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0-612-26103-4
À grand-maman Blanche
Abstract

The work presented in the following pages is the end product of over four years of research in the area of gas phase ion chemistry. During that period of time, different problems related to thermochemical and mass spectrometric aspects of gas phase ion chemistry were addressed.

Combining the available data related to phenyl substituted neutrals (molecules and radicals) and ions (molecular ions and even electron cations) with newly obtained data from electron impact appearance energy measurements, the effect of phenyl substitution on the heat of formation of these species was reviewed. In neutrals, the change in the heat of formation following replacement of an H atom by a phenyl moiety was found to be always destabilizing and the magnitude of the destabilizing effect depended on the functionality at which substitution took place. The enthalpy terms derived empirically were used to revise the heat of formation of a series of substituted alkynes as well as diphenyl methane. In the case of molecular ions and even electron cations, the relationship between the heat of formation and the number of phenyl groups was not straightforward and depended on the chemical nature of the species in which substitution took place. In most cases substitution of a first phenyl group significantly lowered the heat of formation of the ions. This decrease in the heat of formation resulted from a lowering of the ionization energy and, in the case of the even electron cations, from the gained resonance
stabilization energy. As these two stabilizing factors were shown to be much less important when further substitution took place, a monotonic rise in the heat of formation of the ions was observed. This was consistent with the heat of formation associated with the phenyl substituted neutrals becoming the predominant factor in determining the heat of formation of the ions. No general additivity scheme was derived, but for multiple substitution, the linear portion of the relationship between the heat of formation and the number of phenyl groups allowed the estimation of the heat of formation for missing members. A comparison of the effects of vinyl and phenyl substitution showed that vinyl substitution in molecular species was very closely related to the effect of phenyl substitution; whereas, vinyl substitution in radicals behaved very differently than phenyl substitution. From the data available, vinyl substituted radicals appeared to behave like alkyl radicals towards ionization; this was not observed for phenyl substituted radicals.

A controversy surrounding the thermochemical effect of methyl substitution in ketene was investigated by obtaining the heat of formation of ketene and its methyl substituted analogues using the appearance energy measurement method. The heats of formation of CH<sub>2</sub>CO, CH<sub>3</sub>CHCO and (CH<sub>3</sub>)<sub>2</sub>CCO were determined to be -12, -22 and -32±1 kcal mol<sup>-1</sup>, respectively. From these measurements, methyl substitution in ketene was shown to decrease the heat of formation of the methyl substituted species by ca. 10 kcal mol<sup>-1</sup>, which is in keeping with the effect of methyl substitution in structurally related
systems. The heats of formation of CH₃CHCO⁺⁺ and (CH₃)₂CCO⁺⁺ were also determined to be 183 and 165±1 kcal mol⁻¹, respectively. These values were in excellent agreement with the values predicted when using the heats of formation of the neutrals and their corresponding ionization energies. In addition, the heats of formation of C₆H₅CHCO⁺⁺ and (C₆H₅)₂CCO⁺⁺ were determined to be 188 and 212±2 kcal mol⁻¹, respectively, consistent with the behavior of phenyl substitution in structurally related systems. Using these values the heats of formation of the neutral species, C₆H₅CHCO and (C₆H₅)₂CCO, were estimated to be ca. 9 and 30 kcal mol⁻¹, respectively. The proton affinity of CH₂CO was revised to be 197±1 kcal mol⁻¹. In the case of methyl ketene, a proton affinity of 201 kcal mol⁻¹ was consistent with the formation of the lowest energy C₅H₅O⁺ isomer. We suggested that the photoionization data used to obtain the heat of formation of CH₃CH₂CO⁺ be revised and we further suggested that a heat of formation for CH₃CH₂CO⁺ of 145±2 kcal mol⁻¹ be used. From the relationship of the proton affinity with ion size, the proton affinity of (CH₃)₂CCO was estimated to be 206 kcal mol⁻¹.

The dissociation characteristics of phenyl acetate, propanoate and isobutyrate were investigated. Metastable phenyl acetate and propanoate dissociated to ionized phenol and the corresponding neutral ketene. Metastable phenyl isobutyrate dissociated mainly by loss of ionized dimethyl ketene and neutral phenol but also by loss of ionized phenol and neutral dimethyl ketene. The relative intensity of these two peaks was not consistent with predictions
based on thermochemical grounds. Dissociation characteristics of collisionally activated ionized phenyl acetate and propanoate suggested that the molecular ions rearrange to the ion-neutral complexes \([\text{CH}_2\text{CO} \cdots \text{C}_6\text{H}_5\text{OH}^{+\cdots}]\) and \([\text{CH}_3\text{CHCO} \cdots \text{C}_6\text{H}_5\text{OH}^{+\cdots}]\), before dissociating. However, we proposed that ionization of phenyl isobutyrate produced the enol form of the ester which further rearranged to an ion-neutral complex, \([(\text{CH}_3)_2\text{CCO}^{+\cdots} \cdots \text{C}_6\text{H}_5\text{OH}]\) before dissociation. The participation of both intermediates, the enol and the ion-neutral complex form of the ionized ester, was used to rationalize the relative abundance of the fragment ions in the metastable ion mass spectrum of phenyl isobutyrate. Neutralization-reionization mass spectra of all these species showed no recovery signal, supporting the participation of non-bonded intermediates such as the proposed ion-neutral complexes.

The 1-adamantyl \((1\text{Ad}^+)\) cation is particularly interesting because the charge is thought to be formally located at the bridgehead position. Very little data concerning this ion and the 2-adamantyl cation \((2\text{Ad}^+)\) in the gas phase, are available in the literature. A thermochemical study, using electron impact appearance energy measurements determined the heats of formation of the \(1\text{Ad}^+, 2\text{Ad}^+\) and \(1\text{Ad}^+\) to be 153±2 kcal mol\(^{-1}\), 170±2 kcal mol\(^{-1}\) and 11±2 kcal mol\(^{-1}\), respectively. The heat of formation of \(2\text{Ad}^+\) was estimated to be 15 kcal mol\(^{-1}\). The thermochemical measurements suggested that \(1\text{Ad}^+\) and \(2\text{Ad}^+\) ions produced at threshold were indeed tertiary and secondary carbocations that retained their tricyclic structure. A combination of mass spectrometric
techniques showed that 1Ad+ and 2Ad+ ions occupied distinct potential energy wells, separated by an energy barrier high enough to prevent their interconversion. However, at higher energies the two isomers were shown to share a common potential energy surface accounting for their similar dissociation characteristics and the statistical mixing of all the H/D in the 1-C_{10}H_{14}D+ ions which took place before their dissociation by any of the four major accessible channels on the microsecond time scale. The study of the dissociation characteristics of 1-C_{10}H_{15}CH_{2}NH_{2}+ and 1-C_{10}H_{15}CH_{2}OH+ ions, precursor molecules for 1Ad+ ions, and several of their isotopomers revealed that the interaction between the side chain and the adamantyl nucleus was limited to the hydrogens on the heteroatom of the side chain and the methylene hydrogens on the carbon α to the substituted carbon of the ring system. To rationalize the H/D mixing observed, we proposed a simple model in which the side chain can freely rotate.
Acknowledgments

I would like thank the people who have contributed, directly or indirectly, to this thesis.

Thank you Dr. Holmes for providing me with an enthusiastic and productive environment in which to carry out my research. I gained a solid background in mass spectrometry and in physical chemistry in general. I learned to be self-critical of my work, to be persistent and to be patient. I will always try to keep in mind that chemistry should be fun and be considered as a game, and that although it often seems as if chemistry is going to win hands down, there are times when scientists do also score some points!!! It is these moments that make it all worth while!!! I feel very privileged to have been part of your lab.

Thank you Sander for always being there. You are a very patient man; I sometimes think that I would still be trying to understand the electric diagrams of the monochromator if it had not been for you!!! Thank you Clem for your help in figuring out what I had synthesized. Somehow you made it seem not too bad when the synthesis did not work!!! I would also like to thank Fred Lossing for his help with the monochromator as well as for all the interesting anecdotes. I feel privileged to have had the chance to work with him. A special thank you to all my colleagues, Martin, Paul, Hongwen, Dmitri, Andrew, Yan, Don, Jie and Michael, for all your help and also your friendship.

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<th>Description</th>
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<tbody>
<tr>
<td>AE</td>
<td>Appearance energy</td>
</tr>
<tr>
<td>CI</td>
<td>Chemical ionization</td>
</tr>
<tr>
<td>CID</td>
<td>Collision induced dissociation</td>
</tr>
<tr>
<td>CIDI</td>
<td>Collision induced dissociative ionization</td>
</tr>
<tr>
<td>CR</td>
<td>Charge reversal</td>
</tr>
<tr>
<td>CS</td>
<td>Charge stripping</td>
</tr>
<tr>
<td>$\Delta H^0$</td>
<td>Standard heat of formation</td>
</tr>
<tr>
<td>DMA</td>
<td>Dimethylamine</td>
</tr>
<tr>
<td>EI</td>
<td>Electron impact</td>
</tr>
<tr>
<td>ESA</td>
<td>Electrostatic analyzer</td>
</tr>
<tr>
<td>FFR</td>
<td>Field free region</td>
</tr>
<tr>
<td>IE</td>
<td>Ionization energy</td>
</tr>
<tr>
<td>IE$_a$</td>
<td>Adiabatic ionization energy</td>
</tr>
<tr>
<td>IE$_v$</td>
<td>Vertical ionization energy</td>
</tr>
<tr>
<td>KER</td>
<td>Kinetic energy release</td>
</tr>
<tr>
<td>NR</td>
<td>Neutralization-reionization</td>
</tr>
<tr>
<td>PA</td>
<td>Proton affinity</td>
</tr>
<tr>
<td>PIE</td>
<td>Photoionization efficiency</td>
</tr>
<tr>
<td>TMCBD</td>
<td>2,2,4,4-tetramethyl-1,3-cyclobutanedione</td>
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Chapter 1

Introduction

Gas phase ion chemistry is concerned with the production and study of gas phase ionic and neutral species. Its aims are to obtain information on the structural characteristics of species (How are the atoms connected together?), on the reactivity of these species (What unimolecular dissociations and/or rearrangements do they undergo?) and on their thermochemical stability (What is the heat of formation of the species?). The study of these species may be undertaken by a variety of means and mass spectrometry is one method of choice. Using mass spectrometry, a number of different and yet complementary experiments can provide sufficient information to answer the questions just presented.

The technique of mass spectrometry began in J.J. Thompson’s vacuum tube where he studied the nature and behavior of positive rays. From the beginning, Thompson, although not himself a chemist, urged his chemist colleagues to use his newly developed technique for their analysis. The following statement from Thompson’s book entitled “Rays of Positive Electricity and their Application to Chemical Analysis” clearly indicates that he was quite
confident that his technique would serve chemists well: "...I feel sure that there are many problems in chemistry which could be solved with far greater ease by this than by any other method...".

In spite of this far-sighted observation, mass spectrometry stayed in the realm of physicists for quite some time. It was essentially used in the identification of the isotopes of the elements.
F.W. Aston built the first mass spectrometer capable of separating and enriching the isotopes of a given element. This technique was later used to produce enriched uranium samples for use in the Manhattan Project. As the resolving power of the instruments increased, the technique was used in the determination of atomic masses. One field in which this was particularly useful was the petrochemical industry. Characterization of the petroleum distillates were, in the past, based on a series of physico-chemical determinations such as fractional distillation, boiling point measurements and refractive index. Complete analysis of each fraction could take as long as 24 hours. The use of mass spectrometry for the identification of hydrocarbons reduced the time of analysis considerably, and consequently, stimulated a lot of interest towards mass spectrometry.

Using magnetic and electrostatic analyzers, the modern day mass spectrometer has become a high resolution, high sensitivity analytical instrument. The development of ionization methods softer than electron impact, combined with the availability of a variety of mass analyzers, has made mass spectrometry a very powerful and versatile technique. Its use now extends into almost every field of chemistry and beyond.

As the title of this thesis implies, both aspect of gas phase ion chemistry, i.e., thermochemical and mass spectrometric analysis, were used either separately or in combination, in the study undertaken. Chapters 1, 2 and 3 are
introductory chapters. They provide the reader with a short historical account on mass spectrometry in general, a detailed description of the mass spectrometers and the experiments used to characterize ions of interest. Chapter 4 deals with the thermochemical effect of phenyl substitution in neutrals and in ions. It addresses the factors that govern how the heat of formation of the ions and neutrals are affected by phenyl substitution. These ideas are then extended to the investigation of the thermochemical effect of vinyl substitution, another type of \( \pi \) substituent. Chapter 5 addresses the thermochemical effect of methyl substitution in ketene. Experimental results are compared with high level \textit{ab initio} molecular orbital theory calculations and discrepancies between the two series of values are discussed. The proton affinities of ketene and it’s methyl substituted analogue are also revisited. Chapter 6 looks at the dissociation characteristics of phenyl acetate, propanoate and isobutyrate. The difference in behavior is accounted for by the nature of the intermediates involved in the dissociations. Chapter 7 is a combined thermochemical and mass spectrometric investigation on the structure of the 1-adamantyl cation and its isomer, the 2-adamantyl cation. It also addresses the possible interconversion of the two isomers. A discussion on the dissociation characteristics of two precursor molecules used to generate the 1-adamantyl cation is also presented.
Chapter 2

Instrumentation: Production and detection of ions

Fifteen years ago, a mass spectrometer was said to function as a complete chemical laboratory. Inside the mass spectrometer, a gas phase ion chemist prepares his/her ions (ion source), separates the ions of interest (magnetic sector), allows the ions to react unimolecularly or under collisional activation (field free region) and finally analyses the reaction products (electric sector). In the course of our study, three mass spectrometers of different design and characteristics were used to obtain as much information as possible on the ions and neutrals under investigation. The modified VG ZAB-2F was the instrument of choice for all ion and neutral structure characterization experiments, while both the AEI-MS902 and the Monoenergetic Electron Impact Appearance Energy Apparatus allowed thermochemical measurements to be made. In the this chapter a description of these instruments will be presented.
2.1 Modified VG ZAB-2F

2.1.1 Introduction

The VG ZAB-2F\textsuperscript{2} mass spectrometer is a double focusing instrument of reverse geometry. Double focusing because the beam of ions is submitted to the focusing action of both a magnetic and an electric sector and of reverse geometry since the magnetic sector precedes the electric sector. Over the past 12 years, it has been extensively modified to allow novel experiments to be carried out. The last major modification (1992) was the addition of a third field free region and hence a second electric sector, making the instrument triple focusing. A schematic diagram of the instrument is given in Figure 2.1. The individual components of the ZAB will be described in the following sections.
Figure 2.1: Schematic diagram of the modified VG ZAB-2F: 1: source, 2: α-slit, 3: magnetic sector, 4: collision cell 1, 5: deflector electrode, 6: collision cell 2, 7: electric sector 1, 8: collector slit, 9: detector, 10: collision cell 3, 11: deflector electrode, 12: collision cell 4, 13: electric sector 2, 14: collector slit and 15: detector.
2.1.2 Ion source and focusing lenses

Ions are generated by either electron impact or chemical ionization in the source of the mass spectrometer. A schematic diagram of the ion source is given in Figure 2.2.

If electron impact (EI) is the ionization method used, electrons are generated from a heated helical tungsten filament. 2.5 to 3 A of current are needed to increase the temperature of the filament (>2000°C) high enough for the emission of electrons. The efficiency of electron emission from the filament is measured by an electrode placed behind the filament. The current induced by the electrons hitting this plate is of the order of 0.3 mA. The electrons are accelerated into the ionization chamber by a potential energy difference between the filament and the electron exit slit which is generally of the order of 70V. Changing this potential energy difference changes the kinetic energy of the electrons. The ionization chamber is essentially free of electric fields and so the electrons move at constant velocity. It is within the ionization chamber that the electrons come into contact with the gas sample.

When chemical ionization (CI) is the ionization method used, an ionized reagent, such as CH₅⁺, is used to ionize the sample by proton transfer. The CH₅⁺ species are produced by an ion/molecule reaction between a methane molecular ion, produced by electron impact, and a methane molecule.
Figure 2.2: Schematic representation of ion source in the modified VG ZAB-2F: 1: block, 2: direct liquid inlet, 3: magnet, 4: trap, 5: \( \alpha \)-slit, 6: grounded plate, 7: CI/EI slit, 8: gas inlet, 9: solids probe inlet, 10: filament, 11: electron slit, 12: ionization chamber and 13: repeller.
Samples may be introduced in the vapor phase via three different types of sample inlets. The direct liquid inlet is a variable temperature inlet used for most liquid samples. The Granville-Phillips inlet is a variable leak valve used for high boiling point liquids or solids which have an appreciable vapor pressure at room temperature. The solids probe is also a variable temperature inlet, the tip of which contains the solid sample held in a capillary tube. The measured sample pressure in the source is usually of the order of $10^{-7}$ to $10^{-6}$ mbar and the pressure readings are made by means of an ionization gauge situated outside the source, above a diffusion pump. The actual pressure in the ion source is three to four orders of magnitude higher.

Once the sample is ionized, the ions formed are pushed out of the ionization chamber by the repeller electrode which has a slight positive potential with respect to the source block. These ions exit the block through the CI/EI slit which is set in accordance with the ionization technique being used. For an effective ion/molecule reaction, it is necessary that the pressure in the ion source be kept relatively high (i.e., measured pressure $10^{-5}$-$10^{-4}$ mbar. The actual pressure in the ion source is of the order 1 mbar). The CI slit is thus narrower than the EI slit in order to obtain this pressure.

The source block is at 8 kV with respect to a grounded plate situated outside and isolated from the block. The ions exiting the CI/EI slit are thus
accelerated towards the grounded plate acquiring 8 kV of kinetic energy following:

\[ \frac{mv^2}{2} = zeV \]  \hspace{1cm} (2-1)

where \( m, v \) and \( ze \) are respectively the mass, the velocity and the charge of the ion and \( V \) the accelerating voltage (8 kV). A beam of ions having the full accelerating voltage will be referred to as the main beam. The ion beam then passes through a variable slit (\( \alpha \) slit) and through an assembly of focusing lenses. The lens assembly consists of a series of shaped plates onto which electric potentials are applied in order to collimate the ion beam in both the \( y \) and the \( z \) directional axes (the \( x \) axis being the trajectory direction) in order to maximize both the shape and the transmission efficiency of the ion beam. The name of the instrument, ZAB, comes from these lenses that should, in principle, produce an ion beam with Zero ABerration.

The electrons that cross the ionization chamber are accelerated towards the trap which sits at a slightly positive potential with respect to the block. The current at the trap is measured to be approximately 20\( \mu \)A. In order to keep the electrons on their path, two small magnets are placed in parallel with the electrons' path. Due to the heating of the filament, the source temperature is usually maintained at about 150°C.
2.1.3 Magnetic sector - momentum analyzer

After exiting the source, all ions irrespective of their mass are part of one beam of quasi uniform kinetic energy. The magnetic sector allows the components of different mass to be separated. If a magnetic field, $B$, is applied in a direction perpendicular to the direction of ion motion, an ion of mass $m$, of velocity $v$ and charge $ze$ will follow a circular path of radius $r$ following:

$$r = \frac{mv}{Bze} \quad (2-2)$$

A magnetic sector is thus often referred to as a momentum analyzer. By rearranging and combining equations 2-1 and 2-2, the following relationship is obtained:

$$\frac{m}{ze} = \frac{B^2 r^2}{2V} \quad (2-3)$$

The magnetic sector acts as a focusing lens in the direction perpendicular to the applied magnetic field i.e., the $y$ direction. Hence, by scanning the magnetic field, it is possible to sequentially bring to focus at position $r$, components of the main beam of different mass to charge ratios (Figure 2.3).
Figure 2.3: Focusing action of magnetic sector.

Figure 2.4: Focusing action of electric sector.
2.1.4 Electric sector - energy analyzer

The directional focusing of the magnetic sector limits the mass resolution because not all ions have exactly the same kinetic energy, i.e., there is a small energy dispersion. The mass resolution may be improved by the addition of an energy focusing lens in series with the magnetic sector. This lens, the electrostatic analyzer (ESA), is made up of two parallel plates, the outer plate being positive with respect to the inner plate. The ion beam is injected mid-way between the two plates and follows a circular path of radius \( r_0 \). Ions pass through the ESA when the electrostatic force balances the centrifugal force according to:

\[
ze E = \frac{mv^2}{r_0} \tag{2-4}
\]

where \( ze \) is the charge on the ion, \( E \) is the applied electric field, \( m \) and \( v \) are the mass and velocity, respectively, and \( r_0 \) is the radius of the trajectory. By combining and rearranging equations 2-1 and 2-4 the following relationship is obtained:

\[
r_0 = \frac{2V}{E} \tag{2-5}
\]

Scanning \( E \) will allow the ions of different kinetic energy to be sequentially focused at \( r_0 \) (Figure 2.4).
2.1.5 Field free regions

Between the source and the magnet, the magnet and ESA1 and ESA1 and ESA2 are the first, second and third field free region (FFR) of the instrument. In these regions ions may dissociate spontaneously or following collisional activation. The second and third FFR house the four collision cells (refer to Figure 2.1). The cells consist of 2-3 cm long blocks of steel through which a 2 mm groove is cut. Gas lines are connected to each of the collision cells. The pressure in the cells is monitored by ionization gauges placed in close proximity. The differential pumping in these regions produces a pressure gradient between the cells and their surroundings preventing the gas from spreading throughout the flight tube. Cell 1 and cell 2 are 10 cm apart while the distance between cell 3 and cell 4 is variable, but is usually set to 6 cm. An assembly of focusing lenses follows cell 2. Half way between each pair of cells is placed a deflector electrode allowing the ions to be expelled from the beam if a negative or a positive potential is placed on the deflector electrode. This enables the study of the neutral species co-generated in the FFR, as will be described later.

2.1.6 Detectors

Detection of the ions is achieved by off-axis Daly detectors (Figure 2.5). The detectors are made up of two parts. On one side of the ion beam, is placed a conversion dynode onto which a high negative potential is applied (-20 kV).
Figure 2.5: Daly detector: 1: conversion dynode, 2: CaF$_2$ scintillator and 3: photomultiplier tube.
The positive ions are attracted towards the dynode, impinge on the central portion of the conversion dynode and secondary electrons are emitted. These electrons are accelerated towards a CaF₂ scintillator. The scintillations produced are detected by an optically coupled photomultiplier and the signal is amplified. The ions may be detected after double or triple focusing. The detectors used in the ZAB allow both the detection of positive and negative ions. Due to this flexibility, a restriction on the maximum possible potential applied to the dynode may result in mass discrimination. The ions with low translational kinetic energy (i.e., low mass fragment ions) may be discriminated against.

2.2. AEI-MS902

2.2.1 Description

As opposed to the ZAB, the MS9 is a double focusing instrument but of forward geometry; the electric sector thus precedes the magnetic sector. A schematic diagram of the MS9 is shown in Figure 2.6. Although the physical design of the MS9 is different from that of the ZAB, the underlying principles of all the major components are essentially as previously described for the ZAB. The major differences distinguishing the MS9 from the ZAB are discussed below.
Figure 2.6: Schematic diagram of the AEI-MS902S: 1: ion source, 2: α-slit, 3: electric sector, 4: magnetic sector, 5: collector slit and 6: detector.
Only two types of sample inlets, namely the Granville-Phillips variable leak valve and a solids probe, are used to introduce a sample. There is no EI/CI slit. The MS9 lacks the focusing lens placed after the source which is essential to the ZAB. Alignment is achieved by adjusting a beam centering lens as well as two y-directional focusing lenses.

In addition, unlike the ZAB, the first FFR of the MS9 is very short. This characteristic, as well as the possibility to monitor the electron energy accurately and reproducibly, makes the MS9 suitable for thermochemical measurements.

