 kV²</td>
</tr>
<tr>
<td>CH₃⁺</td>
<td>3.5</td>
<td>0.5</td>
</tr>
<tr>
<td>C₂H₂⁺⁺⁺</td>
<td>36</td>
<td>10</td>
</tr>
<tr>
<td>C₂H₅⁺</td>
<td>100</td>
<td>48</td>
</tr>
<tr>
<td>CF⁻</td>
<td>21</td>
<td>9.7</td>
</tr>
<tr>
<td>CHF⁺⁺⁺</td>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>CH₂F⁺</td>
<td>8.3</td>
<td>6.7</td>
</tr>
<tr>
<td>C₂F⁺</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>C₂HF⁺⁺</td>
<td>9.7</td>
<td>19</td>
</tr>
<tr>
<td>C₂H₂F⁺</td>
<td>25</td>
<td>64</td>
</tr>
<tr>
<td>C₂H₃F⁺⁺⁺</td>
<td>32</td>
<td>100</td>
</tr>
</tbody>
</table>

1. The C₂H₄F⁺ is produced from BrCH₂CH₂F⁺⁺⁺ and the collision gas is O₂ with 90% transmission of the ion current.
2. The translational energy.
3. The CID mass spectrum of C₂H₄F⁺, generated from MI of BrCH₂CH₂F⁺⁺⁺.
Table 3.8  The energies of the dissociation products of C_{2}H_{4}X\textsuperscript{1}

<table>
<thead>
<tr>
<th></th>
<th>C\textsubscript{2}H\textsubscript{4}F</th>
<th>C\textsubscript{2}H\textsubscript{4}Cl</th>
<th>C\textsubscript{2}H\textsubscript{4}Br</th>
<th>C\textsubscript{2}H\textsubscript{4}I</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{2}+CH\textsubscript{2}X</td>
<td>85</td>
<td>124</td>
<td>135</td>
<td>-</td>
</tr>
<tr>
<td>CH\textsubscript{3}+CHX</td>
<td>61</td>
<td>106</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{2}+HX</td>
<td>-2</td>
<td>41</td>
<td>54</td>
<td>69</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{2}+X</td>
<td>32</td>
<td>42</td>
<td>40</td>
<td>39</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{2}X+H</td>
<td>19</td>
<td>57</td>
<td>71</td>
<td>83</td>
</tr>
</tbody>
</table>

1. All values from reference 38 in kcal mol\textsuperscript{-1}. Some heats of formation of the neutrals are not available.

Table 3.9  Partial CID mass spectra of C\textsubscript{2}H\textsubscript{2}D\textsubscript{2}X\textsuperscript{+} (X = Cl, Br)

<table>
<thead>
<tr>
<th>Fragment ion</th>
<th>ClCH\textsubscript{2}CD\textsubscript{2}\textsuperscript{+}</th>
<th>ClCD\textsubscript{2}CH\textsubscript{2}\textsuperscript{+}</th>
<th>BrCH\textsubscript{2}CD\textsubscript{2}\textsuperscript{+}</th>
<th>BrCD\textsubscript{2}CH\textsubscript{2}\textsuperscript{+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CX\textsuperscript{+}</td>
<td>23</td>
<td>23</td>
<td>33</td>
<td>32</td>
</tr>
<tr>
<td>CHX\textsuperscript{++}</td>
<td>14</td>
<td>14</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH\textsubscript{2}X\textsuperscript{+}, CDX\textsuperscript{++}</td>
<td>33</td>
<td>33</td>
<td>42</td>
<td>45</td>
</tr>
<tr>
<td>CD\textsubscript{2}X\textsuperscript{+}</td>
<td>30</td>
<td>30</td>
<td>25</td>
<td>23</td>
</tr>
</tbody>
</table>

60
<table>
<thead>
<tr>
<th>X =</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂X</td>
<td>141</td>
<td>151</td>
<td>171</td>
<td>-</td>
</tr>
<tr>
<td>CH₃X</td>
<td>145</td>
<td>163</td>
<td>166</td>
<td>171</td>
</tr>
<tr>
<td>C₂H₃X</td>
<td>168</td>
<td>172</td>
<td>179</td>
<td>185</td>
</tr>
<tr>
<td>C₂H₅X</td>
<td>165</td>
<td>169</td>
<td>171</td>
<td>176</td>
</tr>
</tbody>
</table>

1. The values are taken from Reference 38.
Figure 3.1  The CID and NR mass spectra of CH₃CHF⁺

a. The CID mass spectrum of CH₃CHF⁺, O₂
b. The NR mass spectrum of CH₃CHF⁺ in 2fr, DMA/O₂
c. The NR mass spectrum of CH₃CHF⁺ in 3fr, DMA/O₂
Figure 3.2  The CID and NR mass spectra of CH₂CHCl⁺

a. The CID mass spectrum of CH₂CHCl⁺, O₂
b. The NR mass spectrum of CH₂CHCl⁺ in 2 ffr, DMA/O₂
c. The NR mass spectrum of CH₂CHCl⁺ in 3 ffr, DMA/O₂
Figure 3.3 The CID and NR mass spectra of CH$_2$Cl$^+$/CH$_2$ (IIb)

a. The CID mass spectrum of IIb, O$_2$

b. The NR mass spectrum of IIb in 2ffr, DMA/O$_2$

c. The NR mass spectrum of IIb in 3ffr, DMA/O$_2$
Figure 3.4  The CID and NR mass spectra of CH$_2$CHBr$^+$

a.  The CID mass spectrum of CH$_2$CHBr$^+$, O$_2$

b.  The NR mass spectrum of CH$_2$CHBr$^+$ in 2ffr, DMA/O$_2$

c.  The NR mass spectrum of CH$_2$CHBr$^+$ in 3ffr, DMA/O$_2$
Figure 3.5  The CID and NR mass spectra of $\text{CH}_2\text{Br}^+\text{CH}_2$ (IIc)
a. The CID mass spectrum of IIc, $\text{O}_2$
b. The NR mass spectrum of IIc in 2ffr, DMA/$\text{O}_2$
c. The NR mass spectrum of IIc in 3ffr, DMA/$\text{O}_2$
Figure 3.6 The CID and NR mass spectra of CH$_3$CHI$^+$ (Id)

a. The CID mass spectrum of Id, He
b. The NR mass spectrum of Id, Xe/O$_2$
Figure 3.7  The CID and NR mass spectra of CH₂-CH₃ (IIId)

a. The CID mass spectrum of IIId, He
b. The NR mass spectrum of IIId, Xe/O₂
Figure 3.8 $\Delta_f^0$ of $C_2H_xX$ vs $Vx$

- x Line 1, CH3CHX
- o Line 2, cyclic-CH2XCH2
Figure 3.9 \( \Delta \Delta H_f \) vs. \( \log \alpha \)

\[
\begin{array}{c|c|c|c|c}
\text{X} & F & Cl & Br & I \\
\hline
\log \alpha \text{ (polarizibility of X)} & -0.4 & -0.2 & 0 & 0.2 & 0.4 & 0.6 & 0.8 \\
\end{array}
\]

\( \Delta \Delta H_f \), kcal/mol

-10

0

10
Chapter 4

Halogen substituted triethylxonium ions

4.1 Introduction

The triethylxonium ion is a well known ethylating agent in the liquid phase. It is easily attacked by a nucleophile, which can be either an anion or a neutral, as shown in the following reactions:\[1\]

\[
(C_2H_5)_3O^+ + Y \rightarrow C_2H_5Y + (C_2H_5)_2O \tag{1}
\]

\[
(C_2H_5)_3O^+ + :Y \rightarrow C_2H_5Y^+ + (C_2H_5)_2O \tag{2}
\]

With both field desorption (FD) and fast atom bombardment (FAB) mass spectrometries \((C_2H_5)_3O^+, (Et_3O^+)\) was observed as an intact cation from the salt \((C_2H_5)_3O^+ Sb_2Cl_6\).\[2\] Whereas in a FD mass spectrometer the dissociation products of \((C_2H_5)_3O^+ SbCl_6\) are \((C_2H_5)_3O^+ (100\%), (C_2H_5)_2O^{\text{++}} (33\%)\) and \(C_2H_5Cl^{\text{++}} (23\%)\), in a FAB mass spectrometer the products are \((C_2H_5)_3O^+ (100\%), (C_2H_5)_2OH^+ (C_2H_4 loss, 52\%), C_2H_5O^+ (C_2H_6 loss, 55\%), C_2H_5OH_2^+ (68\%), C_2H_5O^+ (85\%)\) and \(C_2H_5^+ (95\%)\). The authors\[3\] indicated that the \(C_2H_5O^+\) was produced by \(C_2H_4\) loss from the cation. However recent studies on the triethylxonium ion in a ZAB-3F mass spectrometer\[3\] showed that in the metastable timeframe only \(C_2H_4\) loss was observed. The \((C_2H_5)_3O^+\) was derived from the ion-molecule reactions 3 and 4 in the ion source of the ZAB-3F mass spectrometer.

\[
(C_2H_5)_2O^{\text{++}} + C_2H_5I \rightarrow (C_2H_5)_3O^+ + I^+ \tag{3}
\]

\[
C_2H_5I^{\text{+++}} + (C_2H_5)_2O \rightarrow (C_2H_5)_3O^+ + I^+ \tag{4}
\]
Although the C$_2$H$_6$ loss (reaction 6) has a lower endothermicity than C$_2$H$_4$ loss (reaction 5), it was not observed in the MI mass spectrum of (C$_2$H$_3$)$_3$O$^+$ and was only a very weak peak in its CID mass spectrum.

\[
(C_2H_5)_3O^+ \rightarrow (C_2H_5)_2OH^+ + C_2H_4 \tag{5}
\]

\[
\Delta H_f^0 \quad 105 \quad 13 \quad \text{ kcal mol}^{-1}
\]

\[
(C_2H_5)_3O^+ \rightarrow C_4H_9O^+ + C_2H_6 \tag{6}
\]

\[
\Delta H_f^0 \quad 125 \quad -20 \quad \text{ kcal mol}^{-1}
\]

Based on the MI and CID mass spectra of various deuterium labelled precursors the authors\cite{1} proposed that the loss involves a simple β-H$^+$ transfer from ethyl to oxygen followed by the C$_2$H$_4$ loss from a protonated diethylether-ethene ion-molecule complex. Therefore the (C$_2$H$_5$)$_3$O$^+$ ion produced from Reactions 3 and 4 has structure a in which the C$_2$H$_5$ groups have classical configuration.

\[
\begin{array}{c}
(C_2H_5)_2O^+CH_2CH_3 \\
\quad a
\end{array}
\begin{array}{c}
(C_2H_5)_2O^+CH_2CH_3 \\
\quad b
\end{array}
\]

It was also proposed that the (C$_2$H$_5$)$_3$O$^+$ ion formed from reaction of protonated diethyl ether and C$_2$H$_3$I (reaction 7) has structure b in which one C$_2$H$_5$ group has a proton-bridged non-classical configuration. The observation of H/D mixing, which is the evidence for a non-classical structure ethyl group\cite{4}, supports the proposal of structure b.

\[
(C_2H_5)_2OH^+ + C_2H_3I \rightarrow (C_2H_5)_2O^+(C_2H_5) + HI \tag{7}
\]
 Whereas the C₂H₆ loss from (C₂H₅)₂O⁺ is only a very minor reaction,² it was a major MI reaction of the diethylhalonium ions, (C₂H₅)₂X⁺ (X = Cl and Br), as shown in the following.⁵

<table>
<thead>
<tr>
<th>X =</th>
<th>Cl</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensities (%)</td>
<td>74</td>
<td>39</td>
</tr>
<tr>
<td>(C₂H₅)₂X⁺ → CH₃CHX⁺ + C₂H₆</td>
<td>0.7</td>
<td>58</td>
</tr>
</tbody>
</table>

As shown above (C₂H₅)₂Cl⁺ and (C₂H₅)₂Br⁺ exhibited different behaviours in the C₂H₄ loss (reaction 9). The C₂H₄ loss was a minor peak in the MI mass spectrum of (C₂H₅)₂Cl⁺, whereas it was a major peak in the MI mass spectrum of (C₂H₅)₂Br⁺.

The diverse reactivity of the ethyl group in triethylxonium ions and diethylhalonium ions challenged us to investigate onium ions which contain both an oxygen atom and a halogen atom, e.g. (C₂H₅)₂O⁺C₂H₄X and C₂H₅OC₂H₄X⁺C₂H₅ ions.

4.2 Experimental

Electron impact (ionizing electron energy - 70 eV), metastable ion (MI), collision induced dissociation (CID) and collision induced dissociative ionization (CIDI) mass spectra were recorded⁶ using a modified VG Analytical ZAB-2F mass spectrometer with BEE geometry. Oxygen and helium were used for the collisional activation of ions. Oxygen was also used for the ionization of neutrals originating from metastable and collisionally activated ions. In all cases the target gases pressure reduced the main beam by 15%. In the MS/MS/MS experiments, ions formed in the second field-free region (2-FFR) by the metastable or collision induced dissociation of mass selected precursor ions, were transmitted into the 3-FFR and then collisionally activated. Recording the MI, CID and
CID mass spectra was carried out using the ZABCAT program.\textsuperscript{[68]} Kinetic energy release (KER) measurements have been performed on the same mass spectrometer at sufficient energy resolution to reduce the main ion beam width at half height to 3-5 V. The reproducibility of T\(_{0.5}\) values was better than 10%.

To produce theonium ions, precursor molecules were introduced into the ion source in about a 1:1 mixture. The total ion source pressure was set at 1-3 \times 10^{-5} \text{ mbar}.

4.3 Results and discussion

4.3.1 Observation of the halogen substituted triethylxonium ions

The halogen substituted triethylxonium ion \((\text{C}_2\text{H}_5)_2\text{O}^+\text{C}_2\text{H}_2\text{X}\) was observed in the normal mass spectra of mixtures of \(\text{C}_2\text{H}_4\text{XY} + (\text{C}_2\text{H}_5)_2\text{O} (X, Y = \text{Cl, Br})\) at m/z 137 (for \(X = \text{Cl}\)) and m/z 181 (for \(X = \text{Br}\)), as shown in Figure 4.1. No molecular adduct \((\text{C}_2\text{H}_5)_2\text{O}^+\text{C}_2\text{H}_2\text{XY}^+\) was detected. The oxonium ions formed from different \(\text{C}_2\text{H}_4\text{XY}\) precursors have different dissociation characteristics as shown in Table 4.1. Thus the ion formed from \(\text{XCH}_2\text{CH}_2\text{Y} + (\text{C}_2\text{H}_5)_2\text{O}\) is of type I and the ion formed from \(\text{XYCHCH}_3 + (\text{C}_2\text{H}_5)_2\text{O}\) is of type II. The subscripts a and b refer to \(X = \text{Cl}\) and \(X = \text{Br}\), respectively.

\[
\begin{align*}
\text{Ia} & \quad (X = \text{Cl}) \\
\text{Ib} & \quad (X = \text{Br}) \\
\text{Ila} & \quad (X = \text{Cl}) \\
\text{IIb} & \quad (X = \text{Br})
\end{align*}
\]

4.3.2 Formation of ions I and II

Ions I and II may be produced from the following reactions in the ion source:

\[
\begin{align*}
\text{C}_2\text{H}_4\text{XY}^+ (X=\text{Cl}, Y) + (\text{C}_2\text{H}_5)_2\text{O} &\rightarrow [(\text{C}_2\text{H}_5)_2\text{OC}_2\text{H}_2\text{XY}]^+ \rightarrow (\text{C}_2\text{H}_5)_2\text{OC}_2\text{H}_2\text{X}^+ + Y^+ \quad (10) \\
\text{C}_2\text{H}_4\text{XY} + (\text{C}_2\text{H}_5)_2\text{O}^+ &\rightarrow [(\text{C}_2\text{H}_5)_2\text{OC}_2\text{H}_2\text{XY}]^+ \rightarrow (\text{C}_2\text{H}_5)_2\text{OC}_2\text{H}_2\text{X}^+ + Y^+ \quad (11)
\end{align*}
\]
\[ C_2H_4XY^{**} + (C_2H_5)_2O \rightarrow C_2H_4X^+ + Y^+ + (C_2H_5)_2O \rightarrow (C_2H_5)_2OC_2H_4X^+ + Y^+ \] (12)

Although no molecular adduct was observed in the normal mass spectra, reactions 10 and 11 cannot be excluded if the lifetime of the adduct is \(< 10^{-6}\) s. However, reaction 11 is unlikely to produce the oxonium ions \(\text{I}^+\) and \(\text{II}^+\), since if the charge were located on the oxygen the halogen would be attracted to the charged oxygen, which is not a favorable geometry to form the oxonium ions. It is also shown in Table 4.2 that when the proportion of \((C_2H_5)_2O\) is high \((\text{ClCH}_2\text{CH}_2\text{Br} / (C_2H_5)_2O = 1:3)\) the yield of the oxonium ions is the lowest. This indicates that the high \((C_2H_5)_2O^{**}\) concentration does not favor the formation of \(\text{I}\).

Reaction 12 is also unlikely. If it were the case, the yield of the oxonium ion would be only proportional to the intensity of \(C_2H_4X^+\) no matter what kind of precursor was used. However, when the precursor is \(\text{ClCH}_2\text{CH}_2\text{Br}\) the ratio of \(\text{Ib}^+\) to \(C_2H_4Br^+\) is 0.11 and when the precursor is \(\text{BrCH}_2\text{CH}_2\text{Br}\) the ratio of \(\text{Ib}^+\) to \(C_2H_4Br^+\) is 0.02. Reaction 10 is the most plausible. The overall reaction is an addition-elimination process, as shown in Scheme 4.1.

\[
\begin{align*}
X\text{CH}_2\text{CH}_2\text{Br}^{**} + (C_2H_5)_2O & \rightarrow [X\text{CH}_2\text{CH}_2] \rightarrow X\text{CH}_2\text{CH}_2\text{O}^+(C_2H_5)_2 + \text{Br}^- \\
& \text{O}(C_2H_5)_2 \\
\text{Br}^{**} \\
\text{CH}_3\text{CHXBr}^{**} + (C_2H_5)_2O & \rightarrow [\text{CH}_3\text{CHX}] \rightarrow \text{CH}_3\text{CH}(X)\text{O}^+(C_2H_5)_2 + \text{Br}^- \\
& \text{O}(C_2H_5)_2
\end{align*}
\]

Scheme 4.1

75
Three observations support this mechanism:

(i) It is shown in Table 4.2 that when the ratio of \( \text{ClCH}_2\text{CH}_2\text{Br} \) (or \( \text{BrCH}_2\text{CH}_2\text{Br} \)) : \( \text{(C}_2\text{H}_5\text{)}_2\text{O} \) is 1:1 the yield of \((\text{C}_2\text{H}_5)_2\text{O}^+\text{CH}_2\text{CH}_2\text{Cl} \) (Ia) or \((\text{C}_2\text{H}_5)_2\text{O}^+\text{CH}_2\text{CH}_2\text{Br} \) (Ib) is greater than that at ratios 1:3 and 3:1. Both low concentrations of \( \text{XCH}_2\text{CH}_2\text{Y}^{++} \) and low concentrations of \((\text{C}_2\text{H}_5)_2\text{O} \) will lower the yield of I.

(ii) It is also shown in Table 4.2 that the yield of Ib is higher when the precursor is \( \text{BrCH}_2\text{CH}_2\text{Br} \) than when the precursor is \( \text{BrCH}_2\text{CH}_2\text{Cl} \). This is expected by the Scheme 4.1 since Br is a better leaving atom (i.e., more weakly bonded) than Cl.

(iii) The much lower yield of \((\text{C}_2\text{H}_5)_2\text{O}^+\text{CHXCH}_3 \) (II) than that of I may be accounted for by both the shielding effect and steric effect of the X atom on the \( \alpha \)-position.

In Scheme 4.1 the oxonium ions I and II are formed by the covalent binding of O-C as \((\text{C}_2\text{H}_5)_2\text{O}^+\text{C}_2\text{H}_5\text{X} \) isomers. Ion I has the halogen on the \( \beta \)-position and ion II has the halogen on the \( \alpha \)-position. It is shown in Table 4.3 that the dissociation of I is not affected by the composition in the ion source, indicating I is a thermochemically stable species. As a halogen substituted triethylxonium ion both I and II should have some reactions in common with \((\text{C}_2\text{H}_5)_2\text{O}^+ \), which shows the major dissociation by \( \text{C}_2\text{H}_4 \) loss. In addition I and II may have some specific reaction related to the halogen atom. Moreover since I and II have the halogen atom in different positions (\( \beta \)- and \( \alpha \)-), the isomers should display different dissociation characteristics.

4.3.3 Fragmentation of \((\text{C}_2\text{H}_5)_2\text{O}^+\text{CH}_2\text{CH}_2\text{X} \) (I)

From the MI and CID mass spectra of Ia and Ib (Table 4.1) and the CIDI mass spectra of Ia and Ib (Figure 4.2) their dissociations can be characterized by \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_5\text{X}, \)
and (C\textsubscript{2}H\textsubscript{3})\textsubscript{2}O losses as shown in reactions 13-15.

\[

tables
\]

\[
\begin{array}{c}
\text{Product Enthalpies, kcalmol}^{-1} \\
X = \text{Cl} & \text{Br} \\
(C\textsubscript{2}H\textsubscript{3})\textsubscript{2}O*CH\textsubscript{2}CH\textsubscript{2}X & \rightarrow C\textsubscript{2}H\textsubscript{5}O* + C\textsubscript{2}H\textsubscript{4} & 117 & 128 & (13) \\
& \rightarrow C\textsubscript{2}H\textsubscript{5}O* + C\textsubscript{2}H\textsubscript{5}X & 124 & 136 & (14) \\
& \rightarrow C\textsubscript{2}H\textsubscript{4}X* + (C\textsubscript{2}H\textsubscript{3})\textsubscript{2}O & 142\pm2 & 146\pm1 & (15)
\end{array}
\]

The product enthalpies were obtained either from Reference 7 or from the estimations which will be discussed in 4.3.6. The above values show that the C\textsubscript{2}H\textsubscript{4} loss has the lowest endothermicity and the (C\textsubscript{2}H\textsubscript{3})\textsubscript{2}O loss has the highest endothermicity among these three MI dissociations. The energy differences between the two processes are 25 kcalmol\textsuperscript{-1} and 18 kcalmol\textsuperscript{-1} for Ia and Ib, respectively. Reactions 13 and 14 were not sensitive to collisional activation indicating the involvement of other intermediates or isomers. However, reaction 15 was sensitive to collision indicating it is a direct bond cleavage without involving other intermediates. The different kinetic energy release (KER) values for the (C\textsubscript{2}H\textsubscript{3})\textsubscript{2}O loss (Ia, 109 meV; Ib, 33 meV) indicate different reverse energy barriers. In the MI mass spectrum of Ib the (C\textsubscript{2}H\textsubscript{3})\textsubscript{2}O loss (48%) was competitive with C\textsubscript{2}H\textsubscript{4} loss (100%), even though it is 18 kcalmol\textsuperscript{-1} more endothermic, indicating that C\textsubscript{2}H\textsubscript{4} loss involved an energy barrier of this magnitude for either dissociation or isomerization. The latter is pronounced since this process was insensitive to collisional activation and the KER values were relatively small (Ia, 38 meV; Ib, 26 meV).

The weak signal of C\textsubscript{2}H\textsubscript{4}Cl\textsuperscript{+} in the MI mass spectrum of Ia may be accounted for by collision induced dissociation by residual gas in the field-free region. Thus the energy barrier for Ia to dissociate via (C\textsubscript{2}H\textsubscript{3})\textsubscript{2}O loss is much higher than that for Ib to dissociate.
via \((\text{C}_2\text{H}_5)_2\text{O}\) loss. This explains why the KER value for \((\text{C}_2\text{H}_5)_2\text{O}\) loss from \text{Ia} is greater than that from \text{Ib}.

Another common fragmentation in the MI mass spectra of \text{Ia} and \text{Ib} is \text{C}_2\text{H}_3\text{X} loss. In the MI mass spectrum of \text{Ia} the relative intensity of \text{C}_2\text{H}_3\text{Cl} loss was \(\sim 13\%\) of that for \text{C}_2\text{H}_4 loss and it was not sensitive to collision activation, indicating that another isomer may be involved. This will be discussed later in detail (4.3.5). The energy barrier for \text{C}_2\text{H}_3\text{Cl} loss is approximately 5-10 kcal\text{mol}^{-1} higher than the energy barrier for \text{C}_2\text{H}_4 loss.

In the MI mass spectrum of \text{Ib} the relative intensity of \text{C}_2\text{H}_3\text{Br} loss was \(\sim 6\%\) of that of \text{C}_2\text{H}_4 loss and it was collision sensitive. Thus the energy barrier for \text{C}_2\text{H}_3\text{Br} loss is approximately \(\geq 10\) kcal\text{mol}^{-1} higher than the energy barrier for \text{C}_2\text{H}_4 loss. The discussion of the above thermochemistry will be presented in 4.3.6.

4.3.3.1 \text{C}_2\text{H}_4 loss

The MI and CID mass spectra of both \text{Ia} and \text{Ib} (Table 4.1) are dominated by \text{C}_2\text{H}_4 loss. The ionic product is \text{C}_2\text{H}_{10}\text{OX}^\ast, which was examined by recording its CID mass spectra (Table 4.4) and found be \text{C}_2\text{H}_5\text{O}^\ast(\text{H})\text{CH}_2\text{CH}_2\text{X}. This reaction resembles the \text{C}_2\text{H}_4 loss from \((\text{C}_3\text{H}_5)_3\text{O}^\ast\) which produced \text{C}_2\text{H}_5\text{O}^\ast(\text{H})\text{C}_2\text{H}_5^\text{[6]}. The deuterium labelling experiments showed that the \text{C}_2\text{H}_4 lost from \text{Ia} and \text{Ib} originates only from the diethyl ether and that the hydrogen transferred to the oxygen originated in the methyl group of the diethyl ether (Table 4.5).

\[
\begin{align*}
(\text{C}_2\text{H}_5)_2\text{O}^\ast\text{CD}_2\text{CD}_2\text{X} & \rightarrow \text{C}_2\text{H}_5\text{O}^\ast(\text{H})\text{C}_2\text{D}_4\text{X} \quad + \quad \text{C}_2\text{H}_4 & \quad (16) \\
\text{CD}_3\text{CH}_2\text{O}^\ast(\text{C}_2\text{H}_5)\text{C}_2\text{H}_\text{X} & \rightarrow \text{C}_2\text{H}_5\text{O}^\ast(\text{D})\text{C}_2\text{H}_4\text{X} \quad + \quad \text{C}_2\text{H}_2\text{D}_2; \\
& \rightarrow \text{CD}_3\text{CH}_2\text{O}^\ast(\text{H})\text{C}_2\text{H}_\text{X} \quad + \quad \text{C}_2\text{H}_4 & \quad (17)
\end{align*}
\]
The isotope effect for this process was obtained from the ratio of $\text{C}_4\text{H}_7\text{D}_3\text{OX}^*$ to $\text{C}_4\text{H}_7\text{DOX}^*$ (Table 4.5) in the MI mass spectrum of $\text{CD}_3\text{CH}_2\text{O(C}_2\text{H}_5)\text{C}_2\text{H}_2\text{X}^*$. The values are 100/49 and 100/51 for $\text{X} = \text{Cl}$ and $\text{Br}$, respectively. This result indicates the existence of a transition state TS (Scheme 4.2) involving direct transfer of $\text{H}$ or $\text{D}$ in a rate determining step. It is generally observed that a transition state involving a direct hydrogen transfer will result in a significant isotope effect.\(^8\) Compared to the dissociation of $(\text{C}_2\text{H}_5)_3\text{O}^*$ \(^{10}\) an ion-neutral complex $[\text{C}_2\text{H}_5\text{O(C}_2\text{H}_5\text{X})\text{H}^*-*\text{C}_2\text{H}_4]$. $\text{Cl}$ (Scheme 4.2) may be involved in this process, although the KER values ($T_{\text{0.5}} = 26-38$ meV, Table 1) are not small enough to support such a proposal.

\[
\begin{align*}
\text{H-CH}_2
\end{align*}
\]

\[
\begin{align*}
(\text{C}_2\text{H}_5)_2\text{O}^+\text{CH}_2\text{CH}_2\text{X} \rightarrow \text{CH}_2\text{CH}_2\text{O}^+\text{CH}_2 \rightarrow [\text{C}_2\text{H}_5\text{O}^+\text{H}^+\text{C}_2\text{H}_4] \rightarrow \text{C}_2\text{H}_5\text{O}(\text{H})\text{CH}_2\text{CH}_2\text{X}^+\text{C}_2\text{H}_4
\end{align*}
\]

(I)

\[
\begin{align*}
\text{XCH}_2\text{CH}_2
\end{align*}
\]

(TS)

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{X}
\end{align*}
\]

(CI)

Scheme 4.2

It is also noticeable that no $\text{H/D}$ exchange was observed in this process. Harrison suggested\(^9\) that when the $\Delta\text{PA}$ of the two partners is $> 12$ kcal mol$^{-1}$ there would be no $\text{H/D}$ exchange. Since the PA of $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{X}$ is $\sim 200$ kcal mol$^{-1}$ (assumed to be the same as $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$\(^7\) and the PA of $\text{C}_2\text{H}_4$ is 163 kcal mol$^{-1}$\(^7\) the $\Delta\text{PA}$ is larger than the suggested limit. Therefore the observation of no $\text{H/D}$ exchange is reasonable. However, the absence of $\text{H/D}$ exchange in the dissociation of $\text{D}$-labelled Ia and Ib indicates that their ethyl groups must likely have the classical configuration.\(^3\)
4.3.3.2 C₂H₅X loss

In the MI and CID mass spectra of Ia and Ib (Table 4.1) the second most important fragment is C₂H₅O⁺, corresponding to a C₂H₅X loss. The intensity of C₂H₅O⁺ in the MI mass spectra of Ia and Ib is 6 - 13 % of the major peak C₂H₁₀OX⁺. The CID1 mass spectra of Ia and Ib (Figure 4.2) further confirmed the lost neutrals to be C₂H₅X. The deuterium labelling experiments showed that the C₂H₅ in the C₂H₅X lost originates from the diethylether (Table 4.5).

\[(C₂H₅)₂O⁺CD₂CD₂X → C₂H₅OC₂D₄⁺ + C₂H₅X\]  \hspace{1cm} (18)

\[CD₃CH₂O⁺(C₂H₅)C₂H₅X → CD₃CH₂OC₂H₄⁺ + C₂H₅X; \]
\[C₂H₅OC₂H₄⁺ + C₂H₂D₃X\]  \hspace{1cm} (19)

Two possible mechanisms which account for this C₂H₅X loss (Scheme 4.3) are a concerted reaction (1,3-elimination) or one involving an intermediate halonium ion C₂H₅OC₂HLX⁺C₂H₅ (III).

\[
\text{I } → \text{CH₃CH₂-O-CH₂CH₂} \quad \text{1,3 elimination} \quad \text{C₂H₅OC₂H₄⁺ + C₂H₅X}
\]

\[\hspace{1cm} \text{CH₃CH₂} \quad \text{X} \quad \text{CH₃CH₂} \hspace{1cm} \]

\[(\text{III})\]

Scheme 4.3

It is shown in the energy diagram (Figure 4.11) that the isomers IIIa (ΔᵣH⁰ 114 kca/mol) and IIIb (ΔᵣH⁰ 123 kca/mol) lie below the dissociation limit for reaction (18), even though they are higher in energy than isomers Ia (ΔᵣH⁰ 93 kca/mol) and Ib (ΔᵣH⁰
104 kcal mol$^{-1}$). The smaller KER value of IIIa (T$_{0.5}$, 22 meV, Table 4.7) in the MI dissociation via C$_2$H$_5$Cl loss, compared to that of Ia (T$_{0.5}$, 34 meV) illustrated that the isomerization barrier from Ia to IIIa is higher than the product enthalpies, thus only the Ia ions containing higher internal energy can isomerize to IIIa and release more kinetic energy in dissociation via C$_2$H$_5$Cl loss than stable IIIa ions.

That I having isomerized to III showed C$_2$H$_5$Cl loss could explain the absence of C$_2$H$_6$ loss from (C$_2$H$_5$)$_3$O$^+$ ions$^{[3]}$ which cannot form isomers such as III. Moreover, the proposed C$_2$H$_6$ loss in the dissociations of (C$_2$H$_5$)$_3$O$^+$SbCl$_5^-$ in FAB mass spectrometry$^{[2]}$ could possibly be C$_2$H$_5$Cl loss instead.

The structure of the ionic product C$_2$H$_5$O$^+$ in the dissociation of I via C$_2$H$_5$X loss is most likely C$_2$H$_5$O$^+$CHCH$_3^{[10]}$ (Figure 4.3). However the instantly formed species could be C$_2$H$_5$OCH$_2$CH$_2^+$, which rapidly isomerized to the more stable isomer C$_2$H$_5$O$^+$CHCH$_3$ on the time scale of $< 10^{-5}$ s.

In the CID mass spectra of Ia and Ib (Table 4.1), the fragments C$_2$H$_6$OX$^+$ and C$_2$H$_5$O$^+$ are the results of two consecutive neutral losses, as shown in reactions 20 and 21. The structure of C$_2$H$_5$O$^+$ was shown by its CID mass spectrum to be CH$_3$CHOH$^+$ (Figure 4.4 a) and the structure of C$_2$H$_6$OX$^+$ was found similarly to be H$_2$OC$_2$H$_4$X$^+$ (Figure 4.4 b).

\[
\begin{align*}
(C_2H_5)_2O^+CH_2CH_2X & \rightarrow C_2H_5O^+(H)CH_2CH_2X & \rightarrow & \text{H}_2O^+CH_2CH_2X (20) \\
(C_2H_5)_2O^+CH_2CH_2X & \rightarrow C_2H_5OC_2H_4^+ & \rightarrow & \text{CH}_3\text{CHOH}^+ (21)
\end{align*}
\]
4.3.3.3 (C₂H₅)₂O loss

The loss of (C₂H₅)₂O is a major fragment in the MI dissociation of Ib, but is only a minor peak in the MI mass spectrum of Ia (Table 4.1). A deuterium labelling experiment (Table 4.5) confirmed that the dissociation is an O–C bond cleavage.

\[
(C₂H₅)₂OCD₂CD₂X \longrightarrow C₂D₄X^+ + (C₂H₅)₂O
\]  

The CID mass spectra of C₂H₄X⁺ ions produced from I are similar to the CID mass spectra of CH₂X⁺CH₂ produced from CH₂XCH₂Y⁺ via Y⁺ loss (Y = Cl or Br, Figure 4.5), indicating that the cyclic structure CH₂X⁺CH₂ was formed from the (C₂H₅)₂O loss. The high reverse energy barrier (T₀.₅ = 109 meV) in the formation of CH₂Cl⁺CH₂ from Ia may be indicative of the O–C bond cleavage being followed by isomerization of ClCH₂CH₂⁺ to a more stable CH₂Cl⁺CH₂. In the dissociation of Ib the relatively smaller KER value (T₀.₅ = 33 meV) may be accounted for by the concerted formation of the cyclic CH₂Br⁺CH₂ at the same time as the O–C bond cleavage. In MI dissociations of Ib the (C₂H₅)₂O loss (48%) was competitive with C₂H₄ loss (100%) indicating that the two processes have similar activation energies. In contrast, the dissociation of Ia by (C₂H₅)₂O loss (3%) has a significantly higher activation energy than C₂H₄ loss (100%).

