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PHOTOIONIZATION MASS SPECTROMETRIC

STUDY OF

SELECTED ORGANIC COMPOUNDS

By

Mehdi Moini

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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Department of Chemistry

ABSTRACT

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Photoionization mass spectrometry (PIMS) is a technique for investigating the interaction of ionizing radiation with gases. Threshold energies for simple and dissociative ionization can be measured, and the data combined with other thermochemical information to provide enthalpies of formation of the product.

The ionization and fragmentation of o-, m- and p-dibromobenzene upon excitation in the 8.5-13 eV range have been studied, and threshold energies for formation of CeHeBrs⁺, CeHeBr⁺ and CeHe⁺ from each precursor have been measured. The ionization energies of o-, m- and p-CeHeBrs are distinct, but the appearance energies of CeHeBr⁺ agree within experimental error for all three isomers and those of CeHe⁺ are also the same (higher in value, but within experimental error to that for Br loss), independent of the substituent distribution on the parent neutral. The results show that substituent isomerization occurs in CeHeBrs⁺⁺ prior to dissociation. Heats of formation for the ions have been calculated, and a estimate is given for that of neutral o-benzyne: $AH[*]nee(CeHe) = 370 \pm 20$ kJ mol⁻¹.

Ionization and fragmentation of p-dioxane ($C_6H_6O_2$) and p-dioxane-De have been followed by photoionization mass spectrometry, with particular emphasis on their dependence on photon energy and sample pressure. Appearance energies for the major ions have been determined and combined with other thermochemical data to obtain heats of formation of the cations. The mass spectra are strongly pressuredependent, and show that some ions are formed by both unimolecular and bimolecular steps. Both CaHsOs⁺ and CaHrOs⁺ are observed and their appearance energies have been measured. Ion-molecule reaction mechanisms which lead to these and other fragment ions are discussed. The role of hydrogen bonding in the ion-molecule reactions has also been studied.

The appearance energies for the protonated parent and twelve cationic fragments of 12-crown-4 have been measured and their heats of formation have been calculated. The ionization energy of 12-crown-4 is 8.86 ± 0.1 eV. The threshold energies for fragmentation indicate that most of the decompositions occur with insignificant kinetic shift. Possible mechanisms for the fragmentation and probable structures for some of the daughter ions are suggested. TO: Farrokh Azadeh My Mother My Father

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CHAPTER I

INTRODUCTION

The precise determination of heats of formation for cations in the gas phase has assumed considerable importance in recent years. The most precise ionic heats of formation have been obtained from photoionization experiments.¹

Photoionization mass spectrometry (PIMS)² is primarily a spectroscopic technique in which the yield of ions from a sample gas is measured as a function of ion mass and photon energy. Thus, relative photoionization and fragmentation cross sections are measured, and they provide a wealth of information about the ions. Quantities such as appearance energies ionization and of various ionization and fragmentation processes as well as vibrational and electronic energy level spacings of molecular ionic states often can be directly determined from PIMS experiments. Modern photoionization measurements^{3,4} can provide information on these subjects with a precision of about one kJ. PIMS, coupled with a few other techniques,⁵ can often fully characterize molecular ionization and fragmentation processes.

The gas phase chemistry of ions has been an active area of research ever since the advent of mass spectrometry. The study of gas phase ions is of interest because it can provide information about the structure of the neutral precursor molecule from the distribution of fragment ions observed in mass spectrometry, because of its importance in the study of interstellar clouds of gas and dust, and also because it makes possible comparisons between the reactions of gas phase ions and those of ions in solution. Two major differences between these two phases are the stability and de-excitation of ions. In solution, ions are stabilized by solvation and any excited states are rapidly de-excited by collisions. In contrast, at low pressures gas phase ions are isolated and collision free.

This thesis describes the photoionization mass spectrometric investigation of ortho-, meta- and para-dibromobensene, of unlabelled and perdeuterated 1,4-dioxane, and of the macrocyclic crown ether 12crown-4.

The interaction of ionizing radiation with gases leads first to ions with a distribution of internal energies. In competition with other deactivation channels these ions may isomerize and/or dissociate if their internal energy exceeds the thresholds for such reactions. Isomerization among dihalobenzenes has been observed both in solution⁶ and in rare gas matrices.^{7,6} Reported here are the results of a PIMS study of o-, m-, and p-dibromobenzene in the gas phase in which both ionization and dissociation are observed. From the measured appearance energies and auxiliary thermochemical data, upper limits for the heats of formation of the parent ions and for CeH4Br⁴ and CeH4⁺ have been obtained which are more reliable than previously-reported values. The enthalpy of

formation of neutral o-benzyne (C_6H_4), a likely intermediate in many organic reactions,⁹ is also estimated.

In the case of p-dioxane, threshold ionization or appearance energies have been measured for the following ions: $C_4H_9O_5^+$, $C_4H_8O_5^+$, $C_4H_7O_5^+$, $C_5H_8O^+$, $C_5H_8O^+$, $C_2H_4O^+$, $C_2H_9O^+$, $C_4D_9O_5^+$, $C_4D_7O_5^+$, $C_3D_8O^+$ and $C_3D_5O^+$. In order to follow ion molecule reactions in this system, the mass spectra have been studied as functions of the sample gas pressure, the ion source repeller voltage, and the photoionization energy. Perdeuterated p-dioxane was studied in order to more firmly distinguish PIEs of "adjacent" ions and to measure possible isotope effects on threshold energies.

For 12-crown-4, the PIEs of thirteen major fragments have been measured and its fragmentation pattern has been compared with that of the proton-bound¹⁹ dimer of p-dioxane.

CHAPTER II

AN OVERVIEW OF PIMS

The absorption of a monochromatic beam of light by a homogeneous absorbing system is well described by the familiar combined Beer-Lambert law. One form of the law commonly employed in photochemical studies is

where I. represents the light intensity (or number of photons) of strictly monochromatic light incident per unit of time at the front of a column of a single absorbing species of concentration C moles per liter; I is the light intensity per unit time transmitted through the column of material, \pounds is the column length in centimeters; and ε (liter/mole-cm), the molar extinction coefficient, is a constant for a given pure absorbing species at a given wavelength and is a measure of the probability that the photon-molecule interaction will lead to absorption of the photon.

The simplest of the photoabsorption systems are those involving absorption of light by atoms. The essential feature of the absorption of radiation by atoms or molecules is that these processes are quantized; that is, transitions occur between discrete, well-defined energy levels. The simplest line spectrum is that of the hydrogen atom. This spectrum consists, in the visible and near ultraviolet, of series of lines whose separations and intensities decrease in a regular manner toward shorter

wavelengths. Balmer was first to describe precisely the location and distribution of these lines by means of the simple formula¹¹

$$\lambda = \frac{n_1^2}{n_1^2 - 4} G$$
 (II-2)

where n_1 is an integer equal to 3,4,5..., G is a constant equal to 3645.6A and λ is the wavelength in Angstrom units. Today this equation is normally written as

$$\bar{\nu} = R(1/2^2 - 1/n_1^2)$$
 (II-3)

where $\bar{\nu}$ is the wave number of the line characterized by integer n₁ and R is the Rydberg constant, equal to 109,737.32 cm^{-1,12} Other series can also be obtained by changing n₂ in equation (II-3) from 2 to n₂ = 1,3,4... and allowing n₁ to take the value 2,3...; 4,5...; 5,6... respectively. Therefore, in general for the hydrogen atom one can write

$$\bar{\nu} = R(1/n_2^2 - 1/n_1^2)$$
 (II-4)

where $n_1 > n_2$ and both are integers. For the ground state of the hydrogen atom $n_2 = 1$ and n_1 can take any integer number from 2 to ∞ . When n_1 approaches a high limit which is called the series limit,

$$\bar{\mathbf{v}} = \mathbf{R}/\mathbf{n}_2^2. \tag{II-5}$$

In principle, an infinite number of lines lie at the series limit. Later, Bohr formulated the fundamental relation between the terms of an atom and its structure. In general for spectra of hydrogen-like ions Bohr's general formula is

$$\bar{v} = \mathbf{R}\mathbf{Z}^2(1/n_2^2 - 1/n_1^2)$$
 (II-6)

where Z is the atomic number and R is the Rydberg constant. $R = 2\pi^{\mu}\mu e^{4}/ch^{3}$ in which μ is the reduced mass, e the charge of an electron, c the velocity of light and h is Planck's constant. By solving the

Schrodinger equation for the hydrogen-like atoms one derives the same equation as the Bohr equation. Extending from the limit of the discrete energy levels there is a continuous region of possible energy values, also called the continuum. In absorption the series limit corresponds to the separation of an electron from the atom with zero velocity; that is, where the electron and proton are at infinite separation but at "rest". If the transition takes place from the ground state of the neutral atom to the ground states of the ionized atom, the energy of the series limit gives directly the ionization energy. This for the H-atom is equal to 13.636 eV. Beyond this limit there is a region of continuous absorption. This absorption corresponds to photoionization of the atoms and is continuous because any excess energy can be removed as kinetic energy of the electron and positive ion. This process may be represented by

$$h\nu = IB + k \qquad (II-7)$$

where IE is ionization energy of the atom and k is the sum of the kinetic energies of the electron and the positive ion. The ion is always several thousand times heavier than the electron, so that, in order to conserve momentum, nearly all the kinetic energy must be taken by the electron. It is therefore usual to neglect the kinetic energy of the positive ion in most discussions. The energy dependence of the intensity of the absorption lines as they merge into the continuum is of great interest. This behavior may be conveniently discussed in terms of the (unitless) oscillator strength, f, originally a concept of the classical theory of radiation. The relation between the absorption cross section ϵ_n (cm³) for a discrete transition and the oscillator strength for that discrete transition to an excited state n is given by^{13,14}

$$\mathbf{f}_n = (\mathbf{m}c/\mathbf{w}^2) \int \mathbf{f}_n \, \mathrm{d} \mathbf{v} \qquad (II-8)$$

where m is the mass of the electron, ν is the frequency of light, e is the electron charge, and c is the velocity of light; the integral is carried out over the entire absorption line. The cross section ϵ in the photoionization continuum is related to df/dE, the density of oscillator strength, by the equation¹⁶

$$\boldsymbol{\sigma} = (\mathbf{m}^2 \mathbf{h}/\mathbf{m}\mathbf{c}) \mathbf{d}\mathbf{f}/\mathbf{d}\mathbf{R}$$
(II-9)

 $\mathbf{\mathcal{I}} = (1.098 \times 10^{-16} \text{ cm}^2 \text{ eV}) df/dB; df/du \text{ is of order}^{16} 2m/3h |\langle un | \Sigma_{V} ry | u_0 \rangle|^2$

or

$$f(u) \sim 4\pi^2 e^2/3hc |\langle u_h | \Sigma_r r_y | u_h \rangle |^2$$
 (II-10)

here e^{2}/hc = fine structure constant which is $\approx 1/137$ (a pure number) and ry will be of the magnitude of $1A^{\circ} = 10^{-4}$ cm. Therefore,

$$|\langle \psi_{h} | \Sigma_{ry} | \psi_{b} \rangle|^{2} \approx 10^{-16} \text{ cm}^{-2}$$
,

an order of magnitude estimate of $\epsilon(u)$ for the continuum will be

$$\epsilon(\mathbf{u}) = 4\pi^2/3(10^{-2}\times10^{-16}) \approx 10\times10^{-18} \text{ cm}^2 = 10 \text{ Mb}.$$

Indeed the values of absorption cross sections for molecules in the continuum are in the range of one to many tens of megabarns.

Much of the above discussion on hydrogen-like atoms also applies to all atoms and molecules. That is, at energies below the onset of dissociation and ionization, absorption will occur to discrete states. Low-lying states are usually referred to as valence states, higherenergy ones as Rydberg states. To any given, precisely-specified quantum state of an atomic or molecular ion which can be provided by direct photoionization there corresponds one or more optically-allowed Rydberg series.¹⁷ The energy levels of the series are given by

$$\mathbf{R}_{n} = \mathbf{I}\mathbf{E} - \mathbf{R}/(n-\delta)^{2} \qquad (\mathbf{I}\mathbf{I}-\mathbf{I}\mathbf{I})$$

where E_n is the energy of the nth Rydberg level, R the Rydberg constant, n the quantum number of the level considered, δ the quantum

defect-a factor which accounts for penetration of the Rydberg orbital into the ion core and is very nearly constant for large values of n-and IE is ionization energy of the molecule to which the series converges. The atomic values of δ for first and second row elements are characteristic of the orbital angular momentum of the loosely-bound (Rydberg) electron and may be quoted to ± 0.1 as:¹⁸

orbital:	8	P	<u>d</u>	f	
quantum defect (C to Ne)	1.1	0.7	0.0	0.0	
quantum defect (Si to Ar)	2.0	1.5	0.4	0	

The extension of these quantum defect rules to small molecules has been made mainly by Lindholm.¹⁹ The general rule for molecules composed of second row atoms is that ns orbitals are highly penetrating and so have values of δ near 1, np orbitals are less penetrating and require a δ of about 0.6, and nd orbitals are nearly nonpenetrating and have δ very close to zero.^{20,21} Experimental Rydberg state energies can be utilized with equation (II-11) to obtain very accurate ionization energies. Photoelectron spectroscopy (PES) provides an initial estimate of the series limit. The location of the first excited state of an ion is also know from PES. . The quantum defect, which is a primary consideration in the assignment of a Rydberg transition, can then be calculated by using the photoelectron ionization energy of that orbital in the Rydberg equation. However, another option is to fit a series of transitions to the Rydberg equation with the ionization energy and the quantum defect taken as adjustable parameters. KINFIT 4, a general non-linear, least-squares curve-fitting computer program²³ can be used for this purpose. The quantum defect can be assumed to be constant

and independent of n; the error that results for $n \ge 5$ for a molecule composed of second row atoms is negligible.²³

Autoionization in Atoms

For all systems more complicated (i.e. having more electrons) than a hydrogen atom, there exist states whose energy of excitation is greater than the first ionization energy. In atomic systems these states can be produced in two ways: two-electron excitation and inner-shell ' excitation. An example of the former is the transition²⁴

$$He(1s)^2 th \nu \rightarrow He(2s^1 2p^1)$$

This transition needs 60.1 eV, whereas the first ionization energy of He is 24.6 eV, see Figure II-1. An example of inner-shell excitation is

$$Ar(ls)^2(2s)^2(2p)^6(3s)^2(3p)^6 + h\nu \Rightarrow Ar(ls)^2(2s)^2(2p)^63s(3p)^6np$$

requiring an energy between 26.5-29.24 eV for n = 4 to infinity. As to be expected, photon energies required for inner electron excitation are greater than for normal outer electron transitions and these absorption lines are to be found in the vacuum ultraviolet region of the spectrum converging to series limits which correspond to excited ionic states, See Figure II-2.

The first ionization energy of Ar is 15.76 eV. Hence, one can consider a Rydberg series superimposed upon the ionization continuum and converging to the inner-shell excited ion at the 29.24 eV limit;²⁵ see Figure II-3. The ground-state configuration of the Ar⁺ ion is split by spin-orbit interaction into a ${}^{2}P_{3/2}$ ground state and a ${}^{2}P_{1/2}$ state lying 1432 cm⁻¹ above the former. Optically-allowed Rydberg series converge to both limits. Members of the series converging to the higher ${}^{2}P_{1/2}$ limit can autoionize if they lie above the ${}^{2}P_{3/2}$ limit. This is shown in



Figure II-1 Autoionization of Two-Electron Excited States in Helium (from reference 24).



Figure II-2

Autoionization-Inner reference 3).

r Electron

Transitions

(from



Figure II-3 Autoionization Resulting from Excitation of an Electron from the (inner) 3s Orbital of Argon to np Levels (from reference 25).

Figure II-4. X-ray and Auger spectroscopy are based on inner-shell excitation. These two processes are shown schematically in Figure II-5.

These kinds of ionization, in contrast to direct ionization, are called autoionization. Autoionization is an indirect process. Atoms and molecules are first produced in a neutral excited state with energy above an ionization limit, and then spontaneously emit an electron:

$$M + h\nu \rightarrow M^* \rightarrow M^+ \rightarrow e$$

The first step is a resonance process; it can be brought about only by light of the correct energy and the nature of accessible excited states is governed by the normal optical selection rules. Autoionization is the second step, and as no radiation is involved it follows the monopole selection rule that the symmetry species of the autoionizing state and final state of the ion plus free electron must be identical.

Autoionization in Molecules

The absorption of ultraviolet radiation by molecules is observed to be considerably more complex than that of atoms. For atoms, interaction with a photon produces either excitation or ionization. If a discrete state in the atom can have an energy identical with an ionization continuum, then, under certain circumstances, excitation followed by a radiationless transition into the continuous state may take place, leading to autoionization in the photoionization absorption continuum. For molecules, on the other hand, several other processes are also possible which can mask or even completely obliterate the photoionization processes. Thus the interaction of a photon with a molecule can lead to excited electronic states which in turn dissociate or ionize in competition with direct photoionization. Such effects include predissociation and



Figure II-4 Autoionization Converging to the Higher Energy Spin-Orbital Component of the Ground State Configuration of the Ar⁺ Ion (from reference 24).



Figure II-5 Two alternative modes of atomic De-Excitation Which Follow Creation of an Inner Shell Vacancy. (From K. Siegbahn, et al.; ESCA Almquist and Wiksells, Uppsala, 1967)

preionization, caused by the presence in the same energy region of overlapping repulsive potential curves. Photoionization of the molecule may also leave the ion in an excited state, leading to the process of fluorescence as the ion decays to its own ionic ground state.

The number of excited states of a neutral polyatomic molecule is large because there are many electrons in many orbitals to excite, and the number of possible combinations is therefore considerable; in principle, their number is infinite. The number of states of a polyatomic ion is even larger because the removal of an electron from any one of the orbitals can be accompanied by simultaneous excitation of the remaining electrons. thus increasing the number of possible combinations. Connected with the existence of such a large number of excited states in the neutral molecule and its ion is the phonomenon of autoionization. Among the excited states of the neutral molecule may be some that will be energetically degenerate with one or more ionic states; that is, a neutral molecule will contain energy in excess of its first ionization energy. Such states have been called "superexcited" by Platzman.³⁶ If the potential energy surfaces for the energetically degenerate neutral and ionic states cross, as is likely, the superexcited state may autoionize, i.e., ionize by a radiationless transition; this is a resonance process. However, such a potential energy surface crossing is relatively slow, occurring in approximately 10⁻¹³-10⁻¹² sec, which amounts to the period of one or more vibrations. By contrast, direct ionization is essentially immediate (10⁻¹⁵-10⁻¹⁶ sec). The excited (neutral) states that autoionize may be those in which two or more electrons are excited, or an inner-shell electron is excited, or in which only one electron is excited but there is at the same time appreciable

vibrational excitation. This latter case appears to be the dominant one in polyatomic molecules;²⁷ the decay into an ion plus electron is caused by the exchange of energy between electronic and vibrational motion, which of course constitutes a breakdown of the Born-Oppenheimer approximation.