2.3 Monoenergetic electron impact appearance energy apparatus

Thermochemical measurements may be made using a conventional mass spectrometer such as the MS9 but one draw-back of this type of instrument is that the electrons produced from a heated filament are not monoenergetic but rather have a large inherent thermal energy distribution. This energy dispersion is taken into account by the method used for the thermochemical measurements as will be described in a later chapter. With the intent of improving the accuracy of thermochemical data obtained from electron impact measurements, the electron monochromator was designed\(^3\). The major improvement of the monochromator over an instrument such as the MS9 comes from it's capacity to produce a beam of electrons characterized by a very narrow energy distribution.
2.3.1 Electron monochromator

A schematic diagram of the electron monochromator is shown in Figure 2.7. Electrons are produced from a heated helical tungsten filament. The electrons are then accelerated towards the electron gun, through a pin-hole and into the first of two pairs of hemispherical electrodes. The energy dispersion of the beam causes the image of the slit to spread along a line. Part of the beam falls on the interstage aperture and enters the second pair of hemispherical electrodes. Again, the energy dispersion causes the image of the aperture to spread along a line and a small fraction of the beam is selected by the aperture leading to the collimator. The two pairs of hemispheres are positioned such that the electron trajectories are mutually perpendicular and the beam is energy selected twice. The electric potentials on the hemispheres are adjusted to yield a maximum electron flux. Once the electron beam leaves the second hemisphere it enters the collimator. A series of lenses focuses the electron beam onto the exit aperture. An o-ring serves to insulate the collimator from the housing and provides a partial vacuum seal between the monochromator and source housings.
Figure 2.7: Schematic diagram of the electron monochromator: 1: filament, 2: electron gun, 3: 1st inner hemisphere, 4: 1st outer hemisphere, 5: 2nd outer hemisphere, 6: 2nd inner hemisphere, 7: collimator and 8: focusing lens.
2.3.2 Ion source and mass filter

The design of the ion source is very simple and straightforward. It includes the ionization chamber, the energy controlling electrode and the electron trap. A schematic diagram of the ion source is shown in Figure 2.8. As the electron beam leaves the collimator, it is subjected to the potential energy difference applied between the collimator and the energy controlling electrode. The energy of the electrons may thus be varied as needed. The electron beam enters the ionization chamber where it encounters the sample. The sample is leaked into the ionization chamber via a variable valve along a long glass tube at the end of which is a jet separator.

The ionization chamber is simply a cylindrical tube constructed from gold plated platinum mesh. The electrons cross the ionization chamber and are collected at the electron trap whereas the ions produced are extracted from the chamber by an ion extractor plate which sits at a negative potential with respect to the chamber. A field adjuster plate and a focus plate guide the ions to the quadrupole mass filter. A constant ion acceleration of 16 V is maintained between the ionization chamber and the grounded plate. The quadrupole mass filter is used to analyze the ions produced.
Figure 2.8: Schematic diagram of the ion source of the Monoenergetic Electron Impact Appearance Energy Apparatus: 1: electron trap, 2: ionization chamber, 3: energy controlling electrode, 4: collimator, 5: extractor plate, 6: field adjuster plate and 7: grounded plate.
2.4 References

Chapter 3

Experimental: Characterization of ions and neutrals

Two types of experimental information may be combined to characterize gas phase ions; these are the ion structure and the heat of formation ($\Delta_r H^o$) of the ion. The structure of the ion refers only to how the atoms are linked together and does not include more detailed information such as bond lengths and bond angles. In the following chapter, a description of the experiments allowing structural and thermochemical information to be determined will be presented.

3.1 Introduction: Types of ions produced after electron impact

If, in the ionization chamber, an electron passes in close proximity to one of the valence electrons of the sample molecule, it may repel this electron out of the molecule producing a positively charged molecular ion following:

$$M + 1e \rightarrow M^+ + 2e$$  \hspace{1cm} (3-1)

Generally, 70 eV electrons are used for ionization and by combining the kinetic energy and the mass of the electron, the velocity of these electrons is calculated
to be $5 \times 10^8$ cm s$^{-1}$. The electrons will thus traverse a typical molecular diameter of the order of 10 Å in a time of $2 \times 10^{-16}$ s allowing ionization to take place during this time. The fastest molecular vibration, a C-H stretching vibration, has a period of $10^{-14}$ s so that the atoms may be considered to be effectively at rest during ionization. Consequently, electron impact ionization is considered to be essentially a vertical rather than an adiabatic ionization process.

The ions formed will often be in an electronically excited state, and since dissociation is slow enough compared to ionization, the excess energy contained in the molecular ions will be redistributed in all degrees of freedom as vibrational or other forms of internal energy. Since electrons having 70 eV of kinetic energy are generally used in electron impact ionization, a large amount of energy, well above the ionization energy, may be transferred during the process. Consequently, the fate of the molecular ion depends upon the amount of excess energy it contains. A singly charged ion of mass 100 falling through an accelerating voltage of 8 kV, will have a flight time through the ZAB of the order of 40 μs. It is during this time that the ions, according to their energy content, may or may not undergo dissociation. Figure 3.1 describes three types of ions which are formed following ionization.

If the excess energy of the molecular ion is below the dissociation threshold and the ion has a dissociation rate constant smaller than $10^4$ s$^{-1}$, a
Figure 3.1: Different types of ions produced by electron impact.
stable ion is produced. These ions live long enough to traverse the instrument without fragmentation. They correspond in the normal mass spectrum to the molecular ions and all fragment ions having insufficient energy to dissociate on this time scale. The m/z of the molecular ions corresponds to the value of the mass of the corresponding neutral sample molecule.

If the excess energy of the molecular ions is well above the dissociation threshold and the ions have a dissociation rate constant greater than $10^6 \text{ s}^{-1}$, dissociation will follow, yielding an ion and a neutral species according to one of two possibilities:

$$M^{+*} \rightarrow F^{+*} + N$$  \hspace{1cm} (3-2)

$$M^{+*} \rightarrow F^+ + N^*$$  \hspace{1cm} (3-3)

These ions are referred to as unstable ions and dissociate in the ion source of the mass spectrometer giving rise to the fragment ions seen in the normal mass spectrum.

If the excess energy in the ions is slightly above the dissociation threshold and the dissociation rate constant lies somewhere between that of stable and unstable ions, $10^4 \text{ s}^{-1}$ and $10^6 \text{ s}^{-1}$, the ions are referred to as metastable ions. These ions dissociate in flight between the ion source and the detector. If the dissociation takes place in one of the FFR of the mass spectrometer, it may be possible to see these ions in the normal mass spectrum.
All singly charged ions $m_1^+$ will acquire, after leaving the ion source, translational kinetic energy according to:

$$ zeV = \frac{m_1 v_1^2}{2} \tag{3-4} $$

When a metastable ion $m_1^+$ dissociates in the FFR of the mass spectrometer, yielding a fragment ion $m_2^+$ and a neutral fragment $m_3$, the translational kinetic energy of $m_1^+$ is partitioned amongst the fragments according to:

$$ zeV = (1/2)m_1 v_1^2 = (1/2)m_2 v_2^2 + (1/2)m_3 v_3^2 \tag{3-5} $$

The fragment $m_2^+$ will thus have the same velocity as $m_1^+$ and will be transmitted through the magnet according to:

$$ r = \frac{m_2 v_1}{Bze} = \frac{m_2}{Bze} \left( \frac{2zeV}{m_1} \right)^{1/2} \tag{3-6} $$

By rearranging equation 3-6, it can be seen that the ion $m_2^+$ will be transmitted at an apparent mass, $m^*$, given by:

$$ \frac{m_2}{m_1} = \frac{1}{ze} = \frac{m^*}{B^2r^2} = \frac{B^2r^2}{2V} \tag{3-7} $$

Due to their narrow range of internal energies ($< 2$ eV$^i$) and average internal energy not much in excess of the activation energy, $\varepsilon_0$, metastable ions
are particularly informative and will be discussed in more detail in the next section.

3.2 Metastable ions

The recognition of metastable peaks and the first quantitative measurements on them were carried out by Hipple and Condon in 1945\(^2\). Since then, very extensive descriptions of metastable ion phenomena have been written\(^1,\(^3\) and only a summary of the more important features of these ions will be presented.

3.2.1 Experimental conditions for observation of metastably generated ions

Because the translational kinetic energy of the fragment ion \( m_2^+ \) is not the full acceleration voltage, particular experimental conditions are needed to observe the metastably generated ions. These conditions depend on the type of instrument used, \textit{i.e.}, forward vs. reverse geometry, and will be described in the following sections.
3.2.1.1 Detection of metastable ions in the ZAB mass spectrometer

This method is used when working with an instrument of reverse geometry (the magnetic sector precedes the electric sector) such as the ZAB described in section 2.1.4. In this case, the metastable dissociation is studied in the second (or third) FFR of the instrument. The precursor ion $m_1^+$ is mass selected by the magnet. Because the metastably generated fragment ions possess only a fraction of the translational kinetic energy of the precursor molecule, they are detected by scanning the electric sector from the translational kinetic energy of the precursor molecule downwards and will appear at a sector voltage of $m_2^+/m_1^+ \cdot V_{acc}$.

3.2.1.2 Detection of metastable ions in the MS9 mass spectrometer

In this case, the metastable dissociation of interest occurs in the first FFR of the instrument, that is between the ion source and the electric sector. In order for the fragment ion $m_2^+$ to be transmitted through the electric sector, the electric sector voltage should be set to match the translational kinetic energy of the fragment ion $m_2^+$. This energy is a fraction of the full acceleration voltage and is given by $m_2^+/m_1^+ \cdot V_{acc}$. Experimentally, the accelerating voltage and the electric sector voltage are set to $m_2^+/m_1^+ \cdot V_{acc}$. The ion $m_2^+$ is then mass selected with the magnet and increasing the accelerating voltage to its initial value allows the observation of the metastably generated $m_2^+$ ions only. The source generated
having a translational kinetic energy corresponding to the full acceleration voltage will not be transmitted through the electric sector.

3.2.2 Release of kinetic energy and metastable peak shape

In addition to the translational kinetic energy of the metastable ion, which is partitioned amongst the fragments in proportion to their mass, both the excess energy ($\Delta E^*$) of the activated complex and the reverse activation energy ($\Delta E_a^*$) may be released as transitional energy during the metastable ion's dissociation. The fragment ion peak will be broadened as a consequence of this release of translational kinetic energy. The kinetic energy release (KER) associated with a given fragmentation is commonly expressed as $T_{0.5}$ (KER at 50% of the maximum height of the signal) which is calculated according to:

$$T_{0.5} \text{(eV)} = \frac{m_1^2}{16 \cdot m_2^* \cdot m_3 \cdot 8000} \left( w_{1/2(\text{fragment})}^2 - w_{1/2(\text{main beam})}^2 \right)$$ (3-8)

where $m_1^*$, $m_2^*$ and $m_3$ are the masses of the precursor molecule, the ionic and the neutral fragments, respectively, and $w_{1/2}$ are the widths at half height of the fragment ion and main beam. The experiment is carried out at high resolution, which is obtained by narrowing down the y-slits in the instrument so that the width at half height of the fragment peaks are indicative of the kinetic energy released.
The most commonly observed metastable peak shape is of Gaussian-type (Figure 3.2a). These peaks are associated with relatively small kinetic energy releases. As the kinetic energy released increases, flat and eventually dish-topped metastable peaks are observed (Figure 3.2b). The dish observed in some of the peaks has no physico-chemical meaning but results from instrumental discrimination. If fragment ions receive large kinetic energy components along the z axis, that is along the plane of the long axis of the energy resolving slit, these ions will not be transmitted because of the finite length of the energy resolving slit, the result of which is a dish topped peak.

Metastable peaks which are characterized by marked discontinuities in their profile are referred to as composite metastable peaks. They can be seen to consist of a Gaussian type peak atop a dished peak or a pair of superimposed dished peaks (Figure 3.2c). These peaks may arise when two isomeric precursor ions decompose by loss of a common neutral fragment to yield one or two fragment ion structures, when a single precursor ion structure fragments to yield a pair of isomeric fragment ions or when a pair of isomeric precursor ions fragment via different reacting configurations to yield a common fragment ion.

Because the KER associated with the fragmentation of a given metastable ion is characteristic of the reacting configuration of the ion, this information is used when distinguishing isomeric ions.
Figure 3.2: Metastable peak shapes: a) Gaussian b) dished-topped and c) composite.
3.3 Collision experiments

In the earlier days of mass spectrometry, diffuse low intensity peaks were observed in certain mass spectra. These peaks were called “Aston bands” and were the product of collisions between the ions and the residual gas molecules in the mass spectrometer. In the modern era of mass spectrometry, processes involving collisions between ions and neutral gases are key experiments for probing the structure and reactivity of ions. These are the experiment which will be described in the following pages.

3.3.1 Collision induced dissociation

As opposed to unimolecular metastable dissociations, collision induced dissociations (CID) (also unimolecular) occur following excitation from collisions between the high velocity ions and a (stationary) neutral target gas. During this process, part of the translational energy of the ion is converted into internal energy. The resulting mass spectrum will be different from the metastable ion mass spectrum in two major aspects: 1) the total abundance of the fragment ions will be generally increased and 2) there will be a greater variety of fragment ions. The fragment ions thus generated will be characteristic of the structure of the mass selected ions if the precursor ions retain their structure irrespective of their internal energy. However, if some isomerization occurs following activation, the CID mass spectrum obtained will be a superposition of the dissociation characteristics of the isomeric ions.
The average internal energy deposition is usually estimated to be a few eV (1-3 eV) and the distribution of internal energy deposited is wide and characterized by a high energy tail. It has been shown however, that the amount of energy transferred during the collision event increases proportionally with the square root of the translational kinetic energy of the incoming ion.

The collisions take place in the FFR of the mass spectrometer. Gas is introduced into the collision cell and the pressure of the gas is monitored at a point outside the collision cell; it is thus more convenient to rely on the amount by which the intensity of the main beam of ions is reduced due to the presence of the gas, than on the gas pressure itself. It has been shown that in conditions where the main beam is reduced by 10%, 95% of the collision events are single encounters. Increasing the beam reduction to 40% generates conditions in which double and triple encounters account for 20% and 5% of the collision events, respectively. Under multiple collision conditions, higher internal energy dissociation pathways become more probable and so the structure characteristic features may often be reduced significantly or obscured. Conditions yielding single collisions are generally used. Helium is by far the most common collision gas. It is readily available in high purity, at low cost, is most effective for energy deposition processes and is somewhat ineffective for neutralization and/or charge stripping (see below).
The effect of ion initial internal energy on a CID mass spectrum is somewhat controversial but it is generally accepted that only the metastable reaction channels may depend upon the initial internal energy distribution of the precursor molecules. All other "high critical energy" dissociation channels should be independent of the internal energy of the precursor ion and thus ion relative abundances should be independent of the initial internal energies. Consequently, identical ions generated from a variety of precursor molecules should have indistinguishable CID mass spectra, whereas isomeric ions, in general, will have distinctive CID characteristics. The effect of internal energy may be best observed when comparing CID mass spectra of both source and metastably generated ions. The two CID mass spectra will be indistinguishable if the structure of the ions is the same irrespective of their internal energy content. However, the two CID mass spectra will be distinct when the structure of the ions is dependent upon their internal energy content i.e., low internal energy ions, those produced by metastable dissociations, are structurally different from the ions containing more internal energy, those produced in the ion source.
3.3.1.1 Experimental conditions for recording CID mass spectra

For all CID mass spectra referred to in the Results sections, helium was used as collision gas, unless otherwise stated. The ions of interest were mass selected by the magnet and sufficient helium was introduced in collision cell 2 (or cell 4) to cause a 10% decrease in the main beam intensity. The pressure reading corresponding to this decrease in beam intensity is of the order of $10^{-7}$ mbar. The fragment ions generated by the collision with the target gas, in addition to the ions produced from metastable dissociations, were analyzed by the ESA1 (or ESA2).

It is possible to separate the metastably generated ions from those produced inside the collision cell by applying an electric potential onto the collision cell. If a negative electric potential is applied to the cell, the incoming ions will be accelerated towards the cell, and upon exiting the cell, will be decelerated by the same amount, according to:

$$\left(\frac{m_2^+}{m_1^+} \times V_{\text{acc}} \right) + V - V$$

(3-9).

where $V$ is the electric potential applied on the cell. The presence of the electric potential on the cell will thus in no way affect the fragment ions produced prior to entering the collision cell (metastably generated ions).
However, the fragment ions produced by collisions inside the cell will exit the cell with a transitional kinetic energy that will depend on the voltage applied to the cell:

\[
\left( \frac{m_2^*}{m_1^*} \times (V_{\text{acc}} + V) \right) - V \quad (3-10)
\]

### 3.3.2 Charge stripping and charge reversal

When helium is replaced with a diatomic target gas, such as oxygen, a marked increase in the amount of doubly charged ions is observed in the resulting spectrum. This process is referred to as Charge Stripping\(^8\) (CS) and occurs when ions gain enough internal energy to expel a second electron, thus producing a doubly charged ion as described by:

\[
A^+ + T \rightarrow A^{++} + T + 1e \quad (3-11)
\]

In the resulting mass spectrum, these peaks are characteristically narrow (no KER because these ions do not originate from the fragmentation of a higher mass precursor) and appear at half their actual mass (i.e., apparent mass = m/z, and for doubly charged ions z = 2).

It is also possible to induce, through collisions, processes involving the loss of two electrons. This technique is referred to as Charge Reversal\(^9\) (CR),
and allows positive ions to be generated from the corresponding negative ion precursor as described by:

\[ A^- + T \rightarrow A^+ + T + 2e \]  \hspace{1cm} (3-12)

This may allow the production of cations which otherwise may not be directly obtained, but is structure indicative only if the cation produced has the same structure as the anion precursor. Conditions for carrying out these experiments are very similar to those discussed previously for obtaining CID mass spectra.

3.3.3 Collision induced dissociative ionization

The neutrals co-generated in metastable dissociations may also be investigated. The identification of these neutral species is achieved by collisional ionization. When kilovolt neutral projectiles encounter a target gas, the collision may produce an ion which contains sufficient internal energy to fragment. This technique is referred to as collision induced dissociative ionization (CIDI)\textsuperscript{10} and produces a mass spectrum which can be used to characterize the structure of the neutral species co-generated in the metastable decomposition of the precursor molecule. This information is necessary if the thermochemistry of the process is to be investigated and also provides ancillary
information that may prove useful when identifying the nature of the ionic species produced.

3.3.3.1 Experimental conditions for recording CIDI mass spectra

The CIDI mass spectra referred to in the result sections, oxygen was used as target gas. The ion of interest was mass selected by the magnet and the unimolecular dissociation of this ion took place in the second FFR (or third FFR) of the instrument. The oxygen was introduced into cell 2 (or cell 4) in quantities such that a 10% decrease in the main beam intensity was observed. By applying a potential of several hundred volts on the deflector electrode situated in front of the collision cell, all ions were expelled from the beam. The neutrals, unaffected by this potential, continued their trajectory and entered the collision cell. The resulting ion beam was analyzed by scanning ESA1 (or ESA2).

3.3.4 Neutralization-reionization mass spectrometry

In addition to the study of the neutrals co-generated in metastable dissociations, it is also possible to generate neutral species by neutralizing cations. This allows the production, and upon reionization, the characterization of molecules and radicals of unusual structure derived from the corresponding stable cation. The technique, neutralization-reionization (NR) mass spectrometry\textsuperscript{11} consists of two sequential steps: neutralization and reionization:
step 1: neutralization: \[ M^{*} + N \rightarrow M + N^{*} \]  \hspace{1cm} (3-13)

step 2: reionization: \[ M + R \rightarrow M^{*} + R + 1e \]  \hspace{1cm} (3-14)

Neutralization occurs by an electron transfer process considered as a vertical Franck-Condon process so that if the geometries of the ion and neutral are similar, a stable neutral should be produced. If the neutral produced survives, it is then reionized by collisional activation. If the experiment is successful, the resulting mass spectrum will show a peak corresponding to the reionized species (this peak is referred to as a recovery signal) and fragment ions characteristic of the reionized species. The presence of a recovery signal indicates that the neutral produced was stable at least for a period of approximately 0.5 - 5 \( \mu \text{s} \) (depending on the mass of the ion and the distance between the collision cells).

3.3.4.1 Experimental conditions for recording NR mass spectra

The ion of interest was mass selected by the magnet and reached collision cell 1 (or cell 3) where it was to be neutralized. In general a target gas of low ionization energy was chosen for this step although it has been shown that this is not the sole determining factor for the efficiency of the neutralization\(^ {12} \). All NR mass spectra reported in the result sections were obtained using dimethylamine or xenon (DMA, IE = 8.23 eV\(^ {13} \) and Xe, IE = 12.12
eV\(^{13}\)). A target gas pressure corresponding to a 10% reduction in the intensity of the main beam was generally used. A potential of several hundred volts was applied to the deflector electrode in order to expel all residual ions from the beam. The neutral beam reached collision cell 2 (or cell 4) where it encountered a second target gas. For the reionization, oxygen was used in all reported NR mass spectra. The oxygen pressure was adjusted to yield an overall decrease in the intensity of the main beam of 20%. The resulting ion beam was then analyzed by scanning the ESA1 (or ESA2).

3.4 Thermochemistry

Complementary information to the study of the unimolecular and collision induced dissociation characteristics of a species of interest is provided by the knowledge of the heat of formation (\(\Delta_{f}H^{0}\)) of this species. In the following paragraphs, the means by which \(\Delta_{f}H^{0}\) of neutrals and ions are determined, using electron impact methods, will be described.

3.4.1 Basic principles

For every ionic species formed in the mass spectrometer, there is a characteristic threshold electron energy below which these ions will not be produced. When dealing with the energetics of the production of molecular ions, the minimum electron energy needed to produce \(M^{+}\) from \(M\) according to:
\[ M \rightarrow M^{+} + 1e \] (3-15)

is referred to as the ionization energy (IE) of M. Adiabatic (IE\(_a\)) and vertical (IE\(_v\)) ionization energies are frequently referred to. The latter relates to the energy difference between the ground state (electronic and vibrational) of the neutral and the point at which the value for the equilibrium internuclear spacing in the neutral molecule, \( r_0 \), cuts the potential energy surface for the ionized state; whereas the former, refers to the energy difference between the ground states (electronic and vibrational) of both the neutral and ionized species. In the case where there is little or no geometry change between the neutral and the ionized species, both the IE\(_a\) and IE\(_v\) are the same (refer to Figure 3.3a). As the \( r_0 \) for the neutral and the ionized states differ, the difference between the IE\(_a\) and the IE\(_v\) increases (refer to Figure 3.3b and c). Because the transition probability (i.e., the cross section) associated with the adiabatic transition is not negligible in such cases, the IE\(_a\) is accessible in the majority of cases studied by an electron impact method. Alkanes and cycloalkanes are classes of compounds for which the determination of the IE\(_a\) is difficult due to the very small cross-section for ionization close to the threshold. Thus, the reported IE for n-pentane (10.35 eV\(^{13}\)) was re-investigated and a value of 10.22 eV was determined to be more accurate\(^{14}\). As the geometry changes are more pronounced, it becomes difficult to determine precisely the cut-off at the x axis and so the value obtained should only be considered as an upper limit to the IE\(_a\)\(^{15}\).
Figure 3.3: Transition probability curves to be expected when a) $r_n$(neutral) = $r_n$(ionized) and b) and c) $r_n$(neutral) ≠ $r_n$(ionized). Superimposed on each is the expected ionization efficiency using monoenergetic electron impact.
When dealing with the energetics of a fragment ion, the minimum electron energy needed to produce $F^+$ and $N^+$, the neutral co-generated, from $M$ according to:

$$M \rightarrow F^+ + N^+ + 1e$$  

is referred to as the appearance energy (AE) of $F^+$.

When molecules fragment to produce $F^+$, the AE of $F^+$ is thus a measure of the $\text{IE}_0$ of $M$ plus the activation energy ($\epsilon_0$) that must be provided to $M^{\infty}$ in order to produce $F^+$. In addition, some excess energy, allowing for the production of $F^+$ in sufficient yield to be observable on the time scale of the experiment, is also necessary. This last term is referred to as the kinetic shift (Figure 3.4).

The $\Delta H^0$ of an ion or neutral is not measured directly, but is determined from the experimentally obtained IE and AE. These measured quantities are related to the $\Delta H^0$ of the species involved in the process by:

$$\text{IE} = \Delta H^0 (M^{\infty}) - \Delta H^0 (M)$$  

$$\text{AE} = \Delta H^0 (F^+) + \Delta H^0 (N^+) - \Delta H^0 (M)$$

where $N$ is the neutral species co-generated.