In summary, (C₂H₅)₂O⁺CH₂CH₂X (X = Cl and Br), formed from BrCH₂CH₂X⁺ + (C₂H₅)₂O - Br, is a covalently bound species. The C₂H₄ loss from I is a similar process to that from (C₂H₅)₃O⁺. The C₂H₅X loss indicates the involvement of an isomer III, which is the dissociation configuration for C₂H₅X loss. This result leads to the conclusion that
when the halogen is substituted at the β-position, it will show strong tendency to form a C-X bond. According to the fragment intensities in the MI mass spectra of Ia and Ib the activation energy for O-C bond cleavage of I increases in the following series:

\[
\text{C}_2\text{H}_5\text{O}^+\text{[(C}_2\text{H}_4\text{X})\text{-CH}_2\text{CH}_3] < (\text{C}_2\text{H}_5)_2\text{O}^+\text{-CH}_2\text{CH}_2\text{Br} < (\text{C}_2\text{H}_5)_2\text{O}^+\text{-CH}_2\text{CH}_2\text{Cl}
\]

4.3.4 Fragmentation of (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}O*CHXCH\textsubscript{3} (II)

The MI and CID mass spectra of (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}O*CHXCH\textsubscript{3} (II\textsubscript{a}, X = Cl; II\textsubscript{b}, X = Br) formed from the reaction of XCH\textsubscript{2}CH\textsubscript{3} + (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}O - Y are given in Table 4.1. The CID mass spectra of II\textsubscript{a} and II\textsubscript{b} are shown in Figure 4.6. The MI dissociations of ions Ia and Ib are characterized by C\textsubscript{2}H\textsubscript{5}X, C\textsubscript{2}H\textsubscript{4}, and (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}O losses.

<table>
<thead>
<tr>
<th>Relative intensity (%)</th>
<th>X</th>
<th>Cl</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C\textsubscript{2}H\textsubscript{5})\textsubscript{2}O<em>CHXCH\textsubscript{3} → C\textsubscript{2}H\textsubscript{11}O</em> + C\textsubscript{2}H\textsubscript{5}X</td>
<td>100</td>
<td>100</td>
<td>(23)</td>
</tr>
<tr>
<td>→ C\textsubscript{2}H\textsubscript{10}OX* + C\textsubscript{2}H\textsubscript{4}</td>
<td>2</td>
<td>3</td>
<td>(24)</td>
</tr>
<tr>
<td>→ C\textsubscript{2}H\textsubscript{3}X* + (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}O</td>
<td>-</td>
<td>7</td>
<td>(25)</td>
</tr>
</tbody>
</table>

Unlike the MI dissociations of I, which showed C\textsubscript{2}H\textsubscript{4} loss as the major process, the MI dissociations of II showed C\textsubscript{2}H\textsubscript{5}X loss as the dominant fragmentation. Even though C\textsubscript{2}H\textsubscript{4} loss has approximately the same endothermicity as C\textsubscript{2}H\textsubscript{5}X loss, its intensity was only 2-3% of that of C\textsubscript{2}H\textsubscript{5}X loss. The different intensities may indicate the different energy barriers for the hydrogen shift, since the two processes involve a hydrogen shift from the C\textsubscript{2}H\textsubscript{4}X group or the C\textsubscript{2}H\textsubscript{5} group to the oxygen.
4.3.4.1 \( \text{C}_2\text{H}_3\text{X} \) loss

The dissociations of IIa and IIb are dominated by \( \text{C}_2\text{H}_3\text{X} \) loss, (reaction 23). The CID mass spectrum of the product \( \text{C}_2\text{H}_1\text{_{11}}\text{O}^+ \) ions (Figure 4.7) is identical to that of protonated diethyl ether \( (\text{CH}_3\text{CH}_2)_2\text{OH}^+ \). The deuterium labelled ion \( (\text{C}_2\text{D}_3)_2\text{O}^+\text{CH(Cl)}\text{CH}_3 \) dissociated to \( (\text{C}_2\text{D}_3)_2\text{OH}^+ + \text{C}_2\text{H}_3\text{Cl} \) without H/D exchange, which confirmed that this reaction involves a hydrogen transfer from haloethyl to the diethyl ether, as shown in Scheme 4.4.

\[
\begin{align*}
\text{H-CH}_2 \\
\text{II} \rightarrow (\text{C}_2\text{H}_3)_2\text{O-CHX} \rightarrow (\text{C}_2\text{H}_3)_2\text{OH}^+ + \text{C}_2\text{H}_3\text{X}
\end{align*}
\]

Scheme 4.4

Heck et al.\(^{111}\) investigated the reactions between \( \text{CH}_3\text{CHX} \) and \( \text{D}_2\text{O} \) by ICR-MS. It was shown that the total population of the ions rapidly exchanges up to three hydrogen atoms for deuterium atoms. It was proposed that the three chemically identical methyl hydrogen atoms can be involved in the reaction with water. No fourth hydrogen atom exchange was observed because the exchange of the \( \alpha \)-hydrogen atom was energetically inaccessible. From this point of view, the proton in adduct IIa and IIb likely originated from the methyl hydrogens in the \( \text{CH}_3\text{CHX}^+ \) ion.

The major \( \text{C}_2\text{H}_3\text{X} \) loss from II indicates that the \( (\text{C}_2\text{H}_3)_2\text{O}^+ \cdot \text{CHXCH}_3 \) bond must be weaker than the \( (\text{C}_2\text{H}_3)_2\text{O}^+\text{CH}_2\text{CH}_2\text{X} \) and \( \text{C}_2\text{H}_5\text{O}^+(\text{C}_2\text{H}_4\text{X})\cdot\text{CH}_2\text{CH}_3 \) bonds.
4.3.4.2 C$_2$H$_4$ loss

Ethene loss, which is predominant in the dissociations of ion I, is only a minor process in the dissociations of ion II. The ionic fragment C$_{4}$H$_{10}$OX$^+$, produced in reaction 24, is different from that produced in reaction 13. It is shown in Figure 4.7 that the major fragment in the former ion's CID mass spectra is C$_2$H$_3$O$^+$, corresponding to C$_2$H$_3$X loss. The C$_{4}$H$_{10}$OX$^+$ ions produced from C$_2$H$_4$ loss from I, however, prefer lose C$_2$H$_4$ (Table 4.4). This result reveals that the C$_2$H$_4$X groups in the two C$_{4}$H$_{10}$OX$^+$ isomers (I - C$_2$H$_4$ and II - C$_2$H$_4$) are indeed completely different (Scheme 4.5) and so confirms that the (C$_2$H$_3$)$_2$O$^+$C$_2$H$_4$X isomers (I and II) are in no way interconvertible.

\[
\begin{align*}
\text{I} & \quad \xrightarrow{-\text{C}_2\text{H}_4} \quad \text{C}_2\text{H}_3\text{O}^+(\text{H})\text{CH}_2\text{CH}_2\text{X} \quad \rightarrow \quad \text{H}_2\text{O}^+\text{CH}_2\text{CH}_2\text{X} + \text{C}_2\text{H}_4 \\
\text{II} & \quad \xrightarrow{-\text{C}_2\text{H}_4} \quad \text{C}_2\text{H}_5\text{O}^+(\text{H})\text{CH}(\text{X})\text{CH}_3 \quad \rightarrow \quad \text{H}_2\text{O}^+\text{C}_2\text{H}_5 + \text{C}_2\text{H}_3\text{X}
\end{align*}
\]

Scheme 4.5

The C$_2$H$_3$X loss in the CID mass spectrum of C$_{4}$H$_{10}$OX$^+$ (II - C$_2$H$_4$) indicated that the X is still at the $\alpha$-position, i.e. the ion is C$_2$H$_5$O$^+(\text{H})\text{CHXCH}_3$. An ion-neutral complex, [C$_2$H$_6$O(CHXCH$_3$)H$^+$$\cdots$C$_2$H$_4$] (C2) could be involved in the dissociation of II via C$_2$H$_4$ loss.

The different behaviours of II and I shows that when X is on the $\alpha$-position (II), it promoted the hydrogen transfer from the neighbouring methyl group (C$_2$H$_2$X loss) and the hydrogen transfer from the ethyl group (C$_2$H$_4$ loss) was less competitive. When X sits at the $\beta$-position (I), the hydrogen transfer originated only from the ethyl group. A
comparison of all the hydrogen transfers in I and II showed that the activity of hydrogen decreases in the following series:

$$\text{(C}_2\text{H}_5\text{)}_2\text{OCHXCH}_2 - \text{H} > \text{XC}_2\text{H}_4\text{O}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2 - \text{H} > \text{(C}_2\text{H}_5\text{)}_2\text{OCH}_2\text{CHX} - \text{H}$$

(II) (I) & (II) (I)

4.3.4.3 (C₂H₅)₂O loss

The loss of (C₂H₅)₂O is a major fragmentation in the MI dissociation of IIb, but is not observed in the MI mass spectrum of IIa (Table 4.1). The CID mass spectrum of the daughter ion C₂H₄Br⁺ confirmed its structure as CH₃CHBr⁺. Thus the dissociation is a simple bond cleavage producing CH₃CHBr⁺ + (C₂H₅)₂O. This shows that there is no hydrogen shift between the two carbons in the haloethyl group, and again the isomers I and II are not interconvertible with each other.

4.3.5 Reaction of C₂H₅I⁺ + ClCH₂CH₂OC₂H₅

The gas-phase diethylhalonium ions have been thoroughly studied.⁵,¹² To search for the possible formation of CH₃CH₂OCH₂CH₂X⁺CH₂CH₃ (III), an ethoxy diethylhalonium ion, we investigated the reaction between CH₃CH₂OCH₂CH₂Cl and C₂H₅I⁺. Unlike the system of C₂H₅OC₂H₅ + C₂H₄ClBr⁺, which showed no molecular adducts, the molecular adduct ion of ClCH₂CH₂OCH₂CH₃⁺C₂H₅I⁺ (A, m/z 264) was observed in the normal mass spectrum of C₂H₅I⁺ + ClCH₂CH₂OCH₂CH₃ (Figure 4.8). The MI and CID mass spectra of A (Table 4.6) showed a major fragment C₄H₉OCl⁺ (IIIa, m/z 137), corresponding to I loss. The MI and CID mass spectra of IIIa are given in Table 4.7, and they showed the same fragments as Ia but with a different ratio of C₄H₉O⁺ / C₆H₁₀ClO⁺.
(Table 4.1). Figure 4.9 shows the same structure of \(\text{C}_2\text{H}_5\text{O}^+(\text{H})\text{CH}_2\text{CH}_2\text{Cl}\) from IIIa - C\(_2\text{H}_4\) as produced from Ia - C\(_2\text{H}_4\) (Table 4.4). Two possible C\(_2\text{H}_4\text{OCl}^+\) isomers could be formed and may be interconvertible, as shown in Scheme 4.6.

A comparison of deuterium labelled IIIa and Ia is given in Table 4.8, which showed that ion IIIa from \{ Cl\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{CH}_3\text{CD}_2\text{I}^+ \} - I lost more \text{CH}_3\text{CD}_2\text{Cl} \) (or CD\(_3\)CH\(_2\)Cl) than \text{CH}_3\text{CH}_2\text{Cl}. The CID mass spectrum of metastably generated IIIa showed an even higher ratio of C\(_2\text{H}_5\text{O}^+/\text{C}_4\text{H}_{10}\text{ClO}^+. Furthermore the CIDI mass spectrum of IIIa (Figure 4.10) barely showed (C\(_2\text{H}_5\))\(_2\text{O}^+, but only C\(_2\text{H}_5\text{Cl}^-\). Those results support the proposal that the structure of IIIa is \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}^+\text{CH}_2\text{CH}_3. Thus the adduct A produces ion IIIa by I loss. Ion IIIa dissociates competitively to C\(_2\text{H}_5\text{Cl}^-\) loss and C\(_2\text{H}_4\) loss.

\[
\begin{align*}
\text{C}_2\text{H}_5\text{I}^+ + \text{ClCH}_2\text{CH}_2\text{OCl}_2\text{H}_5 \\
\text{(I)} & \rightarrow \text{(II)} & \text{(III)} \\
\text{[CH}_3\text{CH}_2\cdots\text{O(C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{Cl]} \downarrow & \text{[CH}_3\text{CH}_2\cdots\text{ClCH}_2\text{CH}_2\text{OCl}_2\text{H}_5] \downarrow \\
\downarrow & \downarrow \\
\text{Ia} & \text{IIIa} \\
\downarrow & \downarrow \\
\text{C}_2\text{H}_5\text{O}^+(\text{H})\text{C}_2\text{H}_4\text{Cl} + \text{C}_2\text{H}_4 & \text{C}_2\text{H}_5\text{OC}_2\text{H}_4^+ + \text{C}_2\text{H}_5\text{Cl}
\end{align*}
\]

Scheme 4.6

4.3.6 Thermochemical evaluations

To thoroughly understand the dissociation processes of I, II and III a knowledge of their energetics is needed, including the heats of formation of I, II, III, their fragmentation

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products, the energy barriers for both isomerization and dissociation, and also the energies of the possible intermediates such as ion-neutral complex C₁. All estimated heat of formation values are summarized in Table 4.9 and the energetics of configurations involved in the dissociation processes are illustrated in Figure 4.11.

4.3.6.1 Heats of formation of I and III

The heats of formation of I, II and III are not available from experiment. However the heats of formation of onium ions can be obtained by estimation using the ethyl cation affinity (ECA) of the molecules based on Eq. 1.\[^5\]

\[
\begin{align*}
\Delta H_r & \quad \text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2X + \text{C}_2\text{H}_5^+ \rightarrow (\text{C}_2\text{H}_5)_2\text{O}^+\text{CH}_2\text{CH}_2X \\
& \quad \text{Ia} \& \text{Ib}
\end{align*}
\]

\[
\text{ECA(C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{X}) = -\Delta H_r = \Delta H_f^0(\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{X}) + \Delta H_f^0(\text{C}_2\text{H}_5^+) - \Delta H_f^0[(\text{C}_2\text{H}_5)_2\text{O}^+\text{CH}_2\text{CH}_2\text{X}] \quad \text{Eq.1}
\]

The heat of formation of C₂H₅⁺ is readily obtained from Reference 7 to be 216 kcal/mol\(^1\) and the heat of formation of C₂H₅OC₂H₄X can be obtained using the additivity rule\[^13\].

\[
\begin{align*}
\Delta H_f^0 (\text{kcal/mol}^-1) \\
\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{Cl} & \quad -66.6 \\
\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{Br} & \quad -54.2 \\
\text{C}_2\text{H}_5\text{OCHClCH}_3 & \quad -73.6
\end{align*}
\]

The key step to get the heats of formation of Ia and Ib is to estimate the ECA values. First we need to estimate the ECA of C₂H₅OC₂H₅, and then find the correction term for substitution of the β-halogen. It has been found that for some homologous
molecules the difference between the MCA (methyl cation affinity) and the ECA is approximately constant\textsuperscript{15, 141}, as shown below.

<table>
<thead>
<tr>
<th></th>
<th>MCA</th>
<th>ECA</th>
<th>Δ = MCA - ECA (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>67</td>
<td>37</td>
<td>30</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>83</td>
<td>50</td>
<td>33</td>
</tr>
<tr>
<td>C$_2$H$_5$OH</td>
<td>87</td>
<td>55</td>
<td>32</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>32±2</td>
</tr>
</tbody>
</table>

Thus it is reasonable to assume that the difference between MCA (C$_2$H$_5$OC$_2$H$_5$) and ECA (C$_2$H$_5$OC$_2$H$_5$) is also about 32 kcal/mol\textsuperscript{1}. The measured MCA of (CH$_3$)$_2$O was 92±5 kcal/mol\textsuperscript{115}, which may be close to the MCA of (C$_2$H$_5$)$_2$O. Thus the ECA of diethyl ether is estimated to be 92±5 - 32 = 60±5 kcal/mol\textsuperscript{1}. The correction term for the presence of the β-halogen is estimated from the differences between the proton affinity (PA) values of C$_2$H$_5$OH (188 kcal/mol\textsuperscript{1}), ClCH$_2$CH$_2$OH (184 kcal/mol\textsuperscript{1}) and BrCH$_2$CH$_2$OH (185 kcal/mol\textsuperscript{1})\textsuperscript{111}. The β-position effect of halogens is thus taken as 3 ± 1 kcal/mol\textsuperscript{1} and so the ECA(C$_2$H$_5$OCH$_2$CH$_2$X) is taken as ECA(C$_2$H$_5$OC$_2$H$_5$) - 3 = 57±5 kcal/mol\textsuperscript{1}. Thus from Equation 1 the heats of formation of la and lb are obtained to be 93 kcal/mol\textsuperscript{1} and 104 kcal/mol\textsuperscript{1}, respectively, with an uncertainty of ±5 kcal/mol\textsuperscript{1}.

The heat of formation of III was estimated from the ECA of C$_2$H$_5$X (36 kcal/mol\textsuperscript{1} for X = Cl and 38 kcal/mol\textsuperscript{1} for X = Br\textsuperscript{51}). The estimated values are 114 kcal/mol\textsuperscript{1} and 123 kcal/mol\textsuperscript{1} for IIIa and IIIb, respectively.

The heat of formation of II cannot be evaluated since the halogen effect at an α-position (C$_2$H$_5$OCHXCH$_3$) is not available.
4.3.6.2 Heats of formation of the product ions

The heats of formation of $C_2H_5O^+(H)CH_2CH_2X$ were estimated from PA ($C_2H_5OCH_2CH_2X$), which can be obtained from PA($C_2H_5OC_2H_5$) - 3 kJ mol$^{-1}$ (a correction term for the halogen in the neutral ether). The results are given in Table 4.9.

The heat of formation of $C_2H_5OCH_2CH_2^+$ was estimated by comparing $\Delta H_f^0$($HO^*CHCH_3$) (139 kJ mol$^{-1}$) and $\Delta H_f^0$ ($HOCH_2CH_2^+$) (165 kJ mol$^{-1}$). The stable isomer is 26 kJ mol$^{-1}$ lower in energy. By the same consideration it is reasonable that $\Delta H_f^0$($C_2H_5OCH_2CH_2^+$) > $\Delta H_f^0$ ($C_2H_5O^*CHCH_3$) + 26 kJ mol$^{-1}$ = 125 kJ mol$^{-1}$ + 26 kJ mol$^{-1}$ = 151 kJ mol$^{-1}$.

4.3.6.3 The energy of intermediate C$_1$

An ion-neutral complex $[XCH_2CH_2O(C_2H_5)H^*\cdots C_2H_4]$ (C$_1$) has been proposed as an intermediate in the dissociation of I via $C_2H_4$ loss. The energy of C$_1$ could be estimated through the stabilization energy (SE) in the complex. The SE values in some analogous ion-neutral complexes have been calculated. For instance, the SE of $[H_3O^*\cdots C_2H_4]$ has been calculated to be 21.5 kJ mol$^{-1}$ or 19.6 kJ mol$^{-1}$ and the SE of $[CH_3OH_2^*\cdots C_2H_6]$ to be 12 kJ mol$^{-1}$.

The SE decrease from $[H_3O^*\cdots C_2H_4]$ to $[CH_3OH_2^*\cdots C_2H_6]$ is expected since the charge density decreases from $H_3O^+$ to $CH_3OH_2^+$. Consequently the SE of $[XCH_2CH_2O(C_2H_5)H^*\cdots C_2H_4]$ should likely be less than 12 kJ mol$^{-1}$. We will assume an SE of ca. 10 kJ mol$^{-1}$, and so the energy of C$_1$ is estimated to be about 107 kJ mol$^{-1}$ and 118 kJ mol$^{-1}$ for X = Cl and Br, respectively.
4.3.6.4 Energetics of dissociations

It is known that metastable ions contain a narrow range of internal energies. In other words, for dissociations detected in an MI spectrum, their energy requirements will be similar (covering an energy range of $\text{ca} \leq 10$ kcal mol$^{-1}$). In the case of the MI dissociations of Ib the $\text{C}_2\text{H}_4$ loss and $(\text{C}_2\text{H}_5)_2\text{O}$ loss are competitive, so both processes may involve a similar energy barrier. Dissociation via $(\text{C}_2\text{H}_5)_2\text{O}$ loss has been shown to be a direct O–C bond cleavage without isomerization. So the activation energy barrier could be set above the product energies [$\Delta H^\circ_f (\text{C}_2\text{H}_4\text{Br}^+) = 206$ kcal mol$^{-1}$ and $\Delta H^\circ_f (\text{C}_2\text{H}_5\text{OC}_2\text{H}_5) = -60$ kcal mol$^{-1}$]. The KER value ($T_{0.5}$, 33 meV) for this process is a little higher than a simple bond cleavage and so a small reverse barrier should be considered. Thus the activation energy barrier is estimated to be $> 206 - 60 - 116$ ($\Delta H^\circ_f$ of Ib) = 30 kcal mol$^{-1}$, ca. 32 kcal mol$^{-1}$, which is the same as the activation energy barrier for dissociation via $\text{C}_2\text{H}_4$ loss (Figure 4.11). Radom et al. calculated the energy of the transition state for hydrogen transfer in $\text{CH}_3\text{CH}_2\text{OH}_2^+$ followed by $\text{C}_2\text{H}_4$ loss. The transition state is 23 kcal mol$^{-1}$ above $\text{C}_2\text{H}_5\text{OH}_2^+$. In the case of $(\text{C}_2\text{H}_5)_2\text{O}^+\text{CH}_2\text{CH}_2\text{X}$ (I) the difficulty for hydrogen transfer can arise for two reasons: the steric and the inductive effects of the $\text{C}_2\text{H}_4\text{X}$ and $\text{C}_2\text{H}_5$ groups. By the same arguments the activation energy barrier for Ia to dissociate via $\text{C}_2\text{H}_4$ loss was also set 32 kcal mol$^{-1}$ above Ia.

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4.4. Conclusion

The isomeric (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}O\textsuperscript{+}C\textsubscript{2}H\textsubscript{4}X ions (I and II) are not interconvertable. Only the hydrogen in a methyl group will transfer to oxygen. The halogen substituted at the \(\beta\) position has a strong tendency to form a C-X bond with an ethyl group, however, in the \(\alpha\) position the halogen promotes O-C\textsubscript{2}H\textsubscript{4}X bond cleavage. The dissociation energy of the O-C bond increases in the following series:

\[(C\textsubscript{3}H\textsubscript{5})\textsubscript{2}O\textsuperscript{+}-CHXCH\textsubscript{3} < C\textsubscript{2}H\textsubscript{5}O\textsuperscript{+}(C\textsubscript{3}H\textsubscript{4}X)-CH\textsubscript{2}CH\textsubscript{3} < (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}O\textsuperscript{+}-CH\textsubscript{2}CH\textsubscript{2}X\]
4.5 References

1. a: D. N. Kevill and E. K. Fujimoto, J. Chem. Research, Symposia, 408 (1988);


   b: D. V. Zagoreskii and J. L. Holmes, in preparation


8. a: L. Melander and W. H. Saunders, Jr, Reaction rates of isotopic molecules,
Wiley, New York (1980);


Table 4.1 MI and CID\textsuperscript{1} mass spectra of I and II\textsuperscript{2}

<table>
<thead>
<tr>
<th>Fragments</th>
<th>Ia</th>
<th></th>
<th>Ia</th>
<th></th>
<th>Ia</th>
<th></th>
<th>Ia</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MI</td>
<td>CID</td>
<td>MI</td>
<td>CID</td>
<td>MI</td>
<td>CID</td>
<td>MI</td>
<td>CID</td>
</tr>
<tr>
<td>(C_4H_{10}OX^+ + C_2H_4)</td>
<td>100(38)</td>
<td>100</td>
<td>100(26)</td>
<td>90</td>
<td>2(34)</td>
<td>3</td>
<td>3(27)</td>
<td>3</td>
</tr>
<tr>
<td>(H_2OC_2H_4X + 2 C_2H_4)</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(C_4H_{11}O^+ + C_2H_3X)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100(33)</td>
<td>100</td>
<td>100(21)</td>
<td>100</td>
</tr>
<tr>
<td>(C_4H_9O^+ + C_2H_5X)</td>
<td>13(34)</td>
<td>15</td>
<td>6(29)</td>
<td>11</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>(C_2H_{11}X^+ + (C_2H_5)_2O)</td>
<td>3(109)</td>
<td>6</td>
<td>48(33)</td>
<td>100</td>
<td>-</td>
<td>2</td>
<td>7(29)</td>
<td>13</td>
</tr>
<tr>
<td>(C_2H_7O^+ + C_2H_4 + C_2H_5X)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>(C_3H_3O^+ + C_2H_4 + C_2H_5X)</td>
<td>2</td>
<td>4</td>
<td>&lt;1</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1. Oxygen is the target gas with 90% transmission of the mass selected ion current.
2. KER values (\(T_{a5}, \text{meV}\)) are given in parentheses.
Table 4.2 The effect of the composition of C₂H₄XY and (C₂H₅)₂O on the yield of Ia and Ib

<table>
<thead>
<tr>
<th>Precursor ratio</th>
<th>BrCH₃CH₂Cl / (C₂H₅)₂O</th>
<th>Intensity Ratio</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BrCH₃CH₂Br / (C₂H₅)₂O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 / 1</td>
<td>BrCH₃CH₂Cl / (C₂H₅)₂O</td>
<td>0.20</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>1 / 1</td>
<td>BrCH₃CH₂Br / (C₂H₅)₂O</td>
<td>0.22</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>1 / 3</td>
<td>BrCH₃CH₂Cl / (C₂H₅)₂O</td>
<td>0.10</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BrCH₃CH₂Br / (C₂H₅)₂O</td>
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<td>0.62</td>
<td></td>
</tr>
<tr>
<td>1 / 1</td>
<td>BrCH₃CH₂Br / (C₂H₅)₂O</td>
<td></td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>1 / 3</td>
<td>BrCH₃CH₂Br / (C₂H₅)₂O</td>
<td></td>
<td>0.23</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.3 The effect of composition of BrCH₂CH₂Cl and (C₂H₅)₂O mixtures on the dissociation of Ia

<table>
<thead>
<tr>
<th>ClCH₂CH₂Br/ (C₂H₅)₂O</th>
<th>1/3</th>
<th>1/1</th>
<th>3/1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fragment</strong></td>
<td><strong>MI</strong></td>
<td><strong>CID</strong></td>
<td><strong>MI</strong></td>
</tr>
<tr>
<td>C₆H₁₀OCl⁺</td>
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<td>100</td>
<td>100</td>
</tr>
<tr>
<td>C₃H₆OCl⁺</td>
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<td>5</td>
<td>-</td>
</tr>
<tr>
<td>C₄H₇O⁺</td>
<td>13</td>
<td>14</td>
<td>13</td>
</tr>
<tr>
<td>C₂H₅Cl⁺</td>
<td>3</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>C₂H₅O⁺</td>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

Oxygen is the target gas with 90% transmission of the mass selected ion beam.

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<table>
<thead>
<tr>
<th>Fragments</th>
<th>Ia - C₂H₄</th>
<th>C₂H₂O⁺(H)CH₂CH₂Cl</th>
<th>Ib - C₂H₄</th>
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</thead>
<tbody>
<tr>
<td>H₂O⁺C₂H₄X+C₂H₄</td>
<td>100</td>
<td>100</td>
<td>51</td>
</tr>
<tr>
<td>C₂H₄X⁺+C₂H₅OH</td>
<td>29</td>
<td>27</td>
<td>100</td>
</tr>
<tr>
<td>HOCH₂H₄⁺+C₂H₅Cl</td>
<td>14</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>Precursors</td>
<td>C₂H₂D₂Cl⁺·(C₂H₅)₂O</td>
<td>C₂H₂D₂Br⁺·(C₂H₅)₂O</td>
<td>C₂H₄Cl⁺·CD₃CH₂OC₂H₅</td>
</tr>
<tr>
<td>------------</td>
<td>----------------------</td>
<td>----------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Fragments</td>
<td>MI</td>
<td>CID</td>
<td>MI</td>
</tr>
<tr>
<td>CD₂H₂O⁺·(H)C₂H₄X+C₂H₄</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>C₂H₂O⁺·(H)C₂H₂D₂X+C₂H₄</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>C₂H₂O⁺·(D)C₂H₄X+C₂H₂D₂</td>
<td>49</td>
<td>52</td>
<td>51</td>
</tr>
<tr>
<td>CD₃CH₂OC₂H₄⁺·C₂H₅X</td>
<td>9</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>C₂H₅OC₂D₂H₂⁺·C₂H₅X</td>
<td>9</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>C₂H₅OC₂H₄⁺·C₂H₂D₂X</td>
<td>6</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>C₂H₂D₂X⁺·(C₂H₅)₂O</td>
<td>1</td>
<td>4</td>
<td>49</td>
</tr>
<tr>
<td>C₂H₄X⁺·CD₃CH₂OC₂H₅</td>
<td>1</td>
<td>5</td>
<td>94</td>
</tr>
<tr>
<td>HO₂C₂D₂⁺·C₂H₄X+C₂H₄</td>
<td>1</td>
<td>3</td>
<td>&lt;1</td>
</tr>
<tr>
<td>DO₂C₂H₄⁺·C₂H₃X+C₂H₂D₂</td>
<td>1</td>
<td>4</td>
<td>&lt;1</td>
</tr>
<tr>
<td>HO₂C₂H₄⁺·C₂H₂D₃X+C₂H₄</td>
<td>1</td>
<td>5</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
Table 4.6  MI and CID mass spectra of the adduct ion
\( \text{C}_2\text{H}_5\text{I}^+ : \text{ClCH}_2\text{CH}_2\text{OC}_2\text{H}_5 \)

<table>
<thead>
<tr>
<th>Fragments</th>
<th>MI</th>
<th>CID</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{ClCH}_2\text{CH}_2\text{O}^+(\text{H})\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4\text{I} )</td>
<td>33</td>
<td>37</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{Cl}^+\text{C}_2\text{H}_5 + \text{I} )</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{I}^+ + \text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{Cl} )</td>
<td>14</td>
<td>34</td>
</tr>
</tbody>
</table>

Table 4.7  MI and CID\(^1\) mass spectra of III\(^a^2\)

<table>
<thead>
<tr>
<th>Fragments</th>
<th>MI</th>
<th>CID</th>
<th>CID(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_4\text{H}_10\text{ClO}^+ + \text{C}_2\text{H}_4 )</td>
<td>100 (31)</td>
<td>100</td>
<td>67</td>
</tr>
<tr>
<td>( \text{C}_4\text{H}_9\text{O}^+ + \text{C}_2\text{H}_5\text{Cl} )</td>
<td>79 (22)</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4\text{Cl}^+ + (\text{C}_2\text{H}_5)\text{C}_2\text{O} )</td>
<td>1</td>
<td>25</td>
<td>17</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{O}^+ + \text{C}_2\text{H}_5\text{Cl} + \text{C}_2\text{H}_4 )</td>
<td>2</td>
<td>24</td>
<td>17</td>
</tr>
</tbody>
</table>

1. \( \text{O}_2 \) is the target gas with 90% transmittance of the mass selected ion.
2. KER values (T\(_{0.5}\), meV) are shown in brackets.
3. Metastably generated III\(^a^2\) in 2fcr.
Table 4.8  MI and CID mass spectra of deuterium labelled Ia and IIIa

<table>
<thead>
<tr>
<th>Fragments</th>
<th>MI</th>
<th>CID</th>
<th>MI</th>
<th>CID</th>
<th>MI</th>
<th>CID</th>
<th>MI</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD₃CH₂⁺⁺⁺ + ClC₆H₄OC₂H₃</td>
<td></td>
<td></td>
<td>C₂H₅ClBr⁺⁺⁺ + CD₃CH₂OC₂H₃</td>
<td></td>
<td></td>
<td>CH₃CD₂⁺⁺⁺ + ClC₂H₄OC₂H₃</td>
<td></td>
</tr>
<tr>
<td>C₄H₂O⁺</td>
<td>76</td>
<td>75</td>
<td>40</td>
<td>41</td>
<td>82</td>
<td>75</td>
<td>44</td>
</tr>
<tr>
<td>C₄H₆D₂O⁺</td>
<td>24</td>
<td>25</td>
<td>60</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₄H₇D₂O⁺</td>
<td></td>
<td></td>
<td>18</td>
<td>25</td>
<td>56</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

------------

C₄H₅DClO⁺     | 37  | 32  | 33  | 34  |
C₄H₇D₂ClO⁺    | 63  | 68  | 67  | 66  |
C₄H₆ClO⁺      |     |     | 52  | 51  | 50  |
C₄H₇D₂ClO⁺    |     |     | 48  | 49  | 50  |
### Table 4.9  Estimated heats of formation, in kcal mol\(^{-1}\).