Autoionization mechanisms in molecules are classified according to the nature of the molecular ion excitation energy which is exchanged for kinetic energy of the ejected electron. If the excitation energy actually used is in the form of molecular rotation we speak of rotational autoionization, meaning that only the rotation quantum numbers of the core change in the transition from molecule to ion. If the vibrational quantum number(s) change we have vibrational autoionization, while if the electronic state of the core changes we speak of electronic autoionization. Many excited molecular states are energetically capable of autoionizing by two or three of these mechanisms which are in competition with one another. The forms of autoionization which involve nuclear motion rather than electronic motion are generally less rapid than electronic autoionization, and are observed most frequently in molecular Rydberg states which have electronically ground-state cores. Rotational autoionization has been characterized only in H₂,^{28,29} while vibrational autoionization has been studied, for example, in H2^{30,31} and NO32,33,34 in detail. Figure II-6 shows electronic autoionization of a diatomic molecule,^{35,36} and Figure II-7 shows vibrational autoionization in a diatomic molecule.³⁷ In Figure II-7, vertical lines from M₂ to upper states indicate excitation processes. Curved arrows labelled A, B, and C indicate respectively: a $\Delta \nu = -3$ inter-Rydberg transition from Ms² to M_2^{ss} ; a $\Delta \nu = -1$ transition from M_2^{sss} to M_2^* + e; and a two-step



Figure II-6 Autoionization (Thick-Line) and Direct Ionization (Dashed Line) in the Oxygen Molecule (from reference 35).



Figure II-7 Schematic Diagram of Potential Curves of Electronic States and Vibronic Transitions in a Diatomic Molecule (from reference 27).

process involving a $\Delta \nu = -2$ transition from M_3^{22} to M_3^2 , followed by a transition with $\Delta \nu = -1$ from M_3^2 to $M_2^+ + e$.

Dissociation and Predissociation

Comparison of absolute photoionization with absorption crosssection measurements shows that ϵ_i/ϵ_0 , the photoionization yield, is less than unity and varies with photon energy to converge to unity at high energy. Dissociation into neutral fragments and fluorescence are the two processes that can effectively compete with ionization. However. fluorescence is normally considered as negligible since the coupling with the vacuum radiation field is usually very small compared with other Thus when considering the problem of molecular ion perturbations. formation one should understand the effects of dissociative channels. For atoms a continuous energy range joins onto each series of electronic states and corresponds to the removal of an electron (ionization) with more or less relative kinetic energy or, conversely, to the capture of an electron by the ion (recombination). In molecules, however, in addition there are continuous ranges that correspond to a splitting of the molecule into smaller components (normal or excited neutral fragments, or positive and negative ions), that is, which correspond to a dissociation. Such a continuous range joins onto the series of vibrational levels of every electronic state and is the only feature present if the electronic state under consideration has no discrete vibrational levels at all (repulsive state). As in a preionization, when discrete electronic states are overlapped by a continuous range of states that correspond to the separation of an electron (ionization), for molecules we have in addition the much more frequent case of overlap by one of the continuous ranges that correspond to a dissociation into atoms or ions and that occur for every electronic state irrespective of whether it is a stable or an unstable state. In the schematic diagram in Figure II-8 the vibrational levels of the upper state B with $\nu > 4$ on are overlapped by the continuum of the lower state. In this case the system can cross, by radiationless transition, from a discrete state into the continuous state which corresponds to dissociation; this process is called predissociation. Herzberg³⁸ divides predissociation into three types corresponding to the three forms of energy of the molecule (electronic, vibrational, or rotational).

I. Overlapping of a certain <u>electronic</u> state (that is, of its vibrational or rotational levels) by the dissociation continuum belonging to another electronic state; radiationless transition into this other dissociated electronic state may occur.

II. Overlapping of the higher <u>vibrational</u> levels of an electronic state of a polyatomic molecule by a dissociation continuum joining onto a lower dissociation limit of the same electronic state; radiationless splitting off of the particular atom or group of atoms (predissociation by vibration) may occur.

III. Overlapping of the higher <u>rotational</u> levels of a given vibrational level of a molecule by the dissociation continuum belonging to the same vibronic state; radiationless decomposition of the molecule with no change of electronic or vibrational state (predissociation by rotation).

Figure II-9 shows a schematic illustration of several possible types of photodissociation of a polyatomic ion; (a) electronic predissociation; (b) excitation to a dissociative vibrational level of the






Figure II-9 A Schematic Illustration of Several Possible Types of Photodissociation of a Polyatomic Ion; (a) Electronic Predissociation; (b) Excitation to a Dissociative Vibrational Level of the Ground Electronic State; (c) Vibrational Predissociation; (d) Direct Photodissociation on a Repulsive Surface (from Reference 39).

ground electronic state; (c) vibrational predissociation; and (d) direct photodissociation on a repulsive surface.

As a window into the optical spectroscopy of gas phase ions, photodissociation has aroused the most widespread interest. To suggest why the spectroscopist has welcomed this concept so eagerly, one needs only to observe that the maximum concentration of mass-selected ions which can be assembled in a spectrometer cell with current methods is of the order of 10⁻¹⁴M, which is discouraging in attempts to obtain [•] direct optical absorption spectra. Since photodissociation methods deal usefully with ion populations of tens of ions/cm³ or less, their potential spectroscopic importance is clear.

Quasiequilibrium Theory

The process denoted (b) in Figure II-9 is the direct excitation to a high predissociating vibrational level of the ground electronic state of a molecule. In most cases, this process is unfavorable because of the extreme violation of vibrational selection rules. However, these same levels can be reached as in process (c) in twosteps by photoexcitation to a bound excited level; followed by internal conversion (dashed arrow) to the vibrationally hot ground state. It appears as if this internal conversion or vibrational predissociation mechanism dominates the dissociation of the great majority of the larger polyatomic ions so far studied.²⁹ This situation is usually well described by the energy randomization hypothesis which forms the basis of the quasiequilibrium theory (QET) of unimolecular decay.⁴⁰

A major advance in our understanding of unimolecular dissociations was the application of this statistical theory (QET) to reactions occurring in a mass spectrometer. At about the same time and

independently, Marcus and Rice⁴¹ developed an important version of the old RRK42,43 theory, which is now referred to as the RRKM theory. Although the two theories are identical in their fundamental statistical assumptions, the QET expressed the dissociation rate k(E) as a function of the internal energy, E, while the RRKM theory went beyond this form to the thermalized rate, k(T), which is more appropriate to the thermalized neutral experimental systems. Another approach is the Slater⁴⁴ theory which characterizes a molecule by a potential function having only quadratic terms and internal normal modes of motion which are orthogonal to one other, so that the system does not relax through its vibrational manifold before decomposing. The question of which is the more correct theory of unimolecular dissociation was subsequently resolved in favor of statistical models for molecules having lifetimes longer than 10-10 8.45 If the internal energy is statistically distributed among the vibrational modes both in the excited polyatomic molecule and in the activated complex located at the saddle point of the potential surface, the dissociation rate of a molecule or ion with internal energy, E, and an activation energy of E₀ is given by equation⁴⁶

$$\mathbf{k}(\mathbf{E}) = \mathbf{\epsilon} \sum_{\boldsymbol{z}=0}^{\mathbf{E}-\mathbf{E}_0} \rho^{\ddagger}(\boldsymbol{z})/h\rho(\mathbf{E}) \qquad (\text{II-12})$$

where ρ^{\ddagger} and ρ are density of vibrational and internal rotational states of the transition state and the molecule or ion, respectively, ϵ is number of equivalent ways the molecule can dissociate, and h is Planck's constant. The numerator sums over the number of energetically allowed ways of passing through the region of the transition state. This is because E - E, the energy in excess of that required to pass over the transition state, can be partitioned among the vibrational and internal rotational activation energies for various reactions. In terms of phase space one can visualize this model as in Figure II-10. For a molecular ion configuration with total energy E there will be some large number of combinations of vibrational quantum numbers (micro states). Each micro state is shown by a square in phase space and for each combination $E \approx$ Σ_{hys} (V₁ + 1/2). The number of micro states is reduced in the transition state configuration (bottleneck) because only E-E. energy is available for distribution among vibrational modes. In this model dissociation is a random walk in this phase space. Since the statistical assumption is that all steps between the squares have equal probability, therefore, the probability for dissociation is related to the ratio of the area of the bottleneck to area of the bottle, which is the same as equation (II-12). In more recent RRKM models a distinction between loose and tight complexes is made.²⁴ A loose complex is one which involves simple bond stretching in the direction of the reaction coordinate and no coupling between radial and internal coordinates exists; distribution of the final products reflects the internal distribution of the complex. In a tight complex coupling between radial and internal coordinates affects the final product energy distribution, and some kind of rearrangement happens before the fragmentation. Although there is extensive experimental support of the fact that ion yield curves are smooth functions of energy alone, that is the molecular ion has reached a state of microcanonical equilibrium, a few counter examples are known which are referred to as "isolated state decay".⁴⁷ CH2OH* shows both behaviors.48 Most of the ions are produced by a statistical RRKM/QET mechanism, except the CHs⁺ ions. This results from a branching in the reaction path brought about by an avoided crossing



Figure II-10 Potential Energy Surface Showing a Random Walk in Phase Space leading to Dissociation of a Polyatomic Ion or Molecule (from reference 47).

between two potential energy surfaces. One of the reactive paths gives rise to QET, whereas the other leads directly to the $CH_{3^+} + OH$ dissociation asymptote, Figure II-11. This path which is called "isolated state decay" takes place by a fast, diatomic-like, non-statistical mechanism which escapes energy redistribution. It has been found⁴⁹ that for polyatomic ions with lifetimes from 10^{-3} to 10^{-11} s randomization of energy takes place prior to decomposition. The early work of Wolfgang⁵⁰ and Henglein⁵¹ showed that the time scale for energy randomization in the collision complex in ion-molecule crossed beam experiments is about 10^{-12} s.

Kinetic Shift Measurements

Metastable decompositions in a mass spectrometer are those which occur after the parent species has been accelerated out of the ion source, and hence, at a later time than usual. If, as is normally the case, the parent species is not homogeneous in energy, and if rate constants for decomposition increase with increasing energy, then those ions undergoing a metastable decomposition will have had less energy than those decomposing in the ion source itself. That is why the appearance energy (AE) of a metastable ion gives a better estimate of the thermochemical threshold than does the AE of the ion itself.⁵³⁻⁵⁴ The difference between these two appearance energies has been referred to as the "measurable part" of the kinetic shift.⁵⁴ Since even metastable decompositions need some excess energy to be observable, the translational energy release of this metastable decomposition must be measured to obtain this additional kinetic shift.⁵⁴ Franklin and his



Figure II-11 Fragmentation of the Methanol Cation Showing Both Statistical Decomposition [CH₂OH⁺ + H] and Non-Statistical Dissociation Through an Isolated Excited Electronic State [CH₃⁺ + OH] (from reference 48).

coworkers⁵⁶ have proposed the following relation for linking translational energy release 4 with total excess energy E

$$\epsilon_{t} = B/(0.44N),$$
 (II-13)

in which N is the number of vibrational degrees of freedom of the dissociating ion and 0.44N is called the "effective number of oscillators." Kinetic energy release is easily detectable due to the broadening of the corresponding metastable peak in the mass spectrum. Beynon⁵⁷ has shown that the average value of the kinetic energy released, T, is related to the width of the peak by the expression,

$$d = (4m_2^2/m_1)(\mu T/eV)^{1/2}$$
(II-14)

where d is expressed in a.m.u. m_1 and m_2 are the precursor and daughter ion masses, V the full accelerating voltage the metastable ion crosses before decomposing, and $\mu = (m_1-m_2)/m_2$.

Ionization Threshold Laws

For the first ionization and multiple ionization, Wigner⁵⁸ and then Geltman⁵⁹ theoretically showed that the energy dependence of the photoionization and electron impact cross-section in the neighborhood of the threshold follows a power law of the form:

$$\boldsymbol{\boldsymbol{\sigma}}(\boldsymbol{\boldsymbol{\varepsilon}}) = \mathbf{C}(\mathbf{B}-\mathbf{E}_{\mathbf{o}})^{n-1}, \qquad (II-15)$$

where E is the ionizing photon or electron energy, E₀ the threshold energy, C a constant, and n the total number of outgoing electrons for the ionizing process.¹ According to this equation photoionization will give rise to a step function threshold, Figure II-12b, whereas linear threshold laws are expected for direct electron impact ionization, Figure II-12a, and for photoexcitation and electron attachment, which are resonance absorption processes, (Figure II-12c). Figure II-13 shows experimental cross sections near threshold for (a) electron impact



PROJECTILE ENERGY (E)

Bypothetical Threshold Cross-Section Behavior for Frequently Encountered Excitation Processes (a) Direct Ionization by Electrons, (b) Photoionization, (c) Photoexcitation (from Reference 15). Figure II-12



Bxperimental Cross-Section near Threshold for (a)
Blectron Impact Ionization of Helium, (b)
Photoionization of Nitric Oxide, (c) Double Ionization of helium by Blectrons (from Reference 15). Figure II-13

ionization of helium,⁴⁰ (b) photoionization of nitric oxide,⁴¹ and (c) double ionization of helium by electrons,⁴² which all agree well with equation (II-15). Although these experiments are in accord with the theoretical predictions, other studies indicate quite different forms.⁴⁹⁻⁴⁵ Deviations from the step-function threshold law in photoionization are due to numerous factors. In general one can divide these causes in two parts, internal and external.

I. Internal Causes

(a) Autoionisation. Since radiation is absorbed in a transition to a discrete state of the neutral, autoionization is a resonant process and ions will be produced only at the energy of the transition. Autoionization often appears as a sharp, peak-like structure superimposed on the normally featureless direct ionization continuum. However, autoionization exhibits a great variety of asymmetrical line shapes and may appear as a "window resonance" in which there is a decrease or dip in the photoionization cross section.^{13,99,14} The lifetimes of autoionizating levels can vary a great deal, ranging from ~10⁻¹⁴ seconds to ~10⁻⁶ seconds.⁴⁴ For states with short lifetimes, the autoionization structure may be so broad that it is indistinguishable from the continuum for direct ionization. Autoionization structure on a photoionization efficiency curve (PIE) may also be broadened by emission, in which case it may also be indistinguishable from the continuum.

(b) **Dissociation and Predissociation.** In interpreting ionization efficiency curves, it is necessary to remember that what is measured is

the relative amount of various ions present several microseconds after electron or photon impact. In general, this relatively long delay makes the mass spectrometer a much more sensitive instrument for the detection of predissociation than an optical instrument. Predissociation is detectable in a mass spectrometer if the lifetime of the predissociating state is about 10⁻⁴ sec or less. Figure II-14 shows a strong predissociation leading to fragmentation, which causes a dip in the PIE curve.⁶⁷

Internal Energy Distribution. It is frequently possible to (c) prepare an ion with little or no internal energy by photoionization at a wavelength corresponding closely to the ionization threshold. Smaller molecules that are nearly all in the vibrational ground state at room temperature can usually be ionized to give an abundant yield of parent ions which are also nearly all in the vibrational ground state, unless the appropriate Franck-Condon factor is very small. In the case of larger molecules, which contain more thermal vibrational energy, the parent ion can usually be prepared with about the same amount of vibrational Some "cooling" of the ion can be achieved by energy at threshold. photoionization at "hot band" wavelengths corresponding to energies below the ionization energy, but this is usually not very significant.¹⁵ Figure II-15 shows the internal energy distribution of benzene at 25°C.

(d) Franck-Condon Effect. If the Born-Oppenheimer approximation is assumed, w is independent of the nuclear coordinates, and the total time-independent wavefunction is written,



Figure II-14 Potential Curves for a Diatomic Molecule AB, Showing the Effect of Predissociation on the Electron or Photon Impact Spectrum (from Reference 67).



Figure II-15 Internal Thermal Energy Distribution for Benzene at 25°C (from Reference 80).

where the subscripts signify electronic, vibrational, rotational, and electronic spin wavefunctions. Direct ionization is exactly similar to an electronic transition to a neutral state, except here the final state wavefunction includes both the ion and the photoelectron. Therefore, for a dipole transition one can write:

$\langle \psi' | \mu | \psi' \rangle = \langle \psi ' \psi ' \psi ' \psi ' \psi | \mu | \psi ' \psi ' \psi ' \psi ' \psi ' \rangle \quad (II-17)$

where μ is the dipole moment operator, and prime and double prime superscripts are final and initial states, respectively. The total dipole moment is divided into two parts, one due to the electrons and the other due to the nuclei, i.e. $\mu = \mu_{e}\mu_{m}$. Since the electronic wavefunctions are orthogonal, $\langle \psi_{e} \rangle |\psi_{e} \rangle = 0$, equation (II-17) will reduce to:

The separate electronic spin integral is based on the approximation **me = mm**, where it is assumed that the spin-orbit interaction is small. This approximation is good for light diatomic molecules, but it breaks down for heavier species, for which spin-orbit interaction is strong. For a spin-allowed transition $\langle \mathbf{w}' | \mathbf{w}' \rangle$ is equal to one, i.e. AS = 0. The rotational integral normally gives the general selection rules: $\Delta J = 0$, ± 1 and $\Delta M = 0, \pm 1$. The product separation of the two remaining integrals is based on the assumption that $w_r = w$ (q, Q.) w(Q), where q and Q are generalized electronic and nuclear coordinates; Q. corresponds to a fixed nuclear separation at roughly the equilibrium nuclear distance in one of the two electronic states. Based on these assumptions, the first integral of equation (II-18) is called the electronic transition moment matrix; the second is the vibrational overlap integral, whose square is called the Franck-Condon factor.... Figure II-

16 shows the effect of the Franck-Condon factor on the direct ionization threshold of a diatomic molecule.⁴⁸ The photoionization cross-section curves for H₂O and CH₄ shown in Figures II-17 and II-18 illustrate two quite different cases. The data for H₂O show a rather intense step at threshold corresponding to the abundant production, by direct ionization, of the parent ion in the vibrational ground-state. The data for CH4 show a very low probability for forming the ground state of the CH4⁺ ion. The reason is that the equilibrium configuration of the ion is considerably distorted from the tetrahedral form of the neutral, and therefore the Franck-Condon factor for the transition to the vibronic ground state of the ion is very small.⁵⁶ In the case of CH4, the electronic state of the ion is orbitally degenerate and nuclear displacement will occur that destroys the orbital degeneracy. Such displacement is called Jahn-Teller or Renner (for linear molecules) distortion...

II. External Causes

(a) Temperature. The effect of thermal energy on the photoionization threshold has been theoretically investigated by Chupka.⁷⁰ He provides an elegant demonstration that the thermal shift of such a photoionization threshold to lower values is just the average thermal energy of the neutral molecule, provided that the ionization efficiency curve for the molecular or fragment ion is linear in photon energy at absolute zero.

The importance of thermal energy for the interpretation of appearance energies of fragment ions determined by photionization techniques has been recognized for some time.^{67,77} Methods employed



Figure II-16 Franck-condon Factors and Hypothetical Direct Photoionization Yield Curves Expected for Small, Moderate and Large Bond Length Changes in a Vertical Ionization (from Reference 48).



Figure II-17

Photionization Cross-Section of H_2O (from Reference 15).



Figure II-18

Photoionization Cross-Section of CH₄ (from Reference 15).

to minimize thermal contributions include: decreasing the temperature of ion-source to as low as 118K,⁷² or introducing the parent molecule as a supersonic molecular beam⁷³ with rotational temperatures of just a few degrees above absolute zero and also fairly low vibrational temperatures.