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Figure 3.4: Production of $M^{\infty}$ and $F^+$ from $M$. 
In order for the desired $\Delta H^o$ to be determined accurately from the IE and AE measurements, the following conditions must be met: 1) the $\Delta H^o$ of the other species involved must be known. If no experimental datum exists for the neutral molecule or radical, the $\Delta H^o$ may be estimated using Benson's Additivity Scheme\textsuperscript{16}, 2) the fragmentation of M$^{+*}$ must have no significant kinetic shift and 3) the reverse reaction, F$^+$ + N$^-$ $\rightarrow$ M$^{+*}$, must have no significant energy barrier ($\varepsilon_r$).

A fragmentation reaction will have a significant kinetic shift when its rate constant rises slowly with the increase of internal energy. In this case, the AE measured will depend considerably on the time scale of the method used for the measurement\textsuperscript{17}. Comparing the AE of F$^+$ produced metastably with the AE of F$^+$ produced in the source may provide some information on the presence of an important kinetic shift. In general, when the energy difference between the IE of the precursor molecule and the metastable AE for the ion of interest is small, there should be no appreciable kinetic shift but in cases where the difference is large, a kinetic shift may be present. The KER in a metastable dissociation may also provide information concerning the presence of either an appreciable kinetic shift or a reverse activation energy barrier. As a general rule in small molecules, if the average KER is relatively small (0 to ca. 30 meV), it is probable that the reaction involves neither a large kinetic shift nor a reverse activation energy barrier. In cases where the kinetic shift is large and/or in the presence of
an important $\varepsilon$, the measured AE must be considered as an upper limit and the 
$\Delta H^\circ$ value obtained for any product will consequently also be an upper limit.

One concern when interpreting the AE measured using monoenergetic 
electrons, is the temperature applicable to the fragment ion and neutral at the 
measured threshold. This has been considered in detail for the threshold 
obtained from photoionization work. It was argued that for photoionization 
experiments, extrapolating a selected post-threshold portion of the ion yield vs. 
photon energy curve to zero, gave $AE_{\text{exp}}$; this is equal to:

$$AE_{\text{exp}} = AE_0 - E_i$$

(3-19)

where $AE_0$ is the zero Kelvin enthalpy change for the reaction and $E_i$ is the 
average internal thermal energy of the precursor molecule effective in the 
dissociation. When the desired product enthalpies are for 298 K, the $AE_{298}$ can 
be derived from an experiment conducted at that temperature. If it is assumed 
that all the vibrational and rotational energies of the precursor molecule are 
effective in the dissociation, $E_i$ can be evaluated by the usual thermodynamic 
heat capacity terms, as described in the following equation:

$$AE_{298}(Y^+) = \Delta_i H^\circ_{298}(Y^+) + \Delta_i H^\circ_{298}(R^+) - \Delta_i H^\circ_{298}(RY)$$

$$- \left[ \int_0^{298} C_p(Y^+) + \int_0^{298} C_p(R^+) - 5/2RT \right]$$

(3-20)
where $C_p(Y^*)$ and $C_p(R^*)$ are the molar heat capacities of the products and $5/2RT$ relates to the translational energy deficit of the products. This approach has been justified for a number of small molecules such as NH$_3$ and H$_2$O where absolute values for $\Delta H^\circ_{298}$ of the fragment ion and neutral are known.

Thus, if the threshold energies determined in electron impact experiments have the same significance as those for photodissociation, they should be corrected by adding the term in brackets in equation 3-20 before calculating the $\Delta H^\circ_{298}$ of the product ion and neutral. In general, linear extrapolation of the energy selected electron impact AE curves is not possible because a small part of their curvature at the foot arises from the electron energy distribution. We are not convinced that the measured electron impact AE represents a threshold lower than the correct value by an energy equal to the sum of the heat capacity terms in equation 3-20. Indeed it can be questioned, at least for larger molecules, whether all or even the major fraction of the internal thermal energy is effective in the dissociation. For example, the AE experimentally measured for the production of but-2-ene from hexanal was 9.89 eV compared with 9.87 eV which is calculated using the appropriate $\Delta H^\circ_{298}$ values. The inclusion of the remaining correction term in equation 3-20, the translational energy loss, should probably be made only if the other correction factors can be identified and quantified. But without clear evidence for the degree of participation of the internal thermal energy in polyatomic ion fragmentations, one can argue that no
correction is better than one incorrectly identified and applied. Therefore, no corrections have been added to the AE reported in this work.

3.4.1 Experimental conditions for IE and AE measurements

As mentioned previously, two different instruments have been used to measure IE and AE. The next sections will describe how these quantities are obtained.

3.4.1.1 IE and AE using the Monoenergetic Electron Impact Appearance Energy Apparatus

Water is first introduced into the instrument as described in the instrumentation section (to pressures less than $1 \times 10^{-6}$ mmHg). The quadrupole mass filter is adjusted so that the water ions formed in the source are extracted and detected. The focusing plates are set to give maximum ion yield. The electron energy is decreased below the IE of water and once the minimum energy needed to produce water ions is determined, a range of 0.8 eV in electron energy is scanned in increments of 0.02 eV. The signal is averaged to obtain good signal to noise ratio and the data points, consisting of the ion intensity as a function of electron energy, are plotted. From the curve obtained, the apparent threshold for the IE of water is determined (Figure 3.5a). Due to contact potentials in the instrument, the apparent threshold is usually lower than the true IE. The apparent value is thus compared with the actual value for the IE of water (12.60 eV$^{13}$) and a Δ value is obtained. With the water still in the
source, the compound of interest is introduced so that the overall pressure does not exceed 2x10^{-6} mmHg. The quadrupole mass filter is then adjusted so that the appropriate ion is detected, and the threshold energy for the appearance of the ion is measured in the same way as for the water. Scans are accumulated until a good signal to noise ratio is obtained. After plotting the data points, the apparent threshold energy is determined and to this value is added the Δ previously measured to obtain the actual threshold energy for the process of interest (Figure 3.5b). The curves for the IE of the water and of the sample are then repeated. The measurements are accurate to within ± 0.05 eV. Using the other thermochemical data available, the ΔH° of the species of interest is calculated.
Figure 3.5: Determination of the ionization energy of $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{OCH}_3$

a) determination of $\Delta$ using water as standard and b) determination of threshold energy for the production of $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{OCH}_3^\text{+}$. 

$\Delta = 2.62$

$\text{IE} = 9.10\text{eV}$
3.4.1.2 IE and AE measurements using the MS9 mass spectrometer

The MS9 is used instead of the monochromator in two instances: if the compound of interest cannot be introduced into the monochromator due to a lack of volatility or if the measurement of a metastable AE\textsuperscript{20} is desired.

The sample is introduced into the source of the MS9 through the appropriate inlet to pressures usually below 1x10\textsuperscript{-6} torr. The electric sector and the magnet are set so that the metastably generated ions (in the first FFR) or the source generated ions of interest are transmitted and detected. The intensity of the ion beam is maximized using the various focusing plates. The repeller is usually set to zero. After this, no ion source conditions, other than the electron energy, may be changed. The electron energy is then lowered to the point where the ion beam vanishes. Using a chart recorder, the multiplier and amplifier gain are adjusted so that the signal is full scale approximately 2 V above the vanishing point. This sensitivity setting is not therefore to be changed either.

The ion intensity is then measured as a function of electron energy over the 2 V range in steps of 0.2 V. The standard sample is then introduced in the source in quantities such that at the same multiplier and amplifier gain setting (i.e., apart from the electron energy, no source focusing conditions have been changed) a comparable signal is obtained 2 V above the vanishing point. Again, the intensity of the ion beam is measured as a function of electron energy over
the 2 V range. The two curves are plotted (Figure 3.6a) and normalized so that they are parallel. Normalization is achieved in the following way: The height of the standard and sample are measured 3 cm away from the curves at 0.5 cm and 1.0 cm from the base of the curves. The curve for the sample is normalized to the standard curve by multiplying the points by the ratio of the heights \( h_{\text{std}}/h_{\text{sample}} \) (Figure 3.6a). After this normalization, the energy displacement between the two parallel curves is measured and plotted against the peak height near the threshold (Figure 3.6b). By extrapolating to 0 cm, the foot of the curve, a value of \( \Delta \), corresponding to the energy difference between the two curves, is obtained. This \( \Delta \) value is either added or subtracted from the value of the AE of the process associated with the standard, to obtain the AE of the process being investigated. In general, the \( \Delta \) plot had only a small slope. If it the \( \Delta \) values were spread over more than (say) 5 mm, the experiment was repeated.

For all metastable AE measurements reported in the result sections, the following metastable dissociation was used as a standard:

\[
\text{CH}_3\text{COOCH}_3 \rightarrow \text{CH}_3\text{CO}^* + \text{CH}_3\text{O}^* \quad \text{AE} = 10.94 \text{ eV}^{20}
\]

For source generated ions the same standard was used and in the case of IE measurements, one of the two following standards was used:

\[
\text{CH}_3\text{COOCH}_3 \rightarrow \text{CH}_3\text{COOCH}_3^{\sim} \quad \text{IE} = 10.17 \text{ eV}^{13}
\]

\[
\text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_6^{\sim} \quad \text{IE} = 9.24 \text{ eV}^{13}
\]
Figure 3.6: Determination of the appearance energy of (C₅H₅)₂CH⁺OH from (C₅H₅)₂CH(CH₃)OH: a) threshold curves for (C₅H₅)₂CH⁺OH and standard (CH₃CO⁺ from CH₃CO₂CH₃) and b) determination of Δ.
3.5 References


Chapter 4

The thermochemical effect of phenyl substitution

in gas phase neutral and ionic species

4.1 Introduction

Much of the available information concerning the thermochemistry of gas
phase neutral and ionic species has been compiled in the form of compendia\(^1\).
Although incomplete, the compendia provide a large collection of data on the
heat of formation (\(\Delta H^\circ\)) of neutrals and ions and on ionization energies (IE).
Most of the data presented in the compendiums are from experiment, but in
cases where no experimental data are available, estimated values are reported.
Additivity schemes for estimating thermochemical data are now widely accepted
and used, and provide gas phase chemists with data of relative accuracy which
would otherwise be unavailable. The physical basis of such estimation schemes
resides in the fact that forces between atoms in one molecule are very “short
range” \(i.e.,\) appreciable only over distances of 1-3Å\(^2\).

One particular group of compounds for which reliable data are scarce,
especially for ionic species, is phenyl substituted species. The aims of this work
are, using the available data and new experimental data, to assess the effect of
phenyl substitution in neutrals in order to quantitatively determine the effect of
phenyl substitution, and to investigate the effect of multiple phenyl substitution at a carbon center in neutrals and at the charge bearing site in ions.

4.1.1 Additivity in neutrals

Benson and Buss\(^3\) have shown that it is possible to make a hierarchical system of additivity laws in which the simplest order law would be the law of additivity of atom properties. One would assign a partial value for the property to each atom in the molecule, so that the molecular property could be calculated from the sum of all the atom contributions. For a property such as molecular weight, such a law would be precise. However, there are obvious limitations to such a law. In a higher order approximation to additivity behavior, the molecular property is treated as being composed of contributions due to groups\(^2\). A group is defined as a polyvalent atom in a molecule together with all its ligands. To each of these groups is assigned a value for the property of interest, in this case the $\Delta H^\circ$. The $\Delta H^\circ$ is calculated by summing up the contributions of the different groups. In addition to the contributions from the individual groups, corrections for effects such as gauche interaction and ring strain, are also accounted for. The errors associated with the estimated values are in simple molecules $\pm 0.5$ kcal mol\(^{-1}\) and in heavily substituted species $\pm 3$ kcal mol\(^{-1}\).
4.1.2 Additivity in ions

The first additivity type scheme able to reproduce satisfactorily the $\Delta H^\circ$ of odd electron cations of homologous series utilized the following expression\(^4\):

$$\Delta_i H^\circ(\text{ion}^{\ddagger\ddagger}) = A - Bn + C/n$$ \hspace{1cm} (4-1)

where A, B and C are constants for a given homologous series and n is the number of atoms in the molecule. Although the method is empirical, the form of the equation properly reflects the fact that the $\Delta_i H^\circ(\text{ion})$ is the sum of the $\Delta_i H^\circ(\text{neutral molecule})$ and the IE(neutral molecule). The $A - Bn$ part of the equation is analogous to the thermochemical additivity system of Benson which reproduces the linear decrease of the $\Delta_i H^\circ(\text{neutral})$ with increasing homologue size. The IE however, is not linearly related to the size of the molecule (Figure 4.1) but relates to the reciprocal of the molecular size and so is taken into account by the last term of the equation. When A, B and C are known, correction terms accounting for branching are introduced when necessary.

The $\Delta_i H^\circ$ of homologous series for which insufficient data are available to permit useful evaluation of A, B and C can be represented by a simplified linear equation of the form:

$$\Delta_i H^\circ(\text{ion}^{\ddagger\ddagger}) = \alpha - \beta \log n$$ \hspace{1cm} (4-2)
Figure 4.1: IE, $\Delta_r H^0$ of neutrals and ions for $n$-alkanes$^5$. 
where $\alpha$ and $\beta$ are constants and $n$ is again the total number of atoms in the molecule. This simplified equation holds for the lower members of the homologous series ($\leq C_8$). These equations reproduce the experimental values to $\pm 2 \text{ kcal mol}^{-1}$.

This method was extended to ions which could not be described as members of homologous series but which were nevertheless related structurally$^5$. Examples of such series are the even electron cations $\text{CH}_3^+$, $\text{CH}_3\text{CH}_2^+$, $(\text{CH}_3)_2\text{CH}^+$ and $(\text{CH}_3)_3\text{C}^+$ and the odd electron cations $\text{C}_6\text{H}_5\text{CH}_3^{\ddagger\ddagger}$, $\text{C}_6\text{H}_4(\text{CH}_3)\ddagger$, $\text{C}_6\text{H}_3(\text{CH}_3)_2^{\ddagger\ddagger}$, etc. For many series of this kind (multiple substitution of $\text{CH}_3^-$, $\text{HO}^-$, $\text{CH}_2\text{O}^-$) straight line relationships are found (Figure 4.2). Because of the simple linear relationship between the size (as expressed as the log $n$, where $n$ is the number of atoms) and the $\Delta_iH^o$ of the ions, the estimation of the $\Delta_iH^o$ for missing members is therefore straightforward. As will be shown in the following sections such a linear relationship is not strictly observed for phenyl substitution.

A more recent approach used to reproduce the $\Delta_iH^o$ of multi-substituted ionized methyl species takes the form of a simple two term equation$^6$:

$$
\Delta_iH^o([X\text{CH}_3^{\ddagger\ddagger}])/[X\text{C}([\text{CH}_3])_m\text{H}_{3-m}^{\ddagger\ddagger}])
= \Delta_iH^o([X\text{CH}_3]) - \Delta_iH^o([X([\text{CH}_3])_m\text{H}_{3-m}^{\ddagger\ddagger}])
= A + Bm
$$

(4-3)
Figure 4.2: Effect of multiple CH₃⁻ (Δ), HO⁻ (◊) and CH₃O⁻ (□) substitution on ΔH° of CH₃⁻.
where $\Delta r H^\circ ([XCH_3^{+*}] / [XC(CH_3)_mH_{3-m}^{+*}])$ is the difference between the $\Delta r H^\circ$ of the unsubstituted and methyl substituted species, $m$ represents the number of methyl groups and $A$ and $B$ are constants for any given series. When $A$ and $B$ are known, this model has proven to be useful to reproduce the $\Delta r H^\circ$ of a variety of odd-electron cations. The model was also extended to reproduce the effect of multiple phenyl substitutions. Three series of phenyl substituted odd electron cations were investigated $^8$ [C(C_6H_5)_{m+1}H_{3-m}^{+*}], [Si(C_6H_5)_mH_{4-m}^{+*}] and [Si(C_6H_5)_{m+1}H_{3-m}^{+*}]. It was observed that, as opposed to methyl substitution, sequential replacement of a H atom by a C_6H_5 group, when the first member of the series is taken as the monosubstituted species, increases the $\Delta r H^\circ$ of the positive ions, thus exerting a destabilizing effect.

4.2 Results and discussion

All data reported in this section are from reference 1c or otherwise stated. The new experimental data, i.e., our experimentally determined $\Delta r H^\circ$(ion) were obtained from IE and AE measurements.
4.2.1 Phenyl substitution in neutral molecules

Based on the additivity principle, phenyl substitution in neutrals should only depend on the functionality at which substitution takes place and not on long range interactions. Using the available experimentally determined $\Delta_{t}H^{\circ}$, it is possible to empirically establish certain trends quantifying the effect of phenyl substitution in neutral molecules. The quantity $\Delta\Delta_{t}H^{\circ}$, which expresses the difference between the $\Delta_{t}H^{\circ}$ of the monosubstituted and the unsubstituted species, measures the enthalpy change associated with the replacement of an H atom by a $C_{6}H_{5}$ moiety. Table 4.1 summarizes the effect of phenyl substitution on a variety of functionalities. Only cases where sufficiently consistent experimental data was available are presented. Particularities and inconsistencies are discussed in the following text.

Phenyl substitution in neutrals increases the $\Delta_{t}H^{\circ}$ of the species irrespective of the functionality at which substitution takes place, but the size of the $\Delta\Delta_{t}H^{\circ}$ is dependent on the functionality. Consequently, phenyl substitution in neutrals contributes a positive enthalpy term to the $\Delta_{t}H^{\circ}$.
Table 4.1  Effect of phenyl substitution on $\Delta H^\circ$ of neutral molecules (the underlined H atom is replaced) ($\Delta H^\circ$ in kcal mol$^{-1}$).

| Functionality | $\Delta H^\circ$  
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(\Delta H^\circ[R-C_6H_5] - \Delta H^\circ[R-H])$</td>
</tr>
<tr>
<td></td>
<td>(±2)</td>
</tr>
<tr>
<td>CH$_3$R</td>
<td>+27</td>
</tr>
<tr>
<td>H$_2$C=CHR</td>
<td>+23</td>
</tr>
<tr>
<td>HC=CR</td>
<td>+19</td>
</tr>
<tr>
<td>CH$_3$X</td>
<td>+23</td>
</tr>
<tr>
<td>ROH</td>
<td>+32</td>
</tr>
<tr>
<td>RCH$_2$OR</td>
<td>+23</td>
</tr>
<tr>
<td>HCOR</td>
<td>+19</td>
</tr>
<tr>
<td>RCO$_2$H</td>
<td>+37</td>
</tr>
<tr>
<td>RNH$_2$</td>
<td>+25</td>
</tr>
<tr>
<td>RSH</td>
<td>+28</td>
</tr>
</tbody>
</table>

X = halogen, see text

Amongst the hydrocarbons, it is in aliphatic species that the effect of phenyl substitution is the largest. The value of $\Delta \Delta H^\circ$ is unaffected by the type of carbon at which substitution takes place i.e., primary vs. secondary vs. tertiary. This is true as long as there are no contributions from steric effects. In alkenes,
substitution at either one of the two doubly bonded carbons produces the same \( \Delta \Delta H^o \). In the case of alkynes, experimental \( \Delta H^o \) obtained from the measurement of heats of hydrogenation\(^7\) suggest that some of the data reported in the Lias et al. compendium\(^{1c}\) should be revised. Table 4.2 lists the reported\(^{1c}\) and revised values for phenyl substituted alkynes.

### Table 4-2: Revised \( \Delta H^o \) of phenyl substituted alkynes (\( \Delta H^o \) in kcal mol\(^{-1}\)).

<table>
<thead>
<tr>
<th>Species</th>
<th>Reported ( \Delta H^o ) (^{1c})</th>
<th>Revised ( \Delta H^o ) (^7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_6\text{H}_5\text{C}=\text{C}\text{C}_6\text{H}_5 )</td>
<td>96</td>
<td>92</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{C}=\text{CCH}_2\text{CH}_3 )</td>
<td>66(^*)</td>
<td>59</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{C}=\text{C(CH}_2)_2\text{CH}_3 )</td>
<td>61(^*)</td>
<td>53</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{C}=\text{CCH(CH}_3)_2 )</td>
<td>59(^*)</td>
<td>51</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{C}=\text{CC(CH}_3)_3 )</td>
<td>52(^*)</td>
<td>44</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{C}=\text{C(CH}_2)_3\text{CH}_3 )</td>
<td>54(^*)</td>
<td>49</td>
</tr>
</tbody>
</table>

* Estimated values.

In halomethanes, phenyl substitution is independent of the nature of \( X \), the halogen, and appears to be (very few experimental data) independent of the number of halogen substituents. It is in acids and alcohols that phenyl substitution is most destabilizing. It is clear from this observation that the phenyl
moiety acts as an electron withdrawing substituent. When substitution takes place on the carbon α to the oxygen, either in alcohols or esters, the destabilizing effect is much less important. Substitution on nitrogen or sulfur is also quite destabilizing but not as much as substitution on oxygen, as expected based on their relative electronegativities. Although not presented in Table 4.1, a large number of phenyl substituted silicon compounds are tabulated in the Lias compendium\textsuperscript{1c}. It appears that an additivity term of +18 kcal mol\textsuperscript{-1} has been adopted to quantify the effect of phenyl substitution in Si containing compounds, but the lack of experimental data does not allow this to be verified. Similarly, for phosphorous containing compounds, the additivity term used is +24 kcal mol\textsuperscript{-1}.

4.2.2 Multiple phenyl substitution in molecules and molecular ions

Table 4.3 shows the effect of multiple phenyl substitution at a single carbon center on the $\Delta H^\circ$ of a series of molecules and corresponding radical cations.
Table 4.3: $\Delta H^\circ$ and IE of phenyl substituted molecules and corresponding radical cations ($\Delta H^\circ$ in kcal mol$^{-1}$ and IE in eV).

<table>
<thead>
<tr>
<th>Molecules</th>
<th>$\Delta H^\circ$(neutrals)$^a$</th>
<th>$\Delta H^\circ$(ions)$^a$</th>
<th>IE$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>-17.8</td>
<td>271</td>
<td>12.62</td>
</tr>
<tr>
<td>C$_6$H$_5$CH$_3$</td>
<td>12.0</td>
<td>215</td>
<td>8.82</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_2$CH$_2$</td>
<td>33 [39]$^a$</td>
<td>230 [236]$^a$</td>
<td>8.55</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_3$CH</td>
<td>65</td>
<td>257</td>
<td>8.34</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_4$C</td>
<td>95</td>
<td>279</td>
<td>8.0</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>-48.2</td>
<td>202.0</td>
<td>10.85</td>
</tr>
<tr>
<td>C$_6$H$_5$CH$_2$OH</td>
<td>-24.0</td>
<td>183$^c$</td>
<td>9.0$^{b1}$</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_2$CHOH</td>
<td>-1$^d$</td>
<td>197$^c$</td>
<td>8.6$^{b1}$</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_3$COH</td>
<td>25$^d$</td>
<td>205$^c$</td>
<td>7.8$^{b1}$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$OH</td>
<td>-56</td>
<td>185</td>
<td>10.47</td>
</tr>
<tr>
<td>CH$_3$(C$_6$H$_5$)CHOH</td>
<td>-34$^d$</td>
<td>171$^c$</td>
<td>8.9$^{b1}$</td>
</tr>
<tr>
<td>CH$_3$(C$_6$H$_5$)$_2$COH</td>
<td>-11$^d$</td>
<td>190$^c$</td>
<td>8.7$^{b1}$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$OCH$_3$</td>
<td>-51.7</td>
<td>172</td>
<td>9.72</td>
</tr>
<tr>
<td>CH$_3$CH(C$_6$H$_5$)OCH$_3$</td>
<td>-29</td>
<td>181$^c$</td>
<td>9.1$^{b2}$</td>
</tr>
<tr>
<td>CH$_3$C(C$_6$H$_5$)$_2$OCH$_3$</td>
<td>-6</td>
<td>201$^c$</td>
<td>9.0$^{b1}$</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>-26.0</td>
<td>224.8</td>
<td>10.874</td>
</tr>
<tr>
<td>C$_6$H$_5$CHO</td>
<td>-9</td>
<td>210</td>
<td>9.49</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_2$CO</td>
<td>12</td>
<td>221</td>
<td>9.05</td>
</tr>
<tr>
<td>CH$_2$CH$_2$</td>
<td>12.5</td>
<td>255.8</td>
<td>10.507</td>
</tr>
<tr>
<td>C$_6$H$_5$CHCH$_2$</td>
<td>35.3</td>
<td>230</td>
<td>8.43</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_2$CH$_2$</td>
<td>59</td>
<td>243</td>
<td>8.00</td>
</tr>
</tbody>
</table>

$^a$ reference 1c; $^b$ this work (1: MS9; 2: electron monochromator); $^c$ calculated from equation 4-4; $^d$ calculated from additivity, reference 2; $^*$ see text for discussion.
Before discussing the effect of multiple phenyl substitution in radical cations, some discussion on the effect of multiple substitution in neutrals should be addressed. It was discussed in the previous section that phenyl substitution in alkanes increased the $\Delta H^\circ$ of neutrals by $27\pm2$ kcal mol$^{-1}$. It becomes evident that the reported $\Delta H^\circ[(C_6H_5)_2CH_2]$ is too low. The discrepancy is also evident from the comparison of $\Delta H^\circ[(C_6H_5)_2CH_2]$ and $\Delta H^\circ[C_6H_5CH_2CH_2C_6H_5]$, reported as 33 and 32.2 kcal mol$^{-1}$, respectively. A revised value of $39\pm2$ kcal mol$^{-1}$, given in Table 4.3 in brackets is proposed for diphenyl methane. By using this revised value for $\Delta H^\circ[(C_6H_5)_2CH_2]$, the $\Delta\Delta H^\circ$ obtained when going from $(C_6H_5)_2CH_2$ to $C_6H_5CH_2CH_2C_6H_5$ is consistent with the effect of homologue size on the $\Delta H^\circ$ in other hydrocarbons.