<table>
<thead>
<tr>
<th>Chemical</th>
<th>( \Delta H_f )</th>
<th>Chemical</th>
<th>( \Delta H_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{Cl} )</td>
<td>-66±1</td>
<td>( \text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{Br} )</td>
<td>-55±1</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{O}^+(\text{H})\text{CH}_2\text{CH}_2\text{Cl} )</td>
<td>103±3</td>
<td>( \text{C}_2\text{H}_5\text{O}^+(\text{H})\text{CH}_2\text{CH}_2\text{Br} )</td>
<td>114±3</td>
</tr>
<tr>
<td>( \text{(C}_2\text{H}_3)_2\text{O}^+\text{CH}_2\text{CH}_2\text{Cl} ) (Ia)</td>
<td>93±5</td>
<td>( \text{(C}_2\text{H}_3)_2\text{O}^+\text{CH}_2\text{CH}_2\text{Br} ) (Ib)</td>
<td>104±5</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{Cl}^+\text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5 ) (IIa)</td>
<td>114±3</td>
<td>( \text{C}_2\text{H}_5\text{Br}^+\text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5 ) (IIb)</td>
<td>123±3</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2^+ )</td>
<td>≥151±3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.1  Normal mass spectra of $\text{C}_2\text{H}_4\text{XY}^\text{•}$•$\text{O(C}_2\text{H}_5)_2$

a.  BrCH$_2$CH$_2$Cl + O(C$_2$H$_5$)$_2$

c.  Cl$_2$CHCH$_3$ + O(C$_2$H$_5$)$_2$

b.  BrCH$_2$CH$_2$Br + O(C$_2$H$_5$)$_2$

d.  Br$_2$CHCH$_3$ + O(C$_2$H$_5$)$_2$
Figure 4.2  CIDI mass spectra of \((C_2H_5)O^+CH_2CH_2X\)

a.  \(X = Cl\)
b.  \(X = Br\)
Figure 4.3  
CID mass spectra of C$_4$H$_9$O$^+$ ions

a.  ($C_2H_3$)$_2$O$^+CH_2CH_2Cl$ - $C_2H_3Cl$

b.  ($C_2H_3$)$_2$O$^+CH_2CH_2Br$ - $C_2H_3Br$

c.  ($C_2H_2O$)$_2$CHCH$_2$$^+_+$ - $C_2H_3O^+$
Figure 4.4  CID mass spectra of the fragments from \((\text{C}_2\text{H}_5)_2\text{O}^+\text{CH}_2\text{CH}_2\text{Cl}\)

a. \((\text{C}_2\text{H}_5)_2\text{O}^+\text{CH}_2\text{CH}_2\text{Cl} - \text{C}_2\text{H}_4 - \text{C}_2\text{H}_3\text{Cl}\)

b. \((\text{C}_2\text{H}_5)_2\text{O}^+\text{CH}_2\text{CH}_2\text{Cl} - 2 \text{C}_2\text{H}_4\)
Figure 4.5  CID mass spectra of $\text{C}_2\text{H}_4\text{X}'$ ions from I - (C$_2$H$_2$)$_2$O and from ClCH$_2$CH$_2$Br$n$' - Br' (or Cl')

a.  Ia - (C$_2$H$_2$)$_2$O

b.  ClCH$_2$CH$_2$Br$n$' - Br'

c.  Ib - (C$_2$H$_2$)$_2$O

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Figure 4.6  CIDI mass spectra of \((C_2H_5)_2O\cdot CH(X)CH_3\)

a.  \(X = Cl\)

b.  \(X = Br\)
Figure 4.7  CID mass spectra of $\text{C}_4\text{H}_{11}\text{O}^+$ ions
a.  $(\text{C}_2\text{H}_5)_2\text{O}^+\text{CH(Cl)CH}_3 - \text{C}_2\text{H}_5\text{Cl}$
b.  $(\text{C}_2\text{H}_5)_2\text{O}^+\text{CH(Br)CH}_3 - \text{C}_2\text{H}_5\text{Br}$
c.  $(\text{C}_2\text{H}_5)_2\text{O} + \text{H}^+$
Figure 4.8  Normal mass spectrum of ClCH₂CH₂OC₂H₅ + C₂H₅I
Figure 4.9  CID mass spectrum of C₄H₁₀OCl⁺ from III - C₂H₄

Figure 4.10  CIDI mass spectrum of III
Figure 4.11 The Energy diagram for dissociations of Ia and Ib, in kcal mol⁻¹

Ia  \((C_2H_5)_2OCH_2CH_2Cl\)

IIIa  \(C_2H_5Cl'CH_2CH_2OC_2H_5\)

ClIa  \([C_2H_5O(C_2H_5Cl)H'\cdots\cdotsC_2H_4]\)

Ib  \((C_2H_5)_2OCH_2CH_2Br\)

IIIb  \(C_2H_5Br'CH_2CH_2OC_2H_5\)

ClIb  \([C_2H_5O(C_2H_5Br)H'\cdots\cdotsC_2H_4]\)
5.1 Introduction

In Chapter 3 the C₂H₄X⁺ isomers have been described in detail. Studies of the analogous C₃H₆X⁺ ions (X = Cl and Br) will be presented in this chapter.

The possible structures for C₃H₆X⁺ are given in Scheme 5.1. IV to VIII are so-called open halogen cations; IX is a four-membered cyclic halonium ion. Of special interest is the effect of methyl substitution on the C₂H₄X⁺ isomers. CH₃⁺CXCH₃ (IV) and CH₃CH₂⁺CHX (VIII) result from methyl substitution on CH₃⁺CHX; CH₃CHX⁺CH₂ (V) and CH₃⁺CHCH₂X (VI) result from methyl substitution on XCH₂CH₂⁺; propenehalonium ions (X) result from methyl substitution on the cyclic ethylenehalonium ions. XCH₂CH₂CH₂⁺ (VII) and its cyclic isomer, the trimethylene halonium ions (IX) are also important, being analogous to XCH₂CH₂⁺ and CH₂⁺CH₂.

\[
\begin{align*}
\text{CH₃⁺CXCH₃} & \quad \text{CH₃CHX⁺CH₂} & \quad \text{XCH₂⁺CHCH₃} & \quad \text{XCH₂CH₂⁺CH₂} \\
\text{IV} & \quad \text{V} & \quad \text{VI} & \quad \text{VII} \\
\text{CH₃CH₂⁺CHX} & \quad \text{CH₂-CH₂} & \quad \text{CH₂-CH-CH₃} & \quad \text{CH₂⁺X} \\
\text{VIII} & \quad \text{(IX)} & \quad \text{(X)} & \quad \text{(XI)} \\
\end{align*}
\]

Scheme 5.1

When substituted 1,3-dihalo-propanes were dissolved in superacid media,¹⁻³ four
-membered ring halonium ions IX were observed, based on the observation of a 1,3-halogen shift. The participation of the 1,3-shift decreased in the sequence I > Br > Cl.\textsuperscript{[3]} According to theoretical calculations, the four-membered cyclic chloronium ion (IXb) is \(-18\) kcalmol\(^{-1}\) (or \(-21\) kcalmol\(^{-1}\)) lower in energy than the open structured 3-chloropropenyl ion (VIIb). For bromo analogues, the cyclic structure is also \(-20\) kcalmol\(^{-1}\) more stable than the opened form.\textsuperscript{[4]}

Lambert et al suggested that the possible intermediates in the electrophilic
\[
\text{CH}_2X \\
/ \\
\text{\overline{\text{\textbackslash}}}
\]
opening of cyclopropane attacked by \(X^+\) also involve another bridged species, \(\text{CH}_2\text{-CH}_2\) (XIb).\textsuperscript{[6]} The 1-chloro-cyclopropanyl ion (XIb) was calculated to be 6 kcalmol\(^{-1}\) more stable than the 3-chloro-propenyl ion (VIIb).\textsuperscript{[7]}

Olah et al\textsuperscript{[8]} found that when 1,3-dihalo-propanes were treated with \(\text{SbF}_5\text{-SO}_2\) at \(-78^\circ\text{C}\), the propenehalonium ion (X) was formed. Ion X could be formed through the trimethylenehalonium ion (IX) but this latter was not observed as an intermediate. The isomerization to X must therefore be fast. In addition, they found that 1,1-, 1,2- and 1,3-dichloropropanes exhibited identical pmr spectra and behaviour when dissolved in \(\text{SbF}_5\text{-SO}_2\text{ClF}\) solution.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CHCl}_2 & \text{ or } \text{SbF}_5\text{-SO}_2\text{ClF} \\
\text{CH}_3\text{CHClCH}_2\text{Cl} & \rightarrow \text{CH}_3\text{CH}_2\text{CHCl} \leftrightarrow \text{CH}_3\text{CHCH}_2\text{Cl} \leftrightarrow \text{CH}_2\text{CH-CH}_3 \\
\text{ClCH}_2\text{CH}_2\text{CHCl} & \rightarrow \uparrow \uparrow \uparrow
\end{align*}
\]

These observations suggest the formation of rapidly equilibrating ions VIIIb, VIIb, and Xb. The experiment also showed that the methyl hydrogens are not involved in any
exchange with the other three hydrogens. Finally the authors suggested that the chlorine atom, instead of stabilizing the charge by forming a \( \sigma \) bond, \( \text{Xb} \), or via chlorine back donation, \( \text{VIIb} \), destabilizes ion \( \text{VIb} \) by its inductive effect.

Hehre and Hiberty\textsuperscript{[9]} calculated the methyl substituent effects on \( \text{CH}_3\text{CHX}^+ \) and \( \text{XCH}_2\text{CH}_2^+ \) (\( X = \text{F, Cl} \)) from the energies (\( E \)) of the isodesmic reactions (reaction 2) using theoretical calculations at the STO-3G level.

\[
\text{C}_2\text{H}_6\text{X}^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5\text{X}^+ + \text{C}_2\text{H}_6
\]  

(2)

The results showed that when the methyl group was substituted on the \( \alpha \)-carbon (charge site), i.e. \( \text{CH}_3\text{CHX}^+ \rightarrow \text{CH}_3^+\text{CXCH}_3 \) or \( \text{XCH}_2\text{CH}_2^+ \rightarrow \text{XCH}_2^+\text{CHCH}_3 \), the ion will be stabilized by about 22 - 26 kcalmol\(^{-1}\), however, when substituted on the \( \beta \)-carbon, i.e. \( \text{XCH}_2\text{CH}_2^+ \rightarrow \text{CH}_3\text{CHXCH}_2^+ \), the ion is only stabilized by about 6 kcalmol\(^{-1}\) (Table 5.1).

The gas phase \( \text{C}_2\text{H}_5\text{Br}^+ \) isomers have been produced from ionized dibromopropane molecular ions followed by Br loss.\textsuperscript{[10-12]} The heats of formation of \( \text{CH}_3^+\text{CBrCH}_3 \) (IVc) and \( \text{CH}_3^+\text{CHCH}_2\text{Br} \) (Vlc) have been measured using an electron monochromator.\textsuperscript{[10]} The heat of formation of IVc is 178 kcalmol\(^{-1}\) and that of Vlc is 195 kcalmol\(^{-1}\). This shows that the ion with the Br on the \( \alpha \)-position is more stable than that with Br on the \( \beta \)-position. Compared to the heats of formation of \( \text{C}_2\text{H}_5\text{Br}^+ \) ions (Table 3.2), it can be seen that the methyl group is a more effective stabilizer at the \( \alpha \)-carbon of an acyclic isomer than at a ring carbon of the cyclic isomer, as shown in Scheme 5.2.

\[
\begin{align*}
\text{CH}_3^+\text{CHBr} & \quad \text{CH}_3^+\text{CBrCH}_3 \\
(\Delta H^0 = 208 \text{ kcalmol}^{-1}) & \quad (\Delta H^0 = 178 \text{ kcalmol}^{-1})
\end{align*}
\]
Moreover, when methyl substitution is made on the ring carbon of the cyclic Br

\[
\begin{array}{c}
\text{CH}_2 - \text{CH}_2 \\
\text{CH}_2 - \text{CHCl} \\
(\Delta H^\circ = 206 \text{ kcal mol}^{-1})
\end{array}
\]

structure, the calculated angle of C – C increased from 70.6° to 90.7°.\textsuperscript{[13]} In the Cl

\[
\begin{array}{c}
\text{CH}_2 - \text{CHCl} \\
\text{CH}_2 - \text{CHCH}_3 \\
(\Delta H^\circ = 195 \text{ kcal mol}^{-1})
\end{array}
\]

analogous chloronium ion, the angle of C – C increased from 69.6° to 86.8°.\textsuperscript{[14]} These results indicate that the stabilization by the methyl group replaces the electron-donation of the halogen.

Recently, Heck and Nibbering studied the bimolecular reactions of \( \text{C}_3\text{H}_5\text{Br}^+ \) isomers by FT-ICR mass spectrometry. Three stable isomers IVc, IXc and Xc were identified.\textsuperscript{[12]} Isomer IVc reacted with substrate molecules predominantly via proton transfer whereas isomer IXc predominantly reacted via adduct formation. Since the \( \text{C}_3\text{H}_5\text{Br}^+ \) ion, produced from \( \text{BrCH}_2\text{CHBrCH}_3^+ \) by \( \text{Br}^+ \) loss, did not easily transfer a proton to a suitable substrate, the structure Xc was proposed for it.

The \( \text{C}_3\text{H}_5\text{Br}^+ \) isomers will be further distinguished and the \( \text{C}_3\text{H}_5\text{Cl}^+ \) isomers will be characterized in this chapter.

### 5.2 Experimental

All metastable ion (MI), collision induced dissociation (CID) and neutralization reionization (NR) mass spectra were performed with a VG-ZAB-3F mass spectrometer. The conditions are same as described in Chapter 2. Collision induced dissociative
ionization (CID1) mass spectra were recorded using a potential of -1000 V on the ion beam deflector electrode in the 2ffr; the ionization target was oxygen. The CID mass spectra of the daughter ions were obtained by transmitting them to the 3ffr, where the target gas was O₂. Appearance energies (AE) were measured using an electron monochromator.

To examine the reactions of C₃H₆X⁺ ions with diethylether, appropriate halogenated precursor molecules were admitted to the ion source such that the ratio of the ether to the precursor was 1:1. The total ion source pressure was set at 2-4 x 10⁻⁵ mbar.

The C₃H₆X⁺ ions were produced by loss of Y from the ionized dihalo-propane C₃H₆XY⁺ (X and Y = Cl and Br). The dihalo-propanes were commercially available. Table 5.2 shows the formation of C₃H₆X⁺ ions, the structures of which required further examination.

5.3 Results and discussion

5.3.1 Unimolecular dissociations

The MI mass spectra of C₃H₆X⁺ ions were dominated by HX loss (C₃H₆X⁺ → C₃H₅⁺ + HX). The metastable peak for this process was composite. The distribution of released energies, n(T) vs the released energy, T (meV) was obtained by the method described in Reference 62. A representative plot of n(T) vs T (meV) from the metastable peak of CH₃C⁺ClCH₃ is shown in Figure 5.1. The metastable peak components of C₃H₆Cl⁺ isomers were thus separated into a narrow peak with the KER value (T₀.5) ranging from 6 to 16 meV and a wide peak with T₀.5 ranging from 79 to 225 meV. The results are given in Table 5.3.
A detailed CID mass spectrometric study of the C\textsubscript{3}H\textsubscript{5}\textsuperscript{+} daughter ion was attempted by transmitting C\textsubscript{3}H\textsubscript{5}\textsuperscript{+} ions at the center (4260 eV) of the metastable peak from CH\textsubscript{3}°CClCH\textsubscript{3} to the 3fpr, where the C\textsubscript{3}H\textsubscript{5}\textsuperscript{+} ions were collisionally activated by target gas. The ratio of m/z 26 to m/z 27 in the CID mass spectrum thus produced was close to 1.0. It has been demonstrated\textsuperscript{[15]} that at a translational energy of 4200 eV the ratio of m/z 26 to m/z 27 is 2 and 0.67 for CH\textsubscript{3}°CCH\textsubscript{2} and CH\textsubscript{2}CHCH\textsubscript{2}\textsuperscript{+}, respectively. Hence the ratio of 1.0 indicated that the MI dissociation process produced mainly the allyl cation. An attempt to separate the two isomers by transmitting the C\textsubscript{3}H\textsubscript{5}\textsuperscript{+} ions at the edge (4306 eV) of the metastable CH\textsubscript{3}°CClCH\textsubscript{3} peak to the 3fpr failed, because the ratio of m/z 26 to m/z 27 in the CID mass spectrum remained close to 1.0. Possibly some of the C\textsubscript{3}H\textsubscript{5}\textsuperscript{+} ions transmitted from the edge of the peak were collision induced in the 2fpr. Moreover, the components of the metastable peak were not easily separable given the resolution of the mass spectrometer.

Further study by increasing the collision gas pressure in the 2fpr showed that the ratio of m/z 26 to m/z 27 in the CID mass spectrum of the C\textsubscript{3}H\textsubscript{5}\textsuperscript{+} daughter ion did not change, indicating that the two isomers of C\textsubscript{3}H\textsubscript{5}\textsuperscript{+} ions were produced with the same energy barrier. The production of the allyl cation will give a higher kinetic energy release value than the production of CH\textsubscript{3}CCH\textsubscript{2}\textsuperscript{+} since the heat of formation of CH\textsubscript{2}CHCH\textsubscript{2}\textsuperscript{+} is 226 kcal/mol\textsuperscript{[38]}, being 5 kcal/mol lower in energy than isomer CH\textsubscript{3}CCH\textsubscript{2}\textsuperscript{+}. Thus the broad component, which is also the greater component in the MI composite peaks of C\textsubscript{3}H\textsubscript{6}Cl\textsuperscript{+} isomers likely arises from the allyl cation. The cogeneration of CH\textsubscript{3}CCH\textsubscript{2}\textsuperscript{+} with CH\textsubscript{2}CHCH\textsubscript{3}\textsuperscript{+} resulted in the observed composite metastable peak but with CH\textsubscript{3}C°CH\textsubscript{2}
giving rise to the small, narrow component. Moreover the dissociation energy barrier for CH₃CCl⁺CH₃ ions to dissociate to C₂H₅⁺ via HCl loss was estimated to be above 209 kca/mol⁻¹ \[ΔH^0(CH₃CCl⁺) + ΔH^0(HCl) = 231 - 22 = 209 \text{ kca/mol}⁻¹\). The other C₃H₆Cl⁺ isomers also showed a product mixture of C₃H₅⁺ isomers (Table 5.4) and similar kinetic release energy (T_{0.5}) values in their M(I) mass spectra (Table 5.3), indicating they have a similar dissociation energy barrier for HCl loss.

The CID mass spectra of the C₃H₆X⁺ ions are still dominated by the HX loss (Tables 5.5 and 5.6), which is the dissociation of lowest energy requirement. The next fragmentation process is C₂H₄ loss, which requires 38 kca/mol⁻¹ (X = Cl) or 20 kca/mol⁻¹ (X = Br) more energy than HX loss.

\[
\begin{align*}
\text{C}_3\text{H}_6\text{X}^+ & \rightarrow \text{C}_3\text{H}_5^+ + \text{HX} \\
\text{C}_3\text{H}_6\text{X}^+ & \rightarrow \text{CH}_2\text{X}^+ + \text{C}_2\text{H}_4
\end{align*}
\]

\[
\begin{array}{|c|c|c|}
\hline
\text{X} & \text{Cl} & \text{Br} \\
\hline
\text{Cl} & 204 & 217 \\
\text{Br} & 242 & 236.5 \\
\hline
\end{array}
\]

5.3.1.1 The C₃H₆Cl⁺ isomers

The CID mass spectrum of CH₃⁺CClCH₃ is distinguishable from the other C₃H₆Cl⁺ ions by the production of C₃H₆⁺ (Table 5.5), indicating an easy hydrogen shift from a methyl group to the center carbon. In radical ions hydrogen tends to act as an electrophile. The center carbon atom may have some electron density which could be obtained by electron-donation from the halogen atom. A mechanism is shown in Scheme 5.3.
The ions of formal structure CH$_3$CHCH$_2$Cl (VIIb), CH$_3$CH$_2$CHCl (VIIIb) and ClCH$_2$CH$_2$CH$_2$ (VIIIb) are indistinguishable (Table 5.5). A more detailed CID mass spectrometric study on the region of C$_2$HX$^+$ to C$_2$H$_2$X$^+$ (Figure 5.2) also failed to clearly distinguish these isomers. This indicates that the hydrogen atoms may be able to transfer freely between carbons.

VIIb is approximately 20 kcal mol$^{-1}$ lower in energy than VIIb, analogous to that of CH$_3$CHCH$_3$ ($\Delta H_f^0 = 191$ kcal mol$^{-1}$) and CH$_3$CH$_2$CH$_2$ (Δ$H_f^0 = 211$ kcal mol$^{-1}$). VIIIb may be similar in energy to VIIb, but the latter can also form a more stable isomer Xb involving a Cl bridge. Thus a sequence of hydrogen shifts may be proposed, as shown in Scheme 5.4. The estimation of the heats of formation of these isomers will be discussed later.
As the CID mass spectrum of VIIb was identical with that of VIIb and VIIIb, the four-membered isomer IXb could not be identified by CID mass spectrometry.

The NR mass spectrum of CH$_3$CCH$_3$ (Figure 5.3) showed an intense recovery signal of C$_3$H$_6$Cl$^+$, indicating that stable neutral C$_3$H$_6$Cl survived the neutralization process. Moreover, the NR mass spectrum of CH$_3$CCH$_3$ is generally similar to its CID mass spectrum, indicating no geometric change in the neutralization process. The observed Cl$^+$ and HCl$^{*+}$ in the NR mass spectrum of CH$_3$CCH$_3$ likely results from the collision induced dissociation of CH$_3$CCH$_3$ accompanying the neutralization process with dimethylamine (DMA), as shown by reaction 4. The dissociations of CH$_3$CCH$_3$ via Cl and HCl losses are reactions of low energy requirement, the latter producing the pase peak in the CID mass spectrum. The dissociation of neutral CH$_3$C$^+$ClCH$_3$ (reaction 6) may contribute to the flux of neutral Cl$^+$ and HCl. Note that the ionization energies (IE) of Cl$^+$ and HCl$^{*+}$ (13.0 eV and 12.7 eV) are much higher than those of C$_3$H$_5^+$ and C$_3$H$_6^{*+}$ (8.13 eV and 9.73 eV).

\[
\begin{align*}
\text{DMA} & \text{ defector} & \text{O}_2 \\
\text{CH}_3\text{CCH}_3 & \rightarrow & \text{C}_3\text{H}_5^+ + \text{HCl} & \rightarrow & \text{HCl} & \rightarrow & \text{HCl}^{*+}, \text{Cl}^+ \\
& & \text{C}_3\text{H}_6^{*+} + \text{Cl} & \rightarrow & \text{Cl} & \rightarrow & \text{Cl}^+ \\
\end{align*}
\]

(4)

\[
\begin{align*}
\text{DMA} & \text{ O}_2 \\
\text{CH}_3\text{CCH}_3 & \rightarrow & \text{CH}_3\text{CCH}_3 & \rightarrow & \text{CH}_3\text{CCH}_3 & \rightarrow & \text{C}_3\text{H}_5^+ + \text{HCl} & \rightarrow & \text{C}_3\text{H}_6^{*+} + \text{Cl}^+ \\
\end{align*}
\]

(5)

\[
\begin{align*}
\text{DMA} & \text{ O}_2 \\
\text{CH}_3\text{CCH}_3 & \rightarrow & \text{CH}_3\text{CCH}_3 & \rightarrow & \text{C}_3\text{H}_5^+ + \text{HCl} & \rightarrow & \text{C}_3\text{H}_5^+ + \text{HCl}^{*+} & \rightarrow & \text{C}_3\text{H}_6^{*+} + \text{Cl}^+ \\
& & \text{C}_3\text{H}_6 + \text{Cl}^+ & \rightarrow & \text{C}_3\text{H}_6^{*+} + \text{Cl}^+ \\
\end{align*}
\]

(6)

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The NR mass spectra of the other isomers VIIb, VIIb and VIIIb showed very weak recovery signals (Figures 5.4 - 5.6), suggesting either a low neutralization probability or production of unstable neutral C₂H₅Cl⁺, which rapidly dissociates to fragments such as C₂H₅⁺ + HCl or C₂H₆ + Cl⁺ (reaction 7). Note that for these isomers, HCl⁺⁺ and Cl⁺ are relatively much more important than for CH₃C⁺ClCH₃ ions. Since little C₂H₆⁺⁺ is observed in the CID mass spectra of these C₂H₆Cl⁺ isomers, the observation of Cl⁺ in their NR mass spectra may result from the dissociation of HCl⁺⁺.

\[ \text{DMA} \]
\[ \text{C}_2\text{H}_6\text{Cl}⁺ \rightarrow \text{CH}_3⁺\text{CClCH}_3 \rightarrow \text{C}_2\text{H}_5⁺ + \text{HCl} \rightarrow \text{C}_2\text{H}_5⁺ + \text{HCl}⁺⁺ \]
\[ \text{C}_2\text{H}_6 + \text{Cl}⁺ \rightarrow \text{C}_2\text{H}_6⁺⁺ + \text{Cl}⁺ \] (7)

\[ \text{DMA} \]
\[ \text{C}_2\text{H}_6\text{Cl}⁺ \rightarrow \text{C}_2\text{H}_5⁺ + \text{HCl} \rightarrow \text{HCl}⁺⁺, \text{Cl}⁺ \] (8)

The intense peak at C₂H₅Cl⁺⁺ in the NR mass spectra of VIIb, VIIb and VIIIb indicated that neutral C₂H₅Cl⁺ preferably dissociated via CH₃⁺ loss, which is rarely observed in their CID mass spectra. Thus the structure of neutral C₂H₅X⁺ is likely to be CH₃CHClCH₂⁺, which may easily lose CH₃⁺ compared to the other isomers.

5.3.1.2 The C₂H₂Br⁺ isomers

By CID mass spectrometry CH₃⁺CBrCH₃ (IVe) and BrCH₂CH₂CH₂⁺ (VIIc) are distinguishable from CH₃CHBrCH₂⁺ (Ve) and CH₃⁺CHCH₂Br (VIc), see Table 5.6 and Figure 5.7.

\[
\text{CH}_2 - \text{Br}⁺
\]

The formation of the four-membered isomer CH₂ - CH₂ (IXc) from VIIc has been
observed by FT-ICR mass spectrometry\cite{12}. Since the ion IXc is calculated to be about 20 kcal/mol more stable than VIIc\cite{4}, the isomer produced from BrCH₂CH₂CH₂Br⁺⁺⁺ is indeed likely to be IXc. This indicates that the bromonium ion has a stronger tendency to form the four-membered ring than the analogous chloronium ion, a result consistent with the observations in the condensed phase. The identical CID mass spectra of IVc and VIc (Table 5.6 and Figure 5.7) suggests that both ions likely form the propenebromonium ion CH₃·CHBr⁺⁺⁺CH₂ (Xc). The three isomers, IVc, Xc and XIc can be identified by CID mass spectrometry indicating that hydrogen transfer is not competing with brominium ion transfer (or bridging), as shown in Scheme 5.5.

\[
\begin{align*}
\text{Br}^+ & \quad / \quad \text{1,2-Br} & \downarrow \quad \text{1,2-Br} & \downarrow \\
\text{CH₃·CHCH₂Br} & \rightarrow \quad \text{CH₂CH·CH₂} & \leftarrow \quad \text{CH₃CHBrCH₂}^+ \\
\quad & \quad \downarrow \quad \text{X 1,2-H} & \quad \downarrow \quad \text{X 1,2-H} \\
\quad & \quad \downarrow \quad \text{1,3-Br} & \quad \downarrow \quad \text{1,3-Br} \\
\quad \text{CH₂CH₂CH₂Br} & \rightarrow \quad \text{CH₂·CH₂} & \quad \text{CH₃·CBrCH₃} \\
\end{align*}
\]

Scheme 5.5

The NR mass spectra of C₃H₆Br⁺⁺⁺ isomers were dominated by neutral dissociations, as shown in Figures 5.8 - 5.10. The most intense peaks of HBr⁺⁺⁺ and Br⁺ may result from the collision process shown in reaction 9, which is the lowest energy requirement process in the dissociations of C₃H₆Br⁺⁺⁺, see Table 5.9.

\[
\text{C₃H₆Br}^+ \rightarrow \text{C₃H₅}^+ + \text{HBr} \rightarrow \text{HBr} \rightarrow \text{Br}^{+}, \text{Br}^+ \quad (9)
\]
\[
\text{DMA} \\
\text{C}_3\text{H}_5\text{Br}^+ \rightarrow \text{C}_3\text{H}_6\text{Br}^- \rightarrow \text{C}_3\text{H}_6 + \text{Br}^- \rightarrow \text{C}_2\text{H}_5^- + \text{Br}^+ \\
\text{C}_3\text{H}_5^+ + \text{HBr} \rightarrow \text{C}_3\text{H}_5^+ + \text{HBr}^+ \\
(10)
\]

The intense Br\(^+\) peak may also result from the radical dissociation to Br\(^-\) shown in reaction 8. The C-Br bond in C\(_3\)H\(_6\)Br\(^+\) neutrals will be much weaker than that in C\(_3\)H\(_5\)Br\(^+\) and those in C\(_3\)H\(_6\)Br\(^+\) and C\(_3\)H\(_4\)Br\(^+\), i.e.

\[
\begin{array}{c}
\Delta H_f^\circ(\text{kcalmol}^{-1}) \\
32 \\
\hline
\text{BrCH}_2\text{CH}_2^- \rightarrow \text{C}_3\text{H}_4^- + \text{Br}^- \\
12.5 \\
\text{CH}_2\text{Br}^+\text{CH}_2^- \rightarrow \text{C}_3\text{H}_4^+ + \text{Br}^- \\
206 \\
\end{array}
\]

\[
\begin{array}{c}
\text{Bond energy (kcalmol}^{-1}\) \\
7.5 \\
27 \\
76 \\
\end{array}
\]

However, as in the case of C\(_3\)H\(_6\)Cl\(^+\), the ionization energies of Br\(^-\) and HBr (11.8 eV and 11.7 eV) are higher than those of C\(_3\)H\(_5\)^+ and C\(_3\)H\(_6\), reaction 10 may only produce minor Br\(^+\) and HBr\(^+\). Thus in the NR mass spectra of Br\(_2\)CH\(_2\)CH\(_2\)CH\(_2\) and BrCH\(_2\)CH\(_2\)CH\(_3\) (Figures 5.9 and 5.10) the major process is the collision induced dissociation of C\(_3\)H\(_6\)Br\(^+\) in the neutralization process. This is consistent with the fact that no recovery signal was observed. In the NR mass spectrum of CH\(_3\)^+CBrCH\(_3\) the observation of a recovery signal and the similarity to its CID mass spectrum indicated that the neutral CH\(_3\)CBrCH\(_3\) is stable and survived the reionization process.

\[
\text{DMA} \\
\text{CH}_3^+\text{CBrCH}_3 \rightarrow \text{CH}_3^+\text{CHBrCH}_3 \rightarrow \text{CH}_3^+\text{CBrCH}_3 \rightarrow \text{C}_3\text{H}_5^+ + \text{HBr} \rightarrow \text{C}_3\text{H}_6^+ + \text{Br}^+ \\
(11)
\]

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5.3.2 Reaction with diethyl ether

When dihalopropanes (except CH₂CX₂CH₃) were reacted with diethylether in the ion source, oxonium ions \((C₂H₅)₂O⁻C₃H₆X\) were observed in the normal mass spectra at \(m/z\) 151 \((X = Cl)\) and \(m/z\) 195 \((X = Br)\). The formation of the oxonium ions is discussed in Chapter 7 where it is proposed that the oxonium ions were formed from molecular adducts by a halogen loss.

\[
\begin{align*}
XCH₂CH₂CH₂Br^{+*} + (C₂H₅)₂O & \rightarrow XCH₂CH₂CH₂Br^{+*}(C₂H₅)₂O \\
\downarrow & \\
(C₂H₅)₂O⁻C₃H₆X + Br^+ 
\end{align*}
\]

The oxonium ions \((C₂H₅)₂O⁻C₃H₆X\) showed competing dissociations by \(C₂H₄\), \((C₂H₅)₂O\), \(C₂H₅X\) and \(C₃H₆X\) losses in their CID mass spectra (Tables 5.7 and 5.8). The neutral structures were confirmed by their CIDI mass spectra (Figures 5.11 and 5.12).

\[
\begin{align*}
(C₂H₅)₂O⁻C₃H₆X & \rightarrow C₃H₁₂OX^+ + C₂H₄ \\
& \rightarrow C₃H₁₁O^+ + C₂H₅X \\
& \rightarrow C₃H₆X^+ + (C₂H₅)₂O \\
& \rightarrow (C₂H₅)₂OH^+ + C₂H₅X
\end{align*}
\]

The first three dissociation channels resemble the dissociations of \((C₂H₅)₂O⁻CH₂CH₂X\), however the last resembles the dissociation of \((C₂H₅)₂O⁻CHXCH₃\) (Chapter 4). The CID mass spectrum of the daughter ions from \([(C₂H₅)₂O⁻CH₂CH₂CH₂X]^+\) showed that the structure of \(C₃H₁₂OX^+\) (from \(C₂H₄\) loss) is likely to be \(C₂H₅O^+(H)CH₂CH₂CH₂X\) (Figures 5.13a and 5.14a), an ion which dissociated by \(C₂H₄\), \(C₂H₅OH\), \(C₂H₅X\) and \(C₃H₆X\) losses. The structure of \(C₃H₁₁O^+\), (the daughter ion...
from C₂H₅X loss) was C₂H₅O*C₃H₆⁺ which in turn dissociated predominantly by C₂H₄ loss
(Figure 5.13 b). The (C₂H₅)₂O loss from [(C₂H₅)₂O*CH₂CH₂CH₃X]⁺ produces a C₃H₆X⁺
ion as shown in Figures 5.13c and 5.14b. The structure of the daughter ion C₄H₁₀O⁺
(C₃H₅X loss) was shown to be (C₂H₅)₂OH⁺ which also dissociated predominantly by C₂H₄
loss (Figure 5.13d). Analogous to the dissociations of (C₂H₅)₂O*CH₂CH₂CH₃X, the structure
of [(C₂H₅)₂O*CH₂CH₂CH₃X]⁺ is most likely (C₂H₅)₂O*CH₂CH₂CH₂X, with a covalent O-
C bond. The C₃H₆X loss indicates a hydrogen transfer from the C₃H₆X group to oxygen.
Note that the β-H shift was not observed in the MI and CID mass spectra of
(C₂H₅)₂O*CH₂CH₂CH₂Cl (Chapter 4). Thus the hydrogen in the group CH₂CH₂CH₃X is more
active than that in the CH₂CH₂X group, indicating that the C-H bond was strengthened by
the α-halogen in the CH₂CH₂X group. Since XCH₂CH₂CH₂⁺ has a similar reactivity to
diethylether as that of CH₂X⁺CH₂ (Chapter 4), the identity of the four-membered ring
isomer IX is thus further confirmed.