(b) **Pressure.** When the pressure in the ion source is high, so that collision may occur before an ion leaves the source, the apparent ionization energy may shift. In the case of p-dioxane (which is discussed in Chapter (V), this shift is toward lower energy. In general, molecules which are excited by photons close to their ionization energy can lose an electron by collisionally-assisted ionization.¹³

(c) Instrumental Effects.⁷⁴ Two examples are the slit effect and The former is due to the finite slit width of the the kinetic shift. photoexcitation monochromator. Its treatment has been discussed by Rider.⁷⁶ The latter is defined as the excess energy which is required to produce a detectable yield of photofragmented ions on the time scale of the mass spectrometric measurement, which is about 10^{-6} to 10^{-7} seconds.^{76,77} According to Rosenstock, et al.,⁷⁸ in order to observe a fragmentation threshold by mass spectrometry it is necessary that the fragmentation process occur prior to departure of the parent ion from the ion source where it typically resides for -10^{-6} sec. If the rate constant for decomposition is less than ~10⁶s⁻¹ no fragments will be detected. Additional excitation energy must be supplied to increase the Therefore, the apparent threshold energy for decomposition rate. fragmentation will be an upper limit of the true activation energy for dissociation. Chupka⁶⁷ has pointed out that for larger molecules the

kinetic shift effect is offset to some extent by the distribution of internal thermal energy of the molecule, all of which is assumed to be available for decomposition, in addition to the excitation energy imparted in the ionization process. Vestal⁷⁹ has made calculations which indicate the magnitude of the kinetic shift for a number of typical fragmentation The magnitude of the kinetic shift, apart from rate processes. constants, also depends upon the value of the residence time and the sensitivity of the mass spectrometer. Rosenstock et al.⁸⁰ have emphasized that for large molecule fragmentation processes the kinetics of decomposition lead to a gradual increase in fragment ion current, so that there is no well-defined threshold. Kinetic energy release measurements can be used to estimate that part of the kinetic shift and reverse activation energy (energy barrier for fragmented ions and neutral partners to revert back to the transition complex) which is converted to translational energy of the fragment ion.⁸¹ Recently timeresolved photoionization mass spectrometry in the millisecond range has been employed to study ultraslow unimolecular dissociations having rate coefficients $k(E) \leq 10$ s⁻¹ near threshold energies.⁸⁵ Application of this method to the measurement of the threshold energy for fragmentation of bromobenzene to yield the phenyl cation and a neutral bromine atom is shown in Figure II-19. It is clear that the difference in appearance energy with respect to typical conditions is significant (about 0.3 to 0.4 eV). Such experiments can also provide very good estimates for the rate constants for slow decompositions.

Heats of Formation for Gas Phase Cations

The precise determination of heats of formation for cations in the gas phase has assumed considerable importance in recent years. With





the development of experimental techniques for measurement of equilibrium constants associated with proton-transfer reactions among positive ions, extensive networks of relative gas phase basicities and proton affinities have been compiled.⁸³ The assignment of absolute proton affinities relies on the use of suitable reference standards which are usually derived from heats of formation for positive ions. However, these are still not firmly established, with uncertainties in appearance energies, ionization energies, and supplementary thermochemical data giving rise to values over ranges of several kilocalories per mole.⁷⁸ The study of proton-transfer reactions involving alkyl ions and alkenes⁸⁴ has produced a set of relative ionic heats of formation which may assist in their absolute determination.

The most precise ionic heats of formation have been obtained from variable-temperature photoionization experiments.¹ These can lead to reliable OK values, provided that the auxilary thermochemical data at OK is available or can be estimated; in most cases this is the major source of uncertainty in AH® (ion). Extrapolation of data from experiments performed at room temperature is of limited application because of possible thermal decomposition effects; there is also the likelihood of errors being introduced as a result of extrapolation over a large temperature range. The best technique is to perform low-temperature experiments, although these are not always practicable due to problems with sample condensation and reduced sample pressure. It would thus be useful if a method could be developed to enable ionic heats of formation to be accurately estimated from room-temperature photoionization measurements.

For the ionization reaction $A \rightarrow A^* + e$ the adiabatic ionization energy (IE) at 0K corresponds to the formation of a cation and an electron with zero translational energy, i.e. at rest. For the reaction at a temperature T, it is possible to consider the ΔH^{e_1} of an electron to be zero (stationary electron) or 3RT/2, the translational energy (thermal electron). At 298K there will be a difference of 1.48 kcal mol⁻¹ between the two differently-defined heats of formation ($H^{e_{200}} - H^{e_0} = 1.48$ kcal mol⁻¹ for an unexcited monatomic gas). The stationary electron convention has been used throughout the course of this work. For a generalized process

$AB + h\nu \rightarrow A^+ + B + e$

the potential barrier to the reverse reaction is generally assumed to be zero. Constraints on the reaction (unimolecular decomposition) require that the initial translational momentum of the center of mass (CM) and the angular momentum about the CM of the precursor molecule must be conserved.

If the unimolecular decomposition is sufficiently rapid that there is no kinetic shift effect, then the observed appearance energy (AEr experimental) corresponds to the adiabatic appearance energy (AEr adiabatic), which represents the minimum energy to form $A^* + B + e$ from AB at temperature T. The products of this process ($A^* + B + e$) are not formed at any well-defined equilibrium thermodynamic temperature because the reaction occurs in isolation (unimolecular decomposition).⁴⁵ In reality both reverse activation energy and kinetic shift are present; therefore, a reported appearance energy will be an upper limit to the desired adiabatic value. Figure II-20 shows the AE for the reaction $M \rightarrow F^* + N$ in which zein is the experimental AE, ze is



Reaction Coordinate -----

Figure II-20 Schematic Diagram Showing Kinetic Shift and Reverse Activation Energy in the Experimental Observation of the fragmentation: $M + h\nu + F^* + N$ (from Reference 86).

the activation energy, ε^{\ddagger} is the excess energy, ω^{r} is the reverse activation energy and T^{\ddagger} and T^{\bullet} are some portion of ε^{\ddagger} and ω^{r} which appear as kinetic energy.⁶⁶ From the experimental AE of the above reaction, ΔH^{\bullet} ; of A⁺ at room temperature can be calculated from the following equation:

$$\Delta \mathbf{H}^{\mathbf{o}}_{fT}(\mathbf{F}^{+}) = \mathbf{A}\mathbf{E}_{T} + \Delta \mathbf{H}^{\mathbf{o}}_{fT}(\mathbf{M}) - \Delta \mathbf{H}^{\mathbf{o}}_{fT}(\mathbf{N}) \qquad (II-19)$$

where all ΔH^{o}_{ff} are at 298K. To convert this heat of formation to the heat of formation at 0K, one can use the following equation

$$\Delta H^{o}_{fo} = \Delta H^{o}_{fT} + \int \Delta C_{p} dT \qquad (II-20)$$

 ΔCp is the difference between the heat capacities of products and reactants. The N-F⁺ bond energy can be also calculated for the above reaction (M + h $\nu \rightarrow$ F⁺ + N) by subtracting the IE of the parent ion from the AE of the M dissociation, i.e.,

$$D(N-F^+) = AB (F^+, M) - IB(M)$$
(II-21)

Complementary Experimental Techniques

In addition to photoionization mass spectrometry, which is the subject of the next chapter, two other techniques which are widely used for ion spectroscopy are photoelectron spectroscopy (PES) and photoelectron-photoion coincidence spectroscopy (PEPICO). The principles of the PES and PEPICO have been described in detail in several monographs^{97,28} and review articles;⁴ therefore, only an outline will be presented here.

A-Photoelectron Spectroscopy

When a molecule is irradiated by light with wavelength shorter (energy greater) than the first ionization energy of the molecule, it will ionize:

$M + h\nu \rightarrow M^{+} + e^{-}$.

PES is the study of the kinetic energy distribution of the ejected photoelectrons. The HeI resonance source (584 A°, 21.22 eV) has made it possible to obtain ionization energies in the region up to about 21 eV, including ϵ , π , and non-bonding electrons, by the technique which is sometimes called UVPES. This singling-out of individual molecular orbitals is the most important characteristic of PES. Since the photon energy used in PES is fixed, the binding (ionization) energy of each molecular orbital, I_j, can be obtained by measuring the kinetic energy of the ejected electrons:

$$KE = hv - I_{j}. \qquad (II-22)$$

The ejected photoelectrons are separated according to their kinetic energies in an electron energy analyzer, detected and recorded. The intensity of the photoelectron current plotted against ionization (binding) energy is called a photoelectron spectrum. The principles of photoelectron spectroscopy are illustrated schematically in Figure II-21 for a normal, closed-shell molecule. Since according to Koopman's theorem, each ionization energy is equal in magnitude to an orbital energy, each peak in Figure II-21a shows an ionization energy from a different orbital of the neutral molecule as is shown in Figure II-21b. (In this figure fine structure such as vibrational structure, spin-orbit splitting, etc. has been ignored for simplicity.) The energy level diagram in Figure II-21c indicates that the ionization energies are given by the energy difference between the final states (the ionized states) and the initial state.

Two types of ionization energy, "adiabatic" and "vertical", are defined as ionization from the vibrational ground state of the initial



Figure II-21 Principles of UV Photoelectron Spectra. (a) Photoelectron Spectrum, (b) Electronic Configurations of a Molecule and its Ionized States, (c) Energy Level Diagram (from Reference 93).

state $(v^{\prime\prime} = 0)$ to $v^{\prime} = 0$ of the final state, and from $v^{\prime\prime} = 0$ to vibrationally-excited levels of the positive ion with maximum photoionization probability, respectively. The schematic PES band in Figure II-22 is drawn such that the vertical-ionization peak appears at $v^{\prime} = 5$. When there is no vibrational structure in photoelectron spectra, experimental values for the vertical ionization energies are generally determined from the positions of the individual band maxima. Ionization energies reported by PES are generally vertical ionization energies.

B-Photoelectron-Photoion Coincidence Spectroscopy (PEPICO)

The basic purpose of PEPICO spectroscopy is to study the reactions of molecular ions which contain a defined amount of internal energy. This is done using photoionization, by selecting events in which both the incoming photon energy, $h\nu$, and outgoing electron energy, KE_{0} , are known:⁴⁶

$M + h\nu \rightarrow M^+ + e^-$.

The excitation energy of the molecular ions of interest, E_m^+ can be measured if the original thermal energy content, E_{th} , and ionization energy, IE, are known

$$\mathbf{E}_{\mathbf{m}+} = \mathbf{h}\boldsymbol{\nu} - \mathbf{K}\mathbf{E}_{\mathbf{e}} - \mathbf{I}\mathbf{E} + \mathbf{E}_{\mathbf{th}}.$$
 (II-23)

At very low temperature, E_{th} is assumed to be zero. The quantity defined by the experiment is actually $h\nu$ -KE, the energy transferred in ionization.

Two distinct versions of PEPICO spectroscopy-termed fixed⁶⁰ and variable⁹⁰ wavelength technique-have been developed. The two approaches are more complementary than competitive, as the following brief comparison reveals. In both of the two current versions of the PEPICO experiment, mass-selected ions are detected in delayed



Figure II-22 Vibrational Structure of a Phtoelectron Band and Vertical and Adiabatic Ionization Energies (from Reference 93).

coincidence with energy-analyzed photoelectrons. The coincidence signal identifies photoionization events from which both the ion and the electron have been detected. In the fixed wavelength technique the sample is irradiated by a fixed photon wavelength, usually the HeI (21.22 eV) live from a discharge lamp, and the molecular ion internal energies are chosen by varying the kinetic energies at which electrons are accepted by the energy analyzer.

In the variable wavelength technique a special analyzer is employed for selecting those photoelectrons which have essentially zero kinetic energy and the internal energy of the ion is changed by varying the frequency of the ionizing light. The most promising light source for this kind of coincidence experiment is synchrotron radiation, but a standard laboratory light source such as the hydrogen many-line spectrum or the helium continuum can also be used.

The most important difference between these two coincidence experiments arises because indirect autoionizing processes which emit threshold electrons can populate parts of the molecular ion potential energy surface in the variable wavelength option; these processes are not accessible by direct ionization.

CHAPTER III

EXPERIMENTAL APPARATUS AND PROCEDURES

A. Introduction

The purposes of this chapter is threefold; to present a brief description of the MSU PIMS instrument, to document the experimental conditions under which the data presented in succeeding chapters were recorded, and to discuss experimental problems which were encountered in the course of this work. The instrument has been described in considerable detail elsewhere,^{91,76} and a brief overview is included here for completeness and to facilitate the discussion in this chapter. A diagram of the apparatus is shown in Figure III-1. The instrumental problems encountered during the course of this investigation were innumerable, many of them due to lack of experience with the instrument, whose construction was completed several years ago. Many of these problems have been resolved; however, some are likely to occur again, and it is hoped that the following discussion will be of help to future users of the instrument.

B. The Instrument

1. Light Source

The light source is a Hinterregger-type windowless discharge lamp with water-cooled anode and cathode. The discharge tube is a 25 cm long x 4 mm I.D. water-jacketed quartz capillary to which the discharge gas is admitted at the anode after it has passed through a molecular sieve trap immersed in liquid nitrogen. A small pressure differential is



Figure III-1 BA-Baffle; EN-Entrance Slit; EX-Exit Slit; GR-Grating; IS-Ion Source; IT-Ion Transducer; LP-Lamp; Pl-First Differential Pumping Port; P2-Second Differential Pumping Port; P3-Monochromator Pumping Port; P4-Sample Chamber Pumping Port; P5-Quadrupole Chamber Pumping Port; PT-Photon Transducer; QP-Quadrupole; QS-Quadrupole Support; LE-Ion Lense.

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maintained down the length of the discharge by pumping on the cathode end of the lamp; this stabilizes the discharge and helps eliminate sputtering of the cathode onto the monochromator entrance slits. The cathode vacuum pump is throttled with a needle valve.

The rare gas continua can be produced by a high-power pulsed discharge in the pure gas. The MSU instrument utilizes a home-built, single vacuum tube, high-power switching circuit to pulse the output of a (Megavolt) high voltage d.c. power supply. The switching circuit is in turn driven by a Cober A model 605P high-power pulse generator.

The hydrogen many-line pseudo continuum is produced by a d.c. discharge in pure hydrogen at a pressure of 2-4 torr. The d.c. high voltage power supply used in the switching circuit, from which it is disconnected in this application, powers the hydrogen discharge. A 15009, 1500 W resistor limits the current drawn from the supply.

The helium discharge produces light in a higher energy range than does the hydrogen lamp. However, the Roots blower which forms part of the lamp gas vacuum system was broken during the course of these experiments. Thus it was not possible to put 70 torr, which is the necessary operating pressure for helium, into the discharge lamp. Even for the hydrogen lamp, the normal operating pressure of 3 torr was too high. The pressure was decreased to 2 torr and the Megavolt supply was maintained at 2.75 kV and 700 mA. This gave a negligible decrease in the intensity of the hydrogen many-line spectrum and these operating conditions were used for all of the experiments described in this thesis.

Ionization and appearance energies of p-dioxane and 12-crown-4 and their fragments fall in the region where the hydrogen pseudo continuum is a suitable light source (9-13 eV). In the case of the isomers of dibromobenzene threshold PIEs of the parent ions are also easily measured with the hydrogen pseudo continuum, but with this light source only two of the fragments, CeH4Br⁺ and CeH4⁺ could be formed. Other fragments, either due to higher AE's or lower intensities, were not measurable when the hydrogen lamp was used as the irradiation source. Even the benzyne cation (CeH4⁺) has very low intensity in the energy range of the hydrogen lamp, and it's AE is very difficult to measure.

2. Monochromator

The monochromator is a McPherson model 225, 1-meter, nearnormal-incidence instrument. The dispersing element used for this research is a concave osmium-overcoated aluminum grating, ruled with 600 lines/mm and blazed at 900A (Another grating, magnesium fluoride overcoated, ruled with 1200 lines/mm and blazed at 1200A is also available in the laboratory.) The grating has a reciprocal dispersion of 16.8A per mm.

Two interchangeable entrance slit plates are available. Each plate has a blank port plus three fixed slit widths: 10µm, 50µm and 100µm, or 100µm, 300µm, and 500µm. For a given plate, the entrance slit can be changed without breaking vacuum via a knob located outside of the vacuum changer. Interchangeable exit slit tracks are also available, each of which has four fixed slit widths: 10µm, 50µm, 100µm, and 300µm, or 100µm, 300µm, 500µm and 1000µm. Any one of the four slits on a given track can be selected from outside the vacuum via a knob-chaingear system.⁷⁵ The procedure for interchanging entrance and exit slit mounts is given in the PIMS operations manual. The grating is driven

by a stepping motor which can be operated manually or with a computer.

The grating should be cleaned when the helium lamp spectrum shows significant scattered light below 500A To clean the grating, first rinse with Freon 11 (CFC1₂), followed by high purity methanol. The methanol rinse is best done by simultaneously applying the methanol from a squeeze bottle and drying the grating with low pressure (10 torr), clean, compressed air, working from top to bottom. The removal, cleaning, replacement, realignment and focusing procedures are listed in the McPherson monochromator manual. Because realignment of the grating requires adjustment of many parameters. a great deal of time can be saved if the grating is cleaned in situ. In this case, care should be taken to direct the cleaning solvents only on the grating (some absorbing material--such as Kimwipes--can be placed around the bottom of the grating mount), and sufficient time thereafter (about one day) should be allotted to allow vaporization of the solvents from the loosely-covered monochromator under moderate nitrogen gas flow.

3. Interaction Region and Sample Inlet System

The ion source is a cubical stainless steel box, one inch per side, located one centimeter beyond the exit slit of the monochromator. It has two rectangular apertures on opposite sides to enable transmission of the photon beam. The widths of the rectangular apertures are adjustable to allow uninhibited passage of the photon beam with any chosen exit slit. On the horizontal plane perpendicular to the optic axis is a one-quarter inch diameter ion exit hole. The ion aperture is covered with a high-transmission fine wire grid to minimize penetration into the source of electric fields from the ion focusing lenses located
just outside. The repeller, an electrically-insulated stainless steel plate, is positioned inside the ion source across from the ion exit aperture. An adjustable voltage is applied to the repeller to accelerate the ions from the source into an ion lens system.

The sample is admitted through a tube located behind the repeller and the sample pressure is measured through a tube in the top of the ion source. The sample pressure is controlled with a Granville-Phillips model 203 adjustable leak valve and measured with a Datamatrics model 1014-A Barocell capacitance manometer. The leak valve and manometer are outside of the high vacuum.

4. Photon Transducer

The photon transducer is a sodium salicylate phosphor whose emission intensity is measured with an RCA 8850 photomultiplier tube. Because sodium salicylate possesses a nearly constant quantum yield throughout the helium continuum, and that portion of the hydrogen many-line output of interest in this work, it is superior to ordinary (bare) photomultiplier dynode chains. The sodium salicylate emission intensity can be accurately measured with a standard photomultiplier and the emission band does not shift with the exciting wavelength. The output current of the photomultiplier is amplified with a Keithley 1800 current amplifier and converted to a voltage. Then it is digitized with a voltage-to-frequency converter and a computer-interfaced counter.⁹¹

When used with the Hopfield helium continuum, the sodium salicylate transducer detects a great deal of scattered light. This effect is corrected by automatically making repeated measurements of the scattered light during the course of an experiment, then subtracting this contribution from the observed intensities. The scattered light problem is much less bothersome when the hydrogen lamp is used, since this source emits less visible and near ultraviolet radiation and since the many-line spectrum does not begin until wavelengths greater than 800A, which is a region where the scattered light distribution has fallen off considerably.

5. Ion Optics and Mass Spectrometer

The ions are guided from the ion source and focused onto the quadrupole mass filter with four electrostatic aperture lenses. The electrostatic lens system was supplied with the commercial mass filter, and has been modified by removal of the electron impact source. The mass filter is an Extranuclear 324-9 quadrupole mass filter, with rods 1.9 cm in diameter times 22.0 cm long. It is powered by a model 311 power supply, equipped with a model E (mass range 0-200 amu) or a model 13 (mass range 0-400 amu) high Q head. The quadrupole (as well as the lenses and ion transducer which are connected to it) is mounted on a support which is easily moved several inches in a direction parallel to the quadrupole axis. This permits placement of the quadrupole at an appropriate distance from the photon beam for use with single or dual chamber ion sources of various depths. The mass of the ions transmitted by the mass filter is controlled by a dial on the front panel of the quadrupole power supply or by a voltage applied to a connector on the back side of power supply. To obtain a mass spectrum, the transmitted mass is scanned by a mass scanner which applies a voltage ramp to the connector on the back panel of quadrupole power supply; the mass scanner was designed and constructed by David Rider.75

When the high Q head is changed or after about six months of continuous use of a given head, the mass filter needs to be "tuned up" to rematch the RF frequency of the quadrupole power supply and the high Q head. The detailed procedures are listed in the Extranuclear quadrupole filter manual.