The data presented in Table 4.3 clearly indicates that addition of sequential phenyl substituents increases the $\Delta H^\circ$ of the neutrals in increments corresponding to the additivity terms discussed in the previous section.

To illustrate the effect of phenyl substitution on both the $\Delta H^\circ$ of neutrals and radical cations, Figure 4.3 shows plots of the variation of the $\Delta H^\circ$ of CH$_4$, CH$_3$OH and CH$_3$CH$_2$OCH$_3$ and their corresponding ions as a function of the number of phenyl groups. It can be seen, that as predicted by additivity, the $\Delta H^\circ$ of the neutral multi-substituted species increases linearly with the number of phenyl groups and the resulting slope is indicative of the size of the $\Delta\Delta H^\circ$. This simple relationship is not observed for the corresponding radical cations.
Figure 4.3: Effect of multiple phenyl substitution on $\Delta H^\circ$ in molecules (○) and their corresponding radical cations (□) a)CH$_4$, b)CH$_3$OH and c)CH$_3$CH$_2$OCH$_3$. 
For CH₄ and CH₃OH, Figure 4.3a and 4.3b, the addition of a single phenyl group contributes significantly to the stabilization of the ions, while subsequent substitutions do not. As described by the following equation, the $\Delta_r H^\circ(\text{ion})$ is related to both the $\Delta_r H^\circ$ and the IE of the neutral, according to:

$$\Delta_r H^\circ(\text{ion}) = \text{IE} + \Delta_r H^\circ(\text{neutral})$$  \hspace{1cm} (4-4)

The stabilization observed when a hydrogen atom is substituted by a phenyl group in radical cations is the result of an appreciable decrease of the IE of the corresponding neutral. This is due to a change in the ionization site: in the case of alkanes, such as methane, the electron expelled originates from a bonding orbital, whereas in heteroatom containing neutrals, this electron most likely comes from a non-bonding orbital localized on the heteroatom. In either case, the energy required to expel such an electron surpasses the energy needed to remove an electron from the $\pi$-system of the phenyl ring. In most cases, the decrease of the IE is sufficiently large to overcome the increase in the $\Delta_r H^\circ$ of the neutral and the overall result is a decrease in the $\Delta_r H^\circ$ of the radical cation for the first phenyl substitution. The amount by which the $\Delta_r H^\circ$ of the ion is decreased is related to the size of the decrease in the IE of the neutral. It is thus expected that if substitution takes places in a homologous series, such as CH₃OH to CH₃CH₂OH, the decrease in the IE will be smaller for the higher homologue, so that the stabilization effect of phenyl substitution will decrease with homologue size. In certain systems such as dimethyl ether (Figure 4.3c),
the decrease of the IE following the first phenyl substitution is not important
enough to overcome the increase in the $\Delta H^*$ of the neutral so that the phenyl
substituted radical cation is not stabilized with respect to the unsubstituted
analogue. It thus becomes clear that in order for the phenyl substituted species
to be stabilized, the decrease in the IE must be larger than the positive enthalpy
term associated with the addition of a phenyl group in the neutral. As discussed
in the previous section, this will depend on the functionality at which substitution
takes place.

Addition of a second, and when possible a third substituent, does not
enhance the stabilization effect. Instead, a monotonic rise in the $\Delta H^*$ of the ion
is observed after successive substitutions. Although the IE of the multi-
substituted neutrals slightly decreases with further substitution, this effect is of
small relative importance and does not contribute significantly to the stabilization
of the ion formed. The observed rise in the $\Delta H^*$ of the ions thus results from the
positive enthalpy term associated with the addition of the phenyl moiety in the
neutral. The fact that the slope for the increase of the $\Delta H^*$ of the ions is not as
steep as the slope for the $\Delta H^*$ of the neutrals, shows that although small, the
contribution from the decrease in the IE is not negligible. As in the case of
neutral species, the slope associated with the rise in the $\Delta H^*$ of the ions with
increasing number of phenyl groups is characteristic of the chemical nature of
the ions, so that no universal additivity scheme may be derived to predict the
$\Delta H^*$ of the phenyl substituted radical cations. However, the linear portion of the
curves may be used to estimate the $\Delta H^\circ$ for missing members as predicted by equation 4-3.

4.2.3 Multiple phenyl substitution in radicals and even electron cations

To parallel the study of phenyl substitution in molecules and molecular ions, the effect of successive phenyl substitution in radicals and even electron cations was undertaken. Table 4.4 reports the data concerning these species.

To illustrate the effect of phenyl substitution on the $\Delta H^\circ$ of radicals and their corresponding ions, Figure 4.4 shows plots of the variation of the $\Delta H^\circ$ of both the ionic and neutral species as a function of the number of phenyl groups for $\text{CH}_3^+$, $\text{CH}_3\text{CH}_2^+$ and $\text{CH}_2\text{OH}$ and their corresponding ions. As observed previously for the molecular species, there is a linear relationship between the $\Delta H^\circ$ of the radicals and the number of phenyl groups. However, the behavior of the ionic species is not straight-forward, but follows the same pattern as that observed in the case of the molecular ions. Upon a first phenyl substitution, a noticeable decrease in the $\Delta H^\circ$ of the ion is observed while further substitution produces a monotonic rise in the $\Delta H^\circ$ of the multi-substituted ions. These observations are true for all the species presented in Table 4.4.
Table 4.4: $\Delta H^0$ and IE of phenyl substituted radicals and corresponding even electron cations ($\Delta H^0$ in kcal mol$^{-1}$ and IE in eV).

<table>
<thead>
<tr>
<th>Radicals</th>
<th>$\Delta H^0$(neutrals)$^a$</th>
<th>$\Delta H^0$(ions)$^a$</th>
<th>IE$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>34.8</td>
<td>261</td>
<td>9.84</td>
</tr>
<tr>
<td>C$_6$H$_5$CH$_2$</td>
<td>48</td>
<td>200</td>
<td>6.6</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_2$CH</td>
<td>69$^f$</td>
<td>214$^g$</td>
<td>6.3</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_3$C</td>
<td>93$^f$</td>
<td>234$^g$</td>
<td>6.1</td>
</tr>
<tr>
<td>CH$_2$CH$_3$</td>
<td>28</td>
<td>215.8</td>
<td>8.13</td>
</tr>
<tr>
<td>C$_6$H$_5$CHCH$_3$</td>
<td>39.6</td>
<td>199</td>
<td>6.9</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_2$CCH$_3$</td>
<td>57$^b$</td>
<td>213</td>
<td>6.8</td>
</tr>
<tr>
<td>CH$_2$OH</td>
<td>-6.2</td>
<td>168</td>
<td>7.6</td>
</tr>
<tr>
<td>C$_6$H$_5$CHOH</td>
<td>7$^b$</td>
<td>157</td>
<td>6.5</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_2$COH</td>
<td>22$^b$</td>
<td>167$^{c1}$</td>
<td>6.3</td>
</tr>
<tr>
<td>CH$_2$OCH$_3$</td>
<td>-3</td>
<td>157</td>
<td>6.94</td>
</tr>
<tr>
<td>C$_6$H$_5$CHOCH$_3$</td>
<td>7$^b$</td>
<td>150$^{c2}$</td>
<td>6.2</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_2$COCH$_3$</td>
<td>31$^b$</td>
<td>161$^{c1}$</td>
<td>5.6</td>
</tr>
</tbody>
</table>

$^a$ from reference 1c; $^b$ additivity, reference 2; $^c$ this work (1: MS9; 2: electron monochromator); $^d$ calculated using equation 4-4; $^e$ unpublished data, this laboratory; $^f$ estimated.
Figure 4.4: Effect of phenyl substitution on the $\Delta H^\circ$ of radicals (\(\Diamond\)) and electron cations (\(\Box\)) a)CH$_3$, b)CH$_2$CH$_2$ and c)CH$_2$OH.
Using the arguments presented in the case of the molecular ions, the decrease in the \( \Delta H^\circ \) of the ion results from the decrease in the IE of the corresponding phenyl substituted radical. In addition to the decrease of the IE, a second factor must contribute to the decrease of the \( \Delta H^\circ \) of the ions; the resonance stabilization energy gained from phenyl substitution. To quantify this effect, the resonance stabilization energy may be estimated by comparing the measured \( \Delta H^\circ \) of the substituted species with a value calculated using additivity (which does not take into consideration this stabilization energy). This data is presented in Table 4.5.

Table 4.5: Estimated resonance stabilization energy in a multi-phenyl substituted methyl radical (All data in kcal mol\(^{-1}\)).

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Delta H^\circ ) (additivity)</th>
<th>( \Delta H^\circ ) (measured)</th>
<th>Resonance stabilization energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3^* )</td>
<td>35</td>
<td>35</td>
<td>-</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{CH}_2^* )</td>
<td>62</td>
<td>48</td>
<td>-14</td>
</tr>
<tr>
<td>( \text{(C}_6\text{H}_5)_2\text{CH}^* )</td>
<td>89</td>
<td>69</td>
<td>-20</td>
</tr>
<tr>
<td>( \text{(C}_6\text{H}_5)_3\text{C}^* )</td>
<td>116</td>
<td>93</td>
<td>-23</td>
</tr>
</tbody>
</table>
The resonance stabilization energy is not additive, but levels off after the second substituent is added, an observation previously reported in the study of CH₃CO and C₆H₅CO substitution in radicals⁶. For the mono-substituted species, this contribution is significant and combined with the decrease in the IE, overcomes the positive enthalpy term associated with the addition of the phenyl group. The ion produced is thus stabilized. However, when further substitution takes place, both the decrease in the IE and the resonance stabilization energy are no longer significant, and the dominant effect is the increase in the ΔrH° of the neutral species. The ΔrH° of the multi-substituted species increases with the number of phenyl groups as does the ΔrH° of the neutral, and as was the case for the radical cations, the slope associated with the increase in ΔrH° for the ions is not as steep as that for the neutrals, indicating that the contributions from the decrease in the IE and the resonance stabilization energy are not negligible. The observations made on the CH₃⁺ species may be extended to the other species investigated.

As in the case of the molecular ions, the magnitude of the stabilization effect after the first phenyl substitution and the subsequent rise of the ΔrH° of the multi-substituted ions is characteristic of the chemical nature of the ions, so that no universal additivity scheme may be derived to predict the ΔrH° of phenyl substituted even electron cations.
4.2.4 Phenyl vs. vinyl substitution

The Δ\text{r}H° of vinyl substituted molecular species are related to the Δ\text{r}H° of the phenyl substituted species by the following expression:\textsuperscript{9}:

\[ \Delta\text{r}H^\circ(C_2H_3X) = \Delta\text{r}H^\circ(C_6H_5X) - 7 \pm 1.5 \text{ kcal mol}^{-1} \] (4-5)

Because of this simple relationship, one would expect, a priori, that the effect of vinyl substitution will closely resemble the effect of phenyl substitution. The data concerning vinyl substituted species is very scarce but it is possible to make some conclusions using CH\textsubscript{4} and CH\textsubscript{3}+, as examples. This data are presented in Table 4.6.

The data describing the effect of vinyl substitution in molecular species and corresponding molecular ions are plotted in Figure 4.5a. It is evident that the effect of vinyl substitution on the Δ\text{r}H° of the molecular species is additive, but as was the case for phenyl substitution, this is not strictly true for the molecular ions. The first vinyl substitution lowers the Δ\text{r}H° of the ions, as expected from the decrease of the IE, while further substitution results in an increase of the Δ\text{r}H°, consistent with an increase in the Δ\text{r}H° of the neutral being the dominant factor. The linear portion of both curves can be extrapolated and the Δ\text{r}H° of (CH\textsubscript{2}CH\textsubscript{2})\textsubscript{4}C and (CH\textsubscript{2}CH\textsubscript{2})\textsubscript{4}C\textsuperscript{+} can be estimated. These values are included in Table 4.6. It is apparent from Figure 4.5a that vinyl and phenyl substitution in molecular species thermochemically behave in a parallel manner.
Table 4.6: $\Delta H^\circ$ and IE of vinyl substituted neutrals and corresponding cations ($\Delta H^\circ$ in kcal mol$^{-1}$ and IE in eV).

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H^\circ$(neutrals)$^a$</th>
<th>$\Delta H^\circ$(ions)$^a$</th>
<th>IE$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>-17.8</td>
<td>271</td>
<td>12.62</td>
</tr>
<tr>
<td>CH$_2$CHCH$_3$</td>
<td>4.8</td>
<td>229</td>
<td>9.73</td>
</tr>
<tr>
<td>(CH$_2$CH)$_2$CH$_2$</td>
<td>25.2</td>
<td>247</td>
<td>9.58</td>
</tr>
<tr>
<td>(CH$_2$CH)$_3$CH</td>
<td>44</td>
<td>265</td>
<td>9.5</td>
</tr>
<tr>
<td>(CH$_2$CH)$_4$C</td>
<td>63$^b$</td>
<td>283$^b$</td>
<td>9.5$^c$</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>34.8</td>
<td>261</td>
<td>9.84</td>
</tr>
<tr>
<td>CH$_2$CHCH$_2$</td>
<td>40</td>
<td>227</td>
<td>8.13</td>
</tr>
<tr>
<td>(CH$_2$CH)$_2$CH</td>
<td>53</td>
<td>220$^d$</td>
<td>7.25</td>
</tr>
<tr>
<td>(CH$_2$CH)$_3$C</td>
<td>71$^*</td>
<td>223$^*</td>
<td>6.6$^*$</td>
</tr>
</tbody>
</table>

$^a$ from reference 1c; $^b$ extrapolated from figure 4.5a; $^c$ calculated from equation 4-4; $^d$ reference 10; $^*$ estimated, see discussion.
Figure 4.5: Effect of vinyl substitution on $\Delta H^\circ$ in a)CH$_4$ and b)CH$_3$* (ionic species (□) and neutral species (○)).
Figure 4.5b illustrates the effect of vinyl substitution on the $\Delta H^*$ of the $\text{CH}_3^*$ radical and its corresponding even electron cation. As expected, vinyl substitution in radicals is additive. However, in the case of the even electron cations, the relationship between the $\Delta H^*$ of the ion and the number of vinyl groups is somewhat different from that observed for phenyl substitution. The first vinyl substitution considerably decreases the $\Delta H^*$ of the ion, but from the available data, it appears that subsequent substitutions further stabilize the ion formed. This further stabilization is due to a considerable lowering of the IE of the doubly substituted species. In the case of phenyl substitution, the addition of a second substituent did not significantly affect the IE of the species. The decrease in the IE for vinyl substituted species parallels the decrease in the IE observed when going from a primary to a secondary and from a secondary to a tertiary alkyl radical. The observed decrease of the $\Delta H^*$ of the doubly substituted ion is small compared to the decrease in the IE since not much more resonance stabilization energy is gained after a second substitution, and as observed in the case of phenyl substitution, the contribution of the $\Delta H^*$ of the neutral is thus relatively more important.

From the available data and observations made on the resonance stabilization energy in phenyl substituted analogues, the neutral and ionic $\Delta H^*$ of the last member of the vinyl series can be estimated. Table 4.7 provides the data relevant to the resonance stabilization energy.
Table 4.7: Estimated resonance stabilization energy in multi-vinyl substituted CH₃⁺ (All data in kcal mol⁻¹).

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔH° (additivity)</th>
<th>ΔH° (measured)</th>
<th>Resonance stabilization energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃⁺</td>
<td>35</td>
<td>35</td>
<td>-15</td>
</tr>
<tr>
<td>CH₂CHCH₂⁺</td>
<td>55</td>
<td>40</td>
<td>-15</td>
</tr>
<tr>
<td>(CH₂CH)₂CH⁺</td>
<td>75</td>
<td>53</td>
<td>-22</td>
</tr>
</tbody>
</table>

Again the resonance stabilization energy is not additive and based on the phenyl analogue, an estimated resonance stabilization energy of ~ -24 kcal mol⁻¹ for the last member of the vinyl series, (CH₂CH)₃C⁺, is deduced. Additivity would predict a ΔH° of 95 kcal mol⁻¹ for this radical and combining this with the estimated resonance stabilization energy a ΔH°[(CH₂CH)₃C⁺] ~ 71 kcal mol⁻¹ is estimated. Assuming that the trend in the IE observed for the first two members of the series holds, an estimated IE [(CH₂CH)₃C⁺] would be ~ 6.6 eV. The sum of these two values gives an estimated ΔH°[(CH₂CH)₃C⁺] ~ 223 kcal mol⁻¹. This value is only slightly more positive than the ΔH° of the doubly substituted species and suggests that the stabilizing contribution of the lowering of the IE and resonance stabilization energy are almost equivalent to the increase of the ΔH° of the neutral. However, the decrease of the IE in the doubly substituted radical is quite unexpected, and although rearrangements in neutral species are less
common than in ions, the possibility that the measured IE was not that of the sought radical but rather of the cyclopentenyl radical (a lower energy species) cannot be disregarded. Alas, the lack of available data on vinyl substituted species does not allow verification of these observations to other vinyl containing species.

4.4 Conclusions

Phenyl substitution in either molecules or radicals is always destabilizing. The enthalpy term associated with phenyl substitution in these species depends on the functionality at which substitution takes place. These enthalpy terms may be used to estimate the Δ\text{H}^0 when the data is unavailable.

In the case of ionized species, the relationship between the Δ\text{H}^0 and the number of phenyl groups is not straightforward and also depends on the chemical nature of the species in which substitution takes place. However, in most cases substitution of a first phenyl group significantly lowers the Δ\text{H}^0 of the ions. This decrease in the Δ\text{H}^0 results from a lowering of the IE and, in the case of the even electron cations, from the gained resonance stabilization energy. As these two stabilizing factors are much less important when further substitution takes place, a monotonic rise in the Δ\text{H}^0 of the ions is observed, indicating that Δ\text{H}^0 of the phenyl substituted neutrals becomes the predominant factor in determining the Δ\text{H}^0 of the ions. No general additivity scheme may be derived,
but for multiple substitution, the linear relationship between the $\Delta H^\circ$ and the number of phenyl groups allows the estimation of $\Delta H^\circ$ for missing members.

The effect of vinyl substitution in molecular species, both neutral and ionic, is very closely related to phenyl substitution, as is vinyl substitution in $\text{CH}_3^-$. However, vinyl substituted even electron cations behave unlike their phenyl substituted analogues.
4.5 References


Chapter 5

The thermochemical effect of methyl substitution

in neutral ketene

5.1 Introduction

There has been only one accurate measurement reported for the heat of formation (\(\Delta_H^\circ\)) of a compound containing the ketene function [C=C=O], namely ketene itself, CH\(_2\)CO. The \(\Delta_H^\circ\) value, \(-11.4\pm0.6\) kcal mol\(^{-1}\) is listed in the selected thermochemical data source book of Pedley, Naylor and Kirby\(^1\). The method used to determine \(\Delta_H^\circ\) [CH\(_2\)CO(g)] was not combustion to CO\(_2\) and H\(_2\)O, but a measurement of the heat of reaction of ketene with aqueous sodium hydroxide\(^2\). The result has not been challenged by later experiments or by high level theoretical calculations, thus giving confidence in the 1971 result. The data compilation of Lias et al.\(^3\) also contains \(\Delta_H^\circ\) values for methyl ketene, CH\(_3\)CHCO, and dimethyl ketene, (CH\(_3\))\(_2\)CCO, of -25 and -32 kcal mol\(^{-1}\), respectively. These however, are not experimentally based values and moreover the latter value was quoted as -37 kcal mol\(^{-1}\) in the original estimate\(^4\), presumably to reflect an additivity term of about -12 kcal mol\(^{-1}\) per methyl group.
Other thermochemical data available for CH$_2$CO, CH$_3$CHCO and
(CH$_3$)$_2$CCO include the ionization energy (IE) values experimentally determined
by Bock$^5$ and reported to be 9.64, 8.95 and 8.45 eV, respectively.

Recently, McKee and Radom$^6$, using ab initio molecular orbital theory
calculations at the G2 level, reported $\Delta rH^0$ values for CH$_3$CHCO and CH$_3$CHCO$^{**}$
of -15.6 kcal mol$^{-1}$ and 191 kcal mol$^{-1}$, respectively, and an IE$_c$ for methyl ketene
of 8.93 eV. The measured IE reported by Bock$^5$ (8.95eV) is in excellent
agreement with the calculated value, but in disagreement with an unpublished
value for $\Delta rH^0$ [CH$_3$CHCO$^{**}$] of 183±1 kcal mol$^{-1}$ obtained in our laboratory from
the measured appearance energy (AE) of the ion in the following reaction:

$$\text{CH}_3\text{CH}_2\text{COCH}_2\text{OH} \rightarrow \text{CH}_3\text{CHCO}^{**} + \text{CH}_3\text{OH} \quad \text{AE} = 9.88\pm0.05 \text{ eV} \quad (5-1)$$

A value for $\Delta rH^0$[CH$_3$CHCO] appeared in late 1996$^7$ based on a measured proton
affinity of methyl ketene of 201±1 kcal mol$^{-1}$. Using $\Delta rH^0$[CH$_3$CH$_2$CO$^+$] = 141 kcal
mol$^{-1}$ $^8$ gives a $\Delta rH^0$[CH$_3$CHCO] = -24 kcal mol$^{-1}$, which is in reasonable
agreement with the estimate given above.

Most recently, Scott and Radom$^9$ published a paper on the effect of
methyl substitution in ketene, extending their earlier calculations to ketene and
dimethyl ketene. The calculated values were $\Delta rH^0$[CH$_2$CO] = -12 kcal mol$^{-1}$,
$\Delta rH^0$[CH$_3$CHCO] = -16 kcal mol$^{-1}$ and $\Delta rH^0$[(CH$_3$)$_2$CCO] = -22 kcal mol$^{-1}$. The
remarkably small change in the calculated $\Delta rH^0$ in going from ketene to methyl
ketene, from -12 to -16 kcal mol$^{-1}$ and from methyl ketene to dimethyl ketene, from -16 to -22 kcal mol$^{-1}$, (smaller than that for any other methyl substitution, as discussed in the following section) aroused our interest in trying to measure the $\Delta_f H^\circ$ of CH$_3$CHCO and (CH$_3$)$_2$CCO and in obtaining a new experimental value for the $\Delta_f H^\circ[\text{CH}_2\text{CO}]$.