The oxonium ions (C₂H₅)₂O*C₂H₆X, formed from the reaction of CH₃CHBrCH₂X
(X = Cl or Br) with (C₂H₅)₂O followed by Br loss, dissociated largely by loss of C₂H₅X as
shown in their CID and CIDI mass spectra (Tables 5.7 and 5.8, Figures 5.11 and 5.12)
indicative of the active hydrogen in the methyl group.

\[
\begin{align*}
\text{H} & \\
[(\text{C}_2\text{H}_5)_2\text{O*CHCH}_2]^+ & \rightarrow \text{C}_4\text{H}_{10}\text{OH}^+ + \text{C}_2\text{H}_5\text{X} \\
\text{CH}_2\text{X} &
\end{align*}
\]  

(13)
In the normal mass spectrum of \( \text{CH}_3\text{CX}_2\text{CH}_3 + (\text{C}_2\text{H}_5)_2\text{O} \) no oxonium ions were found. It was shown in Chapter 4 that the possibility of forming \((\text{C}_2\text{H}_5)_2\text{O}^+\text{CHXCH}_3\) ions is much lower than that to form \((\text{C}_2\text{H}_5)_2\text{O}^+\text{CH}_2\text{CH}_2\text{X}\). The formation of these oxonium ions is proposed as an elimination-addition process, i.e. the diethyl ether molecule replaces \(Y\) (the leaving atom being Cl or Br). The methyl group may have strong steric effect and thus in the case of \(\text{CH}_3\text{CX}_2\text{CH}_3\), the two methyl groups will certainly hinder the formation of \([(\text{C}_2\text{H}_5)_2\text{OC}_2\text{H}_5\text{X}]^+\).

5.3.3 Energetic evaluations

5.3.3.1 Methyl substituent effects on \(\text{CH}_3\text{CHX}^+\) and heats of formation of \(\text{CH}_3^+\text{CXCH}_3\)

Referring to the reaction 2 \((\text{C}_2\text{H}_5\text{X}^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_4\text{X}^- + \text{C}_2\text{H}_6)\) the methyl substitution effect on \(\text{CH}_3\text{CHF}^+\) \((\Delta H_f^0, 166 \text{ kcalmol}^{-1})\) can be estimated from the heat of formation of \(\text{CH}_3^+\text{CFCH}_3\) \((138 - 143 \text{ kcalmol}^{-1})\) to be \(-24\pm 3 \text{ kcalmol}^{-1}\) and the methyl substitution effect on \(\text{CH}_3\text{CHBr}^+\) \((\Delta H_f^0, 208 \text{ kcalmol}^{-1})\), estimated from the heat of formation of \(\text{CH}_3^+\text{CBrCH}_3\) \((178 \text{ kcalmol}^{-1})\) to be \(-28 \text{ kcalmol}^{-1}\) [taking \(\Delta H_f^0 (\text{CH}_4) = -18 \text{ kcalmol}^{-1}\) and \(\Delta H_f^0 (\text{C}_2\text{H}_6) = -20 \text{ kcalmol}^{-1}\)]. Thus if the methyl substituent effect on \(\text{CH}_3\text{CHCl}^+\) is within \(-24\text{--28 kcalmol}^{-1}\), then the heat of formation of \(\text{CH}_3^+\text{CClCH}_3\) can be estimated to be \(170 \pm 3 \text{ kcalmol}^{-1}\), using \(\Delta H_f^0 (\text{CH}_3\text{CHCl}^+) = 198 \text{ kcalmol}^{-1}\).

A plot of \(\Delta H_f^0 (\text{CH}_3\text{CHX}^+)\) vs \(V_x\) (a scale of electronegativity\(^{20}\)) values gave an equation for \(\Delta H_f^0 (\text{CH}_3\text{CHX}^+) = 276 - 11.1 \text{ V}_x \text{ (kcalmol}^{-1}\)), see Chapter 3. The heats of formation of \(\text{CH}_3\text{CHX}^+\) are 166 kcalmol\(^{-1}\), 198 kcalmol\(^{-1}\) and 208 kcalmol\(^{-1}\) for \(X = \text{F, Cl}\) and \(\text{Br}\), respectively, and the \(V_x\) values are \(9.915, 7.04\) and \(6.13\) for \(X = \text{F, Cl}\) and \(\text{Br}\), respectively.\(^{20}\) A plot of \(\Delta H_f^0 (\text{CH}_3\text{C}^+\text{XCH}_3)\) against \(V_x\) can be described by the
equation $\Delta H^0 (CH_3CXCH_3) = 239 - 9.85$ Vx (kcalmol$^{-1}$). The heats of formation of $CH_3CXCH_3$ are 141 kcalmol$^{-1}$, 170 kcalmol$^{-1}$ and 178 kcalmol$^{-1}$ for $X = F$, Cl and Br, respectively. The stability of $CH_3CXCH_3$ ions is controlled by the C-X bond energy, like that of $CH_3CHX^+$. However, the slightly lower slope for $CH_3CXCH_3$ (-9.85) compared to that of $CH_3CHX^+$ (-11.1) may indicate another minor effect. This could be a contribution from the electron-donation of the heavier halogen atom to form $CH_3CCH_2$.

5.3.3.2 Heats of formation of $C_3H_6Cl^+$

The heats of formation of $C_3H_6Cl^+$ isomers are not available, however they can be estimated from the calculated methyl substituent effect (Table 5.1), see the estimation of $\Delta H^0 (CH_3CClCH_3)$ shown above. By high level ab initio calculations$^{[21]}$ $ClCH_2CH_2^+$ is 21 kcalmol$^{-1}$ higher in energy than $CH_3CHCl^+$ ($\Delta H^0 198$ kcalmol$^{-1}$), thus the heat of formation of $ClCH_2CH_2^+$ is ~ 219 kcalmol$^{-1}$. The methyl substitution effect on its $\alpha$-position (charged carbon) is ~ 25 kcalmol$^{-1}$, thus the heat of formation of $CH_3^+CHCH_2Cl$ (VIIb) is estimated to be 192 kcalmol$^{-1}$. Methyl substitution on its $\beta$-position (next to charged carbon) is only ~ 6 kcalmol$^{-1}$, and so the heat of formation of $CH_3CHClCH_2^+$ (Vb) is estimated to be 211 kcalmol$^{-1}$. The isomers IVb and VIIb with the charge on the center carbon are more stable than isomer Vb with the charge on the terminal carbon. Moreover IVb with Cl at the $\alpha$-position is more stable than VIIb with Cl on the $\beta$-carbon.

If the methyl substitution effect at the $\beta$-carbon of $CH_3CHCl^+$ is also ~ 6 kcalmol$^{-1}$, then the heat of formation of $CH_3CH_2CHCl^+$ may be estimated to be 191 kcalmol$^{-1}$. Note that $CH_3CH_2CHCl^+$ is about 20 kcalmol$^{-1}$ lower in energy than $CH_3CHClCH_2^+$, indicating
that the C\textsubscript{3}H\textsubscript{4}Cl\textsuperscript{+} isomer with the halogen atom setting at the charged carbon is more stable
than that with the halogen atom setting at the other carbons.

\[
\text{CH}_2\text{Cl}^+\text{CH}_2 \quad (\Delta H^0 = 200 \text{ kcal/mol}, \text{ see Chapter 3}) \text{ is } \sim 19 \text{ kcal/mol} \text{ lower in energy than } \text{ClCH}_2\text{CH}_2^+; \text{ while it is also estimated to be 19 kcal/mol lower in energy than } \text{CH}_3^+\text{CHCH}_2\text{Cl}. \text{ Since the energy difference between } \text{CH}_2\text{Cl}^+\text{CH}_2 \text{ and } \text{ClCH}_2\text{CH}_2^+ \text{ results from the cyclic structure and the linear structure, the energy difference between } \text{CH}_3\text{CHCl}^+\text{CH}_2 \text{ and } \text{CH}_3^+\text{CHCH}_2\text{Cl may result from a cyclic structure and a linear structure as well. The CH}_3\text{CHCl}^+\text{CH}_2 \text{ ion is therefore most likely a cyclic species.}
\]

\[
\text{Cl}^+ \quad \text{Cl}
\]

\text{CH}_3\text{CH} - \text{CH}_2. \text{ However the methyl group has both inductive and steric effects, which will reduce the efficiency of the electron - donation from Cl. The calculated angle in }

\[
\text{Cl} \quad \text{Cl}
\]

\text{CH}_3^+\text{CH-CH}_2 \text{ is 86.8°, higher than that in } \text{CH}_2\text{-CH}_2 \text{ (69.6°),[14]} \text{ indicating an incomplete back-bonding. The heat of formation of C}_3\text{H}_6\text{Cl}^+ \text{ (Table 5.9) increases in the following series:}

\[
\text{CH}_3^+\text{CClCH}_3 < \text{CH}_3\text{CHCl}^+\text{CH}_2 < \text{CH}_3\text{CH}_2\text{CH}^+ \sim \text{CH}_3^+\text{CHCH}_2\text{Cl} < \text{CH}_3\text{CHClCH}_2^+
\]

\[
\Delta H^0 \quad 170 \pm 3 \quad 191 \quad 192 \quad 211
\]

5.3.3.3 Heats of formation of C\textsubscript{3}H\textsubscript{6}Br\textsuperscript{+}

The heats of formation of IVc and VIc have been measured\textsuperscript{[16]} to be 178 kcal/mol\textsuperscript{1} and 195 kcal/mol\textsuperscript{1}, respectively. The \(\Delta H^0(\text{IXc})\) was estimated to be 172 kcal/mol\textsuperscript{1} by the appearance energy value (9.37 eV) for the process BrCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}Br (DBP) \(\rightarrow\) C\textsubscript{3}H\textsubscript{6}Br\textsuperscript{+}
\((\text{Xlc}) + \text{Br}^* [\text{taking } \Delta H_f^\circ (\text{DBP}) = -17 \text{ kcal mol}^{-1}, \ \Delta H_f^\circ (\text{Br}^*) = 26.7 \text{ kcal mol}^{-1}]\). As shown before this ion is most likely a four-membered ring isomer \(\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}^*\) (IXc). From the values shown above IXc has the lowest energy among the three isomers.

Comparing the heats of formation of \(\text{C}_2\text{H}_4\text{Br}^*\) (Table 5.9) gives the following series:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}^* &< \text{CH}_3\cdot\text{CBrCH}_3 < \text{CH}_3\text{CHBr}^*\text{CH}_2 \\
\Delta H_f^\circ (\text{kcal mol}^{-1}) &\quad 172 \quad 178 \quad 195
\end{align*}
\]

5.3.3.4 Comparison of methyl substituent effects on \(\text{C}_2\text{H}_4\text{Cl}^+\) and \(\text{C}_2\text{H}_4\text{Cl}^+\)

The heat of formation of \(\text{CH}_3\cdot\text{CClCH}_3\) can estimated from BDE (bond dissociation energy) values. The BDE of the secondary C-Cl in \(\text{CH}_3\text{CHClCH}_3\) is 86 kcal mol\(^{-1}\), 2 kcal mol\(^{-1}\) higher than the BDE for the primary C-Cl in \(\text{CH}_3\text{CH}_2\text{Cl}\) (84 kcal mol\(^{-1}\)); if it is assumed that the BDE of C-Cl in \(\text{CH}_3\text{CCl}_2\text{CH}_3\) will be 2 kcal mol\(^{-1}\) higher than the BDE of the primary C-Cl in \(\text{CH}_3\text{CHCl}_2\) (78 kcal mol\(^{-1}\)). Then \(\Delta H_f^\circ (\text{CH}_3\cdot\text{CClCH}_3)\) is 9 kcal mol\(^{-1}\) [taking \(\Delta H_f^\circ (\text{CH}_3\text{CCl}_2\text{CH}_3) = -42 \text{ kcal mol}^{-1}\) (additivity rule) and \(\Delta H_f^\circ (\text{Cl}^*) = 29 \text{ kcal mol}^{-1}\)]. This is a reasonable value, typical of the result of replacing \(\text{H}^+\) by \(\text{Cl}^+\).

Analogous to Eq. 2 the methyl substituent effect on \(\text{CH}_3\text{CHCl}^+\) is -7 kcal mol\(^{-1}\), which is smaller than the methyl substituent effect on \(\text{CH}_3\text{CHCl}^+\), namely -23-28 kcal mol\(^{-1}\). Hence the stabilizing effect of the methyl substituent is greater at the charge center than on the radical center.
5.4 Conclusions

Three isomers of C₂H₅X⁺ (X = Cl and Br) have been characterized by their CID, CIDI and NR mass spectra and by the formation of isomeric (C₂H₅)₂O⁺C₂H₅X ions. By MI and CID mass spectrometry CH₃⁺CXCH₃ has been distinguished from CH₃⁺CHCH₂X or XCH₂CH₂CH₂⁺. The latter two isomers have been distinguished by the formation of (C₂H₅)₂O⁺C₂H₅X isomers which showed different dissociation characteristics in their MI and CID mass spectra. By NR mass spectrometry it has been shown that the radical CH₃⁺CClCH₃ is more stable than the radical CH₃⁺CBrCH₃.

Methyl substitution on the charge center of CH₃CHX⁺ and XCH₂CH₂⁺ produces two C₂H₅X⁺ isomers, CH₃⁺CXCH₃ and CH₃⁺CHCH₂X. The former is significantly lower in energy than the latter. As with CH₃CHX⁺, the stability of CH₃⁺CXCH₃ is predominantly controlled by the C-X bond strength, in particular the partial formation of a double bond by electron-donation from the halogen. The C-X bond strength is not a major factor controlling the stability of CH₃⁺CHCH₂X ions because its ΔH° value is closer to that of CH₃⁺CHCH₃ (191 kcalmol⁻¹)⁹, i.e. the effect of halogen in the ion is similar to that in the corresponding neutral radical.
5.5 References


Table 5.1  Calculations for methyl substitution on C<sub>2</sub>H<sub>4</sub>X<sup>+</sup> (STO-3G)<sup>)</sup>

<table>
<thead>
<tr>
<th>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;X&lt;sup&gt;+&lt;/sup&gt;</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;X&lt;sup&gt;+&lt;/sup&gt;</th>
<th>E(kcal mol&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;∗&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CCFH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CHF&lt;sup&gt;−&lt;/sup&gt;</td>
<td>23.2</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CCICH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CHCl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>21.6</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;F&lt;sup&gt;−&lt;/sup&gt;</td>
<td>FCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>25.7</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CHFCH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>FCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>6.8</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>ClCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>24.9</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CHClCH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>ClCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5.7</td>
</tr>
</tbody>
</table>

<sup>∗</sup> The energies of the isodesmic reaction
C<sub>2</sub>H<sub>2</sub>X<sup>+</sup> + CH<sub>4</sub> → C<sub>2</sub>H<sub>4</sub>X<sup>+</sup> + C<sub>2</sub>H<sub>6</sub>

Table 5.2  Formation of C<sub>2</sub>H<sub>4</sub>X<sup>+</sup> ions

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Neutral loss</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;X&lt;sup&gt;+&lt;/sup&gt;</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Cl</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CClCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>IVb</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;CHBrCH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>Br</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CHCHCl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>VIIb</td>
</tr>
<tr>
<td>ClCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CHBr&lt;sup&gt;−&lt;/sup&gt;</td>
<td>Br</td>
<td>ClCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CHBr&lt;sup&gt;−&lt;/sup&gt;</td>
<td>VIIb</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>Cl</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;CHCl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>VIIb</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;CB&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Br</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;CBBr&lt;sup&gt;−&lt;/sup&gt;</td>
<td>IVc</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;CHBrCH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>Cl</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;CHBrCH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Vc</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;CHBrCH&lt;sub&gt;2&lt;/sub&gt;Br&lt;sup&gt;−&lt;/sup&gt;</td>
<td>Br</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;CHCHBr&lt;sup&gt;−&lt;/sup&gt;</td>
<td>VIIc</td>
</tr>
<tr>
<td>BrCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CHBr&lt;sup&gt;−&lt;/sup&gt;</td>
<td>Br</td>
<td>BrCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CHBr&lt;sup&gt;−&lt;/sup&gt;</td>
<td>VIIc</td>
</tr>
</tbody>
</table>
Table 5.3  Kinetic energy release (KER) values of metastable \( C_3H_6X^+ \) ions losing HX to give a composite peak

<table>
<thead>
<tr>
<th>( C_3H_6X^+ )</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Composite peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_3^+CClCH_3 )</td>
<td>16</td>
<td>225</td>
<td>156</td>
</tr>
<tr>
<td>( CH_3^+CHCH_2Cl )</td>
<td>16</td>
<td>145</td>
<td>93</td>
</tr>
<tr>
<td>( ClCH_2CH_2CH_2^+ )</td>
<td>16</td>
<td>165</td>
<td>109</td>
</tr>
<tr>
<td>( CH_3CH_2^+CHCl )</td>
<td>16</td>
<td>145</td>
<td>100</td>
</tr>
<tr>
<td>( CH_3^+CBrCH_3 )</td>
<td>8.8</td>
<td>133</td>
<td>86</td>
</tr>
<tr>
<td>( CH_3^+CHCH_2Br )</td>
<td>12</td>
<td>89</td>
<td>45</td>
</tr>
<tr>
<td>( BrCH_2CH_2CH_2^+ )</td>
<td>8.0</td>
<td>81</td>
<td>32</td>
</tr>
<tr>
<td>( CH_3CHBrCH_2^+ )</td>
<td>6.4</td>
<td>79</td>
<td>37</td>
</tr>
</tbody>
</table>

* Deviation: ± 5 meV.

Table 5.4  Partial CID mass spectra of \( C_3H_5 \) ions.

<table>
<thead>
<tr>
<th>Parent ions</th>
<th>Ratio of m/z 26/27</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_3^+CClCH_3 )</td>
<td>1.1</td>
</tr>
<tr>
<td>( CH_3CH_2^+CHCl )</td>
<td>0.93</td>
</tr>
<tr>
<td>( CH_3^+CHCH_2Cl )</td>
<td>1.0</td>
</tr>
<tr>
<td>( ClCH_2CH_2CH_2^+ )</td>
<td>0.75</td>
</tr>
<tr>
<td>( CH_3^+CBrCH_3 )</td>
<td>1.05</td>
</tr>
<tr>
<td>( CH_3^+CHCH_2Br )</td>
<td>0.89</td>
</tr>
<tr>
<td>( BrCH_2CH_2CH_2^+ )</td>
<td>0.85</td>
</tr>
<tr>
<td>( CH_2CHCH_2^+ )</td>
<td>0.53[51]</td>
</tr>
<tr>
<td>( CH_3ClCH_2^+ )</td>
<td>2.05[51]</td>
</tr>
</tbody>
</table>

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### Table 5.5 CID mass spectra of $C_4H_6Cl^+$ isomers

<table>
<thead>
<tr>
<th>Fragment</th>
<th>$CH_3^+$</th>
<th>$CClCH_4$</th>
<th>$ClCH_2'CHCH_3$</th>
<th>$ClCH_2CH_2CH_3^+$</th>
<th>$CH_3CH_2'CHCl$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CH_2^+$</td>
<td>1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>$CH_3^+$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$C_2H_2^+$</td>
<td>10</td>
<td>10</td>
<td>7</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>$C_2H_3^+$</td>
<td>12</td>
<td>14</td>
<td>13</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>$C_2H_4^+$</td>
<td>-</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>$C_2H_5^+$</td>
<td>-</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>$C_3H_5^+$</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>$C_3H_2^+$</td>
<td>10</td>
<td>8</td>
<td>10</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>$C_3H_3^+$</td>
<td>50</td>
<td>38</td>
<td>32</td>
<td>39</td>
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<td>$C_3H_6^+$</td>
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<td>-</td>
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<td>4</td>
<td>4</td>
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<tr>
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<td>4</td>
<td>4</td>
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<tr>
<td>$CH_2Cl^+$</td>
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<td>20</td>
<td>20</td>
<td>23</td>
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<tr>
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<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
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<td>$C_2HCl^+$</td>
<td>7</td>
<td>3</td>
<td>3</td>
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<tr>
<td>$C_2H_3Cl^+$</td>
<td>7</td>
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<td>3</td>
<td>3</td>
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<tr>
<td>$C_3H_4Cl^+$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td></td>
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<tr>
<td>$C_3H_5Cl^+$</td>
<td>10</td>
<td>2</td>
<td>2</td>
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</table>

* He, 90% transmission of ion beam
<table>
<thead>
<tr>
<th>Fragment</th>
<th>$CH_3^+CBrCH_3$</th>
<th>$BrCH_2^+CHCH_3$</th>
<th>$BrCH_2CH_2CH_3^+$</th>
<th>$CH_2CHBrCH_3^+$</th>
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</thead>
<tbody>
<tr>
<td>$C_3H_2^+$</td>
<td>2.5</td>
<td>1.5</td>
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<td>3</td>
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<tr>
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<td>3.5</td>
<td>2</td>
<td>5</td>
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<tr>
<td>$C_2H_4^+$</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
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<td>$C_3H_3^+$</td>
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<td>14</td>
<td>15</td>
</tr>
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<td>$C_3H_5^+$</td>
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<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td>$C_3H_6^+$</td>
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<td>-</td>
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<td>Br$^+$</td>
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<td>4</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>CBr$^+$</td>
<td>2</td>
<td>5</td>
<td>5</td>
<td>2</td>
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<tr>
<td>CH$_2$Br$^+$</td>
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<td>22</td>
<td>6</td>
</tr>
<tr>
<td>C$_3$HBr$^+$</td>
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<td>&lt;1</td>
<td>-</td>
<td>&lt;1</td>
</tr>
<tr>
<td>C$_2$H$_2$Br$^+$</td>
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<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>C$_2$H$_3$Br$^+$</td>
<td>4</td>
<td>2</td>
<td>&lt;1</td>
<td>1</td>
</tr>
<tr>
<td>C$_2$H$_4$Br$^+$</td>
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<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
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<td>-</td>
<td>-</td>
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</table>

* He, 90% transmission of ion beam; including the MI contributions
Table 5.7  Metastable ion (MI) and partial CID mass spectra of $(C_2H_5)_2O^+C_3H_6Cl$

<table>
<thead>
<tr>
<th>Fragments</th>
<th>MI</th>
<th>CID*</th>
<th>Precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$CH_3CHBrCH_2Cl\cdot(C_3H_2)O^{**}-Br^*$</td>
</tr>
<tr>
<td>$C_3H_11ClO^+{+}C_3H_4$</td>
<td>-</td>
<td>&lt;1</td>
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</tr>
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<td>$C_3H_11O^+{+}C_3H_5Cl$</td>
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<td>-</td>
<td>12</td>
</tr>
<tr>
<td>$C_3H_6Cl^+{(C_3H_2)O}$</td>
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<td>7</td>
<td>18</td>
</tr>
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<td>$(C_3H_5)_2OH^+{+}C_3H_5Cl$</td>
<td>100</td>
<td>100</td>
<td>100</td>
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* Including MI contributions
Table 5.8  MI and partial CID mass spectra of (C₂H₅)₂O⁺C₃H₆Br

<table>
<thead>
<tr>
<th>Precursors</th>
<th>[CH₂CHBrCH₂Br⁺(C₃H₆)O]⁻⁺Br⁻</th>
<th>[BrCH₂CH₂CH₂Br⁺(C₃H₆)O]⁻⁺Br⁻</th>
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</thead>
<tbody>
<tr>
<td>Fragments</td>
<td>MI</td>
<td>CID*</td>
</tr>
<tr>
<td>C₃H₁₁BrO⁺⁺C₂H₄</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>C₃H₆Br⁺⁺(C₂H₅)₂O</td>
<td>8</td>
<td>40</td>
</tr>
<tr>
<td>C₃H₁₁O⁺⁺C₂H₅Br</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(C₂H₅)₂OH⁺⁺C₃H₅Br</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>C₄H₆O⁺⁺C₃H₅Br</td>
<td>-</td>
<td>5</td>
</tr>
</tbody>
</table>

* Including MI contributions.
### Table 5.9  Heats of formation of $C_3H_6X^+$ ions and related species, kcahmol$^{-1}$.1

<table>
<thead>
<tr>
<th>Ions</th>
<th>$\Delta H^0$</th>
<th>Species</th>
<th>$\Delta H^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3^+$CFCH$_3$</td>
<td>IVa</td>
<td>141±3$^2$</td>
<td>C$_3$H$_5^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C$_3$H$_5^+$</td>
</tr>
<tr>
<td>CH$_3^+$CClCH$_3$</td>
<td>IVb</td>
<td>170±3$^3$</td>
<td>C$_3$H$_5$</td>
</tr>
<tr>
<td>CH$_3^+$CHCH$_2$Cl</td>
<td>VIb</td>
<td>192±1$^3$</td>
<td>C$_3$H$_5$**</td>
</tr>
<tr>
<td>CH$_3$CHClCH$_2^+$</td>
<td>Vb</td>
<td>211±1$^3$</td>
<td>Cl$^+$</td>
</tr>
<tr>
<td>CH$_3$CH$_2^+$CHCl</td>
<td>VIIIb</td>
<td>191±1$^3$</td>
<td>Cl$^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Br$^+$</td>
</tr>
<tr>
<td>CH$_3^+$CBrCH$_3$</td>
<td>IVc</td>
<td>178$^4$</td>
<td>Br$^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HCl</td>
</tr>
<tr>
<td>CH$_3$CHBr$^+$CH$_2$</td>
<td>VIc</td>
<td>195$^4$</td>
<td>HCl$^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HBr</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_2$Br$^+$</td>
<td>IXc</td>
<td>172$^5$</td>
<td>HBr$^+$</td>
</tr>
<tr>
<td>CH$_3^+$CClCH$_3$</td>
<td>IVb</td>
<td>9$^3$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>C$_3$H$_5$Br$^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH$_3^+$</td>
</tr>
</tbody>
</table>

1. Data are from Reference 38 except indicated.  
2. From References 15 and 64. Estimations, see text.  
3. From Reference 18.  
4. Estimation from the appearance energy measurement.
Figure 5.1 The distribution of released energies (T) in the MI dissociation of CH$_3$C\textsuperscript{+}ClCH$_3$ via HCl loss

$n(T)$: the distribution of released energies
Figure 5.2  Partial CID mass spectra of C$_2$H$_6$Cl' isomers.

Parent ions:

a. CH$_3'^{+}$CClCH$_3$        b. ClCH$_2$CH$_2$CH$_2'^{+}$

C$_2$H$_6$Cl'  C$_2$H$_6$Cl''

b. C$_2$H$_6$Cl'

C$_2$H$_6$Cl''

c. CH$_3'^{+}$CHCH$_2$Cl
d. CH$_3$CH$_2'^{+}$CHCl
Figure 5.3 The CID and NR mass spectra of $\text{CH}_3\text{CClCH}_3$

a: CID mass spectrum  
b: NR mass spectrum  
* Including the MI contributions
Figure 5.4  The CID and NR mass spectra of ClCH₂CH₂CH₂⁺
a: CID mass spectrum  
b: NR mass spectrum  
* Including the MI contributions
Figure 5.5  The CID and NR mass spectra of CH$_3$CH$_2$*CHCl
a: CID mass spectrum
b: NR mass spectrum
* Including the MI contributions
Figure 5.6  The CID and NR mass spectra of CH$_3^+$CHCH$_2$Cl
a: CID mass spectrum
b: NR mass spectrum
* Including the MI contributions
Figure 5.7  Partial CID mass spectra of C₃H₄Br⁺ isomers.
Parent ions:  a. CH₃'CBrCH₃  b. BrCH₂CH₂CH₂⁺  c. CH₃'CHCH₂Br  d. CH₂CHBr'CH₂
Figure 5.8  The CID and NR mass spectra of CH$_3^*CBr$CH$_3$

a: CID mass spectrum  
b: NR mass spectrum  
* Including the MI contributions.
Figure 5.9 The CID and NR mass spectra of BrCH₂CH₂CH₃⁺

a: CID mass spectrum
b: NR mass spectrum
* Including the MI contributions.
Figure 5.10  The CID and NR mass spectra of BrCH$_2$CHCH$_3$

a: CID mass spectrum
b: NR mass spectrum
* Including the MI contributions.
Figure 5.11  CIDI mass spectra of adduct (C₂H₅₂O)⁺C₆H₆Cl
Precursors:  a.  [ClCH₂CH₂Br·(C₂H₅₂O)]⁻·Br⁺  
b.  [ClCH₂CHBrCH₃·(C₂H₅₂O)]⁻·Br⁺
Figure 5.12  CIDI mass spectra of $(\text{C}_2\text{H}_2)_2\text{O}\text{C}_3\text{H}_6\text{Br}$
Precursors:  
   a. $[\text{BrCH}_2\text{CH}_2\text{Br}^\ast(\text{C}_2\text{H}_2)_2\text{O}]^{\ast\ast}\text{Br}^\ast$
   b. $[\text{BrCH}_2\text{CHBrCH}_3^\ast(\text{C}_2\text{H}_2)_2\text{O}]^{\ast\ast}\text{Br}^\ast$
Figure 5.13 CID mass spectra of the daughter ions from \((\text{C}_3\text{H}_7\text{O})^+\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \ (m/z \ 151)\)

- a. \(\text{C}_5\text{H}_{12}\text{Cl}^+ \ (\text{C}_3\text{H}_4 \text{ loss})\)
- b. \(\text{C}_7\text{H}_{12}^+ \ (\text{C}_2\text{H}_2\text{Cl} \text{ loss})\)
- c. \(\text{C}_3\text{H}_6\text{Cl}^+ \ (\text{C}_2\text{H}_2\text{OC}_2\text{H}_5 \text{ loss})\)
- d. \(\text{C}_4\text{H}_{11}^+ \ (\text{C}_2\text{H}_2\text{Cl} \text{ loss})\)
Figure 5.14  CID mass spectra of the daughter ions from 
$$(\text{C}_2\text{H}_2\text{O}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{Br})$$

a. $\text{C}_6\text{H}_{12}\text{O}^{81}\text{Br}^+$ (C$_2$H$_4$ loss)      b. $\text{C}_6\text{H}_6^{81}\text{Br}^+$ (C$_5$H$_5$OC$_5$H$_5$ loss)
Chapter 6

Disticnic radical cations

6.1 Introduction

The term "disticnic ion" was introduced in 1984 by Radom et al\textsuperscript{[1]} for ions with separated charge and radical sites that formally arise from the ionization of a zwitterion or a diradical. Greek letters were later proposed to indicate the relative location of the charge and radical sites. When using a conventional valence bond description, \(\alpha\)-disticnic ions have the charge and radical sites on adjacent atoms while two and three atoms separate the charge and radical sites in \(\beta\)- and \(\gamma\)-disticnic ions, respectively. This method of identification is now widely accepted.\textsuperscript{[2]}

A developing awareness that things were perhaps not quite that simple led to the appearance in the 1970's of scattered reports\textsuperscript{[3]} describing stable gas-phase radical cations with structures that did not correspond to those of stable, neutral molecules. However, the current interest in the chemistry of these species seems to have been sparked by a number of papers appearing in 1981-1982 from different research groups, notably those of Holmes, Radom, Schwarz, and Terlouw.\textsuperscript{[4-6]}

Disticnic radical cations are of wide current interest for two reasons. First, many distonic ions are more stable than the isomeric conventional molecular ions. Small distonic ions, i.e. \(\alpha\)-disticnic ions, are especially stable and moreover are separated from their conventional isomers by quite large energy barriers. Thus a mutual interconversion between these distonic ions and the isomeric molecular ions is slow or does not occur at all. Secondly, distonic ions play an important role as the central intermediates and
products in the dissociation reactions of many ionized organic molecules, the best-known example being the McLafferty rearrangement of the molecular ions of carbonyl compounds. Further, it now seems likely that the gaseous, long-lived molecular ions of many organic compounds may exist as their distonic forms. This is also true for the condensed phase: ESR studies indicate that stable distonic ions can be generated from many organic molecular ions in low-temperature freon matrices. Furthermore, certain X- or γ-ray-irradiated amino acids have been shown to produce distonic ions in frozen matrices. Thus, studies of distonic ions may lead to a better understanding of the biological consequences of ionizing radiation.

6.2 Results and discussion

In this Chapter the discussion of stable distonic radical cations is concentrated on their generation and characterization and the nature of these ions.

6.2.1 Generation and characterization of distonic radical cations

6.2.1.1 Generation of distonic radical cations

Distonic ions are generally formed from: (i) isomerization of a conventional radical cation; (ii) fragmentation of an isomerized molecular odd electron ion; and (iii) a bimolecular reaction between a distonic ion and a neutral molecule.

Isomerization of a conventional radical cation. When a heteroatom containing molecule is ionized, at first the heteroatom loses one electron from its lone-pair electrons and forms a conventional radical cation. If a hydrogen atom is available in the ion, the heteroatom may abstract this hydrogen to form a distonic ion.
\[
\begin{align*}
&\text{e.g. } RCH_2CH_2CH_2CR' \rightarrow RCH'CH_2CH_2CR' \\
\end{align*}
\]

Even though most distonic ions were first proposed to arise from the isomerization of a conventional radical cation, the confirmation of the presence of such distonic ions is limited by the stability of the distonic ions. The distonic ion must be stable enough to produce distinguishable fragment products, different from those produced from the conventional radical cation. Otherwise it is difficult to confirm or prove the existence of the distonic ions.

Ring opening, or ring cleavage, of small cyclic radical cations is one mechanism expected to lead to stable distonic ions, such as the molecular ion of ethylene oxide (EO).\(^{10}\)

\[
\text{EO}^{\bullet\bullet} \rightarrow \text{CH}_2-O-\text{CH}_2^{\bullet}
\]

The distonic ions thus produced are confirmed by their ability to transfer CH\(_2\)^{\bullet\bullet} to a molecule,\(^{11}\) as well as by their characteristic CID mass spectra.

\[
\text{(CH}_3\text{)}_2\text{C}=\text{O} + \text{CH}_2\text{OCH}_2^{\bullet} \rightarrow (\text{CH}_3\text{)}_2\text{C'}\text{OCH}_2^{\bullet} + \text{CH}_2=\text{O}
\]

**Fragmentation of an isomerized molecular ion.**

The general method for the formation of a desired distonic ion involves a dissociative ionisation in which an appropriate rearrangement is followed by the elimination of a small stable molecule, such as CH\(_2\)O, CO\(_2\), and CO.\(^{12}\) For example, two newly observed distonic ions, 'CH\(_2\)CH\(_2\)C'(OH)\(_2\) and 'CH\(_2\)CH\(_2\)OC'(H)OH (Chapter 7)
were produced from the fragmentation of the following molecular ions.

\[
\text{CH}_3\text{OCH}_2\text{CH}_2\text{COOH}^{++} \rightarrow \text{CH}_2\text{CH}_2\text{C}^+(\text{OH})_2 + \text{CH}_2\text{O}
\]

\[
\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOH} \rightarrow \text{CH}_2\text{CH}_2\text{OC}^+\text{HOH} + \text{HCOOH}
\]

Bimolecular reaction of a distonic ion with a neutral molecule.