6. Ion Transducer

The ion transducer, located on-axis at the exit hole of the quadrupole, is a Channeltron continuous-dynode electron multiplier, model CEM 4816, supplied by Galileo Electro-optics. The channeltron output is measured either in a direct-current or a pulse-counting mode. In the former mode the output is amplified with a Keithley model 417 electrometer. However, since the direct-current method has several disadvantages compared to pulse counting when the output current is small, it was used only for setting up an experiment. All data were collected with a pulse-counting technique, where the output pulses are amplified and discriminated with a circuit developed here.

7. Vacuum System

In order to maintain the required pressure differential between the lamp ($\approx 10^2$ torr) and the monochromator ($\approx 10^{-6}$ torr), two stages of differential pumping are used. The monochromator is equipped with a McPherson model 820 differential pumping assembly, the first stage of which is pumped with a 300 liter/sec Roots blower pump. (It is this pump which failed during the course of this work, thus precluding use of the He lamp.) The second stage is pumped by a 300 liter/sec, fourinch diffusion ejector pump, and the monochromator with a 2400 liter/sec, six-inch diffusion pump. The sample and quadrupole chambers are also pumped with six-inch diffusion pumps, rated at 2400 liter/sec and 1800 liter/sec respectively. A baffle around the quadrupole also provides some measure of differential pumping of the sample gas in these chambers.

The pumping speeds quoted above are for untrapped pumps. All four diffusion pumps are trapped with Freon-cooled baffles to reduce the amount of oil back-streaming into the chambers; thus the actual pumping speed in the various chambers will be significantly lower. When the system was pumped down, the best pressure obtained was $9.0x10^{-7}$ torr. Nevertheless, these pumps are sufficient to maintain a pressure on the order of 10^{-5} torr in the monochromator with 70 torr of helium in the lamp (100 µm entrance slits). The pressure in the quadrupole region can be maintained below $2x10^{-5}$ torr for a sample pressure below $2x10^{-3}$ torr, even with the relatively open ion source currently in use.

8. Interlock System

The vacuum and utility service systems in the PIMS instrument are quite complex. Even though each component in the system may be rather dependable, there are so many components involved that the possibility that something will fail in any given time period is quite high. Moreover, even if the individual vacuum components were completely reliable, the necessary electrical and water utilities supplied by the University are not. Thus occasional failures of the vacuum system are inevitable. If proper procedures are not taken, the expensive components inside the vacuum chambers (the grating, channeltron, and quadrupole rods) may be irreparably damaged. All of these components are extremely sensitive to the presence of even very thin contaminating films of pump oil. Thus a security interlock system which monitors the foreline pressure of all diffusion pumps, water pressure of the diffusion pump cooling system, baffles, lamp gas pressure, electrical part of the lamp, and all mechanical pumps has been implemented⁹¹ to reduce the chance of catastrophic damage to the PIMS apparatus.

The interlock system for this instrument was designed as a "stand-alone" system which is not computer operated; it can thus be used to protect the instrument between experiments as well as during them, allowing the instrument to remain safely under full vacuum conditions at all times. Even so, the interlock system is not sufficiently sophisticated to totally automate the pump-down procedure. However, it does mandate the correct sequence of operations during start-up, which greatly reduces operator errors--although it cannot eliminate them. When used to protect the unattended instrument, the action taken by the safety interlock system when an error condition is detected is very simple: any device which, if left on, could conceivably be harmed or cause harm to another device is deactivated. The vacuum system then remains shut down until an operator decides that it is safe to start again.

9. Instrument Control and Data Acquisition

The computer used to control the PIMS instrument during the course of this research was an antiquated PDP 8/F minicomputer (12-bit word length), which has 16K of memory. A PDP 8/M (12-bit word length, 12K memory) is also available for PIMS experiments. Data and program storage peripherals include a dual floppy disc drive (Sykes 7200 series) and an interchangeable hard disc (WANGCO F-1221). Interaction between

the user and the computer takes place via a Heath Z-19 terminal or a Tektronix 4010 graphics display terminal.

The data are collected by using a variable integration time technique which permits recording data of the desired quality in an optimum amount of time. The monochromator wavelength is stepped in preset intervals, and, after each step, ion and photon counts are accumulated until the datum has the desired signal-to-noise ratio. Photon and ion count rates, wavelengths and integration times are stored on a floppy or hard disc. The course of the experiment is continuously monitored via a computer-interfaced, stepped, stripchart recorder on which the real time PIE is plotted. Periodic measurements of "light" and "dark" photon and ion count rates are made at a reference wavelength so that the data can be corrected for sample pressure and instrument drift. Approximate corrections for stray light are made by measuring the light intensity at two wavelengths where the helium continuum does not emit. Final corrections of the data for sample pressure variations, instrument drift and stray light, as well as the final plot, are discussed in the procedure section of this chapter.

C. Experimental Procedure

This section presents a flow chart to show how to run a photoionization mass spectrometry experiment. The difference between this section and the operations manual is that this discussion indicates when and why to do each procedure, whereas the operations manual describes how to do it.

The experimental procedure introduced will follow the order of an experiment. Sometimes several steps may be started at the same time; higher priority steps will be listed first. To continue an aborted run,

or to start a new experiment upon termination of another, the entire sequence may not have to be repeated. Under these circumstances, just skip unnecessary steps and continue to the next one.

1. Samples

1,4-dioxane was obtained from the J. T. Baker Company; para-C4DeO: was purchased in sealed ampoules from the Stohler Chemical Corp.; 12-crown-4 and ortho- and meta-dibromobenzene were obtained from the Aldrich Chemical Company Inc. Para-dibromobenzene was purchased from the Eastman Kodak Company. All samples were thoroughly degassed by repeated freeze-pump-thaw cycles and used without further purification. For the PIE measurements the sample pressure in the ion source was maintained below $5x10^{-4}$ torr and 100 μ m monochromator entrance and exit slit widths were generally employed. For photon energy- and pressure-dependence studies, 500 μ m slits were employed. The sample pressure was measured with a calibrated ionization gauge which was directly connected to the ion source.

2. System Pump-Down

If the PIMS instrument is completely shut down, the following procedure is required. Two parts of the overall system must be initially pumped down, the main part of the system (monochromator, sample and quadrupole chambers) and the lamp gas system. In the main part of the system, after all the diffusion pumps have been turned on and all the gate valves have been opened, the system pressure should be lower than 1.0×10^{-6} torr. Normally it is easy to reach 2.0×10^{-6} torr with a proper degas; sometimes the pressure can be as low as 9.0×10^{-7} torr. After the main chambers have been pumped down, the sample gas line should be evacuated. The purposes of doing this are: (1) to pump out the air in the sample gas line, (2) to remove any residue of previous gas samples, and thus avoid contamination of the sample, and (3) to check for leaks in the sample gas line connection. Any leak in the sample gas line will allow air to enter the system, which will change the sample gas purity and lead to extra peaks in the mass spectrum. The lamp gas system is pumped by a mechanical pump only. This part of the system must be absolutely leakproof; this is tested by closing the valve between the line and the mechanical pump, and monitoring the pressure change via a thermocouple gauge. If the rate of pressure increase is less than 1.0×10^{-2} torr/min, the lamp gas system is considered sufficiently leakproof. Any leaks in the lamp gas system will contaminate the lamp gas, and produce dirty lamp spectra, including many sharp atomic lines. A dirty lamp gas system (especially when the helium discharge is used) will make data correction harder. The molecular sieve trap in the lamp gas system has to be cleaned periodically when helium gas is used. To clean the sieve, heat the heating tape around it up to 200-210°C and continue pumping until the pressure of whole systems return to normal.

3. Lamp Spectra

The main purpose of running a lamp spectrum is to check the lamp system quality. Are the emission intensities as expected, and do the wavelength settings in the computer coincide exactly with several calibration lines? From a lamp spectrum, one can determine the condition of the lamp, the calibration of the monochromator and the purity of the lamp gas. Different observed phenomena infer different kinds of problems. A lamp spectrum provides not only the information

mentioned above, but also information about the optimum voltage setting of photomultiplier, the scale of the amplifier, the photon signal, etc., which are parameters to be set before an experiment is initiated. The lamp spectrum can be generated with the grating rotation either under manual or computer control.

4. Mass Spectra

Before photoionization efficiency curves from a given precursor can be obtained, the mass spectrum of the sample gas must be acquired on the PIMS instrument. Photoionization of the sample is accomplished under full illumination of the helium or hydrogen light source. То obtain the mass spectrum, set the monochromator to the "central image", i.e., zero A which is offset by $\approx 100A$ on the wavelength counter, whereby all of the light from source is reflected from the grating into the reaction region. If the entrance and exit slits are opened to their widest position, maximum photon intensity from the light source impinges on the sample gas. The mass spectrum serves several purposes. (1) It provides a test of the sample gas purity. Because most standard mass spectra are obtained under bombardment of 70eV electrons, one must be careful when comparing PI and EI mass spectra. Although there was generally good agreement between the mass spectra obtained in this work and those tabulated in the literature, the expected variation in the relative intensities of the peaks (both parent and fragment ion) was observed, and highly fragmented daughter ions produced at high ionization energies were sometimes missing from the PI mass spectra. If the photoionization mass spectrum shows several extra peaks compared to the standard mass spectrum, it is probable that the sample gas may be contaminated by some impurity, or that the sample gas inlet line has

a leak. (2) One can easily determine how many ions can be produced from a given sample gas by the light source. In principle, a PIE curve is obtainable for every ion revealed by a peak in the mass spectrum; the intensity of each peak gives a good idea about how difficult it will be to do that experiment. (3) It is convenient to change the conditions to start the next procedure. Simply change the entrance and exit slits to the desired positions. For a given photon energy range, the lamp gas (helium or hydrogen) can be maintained while PIEs are measured for several different ions from a single sample gas.

5. Experimental Set-Up

After the mass spectrum has been obtained, the next step is the choice of an ion for which the photoionization efficiency curve is to be measured. After a particular ion is chosen, the mass filter is set to the corresponding mass region, and the ion optics are adjusted to maximize the ion intensity. Scan the mass in the appropriate region to confirm that the transmitted ion is indeed the one selected; this is facilitated if the ion of interest contains atoms which have characteristic relative isotopic abundance patterns. Sometimes improper adjustment of the ion optics will still allow ions to pass through the mass filter, but the isotopic ratios will not be correct. Once the desired ion is properly identified, reduce the resolution to broaden the peak and thus increase the ion signal. (However, the resolution must not be lowered so far that ions of different m/z are transmitted.) Find a relatively smooth portion of the broadened mass spectrum and lock the mass filter at this m/zvalue. Then small drifts in the quadrupole tuning during the course of long experiments will not affect the photoionization efficiency. All the procedures described above can be done either by the computer or

manually. Hereafter, all the procedures will be done under computer control.

Many parameters must be considered when setting up a photoionization mass spectrometry experiment; these parameters have a great influence on the resulting photoionization efficiency curve. It is necessary to do a quick experiment (or perhaps several) to help decide how to choose these parameters. From the quick run, one can draw conclusions about the following aspects of the final experimental photoionization efficiency curve: (1) the desired signal-to-noise ratio (consistent with time constraints); (2) the duration of the experiment; (3) the energy region which is to be scanned; (4) the wavelength to be chosen for the reference measurement; (5) the desired wavelength resolution; (6) the wavelength interval between successive data points. and (7) the sample pressure. For the actual experiment one also needs to decide: (1) how frequently and for how long to measure the background and reference signals, and (2) where and for how long to measure the stray light. After all these parameters are determined, one can start an experiment.

6. Data Correction

Once an experiment is set up, data collection and storage are controlled with a PDP 8/M or PDP 8/F minicomputer. The periodic reference measurement is made to correct for sample pressure variation and instrument drift. A shutter is closed in front of the monochromator exit slit under computer control so that the periodic background measurements can be made. Dark counts generated in the detectors are also stored and will be subtracted from the ion and photon signals, which are obtained when the shutter is open, in the later procedures. The stray light measurement is made to correct for the stray light contribution to the photon data. After these three corrections, which are made at the department computer facility (PDP 11/34) or on a PDP 11/23 in the Leroi laboratory, a comparison of the ion signal with the photon signal is made to ascertain whether corrections are necessary for artifacts caused by the finite slit width, scattered light, or detector misalignment. (For more detailed information on these points, see reference 91.) After all of these corrections are made, the final photoionization efficiency curve is plotted out and the experiment is complete.

CHAPTER IV

PHOTOIONIZATION AND FRAGMENTATION OF o-, m- AND p-DIBROMOBENZENE

A. Introduction

In contrast to their monohalo counterparts, very little information is available regarding the ionization and fragmentation of the Thus, although the ionization energies of the three dihalobenzenes. dibromobenzene isomers have been reported from photoelectron spectroscopy (PES) measurements,^{7,92-93} neither the energetics nor the dynamics of fragmentation processes involving the ortho-, meta- or para-dibromobenzene cations have been studied. The interaction of vacuum ultraviolet radiation with o-, m- and p-dibromobenzene has been investigated at low sample pressures in order to obtain thresholds for their ionization and fragmentation. In addition to monitoring the effects of the substituent geometry, the measurements can be combined with available thermochemical data for the neutral (fragmentation products) to provide good estimates of bond dissociation energies and of heats of formation for the parent and daughter cations.

The interaction of ionizing radiation with gases leads first to molecular ions with a distribution of internal energies. In competition with other deactivation channels, these ions may isomerize and/or dissociate if their internal energy exceeds the thresholds for such reactions. Isomerization among dihalobenzenes has been observed both in solution⁶ and in rare gas matrices.^{94,96} A photoionization mass spectrometric (PIMS) study of o-, m- and p-dibromobenzene in the gas phase has been carried out, in which both isomerization and dissociation are observed. From the measured appearance energies and ancillary thermochemical data, upper limits for the heats of formation of the parent ions and for C₆H₄Br⁺ and C₆H₄⁺ have been obtained which are more reliable than previously reported values. The enthalpy of formation of neutral o-benzyne (C₆H₄), a likely intermediate in may organic reactions,⁹⁶ is also estimated.

B. Results

Photoionization efficiency (PIE) curves in the 9 eV region for the ortho-, meta-, and para-dibromobenzene parent ions are shown in Figure IV-1. The ionization energies (IEs) for the molecular ions were determined by expanding the threshold region and extrapolating the straight-line portion of the appropriate PIE curve just above the ionization onset back to the baseline. The IEs of the isomers are distinct and distinguishable. An expanded plot of the paradibromobenzene cation PIE in the 8.5-9.5 eV photon energy range is shown in Figure IV-2. Step-like structure is observed which is attributable to a vibrational progression in the ionic state; the vibrational separation is approximately 0.025 eV ≈ 200 cm⁻¹.

The PIE curves of the C4H4Br⁺ and C4H4⁺ daughter ions generated by dissociative ionization of each of the isomeric dibromobenzenes are collected in Figures IV-3 and IV-4. The appearance energy (AE) of a given fragment cation was chosen as the energy at which the PIE first rises perceptibly from the baseline. Because of possible kinetic shift,





The PIE Curves for the Ortho-, Meta- and Para-Dibromobenzene Parent Ions.







Figure IV-3 The PIE Curves of the CoHABr* Daughter Ions Generated by Photofragmentation of Each of the Isomeric Dibromobenzenes.



Figure IV-4

The PIE Curve of the CoH4⁺ Daughter Ions Generated by Photofragmentation of Each of the Isomeric Dibromobenzenes.

reverse activation energy and other factors,⁷⁰ this value must be considered an upper limit to the desired adiabatic AE. The IE and AE values obtained in this work are listed in Table IV-1, where the relative intensities of the cations from each precursor, obtained under full illumination of the hydrogen discharge and verified by 15-20 eV electron bombardment, are also given. In addition to other factors which vary little from one PIE curve to another the error in an extrapolated IE or AE depends on the available photon intensity. With the hydrogen lamp the intensity is high in the vicinity of the parent ion thresholds, and rather low in the AE range of the daughter ions. Wider slits were employed in the latter cases, which leads to larger error in the measurements. Also, the PIE curves of the parent ions rise more sharply and uniformly than those of the daughters, which permits more accurate extrapolation to the baseline. These factors are responsible for the lower error reported for the parent ion threshold energies.

The threshold energies obtained in this work were combined with literature thermochemical data to obtain the room temperature enthalpies of formation for the cations studied. The identities of the neutral partners, the values of their heats of formation used in the calculations, and the ionic heats of formation determined therefrom are also listed in Table IV-1. The enthalpies of formation of the neutral parents were calculated from group additivity tables;⁹⁷ those of Br and Br: are rather precisely known.⁷⁶⁹ The bond dissociation energy for removing a Br atom from the benzene ring in CaHaBrs⁺ can be determined directly from the difference in the threshold energies of the fragment and molecular ions. [Bond Energy = $\Delta He^{0}(CeHaBr^{+}) + \Delta He^{0}(Br)$ -

AH# (CeHaBrs*) = A.E. (CeHaBr*) - I.E. (CeHaBrs*)]. These bond energies are given in the last column of Table IV-1.

Within the photon energy range of the hydrogen lamp, the ion signal at m/z = 154 is negligible, and that at m/z = 156 can be accounted for by the natural distribution of ¹³C in the CeHeBrs precursors. There is no evidence of the production of CeHeBr⁺ under our experimental conditions, probably because the photon energy is below the activation energy for HBr loss. Moreover, the absence of ions at m/z = 77 (CeHs⁺) indicates that the samples are not contaminated by CeHeBr, a possible impurity.

C. Discussion

The first ionization process in substituted benzenes involves removal of a π -electron from the ring; the value of the ionization energy is sensitive to the nature and symmetry of the substituents.** The vertical ionization energy of bromobenzene is 9.041 eV, and those of the dibromo derivatives are slightly lower. The order and the numerical values of the IEs of the three isomers determined in this PIMS study are compared with those obtained by PES^{7,92,93} in Table IV-2. The agreement is excellent. Photoionization gives IEs about 0.05-0.1 eV lower than the vertical photoelectron values. Although the ortho- IE is lower than that of the meta isomer in each report, their difference is within the combined experimental errors of the determinations. However, the p-CeHaBra IE is lower than those of the other isomers by more than the experimental error. Its enthalpy of formation (Table IV-1) is also the lowest of the three. The highest occupied T-molecular orbital in the benzene cation is split upon monosubstitution into ${}^{2}B_{1}$ and ${}^{3}A_{2}$ components. Para (1,4) disubstitution is predicted^{92,99} to give special

stabilization to the ${}^{3}B_{1}$ orbital (${}^{3}B_{22}$ for identical substituents), and this is reflected in our experimental results. Vibrational structure is clearly evident in the threshold region of the p-CeH4Brs⁺ PIE curve, Figure IV-2. Prominent steps, uniformly separated by approximately 0.05 eV, are evident above 8.85 eV. Less pronounced steps can be identified at the mid-points of these intervals, as designated by the vertical lines in the Figure. Similar vibrational structure is seen in the high resolution [Ne(I)] PES spectrum of p-CeH4Br2, where a progression with separation of about 0.025 eV is observed and identified as ve (aq),¹⁰⁰ the symmetric C-Br stretching vibration in the ground ionic state.