5.1.1 Effect of methyl substitution in analogous systems

Molecules structurally related to ketene can be used to evaluate the effect of methyl substitution on both the IE and $\Delta_f H^\circ$. These molecules include ethene, allene (methyl substitution on a double bond) and formaldehyde (methyl substitution on carbonyl). Table 5.1 gives the IE and $\Delta_f H^\circ$ of these species as well as the $\Delta_f H^\circ$ of their methyl substituted analogues.

The decrease in IE following the first and second methyl substitution in ethene, allene and formaldehyde is of the order of 0.7 eV and 0.5 eV, respectively. The differences between Bock's$^{5}$ IE for CH$_2$CO and CH$_3$CHCO and for CH$_3$CHCO and (CH$_3$)$_2$CCO, are -0.69 and -0.59 eV, respectively, consistent with the effect in analogous systems and thus suggesting that the experimental and calculated IE are correct.
Table 5.1: Effect of methyl substitution in ethene, allene and formaldehyde (IE in eV and $\Delta H^\circ$ in kcal mol$^{-1}$).

<table>
<thead>
<tr>
<th>Species</th>
<th>IE</th>
<th>$\Delta$IE</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta\Delta H^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$CH$_2$</td>
<td>10.507</td>
<td></td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CHCH$_2$</td>
<td>9.73</td>
<td>-0.78</td>
<td>4.8</td>
<td>-7.7</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CCH$_2$</td>
<td>9.24</td>
<td>-0.49</td>
<td>-4</td>
<td>-8.8</td>
</tr>
<tr>
<td>CH$_2$CCH$_2$</td>
<td>9.69</td>
<td></td>
<td>45.6</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CHCCH$_2$</td>
<td>9.03</td>
<td>-0.66</td>
<td>38.8</td>
<td>-6.8</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>10.874</td>
<td></td>
<td>-26.0</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CHO</td>
<td>10.229</td>
<td>-0.65</td>
<td>-39.6</td>
<td>-13.6</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CO</td>
<td>9.71</td>
<td>-0.52</td>
<td>-51.9</td>
<td>-12.3</td>
</tr>
</tbody>
</table>

For ethene and allene and other species such as propene, benzene and toluene, methyl substitution lowers $\Delta H^\circ$ by 6.8 to 8.8 kcal mol$^{-1}$, with no significant difference between the different $\pi$–electron systems. On the other hand, methyl substitution in formaldehyde and other carbonyl containing compounds (ketones, acids, esters) has a much larger effect, ca. -12.3 to -13.6 kcal mol$^{-1}$. The latter may well have been chosen by Deming and Wulff$^d$, e.g. -11 $\rightarrow$ -24 $\rightarrow$ -37 kcal mol$^{-1}$. The theoretically calculated energy change$^e$, CH$_2$CO to CH$_3$CHCO and CH$_3$CHCO to (CH$_3$)$_2$CCO, of only -4 and -6 kcal mol$^{-1}$, respectively, appears to be anomalous for methyl substitution.
5.2 Results and discussion

To determine the $\Delta_f H^\circ$ of ketene, methyl ketene and dimethyl ketene the AE of ionized phenol in the reactions:

$$R_1R_2CHCO_2C_6H_5 \rightarrow R_1R_2CCO + C_6H_5OH^{**} \quad (5-2)$$

where $R_1$ and $R_2$ are either CH$_3$ or H, were measured. The Electron Impact Appearance Energy Apparatus was used for these measurements and the method was described earlier (section 3.4.1). The $\Delta_f H^\circ$ of ionized phenol is accurately known and the $\Delta_f H^\circ$ of the precursor esters can be estimated with confidence. Compounds were synthesized by standard procedures (reaction of phenol with corresponding carboxylic acid) and purified before use. Great care was taken to ensure that phenol was undetectable in the esters by GC/MS. Normal, metastable ion (MI) and collision induced dissociation (CID) mass spectra were recorded using the modified VG ZAB-2F mass spectrometer described earlier (section 2.1).

5.2.1 Mass spectrometry of phenyl esters

The three phenyl esters each show a relatively intense molecular ion in their normal electron impact mass spectra. The metastable ion (MI) mass spectra (Figure 5.1) of the acetate and propanoate contain only m/z 94 whereas the MI mass spectrum of the isobutyrate contains m/z 70, (CH$_3$)$_2$CCO** (100%) and only a very weak m/z 94 (1%). The kinetic energy releases calculated from
Figure 5.1: MI mass spectra of a) phenyl acetate, b) phenyl propanoate and c) phenyl isobutyrate.
the half-height widths of these Gaussian fragment ion peaks, were 7, 9, 10 and 18 meV respectively. The kinetic energy releases associated with these four processes are all small and so corrections for kinetic shift can confidently be disregarded\textsuperscript{11}. Finally the collision induced dissociation mass spectra of the m/z 94 ions, C\textsubscript{6}H\textsubscript{4}O\textsuperscript{+}, produced in the dissociation of the esters were identical to that of ionized phenol\textsuperscript{12}, thus leaving no doubt as to the fragment ions’ structure (Figure 5.2).

5.2.2 $\Delta_f H^\circ$ of CH\textsubscript{2}CO, CH\textsubscript{3}CHCO and (CH\textsubscript{3})\textsubscript{2}CCO

Table 5.2 shows the results of the AE measurements, together with the derived $\Delta_f H^\circ$ values for the ketenes, using the well established $\Delta_f H^\circ$ [C\textsubscript{6}H\textsubscript{5}OH\textsuperscript{+}] of 172 kcal mol\textsuperscript{-1}\textsuperscript{3}.
Figure 5.2: CID(He) mass spectra of a) $C_9H_8OH^{+*}$ ion produced from phenyl esters and b) ionized phenol.
Table 5.2: AE for C₆H₅OH⁺ and derived ΔH° for CH₂CO, CH₃CHCO and (CH₃)₂CCO (AE are in eV and ΔH° in kcal mol⁻¹).

<table>
<thead>
<tr>
<th>Ester</th>
<th>ΔH° [esters]</th>
<th>AE [C₆H₅OH⁺]</th>
<th>ΔH° [ketenes]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CO₂C₆H₅</td>
<td>-67³</td>
<td>9.83</td>
<td>-12 (-11.4)²</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-12)²</td>
</tr>
<tr>
<td>CH₃CH₂CO₂C₆H₅</td>
<td>-71¹⁰</td>
<td>9.58</td>
<td>-22 (-25)⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-16)⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-16.3)²</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-21)⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-24)⁴</td>
</tr>
<tr>
<td>(CH₃)₂CHCO₂C₆H₅</td>
<td>-79¹⁰</td>
<td>9.50</td>
<td>-32 (-37)⁵</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-22)²</td>
</tr>
</tbody>
</table>

² experimental, reference 2; ³ calculated, reference 9; ⁴ estimated, reference 4; ⁵ calculated, reference 6; ⁶ estimated, reference 8; ⁷ calculated from PA[CH₃CHCO], reference 7.

There is very good agreement between our value for ΔH°[CH₂CO] and the previous experimentally determined ΔH°. The new experimental values for ΔH°[CH₃CHCO] and ΔH°[(CH₃)₂CCO], however, do not agree with Radom's calculated values and are somewhat more positive than the estimated values.
The difference between the experimental and estimated $\Delta H^\circ$ is even greater for the $\Delta H^\circ[(\text{CH}_3)_2\text{CCO}]$ suggesting that the additivity term selected by Deming and Wulff$^4$ was too large. From our experimental results, the additivity term reflecting the effect of methyl substitution on the ketene function is ca. -10 kcal mol$^{-1}$ per methyl group as opposed to -4 and -6 kcal mol$^{-1}$ for the first and second methyl substitution predicted by calculations and -12 kcal mol$^{-1}$ chosen by Deming and Wulff$^4$. Consequently, according to our results, methyl substitution in ketene is more stabilizing than in carbon-carbon $\pi$-systems but slightly less stabilizing than on carbonyl groups.

It is possible to argue that the AE values for precursor molecules of this size may be subject to appreciable kinetic shift effects. That this is unlikely is shown by the result for ketene itself, where all the experiments and theory are in excellent agreement. Kinetic shifts would necessarily lead to more positive apparent $\Delta H^\circ$ values for the ketenes, and thus this effect would only increase the discrepancy between theory and experiment.

The likelihood that the neutral species accompanying the phenol ion are isomers of methyl and dimethyl ketene can be disregarded on mass spectrometric grounds. The CIDI mass spectrum of phenyl propanoate is markedly different from the CID of acrolein (the only other $\text{C}_3\text{H}_4\text{O}$ species having a negative $\Delta H^\circ$), the former shows major peaks at m/z 41 and m/z 28, no m/z 29, while the latter has an intense m/z 29 and only a weak m/z 41 (Figure 5.3).
Figure 5.3: $C_3H_4O^{+\cdot}$ isomers: a)ClDI($O_2$) mass spectrum of $C_3H_4O^{+\cdot}$ from phenyl propanoate and b)CID($O_2$) mass spectrum of acrolein.
Three C₄H₆O isomers have negative ΔᵣH°. However, the CID (and normal) mass spectra of methyl vinyl ketone, but-2-ene-al and 2-methyl propenal contain major peaks absent in the mass spectra (normal, CID and CIDI) of the dimethyl ketene (Figure 5.4). The ketone’s spectra are dominated by m/z 55 and the aldehyde’s display m/z 29. The ketene has no m/z 29, a weak m/z 55 and the spectra contain an intense m/z 42 ion, which as shown elsewhere¹³, is ionized dimethylcarbene.

The IE of CH₂CO, CH₃CHCO and (CH₃)₂CCO, 9.58, 8.92 and 8.43 eV, respectively, calculated by Scott and Radom⁹ are all in excellent agreement with those published by Bock⁵. However, the calculated ΔrH° of the two methyl substituted ketenes are far from the experimentally determined values. Although the authors acknowledge the unusual effect of methyl substitution in ketene predicted by their calculations, no physico-chemical explanations are provided to rationalize this result. However, the authors do note that for both methyl ketene and dimethyl ketene the calculated C=C bond lengths are somewhat longer (≈ 0.01 Å) that the experimental values and that the calculated C-C₀ (C₀ is the doubly bonded carbon) bond lengths are somewhat shorter longer (≈ 0.01 Å) than the experimental values⁹. It is only in these two cases that significant discrepancies between the calculated and experimental ΔrH° values are observed. For ketene, the calculated geometry is in very good agreement with the experimentally determined geometry and the close fit of all the ΔrH° values
Figure 5.4: CID(He) mass spectra of C₄H₆O⁺⁺ from a)phenyl isobutyrate, b)2-methyl propene-al and c)methyl vinyl ketone.
suggests that, in the case of methyl and dimethyl ketene, the calculated geometries may be the source of the discrepancies. In effect, it has been shown for sulfine\textsuperscript{14}, CH\textsubscript{2}SO, that when the geometry optimization did not accurately reproduce the experimental structure, significant discrepancies were observed between the calculated and experimental Δ\text{H}^\circ.

5.2.3 Δ\text{H}^\circ of CH\textsubscript{2}CHCO\textsuperscript{−−} and (CH\textsubscript{3})\textsubscript{2}CCO\textsuperscript{−−}

From the available thermochemical data i.e., Bock's IE\textsuperscript{5} and our experimentally determined neutral Δ\text{H}^\circ, it is possible to calculate the Δ\text{H}^\circ of the corresponding ionized ketenes using the following equation:

\[
\Delta \text{H}^\circ[\text{ketene}^{−−}] = \text{IE}[\text{ketene}] + \Delta \text{H}^\circ[\text{ketene}]
\]  \hspace{1cm} (5-3)

Note that the Δ\text{H}^\circ of the ionized ketenes may also be obtained independently from an AE measurement. In order for the determined thermochemical quantities to be consistent, the Δ\text{H}^\circ obtained via these two routes must be the same i.e., Δ\text{H}^\circ values derived from IE and AE measurements must be the same. Table 5.3 shows the results of the AE measurements, together with the derived Δ\text{H}^\circ values for the ionized ketenes, using the well established Δ\text{H}^\circ[\text{C}_6\text{H}_5\text{OH}] and Δ\text{H}^\circ[\text{CH}_3\text{OH}] of -23.0 kcal mol\textsuperscript{−1} and -48.2 kcal mol\textsuperscript{−1}, respectively.
Table 5.3: AE and derived $\Delta H^0$ for CH$_3$CHCOC$^+$ and (CH$_3$)$_2$CCO$^+$. Values in parenthesis are published $\Delta H^0$ (AE in eV and $\Delta H^0$ in kcal mol$^{-1}$).

<table>
<thead>
<tr>
<th>Precursors</th>
<th>$\Delta H^0$[precursors]</th>
<th>AE</th>
<th>$\Delta H^0$[ketenes]$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CH$_2$COCH$_2$OH</td>
<td>-93$^{10}$</td>
<td>9.88</td>
<td>183 (181)$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(191)$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(186)$^c$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CO$_2$C$_6$H$_5$</td>
<td>-71$^{10}$</td>
<td>$\leq$ 10.36$^*$</td>
<td>$\leq$ 191</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CHCO$_2$C$_6$H$_5$</td>
<td>-78$^{10}$</td>
<td>9.52</td>
<td>165 (163)$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(174)$^b$</td>
</tr>
</tbody>
</table>

* not a metastable process; $^a$ calculated using IE and $\Delta H^0$ from reference 4; $^b$ calculated, reference 9; $^c$ estimated reference 15.

The $\Delta H^0$[CH$_3$CHCOC$^+$] derived from the AE of this ion generated from the corresponding phenyl ester can only be taken as an upper limit since the process is not the fragmentation of lowest energy requirement, and so the contribution of a competitive shift cannot be ignored. If Bock’s IE values are used in combination with our $\Delta H^0$ values for the neutral ketenes, the expected values for $\Delta H^0$[CH$_3$CHCOC$^+$] and $\Delta H^0$[(CH$_3$)$_2$CCO$^+$] are 184 and 163 kcal mol$^{-1}$, respectively. These calculated values are in excellent agreement with our independently measured experimental values (183 and 165 kcal mol$^{-1}$) and demonstrate that our results are self consistent.
5.2.4 Dissociation of 2,2,4,4-tetramethyl-1,3-cyclobutanedione

To further support our experimental data, a second precursor molecule namely 2,2,4,4-tetramethyl-1,3-cyclobutanedione (TMCBD), was used to obtain information on the $\Delta H^o$ of $(\text{CH}_3)_2\text{CCO}$ and $(\text{CH}_3)_2\text{CCO}^{**}$. Following electron impact TMCBD, a dimer of dimethyl ketene, undergoes a retro Diels-Alder type reaction to produce ionized and neutral $(\text{CH}_3)_2\text{CCO}$.

$$
\begin{array}{c}
\text{O} \\
\bigg\downarrow
\end{array}
\rightarrow
\begin{array}{c}
\text{O} \\
\bigg\downarrow
\end{array}
\quad
(\text{CH}_3)_2\text{CCO}^{**} + (\text{CH}_3)_2\text{CCO}
$$

From the AE measurement for $(\text{CH}_3)_2\text{CCO}^{**}$ the value of the sum of the products $\Delta H^o$ may be calculated from:

$$
\text{AE}[(\text{CH}_3)_2\text{CCO}^{**}] + \Delta H^o[\text{TMCBD}] = \Delta H^o[(\text{CH}_3)_2\text{CCO}^{**}] + \Delta H^o[(\text{CH}_3)_2\text{CCO}] \quad (5-5)
$$

This quantity can then be compared to the values obtained by our measurements and by Radom's calculations\textsuperscript{9}. The $\text{AE}[(\text{CH}_3)_2\text{CCO}^{**}]$ was measured to be $9.5 \pm 0.1$ eV (using the MS9, section 3.4.1), in excellent agreement with the value measured independently using photoionization mass spectrometry by Traeger ($\text{AE}[(\text{CH}_3)_2\text{CCO}^{**}] = 9.41$ eV\textsuperscript{16}).

The MI mass spectrum of the TMCBD \textbf{does not contain} the ion at m/z 70, $(\text{CH}_3)_2\text{CCO}^{**}$, but rather an ion at m/z 84 $(\text{C}_6\text{H}_{12}^{**})$, indicating that the process leading to the production of ionized and neutral dimethyl ketene is not the lowest
dissociation energy channel. Consequently, the measured AE will set an upper limit to the sum of the products $\Delta r H^\circ$. The CID mass spectrum of the ion at m/z 70 was characteristic of (CH$_3$)$_2$CCO$^{**}$ and so was the collision induced dissociative ionization (CIDI) mass spectrum of the neutral co-generated, thus leaving no doubt as to the ion and neutral structures. The sum of the products $\Delta r H^\circ$ obtained from this measurement (using $\Delta r H^\circ[\text{TMCBD}] = -74$ kcal mol$^{-1}$), from the study of the phenyl isobutyrate and the calculations$^9$ are presented in Table 5.4. The sum of the products $\Delta r H^\circ$ obtained from this measurement, which is an upper limit, lies between that predicted from our experimental data and from the calculations$^9$. This clearly indicates that the calculated $\Delta r H^\circ[(\text{CH}_3)_2\text{CCO}]$ is too positive, thus increasing the sum of the product $\Delta r H^\circ$.

Table 5.4: Sum of the $\Delta r H^\circ$ of (CH$_3$)$_2$CCO$^{**}$ and (CH$_3$)$_2$CCO ($\Delta r H^\circ$ and $\Sigma \Delta r H^\circ$ in kcal mol$^{-1}$).

<table>
<thead>
<tr>
<th>Source</th>
<th>$\Delta r H^\circ[(\text{CH}_3)_2\text{CCO}]$</th>
<th>$\Delta r H^\circ[(\text{CH}_3)_2\text{CCO}^{**}]$</th>
<th>$\Sigma \Delta r H^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>-31</td>
<td>165</td>
<td>134</td>
</tr>
<tr>
<td>AE m/z 70 from TMCBD</td>
<td></td>
<td></td>
<td>145</td>
</tr>
<tr>
<td>Calculations$^9$</td>
<td>-22</td>
<td>174</td>
<td>152</td>
</tr>
</tbody>
</table>
5.2.4 Phenyl substitution in ketene

In order to further demonstrate that the thermochemistry of substituted ketenes is not unique, as implied by the calculated $\Delta H^\circ$ values, the effect of phenyl substitution in ionized ketenes was also investigated. The corresponding phenyl esters, $\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{C}_6\text{H}_5$ and $(\text{C}_6\text{H}_5)_2\text{CHCO}_2\text{C}_6\text{H}_5$, produced in their MI mass spectra ionized phenyl and diphenyl ketenes, respectively. Table 5.5 shows the results of the AE measurements together with the derived $\Delta H^\circ$ values for ionized phenyl and diphenyl ketene, using the well established $\Delta H^\circ[\text{C}_6\text{H}_5\text{OH}]$ of -23.0 kcal mol$^{-1}$ \cite{1}. The measurements were carried out on the MS9.

Table 5.5: AE and derived $\Delta H^\circ$ for $\text{C}_6\text{H}_5\text{CHCO}^{**}$ and $(\text{C}_6\text{H}_5)_2\text{CCO}^{**}$ (AE in eV and $\Delta H^\circ$ in kcal mol$^{-1}$).

<table>
<thead>
<tr>
<th>Precursor</th>
<th>$\Delta H^\circ$[precursor]</th>
<th>AE</th>
<th>$\Delta H^\circ$[ketenes]$^{**}$</th>
<th>$\Delta \Delta H^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{C}_6\text{H}_5$</td>
<td>$-40^{10}$</td>
<td>8.9</td>
<td>188</td>
<td>-22</td>
</tr>
<tr>
<td>$(\text{C}_6\text{H}_5)_2\text{CHCO}_2\text{C}_6\text{H}_5$</td>
<td>$-14^{10}$</td>
<td>8.8</td>
<td>212</td>
<td>+24</td>
</tr>
</tbody>
</table>

$\Delta H^\circ[\text{CH}_2\text{CO}^{**}]$ is 210 kcal mol$^{-1}$, using $\Delta H^\circ[\text{CH}_2\text{CO}]$ = -12 kcal mol$^{-1}$ and IE[CH$_2$CO] = 9.61 eV.
As expected from the study of the effect of phenyl substitution on other ionized species (refer to section 4.2.3), the first phenyl substitution decreases the $\Delta_r H^\circ$ of the ion, $\Delta \Delta r H^\circ = -22$ kcal mol$^{-1}$, because of the decrease in IE accompanying the substitution. The size of the $\Delta \Delta r H^\circ$ is, as in the neutral methyl substituted species, somewhere between the $\Delta \Delta r H^\circ$ observed in ethene and formaldehyde (Table 4.3). Upon the addition of a second phenyl group, the $\Delta_r H^\circ$ of the ion increases, reflecting the positive enthalpy term contribution from the $\Delta_r H^\circ$ of the neutral. These observations indicate that the effect of phenyl substitution on the thermochemistry of the ketene moiety is not singular, but consistent with such effects in structurally related systems.

The additivity term for methyl substitution in neutral ketene was between that expected for olefins and carbonyl species. It can thus be expected that a similar observation be made for phenyl substitution in ketene. In C$_n$H$_{2n}$ species, phenyl substitution increased the $\Delta_r H^\circ$ by 23 kcal mol$^{-1}$ whereas in carbonyl species the $\Delta_r H^\circ$ increased by 19 kcal mol$^{-1}$. Hence, an additivity term of 21 kcal mol$^{-1}$ can reasonably be used to estimate the $\Delta_r H^\circ$ of phenyl and diphenyl ketene: $\Delta_r H^\circ[C_6H_5CHCO] = 9$ kcal mol$^{-1}$ and $\Delta_r H^\circ[(C_6H_5)_2CCO] = 30$ kcal mol$^{-1}$.

It is possible, using thermochemical arguments, to show that the values proposed above are reasonable. A lower limit for the $\Delta_r H^\circ$ of neutral C$_6$H$_5$CHCO and (C$_6$H$_5$)$_2$CCO can be set using the following argument: in the MI mass spectra of the corresponding phenyl esters, only the processes leading to the
production of the ionized phenyl ketenes are observed. This indicates that the process yielding the neutral species is at least ca. 10 kcal mol\(^{-1}\) higher in energy, so that:

\[
\begin{align*}
\Sigma \Delta H^\circ[\text{products}] & \\
C_6H_5CO_2C_6H_5 \rightarrow C_6H_5CHCO^{**} (188) + C_6H_5OH (-23) & 165 \text{ kcal mol}^{-1} \\
\overset{x}{\longrightarrow} C_6H_5CHCO (?) + C_6H_5OH^{**} (172) & \geq 175 \text{ kcal mol}^{-1} \\
(C_6H_5)_2CHCO_2C_6H_5 \rightarrow (C_6H_5)_2CCO^{**} (212) + C_6H_5OH (-23) & 189 \text{ kcal mol}^{-1} \\
\overset{x}{\longrightarrow} (C_6H_5)_2CCO (?) + C_6H_5OH^{**} (172) & \geq 199 \text{ kcal mol}^{-1}
\end{align*}
\]

From these energy considerations, \(\Delta H^\circ[C_6H_5CHCO] \geq 3 \text{ kcal mol}^{-1}\) and \(\Delta H^\circ[(C_6H_5)_2CCO] \geq 27 \text{ kcal mol}^{-1}\). These values are in good agreement with our proposed values and Deming and Wulff's\(^4\) estimated values of 6 and 25 kcal mol\(^{-1}\), respectively.

5.2.6 Vinyl substitution in ketene

Combining the \(\Delta H^\circ[CH_2=CHCH=C=O^{**}]\) and the IE[CH\(_2=CHCH=C=O\)], 194±1 kcal mol\(^{-1}\) and 8.32±0.05 eV\(^17\), respectively, gives a \(\Delta H^\circ[CH_2=CHCH=C=O] = 2±1 \text{ kcal mol}^{-1}\). In terms of vinyl substitution, the experimental \(\Delta \Delta H^\circ\) for ketene is +14±1 kcal mol\(^{-1}\). This change in \(\Delta H^\circ\) lies closer to the effect of vinyl substitution at olefin (\(\Delta \Delta H^\circ = 14±1 \text{ kcal mol}^{-1}\)) than at
carbonyl \( \Delta_{f}H^o = +10 \text{ kcal mol}^{-1} \). Thus this substituted ketene is not atypical in its \( \Delta_{f}H^o \) value, a result which lends further support for the experimentally derived values for the methyl substituted ketenes.