Bimolecular reactions of distonic ions have been established either to produce another distonic ion or to be characteristic of the original distonic ion.\textsuperscript{[21]} The novel ions generated this way include the first stable δ-distonic ion, \(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+\), an acyclic isomer of ionized cyclopentanone.\textsuperscript{[22]}

\[
\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+ + \text{CH}_2=\text{C}=\text{O} \rightarrow \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+ + \text{CO}
\]

6.2.1.2 Characterization of distonic radical cations

The presence of a distonic ion rather than a molecular ion of conventional structure can in some cases be demonstrated experimentally by exclusion; that is, by demonstrating that the properties of the ion in question are different from those of ions generated by direct ionization. Appearance energy (AE) measurements play an important role in the characterization of distonic radical cations. Heat of formation data are used in ion structure determination. If the \(\Delta_h^0\) measured for an ion is different from that of a conventional counterpart the ion may have a distonic structure. \(\Delta_h^0\) has been experimentally determined for several distonic ions by appearance energy (AE)
measurements.\textsuperscript{141} A reliable $\Delta_f^{\text{H}_2\text{O}}$ value can be obtained if (i) the structure of the neutral product is known; (ii) the AE is accurately measured with well defined electron energies to limit the effect of the electron kinetic energy distribution.\textsuperscript{131}

With a conventional double focusing mass spectrometer, most stable distonic ions can be distinguished from their conventional isomers by their structure characteristic fragmentations. The fragmentations of distonic ions are observed by metastable ion dissociation (MI), collision induced dissociation (CID), charge stripping (CS), collision induced dissociative ionization (CIDI) of the lost neutrals and neutralization-reionization (NR) mass spectrometries. Isotopically labelled precursors are used to provide additional evidence. CID is a powerful ion structural tool because high internal energies can be deposited in the ions upon collisional activation and the resultant direct bond cleavages being often favored over the slower and usually less informative rearrangement reactions. The CS mass spectrometry is more specifically used to characterize the distonic ions, since the radical site in a distonic ion may be readily ionized by collision.

NR mass spectrometry can provide valuable structure information in the characterisation of a distonic ion, because a distonic ion forms a diradical in the neutralization process, while the conventional counterpart does not. The dissociation of the diradical will produce a NR mass spectrum which is easily distinguishable from that of the conventional isomer.

Recently, examination of ion-molecule reactions with a Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer has yielded information concerning the structures of low-energy ions. Differences in chemical reactivity may allow the distinction
of isomers that yield similar dissociation product distributions under CID conditions. However, the reactivity of an ion is strongly affected by its internal energy, especially when the ion in question has enough energy to isomerize. Thus the ion-molecule reactions approach to distonic ion characterization depends upon the condition that the ions must be generated with only small amounts of internal energy or that they are kinetically and internally relaxed without isomerisation prior to reaction.

High level ab initio molecular orbital theory studies have provided abundant information about an ion's bond lengths, bond angles, and charge distribution. Ab initio calculations have also been utilized in calculating heats of formation, as well as isomerization energy barriers. This kind of information is very useful to broaden our understanding of distonic ion chemistry.

6.2.2 Stable gas-phase distonic radical cations

To date over 50 distonic radical cations have been well characterized as stable gas-phase ionic species and more than 100 distonic ions have been proposed as the active intermediates involved in the dissociations of organic molecular radical cations. The generation and characterization of stable distonic radical cations will be discussed individually and shown briefly in Table 6.1.

6.2.2.1 Halogen-containing distonic radical cations

The distonic ions 'CH₂F⁺' (1⁺), 'CH₂ClH⁺ (2⁺), and 'CH₂BrH⁺ (3⁺) were produced from the fragmentation of [XCH₂COOH]⁺ via CO₂ loss (X = F, Cl and Br). These distonic ions were readily characterized by their distinctive CID mass spectra in
which the doubly charged \([\text{CH}_2\text{XH}]^{2+}\) cation is significantly stable, while for the conventional ion, \(\text{CH}_2\text{X}^{2+}\) has only marginal stability.\(^{12}\) High level ab initio calculations have confirmed that these singly charged isomers are stable with respect to the high energy barrier between the distonic ions and the conventional isomers.\(^{14}\) The heats of formation of \(\text{CH}_2\text{XH}\) ions have been measured to be 217±4 kcallmol\(^{-1}\), 246±3 kcallmol\(^{-1}\), and 237±3 kcallmol\(^{-1}\) for \(\text{X} = \text{F}, \text{Cl}\) and \(\text{Br}\), respectively.\(^{12}\) Thus \(1^{++}\) is 11 kcallmol\(^{-1}\) more stable than its conventional isomer \(\text{CH}_3\text{F}^{++}\) (\(\Delta H^0, 228\) kcallmol\(^{-1}\))\(^{16}\), \(2^{++}\) is 7 kcallmol\(^{-1}\) less stable than \(\text{CH}_3\text{Cl}^{++}\) (\(\Delta H^0, 239\) kcallmol\(^{-1}\))\(^{16}\), and \(3^{++}\) is 3 kcallmol\(^{-1}\) less stable than \(\text{CH}_3\text{Br}^{++}\) (\(\Delta H^0, 234\) kcallmol\(^{-1}\))\(^{16}\). The recently developed values from theoretical calculations are 230.8 kcallmol\(^{-1}\) for \(1^{++}\) and 251.0 kcallmol\(^{-1}\) for \(2^{++}\).\(^{17}\) By the same calculations \(1^{++}\) is about 1 kcallmol\(^{-1}\) more stable than \(\text{CH}_3\text{F}^{++}\) and \(2^{++}\) is 11 kcallmol\(^{-1}\) less stable than \(\text{CH}_3\text{Cl}^{++}\). The theoretical calculations and the experimental measurements are in fair agreement for the heat of formation of \(2^{++}\) but not so for at the heat of formation of \(1^{++}\). If the energy difference between a distonic ion \(\text{CH}_2(\text{CH}_2)_2\text{XH}\) and its conventional isomer \(\text{CH}_3(\text{CH}_2)_2\text{X}^{++}\) could be considered as the difference in the C-H bond strength and X-H bond strength, the extra stability of the distonic ion may account for the higher bond energy of X-H than C-H. From this point of view, one may expect that \(1^{++}\) should be more stable than \(\text{CH}_3\text{F}^{++}\), since the H-F bond is stronger than a C-H bond. However, in an ionized species the bond strength may be different from the homolytic bond dissociation energy in the analogous neutral molecule.\(^{18}\)

Three stable distonic ions, \(\text{CH}_2\text{CH}_2\text{FH}^{++}\) (\(4^{++}\)), \(\text{CH}_2\text{CH}_2\text{ClH}^{++}\) (\(5^{++}\)) and \(\text{CH}_2\text{CH}_2\text{BrH}^{++}\) (\(6^{++}\)) have been generated from the fragmentations of \([\text{XCH}_2\text{CH}_2\text{CH}_2\text{OH}]^{++}\)
(X = F, Cl and Br) via \( \text{CH}_2\text{O} \) loss.\(^{[19]} \) The \( \alpha \)-distonic isomers \( \text{CH}_3\cdot\text{CHClH}^+ (7^-) \) and \( \text{CH}_3\cdot\text{CHBrH}^+ (8^-) \) were also generated from \( [\text{CH}_3\cdot\text{CHXCOOH}]^{+} \) (X = Cl and Br) via CO\(_2\) loss.\(^{[19,20]} \) By CID mass spectrometry the distonic ions \( \cdot\text{CH}_2\text{CH}_2\text{XH}^+ \) were characterized by the intense peaks at \( \text{CH}_2^- \), \( \text{C}_2\text{H}_4^- \) and \( \text{HX}^- \), whereas the \( \text{CH}_3\cdot\text{CHXH}^+ \) isomers were characterized by the intense doubly charged ion peak \( [\text{CH}_3\cdot\text{CHXH}]^{2+} \). In addition, a third type of distonic \( \text{C}_2\text{H}_5\text{X}^- \) isomer, \( \cdot\text{CH}_2\text{Cl}^+\text{CH}_3 (9^-) \) and \( \cdot\text{CH}_2\text{Br}^+\text{CH}_3 (10^-) \) were generated from \( [\text{XCH}_2\text{COOCH}_2]^+ \) via CO\(_2\) loss.\(^{[19,20]} \) These distonic isomers showed pronounced dissociation via \( \text{CH}_3 \) loss.\(^{[19,20]} \)

Ions \( 4^- \) and \( 5^- \) were found more stable than their conventional isomers. The heats of formation of these ions were indeed calculated to be 17.7 kcalmol\(^{-1} \) (X = F) and 3.1 kcalmol\(^{-1} \) (X = Cl) more stable than their corresponding conventional isomers.\(^{[21]} \) However, the measured \( \Delta H^0 \) values of \( \text{CH}_3\cdot\text{CHClH}^+ (232 \text{ kcalmol}^{-1}) \), \( \text{CH}_3\cdot\text{Cl}^+\text{CH}_2^- (242 \text{ kcalmol}^{-1}) \), \( \text{CH}_3\cdot\text{CHBrH}^+ (238 \text{ kcalmol}^{-1}) \), \( \text{CH}_3\cdot\text{Br}^+\text{CH}_2^- (253 \text{ kcalmol}^{-1}) \)\(^{[20]} \) are all higher than those of the conventional isomers \( \text{C}_2\text{H}_5\text{X}^- \) (\( \text{C}_2\text{H}_5\cdot\text{Cl}^- 226 \text{ kcalmol}^{-1} \) and \( \text{C}_2\text{H}_5\cdot\text{Br}^- 222 \text{ kcalmol}^{-1} \)\(^{[16]} \)). The difference between the heats of formation of \( \cdot\text{CH}_2\text{CH}_2\text{ClH}^- (5^-) \) and \( \text{CH}_3\cdot\text{CHClH}^+ (7^-) \) may indicate the different C-H bond strengths in \( \text{CH}_3\cdot\text{CHClH}^+ \). The hydrogen atom affinity (HA) values for even-electron ions have been thoroughly studied.\(^{[18]} \)

\[
\text{RXH}^+ \rightarrow \text{RX}^{+} + \text{H}^+ \quad \Delta H_r
\]

\[
\text{HA} [\text{RX}^{+}] = \Delta H_r = \Delta H^0 [\text{RX}^{+}] + \Delta H^0 [\text{H}^+] - \Delta H^0 [\text{RXH}^+]
\]

The HAs of \( 5^- \) and \( 7^- \) are thus estimated from the heats of formation of \( 5^- \), \( 7^- \), and \( \text{CH}_3\cdot\text{CH}_2\text{ClH}^+ (170 \text{ kcalmol}^{-1}) \) to be 105 kcalmol\(^{-1} \) and 114 kcalmol\(^{-1} \) for \( \beta\)-H and
α-H, respectively. It followed that the higher ΔH° value of 7** may result from the higher HA value at α-position. This probably results from the inductive effect of the -CIH group. The bond dissociation energies in CH₂CH₂Cl can be estimated from the heats of formation of CH₃CH₂Cl (-26.8 kcal mol⁻¹ [16]), CH₂(CH₂)₂Cl (19.8 kcal mol⁻¹ [22]) and CH₃C'Cl (22.8 kcal mol⁻¹ [22]); they are 101.7 kcal mol⁻¹ and 98.2 kcal mol⁻¹ for β-H and α-H, respectively. The two latter values are much closer than the HA values.

The higher ΔH° value of CH₂ClCH₂⁺ (9**) is indicative of the weak C-Cl bond in the ion. The C-Br bond is also weak in ion 9**. This is expected and follows the same trend as the bond dissociation energy in the neutral counterparts.

6.2.2.2 Distonic isomers of alcohol radical cations, 'CH₂(CH₂)ₙOH₂⁺.

The homologous distonic ions 'CH₂(CH₂)ₙOH₂⁺ (n = 0 - 3) behave differently. The distonic ion 'CH₂OH₂⁺ (11**) was produced from the fragmentation of several appropriate molecule radical cations[12]. In its CID mass spectrum 'CH₂OH₂⁺ was distinguished from CH₃OH⁺⁺ by an intense doubly charged ion peak at m/z 16. [41] Thus CS mass spectrometry readily characterized this isomer. [44] The heat of formation of 'CH₂OH₂⁺ was obtained by high level ab initio calculations to be 195±1 kcal mol⁻¹,[17,23] which is in good agreement with that obtained from an AE measurement 195 ± 2 kcal mol⁻¹.[44] Thus 11** is 8 kcal mol⁻¹ lower in energy than CH₃OH⁺⁺. The energy barrier for 'CH₂OH₂⁺ to isomerize to CH₃OH⁺⁺ was calculated to be 35±2 kcal mol⁻¹.[21,24]

The distonic ion 'CH₂CH₂OH₂⁺ (12**) has also been produced from the fragmentation of the appropriate radical cations[6,25] and its MI and CID mass spectra were dominated by the dissociation process via H₂O loss. The very small kinetic energy release
value for this process was attributed to the involvement of a hydrogen-bridged water/ethene radical cation complex $[\text{CH}_2=\text{CH}^\cdots \text{H}^\cdots \text{OH}_2]^+$,\textsuperscript{25,26} a proposal which was well supported by theoretical calculations.\textsuperscript{25,27} The same calculations also predicted that the distonic ion "\text{CH}_2\text{CH}_2\text{OH}_2^+" is 7-10 kcal mol\textsuperscript{-1} more stable than the conventional isomer \text{CH}_3\text{CH}_2\text{OH}^+ and this is consistent with the experimental value (11 kcal mol\textsuperscript{-1}).\textsuperscript{25} The bimolecular reactions of this distonic ion and its conventional isomer have been investigated in a Fourier transform ion cyclotron resonance mass spectrometer.\textsuperscript{28} Strikingly different reactivity is observed for these two radical cations. The distonic ion undergoes thermoneutral exchange of a water molecule when reacted with $^2$H- or $^{18}$O-labeled water. Acetonitrile readily replaces water in this ion, as well. The ethanol radical cation predominantly reacts by proton transfer to all of these reagents.\textsuperscript{28} Another distonic isomer is \text{CH}_3\text{CHOH}_2^+ (13\textsuperscript{+}), which has been experimentally observed\textsuperscript{29} and theoretically calculated to be 6 kcal mol\textsuperscript{-1} more stable than \text{CH}_3\text{CH}_2\text{OH}^+.\textsuperscript{25,27}

The distonic ion "\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}_2^+ (14\textsuperscript{+})" is the reacting configuration for the H$_2$O loss from the propanol ion \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^+.\textsuperscript{30,31} This distonic isomer has also been generated independently from the fragmentation of [HOC\text{H}_2\text{CH}_2\text{CH}_2\text{OH}]^+ via CH$_2$O loss.\textsuperscript{30} The heat of formation of the ion was determined by an AE measurement to be 171±1 kcal mol\textsuperscript{-1}.\textsuperscript{30} The theoretical prediction gave a value of 175 kcal mol\textsuperscript{-1}.\textsuperscript{21} It has been confirmed by a deuterium-labelling experiment that the hydrogen transfer involved in the isomerization of \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^+ to "\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}_2^+" is specifically from the methyl group.\textsuperscript{30,31} The product ion from the dissociation of "\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}_2^+" via H$_2$O loss has been confirmed to be cyclo-C$_3$H$_6$\textsuperscript{+} by AE measurement\textsuperscript{30} and by charge stripping.
mass spectrometry. Thus the involvement of an ion-molecule complex $[\nabla \rightarrow^+ \text{OH}_2]$ was proposed$^{[31]}$ and supported later by theoretical calculations.$^{[32,33]}$

Competition between collision-activated isomerization and fragmentation of the distonic radical cations "CH$_2$(CH$_2$)$_n$OH$^+$" ($n = 0$ - 2) and their conventional counterparts (CH$_3$(CH$_2$)$_n$OH$^+$, $n = 0$ - 2) was examined under different experimental conditions in a triple quadrupole mass spectrometer and in a Paul-type quadrupole ion trap.$^{[34]}$ All the above pairs of isomers give structurally characteristic fragmentation products upon low-energy (eV) collision activation under single- and multiple-collision conditions in the triple quadrupole instrument. Fast direct bond cleavages dominate the fragmentation. Thus abundant even-electron ionic fragments are obtained for the conventional ions, while the distonic isomers yield predominantly odd-electron ionic fragments. Further, the results suggest that the barrier between the ions CH$_3$CH$_2$CH$_2$OH$^+$ and "CH$_2$CH$_2$CH$_2$OH$_2^+$ is significantly lower than the barriers associated with the shorter chain homologues ($n = 0$ or 1).$^{[34]}$

"CH$_2$CH$_2$CH$_2$CH$_2$OH$_2^+$" (15$^{+}$), formed by CH$_2$O loss from HO(CH$_2$)$_5$OH$^-$. showed very similar CID and NR mass spectra to its conventional isomer CH$_3$CH$_2$CH$_2$CH$_2$OH$^+$, suggesting their facile interconversion.$^{[35]}$ The heat of formation of ion 15$^{+}$ has been measured in this laboratory to be 158 kcal mol$^{-1}$, being 8 kcal mol$^{-1}$ lower than that of CH$_3$(CH$_2$)$_4$OH$^+$.

The distonic ion "CH$_2$OCH$_2$CH$_2$OH$_2^+$ (16$^{+}$) produced from the fragmentation of [CH$_3$OCH$_2$OCH$_2$CH$_2$OH]$^-$. via CH$_2$O loss was characterized by its MI and CID mass spectra.$^{[36]}$ The heat of formation of this distonic ion is not available yet.
6.2.2.3 Distonic isomers of ether radical cations

The smallest distonic isomer of ether radical cations is \textsuperscript{17}\textsuperscript{+} \textsuperscript{+}(H)CH\textsubscript{3}, which was generated from the fragmentation of [CH\textsubscript{3}OCH\textsubscript{2}COOH]\textsuperscript{+} via CO\textsubscript{2} loss.\textsuperscript{[29]} This distonic ion was characterized by the absence of m/z 26 and m/z 27 in its CID mass spectrum. This indicates that the ion has no C-C bond. The major MI fragmentation produced m/z 31. The AE of this metastable peak led to an apparent \(\Delta r\text{H}^\circ\) (m/z 31) = 201 kJ mol\(^{-1}\), well above \(\Delta r\text{H}^\circ\) (CH\textsubscript{2}OH), 169 kJ mol\(^{-1}\) \textsuperscript{[37]}, and below \(\Delta r\text{H}^\circ\) (CH\textsubscript{3}O\textsuperscript{+}), 253 kJ mol\(^{-1}\) \textsuperscript{[38]}. The daughter ion was thus confirmed to be \textsuperscript{17}\textsuperscript{+} \textsuperscript{+}CH\textsubscript{2}OH. In contrast, loss of CH\textsubscript{3}\textsuperscript{+} from [CH\textsubscript{3}OCH\textsubscript{3}]\textsuperscript{+} produces an unstable [CH\textsubscript{3}O\textsuperscript{+}] ion which fragments into \textsuperscript{+}CHO + H\textsubscript{2}.\textsuperscript{[39]} The heat of formation of \textsuperscript{17}\textsuperscript{+} \textsuperscript{+}CH\textsubscript{2}O(H)CH\textsubscript{3} has been calculated to be 186.5 kJ mol\(^{-1}\) \textsuperscript{[38]}, which is close to \(\Delta r\text{H}^\circ\) (CH\textsubscript{3}OCH\textsubscript{3}\textsuperscript{+}), 187.2 kJ mol\(^{-1}\).\textsuperscript{[40]} The high energy barrier measured to be 53 kJ mol\(^{-1}\), separates the two isomers and prevents their interconversion.\textsuperscript{[29]}

Two distonic isomers, \textsuperscript{18}\textsuperscript{+} \textsuperscript{+}CH\textsubscript{2}CH\textsubscript{2}O(H)CH\textsubscript{3} and \textsuperscript{19}\textsuperscript{+} \textsuperscript{+}CH\textsubscript{2}O(H)CH\textsubscript{2}CH\textsubscript{3} were found to dissociate in a manner closely similar to that of ionized propan-1-ol.\textsuperscript{[40]} The energy barriers for the isomerization of these ions have been established and the heat of formation of \textsuperscript{17}\textsuperscript{+} \textsuperscript{+}CH\textsubscript{2}CH\textsubscript{2}O(H)CH\textsubscript{3} was measured to be 170±2 kJ mol\(^{-1}\).\textsuperscript{[41]}

The homologous distonic ion \textsuperscript{20}\textsuperscript{+} \textsuperscript{+}CH\textsubscript{2}CH\textsubscript{2}O(H)CH\textsubscript{2}CH\textsubscript{3} was generated by the fragmentation of [CH\textsubscript{3}CH\textsubscript{2}OCH\textsubscript{2}CH\textsubscript{2}OCH\textsubscript{3}]\textsuperscript{+} via CH\textsubscript{3}CHO loss and found to have lower energy (\(\Delta r\text{H}^\circ = 153\) kJ mol\(^{-1}\))\textsuperscript{[41]} than its conventional isomer C\textsubscript{2}H\textsubscript{5}OC\textsubscript{2}H\textsubscript{5}\textsuperscript{+} (\(\Delta r\text{H}^\circ = 159\) kJ mol\(^{-1}\)).
(CH₃)₂'CCH₂O(H)CH₃ (21) is a distonic isomer of C₅H₁₂O⁺ radical cations. It was formed from the rearrangement-dissociation of [(CH₃)₂C(CH₂OH)CH₂OCH₃]⁺ via CH₂O loss and its ΔrH° was measured to be 6.5 kcalmol⁻¹ lower in energy than that for its conventional isomer, (CH₃)₂CCH₂OH⁺ (being 148 kcalmol⁻¹). The latter isomer rearranges to (CH₃)₂'CCH₂O(H)CH₃ via the formation of a ion-radical complex [(CH₃)₂C⁺ 'CH₂OH], in which the radical can rotate, and so yielding the β-distonic ion (CH₃)₂'CCH₂O(H)CH₃. Another observed distonic isomer of C₅H₁₂O⁺ ions is 'CH₂CH₂O(H)CH₂CH₂CH₃ (22) generated from the fragmentation of 1-ethoxy-2-propoxyethane. In its CID mass spectrum this ion yielded the same products as ionized 1-ethoxypropane (CH₃CH₂OCH₂CH₂CH₃), but with a different branching ratio. This distonic ion was also observed to undergo competitive and successive long-distance H-transfer (1,4-H, 1,5- and 1,6-H shifts), whereas 1,2-H and 1,3-H shifts from a carbon atom to a radical site were not observed.

The γ-distonic isomers of the ether molecule radical cations, CH₃'CHCH₂CH(CH₃)O(H)CH₃, CH₃'CHCH₂CH(CH₃)O(H)CH₂CH₃, •CH₂CH₂CH(CH₃)O(H)CH₃, CH₃'CHCH₂CH₂O(H)CH₃ and CH₃'CHCH₂CH₂O(H)CH₂CH₃ were generated by loss of neutral aldehydes form the appropriate diethers, according to the reasonable fragmentation mechanism depicted in Scheme 6.1.
These distonic radical cations have been studied by CID mass spectrometry and identified by their characteristic decomposition via alcohol loss.\cite{45} However, no thermochemical data have been measured.

The $\delta$-distonic oxonium ions $R_1\text{CHOCH}_2\text{CH}_2\text{O}^\cdot(H)R_2$ ($R_1 = \text{H}, \text{CH}_3$; $R_2 = \text{H}, \text{CH}_3, \text{CH}_2\text{CH}_3$) have been studied.\cite{46} These $\delta$-distonic ions are all derived from ionized $\text{ROCH}_2\text{CH}_2\text{OR}'$ ($R, R' = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$) and fragment, depending on $R$ and $R'$, by three reactions: the loss of an alcohol or a water molecule, the formation of a $\beta$-distonic ion $^\cdot\text{CH}_2\text{CH}_2\text{O}^\cdot(H)R$ and a 1,4-H migration between carbon atoms.\cite{46}

6.2.2.4 Distonic isomers of carbonyl compound radical cations

Intramolecular hydrogen atom transfer in a large number of aldehyde and ketone radical cations has been surmised to give rise to distonic isomers. However, unambiguous evidence for the stability of these ions has not been forthcoming, specially for high mass homologous distonic ions. One of the small distonic isomers among those $\text{C}_n\text{H}_{2n}\text{O}'$ radical cations is $^\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{O}'\text{H}$ (23$^{\ddagger}$), which has been directly generated by the fragmentation of $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}=\text{O}]^{\ddagger}$ via $\text{CH}_2\text{O}$ loss and characterized by MI and CID mass spectrometries.\cite{47} The heat of formation derived from an AE measurement was 180.9 kcalmol$^{-1}$,\cite{47} about 4 kcalmol$^{-1}$ lower than that of $\text{CH}_3\text{CH}_2\text{CHO}^{\ddagger}$. However, it is
about 22 kcalmol\(^{-1}\) \cite{16} higher in energy than the enol isomer CH\(_3\)CH=CHOH\(^{•+}\). This reveals that although a distonic ion can be stabilized by a higher X-H bond energy than C-H, an enol isomer may be the lowest energy species, stabilized by resonance stabilization.

The distonic ion \textsuperscript{16}CH\(_2\)CH\(_2\)C(=O\(^{•+}\))CH\(_3\) (24\(^{•+}\)) was generated from CH\(_3\)COCH\(_2\)CH\(_2\)OCH\(_3\) by CH\(_2\)O loss.\cite{58,59} The MI mass spectrum of 24\(^{•+}\) is very similar to that of CH\(_3\)C(OH)CHCH\(_3\)^{•+}, being distinguished only by the presence of a weak m/z 42 peak in the former spectrum. The CID mass spectra of 24\(^{•+}\) and CH\(_3\)C(OH)CHCH\(_3\)^{•+} are also very similar, differing significantly only in the presence of a very weak m/z 58 in the spectrum of 24\(^{•+}\). The weak m/z 58 in the CID mass spectrum of 24\(^{•+}\) implies the presence of an exposed methylene in the collided ion. The heat of formation of 24\(^{•+}\) was determined by an AE measurement to be 165 kcalmol\(^{-1}\), indicating that the ion is not CH\(_3\)C(OH)CHCH\(_3\)^{•+} \((\Delta H^{\circ}, 139 \text{ kcalmol}^{-1} \text{ \cite{16}})\). The distonic structure was therefore proposed.

The distonic ion 24\(^{•+}\) combined with other distonic isomers, CH\(_3\)CHCH\(_2\)CH(=O\(^{•+}\)) (25\(^{•+}\), \(\Delta H = 164.9 \text{ kcalmol}^{-1}\)) and 'CH\(_2\)CH(CH\(_3\))CH(=O\(^{•+}\)) (26\(^{•+}\), \(\Delta H = 153.9 \text{ kcalmol}^{-1}\)), are believed to be important intermediates involved in the dissociation of CH\(_3\)C(O)CH\(_2\)CH\(_3\)^{•+} and CH\(_3\)CH\(_2\)CH\(_2\)CHO^{•+} radical cations.\cite{48}

The homologous distonic isomers of \(\text{C}_6\text{H}_{10}\text{O}^{•+}\) and \(\text{C}_6\text{H}_{12}\text{O}^{•+}\) ions have been proposed to decompose at low energies in the same way as their conventional isomers and are all interconvertible with each other by three-, five- and six-membered ring hydrogen transfers and three membered ring skeletal rearrangements.\cite{49,50}
Recent studies on the small ester molecular radical cations have shown unambiguously that these small ester molecular ions prefer to rearrange to their distonic isomers in the time scale of $10^{-5}$ s. From double collision experiments on methyl formate ions, it was proposed that the non-decomposing ions have undergone rearrangement into the distonic isomer, $^\cdot\text{CH}_2\text{OC}^+\text{HOH}$ (27$^+$). The proposal was supported by high level ab initio calculations, which showed that first the methyl formate radical cation rearranges via a hydrogen 1,4-shift to the distonic ion, which in turn isomerizes to the hydrogen-bridged complex $[\text{HC}=\text{O} \cdots \cdots \text{H} \cdots \cdots \text{O}=\text{CH}_3]^+$. The calculations also showed that the distonic isomer lies 13.5 kcal/mol$^1$ lower in energy than ionized methyl formate and the rearrangement of methyl formate radical cation to its distonic isomer requires 15.5 kcal/mol$^1$. Vertical ionization of methyl formate produces an ion lying 8.4 kcal/mol$^1$ above ground state ionized methyl formate; consequently, rearrangement to the distonic ion only requires a further 1.4 kcal/mol$^1$. The calculations thus predict that ionization of methyl formate initially produces the σ state of the methyl formate radical cation which may rearrange with a small barrier to the distonic isomer $^\cdot\text{CH}_2\text{OC}^+\text{HOH}$.

$^\cdot\text{CH}_2\text{CH}_2\text{OC}^+\text{HOH}$ (28$^+$), the distonic isomer of ethyl formate radical cation has been generated directly from the fragmentation of 1,4-dioxane-2,3-diol molecule ions via HCOOH loss (Chapter 7). The MI, CID and NR mass spectrometric studies showed that this distonic isomer is the key intermediate involved in the dissociations of ethyl formate radical cations. The rearrangement of ethyl formate ion to this distonic ion was proposed earlier but not substantiated. The heat of formation of this ion, derived from an AE
measurement was 137 kcalmol\(^{-1}\) (Chapter 7), which is 16 kcalmol\(^{-1}\) lower in energy than its conventional isomer HCOOCH\(_2\)CH\(_3\)\(^{+}\) (\(\Delta H = 153\) kcalmol\(^{-1}\))[54]).

The distonic ion, CH\(_3\)CHCH\(_2\)OC\(^{+}\)HOH \(\text{(29\(^{+}\))}\) was also proposed as an intermediate involved in the dissociation of the HCOOCH\(_2\)CH\(_2\)CH\(_3\)\(^{+}\) radical cation.[56] The heat of formation of this distonic ion was estimated to be < 138 kcalmol\(^{-1}\).[56]

The unimolecular chemistry of ionized methyl acetate has received attention anew,[57–62] when it was discovered that the [H\(_3\)C,O\(^{+}\)] radicals formed together with CH\(_3\)CO\(^{+}\) chiefly have the H\(_2\)C\(^{+}\)OH structure rather than the expected methoxy radicals formed by a direct bond cleavage. The reacting configuration for formation of H\(_2\)C\(^{+}\)OH from ionized methyl acetate has been proposed to be the \(\alpha\)-distonic ion \(^{+}\)CH\(_3\)OC\(^{+}\)(OH)CH\(_3\) \(\text{(30\(^{+}\))}\).[61] Extensive deuterium-labelling experiments[58] on methyl acetate and its enol have led to the proposal that this distonic ion is the key intermediate, which accounts for the extensive, but incomplete, loss of positional identity of H and D atoms in the labeled isomers. The proposal was also confirmed by generation of the distonic ion from [CH\(_3\)COOCH\(_2\)OCH\(_3\)]\(^{+}\) via CH\(_2\)O loss.[59] The heat of formation of \(^{+}\)CH\(_2\)OC\(^{+}\)(OH)CH\(_3\) was calculated (MP2/6-31G(d)/3-21G level) to be 127 kcalmol\(^{-1}\) [62], which is in good agreement with the experimentally measured value of 130±1 kcalmol\(^{-1}\).[61] The key intermediate in the fragmentation has not been identified by experiment, but calculations\[62\] indicate that the H-bridged ion [CH\(_3\)C\(^{+}\)O···H\(^{+}\)···OCH\(_2\)] probably plays this role.

The homologous distonic ion \(^{+}\)CH\(_2\)CH\(_2\)C\(^{+}\)(OH)OCH\(_3\) \(\text{(31\(^{+}\))}\) was also proposed to be involved in the dissociations of the CH\(_3\)CH\(_2\)C(=O)OCH\(_3\)\(^{+}\) radical cation from the results of CID mass spectrometry.[61]
The distonic ion \(^{14}\text{CH}_2\text{CH}_3\text{C}^+(\text{OH})_2\) (32\(^+\)) was proposed as an intermediate involved in the dissociation of ionized propanoic acid.\(^{63}\) The experimental evidence showed (Chapter 7) that the ion 32\(^+\) was initially produced from \([\text{CH}_3\text{OCH}_2\text{CH}_2\text{COOH}]^-\) by loss of \(\text{CH}_2\text{O}\), then quickly isomerized to the more stable isomer \(\text{CH}_3\text{CHC(OH)}_2^+\). The CID mass spectrum of 32\(^+\) clearly showed \(\text{CH}_2\) loss, which is absent in CID mass spectra of \(\text{CH}_3\text{CH}_2\text{COOH}^+\) and \(\text{CH}_3\text{CHC(OH)}_2^+\) (generated from \([\text{CH}_3\text{CH}_2\text{CH(CH}_3\text{)}\text{COOH}]^-\) by loss of \(\text{C}_2\text{H}_4\)).