We report the I.E. of $p-C_{6}H_{4}Br_{2}$ as 8.85 eV. Another step is apparent at 8.80 eV in Figure IV-2. We consider the higher value to be more reliable because the height of the lower-energy step is within the noise level of the data below the threshold, and because it could be due to ionization of the neutral in a thermally excited vibrational state (i.e. due to hot bands).

The PIE curves of the CeHeBr^{*} and CeHe^{*} fragment ions from the isomeric dibromobenzenes (Figure IV-3 and IV-4) have been measured for the first time. Within experimental error, the AEs for the (bromineloss (M-Br)^{*} daughter) ions are the same (12.16 \pm 0.05 eV) for all three isomers (see Table IV-1). This does not necessarily lead to the conclusion that the energy required to break the first C_{bs}-Br bond is independent of the position of the second Br substituent. It is likely that the dissociation energy for the loss of one bromine atom lies above the energy required for substituent isomerization (scrambling) in the ion. (Additional evidence in support of this suggestion is presented below.) Thus, the same ionic precursor would dissociate in each case with the same threshold energy. The calculated bond dissociation energy is the same for each isomer within experimental error. The numerical value, $314 = 7 \text{ kJ mol}^{-1}$, matches well the Cbs-Br bond energy tabulated¹⁹¹ on the basis of an empirical bond energy scheme. Although decomposition of $C_{6H_4Br_2}^*$ to form $C_{6H_5Br_4}^*$ + Br involves simple bond cleavage and probably passes through a loose transition state with little reverse activation energy,¹⁰² the experimental threshold may involve a significant kinetic shift.⁷⁷ For example, it has recently been shown by elegant time-resolved photoionization mass spectrometry (TRPIMS) measurements that a kinetic shift on the order of 0.3 eV accompanies a normal PIMS determination of the AE of CeHs⁺ from CeHsBr.³ Thus the CeHaBr* AEs given in Table IV-1 must be considered upper limits to the desired 0 K threshold energy.

The threshold portions of the PIE curves for CaHa⁺ produced from o-, m- and p-dibromobenzene are shown in Figure VI-4. Due to the weakness of the ion signal, competition with Br-loss fragmentation, and kinetic shift effects, the AEs can be determined less precisely than those of the parent ions and CoHaBr*. Not only are the values for the three isomers the same, well within experimental error $(12.4 \pm 0.1 \text{ eV})$, but the appearance energy for production of CeH4⁺ from CeH4Br2 is only very slightly higher than that for formation of CeH4Br⁺. This result is consistent with photoionization results from benzene, where the threshold energies of CaHa⁺ and CaHa⁺ are the same within experimental uncertainty,^{60,105} as well as with multiphoton ionization studies on benzene.^{104,105} It is worth noting that compared to AE (CeH4Br⁺), the experimental AE of CoHa⁺ is likely to be a less reliable upper limit to the threshold energy. (For CeHe⁺ from CeHe the experimentalthermochemical difference is about $1 \text{ eV.}^{90,100}$) With these considerations in mind, it is concluded that within experimental error the activation energies for the formation of CeHeBr⁺ and CeHe⁺ from each of the isomeric CeHeBr²⁺ cations are the same.

Thermochemical information can be used to determine that CeHe⁺ is produced from o-CeHeBr₂ by the reaction:

$$o-C_{eH_4Br_2} + h\nu \rightarrow C_{eH_4} + Br_2 + e^-$$
 AE = 12.40 + 0.1 eV.

If the neutral partner is Br₂ we find $\Delta H^{o}_{f}(298)$ for CeHe⁺, most likely the 1,2 dehydrobenzene (benzyne) cation, to be 1283 + 15 kJ mole⁻¹. This is slightly lower than the value suggested by Rosenstock and coworkers;^{60,107} it is probably a better upper limit. If two Br atoms were formed instead, the heat of formation of CeHe⁺ derived from the experimental AE would be 1088 kJ mol⁻¹, a value well below the expected range.⁷⁶

The same thermochemical arguments can be applied to meta- and para-dibromobenzene. If one combines the heat of formation for CeHe⁺ determined from the o-CeHeBr₂ precursor with the experimental AEs and the enthalpy of formation of the appropriate parent molecule, the heat of formation of the accompanying neutral fragment(s) is calculated to be on the order of 30 kJ. This is consistent only with the formation of Br₂, not two Br atoms. The loss of Br₂ upon photo-fragmentation of CeHeBr₂ to form CeHe⁺ thus is not restricted to the isomer initially possessing adjacent Br ring substituents. This result is consistent with the earlier conclusion that isomer scrambling reactions take place prior to or concurrent with the fragmentation.

Isomerization accompanying fragmentation of benzene cations is now well established.¹⁰⁶⁷ Ion fragments produced from deuterated,¹⁰⁹ ¹³C-labeled and doubly-labeled species¹¹⁰⁻¹¹³ retain no "memory" of the position at which the labels were placed. Mass spectrometric measurements on deuterium-labeled chlorobenzenes also show that label scrambling occurs.¹¹⁴

the dissociative ionization The results of study of the dibromobenzenes are summarized in Scheme IV-1. The mechanism of the isomer scrambling cannot be determined from this PIMS investigation Photoelectron spectroscopy shows that several excited ionic alone. states exist below the photofragmentation thresholds determined here. Their energies and probable symmetry assignments are given in Table IV-3. The state assigned with A-symmetry which lies above 12 eV involves removal of a ϵ C-Br bonding electron, and it is tempting to implicate it as a localized state from which unimolecular decomposition occurs, or at least to consider it a "doorway" state to fragmentation on a lower-lying potential energy surface. However, the true thresholds for Br loss, and probably for Br: loss as well, likely lie at slightly lower energies. Moreover, it is now established from photoelectronphotoion coincidence (PEPICO) measurements and time-resolved PIMS that fragmentation of the mono-halobenzene parent ions to form CeHs⁺ occurs through a loose transition state on the ground ionic state surface in the cases of CeHsI 102 and CeHsBr, 30,115 and perhaps for CeHsCl, also.115-117 The ionic fragmentation of benzene to form CeHs⁺ and CeHe⁺ occurs



competitively on the ground state CeHe⁺ surface,⁸⁰ although as noted earlier, the isotopic scrambling of ring and substituent labels reveals that surface crossings have occurred prior to fragmentation.¹⁰⁰ It is unlikely that photofragmentation of CeHeBr₂ to form CeHeBr⁺ and CeHe⁺ occurs by a different mechanism, although experiments where the threshold kinetic shift and the internal energies of the fragments can be measured are required to confirm this conclusion.¹¹⁰

The vertical ionization of the dibromobenzenes can produce parent ions in any electronic state below the excitation energy. Thus the ions which subsequently fragment initially may be formed with electronic rather than vibrational excitation, and competition among various deactivation channels (e.g direct decomposition, internal conversion, Our results show that the o-, m- and pradiation) will ensue. dibromobenzene parent ions are distinguishable at the ionization threshold, but that the nature of the ion which fragments to form either CeH4Br⁺ or CeH4⁺ is independent of the substituent distribution on the neutral precursor. Substituent scrambling is likely to occur concomitant with internal conversion surface crossings, and in this case the ³B₁ (*B# for $p-C_{sH_4Br_2}$ state [10.64 - 11.08 eV, Table IV-3] may be involved. Elegant photoionization matrix experiments on isomeric di- and tri-chlorobenzenes by the Andrews group^{94,95} have demonstrated that photochemical rearrangements of the molecular cations can be induced. For example, o-CeH4Cl2⁺ is converted first to m-CeH4Cl2⁺ and then to p-CeHeCla⁺ upon continued visible irradiation of an o-CeHeCle*/Ar matrix: similarly, matrix-isolated m-CeHeCla* rearranges to yield the p-CeHeCla* isomer.⁹⁶ The stability coincides with the relative order of the corresponding ²B₁ or ²B₂₀ excited electronic state of the three dichloro isomers. This excited state is formed upon removal of a halogen **m**electron from the neutral molecule,¹¹⁹ which leaves a chlorine lone pair hole in the parent ion. It is suggested that an excited, bridged chloronium cation then forms, and that isomerization occurs via a "chloronium ion walk" around the ring to the most stable isomeric form, which relaxes to the ground cationic state in the matrix.⁹⁵ In the case of the gaseous dibromobenzene cations this mechanism, a bromonium ion walk, could account for the observed isomeric scrambling prior to fragmentation, and for the substituent proximity required for the concerted loss of Br: which accompanies the formation of CaHa^{*}.

The enthalpy of formation of neutral ortho benzyne, CeH4, can be calculated from the CeH4⁺ appearance energy if the other necessary thermochemical data are known. If we accept 9.45 eV as the adiabatic ionization energy of benzyne,¹²⁰ then $\Delta H^{0}_{2299}(CeH4) = AE (CeH4^+) - IE$ $(CeH4^+) + \Delta H4^{0}(CeH4Br_{2}) - \Delta H4^{0}(Br_{2})$ is calculated to be 370 ± 20 kJ mol⁻¹. This value is at the low end of the range suggested previously in the literature on the basis of other experimental^{114,129,121} and theoretical^{122,133} considerations, but we believe that its accuracy is within the quoted uncertainty limits.

m/z	Ion	Neutral	Rel. Int.ª	IE or AE (eV)	ΔH°f298 (kJ/mol)	Cbs-Br Bond Energy ^d (kJ/mol)
234-8	p-Ce He Br2*	p-Ce He Br 2	100	8.85 ± 0.02	966.9 ± 7 113 ± 5 ^b	
155-7	Ce He Br+	Br	17	12.17 ± 0.05	1175.3 ± 10 111.884°	320 ± 7
76	Се На +	Br2	6	12.33 ± 0.1	1271.8 ± 15 30.907°	
234-8	m-Ce He Br2*	∎-Ce He Br2	100	8.95 ± 0.02	976.5 ± 7 113 ± 5¤	
155-7	Ce He Br+	Br	15	12.15 ± 0.05	1173.4 ± 10 111.884°	309 ± 7
76	Ce He +	Br2	5	12.44 ± 0.1	1282.4 ± 15 30.907°	
234-8	0-Ce H4 Br2*	o-Ce He Brz	100	8.91 ± 0.02	976.7 ± 7 117 + 5°	
15 5-7	Ce He Br⁺	Br	14	12.16 ± 0.05	1178.3 ± 10 111.884 ^c	313 ± 7
76	Ce He +	Br2	5	12.40 ± 0.1	1282.5 ± 15 30.907°	

Table IV-1. Threshold Energies and Thermochemical Data Relevant to the Photoionization and Fragmentation of p-, m- and o-Dibromobenzene.

*Under full illumination of the hydrogen discharge; ± 5 %.

^bCalculated using group equivalents, Reference 97.

^cReference 78, pp. I-780-1.

^dFor the reaction: C₆H₄Br₂⁺ → C₆H₄Br⁺ + Br

	I.B. (eV)					
Neutral	PIMS*	PESb	PBSc	PESd		
o-Ce He Brz	8.91	8.99	9.02	9.05		
n-Ce Ha Br2	8.95	9.05	9.10	9.07		
p-Ce Ha Br2	8.85	8.90	8.91	8.90		

Ionization Table IV-2. Comparison of First Energies of the Dibromobenzene Isomers Obtained by PIMS and PES.

^aThis work.

^bCvitas and Klasinc, Reference 7.

^cStreets and Ceasar, Reference 92.

^dKimura, et al, Reference 93.

o-Ce He Br2+		m-Cs	He Br2+	p-Ce He Brz+		
² A2	9.05	² A2	9.07	² B2 s	8.91	
2 B 1	9.45	² B1	9.57	² B1 <i>4</i>	9.79	
² B2	10.33	2 B 1	10.73	² B _{3 u}	10.64	
2 B 1	11.08	2 A 1	10.86	² B _{2 u}	10.04	
² A1	11.3	² B ₂	11.15	² B3∎	10.94	
² B2	11.38	² B ₂	11.95	² B ₂	11.94	
² A1	12.15	² Å1	12.28	2 Ag	12.34	

Table IV-3. Vertical Ionization Energies (in eV)^a and Suggested Symmetry Assignments^b of Dibromobenzene Cation Electronic States.

^aThe energy above the ground electronic state of the neutral for those states below 12.5 eV; ortho- and meta- isomers from Reference 93, paraisomer from Reference 100.

^bFrom Reference 119 and PES peak shapes; some of the assignments differ from those given in Reference 100 on the basis of SCF calculations.

CHAPTER V

PHOTOIONIZATION MASS SPECTROMETRIC STUDY OF 1,4-DIOXANE: THERMOCHEMISTRY AND ION-MOLECULE REACTIONS

I. Introduction

The formation of proton-bound dimers in gas phase ion-molecule reactions and the formation of higher charge held aggregates has been the subject of extensive studies.¹²⁴⁻¹²⁷ A prominent application of gasphase ion chemistry is the determination of intrinsic reactivity of molecules free from complicating solvent effects.¹³⁴⁻¹³⁷ Quantitative measurements of clustering reactions, generalized in equation V-1,¹³⁸

$$M^*B_{\mathbf{B}} + B \rightarrow M^*B_{\mathbf{B}+1} \tag{V-I}$$

provide a detailed description of solvation energetics and help bridge the gap between gas and condensed phases. Typically M^+ is a simple monatomic ion such as H^+ , Li^+ , Na^+ , K^+ , F^- , Cl^- , Br^- or I^- and B is H_2O , NH₂, etc.¹²⁹⁻¹³¹ In the experiment described in this chapter, M^+ is H^+ , B is p-dioxane (p-C₄H₂O₂) and n is one.

The formation of proton-bound dimers of p-dioxane and their reaction with acetone have been studied by ion cyclotron resonance (ICR) experiments.¹³² The role of intramolecular hydrogen bonding in dioxane and other di-, tri-, and tetra-ethers as well as some cyclic crown ethers has also been proposed; from results obtained with a pulsed high-pressure mass spectrometer, a mechanism for cluster formation and fragmentation has been suggested.¹³³

A study of the hydrogen-bonded dimer ion of p-dioxane by photoionization mass spectrometry has been carried out. In one sense, ion-molecule reactions can be considered as the reverse of ionic Thus a detailed photoionization mass spectrometric fragmentations. investigation of 12-crown-4, the symmetric cyclic ether with formula CaH16O4. has also been undertaken. They will be described in the next Chapter. Here the results of the investigation of p-dioxane are Photoionization efficiency (PIE) curves and appearance reported. energies of p-dioxane and its perdeuterated isomer, C4DeO2, have been obtained. Ion-molecule reactions involving p-dioxane under different sample pressures, photon irradiation energies and instrument repeller voltages have also been fully investigated, and the results are compared with previous reports.

II. Results and Discussion

The mass spectrum of p-dioxane at a pressure of 1×10^{-5} torr under full illumination of the hydrogen many-line pseudo continuum in the mass range 40-200 amu is shown in Figure V-I. At this pressure the peak at m/z = 89 is due to ¹³C-substituted parent ion (~4% relative intensity). The intensity of C4HrOs⁺ (m/z = 87), the parent ion minus one hydrogen, is very low. However, when the pressure of p-dioxane in the ion source is to ~5x10⁻⁶ torr the intensities of these two peaks are significantly enhanced. Since the mass of the parent ion is 88 amu, the



 Figure V-1
 Mass Spectrum of p-Dioxane Under Full Illumination of the Hydrogen Many-Line Pseudo Continuum.

ion at m/z = 89 cannot be formed by a unimolecular process. Moreover, because the m/z = 87 intensity is so low at low pressure, we suspect that ion-molecule reactions are responsible for its formation at higher pressure. Indeed, at low pressures the ion count rates for both m/z =89 and 87 depend quadratically on the sample pressure over a pressure range of almost one decade; at the highest pressures employable under our experimental conditions, $C_{4}H_{7}O_{5}$ becomes the most abundant ion. The ionization and appearance energy, respectively, of both the parent and protonated parent cations have been measured at room temperature. The PIEs of the molecular ion and the protonated parent in the threshold region (obtained at $2x10^{-5}$ and $2x10^{-4}$ torr respectively) are shown in Figure V-2. The threshold energies are 9.13 eV and 9.09 eV. That is:

p-dioxane \Rightarrow p-dioxane⁺ + e⁻ IE = 9.13 \pm 0.02eV, and (V-2) p-dioxane \Rightarrow p-dioxane⁺ + e⁻ followed by p-dioxane⁺ + p-dioxane \Rightarrow p-dioxane H⁺ + neutral(s), yields (V-3) 2 p-dioxane \Rightarrow p-dioxane H⁺ + neutral(s) + e⁻ AE= 9.09 \pm 0.02eV (V-4)

A. Protonated p-Dioxane

The appearance energy for the formation of protonated p-dioxane measured at room temperature is 9.09 ± 0.02 eV which is equal to the IE of p-dioxane within experimental error. The closeness of the AE of protonated dioxane and the IE of the parent ion can be understood in terms of reactions (V-2), (V-3), and (V-4), which show that ionization of p-dioxane is a precondition for the formation of protonated p-dioxane. The similarity in the shapes of the PIE curves for these two ions also



Figure V-2

Photoionization Efficiency Curves For Parent Ion (Δ) and Protonated Parent Ion (0).
supports the above-mentioned mechanism. The slightly lower AE for protonated p-dioxane also indicates that the potential energy barrier for the ion-molecule reaction (V-3), is negligible. This mechanism is similar to the general reaction,¹³³

$$BH^{+} + ether \rightleftharpoons ether H^{+} + B, \qquad (V-5)$$

except the protonating agent here is p-dioxane itself. However, the time scale of our experiment is about 1000 times faster than the experiment in which reaction (V-5) was studied and therefore, equilibrium is not established under the current conditions.

The relative intensity of the protonated parent (m/z = 89) in the mass spectra as a function of dioxane sample pressure under two different photon illumination conditions, Lyman- α (1215.6A = 10.20 eV) and central image (full illumination of the hydrogen many-lines psuedo continuum), is given in Figures V-3 through V-7. The relative intensity of protonated p-dioxane first increases with pressure and reaches a maximum, subsequently dropping with increasing pressure. This drop in intensity at higher pressures indicated that the m/z = 89 ion can undergo further reactions, which will be discussed later.

B. C4H7O2⁺

At sample pressures below $5x10^{-5}$ torr, the intensity of C₄H₇O₂⁺ with m/z = 87 is very low. This is consistent with previous reports.^{134,135} Therefore, in order to measure its PIE both entrance and exit slits were increased to 300 µm. This increases the light intensity in the ion source and therefore the number of ions per



Pressure (Torr)





Pressure (Torr)





Pressure (Torr)



.



Pressure (Torr)



Ion Yield vs. p-Dioxane Sample Pressure Under Lyman- α (1215.6 A) Illumination. 177 (0), 133 (Δ), 116 (\Box), 73 (\Diamond), 44 (\bullet), 43 (Δ).