5.2.7 Proton affinities of CH₂CO and CH₃CHCO

Attempts to determine the proton affinity (PA) of ketene have yielded quite a long list of different values. Debrou et al.\(^\text{18} \) found the PA[CH₂CO] to be bracketed by the PA[(CH₃)₂O] and PA[(CH₃)₂CHOH], yielding a PA[CH₂CO] of ca. 190 kcal mol\(^{-1} \). Later, a series of proton transfer equilibria experiments gave, after adjusting to the most recent PA scale\(^\text{19} \) the following values: 192 kcal mol\(^{-1} \), 196 kcal mol\(^{-1} \)\(^\text{20} \), 197 kcal mol\(^{-1} \)\(^\text{21} \), and very recently, 196 kcal mol\(^{-1} \)\(^\text{7} \). Traeger calculated a value for PA[CH₂CO] = 197 kcal mol\(^{-1} \)\(^\text{23} \) based on his experimental \( \Delta_{f}H^o[CH₂CO^+] = 157 \text{ kcal mol}^{-1} \) and \( \Delta_{f}H^o[CH₂CO] = -11.4 \text{ kcal mol}^{-1} \)\(^\text{2} \) and \( \Delta_{f}H^o[H^+] = 366 \text{ kcal mol}^{-1} \)\(^\text{3} \). Finally, \textit{ab initio} molecular orbital calculations at the G2 level found a PA[CH₂CO] = 196 kcal mol\(^{-1} \)\(^\text{24} \). Combining the latter five values gives an average PA[CH₂CO] = 196±1 kcal mol\(^{-1} \) which is in keeping with the value calculated using our \( \Delta_{f}H^o[CH₂CO] \), the accepted \( \Delta_{f}H^o[CH₃CO^+] \) and \( \Delta_{f}H^o[H^+] \).

Only two PA values, both from proton transfer equilibria measurements, are reported in the literature for methyl ketene. Armitage et al.\(^\text{25} \) obtained a
PA[CH$_3$CHCO] = 196 kcal mol$^{-1}$, after adjusting to the latest PA scale$^{19}$, and very recently, Bouchoux et al.$^7$ obtained a PA[CH$_3$CHCO] = 201 kcal mol$^{-1}$. The Armitage et al.$^{25}$ value is unusual in that it implies that the PA of ketene is unaffected by methyl substitution, whereas in related systems, methyl substitution does affect the PA. The variation of PA with molecular size is given in Figure 5.5 for a variety of species. The extent to which the PA is affected by methyl substitution in related species is indicated by the different slopes. The effect is largest in ethene where substitution takes place directly on the charge site (broken lines) and is smallest where substitution is remote from the charge site, as in acetaldehyde (solid line). Using Bouchoux's PA for CH$_3$CHCO, the slope characteristic of the effect of methyl substitution in ketene is much less than for ethene, (but between that of formaldehyde and acetaldehyde). This suggests that methyl substitution in the ketenes takes place away from the formal charge (i.e., proton-receiving) site, an observation which is consistent with the protonated species being the propanoyl cation (which is the lowest of C$_3$H$_5$O$^+$ isomers). This plot allows the PA[(CH$_3$)$_2$CCO] to be estimated to 206 kcal mol$^{-1}$.

The uncertainty surrounding the PA[CH$_3$CHCO] translates into an uncertainty concerning the $\Delta$H°[CH$_3$CH$_2$CO$^+$]. Using Bouchoux's PA[CH$_3$CHCO]$^7$, our experimental $\Delta$H°[CH$_3$CHCO] and the $\Delta$H°[H$^+$] gives a $\Delta$H°[CH$_3$CH$_2$CO$^+$] = 143 kcal mol$^{-1}$. The experimental determination
Figure 5.5: Effect of methyl substitution on the PA.
(photoionization mass spectrometry) gave an average value, after correction for the thermal energy of the products, of 141 kcal mol$^{-1}$. These two values are in good agreement but in a recent study on the dissociation of propanal$^{26}$, (one of the precursor molecules used by Traeger$^{8}$ to determine the $\Delta H^0[\text{CH}_3\text{CH}_2\text{CO}^+]$) it is proposed that the dissociation by $\text{H}^+$ to $\text{CH}_3\text{CH}_2\text{CO}^+$ goes over a reverse activation energy barrier, so that the $\Delta H^0[\text{CH}_3\text{CH}_2\text{CO}^+]$ obtained should be considered as an upper limit. All photoionization efficiency (PIE) curves used to derive $\Delta H^0[\text{CH}_3\text{CH}_2\text{CO}^+]$ show unusual tailing near the thresholds and it is this portion of the curve that was used to determine the onset, as opposed to the linear portion of the curves. Consequently, the derived AE values are somewhat low (difference between the AE values determined from the linear portion and the bottom portion of the curves varies from 0.1 to 0.4 eV), but because a correction for the temperature of the products (+3.5 to +5.0 kcal mol$^{-1}$) is added to the derived $\Delta H^0[\text{CH}_3\text{CH}_2\text{CO}^+]$, this value is only slightly lower than the value calculated using Bouchoux’s PA$^7$ and other uncorrected published and unpublished values: 144 kcal mol$^{-1}$, 151 kcal mol$^{-1}$, 146 kcal mol$^{-1}$ and 145 kcal mol$^{-1}$. Apart from the 151 kcal mol$^{-1}$ value, these values are in agreement with the value proposed based on Bouchoux’s PA measurement. If the linear portion of the PI efficiency curves are used to derive the AE values, the mean corrected $\Delta H^0[\text{CH}_3\text{CH}_2\text{CO}^+]$ is 149 kcal mol$^{-1}$ whereas the uncorrected $\Delta H^0[\text{CH}_3\text{CH}_2\text{CO}^+]$ is 145 kcal mol$^{-1}$. The latter value is in good agreement with the other (uncorrected) values.
5.3 Conclusions

The $\Delta H^\circ$ of CH$_2$CO, CH$_3$CHCO and (CH$_3$)$_2$CCO have been determined to be -12, -22 and -32 kcal mol$^{-1}$, respectively. From these measurements, it has been demonstrated that methyl substitution in ketene decreases the $\Delta H^\circ$ of the methyl substituted species by ca. 10 kcal mol$^{-1}$, which is in keeping with the effect of methyl substitution in structurally related systems. In addition, the $\Delta H^\circ$ of CH$_3$CHCO$^{**}$ and (CH$_3$)$_2$CCO$^{**}$ have been determined to be 183 and 165 kcal mol$^{-1}$, respectively. These values are in excellent agreement with the values predicted when using the $\Delta H^\circ$ of the neutrals and their corresponding IE. In view of these observations, it is suggested that there exists a computational problem associated with the description of the methyl substituted ketenes which in turn leads to erroneous values of $\Delta H^\circ$.

The $\Delta H^\circ$ of C$_6$H$_5$CHCO$^{**}$ and (C$_6$H$_5$)$_2$CCO$^{**}$ were determined to be 188 and 212 kcal mol$^{-1}$, respectively, consistent with the behavior of phenyl substitution in structurally related systems. Using these values it was proposed that the $\Delta H^\circ$ of the neutral species, C$_6$H$_5$CHCO and (C$_6$H$_5$)$_2$CCO, be ca. 9 and 30 kcal mol$^{-1}$, respectively.

The PA of ketene has been revised and it is suggested that PA[CH$_2$CO] = 196±1 kcal mol$^{-1}$. This value is consistent with the determined $\Delta H^\circ[CH_2CO]$ indicating that the lower PA value is erroneous. In the case of methyl ketene, a PA of 201 kcal mol$^{-1}$ is consistent with the formation of the lowest energy C$_3$H$_5$O$^+$.
isomer. It is suggested that the photoionization data used to obtain the 
$\Delta v H^\circ[\text{CH}_3\text{CH}_2\text{CO}^+]$ be revised and we further suggest that a $\Delta v H^\circ[\text{CH}_3\text{CH}_2\text{CO}^+] = 145 \pm 2$ kcal mol$^{-1}$ be used. From the relationship of the PA with ion size, the 
PA[(CH$_3$)$_2$CCO] is estimated to be 206 kcal mol$^{-1}$. 

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5.4 References


(16) J.C. Traeger, private communication.


(30) J.L. Holmes and F.P. Lossing, unpublished data.
Chapter 6

The mass spectrometry of phenyl acetate, propanoate and isobutyrate

6.1 Introduction

Although considerable attention has been given to the dissociation of ionized carbonyl containing compounds in general\(^1\), very few data exist concerning the specific dissociation of phenyl esters. The mechanism by which ionized phenol is produced from phenyl esters is believed to involve the migration of the hydrogens \(\alpha\) to the carbonyl group\(^2\). This was concluded based on the study of the electron impact (EI) mass spectra of a series of phenyl esters including phenyl acetate (I), propanoate (II) and isobutyrate (III). It was shown that all esters possessing hydrogens \(\alpha\) to the carbonyl gave ionized phenol as base peak in their electron impact mass spectra, whereas for esters lacking these hydrogens, ionized phenol was only a minor feature of the EI mass spectra.

The study of the dissociation characteristics of esters I, II and III, presented in the following chapter, provides more detail as to how these phenyl esters generate ionized phenol and the corresponding ketene. As discussed in the previous chapter, both esters I and II generate at threshold ketene and
methyl ketene, respectively, whereas ester III yields ionized dimethyl ketene and only a small amount of ionized phenol. A rationalization based on the nature of the intermediate species involved in the dissociation will provide some insight on this marked change in behavior.

6.2 Results and discussion

6.2.1 Electron impact and metastable ion mass spectra of esters I, II and III

The three phenyl esters show in their 70 eV EI mass spectra a relatively intense molecular ion (I (m/z 136): 18%; II (m/z 150): 29% and III (m/z 164): 32% of the base peak, Figure 6-1). The base peak in the EI mass spectra of I, II and III corresponds to m/z 94, ionized phenol. Also relatively important are the peaks corresponding to the ions formed upon cleavage of the ester bond, namely C₂H₅O⁺ (m/z 43), C₄H₇O⁺ (m/z 57) and C₅H₅O⁺ (m/z 71), 18%, 35% and 44% of the base peak, respectively. The peaks corresponding to the ionized ketene is only important in ester III (C₄H₆O⁺, 31% of base peak). The other fragment ions are related to phenol and the phenyl moiety or the aliphatic side chain.
Figure 6.1: 70 eV EI mass spectra of a) phenyl acetate, b) phenyl propanoate and c) phenyl isobutyrate.
The ionization energy (IE) of ester I is reported in the Lias et al. compendium as 8.6 eV and the effect of methyl substitution on the IE in related systems (IE[CH₃COCH₃] = 9.705 eV; IE[CH₃CH₂COCH₃] = 9.51 eV; IE[(CH₃)₂CHCOCH₃] = 9.30 eV; IE[CH₃CO₂CH₃] = 10.27 eV; IE[CH₃CH₂CO₂CH₃] = 10.15 eV; IE[(CH₃)₂CHCO₂CH₃] = 9.86 eV, available from reference 3) decreases the IE by ~ 0.2 eV per methyl group in the acid moiety. If this analogy is correct, the estimated IE values for the phenyl esters will be IE[CH₃CH₂CO₂C₆H₅] ~ 8.4 eV and IE[(CH₃)₂CHCO₂C₆H₅] ~ 8.2 eV. However, the IE of phenyl acetate, 8.6 eV, indicates that ionization takes place at the aromatic ring rather than at carbonyl and so the more remote methyl substitution will exert less effect on the IE. The IE values for toluene, ethyl benzene, propyl benzene and isobutyl benzene, 8.82 eV, 8.77 eV, 8.72 eV and 8.68 eV, respectively, show an effect of only ca. 0.05 eV per methyl group. It is therefore proposed that IE[CH₃CH₂CO₂C₆H₅] ~ 8.55 eV and IE[(CH₃)₂CHCO₂C₆H₅] ~ 8.5 eV.

Metastable esters I and II yield only ionized phenol (Figure 5.1), whereas metastable ester III yields predominantly ionized dimethyl ketene and only a small amount of ionized phenol. All metastable peaks were Gaussian in shape and the kinetic energy releases (KER) measured from the half height width of these peaks were small, 7, 9, 10 and 18 meV, respectively.
6.2.2 Thermochemistry of the dissociation of the esters I, II and III

For all three esters, two possible dissociation routes leading respectively to ionized phenol or the corresponding ionized ketene, are possible:

\[
\begin{align*}
\text{CR}_2\text{HCO}_2\text{C}_6\text{H}_5 & \rightarrow \text{CR}_2=\text{C}=\text{O} + \text{C}_6\text{H}_5\text{OH}^+ \quad (1) \\
\text{CR}_2\text{HCO}_2\text{C}_6\text{H}_5 & \rightarrow \text{CR}_2=\text{C}=\text{O}^+ + \text{C}_6\text{H}_5\text{OH} \quad (2)
\end{align*}
\]

where R is CH₃ or H. Experimentally, these two processes are observed only in the case of ester III. The thermochemistry governing these reaction channels explains this observation. The appearance energy (AE) associated with the two possible reaction channels are described by the following equations:

\[
\begin{align*}
\text{AE}(1) &= \Delta H^\circ[\text{C}_6\text{H}_5\text{OH}^+] + \Delta H^\circ[\text{CR}_2=\text{C}=\text{O}] - \Delta H^\circ[\text{CR}_2\text{HCO}_2\text{C}_6\text{H}_5] \quad (6-1) \\
\text{AE}(2) &= \Delta H^\circ[\text{C}_6\text{H}_5\text{OH}] + \Delta H^\circ[\text{CR}_2=\text{C}=\text{O}^+] - \Delta H^\circ[\text{CR}_2\text{HCO}_2\text{C}_6\text{H}_5] \quad (6-2)
\end{align*}
\]

By subtracting (6-1) from (6-2), a difference in AE values, \(\Delta\text{AE}\), may be obtained:

\[
\text{AE}(2) - \text{AE}(1) = \Delta\text{AE} = \text{IE}[\text{CR}_2=\text{C}=\text{O}] - \text{IE}[\text{C}_6\text{H}_5\text{OH}] \quad (6-3)
\]

The magnitude of the \(\Delta\text{AE}\) is thus a measure of the energy difference between the two reaction processes and depends only on the difference between the IE of the two fragment species. A \(\Delta\text{AE} > 0\) indicates that reaction (1) is the energetically favored route, whereas a \(\Delta\text{AE} < 0\) indicates that reaction (2) is favored. The IE of phenol is 8.47eV and the IE values of ketene, methyl ketene
and dimethyl ketene are 9.64, 8.95 and 8.45 eV, respectively, so that it is possible to determine the $\Delta AE$ for all three esters. These values are 27, 11 and -0.5 kcal mol$^{-1}$ for ester I, II and III, respectively. The energetics governing metastable dissociation require that in order for reactions to compete on the metastable time frame (µs time scale) the energy difference between the processes, $\Delta AE$, should be $\leq 10$ kcal mol$^{-1}$. Thus, for esters I and II, the $\Delta AE$ is large enough to account for the observation that only ionized phenol is produced on the µs time scale. However in the case of ester III, the difference in energy between the reaction producing ionized phenol and that producing ionized dimethyl ketene predicts that the two dissociation channels should compete well on the µs time scale, and the reaction pathway leading to ionized dimethyl ketene should only be slightly favored over that yielding ionized phenol. Experimentally, the relative intensity of the peaks in the MI mass spectrum of ester III suggests that the channel leading to ionized dimethyl ketene is strongly favored.

The reaction channels are isoenergetic ($\Delta H^0[(CH_3)\_2CCO^+] = 165$ kcal mol$^{-1}$, $\Delta H^0[C_6H_5OH] = -23$ kcal mol$^{-1}$, $\Sigma \Delta H^0[\text{products}] = 142$ kcal mol$^{-1}$ and $\Delta H^0[(CH_3)\_2CCO] = -32$ kcal mol$^{-1}$, $\Delta H^0[C_6H_5OH^+] = 173$ kcal mol$^{-1}$, $\Sigma \Delta H^0[\text{products}] = 141$ kcal mol$^{-1}$) and the respective KER (10 and 18 meV) do not suggest the presence of any appreciable reverse energy barrier in either case, so that the difference between the two reaction channels is only in the nature of the ionized species (i.e., which of the fragments departs carrying the
charge). Because the IE of phenol and dimethyl ketene are essentially the same, as reflected in the ΔAE value, the IE cannot be the determining factors in governing the final position of the charge.

From the estimated IE[ester] it is clear that ionization takes place in the phenyl ring. In esters I and II only ionized phenol is produced, consistent with the difference in IE between the phenyl moiety and the ketene moiety. However in ester III, although ionization takes place in the phenyl moiety, only a small amount of ionized phenol is produced. This suggests that isomerization of the ionized ester to a species in which the charge is localized on the ketene moiety possibly takes place, and that further displacement of the charge is limited. This could be rationalized if the nature of the intermediate was such that displacement of the charge was restricted due to geometrical constraints. The nature of the intermediate species involved in the dissociation of the esters must thus be considered.

6.2.3 Collision induced dissociation mass spectra of esters I, II and III

When non-decomposing molecular ions I, II and III are induced to dissociate by collisional activation, the collision induced dissociation (CID) mass spectra (Figure 6-2) of esters I and II are dominated by ionized phenol (m/z 94), whereas the CID mass spectrum of ester III is dominated by ionized dimethyl ketene (m/z 70) although ionized phenol is also an important feature. In all three
CID mass spectra, additional fragmentation is of minor importance. For esters I and II, the dissociation route leading to ionized phenol is very mildly collision sensitive and the presence of a small amount of collision gas (He) does not affect the peak shape. For ester III, the dissociation channel leading to ionized dimethyl ketene is also only very mildly collision sensitive whereas the channel leading to ionized phenol is significantly more collision sensitive. Consistent with these observations, addition of small amounts of collision gas (He) do not affect the peak shape of the m/z 70 ion, but the width at half height of the m/z 94 peak doubles. This latter observation indicates that some of the internal energy gained from collisions is converted into translation kinetic energy when the molecular ions dissociates to m/z 94.

The CID mass spectra of esters I and II do not exhibit very intense peaks at m/z 43 and m/z 57, respectively, which would be expected from the ester bond cleavage in unrearranged molecular ions. This suggests that the majority of these undissociating molecular ions no longer have the ester configuration. For ester III, the CID mass spectrum does contain a relatively intense m/z 71 (~ 30% of the base peak) suggesting that a larger fraction of molecular ions have retained the ester configuration. For the three esters, the CID mass spectra are quite similar to their respective EI mass spectra, indicating that the ions produced in the source behave in a similar manner to the longer lived metastable molecular ions.
Figure 6.2: CID (He) mass spectra of a) phenyl acetate b) phenyl propanoate and c) phenyl isobutyrate.
The dissociation of esters I and II to ionized phenol and of ester III to ionized dimethyl ketene is essentially not affected by activation through collisions. This may be indicative of the involvement of non-covalently bonded species such as ion-neutral or hydrogen bridged complexes. Recent advances in gas phase ion chemistry have clearly indicated the importance of such intermediate species and the central role they can play in reaction mechanisms.

An ion-neutral complex consists of an incipient ion coordinated to a neutral. The two components of the complex are not connected by a covalent bond, but remain bound by ionic forces such as ion-dipole attraction. One component of the complex may formally react individually (i.e., a cation may isomerize); alternatively, the ionic and neutral species may react with each other (i.e., by hydrogen transfer). The hydrogen transfer between the partners can be envisaged to occur via a hydrogen bridged complex in which the two incipient neutrals are attached to a common proton. These proton bridged species are familiar species in bimolecular reactions, but \textit{ab initio} molecular orbital calculations and experiments\textsuperscript{7} suggest they are also involved in the unimolecular dissociation of gas phase ions. It is very difficult to unequivocally characterize these species experimentally, but some experimental observations do suggest their implication in dissociation processes. For example, complex mediated fragmentations of ionized acetone and isopropyl methyl ether have been shown to become insignificant under CID conditions\textsuperscript{8}. In addition, if such intermediates are involved, the KER of the complex mediated fragmentation is expected to be
relatively small, since upon separation of the two partners, the lack of a common
degree of freedom limits the conversion of internal energy into translational
kinetic energy. In the dissociations discussed above, esters I and II to m/z 94
and ester III to m/z 70, these two characteristics are met.

For ester I and II, the ion-neutral complex formed could result from a 1,3-
H shift of the hydrogen $\alpha$ to the carbonyl to the oxygen of the phenoxy group and
lengthening of the C-O bond according to:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \quad \text{R} \\
\text{O} & \quad \text{O} \\
\text{C}_6\text{H}_5^+ & \quad \rightarrow \quad \text{[C}_6\text{H}_5\text{OH}^+ \rightarrow \text{O} = \text{C} = \text{CHR}]}
\end{align*}
\]

where R is H and CH$_3$ for esters I and II, respectively.

In the case of ester III, to account for the difference in behaviour of the
two reaction channels under collision conditions, two species must be involved:
One to generate ionized dimethyl ketene and a second to generated ionized
phenol. The dissociation to m/z 70 is most likely complex mediated as
discussed previously, but as opposed to esters I and II, the charge would be
localized on the ketene moiety. The dissociation to m/z 94 most likely involves a
covalently bonded species consistent with this dissociation channel being
collision sensitive. In view of the particularities of ester III, further
characterization of this ion is needed.
6.2.4 Production of m/z 164 from dissociative ionization

In order to investigate further the structure of the ions formed following ionization of phenyl isobutyrate (m/z 164), a larger precursor molecule was used to generate m/z 164 ions by dissociative ionization, namely phenyl 2,2-dimethylbutyrate (ester IV). This compound can be expected to dissociate following ionization by a McLafferty rearrangement\(^\text{10}\), involving the loss of a \(\text{C}_2\text{H}_4\) unit via a six centered activated complex, to give the enol form of ester III:

![Chemical structure diagram]

\[
\text{CH}_2\text{CH}_2\text{C} = \text{CH}_3 + \text{C}_2\text{H}_4 \quad \text{m/z 164}
\]

The McLafferty rearrangement is known to generate enol ions\(^\text{11}\). As opposed to in the condensed phase, the enol form of ionized carbonyl compounds is usually thermodynamically more stable than the keto form by \(\sim 15\) kcal \text{mol}^{-1}\(^\text{11}\), and is a very common species in the gas phase\(^\text{12}\).

The MI mass spectrum of the source m/z 164 ions generated from ester IV contained both m/z 70 (KER = 12 meV) and m/z 94 (KER = 6 meV) (Figure 6.3a). Comparison of the CID mass spectra of source generated (Figure 6.3b) and metastably generated (Figure 6.3c) m/z 164 ions indicates that the species produced metastably is different from that produced in the ion source. The CID mass spectrum of source generated ions resembles the CID mass spectrum of
Figure 6.3: Characterization of m/z 164 ions generated from phenyl 2,2-dimethylbutyrate a) MI mass spectrum b) CID (He) mass spectrum of source generated ions and c) CID (He) mass spectrum of metastably generated ions.
ester III (Figure 6.2c) but with a more intense m/z 94. The CID of metastably
generated m/z 164 is wholly dominated by m/z 94 suggesting that source ions
are a mixture of ester III and another isomer which essentially only produces m/z
94. The KER for the production of m/z 70 from the m/z 164 ion generated by
dissociation of ester IV is almost identical to the KER associated to the
production of m/z 70 from ester III, and thus provides additional evidence that
the source ions are partly the same ions as those produced after the ionization
of ester III. It is thus proposed that upon ionization, phenyl isobutyrate ions
isomerize to the enol form. It is this species that forms the bulk of the m/z 164
ions (ester III) and thus from which ionized dimethyl ketene is formed.