The homologues \(\text{CH}_3\text{CHCH}_2\text{C}^+(\text{OH})_2\) and \((\text{CH}_3)_2\text{CCHC}^+(\text{OH})_2\) were also proposed to be the intermediates involved in the dissociations of \(\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}^+\) and \((\text{CH}_3)_2\text{CHCH}_2\text{COOH}^+\), respectively.\(^{64}\)

6.2.2.5 Distonic ions as the isomers of cyclic radical cations

Several stable distonic ions which are the isomers of small cyclic radical cations, such as the molecular ions of ethylene oxide and cyclobutanone, have been well characterized by ion-molecule reactions.\(^{28}\) The distonic ion \(^{14}\text{CH}_2\text{CH}_2\text{CH}_2^+\) (33\(^+\)) is now believed to be formed by ring opening of internally excited, ionized cyclopropane.\(^{65}\) This distonic ion has been calculated (MP2/6-31G\(^\ast\)/UHF/6-31\(^*\) level) to be 21.7 kcal mol\(^{-1}\) higher in energy than the cyclic cyclopropane radical cation.\(^{66}\) An extensive experimental study\(^{65}\) focusing on dissociation as well as bimolecular reactions of the cyclopropane radical cation showed that the low-energy radical cation is cyclic. Upon excitation, this ion isomerizes to the distonic radical cation, \(^{14}\text{CH}_2\text{CH}_2\text{CH}_2^+\),\(^{63}\) and not to ionized propene as suggested earlier.\(^{67}\)
The distonic ion \(^{18}\text{CH}_2\text{OCH}_2^+\) (34 \(^-\)) is the acyclic isomer of ionized ethylene oxide. Ion 34 \(^-\) was formed by electron ionization and subsequent ring opening of ethylene oxide or by loss of \(\text{CH}_3\text{O}\) from ionized 1,3-dioxolane.\(^{38}\) Ethylene carbonate loses \(\text{CO}_2\) to give \(^1\text{CH}_2\text{CH}_2\text{O}^+\) which quickly isomerizes to \(^{18}\text{CH}_2\text{OCH}_2^+\). High level ab initio molecular orbital studies suggested\(^{69}\) that the cleavage of the C-C bond of ionized ethylene oxide requires only 6.5 \(\text{kcalmol}^{-1}\) and yields an ion that is 20 \(\text{kcalmol}^{-1}\) lower in energy than the cyclic ethylene oxide radical cation, in agreement with experimental data.\(^{74a}\) The ion \(^{18}\text{CH}_2\text{OCH}_2^+\) shows\(^{70}\) \(\text{CH}_2^+\) transfer when reacted with neutral reagents and to be facile for n-donor bases. This reaction has not been observed for other \(\text{C}_2\text{H}_4\text{O}^+\) isomers.\(^{38b}\)

The higher homologue of \(^{18}\text{CH}_2\text{OCH}_2^+\), the ion \(^{18}\text{CH}_2\text{CH}_2\text{OCH}_2^+\) (35 \(^-\)), has also been studied. This ion is formed, for example, by the loss of formaldehyde from ionized 1,4-dioxane.\(^{71}\) Ab initio molecular orbital theory calculations (RHF/4-31G//RHF/STO-3G) indicate\(^{72}\) that \(^{18}\text{CH}_2\text{CH}_2\text{OCH}_2^+\) is 193 \(\text{kcalmol}^{-1}\), in agreement with the AE measurement derived value of 194 \(\text{kcalmol}^{-1}\).\(^{71c}\) The ion \(^{18}\text{CH}_2\text{CH}_2\text{OCH}_2^+\) has been well characterized by CID\(^{71}\) and NR\(^{73}\) mass spectrometries. The studies of the bimolecular reactions of this distonic ion showed that the ion rapidly transfers ionized ethylene to neutral molecules such as \(\text{CH}_3\text{COCH}_3\), \(\text{CH}_3\text{COOH}\), \(\text{NH}_3\), and \(\text{CH}_3\text{CN}\), while the conventional counterpart, the ionized trimethylene oxide only reacts by electron transfer.\(^{11,74}\) Abstraction of \(\text{CH}_3\text{S}^+\) from \(\text{CH}_3\text{SSCH}_3\) by 35 \(^-\) has been reported.\(^{74}\) The fact that \(\text{CH}_3\text{S}\) abstraction was not observed for the conventional isomer or for the even-electron analog, \(\text{CH}_3\text{CH}_2\text{OCH}_2^+\) has led to the suggestion that this reaction involves the
radical site in the distonic ion, and that bond-formation most likely occurs at the radical site.\textsuperscript{[74]}

The distonic ion \(^{\text{\textsuperscript{1}}}{\text{CH}}_{2}\text{CH}_{2}\text{CO}^{+}\) (36\textsuperscript{+}) is the acyclic isomer of ionised cyclopropanone. It was calculated to be the second most stable \(\text{C}_{3}\text{H}_{6}\text{O}^{+}\) isomer.\textsuperscript{[75]} Its heat of formation has been calculated to be 201.6 kcal mol\(^{-1}\) at the G2 level\textsuperscript{[75]} and 197 kcal mol\(^{-1}\) at MP4/6-31G\(^{\ast}\)/6-31G\(^{\ast}\)+6-31G\(^{\ast}\) ZPVE.\textsuperscript{[76]} The ion has been produced from fragmentation of the diketene radical cation via CO loss\textsuperscript{[76,77]} or by loss of ethylene from ionized \(\gamma\)-butyrolactone.\textsuperscript{[78]} The structure of this ion was deduced on the basis of its dissociation reactions.\textsuperscript{[76-78]} The ion \(^{\text{\textsuperscript{1}}}{\text{CH}}_{2}\text{CH}_{2}\text{CO}^{+}\) reacts with dimethyl disulfide through abstraction of a thiomethyl group and charge exchange.\textsuperscript{[79]}

Ionization of cyclobutanone has been suggested to lead to the ring-opened distonic ion \(^{\text{\textsuperscript{1}}}{\text{CH}}_{2}\text{CH}_{2}\text{CH}_{2}\text{CO}^{+}\) (37\textsuperscript{+}) on the basis of ab initio molecular orbital calculations (MP2/6-31G\(^{\ast}\)//6-31G\(^{\ast}\)+ZPVE) which indicate that the distonic structure is 18 kcal mol\(^{-1}\) lower in energy than the cyclic isomer.\textsuperscript{[80]} Differences observed in the CID mass spectra and metastable ion dissociation of ionized cyclobutanone and other \(\text{C}_{3}\text{H}_{6}\text{O}^{+}\) isomers provided further support for this proposal.\textsuperscript{[81]} Comparison of the CID mass spectrum of the derivatized ion to those of reference ions, conclusively demonstrated that a stable \(\gamma\)-distonic ion is generated upon ionization of cyclobutanone.\textsuperscript{[82]} While the majority of the bimolecular reactions of distonic ions seem to involve the charge site, the ring-opened cyclobutanone distonic radical cation shows different, radical-type behavior.\textsuperscript{[82]} For example, the ion abstracts a hydrogen atom from acetone in a reaction that involves bond
formation at the radical site of 'CH$_2$CH$_2$CH$_2$CO', as indicated by the CID mass spectra measured for the reaction product and for certain reference ions.$^{[82]}$

Very recently the stable δ-distonic ion 'CH$_2$CH$_2$CH$_2$CH$_2$CO' (38$^{++}$) was observed from the ion-molecule reaction of 'CH$_2$CH$_2$CH$_2$CO' (37$^{++}$) with CH$_2$CO via CO loss.$^{[13]}$ Whereas the CID mass spectrum of ion 38$^{++}$ did not produce structurally informative data, the studies of its ion-molecule reaction showed that ion 38$^{++}$ abstracted CH$_3$S$^*$ from CH$_3$SSCH$_3$.$^{[13]}$ The slower abstraction rate for 38$^{++}$ than for 37$^{++}$ has been rationalized on the basis that 37$^{++}$ can form a favorable six-membered transition state for the abstraction of CH$_3$S$^*$ after addition of CH$_3$SSCH$_3$ to the charge site.$^{[24]}$ The complete lack of electron-transfer reactions for the ion 38$^{++}$ demonstrates that this ion does not exist in equilibrium with any conventional C$_3$H$_8$O$^{++}$ ion.$^{[13]}$

6.2.2.6 Nitrogen-containing distonic radical cations

The well-described gas-phase distonic amine cation 'CH$_2$NH$_3^+$ (39$^{++}$) was generated by the loss of CH$_2$O from ionised ethanolamine.$^{[12]}$ The large differences between its CID mass spectrum and the CID mass spectrum of CH$_3$NH$_2^{++}$, and the presence of an intense 'CH$_2$NH$_2^{2+}$ ion, are similar to those observed in the 'CH$_2$OH$^+$, CH$_3$OH$^{++}$ system and clearly show that ion 39$^{++}$ is a stable species.$^{[12]}$ Ion 39$^{++}$ was characterized by the fragment NH$_3^{++}$ in its NR mass spectrum, which is absent in the NR mass spectrum of CH$_3$NH$_2^{++}$.$^{[83]}$ Recently, theoretical calculations (G2 level) showed the heat of formation of ion 39$^{++}$ (203.6 kcal mol$^{-1}$) is close to that of CH$_3$NH$_2^{++}$ (204.7 kcal mol$^{-1}$).$^{[17]}$ The energy barrier between these two isomers was calculated to lie 42 kcal mol$^{-1}$ above 'CH$_2$NH$_3^+$. $^{[14]}$
The MI and CID mass spectrometric studies on the distonic ion 'C\textsubscript{2}H\textsubscript{2}C\textsubscript{2}NH\textsubscript{3}\textsuperscript{+} (40\textsuperscript{++}), generated by loss of CH\textsubscript{2}=NH from [H\textsubscript{2}NCH\textsubscript{2}C\textsubscript{2}H\textsubscript{2}NH\textsubscript{2}\textsuperscript{2+}, showed that this ion is markedly different from those of CH\textsubscript{3}CH\textsubscript{2}NH\textsubscript{2}\textsuperscript{+} and CH\textsubscript{3}NHCH\textsubscript{3}\textsuperscript{+}.\textsuperscript{[12,84]} The NR mass spectrometric studies further confirmed that ion 40\textsuperscript{++} is distonic.\textsuperscript{[35]} Ion 40\textsuperscript{++} was found (MP3/6-31G\textsuperscript{**} ZPVE) as the most stable C\textsubscript{2}H\textsubscript{2}N\textsuperscript{++} isomers (7.9 kcalmol\textsuperscript{-1} lower in energy than CH\textsubscript{3}CH\textsubscript{2}NH\textsubscript{2}\textsuperscript{+}).\textsuperscript{[85]}

Another C\textsubscript{2}H\textsubscript{2}N\textsuperscript{++} distonic isomer has been identified as CH\textsubscript{3}CHNH\textsubscript{3}\textsuperscript{+} (41\textsuperscript{++}), formed from the fragmentation of H\textsubscript{2}NCH\textsubscript{2}CH(CH\textsubscript{3})NH\textsubscript{2}\textsuperscript{+} via CH\textsubscript{2}=NH loss or from HOCH\textsubscript{2}CH(CH\textsubscript{3})NH\textsubscript{2}\textsuperscript{+} by loss of CH\textsubscript{2}O.\textsuperscript{[84]} The ion 41\textsuperscript{++} was characterized by the presence of CH\textsubscript{3}CHNH\textsubscript{3}\textsuperscript{2+} in its CID mass spectrum and by deuterium-labelling experiments.\textsuperscript{[84]} The heat of formation of 41\textsuperscript{++} has been determined by ab initio calculations carried out at the MP3/6-31G\textsuperscript{**} ZPVE level to be 186.3 kcalmol\textsuperscript{-1}.\textsuperscript{[83]} The two distonic isomers, 40\textsuperscript{++} and 41\textsuperscript{++} have similar \(\Delta H^0\) values and are well separated from their conventional isomers by high energy barriers ( > 40 kcalmol\textsuperscript{-1}).\textsuperscript{[85]}

The \(\gamma\)-distonic ion 'C\textsubscript{2}H\textsubscript{2}CH\textsubscript{2}C\textsubscript{2}NH\textsubscript{3}\textsuperscript{+} (42\textsuperscript{++}) was observed as an intermediate from ion-molecule reaction of ionised cyclopropane with NH\textsubscript{3}.\textsuperscript{[86]} Ion 42\textsuperscript{++} was characterized by decomposing to CH\textsubscript{2}NH\textsubscript{2}\textsuperscript{+} and to another distonic species, 'C\textsubscript{2}NH\textsubscript{3}\textsuperscript{+}.\textsuperscript{[86]} Stable 'C\textsubscript{2}H\textsubscript{2}CH\textsubscript{2}C\textsubscript{2}NH\textsubscript{3}\textsuperscript{+} was prepared from H\textsubscript{2}NCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{3}\textsuperscript{+} by loss of CH\textsubscript{2}=NH. Ion 42\textsuperscript{++} was also characterized by its NR mass spectrum which showed the fragment NH\textsubscript{3}\textsuperscript{++}.\textsuperscript{[35]} However, the CID mass spectrum of 42\textsuperscript{++} differed only slightly from that of the propylamine molecular ion.\textsuperscript{[35]} Ab initio calculations confirm that 42\textsuperscript{++} should be a stable
species,\textsuperscript{[21,87]} lying 6.7 kcalmol\textsuperscript{-1} \textsuperscript{[87]} or 9.3 kcalmol\textsuperscript{-1} \textsuperscript{[21]} lower in energy than ionised propylamine.

The higher homologous nitrogen-containing distonic ions, such as \( \text{CH}_2\text{CH}_2\text{N}^+\text{H}_2\text{R} \) \((R = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2\text{CH}_2\text{CH}_3, \text{CH}(\text{CH}_3)_2, \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\) and \( \text{C}(\text{CH}_3)_3 \), \( \text{CH}_3\text{CRC}_2\text{N}^+\text{H}_3 \) \((R = \text{H}, \text{and CH}_3)\) and \( \text{CH}_2\text{CR}_1\text{R}_2\text{CH}_2\text{N}^+\text{H}_3 \) \((R_1, R_2 = \text{H, CH}_3)\) have been produced from the fragmentations of alkoxyalkylamine molecular ions, which react by loss of a neutral aldehyde or ketone.\textsuperscript{[88]} The predominant fragmentation and isomerization processes shown in their CID mass spectra are (i) simple cleavage of a C-N bond with formation of alkene ions or alkene molecules, (ii) 1,2-migration of protonated amino groups, and (iii) formation of ammonium ions by elimination of alkenyl radicals. The hydrogen abstractions are generally reversible; in the presence of long alkyl groups, isomerization to amine molecular ions (and vice versa) can occur.

6.2.2.7 Sulphur-containing distonic radical cations

The distonic ion \( \text{CH}_2\text{SH}_2^+ \) \( (43^{\bullet\bullet}) \) was generated from \([\text{HOCH}_2\text{CH}_2\text{SH}]^{\bullet\bullet}\) by loss of \( \text{CH}_2\text{O} \).\textsuperscript{[12]} The differences between the CID mass spectra of 43\( ^{\bullet\bullet} \) and \( \text{CH}_3\text{SH}^{\bullet\bullet} \) are not nearly so striking as for the oxy-analogues. Nevertheless, the enhanced charge stripping peak \([\text{CH}_2\text{SH}_2]^{2+}\) and the greater relative abundances of \( \text{H}_2\text{S}^{\bullet\bullet} \) and \( \text{CH}_2^{\bullet\bullet} \) are in keeping with the behavior of the distonic ion \( \text{CH}_2\text{SH}_2^+ \).\textsuperscript{[12]} The heat of formation of 43\( ^{\bullet\bullet} \) is calculated (G2 level) to be 232.1 kcalmol\textsuperscript{-1}, being 18.7 kcalmol\textsuperscript{-1} higher in energy than \( \text{CH}_3\text{SH}^{\bullet\bullet} \).\textsuperscript{[17]} The experimentally obtained heat of formation of 43\( ^{\bullet\bullet} \) was 223 kcalmol\textsuperscript{-1}.\textsuperscript{[12]} The isomerization energy barrier between \( \text{CH}_2\text{SH}_2^+ \) and \( \text{CH}_3\text{SH}^{\bullet\bullet} \) was calculated to be
24.6 kcalmol\(^{-1}\) above 'CH\(_2\)SH\(_2\)'\(^+\), slightly below the dissociation energy barriers.\[^{14}\] This is consistent with the experimental observations.\[^{12}\]

Another sulphur-containing distonic ion is \((\text{CH}_3)_2\text{S}^+-\text{CH}_2\text{CH}_2\text{S}^-\) \((44''')\), which was formed by the ion-molecule reaction of 'CH\(_2\)OCH\(_2\)'\(^+\) + CH\(_3\)SCH\(_3\) followed by CH\(_2\)O loss.\[^{89}\] Ab initio MO calculations at the MP2/6-31G*/6-31G* + ZPVE level suggest that the ion 44''' is 17.9 kcalmol\(^{-1}\) higher in energy than ionized ethyl methyl sulfide. However, this distonic ion is stable towards isomerization to the conventional structure: the two ions showed distinctly different reactivity in an FT-ICR mass spectrometer. This distonic radical cation possesses unique chemical reactivity in that its reactions are associated with the radical site. Most of these reactions involve a homolytic bond cleavage in the neutral molecule, resulting in abstraction of an atom or a radical by the ion. Hence ion 44''' can be described as an electrophilic radical with an inert charge site.\[^{90}\]

6.2.3 The nature of distonic radical cations

6.2.3.1 The stability of distonic ions

The relative stability of distonic ions compared to their conventional isomers are shown in Table 6.2. Most O, N, F-containing distonic ions are more stable than their conventional isomers. If one viewed the distonic ions as being formed from a C-H bond cleavage in the conventional isomers followed by formation of an X-H bond \((X = \text{O, N, F, ...)\), then, the lower heats of formation of distonic ions compared to their conventional isomers may result from the difference between HAs for the C-H bond and X-H bond in the even-electron ions H-CRR'(CH\(_2\))\(_n\)X-H\(^+\). However, the \(\Delta\Delta H\) values in Table 6.2 change from -20 kcalmol\(^{-1}\) to 31 kcalmol\(^{-1}\), indicating a very wide range of BDEs and this
approach appears unsatisfactory. The HA of X-H in some oxygen-containing cations have been investigated.\textsuperscript{[18]} In general, hydroxyl [O-H] HA values for the removal of a hydrogen atom from an aldeydic of ketonic carbonyl cation are not greatly different from the homolytic bond dissociation energies (BDE) of O-H, typically 104±1 kcalmol\textsuperscript{-1}.\textsuperscript{[91]} In marked contrast, HA values for the ionized carbonyl groups are large indeed, generally exceeding the BDE in water, 119 kcalmol\textsuperscript{-1}.\textsuperscript{[91]} For the nitrogen-containing cations, namely protonated amines, the HA values correspond closely to the BDE in NH\textsubscript{3}, 107 kcalmol\textsuperscript{-1}\textsuperscript{[91]} or are a little smaller. The H-CH\textsubscript{2} bond in oxygen-containing cations is significantly stronger than for any neutral counterparts. It follows that the H-C bond and X-H bond in H-CRR'(CH\textsubscript{2})\textsubscript{n}X-H\textsuperscript{+} may both be stronger than those in the neutral counterparts. Therefore, the stability of a distonic ion compared to that of the conventional isomer may not be directly estimated from the different C-H and X-H bond strengths. Alternatively, if one can assume that in a distonic ion the charge site and the radical site are independent, i.e. there is no significant interaction between the two sites, then the two sites may be considered individually, as shown in Scheme 6.2.

\[
\text{H-CRR'(CH}_2\text{)}_n\text{X} \quad \rightarrow \quad \text{CRR'(CH}_2\text{)}_n\text{X} \quad \rightarrow \quad \text{CRR'(CH}_2\text{)}_n\text{XH}^+\]

\begin{align*}
R, R' &= \text{H, CH}_3, \text{C}_2\text{H}_5, \ldots \ldots \\
n &= \text{0, 1, 2, \ldots \ldots} \\
X &= \text{F, Cl, Br, OR, C(=O)R, C(=O)OR, NRR', SR, \ldots \ldots} \\
\end{align*}

Scheme 6.2
Thus, the heat of formation of a distonic ion can be estimated from the BDE in a neutral organic molecule (M) and the proton affinity (PA) of the molecule, as shown in Eq. 1.

\[
\Delta \tilde{H}^\circ(D)_{\text{cal}} = \left[ \Delta \tilde{H}^\circ(M) + \text{BDE(C-H)} - \Delta \tilde{H}^\circ(H') \right] + \Delta \tilde{H}^\circ(H') - \text{PA(M)} \\
= \Delta \tilde{H}^\circ(R') + \Delta \tilde{H}^\circ(H') - \text{PA(M)}
\] (1)

\(\Delta \tilde{H}^\circ(R')\) is the heat of formation of the organic radical produced from the C-H bond cleavage in an organic molecule. Most of \(\Delta \tilde{H}^\circ(R')\) values are from References 16 and 92. The other unknown \(\Delta \tilde{H}^\circ(R')\) values are estimated from BDE data, which for \(\beta\)- and \(\gamma\)-distonic ions are assumed as the BDE in ethane (100 kcalmol\(^{-1}\)).

The estimated heat of formation values of distonic ions are shown in Table 6.3. The estimation is based on the assumption that there is no charge-radical interaction in the distonic ions and so the difference between the estimated value, \(\Delta \tilde{H}^\circ(D)_{\text{cal}}\), and the measured (or calculated) value, \(\Delta \tilde{H}^\circ(D)\), may indicate the presence of significant charge-radical interaction. The new difference values, \(\Delta \tilde{H}\), are shown in Table 6.4.

It is noteworthy that the \(\Delta \tilde{H}\) values of \(\alpha\)-distonic ions are all close, being 14-18 kcalmol\(^{-1}\) except \(\text{CH}_2\text{Br}H^+\), the heat of formation of which may need further examination. It seems that the charge-radical interaction is not effected by the nature of the X group. This result also indicates that the BDE (C-H) adjacent to a protonated center in a cation is strengthened by about 16±2 kcalmol\(^{-1}\).

The charge-radical interaction in a \(\beta\)-distonic ion is much less, with an average value of \(\Delta \tilde{H}\) (Table 6.4) of about 4-5 kcalmol\(^{-1}\), showing that the effect of the
protonated center on the β-position BDE (C-H) in a cation is significantly lower than for an α-distonic ion. The ΔΔH values for the β-distonic isomers of carbonyl containing molecular ions are similar to those of α-distonic ions, indicating some special charge distribution in those ions, i.e. the charge is located within the O-CHR-OH group, or it is possibly a distonic ion such as \( \text{"CH}_2\text{O}^-\text{C}^=\text{ROH} \).

The ΔΔH values of γ-distonic ions are not close to zero as might have been expected with the charge and radical sites further apart. Those ΔH°(D) values perhaps need further examination. The ΔΔH value of \( \text{"CH}_2\text{CH}_2\text{OC}^=\text{HOH} \) is close to those of β-distonic ions. This may again result from the charge dislocation in the O-CH-\text{OH} group.

The nature of distonic radical cations can be further investigated by comparing the methylene ion affinity (MIA) and ethylene ion affinity (EIA) of some small molecules. The MIA and EIA are obtained from the Eq. 2.

\[
\Delta H_r \quad \text{CH}_2^+ \quad (\text{or C}_2\text{H}_4^+) \quad + \quad \text{M} \quad \rightarrow \quad \text{"CH}_2\text{M}^+ \quad (\text{or } \text{"CH}_2\text{CH}_2\text{M}^+) \\
\text{MIA (or EIA)} \quad = \quad - \Delta H_r \\
= \Delta H^0(\text{CH}_2^+, \text{or C}_2\text{H}_4^+) \quad + \quad \Delta H^0(\text{M}) \quad - \quad \Delta H^0(\text{"CH}_2\text{M}^+, \text{or C}_2\text{H}_4\text{M}^+) \quad (2)
\]

It is well known that for some small molecules the differences between methyl cation affinity (MCA) and ethyl cation affinity (ECA) are constant.\(^{[93]}\) The difference values (\( \Delta \)) shown in Table 6.5 give an average of 33 kcalmol\(^{-1} \) except for HF. The same property is also observed among the distonic ions, which are represented by their difference value between MIA and EIA. The difference values (\( \Delta' \)) shown in Table 6.6
give an average of 58 kcalmol⁻¹ except for HF and HCl. By comparing Δ and Δ' values a common trend can be observed. The ECA values are lower than the MCA values, which is due to the CH₃ group in C₂H₅⁺ having already stabilized the cation site. The EIA values are much lower than the MIA values, which reveals that the cation and radical are already separated in C₂H₅⁺ compared to that in CH₂⁺. This kind of stabilization is more effective than that of CH₃ substitution.

6.2.3.2 Isomerization of distonic ions

Both experimental and theoretical results indicated that the isomerization energy barrier between distonic ions and their conventional radical cations decreases with increasing size of the ion.\(^{34,87}\)

The energy barriers between CH₃(CH₂)ₙNH₂⁺⁺ and CH₂(CH₂)ₙNH₃⁺⁺ (n = 0, 1, 2) have been calculated at the MP2-6-31G* level,\(^{87}\) as shown below.

\[
\begin{align*}
\text{CH}_3\text{NH}_2^{++} & \xrightarrow{1,2 \text{ H-shift}} \text{CH}_2\text{NH}_3^+ & \text{E (kcalmol}^{-1}) \\
\text{CH}_3\text{CH}_2\text{NH}_2^{++} & \xrightarrow{1,3 \text{ H-shift}} \text{CH}_2\text{CH}_2\text{NH}_3^+ & 34.4 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2^{++} & \xrightarrow{1,4 \text{ H-shift}} \text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+ & 16.2 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2^{++} & \xrightarrow{1,5 \text{ H-shift}} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+ & 4.3
\end{align*}
\]

The increasing ease of isomerization (hydrogen shift) is partly accounted for by the decreasing ring strain in the corresponding transition structures. The facile intramolecular rearrangements of larger molecular ions indicates that although the distonic ions may widely exist they will be difficult to characterize.
6.2.3.3 Bond cleavage in distonic ions

An examination of bond length change between distonic ions and their conventional isomers reveals that the bond length between the radical bearing carbon and its α-atom in a distonic ion is shorter than that in the corresponding conventional isomers (see Table 6.7), indicating a special interaction between the radical site and the neighbour group.

A detailed examination of the geometries in the isomers of \( \text{CH}_3\text{CH}_2\text{OH} \), \( \text{CH}_3\text{CH}_2\text{OH}^+ \), \( \text{CH}_2\text{CH}_3\text{OH} \), and \( \text{CH}_2\text{CH}_2\text{OH}^+ \) (Table 6.8) indicated that the α-bond shortening is also observed in the corresponding radicals. In contrast, the charge site makes its α-bond loose. This indicates that the radical site in a distonic ion is keeping the neighbour group close and the charge site is keeping the neighbour group apart. Thus the water loss is not observed from \( \text{CH}_2\text{OH}^+ \), whereas water loss is dominant in the dissociations of \( \text{CH}_2\text{CH}_2\text{OH}^+ \). The radical site in a distonic ion is probably more reactive than the charge center. It follows therefore that the common dissociation channel of distonic ions, i.e. the C-X bond cleavage (Scheme 6.3) is understandable.

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{-XH}^+ & \rightarrow \text{C}_2\text{H}_4^{**} + \text{XH} \\
(X = \text{OH, NH}_2, \text{F, Cl, ...})
\end{align*}
\]

Scheme 6.3

Moreover, the radical reactivity may trigger formation of a cyclic isomer.

\[
\begin{align*}
\text{CH}_2 & \quad \quad \quad \quad \quad \quad \text{CH}_2 \\
\mid & \quad \quad \quad \quad \quad \quad / \setminus \\
\text{CH}_2\text{CH}_2\text{-OH}_2 & \rightarrow \quad \quad [\text{CH}_2\text{-CH}_2\text{***OH}_2]^{**}
\end{align*}
\]
If the β-bond cleavage is indeed triggered by the radical reaction, this bond dissociation may be a rate-determining process. Thus an ion-neutral complex may be involved in the dissociation process. Indeed, the involvement of an ion-neutral complex in the dissociation of distonic ions has been proposed for many distonic ion systems.

6.2.3.4 Ring-strain in ionized molecules

Ring-strain (RS) values in many organic molecules are well documented. Whether these values are comparable to the RS in the corresponding ionized molecules needs to be examined. From the available Δ\text{H}^\circ values of distonic ions (Table 6.2) the RS energies of some molecular ions may be evaluated from the following equation:

\[ \text{ΔH}^\circ (\text{Ring-opened distonic ion}) = \text{ΔH}^\circ (\text{Ring molecular ion}) - \text{RS} \]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>RS in molecule[^{[94]}] (kcalmol(^{-1}))</th>
<th>RS in molecular ions (kcalmol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopropane</td>
<td>27</td>
<td>-22</td>
</tr>
<tr>
<td>Oxirane</td>
<td>27</td>
<td>20</td>
</tr>
<tr>
<td>Oxetane</td>
<td>26</td>
<td>10</td>
</tr>
<tr>
<td>Cyclopropanone</td>
<td>46</td>
<td>17</td>
</tr>
</tbody>
</table>

The values shown above indicate that the RS energy in a molecular ion is not consistent with that in neutral molecule. Ring-opening of a cyclopropane is even an endothermic process. Hence the ring-opening of a molecular ion to yield a distonic ion is not a simple ring-strain release process. Other factors may be in control, such as the resonance stabilities in both ring and ring-opened structures. Hence the relationship
between the heats of formation of a ring-opened distonic ion and its cyclic isomer is derived as follows:

\[
\Delta h^\circ(\text{distonic ion}) = \Delta h^\circ(\text{Ring molecular ion}) - RS + R_1 - R_2
\]

- \(R_1\): Resonance effect in the ring structure;
- \(R_2\): Resonance effect in the ring-opened structure

The \(R_1\) can be estimated from the energy difference between [CH\(_2\)CH\(_2\)CH\(_3\)]\(\text{++}\) and [cyclopropane]\(\text{++}\), because there is no resonance effect in [CH\(_2\)CH\(_2\)CH\(_3\)]\(\text{++}\). If the resonance effect in these small cyclic molecular ions were taken to be the same, the resonance effect in the corresponding distonic ion could be estimated.

<table>
<thead>
<tr>
<th></th>
<th>(\Delta h^\circ(\text{Distonic ion}))</th>
<th>(\Delta h^\circ(\text{Molecular ion}))</th>
<th>RS</th>
<th>(R_1)</th>
<th>(R_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CH(_2)CH(_2)CH(_3)](\text{++})</td>
<td>262</td>
<td>240</td>
<td>27</td>
<td>49</td>
<td>0</td>
</tr>
<tr>
<td>[CH(_2)OCH(_2)](\text{++})</td>
<td>211</td>
<td>231</td>
<td>27</td>
<td>(49)</td>
<td>42</td>
</tr>
<tr>
<td>[CH(_2)CH(_2)OCH(_3)](\text{++})</td>
<td>194</td>
<td>204</td>
<td>26</td>
<td>(49)</td>
<td>33</td>
</tr>
<tr>
<td>[CH(_2)CH(_2)CO](\text{++})</td>
<td>197</td>
<td>214</td>
<td>46</td>
<td>(49)</td>
<td>29</td>
</tr>
</tbody>
</table>

The above estimations result in a larger resonance effect in [CH\(_2\)OCH\(_2\)]\(\text{++}\) than [CH\(_2\)CH\(_2\)OCH\(_3\)]\(\text{++}\). This is consistent with that in the former the delocalization region is C-O-C, whereas in the latter the delocalization region is only O-CH\(_2\). However, as the ring resonance effects are different in these molecular ions, we can only estimate the value of \(R_1 + R_2\). Theoretical calculations are required to make accurate evaluations.
6.3 Conclusion

44 stable distonic radical cations have been discussed. By analysis of the available thermochemical data the interaction of the radical site and the charge site was found to be 16±2 kcal mol⁻¹ in α-distonic ions or 3-4 kcal mol⁻¹ (average) in β-distonic ions. The examination of the bond length change in the distonic ions relative to their conventional isomers shows that the radical effect results in a shorter α-bond length and probably is responsible to the special bond cleavage in the distonic ions.
6.4 References


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   (1985)


<table>
<thead>
<tr>
<th>Distonic ion (D)</th>
<th>Generation</th>
<th>Characterization</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{15} \text{CH}_2\text{FH}^+)</td>
<td>([\text{FCH}_2\text{COOH}]^+) → (^{15} \text{CH}_2\text{FH}^+)</td>
<td>CID, AE</td>
<td>12</td>
</tr>
<tr>
<td>(^{15} \text{CH}_2\text{ClH}^+)</td>
<td>([\text{ClCH}_2\text{COOH}]^+) → (^{15} \text{CH}_2\text{ClH}^+)</td>
<td>CID, AE</td>
<td>12</td>
</tr>
<tr>
<td>(^{15} \text{CH}_2\text{BrH}^+)</td>
<td>([\text{BrCH}_2\text{COOH}]^+) → (^{15} \text{CH}_2\text{BrH}^+)</td>
<td>CID, AE</td>
<td>12</td>
</tr>
<tr>
<td>(^{15} \text{CH}_2\text{CH}_2\text{FH}^+)</td>
<td>([\text{FCH}_2\text{CH}_2\text{CH}_2\text{OH}]^+) → (^{15} \text{CH}_2\text{CH}_2\text{FH}^+)</td>
<td>MI, CID, NR</td>
<td>19</td>
</tr>
<tr>
<td>(^{15} \text{CH}_2\text{CH}_2\text{ClH}^+)</td>
<td>([\text{ClCH}_2\text{CH}_2\text{CH}_2\text{OH}]^+) → (^{15} \text{CH}_2\text{CH}_2\text{ClH}^+)</td>
<td>MI, CID, CS, NR</td>
<td>19</td>
</tr>
<tr>
<td>(^{15} \text{CH}_2\text{CH}_2\text{BrH}^+)</td>
<td>([\text{BrCH}_2\text{CH}_2\text{CH}_2\text{OH}]^+) → (^{15} \text{CH}_2\text{CH}_2\text{BrH}^+)</td>
<td>MI, CID, NR</td>
<td>19</td>
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<tr>
<td>(^{15} \text{CH}_2\text{CICH}_2^+)</td>
<td>([\text{CH}_2\text{CICH}_2\text{COOH}]^+) → (^{15} \text{CH}_2\text{CICH}_2^+)</td>
<td>CID, CS, NR, AE</td>
<td>19, 20</td>
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<tr>
<td>(^{15} \text{CH}_2\text{CHBrH}^+)</td>
<td>([\text{CH}_2\text{CHBrCOOH}]^+) → (^{15} \text{CH}_2\text{CHBrH}^+)</td>
<td>MI, CID, NR, AE</td>
<td>19, 20</td>
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<tr>
<td>(^{15} \text{CH}_2\text{ClCH}_3)</td>
<td>([\text{ClCH}_2\text{COOCH}_3]^+) → (^{15} \text{CH}_2\text{ClCH}_3)</td>
<td>CID, CS, NR, AE</td>
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<td>(^{15} \text{CH}_2\text{BrCH}_3)</td>
<td>([\text{BrCH}_2\text{COOCH}_3]^+) → (^{15} \text{CH}_2\text{BrCH}_3)</td>
<td>MI, CID, NR, AE</td>
<td>19</td>
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<tr>
<td>(^{15} \text{CH}_3\text{OH}_2^+)</td>
<td>([\text{HOCH}_2\text{CH}_2\text{OH}]^+) → (^{15} \text{CH}_3\text{OH}_2^+)</td>
<td>CID, CS, CID, AE</td>
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Table 6.1  Generation and characterization of distonic radical cations, continues

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<th>Distonic Ion (D)</th>
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<th>Characterization</th>
<th>References</th>
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<td>( \cdot \text{CH}_2\text{CH}_2\text{OH}_2^* )</td>
<td>( [\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}]^* ) ( \rightarrow ) ( \cdot \text{CH}_2\text{O} ) ( \cdot \text{CH}_2\text{CH}_2\text{OH}_2^* )</td>
<td>MI,CID,AE</td>
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<td>( \text{CH}_3\cdot \text{CHOH}_2^* )</td>
<td>( [\text{CH}_3\text{CH} (\text{OH})\text{COOH}]^* ) ( \rightarrow ) ( \cdot \text{CO}_2 ) ( \cdot \text{CH}_2\text{CHOH}_2^* )</td>
<td>MI,CID</td>
<td>28</td>
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<td>( \cdot \text{CH}_2\text{CH}_3\text{CH}_2\text{OH}_2^* )</td>
<td>( [\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}]^* ) ( \rightarrow ) ( \cdot \text{CH}_2\text{O} ) ( \cdot \text{CH}_2\text{CH}_3\text{CH}_2\text{OH}_2^* )</td>
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<td>( [\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}]^* ) ( \rightarrow ) ( \cdot \text{CH}_2\text{O} ) ( \cdot \text{CH}_2\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}_2^* )</td>
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<tr>
<td>( \cdot \text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}_2^* )</td>
<td>( [\text{CH}_3\text{OCH}_2\text{OCH}_2\text{CH}_2\text{OH}]^* ) ( \rightarrow ) ( \cdot \text{CH}_2\text{O} ) ( \cdot \text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}_2^* )</td>
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<td>( [\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3]^* ) ( \rightarrow ) ( \cdot \text{CH}_2\text{O} ) ( \cdot \text{CH}_2\text{CH}_3\text{O}^* (\text{H})\text{CH}_3 )</td>
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<td>( \cdot \text{CH}_2\text{O}^* (\text{H})\text{CH}_2\text{CH}_3 )</td>
<td>( [\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3]^* ) ( \rightarrow ) ( \cdot \text{CH}_2\text{O} ) ( \cdot \text{CH}_2\text{O}^* (\text{H})\text{CH}_2\text{CH}_3 )</td>
<td>MI,CID</td>
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<td>( \cdot \text{CH}_2\text{CH}_3\text{O}^* (\text{H})\text{CH}_2\text{CH}_3 )</td>
<td>( [\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3]^* ) ( \rightarrow ) ( \cdot \text{CH}_2\text{O} ) ( \cdot \text{CH}_2\text{CH}_3\text{O}^* (\text{H})\text{CH}_2\text{CH}_3 )</td>
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<td>( \cdot \text{CH}_2\text{CH}_3\text{O}^* (\text{H})\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
<td>( [(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})\text{CH}_2\text{OCH}_3]^* ) ( \rightarrow ) ( \cdot \text{CH}_2\text{O} ) ( \cdot \text{CH}_2\text{CH}_3\text{O}^* (\text{H})\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
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<td>( [\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3]^* ) ( \rightarrow ) ( \cdot \text{CH}_2\text{O} ) ( \cdot \text{CH}_2\text{CH}_3\text{O}^* (\text{H})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
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<td>'CH$_3$CH$_2$CH(=O'H)</td>
<td>[CH$_3$OCH$_2$CH$_2$CHO]**</td>
<td>→ 'CH$_3$CH$_2$CH(=O'H)</td>
<td>MI,CID,AE</td>
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<tr>
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<td>[CH$_3$CH$_2$CH$_2$CHO]**</td>
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<td>MI,CID,AE</td>
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<td>'CH$_3$CH(CH$_3$)CH(=O'H)</td>
<td>[CH$_3$CH(CH$_3$)CHO]**</td>
<td>→ 'CH$_3$CH(CH$_3$)CH(=O'H)</td>
<td>MI,CID,AE</td>
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<tr>
<td>'CH$_3$CH$_2$C(=O'H)CH$_3$</td>
<td>[CH$_3$OCH$_2$CH$_2$COCH$_3$]**</td>
<td>→ 'CH$_3$CH$_2$C(=O'H)CH$_3$</td>
<td>MI,CID,AE</td>
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<td>'CH$_3$OC'HOH</td>
<td>[HCOOCH$_2$CH(CH$_3$)$_3$]**</td>
<td>→ 'CH$_3$OC'HOH</td>
<td>CID,NR</td>
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<td>'CH$_3$CH$_2$OC'HOH</td>
<td>[1,4-dioxane-2,3-diol]**</td>
<td>→ 'CH$_3$CH$_2$OC'HOH</td>
<td>MI,CID,NR,AE *</td>
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<td>CH$_3$CH$_2$OCH$_2$OH</td>
<td>[HCOOCH$_2$CH$_2$CH$_3$]**</td>
<td>→ 'CH$_3$CHCH$_2$OC'HOH</td>
<td>MI,CID,AE</td>
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<td>'CH$_3$OC'(OH)CH$_3$</td>
<td>[CH$_3$COOCH$_2$OCH$_3$]**</td>
<td>→ 'CH$_3$OC'(OH)CH$_3$</td>
<td>MI,CID,AE</td>
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<td>'CH$_3$CH$_2$OC'(OH)CH$_3$</td>
<td>[CH$_3$CH$_2$COOCH$_3$]**</td>
<td>→ 'CH$_3$CH$_2$OC'(OH)CH$_3$</td>
<td>MI,CID,AE</td>
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<td>'CH$_3$CH$_2$C'(OH)$_2$</td>
<td>[CH$_3$OCH$_2$CH$_2$COOH]**</td>
<td>→ 'CH$_3$CH$_2$C'(OH)$_2$</td>
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<tr>
<td>'CH$_3$CH$_2$CH$_2$</td>
<td>[cyclopropane]**</td>
<td>→ 'CH$_3$CH$_2$CH$_2$'</td>
<td>Bimole.</td>
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<tr>
<td>'CH$_3$OCH$_2$</td>
<td>[1,3-dioxolane]**</td>
<td>→ 'CH$_3$OCH$_2$'</td>
<td>Bimole.</td>
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<td>[1,4-dioxane]**</td>
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<tr>
<td>'CH₂CH₂CO⁺</td>
<td>[γ-butyrolactone]** → 'CH₂CH₂CO⁺</td>
<td>Bimole.</td>
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<td>[cyclobutanone]** → 'CH₃CH₂CH₂CO⁺</td>
<td>CID,Bimole.</td>
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<tr>
<td>'CH₃CH₂CH₂CH₂CO⁺</td>
<td>'CH₃CH₂CH₂O⁺ + CH₂CO → 'CH₃CH₂CH₂CH₂CO⁺</td>
<td>CID,Bimole.</td>
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<td>[H₂NCH(CH₃)CH₂NH₂]** → CH₃'CHNH₃⁺</td>
<td>CID,NR</td>
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<td>CID,NR</td>
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<td>'CH₂SH₂⁺</td>
<td>[HOCH₂CH₂SH]** → 'CH₂SH₂⁺</td>
<td>CID,AE</td>
<td>12</td>
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<tr>
<td>(CH₃)₂S⁺-CH₂⁺</td>
<td>'CH₂OCH₂⁺ + CH₃SCH₃ → (CH₃)₂S⁺-CH₂⁺</td>
<td>Bimole.</td>
<td>89,90</td>
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<tr>
<td>Distonic Ions (D)</td>
<td>Δ\text{H}^\circ (D)</td>
<td>Ref.</td>
<td>Conventional Ions (C)</td>
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<td>CH₃F⁺</td>
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<td>CH₂CH₂CH₂CH₂OH₂⁺</td>
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<td>CH₂CH₂COCH₂⁺</td>
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Table 6.2  Heats of formation (kcal mol⁻¹) of distonic ions and their conventional isomers, continues

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<th>ΔH°(D)</th>
<th>Ref.</th>
<th>Conventional Ions (C)</th>
<th>ΔH°(C)</th>
<th>Ref.</th>
<th>ΔΔH (ΔH°(D) - ΔH°(C))</th>
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<td>53a</td>
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<td>'CH₃O'('H)CHO</td>
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<td>HCOOCH₂CH₃⁺⁺</td>
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<td>16</td>
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<td>CH₃COOCH₃⁺⁺</td>
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<td>127</td>
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<td>'CH₃OCH₃⁺⁺</td>
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<td>ethylene oxide⁺⁺</td>
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<td>trimethylene oxide⁺⁺</td>
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<td>cyclopropanone⁺⁺</td>
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<td>-17</td>
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<td>cyclobutane⁺⁺</td>
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<td>CH₃NH₂⁺⁺</td>
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<td>16</td>
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<td>CH₃SH⁺⁺</td>
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<td>19</td>
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<td>(CH₃)₂S⁻⁻CH₂⁺⁺</td>
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<td>CH₃CH₂SCH₂⁺⁺</td>
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<td>16</td>
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Table 6.3  Estimation of heats of formation of distonic radical cations, \((\Delta H^0(D))_{est}^1\)

<table>
<thead>
<tr>
<th>Molecule(M)</th>
<th>(\Delta H^0(M))</th>
<th>(\Delta H^0(R))</th>
<th>BDE(C-H)(^2)</th>
<th>PA(M)</th>
<th>Distonic ion (D)</th>
<th>(\Delta H^0(D)_{est})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)F</td>
<td>-59</td>
<td>-8</td>
<td>103</td>
<td>145</td>
<td>'CH(_3)FH'</td>
<td>213</td>
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<tr>
<td>CH(_3)CH(_2)F</td>
<td>-63</td>
<td></td>
<td>(100)</td>
<td>165</td>
<td>'CH(_3)CH(_2)FH'</td>
<td>186</td>
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<tr>
<td>CH(_3)CH(_2)CH(_2)F</td>
<td>-68</td>
<td>(100)</td>
<td>(100)</td>
<td>165</td>
<td>'CH(_3)CH(_2)CH(_2)FH'</td>
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<td>CH(_3)Cl</td>
<td>-20</td>
<td>31</td>
<td>103</td>
<td>163</td>
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<td>CH(_3)CH(_2)Cl</td>
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<td>(100)</td>
<td>169</td>
<td>'CH(_3)CH(_2)Cl'</td>
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<td>CH(_3)CH(_2)CH(_2)Cl</td>
<td>-32</td>
<td></td>
<td>(100)</td>
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<td>(100)</td>
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<td>CH(_3)Br</td>
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<td>-6.2</td>
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<tr>
<td>CH(_3)CH(_2)OH</td>
<td>-56</td>
<td>-14.5(^4)</td>
<td>(100)</td>
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<td>'CH(_3)CH(_2)OH'</td>
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<td>(100)</td>
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<td>(100)</td>
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<td>(100)</td>
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<td>HCOOCH(_3)CH(_3)</td>
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<td>'CH(_3)N(_3)'</td>
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1. Values are from Reference 16, except indicated.
2. From estimations.
3. From reference 22.
4. Values are from Reference 92.
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<th>Distonic ion (D)</th>
<th>$\Delta H_f^o(D)$</th>
<th>$\Delta H_f^o(D)_{\text{est}}$</th>
<th>$\Delta \Delta H_f = \Delta H_f^o(D) - \Delta H_f^o(D)_{\text{est}}$</th>
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<td></td>
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<tr>
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<td>213</td>
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<td>16</td>
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<tr>
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<td>178</td>
<td>18</td>
</tr>
<tr>
<td>CH$_3$CHOH$_2^+$</td>
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<td>16</td>
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<td>171</td>
<td>15</td>
</tr>
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<td>$\cdot CH_2NH_3^+$</td>
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<td>190</td>
<td>14</td>
</tr>
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<td>175</td>
<td>16</td>
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<td>11</td>
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<td>166</td>
<td>4</td>
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<tr>
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<td>185</td>
<td>0</td>
</tr>
<tr>
<td>$\cdot CH_2CH_2O^+$(H)C$_2$H$_5$</td>
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<td>153</td>
<td>0</td>
</tr>
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<td>$\beta$-distonic isomers of carbonyl molecular ions</td>
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<td></td>
<td></td>
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<tr>
<td>$\cdot CH_2OC^+HOH$</td>
<td>156</td>
<td>138</td>
<td>18</td>
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<td>111</td>
<td>16</td>
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<td>$\gamma$-distonic ions</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>185</td>
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<td>159</td>
<td>13</td>
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<td>-2</td>
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<td>$\gamma$-distonic isomers of carbonyl molecular ions</td>
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<tr>
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<td>8</td>
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<tr>
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<td>$\cdot CH_2$CH$_2C(=O^+H)CH_3$</td>
<td>165</td>
<td>156</td>
<td>9</td>
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### Table 6.5 The methyl cation affinity (MCA) and ethyl cation affinity (ECA) of some small molecules, in kcal mol\(^{-1}\)

<table>
<thead>
<tr>
<th>Molecule (M)</th>
<th>(\Delta H^\circ) (M)</th>
<th>(\Delta H^\circ) (CH(_3)M(^+))</th>
<th>MCA (M)</th>
<th>(\Delta H^\circ) (C(_2)H(_2)M(^+))</th>
<th>ECA (M)</th>
<th>(\Delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-65</td>
<td>162</td>
<td>34</td>
<td>138</td>
<td>13</td>
<td>(21)</td>
</tr>
<tr>
<td>HCl</td>
<td>-22</td>
<td>183</td>
<td>56</td>
<td>170</td>
<td>24</td>
<td>32</td>
</tr>
<tr>
<td>HBr</td>
<td>-9</td>
<td>191</td>
<td>61</td>
<td>180</td>
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<td>34</td>
</tr>
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<td>H(_2)O</td>
<td>-58</td>
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<td>67</td>
<td>121</td>
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<td>30</td>
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<td>130</td>
<td>83</td>
<td>118</td>
<td>50</td>
<td>33</td>
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<tr>
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<td>80</td>
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<td>89</td>
<td>59</td>
<td>54</td>
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</tr>
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<td>104</td>
<td>137</td>
<td>68</td>
<td>36</td>
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<tr>
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<td>114</td>
<td>132</td>
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<td>83</td>
<td>164</td>
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\(\text{Average}\) 33

1. All values from reference 16.
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<thead>
<tr>
<th>Molecule(M)</th>
<th>MIA(M)</th>
<th>EIA(M)</th>
<th>( \Delta' )</th>
</tr>
</thead>
<tbody>
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<td>3</td>
<td>(32)</td>
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<td>22</td>
<td>56</td>
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<tr>
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<td>60</td>
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<tr>
<td>HCOOH</td>
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<td>57</td>
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<tr>
<td>CH(<em>2)CO ((\Delta</em>{f}H^0),-11)</td>
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<td>67</td>
<td>56</td>
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<tr>
<td>(\text{CH}<em>2\text{O}) ((\Delta</em>{f}H^0),-26)</td>
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<td>35</td>
<td>59</td>
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<tr>
<td>NH(_3)</td>
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<td>57</td>
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<tr>
<td>Molecular ion</td>
<td>Bond length (Å)</td>
<td>Distonic ion</td>
<td>Bond length (Å)</td>
</tr>
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<td>--------------</td>
<td>-----------------</td>
<td>--------------</td>
<td>-----------------</td>
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<tr>
<td>[FCH₂-CH₃]⁺⁺</td>
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<td>HF⁺CH₂-CH₂⁺</td>
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<td>H₂O⁺CH⁻-H</td>
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<td>CH₃C'HOH</td>
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<td>0.987</td>
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1. Unpublished values from Dr. L. Radom; at MP2//6-31G* level.
Chapter 7

C$_3$H$_6$O$_2$$^{+\ast}$ radical cations

7.1 Introduction

A particular interest in C$_3$H$_6$O$_2$$^{+\ast}$ isomers was evoked by the observation that the majority of low-energy molecular ions of methyl acetate lost 'CH$_2$OH rather than CH$_3$O' in the formation of the acetyl cation, CH$_3$CO$^\ast$. The key experiment was the collision-induced dissociative ionization of the free-radical products from metastable methyl acetate molecular ions.$^{[1]}$ The dissociation process was proposed$^{[2,3]}$ to involve a distonic isomer CH$_3$C'(OH)OCH$_2$' (2), which in turn isomerizes to a hydrogen-bridged radical cation [CH$_3$C=O$^{\cdots\cdots}$H$^{\cdots\cdots}$O=CH$_2$]$^{+\ast}$ (3) followed by direct hydrogen bond cleavage to the products:

\[
\begin{align*}
\text{CH}_3\text{COOCH}_3^{+\ast} & \rightarrow \text{CH}_3\text{C'(OH)OCH}_2' \\
(1) & \quad (2) \\
\downarrow & \\
[\text{CH}_3\text{C}=\text{O}^{\cdots\cdots}\text{H}^{\cdots\cdots}\text{O}=\text{CH}_2]^{+\ast} & \rightarrow \text{CH}_3\text{CO}^+ + '\text{CH}_2\text{OH} \\
(3a) & \\
\end{align*}
\]

Scheme 7.1

The involvement of the O$^{\cdots\cdots}$H$^{\cdots\cdots}$O bridged isomer 3a in the gas-phase ion chemistry of ionized acetol, CH$_3$C(=O)CH$_2$OH$^{+\ast}$ (4) has been considered recently.$^{[4]}$ The MS/MS/MS experiments on D-labeled acetol isotopomers and ab initio MO calculations led to the proposal that ions 4 dissociated to CH$_3$CHOH$^+$ + CHO$^\ast$ via a C$^{\cdots\cdots}$H$^{\cdots\cdots}$O bridged
isomer 3b instead of the O•••H•••O bridged isomer 3a. Although 3b is ~ 11 kcal/mol higher in energy than 3a,\textsuperscript{[3]} it was readily formed from the ion-neutral complex [CH\textsubscript{3}C(=O)•••HOCH\textsubscript{2}•••] (4a), which was found by the calculations to be accessible from ion 4. Thus the most satisfactory pathway was suggested as the following:

\[
[\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{OH}]^{2+} \rightarrow [\text{CH}_3\text{C}(=\text{O})\cdots\cdots\text{HOCH}_2]^{2+} \quad (4) \quad (4a)
\]

\[
[\text{CH}_3\text{C}(=\text{O})\cdots\cdots\text{H}••\cdots\text{CH}_2]^{2+} \rightarrow [\text{CH}_3\text{C}l=\text{O}••\cdots\cdots\text{O=CH}]^{2+} \rightarrow \text{CH}_3\text{CHOH}^+ + \text{CHO}^- \quad (3b) \quad (3c)
\]

Scheme 7.2

These thorough studies on CH\textsubscript{3}COOCH\textsubscript{3}^{2+} and CH\textsubscript{3}COCH\textsubscript{2}OH\textsuperscript{2+} indicated that both distonic isomers and hydrogen-bridged isomers are all actively involved in these C\textsubscript{3}H\textsubscript{6}O\textsubscript{2}^{2+} systems.

Ionized ethyl formate (5) displays characteristics quite different from isomers 1 and 4 in its unimolecular dissociation processes. The important fragmentation in the MI mass spectrum of 5 is H\textsubscript{2}O loss, which lost its priority in the CID mass spectrum of 5, being exceeded by the intensity of the C\textsubscript{2}H\textsubscript{4} \textsuperscript{+} ion (HCOOH loss).\textsuperscript{[5]} The different decay rate constants observed for the formation of C\textsubscript{2}H\textsubscript{4} \textsuperscript{+} and C\textsubscript{2}H\textsubscript{4}O \textsuperscript{+} (H\textsubscript{2}O loss) indicates two separate, prior isomerization processes.\textsuperscript{[6]} The intermediate involved in the formation of C\textsubscript{2}H\textsubscript{4} \textsuperscript{+} was assigned to a distonic ion *CH\textsubscript{2}CH\textsubscript{2}OC^\textsuperscript{+}OH (6), which was formed from ion 5 via a McLafferty rearrangement. The other intermediate, responsible for the formation of C\textsubscript{2}H\textsubscript{4}O \textsuperscript{+} was first suggested to be CH\textsubscript{3}CHC(OH)\textsubscript{2} \textsuperscript{+} (7). The examination of the structure of C\textsubscript{3}H\textsubscript{4}O\textsuperscript{+}, however, showed that it most likely was *CH\textsubscript{2}CH\textsubscript{2}CO\textsuperscript{+}, rather than
CH$_3$CHCO$^{++}$ which is known to be produced from CH$_3$CHC(OH)$_2^{++}$ (7). Hence it was proposed that the fragmentation to "CH$_2$CH$_2$CO" also came from the distonic ion 6.$^{[5]}$ Some more complicated isomerization steps, which remain unknown, may be involved in this dissociation process.

The direct generation and detailed characterization of the distonic ion "CH$_2$CH$_2$OC"HOH (6) will be shown in this Chapter. Moreover, the characterization of ion 7 and its distonic isomer "CH$_2$CH$_2$C"(OH)$_2$ (8) which has been produced for the first time, will be also discussed.

7.2 Experimental

The metastable ion (MI), the collision-induced dissociation (CID) and the neutral-reionization (NR) mass spectra were obtained with the VG ZAB-3F mass spectrometer. Appearance energy (AE) values were measured with the KRATOS MS 902 mass spectrometer. The CID and NR mass spectra (8-keV ions) were obtained in the second field-free region (2ffr) of the ZAB-3F using He to effect collision-induced dissociation or using O$_2$ to effect reionization (main beam transmission 80%) and Xe for neutralization. The structure of the products of spontaneous or collision-induced dissociation of ions in the 2ffr was probed by obtaining their CID mass spectra in the third field-free region (3ffr) using O$_2$ as the collision gas. All compounds used were commercially available (Aldrich) and purified where necessary. Deuteration of the hydroxyl groups in 1,4-dioxane-2,3-diol and CH$_3$OCH$_2$CH$_2$COOH was achieved by dissolving a small amount of sample in D$_2$O, after which water was removed; this was repeated three times.
7.3 Results and discussion

7.3.1 Generation of $\text{C}_2\text{H}_4\text{O}_2^{+*}$ isomers

The distonic ion $^*\text{CH}_2\text{CH}_2\text{OC}^{+*}\text{HOH}$ was produced directly from the fragmentation of ionized 1,4-dioxane-2,3-diol (A) via HCOOH loss.

\[ \text{O} \quad \text{OH} \quad ^* \quad \text{OH} \quad \rightarrow \quad ^*\text{CH}_2\text{CH}_2\text{OC}^{+*}\text{HOH} + \text{HCOOH} \quad \text{(6)} \]

As discussed in Chapter 6, a cyclic molecular ion may well fragment to a distonic ion via loss of a small molecule. Indeed ion 6 (m/z 74) is dominant in the MI and CID mass spectra of A. The kinetic energy release (T<sub>0.5</sub>) in the metastable dissociation of A via HCOOH loss is 19 meV, likely indicating that no reverse energy barrier was involved. It is possible that the ion A first isomerized to an acyclic intermediate (by breaking the C2-C3 bond) which then dissociated directly to ion 6 by HCOOH loss.

The appearance energy (AE) of ion 6 measured from the metastable dissociation of A was 9.26 ± 0.1 eV, leading to the heat of formation of 6 as 137 kcallmol<sup>-1</sup>. The heat of formation of HCOOH is -90.5 kcallmol<sup>-1</sup> and the heat of formation of 1,4-dioxane-2,3-diol is estimated by the additivity rule<sup>[8]</sup> to be -167 kcallmol<sup>-1</sup>. Thus ion 6 is 16 kcallmol<sup>-1</sup> more stable than ionized ethyl formate ($\Delta_{f}H^{O} = 153$ kcallmol<sup>-1</sup>). This result is expected, as the distonic isomers of ester molecular ions are commonly more stable than their conventional isomers. For instance, $^*\text{CH}_2\text{OC}^{+}(\text{OH})\text{CH}_3$ ($\Delta_{f}H^{O} = 127$ kcallmol<sup>-1</sup>) is lower
in energy than CH₃COOCH₃⁺ (Δ_H° = 139 kcalmol⁻¹ [7]), but so stable as the enol ion
*CH₂C'(OH)OCH₃, Δ_H° = 114 kcalmol⁻¹ [7].

The enol isomer of ionized propanoic acid CH₃CHC(OH)₂⁺ (7) was generated
from the fragmentation of CH₃CH₂CH(CH₃)COOH⁺⁺ (B) via C₂H₄ loss or from the
dissociation of CH₃CH(COOH)₂⁺⁺ (C) via CO₂ loss.

\[
\text{CH₃CH₂CH(CH₃)COOH⁺⁺} \quad \rightarrow \quad \text{CH₃CHC(OH)₂⁺⁺} + \text{C₂H₄} \quad (2)
\]

\[
\text{CH₃CH(COOH)₂⁺⁺} \quad \rightarrow \quad \text{CH₃CHC(OH)₂⁺⁺} + \text{CO₂} \quad (3)
\]

Both reactions 2 and 3 are rearrangement-fragmentation processes. Ion 7 is the
second most intense peak in the MI and CID mass spectra of B, which preferably
dissociated via CH₃⁺ loss. The possible product ion by CH₃⁺ (Δ_H°, 34.8 kcalmol⁻¹ [7]) loss
is CH₃CHCHC(OH)₂⁺ (Δ_H°, 78 kcalmol⁻¹ [7]). This dissociation process is slightly less
endothermic than dissociation to CH₃CHC(OH)₂⁺⁺ (Δ_H°, 104 kcalmol⁻¹ [7]) via C₂H₄
(Δ_H°, 12.5 kcalmol⁻¹ [7]) loss. The T₀.₅ value in the metastable dissociation of B for C₂H₄
loss was measured to be 6.2 meV, indicating that no reverse energy barrier was involved.
It is thus suggested that CH₃CH₂CH(CH₃)COOH⁺⁺ (B) rapidly isomerizes to a distonic
isomer CH₃C'CHCH(CH₃)C'(OH)₂ (B') via a 1,4-hydrogen shift. Ion B' is the precursor
which dissociates to both CH₃CHC(OH)₂⁺⁺ (7) and CH₃CHCHC(OH)₂⁺.

The MI dissociation of CH₃CH(COOH)₂⁺⁺ (C) to ion 7 via CO₂ loss (reaction 3)
showed a T₀.₅ value of 721 meV, which may result from a significant reverse energy
barrier for dissociation or a high isomerization energy barrier for C to isomerize to a more
stable isomer. The intensity of m/z 74 increased 73% in the CID mass spectrum of C, indicating it is sensitive to collisional activation. The process is thus believed to involve a transition state higher in energy than that for CH₃CHC(OH)₂⁻ + CO₂, i.e.

\[
\text{CH}_{3}\text{CH(COOH)}_{2}^{+} \rightarrow \left[ \begin{array}{c}
O = C \\
\text{CH} - \\
\text{CH}_{3} \end{array} \right]^{+} \rightarrow \text{CH}_{3}\text{CHC(OH)}_{2}^{+} + \text{CO}_{2}
\]

Scheme 7.3

The distonic ion 'CH₂CH₂C'(OH)₂ (8) was produced from the fragmentation of ionized 3-methoxy-propanoic acid via CH₂O loss.

\[
\text{CH}_3\text{OCH}_2\text{CH}_2\text{COOH}^{+} \rightarrow '\text{CH}_2\text{CH}_2\text{C}'(\text{OH})_2 + \text{CH}_2\text{O} \quad \text{(4)}
\]

\[
\text{CH}_3\text{OCH}_2\text{CH}_2\text{COOH}^{+} \rightarrow '\text{CH}_2\text{CH}_2\text{C}'(\text{OH})_2 + \text{CH}_2\text{O} \quad \text{(8)}
\]

Ion 8 was dominant in the MI and CID mass spectra of ion D. That the intensity of ion 8 (m/z 74) was not increased by introducing collision gas to the 2ffr indicates that this dissociation process may involve a stable intermediate. Moreover, the kinetic energy release (T₀, 13 meV) was not affected by the collisional activation either, indicating that the isomerization energy barrier to the stable intermediate may lie close to the dissociation energy barrier. This intermediate is most likely 'CH₂OCH₂CH₂C'(OH)₂ (D') which is accessible by a 1,6-hydrogen shift from ion D.

7.3.2 Characterization of C₂H₄O₂⁻ distonic isomers 6 and 8

The distonic isomers can be characterized by their MI and CID mass spectrometries. However, if the isomerization energy barrier between the distonic ion and
its conventional isomer is below the lowest energy requirement for dissociation, the
distonic ion may not be distinguishable by MI mass spectrometry but may show some
specific dissociations in its CID mass spectrum.

7.3.2.1 *CH₂CH₂OC'HOH, 6

The distinguishing characteristic of this distonic isomer was the intense peak at m/z
28 in its MI mass spectrum (Table 7.1) compared to that in the MI mass spectrum of
HCOOCH₂CH₃⁺⁺ (9). The m/z 28 daughter ion was confirmed by the fragments of m/z 25
- m/z 27 in its CID mass spectrum to be C₂H₄⁺⁺. The similar small KER (T₀.5) values 2-3
meV, for this dissociation of metastable 6 and 9 indicates that both isomers probably have
the same dissociation energy barrier. It was suggested⁵¹ that isomer 9 isomerized to 6 via
a McLafferty rearrangement followed by dissociation to C₂H₄⁺⁺ via HCOOH loss. The
domination of C₂H₄⁺⁺ in the MI and CID mass spectra (Tables 7.1 and 7.2) of the directly
generated 6 confirmed this suggestion. Whereas in the CID mass spectra of both 6 and 9
the intensities of C₂H₄⁺⁺ increased, the increase in the CID mass spectrum of 6 was
greater, in keeping with it being a direct bond cleavage. It was noticeable that the other
dissociations of metastable 6 other than HCOOH loss, showed different sensitivities to
collisional activation, indicating that they are involved in some other isomerization
processes. These will be discussed in the following section. Thus distonic isomer 6 is the
reacting configuration by which ion 9 loses HCOOH.

Another distinguishing characteristic of 6 was the doubly charged ion C₃H₆O₂²⁺ in
its CID mass spectrum. There was no doubly charged ion peak in the CID mass spectrum
of 9. This characteristic further confirms 6 as a distonic ion. In general, distonic ions show
doubly charged peaks in their CID mass spectra more often than their conventional
isomers. [9]

In the MI dissociations of C₃H₆O₂⁺⁺ isomers (Table 7.1) only 6 showed a fragment
at m/z 45 (CHO loss). This daughter ion was confirmed by the ratio of m/z 19 to m/z 43 in
its CID mass spectrum to be CH₂CHOH₂⁺⁺ [10] see Figure 1. Moreover, in the MI mass
spectrum of 'CH₂CH₂OC'HOD, produced from 1,4-dioxane-2,3-diol-d₂ by HCOOD loss,
the ratio of m/z 45 (CDO loss) to m/z 46 (CHO loss) was 12 (Table 7.3), indicating that
the hydroxyl group is likely involved in CHO loss. It is therefore proposed that a
hydrogen-bridged species [CH₂CH₂O***H***OCH]⁺⁺ may lead to the CHO loss.

7.3.2.2 'CH₂CH₂C'(OH)₂, 8

The MI mass spectrum of 8 was the same as those of CH₂CHC'*(OH)₂ (7) and
CH₃CH₂COOH⁺⁺ (10), see Table 7.1. The only characteristic of 8 was the presence of the
fragment C₂H₄O₂⁺⁺ in its CID mass spectrum (Table 7.2). The fragments of C₂H₄O⁺⁺ (H₂O
loss) and CHO₂⁺ (CH₃ loss) in the CID mass spectrum of this C₂H₄O₂⁺⁺ daughter ion
(Figure 7.2) confirmed that it is CH₂C(OH)₂⁺⁺ [11] Thus the structure of 8 is indeed
'CH₂CH₂C'(OH)₂, which fragments to CH₂C(OH)₂⁺⁺ by CH₂ loss. The C₂H₄O₂⁺⁺ peak in
the CID mass spectrum of 8 generated from metastable CH₃OCH₂CH₂COOH⁺⁺ via CH₂O
loss was more intense (Figure 7.3) than that of the ion source generated species, indicating
that ion 8 having a lower internal energy (MI generated), shows stronger structure
characteristics than those with higher internal energy (ion source generated). Thus the ion
source generated ions 8 most likely (at least in part) isomerize to the more stable isomer 7
(ΔH°, 104 kcalmol⁻¹ [7]). The heat of formation of 8 can be estimated from a
thermochemical cycle (Eq. 1) to be 115 kcal mol\(^{-1}\) by taking PA(CH\(_3\)CH\(_3\)COOH) = 192 kcal mol\(^{-1}\), BDE(H-CH\(_2\)CH\(_2\)COOH) = 100 kcal mol\(^{-1}\) and \(\Delta H^\circ(\text{CH}_3\text{CH}_2\text{COOH}) = -107\) kcal mol\(^{-1}\).[7]

\[
\Delta\text{f}H^\circ (8) = [\Delta\text{f}H^\circ (\text{P}) + \text{BDE(C-H)} - \Delta\text{f}H^\circ (\text{H})] + \Delta\text{f}H^\circ (\text{H}^\circ) - \text{PA (P)} \quad \text{Eq. 1}
\]

\[
P = \text{CH}_3\text{CH}_2\text{COOH}
\]

The MI dissociations of 7, 8 and 10 by H\(_2\)O loss had closely similar \(T_{0.5}\) values, 87-91 meV, indicating that the three isomers have a common dissociation barrier. The dissociation energy barrier for 10 dissociating by H\(_2\)O loss has been measured to be 144.4 kcal mol\(^{-1}\), from its appearance energy of 10.9 eV.[12] Thus the isomerization barrier between 7, 8 and 10 is below 144.4 kcal mol\(^{-1}\), as shown in the energy diagram (Figure 7.4).

7.3.3 Isomerization-dissociation processes of C\(_3\)H\(_6\)O\(_2^{+}\) isomers

The C\(_3\)H\(_6\)O\(_2^{+}\) isomers, 6, 7 and 8 together with ionized ethyl formate, HCOOCH\(_2\)CH\(_3^{+}\) (9) and ionized propanoic acid, CH\(_3\)CH\(_2\)COOH\(^{+}\) (10) were characterized by MI, CID, CIDI and NR mass spectrometries. The MI and CID mass spectra of those C\(_3\)H\(_6\)O\(_2^{+}\) isomers are summarized in Tables 7.1 and 7.2, respectively.

According to the relative intensities in their MI and CID mass spectra, the C\(_3\)H\(_6\)O\(_2^{+}\) isomers 6, 7, 8, 9 and 10 can be divided into two groups. The first group includes HCOOCH\(_2\)CH\(_3^{+}\) (9) and its γ-distonic isomer \(^{1}\text{CH}_2\text{CH}_2\text{OC}^{+}\)OH (6). The second group includes CH\(_3\)CH\(_2\)COOH\(^{+}\) (10), its enol isomer CH\(_3\)CHC(OH)\(_2^{+}\) (7) and its β-
distonic isomer \( \text{CH}_2\text{CH}_2\text{C}^\cdot(\text{OH})_2 \) (8). The significant difference between the two groups is the fragmentation by HCOOH loss for 9 and 6.

7.3.3.1 Dissociation by HCOOH loss

The dissociation by HCOOH loss was only observed in the MI mass spectra of the first group (Table 7.1). The kinetic energy release of this process was very small (\( T_{0.5} \), 2-3 meV). Moreover, the intensity of \( \text{C}_2\text{H}_4^+ \) in the MI mass spectrum of 6 was much higher than that in the MI mass spectrum of 9, indicating that 6 is the direct precursor for \( \text{C}_2\text{H}_4^+ + \text{HCOOH} \). This was further confirmed by the CID mass spectrum of 6, in which \( \text{C}_2\text{H}_4^+ \) was predominant (Table 7.2). As discussed above ion 6 is 16 kcalmol\(^{-1} \) lower in energy than ion 9. The latter may thus easily isomerize to the former via a McLafferty rearrangement.

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\| & \quad \| \\
\left[ \text{CH}_2\text{CH}_2\text{OCH} \right]^+ & \rightarrow \text{CH}_2\text{CH}_2\text{OC}^\cdot\text{H} \rightarrow \text{CH}_2\text{CH}_2^+ + \text{HCOOH} \\
6 & \quad 9
\end{align*}
\]

The MI mass spectrum of \( \text{CH}_2\text{CH}_2\text{OC}^\cdot\text{HOD} \) (Table 7.3) showed little H/D mixing in the HCOOH loss. In the CID mass spectrum of \( \text{CH}_2\text{CH}_2\text{OC}^\cdot\text{HOD} \) the ratio of m/z 28 (\( \text{C}_2\text{H}_4^+ \)) to m/z 29 (most \( \text{C}_2\text{H}_3\text{D}^+ \)) was about 1, indicating a great extent of H/D mixing during collisional activation. Thus the barrier for a hydrogen shift in 9 must be higher than that for the \( \text{CH}_2\text{CH}_2\text{-O} \) bond cleavage. It is noteworthy that the C-O bond cleavage in \( \text{CH}_2\text{CH}_2\text{OC}^\cdot\text{HOH} \) produces ionized ethene. The charge is retained on the alkyl group. Even in the CID mass spectra of 6 and 9 the \( \text{CH}_2\text{O}_2^+ \) ion was absent. However, in the
CID mass spectra of the second group of ions, i.e. 7, 8 and 9, CH₂O₂⁻⁻ was observed, indicating that the charge was retained on the carbonyl group.

7.3.3.2 Dissociation by H₂O loss

The isomers in the first group showed C₃H₅O⁺⁺ as the most intense peak in their MI mass spectra. The structure of this C₃H₅O⁺⁺ daughter ion was examined by being transmitted to the 3ffr, where its CID mass spectrum was produced, as shown in Table 7.4. The base peak of m/z 28 in the CID mass spectra of C₃H₅O⁺⁺ is due to CO loss, it being 80 kcal/mol⁻¹ less endothermic than C₂H₄ loss. The heats of formation of CO, CO⁺⁺, C₂H₄, and C₂H₄⁺⁺ are -26 kcal/mol⁻¹, 296.7 kcal/mol⁻¹, 12.5 kcal/mol⁻¹ and 254.8 kcal/mol⁻¹, respectively. The fragment ion m/z 42 in the CID mass spectra of the C₃H₅O⁺⁺ daughter ions from isomers 6 and 9 clearly indicated the presence of a terminal methylene group and therefore the structure CH₂CH₂CO⁺ was assigned to it. The base peak of m/z 28 in the CID mass spectra of C₃H₅O⁺⁺ daughter ions from isomers 7, 8 and 10 also result from CO loss. The weak peak at m/z 41 and the absence of m/z 42, indicates the structure CH₃CHCO⁺⁺.

The C₃H₆O₂⁺⁺ isomers in the second group dissociate to CH₃CHCO⁺⁺ by H₂O loss with the same kinetic energy release (T₀₅, 87-91 meV), indicating that the same intermediate ion was involved. It has been calculated[13] that the dissociation of CH₃COOH⁺⁺ (I) to CH₃CO⁺⁺ by H₂O loss involves the stable intermediate "CH₂C(=O)OH₂⁺ (II). The isomerization is a stepwise process, i.e. I first isomerizes to CH₂C(OH)₂⁺⁺ (III), which is 20 kcal/mol⁻¹ lower in energy than I. Ion III then isomerizes to II with an energy barrier of 52 kcal/mol⁻¹. Ion II has been experimentally observed and
characterized.[14] By analogy, \( \text{CH}_3\text{CHC}(=\text{O})\text{OH}_2^{+} \) (11) may be the intermediate involved in the dissociation of \( \text{CH}_3\text{CHC(OH)}_2^{+} \) (7), \( \text{CH}_2\text{CH}_2\text{C(OH)}_2^{+} \) (8) and \( \text{CH}_3\text{CH}_2\text{COOH}^{+} \) (10) to \( \text{CH}_3\text{CHCO}^{+} + \text{H}_2\text{O} \). Ions 8 and 10 may readily isomerize to ion 7, since 7 is 26 kca\text{m}ol^{-1} more stable than 10\text{[7]} and about 11 kca\text{m}ol^{-1} more stable than 8. Isomer 10 may isomerize to 8 by a simple 1,4-hydrogen shift. Such a five-membered ring H-transfer has been found to compete with the McLafferty rearrangement in ionized carbonyl compounds.[15] Thus the isomerization of 10 to 8 may require only a small energy barrier.

The isomerization energy barrier between 7 and 8 can be estimated from that for the 1,2-hydrogen shift between \( \text{CH}_3\text{CHCO}^{+} \) and \( \text{CH}_2\text{CH}_2\text{CO}^{+} \), which was calculated to be 25.5 kca\text{m}ol^{-1} (G2 procedure).[16] The isomerization process is shown in Figure 7.4.

The MI mass spectrum of \( \text{CH}_2\text{CH}_2\text{C}^{+}(\text{OH})\text{OD} \) produced from dissociation of \( \text{CH}_3\text{OCH}_2\text{CH}_2\text{COOD}^{+} \) via \( \text{CH}_2\text{O} \) loss showed that the ratio of HDO loss to \( \text{H}_2\text{O} \) loss is about 0.41, which is less than the statistical value of 0.5 and so indicating incomplete H/D mixing before water loss. The intermediate 11 is most likely involved in this dissociation process, as shown in Scheme 7.4.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{COOH}^{+} & \\
(10) & \\
\rightarrow & \\
\text{CH}_3\text{CHC(OH)}_2^{+} & \\
\rightarrow & \\
\text{CH}_3\text{CHC(OH)}_2 & \rightarrow \\
\text{CH}_3\text{CHC(OH)}_2^{+} & \\
\rightarrow & \\
\text{CH}_3\text{CHCO}^{+} + \text{H}_2\text{O} & \rightarrow \\
(7) & \rightarrow \\
(11) & \\
\text{CH}_2\text{CH}_2\text{C}^{+}(\text{OH})_2 & \\
(8) & \\
\end{align*}
\]

Scheme 7.4

The dissociation by \( \text{H}_2\text{O} \) loss of the \( \text{C}_3\text{H}_6\text{O}_2^{+} \) isomers in the first group, \( \text{CH}_2\text{CH}_2\text{C}^{+}\text{HOH} \) (6) and \( \text{HCOOCH}_2\text{CH}_3^{+} \) (9), is more complicated. The two isomers
gave the same kinetic energy release \((T_{0.5}, 37 \text{ meV})\) in this dissociation process (Table 7.1), indicating that they isomerize to the same intermediate before dissociation. As the daughter ion \(C_3H_5O^+\) was confirmed to be \(\text{"CH}_2\text{CH}_2\text{CO}^+\), the question is how isomers 6 and 9 produce this fragment ion. Is the C-O bond cleavage and the C-C bond formation a stepwise or a concerted process?

By analogy with the isomers in the second group, the precursor ion structure for \(\text{H}_2\text{C}^\cdots\text{O}\)

\[\text{CH}_2\text{CH}_2\text{CO}^+\] may well be \(\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}_2^+\), which may arise from \([\text{H}_2\text{C}^\cdots\text{CHOH}]^+\) \((12)\). Hudson and McAdoo suggested that the immediate product from \(\text{H}_2\text{O}\) loss is \(\text{CH}_2\text{CH}_2\text{OC}^+\), higher in energy than \(\text{CH}_2\text{CH}_2\text{CO}^+\), and which might readily collapse to the latter. If it were the case, the reacting configuration for \(\text{H}_2\text{O}\) loss would be \(\text{CH}_2\text{CH}_2\text{OC}^+\text{HOH} (6)\). The water loss would be encouraged by collisional activation as was the dissociation of 6 to \(\text{CH}_2\text{CH}_2^+\) by \(\text{HCOOH}\) loss. However, the water loss was very insensitive to collisional activation, indicating that another intermediate is likely involved. Moreover, the MI mass spectrum of \(\text{CH}_2\text{CH}_2\text{OC}^+\text{HOD}\) showed little H/D mixing in \(\text{HCOOH}\) loss. However, the ratio of \(\text{C}_3\text{H}_4\text{O}^+\) (HDO loss) to \(\text{C}_3\text{H}_3\text{DO}^+\) (\(\text{H}_2\text{O}\) loss) was 0.75 (statistical = 0.5), indicating some extent of H/D mixing in the water loss process. This result supports the proposal that the \(\text{H}_2\text{O}\) loss involves an intermediate other than isomer 6.

An examination of the metastable ion dissociations of several ester radical cations showed that only ionized ethyl esters dissociate by \(\text{H}_2\text{O}\) loss. Ionized methyl or propyl esters do not do so.
<table>
<thead>
<tr>
<th>Ionized alkyl ester</th>
<th>Distonic isomers</th>
<th>H₂O loss in MI mass spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOOCH₃&quot;</td>
<td>HCO(OH)OCH₂&quot;</td>
<td>No</td>
</tr>
<tr>
<td>HCOOCH₂CH₃&quot;</td>
<td>HCO(OH)OCH₂CH₂&quot;</td>
<td>Yes</td>
</tr>
<tr>
<td>HCOOCH₂CH₂CH₃&quot;</td>
<td>HCO(OH)OC₂H₅&quot;</td>
<td>No</td>
</tr>
<tr>
<td>CH₃COOCH₃&quot;</td>
<td>CH₃C(OH)OCH₂&quot;</td>
<td>No</td>
</tr>
<tr>
<td>CH₃COOCH₂CH₃&quot;</td>
<td>CH₃C(OH)OCH₂CH₂&quot;</td>
<td>Yes</td>
</tr>
<tr>
<td>CH₃COOCH₂CH₂CH₃&quot;</td>
<td>CH₃C(OH)OC₂H₅&quot;</td>
<td>No</td>
</tr>
<tr>
<td>CH₃CH₂COGCH₃&quot;</td>
<td>CH₃CH₂C(OH)OCH₂&quot;</td>
<td>No</td>
</tr>
<tr>
<td>CH₃CH₂COOCH₂CH₃&quot;</td>
<td>CH₃CH₂C(OH)OCH₂CH₂&quot;</td>
<td>Yes</td>
</tr>
</tbody>
</table>

(* The distonic isomer involved in the dissociation of CH₃COOCH₂CH₃" was suggested[17] to be CH₃=OCH₂CH₃". However, the latter may readily isomerize to CH₃C(OH)OCH₂CH₂" via a McLafferty rearrangement.)

Thus ionized esters may well have a common behaviour for H₂O loss, which likely

\[
\text{H}_2\text{C} \cdots \cdots \text{O} \rightarrow [\text{H}_2\text{C} \cdots \cdots \text{C}(\text{R})\text{OH}] \cdots \quad (12', \text{R} = \text{H, CH₃, C₂H₅}).
\]

involves a species such as [H₂C\cdots\cdotsC(R)OH]" (12', R = H, CH₃, C₂H₅). It may be formed from an incomplete O-C bond cleavage. The dissociation process is possibly under thermodynamic control, because the hydrogen lost, whether from R or from the ethyl group depends upon which product ion has lower energy.

<table>
<thead>
<tr>
<th>CₙH₂ₙ₋₂O⁺⁺¹</th>
<th>ΔH°(CₙH₂ₙ₋₂O⁺⁺¹), kJ mol⁻¹</th>
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<tr>
<td>CH₂CH₂CO⁺⁺</td>
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<td>CH₂CHCHO⁺⁺</td>
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<tr>
<td>CH₂CHCOCH₂⁺⁺</td>
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</tr>
<tr>
<td>CH₂CH₂COCH₂⁺⁺</td>
<td>219</td>
</tr>
<tr>
<td>CH₂CHCOCH₂CH₃⁺⁺</td>
<td>186</td>
</tr>
<tr>
<td>CH₂CH₂COCH₂CH₃⁺⁺</td>
<td>&gt;194²</td>
</tr>
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</table>

1. The CₙH₂ₙ₋₂O⁺⁺ ions underlined are the product ions.
2. Estimated from methyl substitution on "CH₂CH₂OCH₂", the value of the methyl substitution effect was assumed to be the same as for CH₃CH₂⁺⁺ + CH₃⁺ → CH₅C⁺HCH₃ + H⁺

220
We propose that the O-C bond cleavage in isomer 6 and C-C bond formation to form intermediate 12 are most likely completed before the H$_2$O loss. Note that the ionized methyl esters, [RC(OH)-OCH$_3$]$^+$ only showed C-O bond cleavage and the ionized propyl esters, [RC(OH)O-C$_3$H$_7$]$^+$ only showed complete O-C bond cleavage without the formation of a C-C bond. Therefore the C-C bond formation in ionized ethyl esters may result from the incomplete O-C bond cleavage, followed rapidly by hydrogen abstraction leading to H$_2$O loss. The dissociation process for 6 and 9 by H$_2$O loss is shown in Scheme 7.5.

\[
\begin{align*}
\text{HCOOCH}_2\text{CH}_3^+ & \rightarrow \text{H}^-\text{C}^\equiv\text{O} \rightarrow [ \ \text{H}_2\text{C}^\equiv\equiv\text{CHOH} \\
\text{H}_2\text{C}^\equiv\equiv\text{O} & \rightarrow \text{CH}_2\text{CH}_2\text{CO}^+ + \text{H}_2\text{O}
\end{align*}
\]

\( \text{(9)} \quad \text{(6)} \quad \text{(12)} \)

Scheme 7.5

The appearance energy of C$_3$H$_4$O$^-$ from 9 has been measured to be 10.73 eV, corresponding to an energy barrier at 155.4 kcalmol$^{-1}$. This is 2.4 kcalmol$^{-1}$ above the energy of 9 ($\Delta_f H^0 = 153$ kcalmol$^{-1}$), indicating that the isomer 9 only lies in a shallow well on the potential energy surface of C$_3$H$_6$O$_2^+$ isomers, as shown in Figure 7.5. The isomer 6 being 16 kcalmol$^{-1}$ lower in energy than 9, sits in a relatively deep well in the potential energy surface. By contrast, the species 12 may lie in only a shallow well, because the water loss process lost its priority in collisional activation decompositions, indicating a lower density of states for intermediate 12 relative to more stable isomers.
7.3.3.3 Dissociation by H loss

Dissociation by H loss was dominant in the MI and CID mass spectra of 7, 8 and 10 and also produced the second most intense peak in the MI mass spectra of 6 and 9 (Tables 7.1 and 7.2). However, in the CID mass spectra of 6 and 9, the peak at m/z 73 was only from metastable ions. The structure of the C₃H₅O₂⁺ daughter ions were characterized by their CID mass spectra, which were all identical to that of CH₂CHC(OH)₂⁺ produced from CH₂CHCOOH + H⁺ (Table 7.5). The absence of m/z 43 in these CID mass spectra indicates that neither CH₂CHCOOH⁺ nor CH₂CH₂COOH⁺ was produced.[18]

The dissociations of 7, 8 and 10 by H loss may be straightforward. The precursor is possibly either CH₃CHC(OH)₂⁺ (7) or "CH₂CH₂C"(OH)₂ (8). Ion 7 is the most stable C₃H₆O₂⁺ isomer and so its direct dissociation processes should be sensitive to collisional activation. Indeed the CID mass spectra of these three isomers all showed an intense peak at C₃H₅O₂⁺, even after the substraction of MI contributions.

The CID mass spectrum of "CH₂CH₂C"(OH)OD produced from CH₃OCH₂CH₂COOD⁺ via CH₂O loss, showed a ratio of D loss to H loss of about 0.09 (Table 7.4), indicating either a large isotope effect or that the H loss is almost wholly from the ethylene group with very little H shift between it and the C(OH)(OD) group. It has been observed[19] that the ratio of D loss to H loss in the MI decompositions of deuterium labelled 8 and 10 was about 0.04, indicating that H/D exchange between the α- and β-carbons in these isotopomers was rapid and that between the ethylene group and the carbonyl group was slow.
The dissociation of isomers 6 and 9 by H loss was very insensitive to collisional activation, the C₃H₅O₂⁺ peak in their CID mass spectra being totally from metastable ions. Hence the dissociating species must be an intermediate which is higher in energy than 6, but which lies in a well. One possibility is that the hydrogen shift in the intermediate 12 may lead to isomer 8, "CH₂CH₂C"(OH)₂, which dissociated to CH₂CHC(OH)₂⁺ and H⁺.

\[ 6 \rightarrow 12 \rightarrow "\text{CH}_2\text{CH}_2\text{C}"(\text{OH})_2 \rightarrow \text{CH}_2\text{CHC(OH)}_2^+ + \text{H}^+ \]

Scheme 7.6

The MI and CID mass spectra of "CH₂CH₂OC"HO⁺D produced from 1,4-dioxane-2,3-diol-d₂ via CHDO₂ loss, showed a ratio of D loss to H loss of about 0.61 (Table 7.3), indicating a strong isotope effect preferred for D loss. Note that in the MI dissociations of "CH₂CH₂OC"HO⁺D, the HCOOH loss showed little H/D mixing, while the H₂O or H loss showed a certain extent of H/D mixing, indicating that the reactions involved different intermediates.

Whereas the H loss from "CH₂CH₂C"(OH)₂ (8) did not show H/D mixing, the H loss from "CH₂CH₂OC"HO⁺H (9) showed extensive H/D mixing; the latter involves more complex isomerization steps. Moreover, in the CID mass spectra of 7, 8 and 10 the presence of m/z 55, which was not observed in the CID mass spectra of 6 and 9, indicated a sequential dissociation from C₃H₅O₂⁺ by H₂O loss. This further confirmed that the H loss from 6 and 9 is a slower process, involving several isomerization steps.
7.3.3.4 Dissociation by CO₂ loss

Another common fragment in the MI mass spectra of these C₃H₆O₂⁺⁺ isomers is m/z 30, C₂H₆⁺⁺. The fragments at m/z 24 - m/z 29 in the CID mass spectrum of this daughter ion confirmed that it was C₂H₆⁺⁺. The fragment at m/z 31 in the MI mass spectra of "CH₂CH₂OC"HOD and "CH₂CH₂C"(OH)OD (Table 7.3) further confirmed this structure.

\[
\text{C}_3\text{H}_6\text{O}_2^{++} \rightarrow \text{C}_2\text{H}_6^{++} + \text{CO}_2
\] (6)

Studies\(^{[18]}\) on the C₃H₅O₂⁺ isomers have revealed that the dissociating configuration of C₃H₅O₂⁺ ions by CO₂ loss was CH₃CH₂OCO⁺, which metastably dissociates to C₂H₅⁺ by CO₂ loss with a T₀.5 of ≤ 0.5 meV. In contrast the T₀.5 values for loss of CO₂ from other C₃H₅O₂⁺ isomers CH₂CH₂OC⁺OH, "CH₂CH₂COOH, CH₃C'HOOH, and HOCH₂CH₂CO⁺ (30 - 35 meV), are much larger than that for loss of CO₂ from CH₃CH₂OCO⁺, indicating that an energy barrier exists for interconversion. In the system of C₃H₆O₂⁺⁺ isomers, the analogous isomer cannot be directly obtained. However, a complex intermediate such as [CH₃CH₂***H***OCO]⁺⁺ may be achieved from 9 and 10. The T₀.5 values of 9 and 10 are a little smaller than those of 6, 7 and 8 (Table 7.1) indicating that the above may well be the structure leading to direct CO₂ loss.

7.3.3.5 Dissociation by CO loss

The dissociation channel by CO loss is only observed in the MI mass spectra of isomers 6 and 9. The structure of the C₂H₆O⁺⁺ daughter ion was investigated by its CID mass spectrum performed in the 3ffr (Figure 7.6a). The intense peak at m/z 28 rather than
m/z 29 indicated that the structure was CH₂CH₂OH₂⁺. The fragment at m/z 46 in the CID mass spectra of 7, 8 and 10 is CH₂O₂⁺ which was confirmed by the presence of major fragments at m/z 29 and m/z 45 in its CID mass spectrum (Figure 7.6b).

One possible pathway for 6 and 9 to fragment to CH₂CH₂OH₂⁺ is via a hydrogen bridged complex [CH₂CH₂O(H)･･･H･･･CO]⁺⁺ (13) which may be formed from an intermediate such as ‘CH₂CH₂O(H)’CHO (14). The proposed mechanism for CO loss is shown below:

\[
\begin{align*}
\text{[HCOOCH₃CH₃]⁺⁺} & \quad \xrightarrow{6} \quad [\text{CH₂CH₂O(H)’CHO}] \quad \rightarrow \quad [\text{CH₂CH₂O(H)･･･H･･･CO}]⁺⁺ \quad 14 \\
[\text{’CH₂CH₂OC’HOH}] & \quad \downarrow \quad \text{CH₂CH₂OH₂⁺} \quad + \quad \text{CO}
\end{align*}
\]

Scheme 7.7

It has been observed that at low temperature (77K) ‘CD₂CH₂OC’HOD radicals (presumably formed by isomerization of CD₂CH₂OCHO⁺⁺) rearrange to ‘CH₂CD₂OC’HOD, suggesting a shift of oxygen between the carbons. Thus the isomerization from 6 to 14 may be energetically accessible. The energy for the isomerization-dissociation of HCOOCH₃⁺⁺ (IV) by CO loss has been calculated (MP3/6-31G”/6-31G” + ZPVE). The isomerization energy barrier between IV and ‘CH₂O’(H)CHO (V) lies 44.4 kcalmol⁻¹ above IV, but the energy barrier between ‘CH₂OC’HOH (VI) and V is 51.8 kcalmol⁻¹ above IV. Ion V isomerizes to a hydrogen bridged complex [CH₂O(H)･･･H･･･CO]⁺⁺ followed by its dissociation to CH₂OH₂⁺ +
CO. In the system 6 and 9 the isomerization energy barriers may be lower than for the analogous ions IV and VI, because the energy barriers for hydrogen shift from alkyl carbon to a heteroatom will decrease with increase of size of the chain in the alkyl group. For example, the isomerization energy barrier between $\text{CH}_3(\text{CH}_2)_n\text{NH}_2^{+*}$ and $\text{CH}_2(\text{CH}_2)_n\text{NH}_3^+$ decreases as $n$ increases.\textsuperscript{[23]}

7.3.4 The NR mass spectra of $C_3H_8O_2^{+*}$ isomers

The NR mass spectra of isomers 6$^{+*}$ and 9$^{+*}$ (Figure 7a,b) were different from the CID mass spectrum of 9$^{+*}$ (Figure 7c). The major peaks in their NR mass spectra were m/z 46 and m/z 29, which are most likely from the collision induced dissociations accompanying neutralization with Xe.

$$\text{Xe} \quad \text{Defect} \quad \text{O}_2$$
$$6^{+*}, \quad 9^{+*} \rightarrow C_2H_4^{+*} + CH_2O_2 \rightarrow CH_2O_2 \rightarrow CH_2O_2^{+*} \rightarrow \text{CHO}_2^{+}, \text{CHO}^+$$  \hfill (7)

$$\rightarrow \text{CHO}_2^{+} + C_2H_3^* \rightarrow C_2H_5^* \rightarrow C_2H_5^* \rightarrow C_2H_3^*, \cdots$$  \hfill (8)

Dissociation to $C_2H_4^{+*} + CH_2O_2$ was predominant over $\text{CHO}_2^{+} + C_2H_3^*$ in the collision induced dissociations (CID). However, $C_2H_5^*$ has a lower ionization energy (IE, 8.13 eV\textsuperscript{[71]} than $\text{CH}_2O_2$ (11.33 eV\textsuperscript{[71]} and so is significant in the NR process. The small peaks at m/z 18 and m/z 17 in the NR mass spectra of 6$^{+*}$ and 9$^{+*}$ were also produced from the CID during the neutralization process.

$$\text{Xe} \quad \text{Defect} \quad \text{O}_2$$
$$6^{+*}, \quad 9^{+*} \rightarrow C_3H_4O^{+*} + H_2O \rightarrow H_2O \rightarrow H_2O^{+*}$$  \hfill (9)
H$_2$O loss was only a minor process in the CID of 6$^{**}$ and 9$^{**}$ (most of the intensity is the contribution of MI dissociation) and the IE of H$_2$O is very high (12.61 eV). Hence fragments m/z 18 and m/z 17 were the weakest peaks in the NR mass spectra of the two isomers. The weak recovery signal of m/z 74 in the NR mass spectrum of 9$^{**}$ indicated that a small amount of 9$^{**}$, without isomerization to 6$^{**}$, survived the neutralization process. The peaks at m/z 55-56 are derived from the dissociations of reionized 9$^{**}$. Thus the neutral counterpart of 9$^{**}$, most likely [CH$_3$CH$_2$OCHO], is stable, whereas the neutral counterpart of 6$^{**}$ is unstable. The higher ratio of m/z 28 to m/z 27 in the NR mass spectra of 6$^{**}$ and 9$^{**}$ may indicate that some neutral C$_2$H$_4$ is produced in the dissociation of neutral C$_3$H$_6$O$_2$, followed by reionization with O$_2$.

\[
\text{Xe} \quad \text{Defect} \quad \text{O}_2 \\
6^{**} \rightarrow \text{CH}_2\text{CH}_2\text{OCH}_2\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{CH}_2\text{O}_2 \rightarrow \text{C}_2\text{H}_4^{**} + \text{CH}_2\text{O}_2^{**} \quad (10)
\]

In contrast to 6$^{**}$, the NR mass spectrum of 7$^{**}$ showed a good recovery signal at m/z 74 (Figure 7.8a). Moreover, the NR mass spectrum of 7$^{**}$ was similar to its CID mass spectrum (Figure 7.8b), indicating that the neutral counterpart of 7$^{**}$ was quite stable.

\[
\text{Xe} \quad \text{O}_2 \\
7^{**} \rightarrow \text{CH}_3\text{CHC(OH)}_2 \rightarrow \text{CH}_3\text{CHC(OH)}_2^{**} \quad (11)
\]

In the NR mass spectra of 8$^{**}$ and 10$^{**}$ (Figure 7.8c,d) the smaller recovery signals and intense peaks at m/z 44 and m/z 28, which were the major peaks in their CIDI mass
spectra, indicated that these C$_3$H$_6$O$_2$$^-$ isomers undergo significant collision induced dissociation as well as neutralization when collided with Xe.

7.4 Conclusions

Five C$_3$H$_6$O$_2$$^-$ isomers have been characterized by MI, CID and NR mass spectrometries. Dissociation mechanisms were proposed from the identification of daughter ion structures. The involvement of unusual intermediates has been proposed. The stability of neutral CH$_3$CHC(OH)$_2$ (1,1-dihydroxy prop-1-ene) in the gas phase has been confirmed by NR mass spectrometry.
7.5 References


<table>
<thead>
<tr>
<th>Fragments</th>
<th>'CH₂CH₂OCH₃OH</th>
<th>HCOOCH₂CH₃**</th>
<th>CH₃CHC(OH)₂**</th>
<th>'CH₂CH₂C'(OH)₂</th>
<th>CH₃CH₂COOH**</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂CHC(OH)₂⁺ + H</td>
<td>100 (146)</td>
<td>100 (137)</td>
<td>100 (124)</td>
<td>100 (118)</td>
<td>100 (117)</td>
</tr>
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<td>'CH₂CH₂CO⁺ + H₂O</td>
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<td>98 (37)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH₃CHCO⁺⁺ + H₂O</td>
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<td>-</td>
<td>38 (87)</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₃H₅⁺ + CO₂</td>
<td>16 (37)</td>
<td>17 (33)</td>
<td>6 (49)</td>
<td>6 (46)</td>
<td>5 (26)</td>
</tr>
<tr>
<td>C₂H₄⁺⁺ + HCOOH</td>
<td>55 (2)</td>
<td>6 (3)</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

1. Relative intensities (%). Values in parentheses are kinetic energy releases (T₀₅) in meV.
<table>
<thead>
<tr>
<th>Fragments</th>
<th>'CH₂CH₂OC'HOH (6)</th>
<th>HCOOCH₂CH₃⁺⁺ (9)</th>
<th>CH₃CH(C(OH))₂⁺⁺ (7)</th>
<th>'CH₂CH₃C'⁺(OH)₂⁺⁺ (8)</th>
<th>CH₃CH₂COOH⁺⁺ (10)</th>
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<tbody>
<tr>
<td>C₃H₃O₂⁺⁺</td>
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<td>100</td>
<td>100</td>
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<td>-</td>
<td>-</td>
<td>3</td>
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<td>45</td>
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<td>CH₃O₂⁺⁺</td>
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<td>4</td>
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<td>4</td>
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<td>CH₂O₂⁺⁺, C₂H₄O⁺⁺</td>
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1. Relative intensities (%).
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<th>( ^{1}\text{CH}_2\text{CH}_2\text{C}^{\text{HOD}} ) ( ^{3})</th>
<th>Statistic</th>
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<td>H</td>
<td>0.92 0.92</td>
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<td>0.83</td>
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<td>D</td>
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<td>H(_2)O</td>
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<td>0.57 0.55</td>
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<td>0.33</td>
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1. Relative intensity (%).
2. Generated from \( \text{CH}_3\text{OCH}_2\text{CH}_2\text{COOD} \) by \( \text{CH}_2\text{O} \) loss.
3. Generated from \( \text{DOCH}_2\text{CH}_2\text{OCHOD} \) by \( \text{CHDO}_2 \) loss.
4. Overlapped by \( \text{C}_3\text{H}_5^{+} \) and \( \text{C}_2\text{H}_4\text{D}^{+} \) losses.
Table 7.4  CID mass spectra of $C_3H_4O^{++}$ daughter ions

<table>
<thead>
<tr>
<th>m/z</th>
<th>$^{13}CH_2CH_2OC^{+}$H2O (6)</th>
<th>HCOOCH$_2$CH$_3^{+}$ (9)</th>
<th>CH$_3$CHC(OH)$_2^{+}$ (7)</th>
<th>$^{13}CH_2CH_2C^{+}(OH)H$ (8)</th>
<th>CH$_3$CH$_2$COOH$^{+}$ (10)</th>
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1. Relative intensities (%).
<table>
<thead>
<tr>
<th>m/z</th>
<th>( \text{'CH}_2\text{CH}_3\text{OC'HOH} ) (6)</th>
<th>( \text{HCOOCH}_2\text{CH}_3^{+} ) (9)</th>
<th>( \text{CH}_3\text{CHC(OH)_2}^{+} ) (7)</th>
<th>( \text{'CH}_2\text{CH}_3\text{C'(OH)_2} ) (8)</th>
<th>( \text{CH}_3\text{CH}_2\text{COOH}^{+} ) (10)</th>
<th>( \text{CH}_3\text{CHCOOH}+\text{H}^+ )</th>
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1. Relative intensities (%); He is the target gas.
2. From self protonation of \( \text{CH}_3\text{CHCOOH} \); \(^{13}\text{C} \) interferences were subtracted.
Figure 7.1  CID mass spectrum of C₆H₄O⁺ daughter ions

Figure 7.2  CID mass spectrum of C₆H₄O₂⁻ daughter ions

Figure 7.3  CID mass spectrum of 'CH₂CH₂C⁺(OH)₂ from metastable [CH₃OCH₂CH₂COOH]⁻ by CH₂O loss
Figure 7.4  Energy diagram (in kca/mol\textsuperscript{-1}) for the isomerization-dissociations of CH\textsubscript{3}CHC(OH)\textsubscript{2}\textsuperscript{+} (7), 'CH\textsubscript{2}CH\textsubscript{2}C\textsuperscript{+}(OH)\textsubscript{2} (8) and CH\textsubscript{3}CH\textsubscript{2}COOH\textsuperscript{+} (10)
Figure 7.5  Energy diagram for the isomerization-dissociations of $^1$CH$_2$CH$_2$OC$^+$HOH (6) and CH$_3$CH$_2$OCHO$^{**}$ (9) (kcalmol$^{-1}$).
Figure 7.6a  CID mass spectrum of C\textsubscript{4}H\textsubscript{4}O\textsuperscript{+} daughter ion from 'CH\textsubscript{2}CH\textsubscript{2}C'(OH)\textsubscript{2} (8)

Figure 7.6b  CID mass spectrum of CH\textsubscript{2}O\textsubscript{2}\textsuperscript{+} daughter ion from 'CH\textsubscript{2}CH\textsubscript{2}OC'\textsubscript{H}(OH) (6)
Figure 7.7  CID and NR mass spectra of 6 and 9
a: NRMS of \(^{13}C\text{H}_2\text{CH}_2\text{OC}^+\text{HOH} (6), \text{Xe/O}_2\)
b: NRMS of \(\text{HCOOCH}_2\text{CH}_3^+ (9), \text{Xe/O}_2\)
c: CIDMS of \(\text{HCOOCH}_2\text{CH}_3^+ (9), \text{He}\)
Figure 7.8  CID and NR mass spectra of 7, 8 and 10
a: NRMS of $\text{CH}_3\text{CHC}^{\prime}\text{(OH)}_2$ (7), Xe/O$_2$

b: CIDMS of $\text{CH}_3\text{CHC}^{\prime}\text{(OH)}_2$ (7), Xe/O$_2$

c: NRMS of $\text{CH}_2\text{CHC}^{\prime}\text{(OH)}_2$ (8), Xe/O$_2$

d: NRMS of $\text{CH}_3\text{CH}_2\text{COOH}^{\prime\prime}$ (10), Xe/O$_2$