Pressure (Torr)



second, which makes the PIE measurement possible. At the same time the lower irradiation wavelength precision increases the error in the appearance energy measurements. PIE curves for both $C_4H_7O_2^*$ and $C_4D_7O_2^*$ have been measured. Their AEs agree well within the combined experimental error of 0.1 eV, and the value (see Table V-1 for AE of $C_4H_7O_2^*$) is about 0.5 eV below the AE previously reported¹³⁵ following electron bombardment of 1,4-dioxane. Considering the fact that the AEs measured by the photoionization technique for other fragments of pdioxane are lower by about half an electron volt from the electron bombardment values given in Reference 135, the AE reported here for $C_4H_7O_2^*$ is a better estimate. Therefore one can write

$$C_{4}H_{9}O_{2} \rightarrow C_{4}H_{7}O_{2}^{+} + H + e^{-} AE = 10.41 \text{ eV}. \qquad (V-6)$$

When the pressure of the p-C4HeO2 in the ion source is raised above $5x10^{-6}$ torr the peak at m/z = 87 is significantly enhanced. Figure V-7 shows that the relative intensity of C4HrO2⁺ increases with increasing pressure even when the energy of the ionizing radiation (Lyman- α = 10.20 eV) is below its appearance energy (10.41 eV). This indicates that at higher pressure ion-molecule reactions are responsible for the formation of C4HrO2⁺. Two mechanisms can be postulated for the formation of the C4HrO2⁺ cation at higher pressure:

$$C_{4}H_{4}O_{2} + C_{4}H_{6}O_{2}^{*} \rightarrow C_{4}H_{7}O_{2}^{*} + Fragment(s) \qquad (V-7)$$

$$C_{4}H_{9}O_{2}^{+} \rightarrow C_{4}H_{7}O_{2}^{+} + H_{2} \qquad (V-8)$$

As noted earlier, as the dioxane pressure is increased, the $C_4H_7O_2^*$ ion count rate first depends quadratically on the sample pressure over a range of about one decade and then increases even more rapidly. Figures V-5 and V-7 show that at energies both above and below the AE of $C_{4H_7O_2}$ increasing the pressure above $5x10^{-5}$ torr increases the intensity of this ion whereas the intensities of both $C_{4H_0O_3^*}$ and $C_{4H_{9}O_{2}}$ reach a maximum and then drop. Both reactions (V-7) and (V-8) favor the production of C₄H₇O₂ at the expense of C₄H₈O₃ and C4HeO2⁺, consistent with the pressure study. In the proposed mechanism for the fragmentation of crown ethers by electron impact, it has been suggested that $C_4H_7O_2^+$ is produced by H_2 -loss from protonated p-dioxane, reaction (V-8).136 The cation enthalpies of formation derived in this work (vide infra) indicate that this reaction is endothermic, with endothermicity of 56.8 kJ mol⁻¹ (0.59 eV). But it is exothermic and spontaneous at the energies under which the pressure study has been carried out (10.2 eV and about 13 eV).

C. Unimolecular Dissociation of p-Dioxane at Low Pressure

When the sample pressure in the ion source is below $5x10^{-4}$ torr photoionization efficiency curves for the following ions can be measured: C4HsOs⁺, C4H7Os⁺, C3HsO⁺, C3HsO⁺, C2HsO⁺, C2HsO⁺, C4DsOs⁺, C4DrOs⁺, C2DsO⁺, and C2DsO⁺. Corrected PIE curves for the cations from C4HsOs, obtained over the incident photon energy range 9-13 eV, are shown (on a fairly coarse scale) in Figure V-8. Each curve has been separately normalized; the approximate relative intensities can be gauged from the mass spectrum observed under full illumination of the hydrogen discharge, indicated in the fourth column of Table V-1. The ionization energies (IEs) of C4HsOs and C4DsOs were determined by expanding the threshold region and extrapolating the straight-line portion of the appropriate PIE curve just above onset back to the



Figure V-8 Photoionization Efficiency Curves for Parent and Daughter Ions of 1,4-Dioxane. $C_4H_8O_2^+(\Delta L)$, $C_4H_7O_2^+(\clubsuit)$, $C_3H_6O^+(O)$, $C_3H_5O^-(\Delta 2)$, $C_2H_5O^+(\diamondsuit)$, $C_2H_4O^+(\Box)$, $C_2H_3O^+(\Delta 3)$.

For the fragment ions, the appearance energy (AE) was baseline. chosen as the energy at which the PIE first rose perceptibly from the baseline; because of possible kinetic shifts and other factors, even these values must be considered upper limits to the desired adiabatic AE. The values for the deuterated cations are identical within experimental error to their unsubstituted counterparts, and thus AEs for the hydrogencontaining species only are listed in Table V-I. For the parent ion and fragments with m/z = 58, 45, 44 and 43, agreement with the photoionization threshold energies reported by Baer and coworkers¹³⁴ is excellent; well within the combined experimental uncertainty. The values are consistently lower than those obtained from electron bombardment experiments by Collin and Conde,¹³⁵ by 0.4 eV to as much as 1.7 eV. The photon impact results are clearly more reliable. The AB we measure for the $C_{2}H_{5}O^{+}$ (m/z = 57) fragment is lower than that given in reference 134 by about 0.3 eV. However, this cation is formed in competition with three lower-energy fragmentations, so its threshold may be subject to significant kinetic shift. As noted above, the observed AE is an upper limit, and perhaps our experimental sensitivity has enabled us to detect C3H5O* closer to the adiabatic onset. For each ion the experimental AE or IE has been combined in a Hess' Law calculation with auxiliary thermochemical information for the parent molecule and the presumed neutral partners in the pertinent fragmentation channel to provide the room temperature enthalpy of formation. That value has been adjusted to 0 K using the procedure and vibrational frequency data given in reference 135. Enthalpies of formation at both temperatures are listed for each cation in Table V-1.

In order to ascertain whether ions differing in mass by only 1 amu (e.g. m/z 88 and 87, or 58 and 57) were sufficiently well separated in our mass filter, the perdeuterated molecule was studied. It was reassuring that the threshold energies of the well-separated deuterated species (C4DeO2⁺ and C4D7O⁺, and C2D6O⁺ and C3D6O⁺) were the same as those of the hydrogen-containing ions.

D. Other Products of Ion-Molecule Reactions

The dependence of the p-dioxane mass spectrum on the sample pressure under illumination of the Lyman- α line of hydrogen (1215.6A -10.20 eV) is shown in Figure V-9. The results are striking. Not only are the protonated parent, the molecular ion, and the H-loss cations formed, but ions at m/z = 177, 133, 114, 116, 73, 45, 44 and 43 are detected. At the highest pressure shown (top frame) the mass spectrum is dominated by the C4HrOs⁺ cation. From Table V-1 it can be seen that only the parent ion(m/z = 88) has its appearance energy below 10.2 eV. Thus <u>all</u> of the other species result from ion-molecule reactions involving the parent ion; to form the cation at m/z = 177 at least three molecules must be involved.

The mass spectrum is similarly pressure dependent at other photon energies. Regardless of the sample pressure, the ions at m/z =57, 58, and 59 are not detected under Lyman- α irradiation. However, once the incident energy exceeds about 10.5 eV they occur in the mass spectrum and show pressure dependence which suggests that they arise both from unimolecular decay of C₄H₈O₂⁺ and from ion-molecule reactions. At 1050A = 11.81 eV and 5x10⁻⁴ torr dioxane pressure ions at

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Figure V-9 Mass Spectrum of 1,4-Dioxane, Obtained with Photon Energy of 10.20 eV (1215A), at the Specified Sample Pressures (in torr).

m/z = 177, 133, 116, 114, 89, 88, 87 and 73, as well as the usual (lowpressure) fragments from p-dioxane, are detected. Under full illumination of the hydrogen pseudo-continuum (central image) the same cations are observed at pressures as low as $5x10^{-5}$ torr. The pressuredependence of the electron impact mass spectra confirm these results; for example, at p-dioxane pressures in the 5-7x10⁻⁵ torr range 15 eV electrons generate the same mass spectrum as that produced by photoionization by undispersed radiation from the hydrogen lamp. It is worthy of note that the dioxane dimer ion, m/z = 176, was not observed under any conditions with either photon or electron impact.

The voltage of the repeller plate in the ion source was varied at selected sample pressures in order to alter the ion residence times. The results are consistent with expectations from the pressure dependence of the dioxane mass spectrum. At a given photon energy and pressure of the neutral molecule, increase of the repeller voltage from its normal, nominal value of 0.1 V leads to mass spectra which are similar to those described previously at lower sample pressures. For a given sample pressure, at the higher voltages an ion has less chance to undergo ionmolecule reactions before it leaves the ion source.

E. Ions With m/z Higher Than 89

The intensities of these ions are not sufficiently high to enable their AEs to be measured. This, plus lack of information about both the structures of these cations and their neutral fragmentation partners, as well as their enthalpies of formation, precludes speculation regarding product structures based on the PIMS measurements. In an independent photoionization mass spectrometric study of 12-crown-4, a similar fragmentation pattern to that of 1,4-dioxane at high pressure is observed (Chapter VI). Moreover, the fragment AEs generally match well under the two sets of conditions. These facts suggest that the ionic fragmentation of p-dioxane at the higher pressures employed in this study may proceed through an intermediate with a chemical formula $(C_{8}H_{16}O_{4}^{+}).$ Whether its structure is cyclic, an open chain, or branched cannot be determined since the ion has not been directly observed in either photoionization or electron impact mass spectrometry. (Indeed the geometry of the parent cation from 12-crown-4 has not been established.136,137 In the case of the dioxane intermediate, the dimer ion $(C_{0}H_{16}O_{4}^{*})$ could, in fact, be a short-lived, activated ion, which decomposes before it enters the quadrupole mass filter, and mainly produces protonated p-dioxane, which in turn can undergo further reactions.

The absence of a peak at m/z = 176 indicates that the dioxane dimer ion is not stable on the time scale of this experiment, which is a few microseconds. At higher pressures a peak due to m/z = 177 is detected (see Figure V-6), and its intensity increases with further increase in pressure. At 10.2 eV only the molecular ion can be formed by direct ionization. Collision of this ion with p-dioxane neutral could produce protonated parent ion which in turn, at higher pressure, could react with a second p-dioxane neutral to form CeH17Oe^{*}. Production of CeH17Oe^{*} rather than CeH16Oe^{*} on the time scale of the mass spectrometer experiment highlights the necessity of hydrogen bonding in the reaction and the consequent stabilization of the aggregate ion. Two



Baer and coworkers have shown that the fragmentation of the p-dioxane cation occurs via a tight activated complex,¹³⁴ and that the molecular ion keeps its cyclic structure even a few electron volts above its ionization energy. It has also been shown¹³³ that, although optimal hydrogen bonding geometry is available in crown ethers, if the interaction is between non-adjacent oxygens such as shown in structure B, the internal hydrogen bond is stable, but its enthalpy in most cases falls substantially short of the strength of the strong hydrogen bonds observed in hydrogen-bridged dimer ions such as structure A, where $\Delta H^0_{BB} = 30 \pm 2$ kcal mol⁻¹. On the other hand, it has been proposed¹³⁷ that neutral p-dioxane and protonated p-dioxane are

fragments of protonated 12-crown-4 decomposition, and therefore reaction of protonated p-dioxane with neutral p-dioxane can be considered as the reverse of that fragmentation.

Support for both structures A and B makes the determination of the exact structure of the ion with m/z = 177 difficult; structure A is more probable due to the stability of p-dioxane⁺ at energies above its fragmentation threshold and the stronger hydrogen bonding in that structure. Mautner¹³³ has also shown that the reaction ether H⁺ + ether = ether H⁺ ether reaches equilibrium within 1-2 ms. Here again the proton-bonded dimer is favored over a possible cyclic structure.

Ion with m/z = 133. At 10.20 eV where only the molecular ion can be formed by direct photoionization, the following mechanism can be written for the production of the m/z = 133 cation:

$$C_{4}H_{8}O_{2}^{+} + C_{6}H_{8}O_{2} \rightarrow C_{6}H_{13}O_{3}^{+} + C_{2}H_{8}O_{3} \qquad (V-9)$$

At the highest pressures attainable in these experiments a very small amount of an ion with m/z = 131 was also produced. This cation could be formed by direct ion-molecule interaction, like reaction (V-9), except with CeH11Os⁺ + C2H5O as products, or by H2-loss from the ion with m/z= 133, that is

$$C_{6}H_{19}O_{3}^{+} \rightarrow C_{6}H_{11}O_{3}^{+} + H_{2}, \qquad (V-10)$$

At higher photon energy, where daughter ions are formed following p-dioxane photoionization, it is also possible that $C_2H_5O^+$ (m/z = 45) reacts with neutral p-dioxane to form the m/z = 133 cation:

$$C_{6}H_{8}O_{2} + C_{2}H_{5}O^{+} \rightarrow C_{6}H_{18}O_{3}^{+}. \qquad (V-11)$$

Figure V-3 shows that the intensity of $C_{eH_{10}O_{2}}$ first increases with pressure, reaches a maximum and then drops. This suggests that at higher pressure the m/z = 133 cation is involved in further reactions.

<u>Ions with m/z = 116 and 114</u>. As in the case of CeH13O3⁺, cations with m/z = 116 can be formed from direct reaction of the molecular ion with neutral p-dioxane, and at higher photon energies perhaps also from reaction of the p-dioxane fragment having m/z = 28 with p-dioxane. High resolution mass spectra at various electron impact energies has indicated that at onset the m/z = 28 ion is C₂H₄⁺. Therefore, the m/z =116 ion in the p-dioxane mass spectra is likely to be CeH13O3⁺, and the mass 114 ions arise from H₂-loss from 116:

$$p-C_4H_8O_2 + C_2H_4^+ \rightarrow C_6H_{12}O_2^+(m/z = 116) \rightarrow$$

$$C_{6}H_{10}O_{2}^{+}(m/z = 114) + H_{2}.$$
 (V-12)

One mechanism proposed for the formation of $C_2H_4^*$ from the p-dioxane parent ion is a consecutive dissociation process in which the $C_2H_4^*$ grandaughter ion is produced from $C_3H_6O^*$ (m/z = 58) along with $CH_2O.^{135}$ The intensity of m/z = 116 increases with pressure in the range of the PIMS experiments while m/z = 58 constantly decreases, which is consistent with this mechanism.

F. Ions With m/z Less Than 88

<u>Cations with m/z = 73, 71 and 59</u>. These ions are detected only at fairly high sample pressure. They are not photo-fragments of p-dioxane at low pressure, even under full illumination of the hydrogen discharge, and they must therefore be products of ion-molecule reactions. Ions with these m/z values are indeed photo-fragments of 12-crown-4, and it has been suggested that the daughter ion at m/z = 133 can undergo further decomposition to produce m/z = 73, 71, 61 and $59.^{136}$ Although no ion with mass 61 was detected in this investigation, the observation of ions at m/z = 73, 71 and 59 under conditions where m/z = 133 is maximum, and the increase in their intensity while the intensity of the mass 133 ion subsequently decreases, can be viewed as support for this mechanism. The absence of any further information about these ions precludes speculation regarding their structure. Schemes for the production of the ions discussed in this subsection are given below:

Low Energy:



High Energy:

 $C_{4H_9O_2} + C_{2H_5O^+} \rightarrow C_{6H_{19}O_3^+} \rightarrow [same decomposition products]$

Cations with m/z = 45, 44 and 43. These ions can be produced both by unimolecular fragmentation of the parent cation or from ionmolecule reactions. The mass 43 ion could also be produced from m/z =45 through H₂-loss. In compounds such as the benzo-crowns studied by Gray et al., metastables are observed which confirm the fragmentation $m/z = 89 \Rightarrow 45$. This suggests that, in addition to being the product of unimolecular fragmentation of C4H₂O₂⁺, the cation with m/z = 45 could be produced from protonated dioxane, which itself is a product of an ionmolecule reaction. One possible mechanism for the formation of these ions at high pressure, therefore, will be:

$$C_{2}H_{4}O + C_{2}H_{5}O^{+} (m/z = 45)$$

$$+-H_{2}$$

$$C_{2}H_{6}O + C_{2}H_{3}O^{+} (m/z = 43)$$

$$C_{2}H_{5}O + C_{2}H_{4}O^{+} (m/z = 44)$$

The decrease in the m/z = 44 and 45 ion intensities at higher pressure (FigureV-4) is an indication of their further reaction. The increase in intensity of the m/z = 43 cation at pressures where the mass 45 ion intensity declines can be considered as support for the conversion of $C_{2HsO^{+}}$ to $C_{2HsO^{+}}$ via H_{2} -loss.

m/ Z	Ion	Neutral ^a	Relative Intensity ^b	IE ^c or AE ^c (eV)	(kJ mol ⁻¹)	dH ^o fo ^f , ∈ (kJ mol ⁻¹)
88	C4 He O2 +	C4 Ha O2	93	9.13 ± 0.02	564 ± 4 -316 ± 0.8	595 ± 4 -285.3 ± 0.8
87	C4 H7 O2 *	H	3	10.41 ± 0.1	≤ 469.7 217.8	
58	C3 H5 0+	СЊО	100	10.52 ± 0.05	524 ± 8 -108.8 ± 0.8	-105.0 ± 0.8
57	C3 Ha O⁺	СЊО	6	10.89 ± 0.05	≤740 ±8 14.6	≤752 ±8 21.3
45	C2 H5 O+	С2 Њ3 О	15	10.46 ± 0.05	736 ± 8 -22.6	753 ± 8 -15.9
44	C2 H4 O+	C2 H4 O	8	10.47 ± 0.05	890 ± 8 -165.7 ± 0.4	900 ± 8 -155.2 ± 0.4
43	C₂ H₂ O⁺	C2 H5 0	6	11.90 ± 0.05	≤ 868 17	≤ 873 -2.1

Table V-1.	Threshold	Energies	and	Beats	of	Formation	for	Ions	Produced	From	P -
	Dioxane at	LOW Samp	le Pi	ressure	6.						

*Reference 134.

^bUnder full illumination of hydrogen many-line pseudo-continuum. Ion source Pressure = 1.2x10⁻⁵ torr.

cAt 298°K.

^d Ions are corrected for kinetic energy release (taken from reference 134). Neutrals taken from reference 134.

*Ions are corrected for thermal energy. Neutral taken from reference 134.

^f Alg(e⁻) is taken to be zero. Temperature conversion according to procedure in reference 134.

CHAPTER VI

PHOTOIONIZATION MASS SPECTROMETRIC STUDY OF 12-CROWN-4

Introduction

Since the first report of the syntheses of macrocyclic "crown" polyethers by Pederson,^{139,140} considerable interest has been shown in the properties of these compounds. Crown ethers have been found to be very useful reagents in organic chemistry because they selectively complex alkali metal ions and can be used to carry them through aqueous non-polar solution boundaries.^{141,142} This has been employed as a model for cation transport through membranes.¹⁴³

Ultraviolet photoelectron spectra of crown ethers and their electronic structures have been reported, and with the aid of theoretical calculations, the lower IE bands of the spectra have been assigned.¹⁴⁴ The 70 eV mass spectra of unsubstituted cyclic polyethers, along with their dissociation mechanism and the elemental composition of both ions and neutrals have been suggested.¹³⁶

In this work the ionization and fragmentation of 12-crown-4 (C₈H₁₆O₄) have been followed by photoionization mass spectrometry. Appearance energies for the protonated parent ion and twelve of its daughter cations are reported. Upon ionization 12-crown-4 produces a rich assortment of fragment ions and neutrals. Some of these, such as $C_4H_8O_3^*$, are well-known and stable ions, whose appearance energies can be readily calculated because the heats of formation of the ionic and neutral products are established.^{78,145,146} For these cases comparisons between the new results and previously-reported values are possible. However, in many instances the heats of formation of the fragment cations are not known and even their chemical compositions are not certain, so comparisons with the literature cannot be made. In addition to its inherent interest, the photoionization mass spectrometric study of the fragmentation of 12-crown-4 is also likely to be useful for comparison with ion-molecule reactions of dioxane at higher pressure, which have been described in the preceding chapter.

RESULTS

The PIEs for the protonated parent and twelve fragments of 12crown-4 have been measured; PIE curves for the fragments are shown in Figures VI-1 and VI-2. Under the experimental condition employed in this study the parent ion (m/z = 176) intensity was never above the signal-to-noise level. This result is consistent with mass spectra of 12crown-4 under electron bombardment.¹³⁶ At higher sample pressures an ion with m/z = 177 was detectable and its intensity was sufficiently high that PIE measurements could be made. At low pressures several fragment ions are detected with AEs in the range 8.86 \pm 0.05 eV. From this information the ionization energy of 12-crown-4 was estimated to be 8.86 eV. PES shows four broad peaks around 9.3, 9.9, 11.4 and 12.5 eV;¹⁴⁴ the reported vertical ionization energy is 9.3 eV, although the onset of this band in the PES spectrum is about 8.6 eV. The threshold energies of the fragment ions determined by PIMS, along with probable





Photoionization Efficiency Curves For Protonated and Daughter Ions of 12-Crow-4.