The participation of the enol form of phenyl isobutyrate can explain the
CID characteristics of the molecular ions of ester III (i.e., different collision
behavior for the two reaction channels) but not the specificity of the reaction (i.e.,
especially only ionized dimethylketene is produced). If the intermediate
involved in the dissociation were covalently bonded, displacement of the charge
and radical site could take place without restriction and both ionized dimethyl
ketene and ionized phenol should be observed. However, if the dissociating
species, i.e., the species at the dissociation threshold, was no longer a bonded
entity, but rather an ion-neutral complex, the displacement of the charge and
radical sites between the partners of the ion-neutral complex would be restricted
due to geometrical constraints.
The species from which the rearrangement takes place is the enol form of ester III and so a 1,3-H shift of the hydrogen on the hydroxyl group to the oxygen of the phenoxy group and lengthening of the C-O bond would yield the following ion-neutral complex:

\[
\text{CH}_3\text{C}^-\text{CH}_3 \quad \xrightarrow{\text{[C}_6\text{H}_5\text{OH} - \text{O=C=C(CH}_3)_2^{++}]}
\]

\[
\text{C}_6\text{H}_5\text{O}^-\text{O=C=C(CH}_3)_2^{++}
\]

The intact form of ionized phenyl isobutyrate would be the species generating ionized phenol.

6.2.5 Neutralization-reionization mass spectra of esters I, II and III

The neutralization-reionization (NR) mass spectra of the three esters are shown in Figure 6.4. One common feature to all the species is the lack of recovery signal. This is the case when dimethylamine (DMA) is used, making the neutralization process slightly exothermic (\(\text{IE[DMA]} = 8.23 \text{ eV}\); \(\text{IE[CH}_3\text{CO}_2\text{C}_6\text{H}_5] = 8.6 \text{ eV}\); \(\text{IE[CH}_3\text{CH}_2\text{CO}_2\text{C}_6\text{H}_5] \sim 8.4 \text{ eV (estimate)}\); \(\text{IE[(CH}_3)_2\text{CHCO}_2\text{C}_6\text{H}_5] \sim 8.2 \text{ eV (estimate)}\)), but is also the case when xenon is used, making the neutralization very endothermic (\(\text{IE[Xe]} = 12.13 \text{ eV}\)). The lack
Figure 6.4: NR (Xe/O₂) mass spectra of a) phenyl acetate b) phenyl propanoate and c) phenyl isobutyrate.
of a recovery signal was unexpected since the phenyl esters all show in their EI mass spectra a relatively intense molecular ion, and other esters, such as methyl acetate, are known to exhibit recovery signals. The lack of recovery signal may be due to one of two possibilities: 1) the species formed upon neutralization is unstable on the time frame of our experiment (1 μs) and dissociates into neutral fragments which are subsequently ionized or 2) the species formed upon neutralization is stable but the reionized species does not have a stable molecular ion.

As could be expected from their MI and CID behaviour, both esters I and II exhibit very similar NR mass spectra characteristics which are distinct from those of ester III. The NR mass spectra of esters I and II are dominated by the presence of ionized ketene (m/z 42) and ionized methyl ketene (m/z 56), respectively, which is in keeping with these species being co-generated in the MI and CID processes. The lack of a recovery signal distinguishes the NR mass spectra from the EI mass spectra of these esters, indicating that the neutralized species must no longer have the ester configuration. The presence of ionized phenol clearly indicates that a neutral species was formed upon neutralization since for both ester I and II, all dissociation channels lead to the production of ionized phenol which are separated from the neutral beam by a deflector electrode. The width of the m/z 42, m/z 56 and m/z 94 peaks in the NR mass spectra of esters I and II respectively, suggests that these species are not the product of dissociation (there is no significant KER) but rather are from the
ionization of the neutral fragments. From this information the lack of a recovery signal in the NR mass spectra of esters I and II must be due to the formation of unstable neutrals which then dissociate into neutral phenol and neutral ketenes. This is consistent with the nature of the ion-neutral complexes suggested to be a main proportion of the ions formed upon ionization of ester I and II.

In the case of ester III, both ionized phenol (m/z 94) and ionized dimethylketene (m/z 70) are present as is expected from the MI and CID processes. The width of the m/z 70 and m/z 94 peaks again indicates that these ions are most likely not generated from dissociation, but rather from the ionization of neutral fragments. The lack of a recovery signal combined with this observation is also consistent with the involvement of an ion-neutral complex being neutralized and then dissociating.

6.3 Conclusions

Metastable phenyl acetate and propanoate ions dissociate to ionized phenol according to predictions based on thermochemical arguments. The CID characteristics suggested that the dissociation of these two ionized esters was complex mediated and the following ion-neutral complexes were proposed to be involved: \([\text{CH}_2\text{CO} \cdots \text{C}_6\text{H}_5\text{OH}^+]\) and \([\text{CH}_3\text{CHCO} \cdots \text{C}_6\text{H}_5\text{OH}^+]\).

Metastable phenyl isobutyrate ions, however, show two dissociation products, ionized dimethyl ketene and ionized phenol, as expected from the
thermochemistry, but the relative abundances of the product ions is in
disagreement with the predicted thermochemistry. Based on the CID
characteristics, the two product ions were proposed to originate from two distinct
species. The unrearranged ionized ester dissociated to ionized phenol whereas
a rearranged species generated the ionized dimethyl ketene. Dissociative
ionization was used to generate the enol form of ionized phenyl isobutyrate
which showed very similar MI and CID characteristics to the ionized ester III.
Hence, the bulk of the ions produced from the ionization of phenyl isobutyrate
were proposed to be the enol ion. In order to rationalize the specificity of the
reaction an ion-neutral complex, namely [(CH₃)₂CCO⁺—CC₆H₅OH], was proposed
to be involved in the dissociation to ionized dimethyl ketene. The NR data
provided support for the involvement of non-covalently bonded species.

Further studies are needed to verify the participation of the ion-neutral
complexes proposed in the dissociation of the phenyl esters. More precisely, a
detailed study of the species generated by dissociative ionization would provide
detailed information on other possible isomers of the ester and possibly on the
ion-neutral complex itself. In addition, a study of labeled species would allow
one to determine the origin of the hydrogen transferred in the case of metastable
dissociations which in turn could provide information on the nature of the
intermediate.
6.4 References


(5) C. Aubry, J.L. Holmes and J.K. Terlouw, Accepted for publication in *J. Phys. Chem.*


(9) Ester IV, prepared by reacting 2,2-dimethyl butanoic acid with SOCl₂ to form the acid chloride which was further reacted with phenol to give the ester.


Chapter 7
The 1-adamantyl and 2-adamantyl cations
in the gas phase

7.1 Introduction

The 1- and 2-adamantyl cations (1Ad$^+$ and 2Ad$^+$, respectively) are two isomeric C$_{10}$H$_{15}$$^+$ species generated from the dissociative ionization of the corresponding substituted tricyclic hydrocarbon, following the loss of an appropriate side chain.

![Diagram of 1Ad$^+$ and 2Ad$^+$]

The feature that distinguishes these C$_{10}$H$_{15}$$^+$ ions from other C$_{10}$H$_{15}$$^+$ ions is their tricyclic structure. The electron impact (EI) mass spectra of the 1- or 2-substituted hydrocarbons is usually dominated by a peak at m/z 135 corresponding to C$_{10}$H$_{15}$$^+$ ions, indicating that the side chain loss is an important dissociation route for the precursor molecules.

The 1Ad$^+$ is of particular interest because the charge is thought to be formally located at the bridgehead position. However, knowing that the tert-butyl
cation is essentially a planar species\(^1\), it may be expected that upon formation
the 1Ad\(^+\), also a tertiary carbocation, assumes a flat structure and the tricyclic
ion may open to relieve ring strain energy. It was suggested, in the first mass
spectrometric investigation on the 1Ad\(^+\), that the ion formed by dissociative
ionization may rearrange according to\(^2\):

\[
\begin{align*}
\text{[structure]} & \rightarrow \text{[structure]} & \rightarrow \text{[structure]}
\end{align*}
\]

In solution, the 1Ad\(^+\) ion can readily be prepared by treating adamantane
with super acids. The ions produced in such acidic media are well characterized
by \(^1\text{H}\) and \(^{13}\text{C}\) nuclear magnetic resonance spectroscopies and it is believed that
the ions retain their tricyclic structure\(^3\).

The isomerization of 1Ad\(^+\) to the 2Ad\(^+\) ion or vice-versa, by a 1,2 hydride
shift, is strongly inhibited in the ionic species since the vacant orbital at the
carbon center and the orbital of the migrating group are rigidly held in a
conformation unfavorable for the H\(^-\) migration\(^4\). The observed isomerization in
super acidic media has been shown to originate from bimolecular reactions\(^5\).

In the gas phase, the species formed by loss of Br\(^+\) from 2-
bromoadamantane showed slightly different collision induced dissociation (CID)
characteristics from those of the ions generated from 1-bromoadamantane (loss
of Br\(^+\)) and adamantane (loss of H\(^+\))\(^6\), and it was thus concluded that 2Ad\(^+\) was
distinct from 1Ad\(^+\) and that both ions retained their tricyclic structures.

The thermochemical and mass spectrometric investigation that is
presented in the following chapter is thus concerned with the structures of the
1Ad\(^+\) and 2Ad\(^+\) ions, as well as how these ions relate to each other. In the
process of this investigation, it was found that some of the precursor molecules
used to generate the C\(_{10}\)H\(_{15}\)\(^+\) ions exhibited interesting dissociation
characteristics. These will also be discussed.

7.2 Results and discussion

7.2.1 Thermochemistry of the 1Ad\(^+\) and 2Ad\(^+\) ions

Several attempts to determine the heat of formation (\(\Delta_f H^0\)) of 1Ad\(^+\) have
been made in the past and calculations have provided some information
concerning the energy difference between the \(\Delta_f H^0[1Ad^+]\) and \(\Delta_f H^0[2Ad^+]\). This
information is listed in Table 7.1. Beauchamp et al.\(^8\) and Kebabie et al.\(^11\)
obtained their \(\Delta_f H^0[1Ad^+]\) from the study of bromide and chloride and hydride
transfer reactions, respectively. The values given in Table 7-1 are adjusted to
the presently accepted value for \(\Delta_f H^0[t-Butyl^+] = 170\ \text{kcal mol}^{-1}\). Ridge et al.\(^10\)
obtained their value by studying the reaction of Li\(^+\) with 1-C\(_{10}\)H\(_{15}\)Cl and 1-
C\(_{10}\)H\(_{15}\)Br. In a second study concerning the adamantyl species, Beauchamp et
al.\(^12\) measured the photoelectron spectra of the species generated pyrolytically
from 1- and 2-adamantyl methyl nitrite (by loss of NO and CH₂O), and determined the IEₐ of the 1Ad⁺ and 2Ad⁺ radicals.

Table 7.1: Available thermochemical data related to the 1Ad⁺ and 2Ad⁺ cations and their corresponding radicals (All values in kcal mol⁻¹).

<table>
<thead>
<tr>
<th>Source</th>
<th>ΔH°</th>
<th>ΔΔH°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1Ad⁺</td>
<td>2Ad⁺</td>
</tr>
<tr>
<td>Beauchamp (1977)⁸</td>
<td>159</td>
<td></td>
</tr>
<tr>
<td>Houriet (1979)⁹</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Ridge (1979)¹⁰</td>
<td>161</td>
<td></td>
</tr>
<tr>
<td>Kebarle (1985)¹¹</td>
<td>164</td>
<td></td>
</tr>
<tr>
<td>Beauchamp (1986)¹²</td>
<td>15⁸</td>
<td>12⁸</td>
</tr>
<tr>
<td>Rauk (1989, 91)¹³,¹⁴</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

⁸estimated; ⁹calculated using estimated ΔH°[R⁺] and measured IEₐ[1Ad⁺] = 6.21 eV¹² and IEₐ[2Ad⁺] = 6.73 eV¹².

By estimating the ΔH° of the radicals and combining these values with the appropriate IEₐ, they calculated ΔH° values for the ions. It is noteworthy that the estimated ΔH°[1Ad⁺] is lower than the estimated ΔH°[2Ad⁺], because using the established secondary and tertiary C-H bond strengths in hydrocarbons, the
reverse order of stability would be predicted. In both of their studies, Rauk et
al.\textsuperscript{13,14} used \textit{ab initio} molecular orbital theory calculations, at the MP2/6-31G//6-
31G level, to predict the \textit{1Ad}\textsuperscript{+} to be 15 kcal mol\textsuperscript{-1} more stable than the \textit{2Ad}\textsuperscript{+}.

In view of the lack an experimental $\Delta H^0[2\text{Ad}^+]$ and the disagreement
between the values for $\Delta H^0[1\text{Ad}^+]$ presented in Table 7.1, an experimental
determination of these quantities was performed using metastable peak
appearance energy (AE) measurements.

7.2.1.1 \textit{Measured thermochemistry}

A series of \textit{1-C\textsubscript{10}H\textsubscript{15}X} and the \textit{2-C\textsubscript{10}H\textsubscript{15}Br} were used as precursor
molecules to generate \textit{1Ad}\textsuperscript{+} and \textit{2Ad}\textsuperscript{+}, respectively, by the following reactions:

\[
\begin{align*}
1-\text{C}_{10}\text{H}_{15}\text{Cl} & \rightarrow 1-\text{C}_{10}\text{H}_{15}^+ + \text{Cl}^+ \\
1-\text{C}_{10}\text{H}_{15}\text{CH}_2\text{OH} & \rightarrow 1-\text{C}_{10}\text{H}_{15}^+ + ^*\text{CH}_2\text{OH} \\
1-\text{C}_{10}\text{H}_{15}\text{COCH}_3 & \rightarrow 1-\text{C}_{10}\text{H}_{15}^+ + ^*\text{COCH}_3 \\
1-\text{C}_{10}\text{H}_{15}\text{CH}_2\text{NH}_2 & \rightarrow 1-\text{C}_{10}\text{H}_{15}^+ + ^*\text{CH}_2\text{NH}_2 \\
2-\text{C}_{10}\text{H}_{15}\text{Br} & \rightarrow 2-\text{C}_{10}\text{H}_{15}^+ + \text{Br}^+
\end{align*}
\]
In addition, $1\text{-C}_{10}\text{H}_{15}\text{CH}_{2}\text{NH}_{2}$ was used to generate the $1\text{Ad}^+$ according to:

$$1\text{-C}_{10}\text{H}_{15}\text{CH}_{2}\text{NH}_{2} \rightarrow 1\text{-C}_{10}\text{H}_{15}^+ + \text{^CH}_{2}\text{NH}_{2}$$

In all cases, the $1\text{Ad}^+$, $2\text{Ad}^+$ and $1\text{Ad}^+$ were produced from metastable molecular ions and the accompanying kinetic energy release (KER) was small enough to neglect any kinetic shift effects. Table 7.2 shows the results of the AE measurements as well as the ancillary thermochemical data used to determine the $\Delta_h H^0$ of interest.

A comparison between the previously reported values and our experimental values is given in Table 7.3.
Table 7.2: Experimental determination of the $\Delta H^\circ$ of 1Ad$^+$, 2Ad$^+$ and 1Ad$^*$ (AE in eV, KER in meV and $\Delta H^\circ$ in kcal mol$^{-1}$).

<table>
<thead>
<tr>
<th>Precursor</th>
<th>AE</th>
<th>KER</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta H^\circ[1\text{Ad}^+]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pm0.1$</td>
<td>[molecule]$^a$</td>
<td>[neutral]$^a$</td>
<td>$\pm2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-C$<em>{10}$H$</em>{15}$Cl</td>
<td>9.7</td>
<td>4</td>
<td>-43</td>
<td>29</td>
<td>152</td>
</tr>
<tr>
<td>1-C$<em>{10}$H$</em>{15}$CH$_2$OH</td>
<td>9.6</td>
<td>6</td>
<td>-75$^b$</td>
<td>-4$^c$</td>
<td>151</td>
</tr>
<tr>
<td>1-C$<em>{10}$H$</em>{15}$COCH$_3$</td>
<td>9.4(9.51)$^d$</td>
<td>9</td>
<td>-70$^b$</td>
<td>-6</td>
<td>152</td>
</tr>
<tr>
<td>1-C$<em>{10}$H$</em>{15}$CH$_2$NH$_2$</td>
<td>9.7(9.60)$^d$</td>
<td>17</td>
<td>-31$^b$</td>
<td>38</td>
<td>155</td>
</tr>
</tbody>
</table>

$\Delta H^\circ[2\text{Ad}^+]$

| 2-C$_{10}$H$_{15}$Br | 9.9 | 1   | -30              | 26.7             | 170                           |

$\Delta H^\circ[\text{ion}]^a$  $\Delta H^\circ[1\text{Ad}^+]$

| $\pm2$          |                                |
| 1-C$_{10}$H$_{15}$CH$_2$NH$_2$ | 9.6(9.6)$^d$ | 17  | -31$^b$          | 178               | 11                            |

$^a$reference 15;  $^b$additivity, reference 16;  $^c$reference 17;  $^d$photoionization, reference 18.
Table 7.3: Comparison between reported $\Delta H^\circ$ and $\Delta H^\circ$ from this work (All values in kcal mol$^{-1}$).

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\circ$</th>
<th>$\Delta \Delta H^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1Ad$^+$</td>
<td>2Ad$^+$</td>
</tr>
<tr>
<td>Selected data</td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td>Our work</td>
<td>11±2</td>
<td>15*</td>
</tr>
</tbody>
</table>

*calculated using $\Delta H^\circ[2Ad^+] = 170$ kcal mol$^{-1}$ and IE$_d[2Ad^+] = 6.73$ eV$^{12}$

Our value for $\Delta H^\circ[1Ad^+]$ is somewhat lower than the previously reported $\Delta H^\circ$ obtained from reaction equilibria measurements, but the AE values, when comparison is possible, are in excellent agreement with photoionization measurements$^{18}$. The $\Delta H^\circ[2Ad^+]$ is slightly higher than the value predicted by Beauchamp et al.$^{11}$ Consequently, the experimentally determined $\Delta \Delta H^\circ$ is also larger than the value predicted by them and also higher than the calculated value$^{13,14}$. The $\Delta H^\circ[1Ad^+]$ obtained experimentally is in excellent agreement with the value predicted when combining $\Delta H^\circ[1Ad^+] = 153$ kcal mol$^{-1}$ and the IE$_d[1Ad^+] = 6.21$ eV$^{12}$, which gives $\Delta H^\circ[1Ad^+] = 10$ kcal mol$^{-1}$, thus indicating the consistency of our results. Furthermore, combining the $\Delta H^\circ[2Ad^+] = 170$ kcal mol$^{-1}$ and IE$_d[2Ad^+] = 6.73$ eV$^{12}$ gives $\Delta H^\circ[2Ad^+] = 15$ kcal mol$^{-1}$, making the
relative stability of the 1Ad\textsuperscript{+} and 2Ad\textsuperscript{+} radicals consistent with the usual order of tertiary and secondary C-H bond strengths.

The information obtained from these thermochemical measurements provides only the $\Delta H^0$ values for the ions and neutrals and provides no information concerning the actual structure of the species produced by dissociative ionization of the larger precursor molecules.

However, it has been shown\textsuperscript{19} that a linear relationship between the heterolytic bond strength ($D[R^+\cdot H]$) and the size of the ion formed, exists for hydrocarbons, and this relationship depends on the type of carbocation formed \textit{i.e.}, secondary vs. tertiary. Figure 7.1 shows a plot of the variation of the heterolytic bond strength as a function of size for secondary and tertiary carbocations. The values for 1Ad\textsuperscript{+} and 2Ad\textsuperscript{+} are included in the plot for comparison. Based on this simple empirical argument, it appears that the ions formed at threshold from the dissociative ionization of 1-C\textsubscript{10}H\textsubscript{15}X and 2-C\textsubscript{10}H\textsubscript{15}Br precursor molecules are indeed tertiary and secondary carbocations, respectively. It is noteworthy that other tertiary C\textsubscript{10}H\textsubscript{15}\textsuperscript{+} ions generated by loss of H\textsuperscript{+} from hydrocarbons other than adamantane have estimated $\Delta H^0$ values (estimated using the $D[R^+\cdot H]$ for adamantane, $\Delta H^0[H] = 35 \text{ kcal mol}^{-1}$\textsuperscript{15} and the $\Delta H^0[\text{molecule}]$ from additivity\textsuperscript{16}) which are considerably more positive than the C\textsubscript{10}H\textsubscript{15}\textsuperscript{+} ions generated from adamantane and 1-C\textsubscript{10}H\textsubscript{15}X species.
Figure 7.1: Effect of size on the heterolytic bond strength in secondary and tertiary carbocations.
For example, heterolysis of the tertiary C-H bond in the $C_{10}H_{16}$ isomer shown below ($\Delta H^\circ = 1$ kcal mol$^{-1}$, by additivity$^{11}$) produces a resonance stabilized ion with $\Delta H^\circ[C_{10}H_{15}^+] = 184$ kcal mol$^{-1}$, well above that for $1Ad^*$.  

7.2.2 Mass spectrometric investigation of $1Ad^*$ and $2Ad^*$ ions

The thermochemical data discussed in the previous section provides information concerning the relative energies of the $1Ad^*$ and $2Ad^*$ cations and furthermore indicates that the ions are distinct and retain their tricyclic structure. However, no information concerning the possible interconversion of the two ions (and hence the isomerization barrier) was obtained.

A large number of mass spectrometric investigations on substituted adamantane deal with the effect of the nature and the position of the substituent on the dissociation characteristics of the molecular ions$^{20}$ and do not address in any detail the characteristics of the $C_{10}H_{15}^*$ ions generated. The following sections describe the dissociation characteristics of the $1Ad^*$ and $2Ad^*$ cations and addresses their possible interconversion.

7.2.2.1 Metastable ion (MI) mass spectra

For all the precursor molecules used to generate either $1Ad^*$ or $2Ad^*$, the EI mass spectra were dominated by the peak at m/z 135, corresponding to the
$C_{10}H_{15}^+$ species. Metastable m/z 135 ions produced from all 1-$C_{10}H_{15}X$ precursor molecules studied exhibited four major dissociations corresponding to the losses of $C_2H_4$ (m/z 107), $C_3H_6$ (m/z 93), $C_4H_8$ (m/z 79), and $C_5H_8$ (m/z 67). Reducing the energy of the ionizing electrons shows that the dissociation by loss of $C_3H_6$ is the process of lowest energy requirement. The relative abundance of the peaks as well as the KER are given in Table 7.4, and Figure 7.2 shows the MI mass spectra of the 1Ad$^+$ and 2Ad$^+$ ions.

<table>
<thead>
<tr>
<th>Precursor molecule</th>
<th>m/z 67</th>
<th>m/z 69</th>
<th>m/z 79</th>
<th>m/z 81</th>
<th>m/z 93</th>
<th>m/z 107</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-$C_{10}H_{15}CH_2OH$</td>
<td>21(17)</td>
<td>4(22)</td>
<td>58(19)</td>
<td>16(21)</td>
<td>100(55)</td>
<td>47(320)</td>
</tr>
<tr>
<td>1-$C_{10}H_{15}COCH_3$</td>
<td>20(18)</td>
<td>3(18)</td>
<td>58(20)</td>
<td>16(22)</td>
<td>100(57)</td>
<td>25(309)</td>
</tr>
<tr>
<td>1-$C_{10}H_{15}CH_2NH_2$</td>
<td>17(19)</td>
<td>3(23)</td>
<td>52(23)</td>
<td>13(26)</td>
<td>100(73)</td>
<td>35(278)</td>
</tr>
<tr>
<td>1-$C_{10}H_{15}Br$</td>
<td>12(15)</td>
<td>2(15)</td>
<td>44(20)</td>
<td>12(22)</td>
<td>100(58)</td>
<td>73(285)</td>
</tr>
<tr>
<td>1-$C_{10}H_{15}Cl$</td>
<td>20(20)</td>
<td>3(18)</td>
<td>59(23)</td>
<td>15(23)</td>
<td>100(58)</td>
<td>46(331)</td>
</tr>
<tr>
<td>1-$C_{10}H_{15}I$</td>
<td>20(17)</td>
<td>3(20)</td>
<td>56(19)</td>
<td>15(24)</td>
<td>100(67)</td>
<td>41(285)</td>
</tr>
<tr>
<td>2-$C_{10}H_{15}Br$</td>
<td>78(14)</td>
<td>2(21)</td>
<td>58(18)</td>
<td>15(21)</td>
<td>100(50)</td>
<td>49(270)</td>
</tr>
</tbody>
</table>
Figure 7.2: MI mass spectra of a) $1\text{Ad}^+$ generated from $1\text{-C}_{10}\text{H}_{15}\text{CH}_2\text{NH}_2^{**}$
b) $2\text{Ad}^+$ generated from $2\text{-C}_{10}\text{H}_{15}\text{Br}^{**}$.
For both types of C_{10}H_{15}^+ ions, all the fragment ion peaks are Gaussian, except the peak corresponding to the loss of C_2H_4 (m/z 107). This peak is composite, a narrow component atop a broad component. The narrow component is only a minor feature of the peak and the relative abundance of both components varies with the precursor molecule used to generate the m/z 135 ions, explaining the wider range in KER values. From the data in Table 7.4, it is clear that all m/z 135 ions generated from the dissociative ionization of the 1-C_{10}H_{15}X precursor molecules are indistinguishable on the basis of KER values and relative intensities. However, the MI mass spectrum of the m/z 135 ion produced from the 2-C_{10}H_{15}Br^+ has one distinct feature relative to the MI mass spectrum of the 1Ad^+: the relative abundance of the m/z 67 fragment peak.