Photoionization Efficiency Curves For Daughter Ions of 12-Crown-4.

formulas of the ions and neutrals and the relative ion intensities are listed in Table VI-1.

DISCUSSION

A. PIE Measurement and Thermochemistry

A useful property of an ion or molecule is its heat of formation. AH.º. This is a thermodynamic quantity which, at a nonzero temperature, contains the thermal distribution of internal and translational energies. Photoionization, on the other hand, is a spectroscopic experiment and thus is associated with transitions between specific internal energy states. The dissociation energy refers to the (thermodynamic) energy of the products relative to the reactants. This can be lower than the (spectroscopic) AE because of reverse activation energies and kinetic shifts. Therefore the true value of an jonic heat of formation determined spectroscopically depends on the internal energies of the precursor and the products [ion and neutral(s)], the kinetic shift and reverse activation energy. Where these factors cannot be determined the reported AE value will be only an upper limit. This is in fact the case in this study because no information regarding these matters are available at this time. The AE listed for a given cation in Table VI-1was chosen as the energy at which the corresponding PIE first rose perceptibly from the baseline.

B. Structures and Energies of Fragments

In order to determine the structures and energies of photofragments from PIE measurements one must know the chemical composition of the fragments at the threshold energies. Normal mass

m/z	Ion	Relative Ion Intensity	IE of AE, eV
176	Ce H1 6 O4 +		8.86 ± 0.1ª
133	C6 H1 3 O3 +	5	8.89 ± 0.05
117	C6 H1 3 O2 +	1	8.93 ± 0.05
101	C4 H5 O3 +	2	8.92 ± 0.05
89	C4 H9 O2 +	41	8.86 ± 0.05
88	C4 H8 O2 +	18	9.14 ± 0.05
73	C4 H9 O+	66	8.92 ± 0.05
61	C2 H5 O2 +	9	9.10 ± 0.05
59	$C_3 H_7 O^+$ (or $C_2 H_3 O_2^+$) 7	9.70 ± 0.05
58	$C_3 H_5 O^+$ (or $C_2 H_2 O_2^+$) 14	9.32 ± 0.05
45	C2 H5 0+	100	9.70 ± 0.05
44	C ₂ H ₄ O ⁺	70	9.58 ± 0.05
43	C ₂ H ₃ O ⁺	22	9.70 ± 0.05

.

Table	VI-1.	Ionization and Appearance Energies (298K) of 12-Crown-4 and	ł
		its Fragment Cations.	

^a Inferred from lowest AEs measured.

spectrometers give information only about m/z and not chemical composition or structure. For a given nominal m/z, in most cases, one can write several chemical compositions. Their differences lie in the 0.01-0.1 amu range and they may be distinguished only by high resolution mass spectrometry. Moreover, for thermochemical studies one must also know the structure of the neutral fragments which accompany a particular fragmentation, and but little information concerning these neutrals is available. Metastable ions are useful in this regard since they provide information about the precursor of a fragment ion (i.e. whether the fragment ion was produced directly from the molecular ion or is a product of consecutive reactions) and therefore about the neutral counterparts. In addition, it is necessary to know whether the dissociation path is determined by dynamical (or mechanistic) constraints or by thermochemical ones, and thus whether one might expect the formation of fragments which are not necessarily the most stable ones. If different isomers of one compound isomerize to a common ionic structure, it could indicate that the dissociation paths are determined by thermochemical constraints and therefore that the most stable fragments are to be expected. Kinetic shift and reverse activation energy data are also needed in order to obtain information about heats of formation from the differences between activation energies of forward and reverse reactions. In principle, these data can be gathered from time-resolved photoionization mass spectrometry and kinetic energy release measurements. A more accurate onset for a particular also determined from RRKM/QET decomposition product could be statistical theory calculation of the dissociation rate, 147, 148 which could be compared with PIPECO experiments. If the heat of formation at zero

degrees is desired from an experimental value at 298 K, the average thermal energy, $\langle E_{th} \rangle$, has to be taken into account. $\langle E_{th} \rangle$ is the sum of the average translational <Eu>, vibrational <Evib> and rotational $\langle E_{tr} \rangle$ and $\langle E_{rot} \rangle$ can be obtained by using the <Erot> energies. classical values; (Evib) can be determined by evaluating the vibrational frequencies for each species. For the activated complex these are usually not available and must be estimated. For larger molecules this information becomes less available and therefore the prediction of ionic structures becomes less certain. In this study calculations of heats of formation are limited to those fragment ions whose elemental compositions previous have predicted by EI been mass spectrometry studies.136,137,149

$C_{8}H_{16}O_{4}(m/z = 176)$

At low pressure no ion with m/z = 176 was detectable in our mass spectrometer when 12-crown-4 was irradiated by light from the hydrogen discharge. This result is in agreement with a low pressure, low electron energy study, and with 70 eV mass spectra of crown ethers.¹³⁶ At higher sample pressures an ion with m/z = 177 was detected and its intensity was sufficient to enable measurement of its PIE. The appearance energy of this ion is 8.89 eV. Ions with m/z =177, 133, 117, 101, 89 and 73 show similar AEs (i.e., within experimental error). The AE of an ion with m/z less than 176 must at least be equal to the IE of the parent ion at low pressure. Therefore the IE of 12crown-4 must to be 8.86 + 0.1 eV, the minimum AE observed at low pressure. The vertical IE of 12-crown-4 reported by PES is 9.3 eV;¹⁴⁴ the adiabatic value will be somewhat lower. Ionization of the parent neutral is a precondition for fragmentation; if the molecular ion decomposes on a time scale much faster than the mass spectrometry experiment, then the fragment ions formed at the IE will have no kinetic shift. However, because the dissociation products may be more stable than the parent cation, they may be formed with some internal energy. Thus the experimental AEs will give upper limits to the desired thermochemical reaction enthalpy.

The ionization energy of 12-crown-4 is considerably lower (at least 0.27 eV) than that of 1,4-dioxane . In an earlier investigation it was established that the thermochemical stability of polyethers is strongly dependent on the relative positions of the oxygens.¹⁵⁰ The apparent strain energies calculated for 1,4-dioxane and 12-crown-4 are 13.8 and 32.1 kJ mol⁻¹ respectively.¹⁵¹ The difference (about 0.19 ev) has been described in terms of differences in the conformations of the structural units that constitute the rings.¹⁵¹ The strain has been investigated in the solid phase on the basis of geometrical considerations, and sterically the 1,4 0...0 interaction, which depends on the C-C gauche bond and the 1,4 CH...HC interaction which depends on the oxygen-carbon gauche bond are considered to be responsible for this strain.¹⁵² The interaction energies are in agreement with strain energies determined when similar conformations are assumed for the gas-phase molecule.¹⁵¹ The relative IEs of 12-crown-4 and 1,4-dioxane determined by PIMS are consistent with this result; one can interpret both the lower ionization energy and the fragmentation energy of 12-crown-4 in terms of these steric interactions. From the IE estimated in this work and the known heat of formation of 12-crown-4,78 an upper limit for AHr^o of C₈H₁₆O₄ can be calculated; the value is listed in Table VI-2.

$C_{6}H_{13}O_{3}^{+}$ (m/z = 133) + $C_{2}H_{3}O$

Similar to the IE, the activation energies for fragmentation of 12crown-4 are also smaller than those of p-dioxane. Again, steric effects are likely to be responsible for this observation.

The AE of the m/z = 133 ion is equal to the estimated parent IE within experimental error and therefore kinetic shift is insignificant. If one assumes the lowest energy structure for the neutral fragment, $CH_{3}CO_{,}^{145}$ Hess' law gives $\Delta H^{\circ}_{1290}(C_{6}H_{13}O_{3}^{+}) \leq 248.3$ kJ/mol. (The inequality arises because the kinetic shift and reverse activation energy are not known.) A cyclic structure has been proposed for this ion.¹³⁶

$C_{6H_{13}O_{2}}(m/z = 117) + C_{2H_{3}O_{2}}$

The AE of this ion lies only 0.07 eV above the proposed molecular IE and therefore only very little kinetic shift can be involved. No information concerning the structure and thermochemistry of the neutral(s) are available to enable the calculation of the heat of formation of the ion.

$C_{4}H_{5}O^{+}(m/z = 101) + (C_{4}H_{11}O)$

This cation has AE = 8.92 eV which is only 0.06 eV above the estimated IE and therefore the kinetic shift is not significant. The heats of formation of the neutral fragment with chemical composition C₄H₁₁O is not available, and no information concerning the structure of the neutral (or neutrals) in this reaction has been reported. But if one assumes that this ion is produced through the same mechanism as m/z = 105,¹³⁶ by the subsequent loss of two H₂ molecules, then the neutrals

will be C_2H_3O + C_2H_4 + $2H_2$. The heat of formation of $C_4H_5O_3^+$ can be calculated from the experimental AB and ΔH°_f values for these neutrals; the result is tabulated in Table VI-2.

$C_{6}H_{9}O_{2}^{+}(m/z = 89) + C_{4}H_{7}O_{2}$

Among all the fragment ions from 12-crown-4, CaHeOs⁺ has the minimum AE and the probability that this ion is observed with a very small kinetic shift is high. If the neutral has the same structure as in the case of fragmentation of the p-dioxane dimer cation (for which $\Delta H^{\circ}_{7299}C_{4}H_{7}O_{2} = -156.3 \text{ kJmol}^{-1}$, see previous chapter), then one calculates $\Delta H^{\circ}_{7299}C_{4}H_{9}O_{3}^{+} = 379.1 \text{ kJ mol}^{-1}$. This value is in a good agreement with the reported heat of formation of protonated dioxane, and suggests that the m/z = 89 daughter ion from 12-crown-4 has the same structure as protonated p-dioxane.

Consider the two processes:

- (a) $2C_{4}H_{9}O_{2} \rightarrow C_{4}H_{9}O_{2}^{+} + C_{4}H_{7}O_{2}$, and
- (b) CeH1eOe \rightarrow CeHeOz $^+$ + CeHrOz

The enthalpies of formation of the reactants in both cases are the same⁷⁸ (ΔH^{o}_{rase} 12-C-4 = 151 kcal mol⁻¹ = 2 ΔH^{o}_{rase} p-dioxane). The products of both reactions are also the same. The photon energy at which C4HeO2⁺ is observed in the first case (9.09 eV) is slightly higher than the AE of C4HeO2⁺ (8.86 eV) from reaction (b). The difference attributed to IEs of the oxygen atoms in p-dioxane and 12-crown-4, indicates that reaction (a) has a somewhat higher reverse activation energy (since both reactions have very little, if any, kinetic shift). In that case, the fragments of reaction (a) will be produced with higher

internal or translational energies than the dissociation products in (b). The similarity between the products of reactions (a) and (b) could also indicate a common activated complex for these two reactions.

$C_4H_8O_2^+(m/z = 88) + C_4H_8O_2$

If one assumes that the neutral in this case is p-dioxane then the heat of formation of the cation calculated from the AE listed in Table VI-2 is $\Delta H^{\circ}_{7200}C_4H_5O_2^{+}$ = 364.3 kJmol⁻¹, which is exactly equal to the heat of formation of the p-dioxane cation measured from the direct ionization of p-dioxane. This reaction can be considered as the reverse of the association of neutral and cationic p-dioxane and the similarity between the IE of p-dioxane at high pressures (~9.1 eV) and the AE for production of p-dioxane+ from 12-crown-4 (9.14 ± 0.05 eV) indicates that the latter reaction has almost no reverse activation energy.

$C_4H_9O^+(m/z = 73) + C_2H_3O + C_2H_4O_2$

The suggested structure for this cation is a protonated cyclic ether for which the heat of formation is known in the gas phase. With this information, the experimental AE, plus the heat of formation of C_{2H_2O} we find $\Delta H^{o}_{7290}C_{2H_4O_2} = -262.9$ kJ mol⁻¹. The suggested structure for this neutral is also a cyclic ether. The calculated enthalpy of formation is considerably higher than ΔH^{o}_{f} of other isomers of $C_{2H_4O_2}$ (ΔH^{o}_{7290} methyl formate = -354.9 kJ mol⁻¹ and ΔH^{o}_{f} acetic acid = -432.0 kJ mol⁻¹); the heat of formation of cyclic $C_{2H_4O_2}$ is not known from other work, but one might expect the cyclic forms to be less stable than the well-known isomers.

$C_{2}H_{5}O_{2}^{+}(m/z = 61) + C_{2}H_{3}O + C_{4}H_{8}O$

Since the heats of formation of the neutrals (considering C_4H_0O to be a cyclic ether) are known, the heat of formation of the ion can be calculated and the result is given in Table VI-2. No information concerning the heat of formation of this cation is available with which to compare the experimental value. It has been suggested that both $C_{4H_9O^+}$ and $C_{2H_5O_2^+}$ cations are produced from a common precursor¹³⁶ The results of the PIMS study show that both of these ions (C6H13O3⁺). have AEs close to that of the $C_6H_{13}O_3^+$ ion (0.03 and 0.21 eV higher, respectively), which is consistent with this possibility. (If one of the ions with m/z = 73 or 61 had a lower AE, then $C_{6H_{13}O_{3}}$ could not be the precursor ion.) The results of the p-dioxane pressure study also show that ions with m/z = 73 and 59 (which could be produced from 61⁺ \rightarrow 59⁺ + H₂) start to appear as m/z = 133 reaches its maximum intensity and continue to increase as 133⁺ starts to fall off. These observations support the above mechanism, but some disagreement also exists (see below).

$C_2H_3O_2^+$ (m/z = 59) + C_2H_3O + C_4H_8O + H_2

The AE of this reaction with respect to the threshold for m/z = 61is higher by 0.6 eV, which indicated either that loss of H₂ from C₂H₅O₂⁺ is an endothermic process or this ion has been produced with a considerable kinetic shift. Again, since the m/z = 59 ion has a higher AE than C₂H₅O₂⁺, the possibility exists that this ion has been produced by decomposition of the m/z = 61 cation. On the other hand, the repeller voltage study made for p-dioxane photoionization over a voltage difference of 0.1 to 15 volts shows that the relative intensity of this ion remains constant with respect to those with m/z = 57 and 58, which indicates that this ion could be the protonated analog of the cation with m/z = 58. If this is the case then the chemical composition of m/z = 59is C₃H₇O^{*}, and the likely neutrals would be C₄H₈O₂ + CHO. For the first case, ΔH^{o}_{f} (C₂H₃O₂^{*}) has been calculated and the result is included in Table VI-2. Again, no value is available in the literature for comparison. For the cation with chemical composition C₃H₇O^{*} (the second case) $\Delta H^{o}_{f256} = 581.9$ kJ mol⁻¹ which is very close to ΔH^{o}_{f256} of protonated acetone (i.e. 543.4 kJ mol⁻¹).

$C_{3}H_{5}O^{+}$ (m/z = 58) + $C_{4}H_{8}O_{2}$ + $CH_{2}O$

The calculated heat of formation for this ion is $691.4 \text{ kJ mol}^{-1}$ which lies between the heats of formation of CH₂ =C(OH)-CH₂* [ΔH°_{f} = $660.9 \text{ kJ mol}^{-1}$) and CH₂-CO-CH₂* (ΔH°_{f} = 719.0 kJ mol}^{-1})]. The closeness of the heat of formation of m/z = 58 to that of acetone might be considered as support for the m/z = 59 ion being protonated acetone.

$C_{2}H_{5}O^{+}$ (m/z = 45) + $C_{4}H_{8}O_{2}$ + $C_{2}H_{3}O$

The ΔH°_{f} (C₂H₅O⁺) = 642.1 kJ mol, which falls between the values for CH₃ - C(OH)-H⁺ (608.2 kJ mol⁻¹) and CH₃-O-CH₂⁺ (660.9 kJ mol⁻¹). The heat of formation of the cyclic isomer of C₂H₅O⁺ is 689.7 kJ mol⁻¹; and is being considered as it was the suggested the fragment with m/z = 45 in the electron impact ionization study 12-crown-4.¹³⁶

$C_{2}H_{4}O^{+}$ (m/z = 44) + C_{4}H_{8}O_{2} + C₂H₄O

The calculated heat of formation of the m/z = 44 ion is 775 kJ mol⁻¹, which is very close to $\Delta H^{o}_{f} = 770.0$ kJ mol⁻¹ of CH₂=CH-OH⁺.

$C_2H_3O^+$ (m/z = 43) + $C_4H_9O_2$ + C_2H_5O

The calculated heat of formation of this ion based on these neutrals is 602.3 kJ mol⁻¹ which is close to ΔH^{o}_{f2396} (CH₂CO⁺) = 630 kJ mol⁻¹. If the neutrals are taken to be C₄H₂O₂ + C₂H₂O + H₂, then ΔH^{o}_{f2396} (C₂H₃O⁺) = 642.1 kJ mol⁻¹ which is between those of CH₃-CO⁺ and CH₂=C-OH⁺ (ΔH^{o}_{f} = 787.1 kJ mol⁻¹).

As was mentioned at the beginning of this chapter, prediction of the structure of an ion from PIE measurements alone, without complementary structural and thermochemical data, is in most cases impossible. In the photo-fragmentation of 12-crown-4 more information is necessary in most instances in order to choose the exact structure of the fragment ions.

The results of this PIMS investigation of 12-crown-4 indicate that heats of formation of several of the fragments, such as C4HeO2⁺ and C4HeO2⁺, are very close to those obtained in the p-dioxane study. On the other hand, different heats of formation are calculated for other ions with the same chemical composition, e.g. C₃H₅O⁺, C₂H₅O⁺, C₂H₄O⁺ and C₂H₅O⁺.

One cannot conclude from these data that the fragmentation products of 12-crown-4 are alike or dissimilar to those from p-dioxane because different choices of neutral fragmentation partners (where inadequate information exists) might provide better agreement between calculated heats of formation for a given cation.

m/ Z	ion	neutrals	AR ⁰ f298 kJ mol ⁻¹
176	Ce H1 e O4 +	Са Н1 в О4	223° -631°
133	C6 H1 3 O3 +	C2 H3 O	-631 ^b -23 ^c
117	C6 H1 3 O2 +	C2 H3 O2	
101	C4 H5 O3 *	$C_2H_30 + C_2H_4 + 2H_2$	201ª -23 ^c + 50 ^b
89	C4 H2 O2 *	C4 H7 O2	379• -156ª
88	C4 Ha O2 +	C4 Ha O2	564 • -316 ⁵
73	C4 Ho O+	$C_2 H_3 O + C_2 H_4 O_2$	514 ^b -23 ^c -263 ^b
61	C2 H5 O2 +	$C_2H_3O + C_4H_8O$	453ª −23 ^c −184 ^b
59	C2 H3 O2 +	$C_2 H_3 0 + C_4 H_8 0 + H_2$	511ª -23 ^c -184 ^b
	C₃ H7 0+	$C_4 H_8 O_2 + CHO$	582° -316° + 38°
58	C2 H2 O2 +	$C_2H_4O + C_4H_8O + H_2$	617ª -166 ^p -184 ^p
	C3 Hs 0+	C_4 Ha O_2 + CH ₂ O	691ª -316 ^b -109 ^b

Table VI-2. Thermochemical Data Relevant to the Ionization and Dissociation of 12-Crown-4.
Table VI-2 continued.

m/z	ion	neutrals	∆H°f298 kJ mol ⁻¹
45	C2 H5 O+	$C_4 H_8 O_2 + C_2 H_3 O$	642ª -316 ^b -23 ^c
44	C2 H4 O+	$C_4 H_8 O_2 + C_2 H_4 O$	775 ° -316 ^b -167 ^b
43	C₂ H₃O+	$C_4 H_8 O_2 + C_2 H_3 O + H_2$	642ª -316 ^b -23 ^c

^aDetermined from the present data.

^bReferences 146 and 153.

^cReference 145.

^dFrom Table V-I (Chapter V).

REFERENCES

1.	K.E. McCulloh, Int. J. Mass Spectrom. Ion Phys. 21, 333 (1976).
2.	H.M. Rosenstock, Int. J. Mass Spectrom. Ion Phys. 20, 139 (1976).
3.	Y. Malinovich, R. Arakawa, G. Hasse and C. Lifshitz, J. Phys. Chem. 89, 2253 (1985).
4.	J. Dannacher, Org. Mass. Spectrom. 19, 253 (1984).
5.	T.L. Bunn, A.M. Richard and T. Baer, <u>J. Chem. Phys</u> . In Press (1985).
6.	E.J. Darland, D.M. Rider, R.P. Tully, C.G. Enke and G.E. Leroi, Int. J. Mass Spectrom. Ion Phys. <u>34</u> , 175 (1980).
7.	T. Cvitas and L. Klasinc, Croat. Chem. Acta. 50, 291 (1977).
8.	J.F. Bunnett and C.E. Moyer, Jr., J. Am. Chem. Soc. 93, 1183 (1971).
9.	R.H. Levin: <u>Reactive Intermediates</u> , ed. by M. Jones, Jr. and R. Am Moss (John Wiley and Sons, New York, 1978).
10.	R.Yamdagi and P. Kebarle, J. Am. Chem. Soc. 95, 3504 (1973).
11.	G. Herzberg: Atomic Spectra and Atomic Structure (Dover Publication, New York, 1945).
12.	I.N. Levine: <u>Molecular Spectroscopy</u> (John Wiley and Sons, New York, 1975).
13.	G.V. Marr: Photoionization Processes in Gasses (Academic Press, New York, 1967).
14.	V. Fano and J.W. Cooper, Rev. Mod. Phys. 40, 441 (1968).
15.	W.A. Chupka, "Ion-Molecule Reactions by Photoionization Techniques" in <u>Ion-Molecule Reactions</u> , Vol. 1, ed. by J. L. Franklin (Plenum Press, New York, 1972, pp. 33-77).
16.	J. Berkowitz: Photoionization and Photoelectron Spectroscopy (Academic Press, New York, 1979).
17.	R.S. Mulliken, Acc. Chem. Res. 9, 7 (1976).
18.	J.H.D. Eland, J. Chim. Phys. 77, 613 (1980).
19.	E. Lindholm, Arkiv, Fys. 40, 103 (1969).
20	M.B. Robin: Higher Excited States of Polyatomic Molecules (Academic Press, New York, 1974).

- 21. A.D. Walsh, J. Phys. Radium 15, 501 (1954).
- 22. J.L. Dye and V.A. Nicely, Chem. Ed. 48, 443 (1971).
- 23. P. Houchman, H. Wang, W.S. Felps, S. Foster and S.P. McGlyn, "On the Assignment of Molecular Rydbert Series," in <u>Chemical</u> <u>Spectroscopy and Photochemistry in the Vacuum Ultraviolet</u>, ed. by C. Sandorfy, P. J. Ausloos and M. B. Robin (D. Reidel, Boston, 1974, pp. 385-393).
- 24. R.P. Madden and K. Codling, Astro Phys J. 141, 364 (1965).
- 25. R.P. Madden, D.L. Ederer and K. Coding, Phys. Rev. <u>177</u>, 136 (1969).
- 26. R.L. Platzman, Radiat. Res. 17, 419 (1962).
- 27. R.S. Berry, J. Chem. Phys. 45, 1228 (1966).
- 28. W.A. Chupka and J. Berkowitz, J. Chem. Phys. 51, 4244 (1969).
- 29. Ch. Jungen and O. Atabek, J. Chem. Phys. 66, 5584 (1977).
- 30. J. Berkowitz and W.A. Chupka, J. Chem. Phys. 51, 2341 (1969).
- 31. W.A. Chupka and J. Berkowitz, J. Chem. Phys. 48, 5726 91968).
- 32. P.C. Killgoar, G.E. Leroi, J. Berkowitz and W. A. Chupka, J. Chem. Phys. 58, 803 (1973).
- 33. C.Y. Ng, B. H. Mahan and Y.T. Lee, J. Chem. Phys. 65, 1956 (1976).
- 34. E. Miescher, Y.T. Lee and Gurtler, J. Chem. Phys. 68, 2753 (1978).
- 35. J.H.D. Eland, Journal de Chimie Physique 77, 613 (1980).
- 36. J.H.D. Eland: Photoelectron Spectroscopy (Butterworths, London, 1984).
- 37. R.S. Berry, J. Chem. Phys. 45, 1228 (1966).
- 38. G. Herzberg: <u>Spectra of Diatomic Molecules</u> (D. Van Nostrand, New York, 1950).
- 39. R.C. Dunbar, "Ion Photodissociation" in <u>Gas Phase Ion Chemistry</u>, Vol. 2, ed. by M. T. Bower (Academic Press, New York, 1979, pp. 181-220).
- 40. H.M. Rosenstock, M.B. Wallenstein, A.L. Warhaftingand, H. Eyring, Proc. Natl. Acad. Sci. U.S.A. 38, 667 (1952).
- 41. R.A. Marcus and O.K. Rice, J. Phys. Colloid Chem. 55, 894 (1951).
- 42. O.K. Rice and H.C. Ramsperger, J. Am. Chem. Soc. 49, 1617 (1927).

- 43. L.S. Kassell, J. Phys. Chem. 32, 225 (1928).
- 44. N.B. Slater: Theory of Unimolecular Reactions (Methven, London, 1959).
- 45. L.D. Spicer and B.S. Rabinovitch, Annu. Rev. Phys. Chem. 21, 349 (1970).
- 46. G. Wong and R.A. Marcus, J. Chem. Phys. 67, 1636 (1977).
- 47. J.C. Lorquet and B. Leyh, "Potential Energy Surface and Theory of Unimolecular Dissociation" in Ionic Processes in the Gas Phase, ed. by M. A. Almoster Ferreira (D. Reidel, Boston, 1982, pp 1-6).
- 48. C. Galloy, C. Lecomte and J.C. Lorquet, J. Chem. Phys 77, 4522, (1982).
- 49. C. Lifshitz, Adv. Mass Spectrom. 7, 3 (1977).
- 50. Z. Herman, A. Lee and R. Wolfgang, J. Chem. Phys. 51, 452 (1969).
- 51. A. Henglein, J. Chem. Phys. 53, 458 (1970).
- 52. I. Herteland and Ch. Ottinger, Z. Naturforsch, A22, 40 (1969).
- 53. J.H. Beynon, J.A. Hopkinson and G.R. Lester, Int. J. Mass Spectrom. Ion Phys. 2, 291 (1969).
- 54. R.D. Hickling and K.R. Jennings, Org. Mass Spectrom. 3, 1499 (1970).
- 55. E.G. Jones, J.H. Beynon and R.G. Cooks, <u>J. Chem. Phys.</u> <u>57</u>, 3207 (1972).
- 56. M.A. Haney and J.L. Franklin, J. Chem. Phys. 48, 4093 (1968).
- 57. R.G. Cooks, J.H. Beynon, R.M. Caprioli and G.R. Lester: <u>Metastable</u> Ions (Elsevier Scient, Amsterdam, 1973).
- 58. E.P. Wigner, Phys. Rev. 73, 1002 91948).
- 59. S. Geltman, Phys. Rev. 102, 171 (1956).
- 60. R.E. Fox, J. Chem. Phys. 35, 1379 (1961).
- 61. K. Watanable, J. Chem. Phys. 22, 1562 (1954).
- 62. R.E. Fox, J. Chem. Phys. 33, 200 (1960).
- 63. R.H. McFarland, Phys. Rev. Letters 10, 397 (1963).
- 64. G.J. Schultz and R.E. Fox, Phys. Rev. 106, 1179 (1957).

- 65. C.E. Klots, "Energy Deposition Processes" in Fundamental Process in Radiation Chemistry ed. by P. Ausloos (Interscience, New York, 1968, pp. 1-58).
- 66. N.W. Reid, Int. J. Mass Spectrom. Ion Phys. 6, 1 (1971).
- 67. W.A. Chupka, J. Chem. Phys. 30, 191 (1959).
- 68. E.U. Condon, Phys. Rev. 41, 759 (1932).
- 69. G. Herzberg: <u>Molecular Spectra and Molecular Structure III</u> (Van Nostrand, Princeton, New Jersey, 1967).
- 70. W.A. Chupka, J. Chem. Phys. 54, 1936 (1971).
- 71. B. Steiner, C.F. Giese and M.G. Ingham, J. Chem. Phys. 34, 189 (1961).
- 72. V.H. Dibeler and J.A. Walker, Int. J. Mass Spectrom. Ion Phys. 11, 49 (1973).
- 73. G.R. Parr and J.W. Taylor, Rev. Sci, Instrum. 44, 1578 (1973).
- 74. P.M. Guyon and J. Berkowitz, J. Chem. Phys. 54, 1814 (1971).
- 75. D.M. Rider, Ph.D. Thesis, Michigan State University, 1980.
- 76. L. Friedman, F.A. Long and M. Wolfsberg, J. Chem. Phys. 26, 714 (1957).
- 77. C. Liifshitz, Mass Spectrom. Rev. 1, 309 (1982).
- 78. H.M. Rosenstock, K. Dranl, B.W. Steiner and J.T. Henon, <u>J. Phys.</u> Chem. Ref. Data 6, 1 (1977), Supplement No. 1.
- 79. M. Vestal "Ionic Fragmentation Processes" in <u>Fundamental</u> <u>Processes in Radiation Chemistry</u>, ed. by P. Ausloos (Interscience, New York, 1968, pp 59-118).
- 80. H.M. Rosenstock, J.T. Larkins and J.A. Walker, Int. J. Mass Spectrom. Ion Phys. 11, 309 (1973).
- 81. W.A. Brand and T. Baer, Int. J. Mass Spectrom. Ion Phys. 49, 103 (1983).
- 82. C. Lifshitz, M. Goldenberg, F.Y. Malinovich and M. Peres, Org. Mass Spectrom. 17, 453 (1982).
- 83. D.H. Ave and M.T. Bowers: <u>Gas Phase Ion Chemistry</u>, Vol. II, (Academic Press, New York, 1979).
- 84. S.G. Lias, D.M. Shold and P. Ausloos, J. Am. Chem. Soc. 102, 2540 (1980).

- 85. J.C. Traeger and R.G. McLoughlin, J. Am. Chem. Soc. 103, 3647 (1981).
- 86. R.G. Cooks: Collision Spectroscopy (Plenum Press, New York, 1978).
- 87. D.W. Turner, A.D. Baker, C. Baker and C.R. Brundle: <u>Molecular</u> Photoelectron Spectroscopy (Interscience, London, 1970).
- 88. J.H.D. Eland, Adv. Mass Spect. 7, 17 (1977).
- 89. J.H.D. Eland, Int. J. Mass Spectrom. Ion Phys. 8, 143, (1972).
- 90. R. Stockbauer, J. Chem. Phys. 58, 3800 (1973).
- 91. E.J. Darland, Ph.D. Thesis, Michigan State University, 1977.
- 92. D.G. Streets, G.T. Ceasar, Mol. Phys. 26, 1037 (1973).
- 93. K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki: Mono Series Res. Inst. Appl. Electricity (Hokkaido University 25, 1978).
- 94. R.S. Friedman, B.J. Kelsall, L. Andrews, J. Phys. Chem. 88, 1944 (1984).
- 95. R.S. Friedman, L. Andrews, J. Am. Chem. Soc. 107, 822 (1985).
- 96. R.W. Hoffman: Dehydrobenzene and Cycloalkynes (Academic Press, New York, 1967).
- 97. J.L. Franklin, J.G. Dillard, H.M. Rosenstock, J.T. Herron and F.H. Field: Ionization Potentials, Appearnace Potentials, and Heats of Formation of Gaseous Positive Ions, NSRDS-NBS 26, U.S. Government Print Office, Washington, 1969, Appendix 2.
- 98. A.D. Baker, D.P. May, D.W. Turner, J. Chem. Soc, (B) 22, (1968).
- 99. A.W. Potts, M.L. Lygus, E.P.F. Lee and G.H. Fattahallah, J. Chem. Soc. Faraday II 76, 556 (1980).
- 100. J.H.S. Green, Spectrochim Acta 26A, 1503 (1970).
- 101. J.D. Cox, Tetrahedron 18, 1337 (1970).
- 102. J. Dannacher, H.M. Rosenstock, R. Buff, A.C. Parr and R.L. Stockbover, Chem. Phys. 75, 23 (1983).
- 103. Y.L. Sergeev, A.V. Golovin, M.E. Akopyan and F.I. Vilesov, High Energy Chem (Engl-Transl.) 11, 88 (1977).
- 104. R.S. Pandolfi, D.A. Gobeli and M.A. El-Sayed, J. Phys. Chem. 85, 1779 (1981).
- 105. B.D. Koplitz and J.K. McVey, J. Phys. Chem. 89, 2761 (1985).

- 106. R.D. Levin and S.G. Lias: Ionization Potential and Appearance Potential Measurements, 1971-1981 (NSRDS-NBS 71; U.S. Govt. Printing Office, Washington, 1982).
- 107. H.M. Rosenstock, R.L. Stockbaver and A.C. Parr, J. Chimie Physique 77, 745 (1980).
- 108. H.M. Rosenstock, J. Dannacher, and J.F. Liebman, <u>Radiat. Phys.</u> Chem. 20, 7 (1982).
- 109. K.R. Jennings, Z. Naturforsch. 22A, 454 (1967).
- 110. J. Horman, A.N. Yeo, D.H. Williams, J. Am. Chem. Soc. 92, 2131 (1970).
- 111. W.O. perry, J.H. Beynon, W.E. Baifinger, J.W. Amy, R.M. Caprioli, K.N. Renaud, L.C. Leitch and S. Meyerson, J. Am. Chem. Soc. 92, 7236 (1970).
- 112. R.J. Dickinson and D.H. Williams, J. Chem. Soc. B 249 (1971).
- 113. J.H. Beynon, R.M. Caprioli, W.O. Perry and W.E. Baitinger, J. Am. Chem. Soc. 94, 6828 (1972).
- 114. S.K. Pollack and W.I. Hehre, Tetrahedron Letters 21, 2483 (1980).
- 115. H.M. Rosenstock, R.L. Stockbauer and A.C. Parr, J. Chem. Phys. 73, 773 (1980).
- 116. H.M. Rosenstock, R.L. Stockbauer and A.C. Parr, J. Chem. Phys. 71, 3708 (1979).
- 117. S.T. Prott and W.A. Chupka, Chem. Phys. 62, 153 (1981).
- 118. Such experiments are in progress, T. Baer, personal communication.
- 119. J.P. Maier and O. Marfbaler, Chem. Phys. 32, 419 (1978).
- 120. H.F. Grutzmacher and J. Lobemann, Anv. Chem. 705, 81 (1967).
- 121. P. Natalis and J.L. Franklin, J. Phys. Chem. 69, 2935 (1965).
- 122. J.O. Noel and M.D. Newton, J. Am. Chem. Soc. 101, 51 (1979).
- 123. M.J. S. Dewar, G.P. Ford and H.R. Reynolds, J. Am. Chem. Soc. 105, 3162 (1983).
- 124. J.I. Brauman and L.K. Blair, J. Am. Chem. Soc. 92, 5986 (1970).
- 125. J.L. Beauchamp and M.C. Caserio, J. Am. Chem. Soc. 94, 2638 (1972).

- 126. J.B. Briggs, R. Yamdagni and P. Kerbarle, J. Am. Chem. Soc. 94, 5128 (1972).
- 127. J.E. Barness and R.T. McIver, Jr.: "The Gas-Phase Acidity Scale" in <u>Gas Phase Ion Chemistry</u>, Vol. 2, ed. by M.T. Bowers (Academic Press, New York, 1979).
- 128. D.S. Bomse and J.L. Beauchamp, J. Phys. Chem. 85, 488 (1981).
- 129. P. Kebarle, Ann. Rev. Phys. Chem. 28, 445 (1977).
- 130. A.W. Castleman, Jr., P.M. Holland, D.M. Lindsay and K.I. Peterson, J. Am. Chem. Soc. 100, 6039 (1978).
- 131. R.L. Woodin and J.L. Beauchamp, Chem. Phys. 41, 1 (1979).
- 132. J.W. Larson and T.B. McMahon, J. Am. Chem. Soc. 104, 6255 (1982).
- 133. M. Meot-Ner (Mautner), J. Am. Chem. Soc. 105, 4906 (1983).
- 134. M.L. Fraser-Monteiro, L. Fraser-Monterio, J.J. Butler, T. Baer and J.R. Hass, J. Phys. Chem. 86, 739 (1982).
- 135. J.E. Collin and G. Conde, Bull. Cl. Sci. Acad. Rog. Belg. 52, 978 (1966).
- 136. Y.C. Lee, A.I. Popov and J. Allison, Int. J. Mass Spectrom. Ion Phys. 51, 267 (1983).
- 137. R.T. Gray, D.N. Reinhoudt, K. Spaargaren and J.F. de Bruijn, J. Chem. Soc. Perkins Trans. 2, 206 (1977).
- 138. J.W. Larson and T. McMahon, J. Am. Chem. Soc. 104, 6255 (1982).
- 139. C.J. Pederson, J. Am. Chem. Soc. 89, 7017 (1967).
- 140. C.J. Pederson, J. Am. Chem. Soc. 92, 386 (1970).
- 141. E. Shchori, J. Jagur-Grodzinski and M. Schporer, J. Am. Chem. Soc. 95, 3842 (1973).
- 142. N.S. Poonia, J. Am. Chem. Soc. 96, 1012 (1974).
- 143. A. Pullman, G. Giesstner-Prettre and Yu Y. Kruglyak, Chem. Phys. Lett. 35, 156 (1975).
- 144. M. Kajitani, A. Sugimori, N. Sato, K. Seki, H. Inokuchi and Y. Harada, Bull. Chem. Soc. Japan 32, 2199 (1979).
- 145. S.W. Bensen: Thermochemical Kinetics (Wiley-Interscience, New York, 1976).

- 146. J.B. Pedley and J. Rylance: SUSSEX-N.P.L. Computer Analyzed <u>Thermochemical Data:</u> Organic and Organo-metallic Compounds (University of Sussex, Sussex, 1977).
- 147. T. Baer, G.D. Willett, D. Smith and J.S. Phillips, J. Chem. Phys. 70, 4076 (1979).
- 148. G.D. Willett and T. Baer, J. Am. Chem. Soc. 102, 6774 (1980).
- 149. D.A. Jaeger and R.R. Whitney, J. Org. Chem. 40, 92 (1975).
- 150. M. Mansson, J. Chem. Thermodyn. 1, 141 (1969).
- 151. K. Bystrom and M. Mansson, J. Chem. Soc. Perkin 2, 565 (1982).
- 152. F. Podo, G. Nemethy, P.I. Indovina, L. Radics and V. Viti, Mol. Phys. 27, 521 (1974).
- 153. G.L. Sharon, J.F. Liebman and R.D. Levin, J. Phys. Chem. Ref. Data, 13, 695 (1984).