Introduction of a small amount of collision gas does not affect the process leading to m/z 107, whereas the other processes are all mildly collision sensitive. The fragment ions produced from metastable 1Ad^+ and 2Ad^+ were characterized by transmitting them into the third field free region of the instrument where they were activated by collisions with helium. The CID mass spectra of the ions m/z 107, 93, 79 and 67 exhibited identical dissociation characteristics suggesting that the ions formed by the dissociations of metastable 1Ad^+ and 2Ad^+ are the same. This suggests that rearrangement to common dissociating configurations can take place in both 1Ad^+ and 2Ad^+ at some energy between the bottom of the 2Ad^+ well and the dissociation limit for C_3H_6 loss (see Figure 7.4).
7.2.2.2 Collision induced dissociation (CID) mass spectra

As discussed in section 3.3.1.1, CID mass spectra are a convolution of metastable and collision induced processes. In order to eliminate the MI contribution, the CID mass spectra of metastably generated m/z 135 ions were obtained. The ions sampled are therefore m/z 135 ions with little excess internal energy. Figure 7.3 shows the CID of metastably generated m/z 135 from 1-C\textsubscript{10}H\textsubscript{15}CH\textsubscript{2}NH\textsubscript{2}\textsuperscript{+} and 2-C\textsubscript{10}H\textsubscript{15}Br\textsuperscript{+}. Although not shown in the figure, the CID mass spectra of m/z 135 ions metastably generated from the other precursor molecules are the same as the CID spectrum from 1-C\textsubscript{10}H\textsubscript{15}CH\textsubscript{2}NH\textsubscript{2}\textsuperscript{+}.

As in the MI mass spectra, the distinction between the CID mass spectra of the metastably generated 1Ad\textsuperscript{+} and 2Ad\textsuperscript{+} ions lies only in differences of relative intensities. The most obvious differences are the intensities of the m/z 93 and m/z 67 ions relative to m/z 79 ions. The ratios m/z 93:79 and m/z 67:79 are 0.72 and 0.29 for the 1Ad\textsuperscript{+} and 1.26 and 0.87 for the 2Ad\textsuperscript{+}. The origin of these intensity differences may be rationalized only in the in the 2Ad\textsuperscript{+} species. The flanking bridgeheads to the 2-position allow the potential formation of 5 and 6 membered rings; this is illustrated below. Note that this ion can formally be represented by four equivalent forms.
Figure 7.3: ClID(He) of metastably generated a) 1Ad* from 1-C_{10}H_{15}CH_{2}NH_{2}^{+*} and b) 2Ad* generated from 2-C_{10}H_{15}Br^{+*}. 
This alternative secondary carbocation formally contains an intact C₅H₇ unit and thus may account for the greater ease with which the 2Ad⁺ generates m/z 67 fragment ions. In addition, from the partially opened form, it is also easier to expel a C₃H₆ unit to produce the m/z 93 fragment ions. For the 1Ad⁺, no such simple effect yields another tertiary cation. The tertiary cation thus formally contains only intact C₅H₆ units.

This simple view is supported by the calculations by Rauk et al. ¹³,¹⁴. The ground state structure for 2Ad⁺ was found to be significantly distorted from the symmetrical 2Ad⁺ form ¹³. The Cα-C⁺-Cα bridge is bent towards one face of the cation, the C⁺-H bond becomes more pyramidal and the Cα-Cβ bonds become very unequal. These effects were rationalized in terms of enhanced C-C hyperconjugation rather than the formation of a non-classical "bridged" cation. (2Ad⁺)⁺ is therefore a discrete species and was also investigated by the same authors ¹⁴. Two minima were found on the potential energy surface, one of which is ca. 2 kcal mol⁻¹ above 2Ad⁺, with only a small energy barrier between them.

The CID mass spectra of metastably generated ions are characteristic of low internal energy C₁₀H₁₅⁺ ions i.e., the ions sampled are those near the bottom of the potential energy well. The CID mass spectra of the metastably generated 1Ad⁺ and 2Ad⁺ ions are distinct and thus indicate that these two ions occupy independent potential energy wells, separated by a barrier to interconversion high enough to prevent the ions from interconverting at low internal energies.
However, that these $C_{10}H_{15}^+$ ions show so many similar dissociation characteristics confirms that they are capable of interconverting at energies below the lowest dissociation limit, $C_3H_6$ loss (see above). The depths of the potential energy well of the 1Ad$^+$ and 2Ad$^+$, which are approximately the difference between the sum of the products $\Delta rH^0$ for the lowest energy dissociation channel and the $\Delta rH^0$ of the ions, are of the order of 1 and 2 eV, respectively, so that near the dissociation threshold the density of states is large. At these energies, both the 1Ad$^+$ and 2Ad$^+$ may interconvert and access a large number of different structures. In keeping with this is the total lack of sensitivity to collision gas of the m/z 107 peak in the MI mass spectra of both isomers, which shows that the reacting configuration for the $C_2H_4$ loss in only (just) accessed by $C_{10}H_{15}^+$ ions very close to the dissociation limit. The weak sensitivity of the other MI peaks shows that the reacting configurations for these dissociations are also only reached at high internal energies.

Figure 7.4 shows a potential energy diagram describing the relationship between the two ions. It not possible experimentally to determine the height of the barrier to interconversion, but it is clear from these experiments that it is high enough to prevent isomerization at low internal energies. For comparison, the barrier to the isomerization of sec-butyl and tert-butyl ions (from tertiary to the secondary cation), which behave similarly to 1Ad$^+$ and 2Ad$^+$, has been calculated to be 19.6 kcal mol$^{-1}$. The corresponding relative energies are t-
Figure 7.4: Potential energy surface for the $1\text{Ad}^+$ and $2\text{Ad}^+$ isomers.
\[ C_4H_9^+ = 0 \text{ kcal mol}^{-1} ; \ s-C_4H_9^+ = 13 \text{ kcal mol}^{-1} \]

and the dissociation limit (to 
\[ C_3H_6^+ \text{ and CH}_4 \] = 43 kcal mol\(^{-1}\)\(^{15}\), which are remarkably similar to the adamantyl system.

7.2.2.3 Deuterium labeling in 1Ad\(^+\)

1-Bromoadamantane containing one deuterium atom at a tertiary position was synthesized according to a published procedure\(^{21}\). Dissociative ionization of 1-C\(_{10}\)H\(_{14}\)DBr\(^+\) generates 1-C\(_{10}\)H\(_{14}\)D\(^+\) ions (m/z 136). The MI mass spectrum of this ion shows extensive H/D mixing for all dissociation channels (Figure 7.5). From the relative abundance of each of the peaks, it is possible to calculate experimental ratios describing the loss or retention of the deuterium atom. It is also possible to calculate the expected statistical distribution of the hydrogen and deuterium atoms for each of the dissociations, provided that the number of hydrogen and deuterium atoms involved in the mixing is known. Table 7.5 lists the calculated and experimentally determined ratios for the four most intense metastable processes, assuming that all the hydrogen (14H) and the deuterium (1D) atoms participate in the mixing.
Figure 7.5: MI mass spectrum of 1-C_{10}H_{14}D^{++}.
Table 7.5: Statistical and experimental H/D mixing ratios.

<table>
<thead>
<tr>
<th>Fragmentation</th>
<th>Statistical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>(14H, 1D)</td>
<td>2.75 : 1</td>
<td>2.5 : 1*</td>
</tr>
<tr>
<td>loss of C$_2$H$_4$/C$_2$H$_3$D</td>
<td>1.5 : 1</td>
<td>1.4 : 1</td>
</tr>
<tr>
<td>loss of C$_3$H$_6$/C$_3$H$_5$D</td>
<td>1 : 1.1</td>
<td>1.05 : 1</td>
</tr>
<tr>
<td>loss of C$_4$H$_8$/C$_4$H$_7$D</td>
<td>1 : 1.1</td>
<td>1.05 : 1</td>
</tr>
</tbody>
</table>

*because of the large KER associated with the loss of C$_2$H$_4$, the peaks are not well resolved and consequently, only an approximate ratio is obtained.

When all the hydrogen and the deuterium atoms are involved in the mixing, the experimental and statistical distributions are almost identical. This indicates that the H/D mixing is essentially complete before the m/z 136 ions dissociate by any of the dissociation channels. This observation is consistent with the conclusion that the 1Ad$^+$ ions have access to a wide range of structures, due to the large density of states near the dissociation limit, to allow extensive H/D mixing to occur. The behavior of these ions is similar to that of the 2-norbornyl cation which also displays complete positional loss of identity for H and C atoms prior to C$_2$H$_4$ loss$^{22}$.  

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7.2.3 Dissociation of 1-C_{10}H_{15}CH_{2}NH_{2}^{+} and 1-C_{10}H_{15}CH_{2}OH^{+}

7.2.3.1 Mass spectrometric investigation

1-C_{10}H_{15}CH_{2}NH_{2} and 1-C_{10}H_{15}CH_{2}OH exhibit relatively intense molecular ions in their EI mass spectra (~40% and 10% of the base peak m/z 135, respectively). In addition to generating 1Ad^{+} by loss of CH_{2}NH_{2}, metastable 1-C_{10}H_{15}CH_{2}NH_{2}^{+} ions dissociate by loss of C_{10}H_{15}^{+}, NH_{3}, CH_{3}^{+} and H^{+}, the latter two processes involve considerable reverse activation energy barriers. Metastable 1-C_{10}H_{15}CH_{2}OH^{+} ions behave similarly in that they produce 1Ad^{+} by loss of CH_{2}OH and also dissociate by loss of H_{2}O. The MI mass spectra of 1-C_{10}H_{15}CH_{2}NH_{2}^{+} and 1-C_{10}H_{15}CH_{2}OH^{+} ions are shown in Figure 7.6. The KER accompanying the dissociations are indicated on the spectra.

When non-decomposing 1-C_{10}H_{15}CH_{2}NH_{2}^{+} and 1-C_{10}H_{15}CH_{2}OH^{+} ions are collisionally activated, the resulting spectra are dominated by the MI processes, but show further fragmentation (Figure 7.7). For 1-C_{10}H_{15}CH_{2}NH_{2}^{+} ions the channels leading to the production m/z 164, m/z 150 and m/z 148 do not respond to collisional activation whereas the channels leading to m/z 135 and m/z 30 are slightly sensitive to collision. For 1-C_{10}H_{15}CH_{2}OH^{+} ions, parallel observations are made for the dissociations to m/z 135 and m/z 148.
Figure 7.6: MI mass spectra of a) $\text{C}_{10}\text{H}_{15}\text{CH}_{2}\text{NH}_2^{+*}$ and b) $\text{C}_{10}\text{H}_{15}\text{CH}_{2}\text{OH}^{+*}$.
Figure 7.7: CID(He) mass spectra of a) 1-C_{10}H_{15}CH_{2}NH_{2}^{+} and b) 1-C_{10}H_{15}CH_{2}OH^{+}.
The C_{11}H_{16}^{2+} ions (m/z 148) produced by loss of NH_{3} and H_{2}O from 1-C_{10}H_{15}CH_{2}NH_{2}^{+} and 1-C_{10}H_{15}CH_{2}OH^{+} ions, respectively, exhibit indistinguishable CID characteristics (Figure 7.8) and metastable AE measurements (AE[m/z148] = 9.5±0.1 eV, using ΔH°[1-C_{10}H_{15}CH_{2}NH_{2}] = -31 kcal mol^{-1} \text{ and } ΔH°[NH_{3}] = -11 \text{ kcal mol}^{-1} \text{;} AE[m/z 148] = 9.4±0.1 eV, using ΔH°[1-C_{10}H_{15}CH_{2}OH] = -75 \text{ kcal mol}^{-1} \text{ and } ΔH°[H_{2}O] = -57.8 \text{ kcal mol}^{-1} \text{,) confirming that the ions almost certainly have the same structure. The C_{10}H_{15}^{+} ions produced from these two precursor molecules were also shown to be the same.}

In order to investigate the mechanism by which these molecular ions generate both m/z 135 and m/z 148, a study of deuterium labeled isotopomers was undertaken.
Figure 7.8: CID(He) mass spectra of $C_{11}H_{16}^{+}$ ions generated from a) $1-C_{10}H_{15}CH_{2}NH_{2}^{+}$ and b) $1-C_{10}H_{15}CH_{2}OH^{+}$. 
7.2.3.2 Dissociation of deuterium labeled species

Introducing deuterium atoms in either the side chain or the ring allows one to determine if H/D mixing occurs within the side chain or the adamantyl nucleus alone or whether the mixing involves both parts of the molecule. It has been documented that exchange between the deuterium atom on the side chain in 1-C_{10}H_{15}(CH_2)_nOD^{2-} and 1-C_{10}H_{15}(CH_2)_nCO_2D^{2-} ions, where n = 0-4, and the adamantyl nucleus occurs and that the extent of deuterium intake in the adamantyl nucleus depended on the length of the side chain\textsuperscript{23}. The maximum intake occurred when n = 2 and this observation was rationalized on the basis that a six membered ring was formed, thus facilitating the exchange.

1-C_{10}H_{15}CH_2ND_2 was obtained by H/D exchange of 1-C_{10}H_{15}CH_2NH_2 in acidic (DCI/D_2O) media. The MI mass spectrum of 1-C_{10}H_{15}CH_2ND_2^{2-} ions showed extensive H/D mixing occurring before dissociation by losses of C_{10}H_{15}^{+}, \textsuperscript{13}CH_2NH_2 and NH_3. No exchange occurred for the dissociations by loss of CH_3\textsuperscript{+} and H\textsuperscript{+}, implying that the methylene hydrogens of the side chain do not lose their positional identity. This observation was confirmed by the study of the 1-C_{10}H_{15}CD_2NH_2\textsuperscript{+} analogue (1-C_{10}H_{15}CD_2NH_2 was synthesized by reducing 1-C_{10}H_{15}CN with LiAlD_4) which showed exclusive CD_2H\textsuperscript{+} loss as well as no mixing for all other dissociation channels. The relative intensities of the peaks corresponding to the loss or retention of label in the MI dissociation of 1-C_{10}H_{15}CH_2ND_2^{2-} ions are given in Table 7.6. The relative intensities have been measured at two different ion lifetimes (in the second and third field free regions

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(2FFR and 3FFR, respectively and at two different accelerating voltages of the ZAB) in order to determine if isotope effects were observable. Also included in Table 7.6 are a series of statistically calculated ratios involving different numbers of hydrogen and deuterium atoms. The experimental ratios were corrected for the contribution of the $^{13}\text{C}$ natural abundance of the [1-$\text{C}_{10}\text{H}_{15}\text{CH}_{2}\text{ND}_{2}$] - H peak.

Table 7.6: H/D mixing in 1-$\text{C}_{10}\text{H}_{15}\text{CH}_{2}\text{ND}_{2}$.

<table>
<thead>
<tr>
<th>Relative abundance ratios</th>
<th>C$<em>{11}$H$</em>{15}$D$<em>2^{-}$:C$</em>{11}$H$<em>{15}$D$^{-}$:C$</em>{11}$H$_{16}^{-}$</th>
<th>C$<em>{10}$H$</em>{15}$D$<em>2^{-}$:C$</em>{10}$H$<em>{15}$D$^{-}$:C$</em>{10}$H$_{16}^{-}$</th>
<th>CH$_2$ND$_2$-:CH$_2$NHD-$^{-}$:CH$_2$NH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2FFR (8 kV)</td>
<td>2.8 : 4.5 : 1</td>
<td>9.1 : 8.7 : 1</td>
<td>1 : 8.4 : 8.8</td>
</tr>
<tr>
<td>3FFR (4 kV)</td>
<td>2.9 : 4.3 : 1</td>
<td>10 : 8.7 : 1</td>
<td>1 : 10.2 : 10.5</td>
</tr>
<tr>
<td>Statistical</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6H, 2D</td>
<td>3.3 : 5 : 1</td>
<td>15 : 12 : 1</td>
<td>1 : 12 : 15</td>
</tr>
<tr>
<td>9H, 2D</td>
<td>9.3 : 8 : 1</td>
<td>86 : 18 : 1</td>
<td>1 : 18 : 86</td>
</tr>
<tr>
<td>12H, 2D</td>
<td>18.3 : 11 : 1</td>
<td>66 : 24 : 1</td>
<td>1 : 24 : 66</td>
</tr>
<tr>
<td>15H, 2D</td>
<td>30.3 : 14 : 1</td>
<td>105 : 30 : 1</td>
<td>1 : 30 : 105</td>
</tr>
</tbody>
</table>
For NH₃ loss, the relative abundance ratios of ions C₁₁H₁₄D₂⁺:C₁₁H₁₅D⁺:C₁₁H₁₆⁺ are almost independent of the lifetime of the molecular ions, suggesting that no significant kinetic effect interferes with the data, at least on the time scale of the experiment i.e., that the H/D mixing has equilibrated prior to dissociation. By comparing the experimentally obtained ratios with those obtained from a statistical treatment, it is proposed that 6H and 2D are involved in the H/D mixing. There appears however to be a small isotope effect favoring elimination of label. It is known from the study of the 1-C₁₀H₁₅CD₂NH₂ isotopomer that the methylene hydrogens of the side chain do not participate in the mixing, so a simple model rationalizing the data is one in which the side chain may freely rotate along the axis formed by the C-C bond connecting the side chain to the adamantyl nucleus. Exchange could thus involve the two deuterium atoms on the nitrogen and the six methylene hydrogens on the carbons α to the substituted carbon of the adamantyl nucleus, as shown schematically below:

For the 1-C₁₀H₁₅CH₂OD⁺ ions, the abundance ratios obtained for the H₂O loss also indicate that 6H and 1D atoms are involved in the scrambling, so that the
simple model proposed for the mechanism of NH$_3$ loss in 1-C$_{10}$H$_{15}$CH$_2$ND$_2$$^{**}$ ions, is also applicable to the H$_2$O loss from 1-C$_{10}$H$_{15}$CH$_2$OD$$^{**}$ ions. This is also consistent with the conclusion that the C$_{11}$H$_{16}$$^{**}$ ions produced from both these precursor molecules have the same structure.

The MI mass spectrum of the isotopomer labeled at a tertiary position, the 1-C$_{10}$H$_{15}$CH$_2$OH-3d$_1$$^{**}$ ions, (prepared by a three step synthesis: 1-C$_{10}$H$_{15}$Br-3d$_1$ was prepared following a known procedure$^{21}$; it was then reacted with H$_2$CO$_2$/H$_2$SO$_4$ to produce 1-C$_{10}$H$_{15}$CO$_2$H-3d$_1$$^{24}$ followed by reduction with LiAlD$_4$) showed no mixing i.e., only H$_2$O loss, thus further supporting that only the methylene hydrogens of the carbons $\alpha$ to the substituted carbon of the adamantyl nucleus are involved.

For the processes corresponding to $^{*}$CH$_2$NH$_2$ and C$_{10}$H$_{15}$$^{*}$ losses, the relative abundance ratios of the ions C$_{10}$H$_{13}$D$_2$$^{*}$:C$_{10}$H$_{14}$D$^{*}$:C$_{10}$H$_{15}$$^{*}$ and $^{*}$CH$_2$ND$_2$$^{*}$CH$_2$NHD$^{*}$CH$_2$NH$_2$ depended considerably on the lifetime of the molecular ions, and comparison with the statistically calculated abundance ratios is not as straightforward. However, it appears that, as for the NH$_3$ loss, these losses involve 6H and 2D atoms, but are accompanied by a larger isotopic effect of $\sim$ 1.3 for the retention of 1D in the ions and of $\sim$ 1.5 for the retention of 2D in the ions. The AE of these two processes are slightly higher than the AE for NH$_3$ loss which may account for their greater susceptibility to kinetic effects.
Consequently, the model proposed for H/D scrambling accompanying the NH$_3$ loss, also applies to the simple bond cleavages.

7.3 Conclusions

The $\Delta_r^o$ of the 1Ad$^+$, 2Ad$^+$ and 1Ad$^+$ were measured to be 153±2 kcal mol$^{-1}$, 170±2 kcal mol$^{-1}$ and 11±2 kcal mol$^{-1}$, respectively, and the $\Delta_r^o$ of 2Ad$^+$ estimated to be 15 kcal mol$^{-1}$.

The 1Ad$^+$ and 2Ad$^+$ were proposed to occupy independent potential energy wells, separated by an energy barrier which is high enough to prevent their interconversion. Based on the thermochemical measurements and the mass spectrometric data, the 1Ad$^+$ and the 2Ad$^+$ produced at threshold are indeed tertiary and secondary carbocations that retain their tricyclic structure. However, at higher internal energies, the two isomers were proposed to share a common potential energy surface, accounting for their similar dissociation characteristics. At these elevated energies, the ions must access many structures, due to the high density of states, so that the structure of the dissociating ions may no longer be the closed tricyclic structure. The statistical mixing of all the H/D in the 1-C$_{10}$H$_{14}$D$^+$ ions occurring before the dissociation by any of the accessible channels on the $\mu$s time scale, also suggested that the ions access many structures near the dissociation limit.
The study of the dissociation characteristics of 1-C_{10}H_{15}CH_{2}NH_{2}^{+} and 1-C_{10}H_{15}CH_{2}OH^{+} ions and several of their isotopomers reveals that the interaction between the side chain and the adamantyl nucleus is limited to the hydrogens on the heteroatom of the side chain and the methylene hydrogens on the carbon α to the substituted carbon of the ring system. A simple model is proposed in which the side chain can freely rotate to rationalize the H/D mixing observed.
7.4 References


Claims to Original Research

1. Appearance energy measurements were used to determine the $\Delta_r H^0$ of several phenyl substituted species. Prior to this work, few $\Delta_r H^0$ of multi substituted phenyl species were available. The thermochemical data was used to evaluate the change in $\Delta_r H^0$ following phenyl substitution for neutral and ionic species (1)

2. The effect of methyl substitution on the $\Delta_r H^0$ of ketene was investigated, by the appearance energy measurement method. It was shown that the $\Delta_r H^0$ decreases by 10 kcal mol$^{-1}$ per methyl group, as expected based on the effect of methyl substitution in structurally related compounds. (2)

3. The dissociation characteristics of ionized phenyl acetate, propanoate and isobutyrate were investigated by a combination of mass spectrometric techniques. To account for their dissociation characteristics, ion-neutral complexes and the enol form of phenyl isobutyrate were proposed as intermediate species.

4. The $\Delta_r H^0$ of 1- and 2- adamantyl cations and the 1-adamantyl radical were determined by appearance energy measurements. A mass spectrometric investigation of the ions showed that at low internal energies the ions have distinct potential energy wells with a barrier high enough to prevent interconversion and retain their tricyclic structures. However, at higher internal energies, the ions share a common potential energy surface. (3)

(1) C. Aubry and J.L. Holmes, “The thermochemistry of phenyl substitution in neutrals and in ions", in preparation.

(3) C. Aubry, J.L. Holmes and J.C. Walton, “The 1-adamantyl and 2-adamantyl cations in the gas phase”, submitted for publication.

Other publications:
