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PHOTOIONIZATION AND FRAGMENTATION OF POLYATOMIC MOLECULES

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EXPERIMENTAL

The most detailed studies of photoionization and fragmentation have been carried out with apparatus which consists of a vacuum ultraviolet monochromator with various light sources producing continua or near-continua and a mass spectrometer for ion detection and identification. Several such instruments have been used and are described or referred to in recent reviews.(1,2) One particularly advantageous combination is that of a 1-meter near normal incidence monochromator equipped for windowless operation with rare gas continua lamps and a magnetic-deflection mass spectrometer. Photon band widths as narrow as 0.04 Å have been used but 1.0 Å (~0.01 eV at 1100 Å) is more typical. Such an apparatus has been described in the literature.(3) Of particular interest in the present context are certain temporal characteristics of this apparatus. Between the instant of formation in the photoionization chamber and final detection after mass analysis an ion of typical mass (~100 amu) spends several microseconds in each of the following regions of the instrument: (1) the ionization chamber, (2) acceleration and focusing regions, (3) a first field-free region, (4) the magnetic field, (5) a second field free region. Ions which dissociate in region (1) are detected as fragment ions. Those which dissociate in regions (2) or (4) are effectively lost from the mass spectrum. Ions which do not dissociate at all or dissociate in region (5) are detected as parent ions. Of special interest here are those ions which decompose in region (3). They are known as "metastable ions" in mass spectrometry and appear at a generally non-integral mass position, m^* given by the ratio $(m_f)^2/(m_p)$ where m_f and m_p are the masses of fragment and parent ions respectively. The detection character-

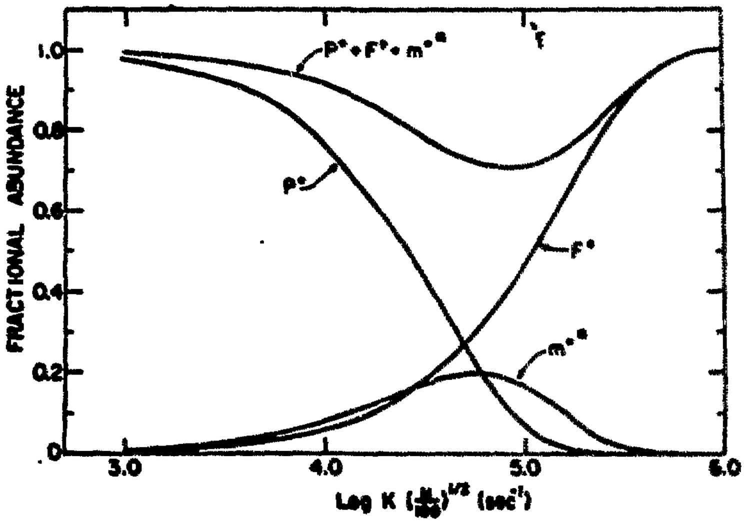

Fig. 1. Fractional abundance of ions detected as parent, fragment and metastable ions as a function of k the rate constant for unimolecular decomposition of a parent ion of mass M in amu. This applies to the apparatus described in ref. 3.

istics of the apparatus described in ref. (3) for parent, fragment and metastable ions have been calculated as described previously(4) for another instrument and are shown in Fig. 1. Of particular interest here is the fact that metastable ions are observed predominantly for decompositions with rate constants in the range 10^4 to 10^5 sec^{-1} and that fragment ions are not observed significantly until the rate constant is of comparable magnitude. It is assumed in these calculations that radiative de-excitation is not a significant competitive process. This point has important consequences as will be discussed later.

The shape and width of the metastable ion peak in the mass spectrum is also a very sensitive measure of the kinetic energy released in dissociation. For a decomposition which is isotropic and monoenergetic in kinetic energy release, it has been shown(5) that, to a good approximation, the metastable peak will be rectangular and of width proportional to the quantity $(eV \cdot T)^{1/2}$ where eV is the kinetic energy to which the parent ions were accelerated (typically of the order of kilovolts) and T is the kinetic energy released in the center of mass system. Neglected effects of components of velocity normal to the ion-optic axis and certain losses of ions from the beam can produce some relatively small distortion from the expected simple rectangular form. However, a more complete analysis and proper instrumental design and operation can yield highly precise absolute measurements of the distribution of kinetic energy released in the decomposition process. Present instruments are capable of measuring values of T less than one millivolt.(6) This high sensitivity is the result of the large "amplification" effect of the transformation from the c.m. to the laboratory system and is the precise opposite of the "de-amplification" effect achieved in "merging-beam" experiments in which the initial collisions are essentially the reverse of the metastable decomposition process. Such amplification and de-amplification effects are common and very important in a wide variety of collision and dissociation phenomena.(7) Various techniques have also been used to measure the kinetic energy distribution of fragment ions formed in the ionization chamber.(8) These latter techniques are particularly valuable for decompositions which are not observable as metastable ions. However, the metastable ion measurements have the great advantage that they refer to ions with a narrow range of dissociation rate constants which implies a narrow range of internal energy.(8) This latter condition makes comparisons between theory and experiment much easier and more direct.

GENERAL CONSIDERATIONS

Absorption by molecules of photons of wavelengths shorter than the first ionization limit of the molecule can lead to a number of competitive and consecutive processes which may be described briefly as follows. In this description the molecule AB may be polyatomic and A and B may be atoms or groups of atoms. Direct excitation to continua may occur:

$$\begin{aligned} AB + h\nu &\rightarrow AB^{+} + e^{-} &&\text{(Direct Ionization)} \\ &\rightarrow A^{*} + B &&\text{(Direct Dissociation)} \\ &\rightarrow A^{+} + B^{-} &&\text{(Direct Dissociation to an Ion Pair)} \end{aligned}$$

Excitation may also occur to quasi-discrete ("superexcited") states AB^{*} which may interact strongly with each other and with one or more of the continua described above. The resulting indirect processes of autoionization (preionization) and predissociation are prominent and important in the photoionization spectral region. The resulting fragments of both direct and indirect processes may be sufficiently excited to undergo further decomposition. The most commonly observed such decomposition is that of the parent ion, $AB^{+*} \rightarrow A^{+} + B$. In the case of a polyatomic parent ion, several competing modes of decomposition may occur and the resulting fragments may have sufficient internal energy to undergo still further competitive and successive decompositions. Another possible decomposition process is that of autoionization of an excited neutral fragment produced by direct dissociation or predissociation. This latter process has never been positively identified and is not expected to account for anything but a minor fraction of observed ionic fragments.

The above description may be too simplistic in some cases. A more rigorous description would recognize the possibility that the observed quasi-discrete states may interact strongly not only with each other and with the continua described above, but also with other optically weak or forbidden quasi-discrete manifolds (i.e. internal conversion or intersystem crossing) and also directly with three-body continua in a way such that it may not be a good approximation to consider the processes of ionization and dissociation to occur successively as described above. There is very little experimental evidence bearing on the importance of these latter processes. At present, the simple model of ionization followed by dissociation is capable of explaining practically all experimental observations. It should be noted that this model need not fail for transitions to a three-body continuum. For example, the direct ionization of H_2 to produce H_2^+ in the repulsive $^2\Sigma_u^+$ state is a process for which application of the Franck-Condon principle predicts well the kinetic energy distribution of the fragments, i.e. the Born-Oppenheimer separation of electronic and nuclear motions is a good approximation and the ionization and dissociation can be considered to occur consecutively. However, the possibility of serious failure in some cases of decay of quasi-discrete states should be kept in mind.

PHOTOIONIZATION AND ENERGY DEPOSITION

The general features of the photoabsorption curve of a molecule above its first ionization limit are readily understood at least qualitatively from the photoelectron spectrum of the molecule taken at a wavelength at which negligible autoionization occurs. The absorption consists of direct ionization continua corresponding to the formation of the states of the ion displayed in the photoelectron spectrum and of one or more Rydberg series converging to each of these states of the ion. In some cases an excited valence state (or at least a state which cannot be unambiguously assigned as a Rydberg state) may be above the first ionization limit also. Thus the $^1A(\pi \rightarrow \pi^*)$ valence state of formaldehyde is estimated to lie above the first I.P. and to be strongly autoionized.(9) Some such valence states can be considered to be formed by excitation of one of the more strongly bound electrons (corresponding to one of the higher I.P.'s of the photoelectron spectrum) into one of the normally unfilled valence orbitals. A crude estimate of the excitation energy of such a state may be given by the difference of the higher I.P. and the term value of the unfilled valence orbital as determined from other transitions to the latter orbital observed at longer wavelengths. Identification of such valence states is expected to be difficult since they will usually be very short-lived with respect to autoionization or predissociation and have a broadened band envelope not readily recognizable from other data in contrast to the situation for Rydberg states.

The vibrational structure of the Rydberg transitions, particularly higher members, approach those of the photoelectron spectrum and the interaction of these quasi-discrete states with the underlying continua often produces recognizable Beutler-Fano profiles.(10) However, especially for the larger polyatomic molecules, the overlapping and mutual interaction of rich vibrational structure together with rotational and lifetime broadening often produce an absorption curve with little assignable structure. The well known continuity of oscillator strength density through ionization limits(10) ensures that the thresholds for formation of various states of the ion are not apparent in the absorption spectrum.

If all absorption above the ionization limit led to ionization, the ionization and absorption cross section curves would, of course, coincide in this region. Except for atoms, this is rarely the case due to the competitive decay of some superexcited states via processes which do not produce charged particles, most importantly dissociation or predissociation into neutral particles. In the extreme case of strong predominance of predissociation of all intense Rydberg states converging to a particular limit, the resulting photoionization cross section curve will show a step-like rise at the limit, the height of the step being approximately proportional to the corresponding feature of the photoelectron spectrum. This behavior is most often observed just above the first ionization threshold and can lead to the display of a series of steps which correlate with the vibrational structure of the ground state photoelectron band. Some molecules which display this behavior fairly clearly are NH_3, NO, C_2H_2 and C_2H_4 although careful measurements still show remnant autoionization structure in this region.(11,12)

While the presence of autoionization has the disadvantage of preventing the determination of excited state thresholds in most cases from simple inspection of ionization cross section curves, it has an important advantage in the study of fragmentation thresholds, in that it can result in the population of excited states of the parent ion which are not accessible by direct ionization as indicated by the photoelectron spectrum taken at a non-autoionizing wavelength (the usual case for the HeI and HeII lines most frequently used). In the case of autoionization of a particular vibronic state, the vibrational distribution in the final ionic state is governed by the Franck-Condon factors between the initial and final state. Since the ion in the excited vibronic state often has several quanta of vibrational energy and a geometry significantly different from that of the ground state, the resulting distribution of internal energy in the ion produced is broader than that produced by direct ionization. Furthermore, for larger polyatomic molecules, the autoionizing Rydberg bands are often so overlapped that at any given wavelength many autoionizing bands may be excited so that this broadening of the internal energy distribution beyond that of the photoelectron spectrum is further enhanced. Several examples of marked changes in the vibrational envelope of a photoelectron band due to excitation of a strong autoionizing level are known in photoelectron spectroscopy,(13) and many more may be inferred from photoionization efficiency curves for certain fragment ions which have thresholds at energies at which the photoelectron spectra show no detectable intensity for formation of excited ions.

Within the framework of the simple atomic and molecular orbital description in which configuration interaction is neglected, only single electron excitation or ejection is permitted by photon absorption and very nearly all photoelectron bands have been assigned on this basis. However, many examples of two-electron excitation processes, otherwise allowed by selection rules, are known in atomic spectroscopy and photoionization(10,14,15) although the intensities are typically one to two orders of magnitude lower than single-electron allowed transitions. Recently a few examples of photoelectron bands which can be ascribed to formation of ionic states by simultaneous ejection of one electron and excitation of another have been identified in the photoelectron spectra of O_2 (16,17), N_2O(18) and I_2(19). Undoubtedly many more such two-electron excitation bands are present in photoelectron spectra but are in most cases obscured by the stronger single-electron bands or buried in the noise of the typical photoelectron spectrum. Such states would, of course, be accompanied by associated Rydberg series converging to their limit and would also be formed (usually weakly) by autoionization of singly-excited states. The formation of such excited ionic states can have significant effects in photoionization mass spectrometric studies in spite of the low intensity. Thus, if such a state occurs in the energy region of a threshold for fragmentation and this region is devoid of states produced by single electron excitation, the intensity of the fragment ion can be due entirely to the multiple excitation process. It is very commonly the case that ion fragment intensities lower than parent ion intensities by factors of 10^{-3}—10^{-5} are readily detectable by mass spectrometry. It is fairly common to observe a fragmentation threshold in an apparently "blank" region of the photoelectron spectrum at, or very near, the calculated thermochemical threshold. In many cases, it is obvious from the structure in the ionization efficiency curve that autoionization is the major process responsible for populating the "blank" region. In other cases an underlying continuum appears to be present and the mechanism is not clear.

DISSOCIATION PROCESSES AND THE DETERMINATION OF THERMOCHEMICAL QUANTITIES

Ions, as well as neutral molecules, may fragment by direct dissociation or by predissociation. Predissociation may be divided into three cases:(20) (I) electronic predissociation in which the molecular ion makes a radiationless transition into the dissociation continuum of another electronic state; (II) vibrational predissociation, in which the molecular ion remains in the same state and only vibrational motion is involved; (III) rotational predissociation, in which only the higher rotational levels of a particular vibronic state may predissociate. Rotational predissociation can be significant in the precise determination of dissociation thresholds especially for smaller ions.(21) However, the process accounts for only a very small fraction of observed fragmentation and is not significant to the main thrust of this paper. It will not be discussed further. It should also be noted that predissociation can involve a radiationless transition followed by vibrational predissociation. This is probably common for larger polyatomic molecules.

The observation and determination of thresholds for fragment ion formation by photoionization mass spectrometry is a very powerful and widely applicable technique for the determination of heats of formation of charged and neutral molecules, free radicals and atoms. From these quantities values of bond dissociation energies, ionization potentials and electron affinities can be determined reliably and accurately. The technique is not without its pitfalls, but by careful experiment and interpretation these can be almost always either eliminated or at least questionable value recognized.

The power and scope of the technique derives from several characteristics. The onset of fragmentation is unambiguously recognized by the appearance of the fragment ion in the mass spectrum. The minimum rate constant for observation of fragmentation is very low, - of the order of 10^4 sec^{-1}. This minimum can, and has been, decreased by the use of well-developed ion storage techniques or of other types of mass spectrometers such as the Ion-Cyclotron-Resonance type, but difficulties associated with secondary collision processes limit the decrease to a few orders of magnitude. Detection of such slow dissociations minimizes the effects of selection rules or other inhibiting kinetic factors. The identity of the fragment ion is usually unambiguously determined by its mass. In the case of possible isomers, experiments on several compounds often settle the question and can give heats of formation of different isomers. Fragmentation processes of very low intensity can be determined (typically 10^{-3}—10^{-4} and sometimes as low as 10^{-6} of parent ion intensity). Parent ions can be formed readily in electronic states spanning such large ranges of energy that very often all values of internal energy are effectively accessible. A large number of fragmentation processes are typically observed, although many are not suitable for thermochemical determinations as will be discussed later. The kinetic energy released in fragmentation, especially of "metastable" ions, is measurable, often with high sensitivity and precision.

There are two general approaches used to determine the heat of formation of an ion. In the first and more accurate approach, one judiciously chooses a parent molecule and fragmentation process such that the observed threshold is likely to be equal to the thermochemical one. Various characteristics of the data will usually indicate whether this circumstance is true or not. In the other approach, one investigates a process, the threshold for which is significantly higher than the "true thermochemical" threshold and then applies a correction derived from other experimental data (such as kinetic energy released in fragmentation) or by application of theory based on a plausible model (e.g. the RRKM theory of unimolecular decomposition of an isolated molecule). In any case, an observed threshold always yields at least an upper limit to the value of ΔE for the process.

The major factors which can cause fragmentation to appear at a higher threshold than that calculated thermochemically are listed below.

(1) There may be a negligibly small probability for forming the parent ion in the internal energy range of the thermochemical threshold, in which case the observed threshold often coincides with the threshold of the next highest band in the photoelectron spectrum. The presence of significant band intensity in the photoelectron spectrum at and below the observed fragmentation threshold is sufficient to rule out this possible source of error. However, the above is not at all a necessary condition since an apparently "blank" region may be populated by processes mentioned earlier.

(2) There may be a potential barrier in every potential curve or surface leading to the product fragments. This seems to be relatively rare for simple bond rupture processes but a few cases for small parent ions seem to be established. Thus adiabatic correlation diagrams, theoretical calculations and some experiments indicate that the fragments of lowest energy from NO_2^+ ($NO^+ + O$ in their ground states) and from N_2O^+ ($NO^+ + N$ in their ground states),(22) upon approaching to form the triatomic ion, do so

upon potential surfaces which are all initially repulsive (excluding the small ion-induced-dipole attraction at long distances). In such cases dissociation of the parent ion cannot occur at the thermochemical threshold other than by tunnelling which is far too slow for heavy atoms and thick barriers. This circumstance of large potential barriers is far more common for decomposition processes involving rearrangement where it should always be suspected.

(3) Spin conservation or correlation rules may require potential surface hopping (intersystem crossing or internal conversion) in order to yield ground state products at the thermochemical threshold from the electronic state in which the parent ion is initially formed. Such selection rules are considerably less effective than is found to be the case in ordinary optical spectroscopy in great part due to the far longer time ($\sim 10^{-4}$sec) available for observable predissociation and the high detection sensitivity of mass spectrometry. Thus, more cases are known in which such rules are broken than in which they are sufficiently effective as to prevent observable dissociation. Such rules should be more effective when the electronically excited parent ion has a fast radiative decay which reduces the available time.

(4) In the case of polyatomic molecules with a sufficiently large number of internal degrees of freedom, there may be a significantly large "kinetic shift".(4) That is, dissociation of the molecular ion may occur at the thermochemical threshold but with such a very low rate constant as to be practically undetectable and a significant amount of excess internal energy (the "kinetic shift") may be required to increase the dissociation rate constant to the readily detectable range of 10^4—10^5sec^{-1}. The observation of a corresponding intense metastable peak is a reliable warning of this possible source of error, since it indicates a significant fraction of ions with rate constants in the 10^4—10^5 sec^{-1} range and thus the strong possibility of a significant fraction with still lower rate constants. This behavior, expected for dissociation processes which are statistically controlled, e.g. describable by the RRKM theory, will be discussed in more detail later.

(5) In the case of those larger polyatomic molecules whose decompositions are describable statistically, only the decompositions having the lowest threshold energy or those within a small fraction of an eV of the lowest threshold are usually useful for the determination of accurate thermochemical thresholds. This limitation is due to the fact that decomposition processes occurring at higher energies must compete with those having lower thresholds resulting almost invariably in ionization efficiency curves for the higher processes which rise asymptotically from zero, have poorly defined thresholds and effectively larger

kinetic shifts. The same behavior occurs for processes in which three or more fragments are formed overall, since these generally occur successively and the energy carried off by the neutral fragment of the initial decomposition can have a wide distribution with a vanishingly small probability of zero energy loss.

In spite of the problems enumerated above the major fraction of simple bond scission decompositions of lower thresholds studied by photoionization mass spectrometry have yielded accurate and reliable thermochemical quantities. Unreliable thresholds are usually readily recognized and questionable heats of formation confirmed by investigating several processes in different molecules.

DIATOMIC MOLECULES

The processes leading to formation of fragment ions by photoionization of diatomic molecules are relatively well understood due to the wealth of optical spectroscopic information on dissociation and predissociation processes of neutral molecules.(23) The major experimental difference is the nearly universal observation of fragmentation due to the far greater sensitivity of mass spectrometric detection. For very nearly all molecules investigated by photoionization mass spectrometry, fragmentation has been observed at or at least very near the lowest thermochemical threshold. The shape and structure of the ionization efficiency curves for the fragment ions vary greatly from case to case depending on the characteristics and relative amounts of direct ionization and autoionization, on the shapes and relative positions of the potential curves for the ground state molecule, intermediate superexcited states and the various states of the ion, and on the interactions among the latter states.

SMALL POLYATOMIC MOLECULES

Optical spectroscopy provides relatively little information on dissocation and predissociation processes of polyatomic molecules due to the inherently greater complexity of the spectra. Nevertheless, analyses of spectra for several cases have provided useful examples of different decomposition mechanisms. Direct dissociation (i.e. within the time of a vibrational period) of neutral molecules is apparently well established for several cases from the appearance of true continua (20). It is much more difficult to establish the occurrence of direct dissociation of a polyatomic ion formed by photoionization. The observation of an apparent continuum in the photoelectron spectrum of a polyatomic molecule taken with present limits of resolution (~10 mV) is not convincing evidence for direct dissociation unless one can exclude the possibility of a quasi-continuum due to crowded vibrational structure. Such quasi-continua have been observed in a number of instances in which dissociation is energetically impossible (e.g. the lowest photoelectron band of NO_2).(24) While no well established case of direct dissociation following photoionization of a polyatomic ion at or near threshold is known, such cases very probably occur. For example, direct dissociation seems likely for that class of molecules (e.g. CF_4 SF_6) for which only fragment ions are observed at the lowest ionization threshold.

Predissociation of small polyatomic molecules is well established for a number of cases by optical spectroscopy and is often a very obvious and common occurrence for polyatomic ions. Predissociation is obvious in the latter case from the appearance in the photoelectron spectrum of well defined vibrational structure in bands which correspond to the formation of fragment ions as observed by photoionization mass spectrometry, by the charge transfer technique developed by Lindhom,(25) and by the recently developed photoelectron-photoion coincidence techniques.(26-30)

The selection rules governing predissociation processes are discussed in detail by Herzberg.(20) The rigorous selection rules (conservation of total angular momentum and of overall symmetry) are not expected to be significant in excluding predissocation since appropriate final states are practically always available. However, the operation of various approximate selection rules (e.g. conservation of spin) can greatly affect rates of predissociation which may then depend on the strength of spin-orbit, vibronic or electronic-rotational interactions.

A number of examples of fragmentation of triatomic ions occurring from excited states which show distinct vibrational structure in the photoelectron spectrum have been discussed by Turner et al.(13) More extensive data of higher quality obtained with a variety of techniques have since become available for these and other triatomic molecules and a few examples will be discussed here.

The photoionization and ionic fragmentation of H_2O(13) provides an interesting example of predissociation processes in small polyatomic ions. Two fragmentation processes are observed to occur with high intensity at their thermochemical thresholds. The products (1) $OH^+(^3\Sigma^-) + H(^2S)$ appear at about 684.0Å (18.13 eV) and the products (2) $OH(^2\Pi) + H^+(^1S)$ appear at about 661.1Å (18.75 eV). (These values have been measured in this laboratory, are corrected for thermal energy effects and are somewhat more accurate than previously reported data.(31)) The shapes of the ionization efficiency curves indicate that process (2) becomes quite intense and possibly dominant within a few tenths of an eV above its threshold. In the energy range of both thresholds the parent ion must be initially formed in the $^2B_2$ second electronically excited state which has its adiabatic threshold at 17.22eV(13) and a photoelectron band with vibrational structure which persists well above both dissociation thresholds although some broadening appears to set in at about the first threshold and to become progressively more pronounced at higher energies. The $^2B_2$ state does not correlate with either set of products in their ground states. Thus this is a clear-cut case of two predissocations occurring from the same excited state of the ion. Process (1) has been attributed to predissocation by a $^4A''$ repulsive state by spin-orbit coupling and process (2) to predissociation by a $^2A''$ repulsive state by rotational coupling.(32,33) Some other possibilities exist which cannot be discussed in this space. Nevertheless, in summary, all possible predissociation processes of the $^2B_2$ state of H_2O^+ are forbidden by some (non-rigorous) selection rule, yet both decompositions are rapid (no metastable ions are detected) and occur readily at the thermochemical threshold. This is a common circumstance in photoionization mass spectrometry.

Photoionization and fragmentation of CO_2 into (1) $O^+(^4S)$ + $CO(^1\Sigma^+)$ and (2) $O(^3P)$ + CO^+ $(^2\Sigma^+)$ are both observed to occur at their thermochemical thresholds.(34,35) Process (2) is relatively low in intensity and will not be discussed further. The photoionization efficiency curve for O^+ and CO_2^+ from CO_2 is shown in Fig. 2. Process (1) is seen to have its threshold at about

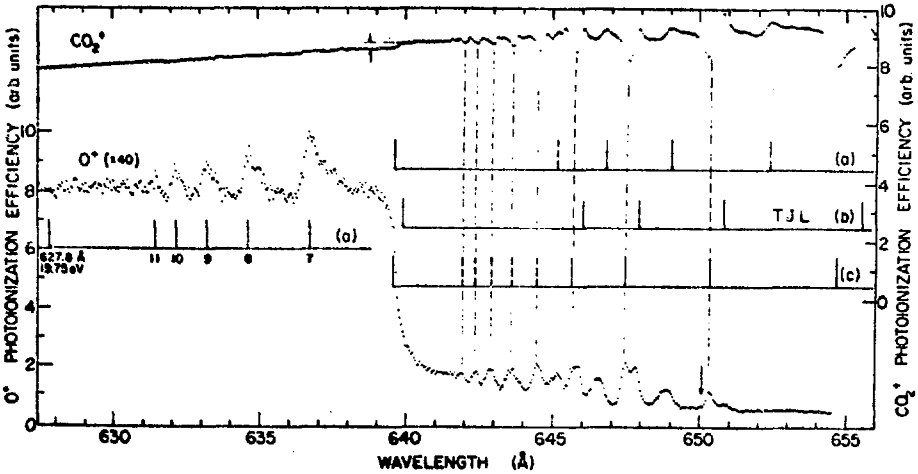

Fig. 2. Photoionization of CO_2 showing formation of O^+ at threshold (650 Å) and also by predissociation of C state of CO_2^+.

650.2 Å (19.07 eV) which corresponds to a gap in the photoelectron spectrum. In the region immediately above threshold, the data show clearly that the process occurs via initial formation of Rydberg states converging to the C $^2\Sigma_u^+$ excited state of the parent ion. The Rydberg states predominantly autoionize to form CO_2^+ in one or more of the several electronic states of lower energy ($X^2\Pi_g$, $A^2\Pi_u$, $B^2\Sigma_u^+$). The formation of O^+ probably occurs by predissociation of the small fraction of sufficiently highly vibrationally excited CO_2^+ ions in either the A or B states. At about 19.40 eV the CO_2^+ ion is formed in the $C^2\Sigma_g^+$ state. The photoionization efficiency curves for parent and fragment ions, the absence of fluorescence from the C state (36) and, most conclusively, a photoelectron-photoion coincidence study(28) show that the C state is completely predissociated, predominantly by process (1). Since the products can only form quartet states, predissociation of the C state as well as the lower energy fragmentation processes occur in violation of spin conservation.

Fragmentation of NO_2^+ has several unusual and interesting features (see Fig. 3). The energetically lowest possible fragmentation producing NO^+ + O in their ground states is observed to occur together with an unexpected associated metastable ion.

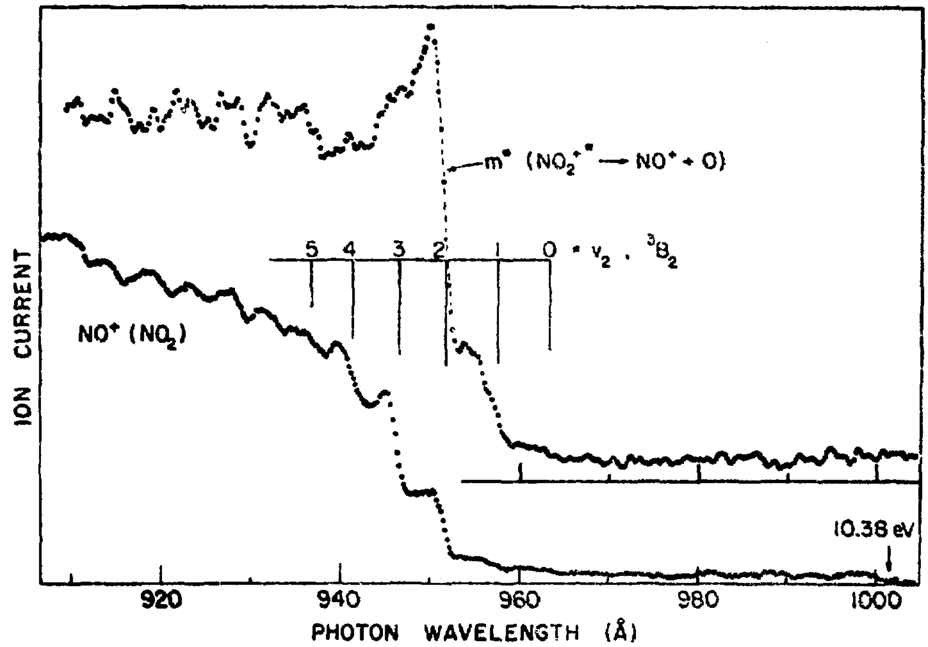

Fig. 3. Photoionization of NO_2 showing formation of NO^+ fragment fragment and associated metastable ion from various vibrational levels of the $^3B_2$ state of NO_2^+.

The thermochemical threshold is at 1001.5 Å (12.38 eV). There is some evidence for a threshold in this region although repeated experiments could not verify it and it is very doubtful at best. At about 964.0 Å (12.86 eV) the ion is formed in the first electronically excited $^3B_2$ state and the photoelectron spectrum(24) shows a strong progression in the bending vibrational mode. The photoionization data show that this predissociates with a rate that is very small and possibly zero for v = o but increases very rapidly with vibrational quantum number. Metastable ions corresponding to the decomposition are seen to be formed from the v = 1 and 2 (and possibly v = o) vibrational states. By comparing the relative intensities of the metastable ions formed from these states in the photoelectron spectrum and considering the flight-time characteristics of the mass spectrometer, the following dissociative lifetimes were deduced:

$v = 0, \tau \geq 150$ µsec

$v = 1, \tau = 55 \pm 10$ µsec

$v = 2, \tau = 15 \pm 5$ µsec

$v = 3, \tau \leq 5$ µsec

Measurements of the metastable peak width show that nearly all of the excess energy available in the decomposition is released as kinetic energy.

The characteristics of the above decomposition process are very unusual. The $^3B_2$ state of the ion should correlate adiabatically to the ground state products but obviously must do so over a potential barrier at least in most of its configurations.

A survey of the available data shows that most fragmentation of small polyatomic molecular ions produced by valence shell photoionization proceeds by predissociation. Electronic predissociation is involved in most cases but it is usually not clear whether the process is purely case I or also involves vibrational predissociation of the final electronic state.

LARGE POLYATOMIC MOLECULES

While the decomposition of small polyatomic ions can be usefully discussed and explained in terms of details of potential surfaces, some features of which can be determined from experimental data, adiabatic correlation diagrams and theoretical calculations, such an approach for larger polyatomic ions is usually not fruitful due to the far greater complexity of the systems. The most commonly used and most successful approach which provides quantitative results with modest computational effort involves the use of statistical theories. The RRKM theory(37) in microcanonical form appropriate to isolated molecules of specific internal energy has been most useful. It is based on the assumption of effective randomization of internal energy such that the rate of reaction is proportional to the ratio of volume of phase space available to the molecule in the critical configuration for reaction to that available to the activated molecule. The theory has been tested most extensively and critically for neutral molecules decomposing on a single potential surface. It has been extensively successful(38) although evidence of failure of energy randomization has been found for some cases of very non-random chemical activation.(39,40)

The basic equation of RRKM theory for $k_a(E^*)$, the unimolecular rate constant for decomposition of a molecule of internal excitation energy E^*, is

$$(1) \qquad k_a(E^*) = C \frac{1}{hN^*(E^*)} \sum_{E^\dagger}^{E^\dagger} P(E_{vr}^{\dagger})$$

where $E^\dagger = E^* - E_a$, E_a is the activation energy for reaction, $N^*(E^*)$ the density of states (number of states per unit energy) of the activated molecule, $P(E^\dagger_{vr})$ is the degeneracy of the state of the activated complex having vibrational and internal rotational energy $E^\dagger_{vr}$, and C is a dimensionless number (of the order of magnitude of unity) which includes ratios of symmetry numbers and moments of inertia as discussed in detail elsewhere.(37,41) Many methods for evaluating $N^*(E^*)$ and the summation in equation (1) have been described.(37,42) It is worth noting that the usual methods for evaluating k_a and especially the summation in equation (1) do not specifically conserve total angular momentum. This does not usually lead to significant errors except for certain cases of loose activated complexes in which so-called "Gorin-tumbling" rotational degrees of freedom of the separating fragments are active and are summed over without regard to conservation of angular momentum. Conditions for which the standard statistical calculations for dissociation of a molecule into an atom plus another molecule are very bad approximations were first pointed out by Nikitin(43) who also derived more valid approximations. Klots(44) has considered this problem for a wide variety of fragment products and gives convenient approximate formulae.

At threshold ($E^* = E_a$), equation (1) reduces to $k_a \approx 1/hN^*(E^*)$, that is it predicts a minimum rate(45) which is readily calculable. This minimum rate is inversely proportional to N^* which is a rapidly increasing function of E^* and of the number of internal degrees of freedom. Above threshold the calculated rate is practically a monotonically increasing function of E^*. If RRKM theory is applicable to decomposition of molecular ions formed by photoionization, we expect that metastable ions will be undetectable for molecules with sufficiently few internal degrees of freedom and/or such low activation energies that the minimum rate is $>10^6$ sec^{-1}. For sufficiently large molecules and large activation energies, metastable ions are expected to be observable and the kinetic shift is expected to increase with activation energy and number of degrees of freedom. These expectations are amply borne out by a large amount of data with relatively few exceptions.

The RRKM theory (or one of its variant forms) can also be extended to calculate the distribution of various forms of energy in the fragment products. A number of such extensions have been made, some specifically for ionic decompositions with their characteristic long range forces between fragments (see references 40, 43, 44 and references therein). Of particular importance here are calculations of the distribution of relative kinetic energy of the products since this is readily measured experimentally. The validity of straightforward applications of statistical theory to fragment energy distributions depends on the characteristics of the activated complex and particularly on the interaction between fragments after passing through the critical configuration. For simple bond dissociation of a molecular ion with no excess activation energy, the theory would be expected to be adequate and predicts a quasi-Maxwellian kinetic energy distribution which is a measure of the total excess energy available. For reactions involving potential barriers and excess activation energy, as is often the case with rearrangements, the observed kinetic energy distribution is very often higher than the simple statistical prediction and can be interpreted to give information on the characteristics of the potential barrier.

Statistical theory of mass spectra.(46,47)

From its considerable success for neutral molecules the RRKM theory would be expected to be applicable to the decomposition of molecular ions occurring on a single potential surface. There are a number of well known cases in which the lowest energetically possible dissociations of polyatomic molecular ions occur from vibrationally excited ions in the ground electronic state (e.g., n-alkyl amines and many alkanes). However, in many other cases, fragmentation thresholds occur at energies corresponding to the production of ions in electronically excited states. In any case, at higher photon energies it is clear that the molecular ion is initially prepared in a large number of electronically excited states as shown by the photoelectron spectrum at that photon energy. Photoionization mass spectrometry, charge-exchange mass spectrometry and the limited data available for larger molecules by the photoelectron-photoion coincidence technique show that most, if not all, ions with internal energies above the first fragmentation threshold dissociate. Strong arguments, based on theory and experiment, support the assumption that normally a negligible fraction of parent ions undergo direct dissociation (see reference 46). The dominant process of predissociation can occur in many ways. At one extreme, the ions may predissociate by vibration, remaining on the initial electronic potential surface, in which case RRKM theory is applicable with appropriate parameters. At the other extreme, the ions could undergo a series of rapid (compared to intervening dissociation) radiationless transitions, forming all isoenergetic states with equal probability, predominantly highly vibrationally excited ions in the ground electronic state. Again, RRKM theory is applicable with an appropriate set of structural and energy parameters. The latter case is that assumed in the usual form of the Statistical Theory of Mass Spectra (STMS) or, as it is now more commonly called, Quasi-Equilibrium Theory (QET). Predissociation (predominantly vibrational and describable by RRKM theory) is then assumed to occur along competitive reaction paths each with an activation energy and activated complex appropriate to the specific fragmentation process. For larger values of E^* many of the primary product ions will in turn possess sufficiently large (and statistically calculable) internal energies such that they can undergo still further competitive and successive decompositions until the resulting product ions have insufficient internal energy to decompose further. The result of a QET calculation is conveniently displayed as a "breakdown graph" showing the relative abundance of various ions (after a time of $\approx 10^{-5}$ sec) as a function of internal energy of the initial parent ion.

The general model of competitive and successive decomposition occurring on a time scale much larger than 10^{-14} sec is abundantly supported by a vast body of data (46,47) on ion abundances, ionization efficiency curves, measurements of metastable ions and of the kinetic energy released in formation of fragment and metastable ions. However, accurate and unambiguous quantitative tests of the theory are not readily made and probably the major uncertainty concerns the degree to which the assumption of complete electronic relaxation before dissociation is valid. This uncertainty should not be considered a fatal flaw of the model. It is similar to the uncertainty which accompanies the application of statistical thermodynamics in that it concerns the regions of energetically available phase space which are effectively excluded to the system during some time interval. At present, comparison of theory and experiment can be very helpful in inferring the degree of electronic relaxation and its correlation with pertinent parameters such as energy gaps between electronic states.

Radiationless transitions

Enormous advances in this area have been made in the past decade as a result of much experimental and theoretical work on fluorescence and phosphorescence phenomena. A number of good reviews are available(48-51) and a very recent one(52) is particularly helpful in removing earlier confusion in the theory regarding proper choice of basis sets. Only the briefest outline of those aspects of this topic most relevant to the present subject can be presented here.

Practically all of the experimental and theoretical work on non-dissociative radiationless transitions deal with molecular systems whose ground and relevant excited state potential surfaces are "nested", i.e. do not intersect in the region accessible by photon absorption. Two major experimental generalizations, which apply to gaseous molecules under collisionless conditions as well as to molecules in the condensed phase are (1) the "energy gap law" according to which the rate of radiationless transition decreases approximately exponentially with increasing energy gap between the two potential surfaces, and (2) the isotope effect whereby perdeuteration results in a strong decrease in the rate. The simpler theoretical treatments which have explained these rules have employed a model of (not too greatly) displaced and distorted oscillators. The theoretical expression for the transition rate can be written in a very crude approximation as a product of an electronic and a Franck-Condon factor. Nearly all quantitative calculations have been concerned with the latter factor which is capable of explaining the energy gap and isotope effects. Accurate theoretical calculations of electronic factors have not yet been achieved although the perturbations responsible have been formally considered in some detail (spin-orbit coupling for intersystem crossing and vibronic coupling for internal conversion within the same spin-multiplicity manifold) and crude estimates made. It has been estimated (53) that variation of the vibronic coupling term for different molecules may introduce an uncertainty of only about two orders of magnitude in the rate so that it is useful to note its magnitude for a large number of aromatic molecules (see reference 48, chapter 5). If k_{nr}, the rate of non-radiative transition is written as

$$k_{nr} = A \cdot F$$

where A is the elctronic factor and F the Franck-Condon factor, A has been given the value of $\sim 4 \times 10^{12}$ sec^{-1} for internal conversion and ~4 × 10^4 sec^{-1} for intersystem crossing.(48) The value of F can be taken from Fig. 5.2, p. 148 of reference 48 or estimated for the perprotonated compound from the equation for the line of that figure:

$$- \log F \cong + 0.11\ (\Delta E - E_o)/\eta + 0.7$$

where $(\Delta E - E_o)/\eta$ is the normalized energy gap in units of $10^3 cm^{-1}$, i.e. ΔE is the energy gap between zero-point levels of the two electronic states, $E_o \cong 4000\ cm^{-1}$ for the fully protonated compound and η is the relative number of hydrogen atoms as given in the formula $C_{1-\eta}H_\eta$. Englman and Jortner(53) give still simpler expressions with an estimated error of two orders of magnitude.

It should be emphasized that the internal conversion rates discussed above, which can be of the order of 10^{12} sec^{-1} (see table 5.7, p. 187 of reference 48) apply to what Englman and Jortner (53) call the "weak coupling case" for which energy gaps are larger than typical vibrational frequencies and displacements between potential surfaces are small ("nested" surfaces). These authors also treat a "strong coupling case" characterized by a large displacement of the potential energy surfaces along at least one normal coordinate so that the surfaces intersect in the vicinity of the minimum of the upper surface. The corresponding rate equation has the Arrhenius form with activation energy corresponding to the energy difference between the zero point level of the upper state and the minimum intersection energy.

Recently the variation of radiationless transition rates as a function of vibronic energy and even of specific vibronic states has been investigated(51-55) experimentally and theoretically. The experimental data show the rates to increase, often quite rapidly, with increasing vibronic energy although the theory indicates that the increase may sometimes be small or even negative, depending strongly on the specific vibrational modes excited.

A survey of photoelectron spectra(13) of larger molecules for which QET is expected to be applicable shows that energy gaps larger than ~2.0 eV are relatively rare (and this observation does not consider states which do not appear in the photoelectron spectra but may participate in electronic relaxation). Smaller gaps and overlapped bands which indicate a good possibility of the faster strong-coupling case are very common. From the above considerations we may then estimate that radiationless transition rates are usually much greater than 10^9 sec^{-1}. Thus, it is very likely that extensive if not virtually complete electronic relaxation occurs before the lowest energy decompositions accompanied by metastable ions indicating dissociation rate constants of the order of 10^5 sec^{-1}. Less reliable predictions can be made regarding the extent of electronic relaxation before dissociation for the more highly excited states of ions well above one or more dissociation limits. From the energy gap law, one expects the relaxation to occur stepwise and, for equal energy gaps, with usually increasing rate for successive steps due to the effect of increasing vibrational energy and to the greater possibility of surface crossings and strong-coupling behavior. Estimates of relaxation rates could be made for individual cases but the estimation of the rates of competing dissociations of excited electronic states would usually suffer from more uncertainty in the appropriate activation energies as compared with the case of the ground state of the ion. For certain classes of compounds, such as the alkanes for instance, for which the photoelectron spectra indicate only broad and strongly overlapped bands, extensive electronic relaxation seems very likely and these compounds have generally shown very good agreement between experiment and the predictions of QET based on complete electronic relaxation.

Recent tests of QET

For a comprehensive presentation of experimental data relating to tests of QET, the reader is referred to review articles (46,47) which may be summarized fairly as showing that QET accounts well for the general features of mass spectra and decomposition behavior of large molecular ions, but that there is evidence for its failure in some instances. The theory is sufficiently successful as to become useful in practical applications of mass spectrometry to molecular structure determination.(56) This section will emphasize recent tests of QET, particularly those employing more powerful techniques.

Many earlier tests of QET have involved the experimental measurement of breakdown curves by photoionization(4,57) techniques. The interpretation of these experiments required assumptions regarding cross section behavior. Charge transfer(25) techniques which yield data points at widely separated energies and sometimes suffer from difficulties of interpretation have also been used. The recently developed technique(26-30) of detecting mass-analyzed ions produced in coincidence with energy-analyzed photoelectrons by monochromatic photons yields breakdown curves unambiguously. Stockbauer(30) has recently published breakdown curves of very high quality for methane and ethane. His data for ethane are shown in Fig. 4, together with the results of an earlier theoretical calculation. The small discrepancy is readily attributed to the use of somewhat inaccurate thermochemical data in the calculation. The complete absence of parent ions above the first fragmentation threshold, the behavior of the competitive decompositions producing $C_2H_5^+$ and $C_2H_4^+$ and of the succeeding

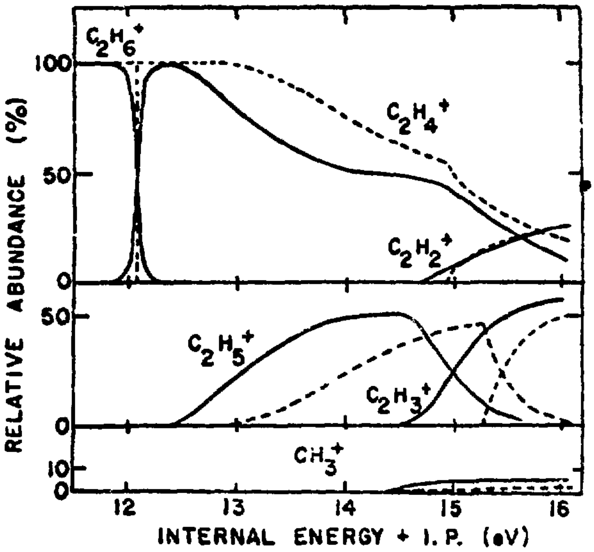

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Fig. 4. Comparison of experimental (solid lines) breakdown curves of Stockbauer (ref. 30) with results of QET calculations (dashed lines).

decomposition of these ions by elimination of H_2 are as predicted by the theory. Of particular importance is the smooth behavior of the curves (except at thresholds as expected) although the photoelectron spectrum shows at least three electronic bands in this region. The data show that the decomposition behavior is a smooth function of the internal energy of the parent ion independent of initial electronic state. Such data for a number of molecules will provide excellent tests of theory. Lack of electronic relaxation can evidence itself by persistence of parent ions well above the first dissociation limit and by abrupt changes in breakdown curves at thresholds for formation of excited states.

Another series of important developments have been made by Osberghaus, Ottinger and their co-workers.(58-60) By producing initial ionization along a thin equi-potential plane in a strong electric field and measuring the kinetic energy distribution of fragment ions, they were able to measure decomposition times over a range from 5×10^{-9} sec to 5×10^{-6} sec. The earlier work employed electron impact ionization which produced ions with a range of internal energies and they showed that the resulting ions decayed with a distribution of rate constants as predicted by QET. In the most sophisticated version of their experiment, Andlauer and Ottinger(61) initiated ionization by charge-transfer by which

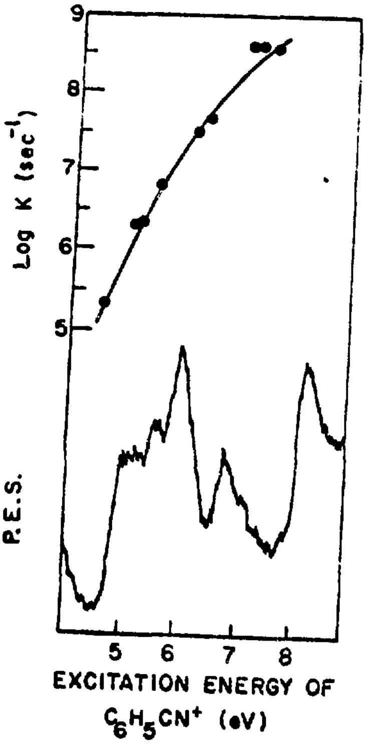

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Fig. 5. Comparison of the rate constant for decomposition of benzonitrile ion into $C_6H_4^+$ + HCN with the photoelectron spectrum.

parent ions were formed with specific amounts of internal energy. For two molecules, they were able to measure the rate constant as a function of excitation energy of the parent ion. The first case was that of benzonitrile for which the experimental data, together with the corresponding region of the photoelectron spectrum(13) is shown in Fig. 5. The data of Fig. 5 show that k is a smoothly and monotonically increasing function of E^* even though the photoelectron spectrum shows at least four different electronic bands in the energy region covered. A theoretical rate curve calculated by Klots(44) has the same general shape but the quantitative agreement is poor, in great part due to the use of an incorrect heat of formation for the fragmentation. Of far more significance is the experimental evidence for electronic relaxation as indicated by the monotonic behavior of k.

The other molecule investigated by Andlauer and Ottinger is benzene. Four decompositions occur with roughly the same thresholds and these workers were able to measure the decomposition rate by monitoring two fragments, $C_4H_4^+$ and $C_6H_5^+$. If these two fragmentation processes are competitive, the decay rates of the parent ion inferred by measuring the formation of each of the ions should be identical. The results are shown in Fig. 6 where it is seen that for E^* above 5.0 eV the two ion fragments yield different curves. Unfortunately the apparent discrepancy depends on only two sets of points but if correct, the data clearly indicate lack of complete randomization and apparently require that the two fragments come from different states or forms of the parent ion. Also shown in Fig. 6 is a dashed line obtained by photoionization as will be described later. The latter results indicate that for values of E^* below 5.0 eV all four decompositions are in competition. The facile conclusion from the above data is that randomization occurs very near the fragmentation threshold but fails at some higher energies.

Benzene and some derivatives

The fragmentation of the benzene ion has a long history in connection with QET. It was once proposed(46) as an obvious case of failure of QET since four metastable ions produced by decomposition of the parent ion were observed although the appearance potentials of the corresponding fragments measured by electron impact differed by more than 1.0 eV whereas QET requires that they be very nearly the same. Vestal(47) pointed out some reasons for the apparent discrepancy and recent photoionization mass spectrometric studies(62,63) have cleared up this problem entirely. Some of the relevant data and the photoelectron spectrum are shown sketched semi-quantitatively in Fig. 7 for both C_6H_6 and C_6D_6. In one photoionization study(63) the ionization efficiency curves of the four metastable ions were also measured and found to be very nearly identical (except for intensity) as required by QET for competitive decompositions. The metastable curves have the form of moderately sharp steps located in the threshold region for fragment production. The curvature and asymptotic form of the curves for the fragment ion make "threshold" an inappropriate description. The shape and position of the metastable curves are far more meaningful as will be described shortly. The fragment and metastable curves for C_6D_6 appear very similar to those of C_6H_6 except that they are shifted upward in energy by about 0.35 eV. The normalized derivative curve for an ion yields its breakdown curve(4) to an approximation which is especially good for a metastable ion. This experimental breakdown curve can be compared with the calculated one of Fig. 1 to determine a short segment of the curve of log k vs. E^* as illustrated in Fig. 8 for

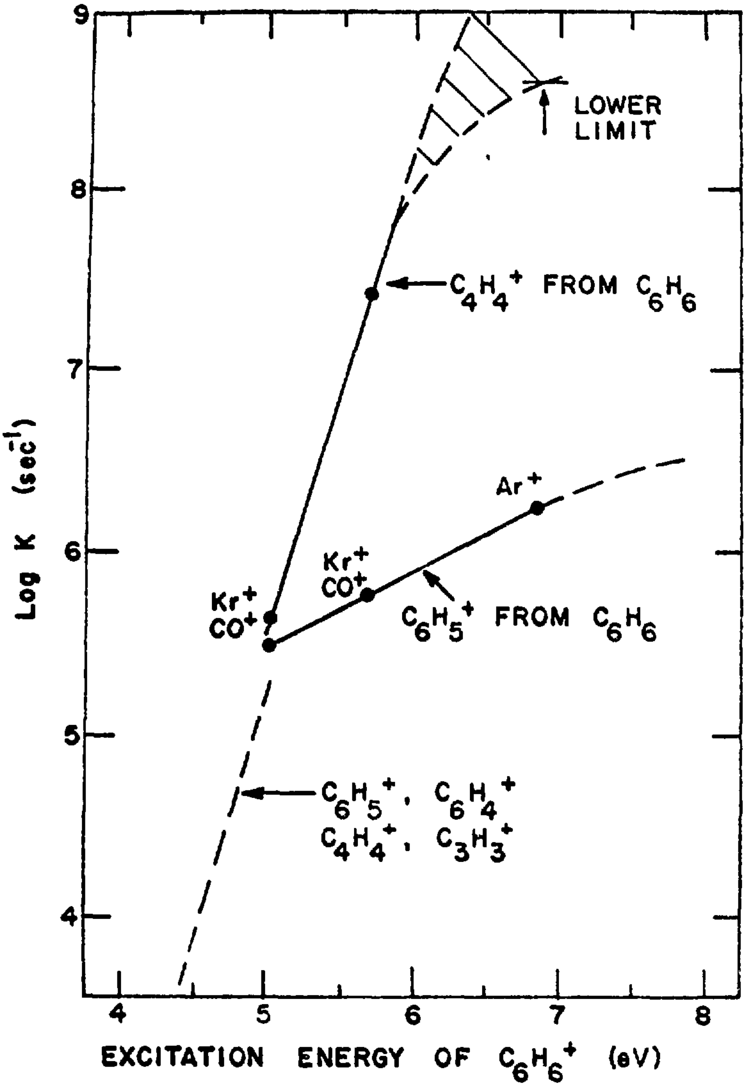

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Fig. 6. Rate constants as a function of internal energy for decomposition of the $C_6H_6^+$ ion as determined by charge-transfer excitation (points and solid lines, ref. 61) and by photoionization measurements of the corresponding metastable ions (dashed line, ref. 63).

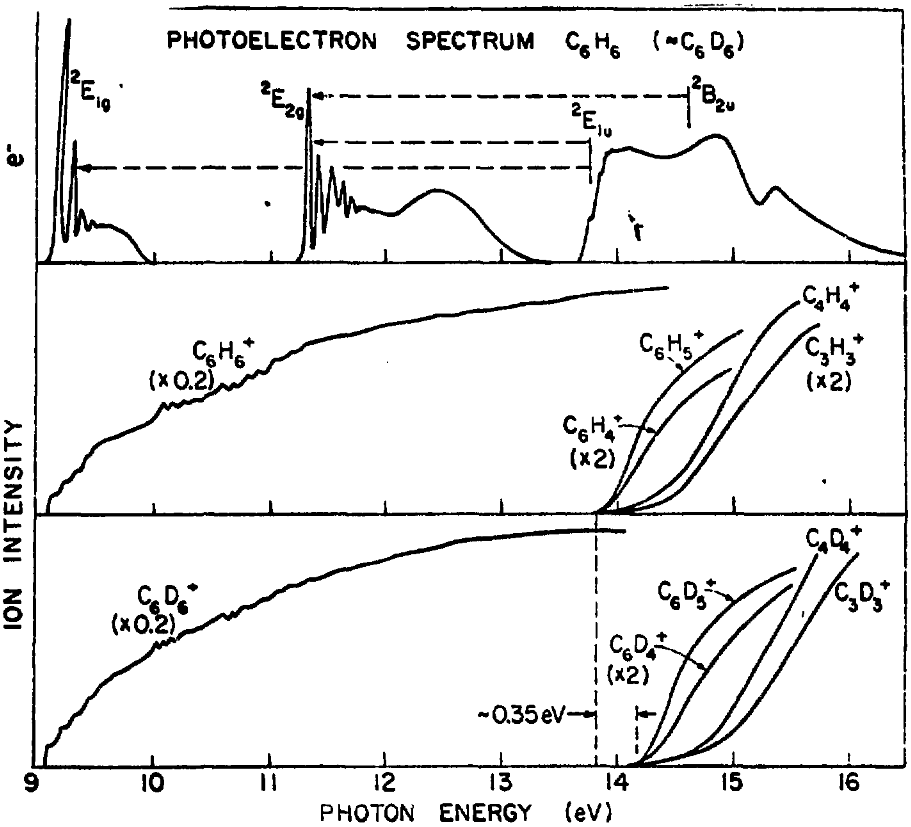

Fig. 7. Photoelectron spectrum of benzene (top) and photoionization efficiency curves for parent and fragment ions of benzene and perdeuterobenzene.

C_6D_6. Thus k = 6.0×10^4 sec^{-1} at 859 Å (14.43 ev) which corresponds to E* = 14.43 - 9.25 = 5.18 eV and the slope is 2.87 eV^{-1} as shown. The dashed line of Fig. 6 was so obtained for C_6H_6. The analogous line for C_6D_6 has very nearly the same slope but is displaced to higher energies by about 0.35 eV.

The data of Fig. 7 show that fragmentation at threshold occurs from parent ions initially formed in the $^2E_{1u}$ excited state and at somewhat higher energies in the $^2B_{2u}$ state as well. At threshold, i.e. in the region of metastable ion formation, it is almost certain that a significant amount of electronic relaxation occurs for the following reasons. Both of the excited electronic states mentioned above have one or more optically allowed transitions to lower states as shown by the dashed lines

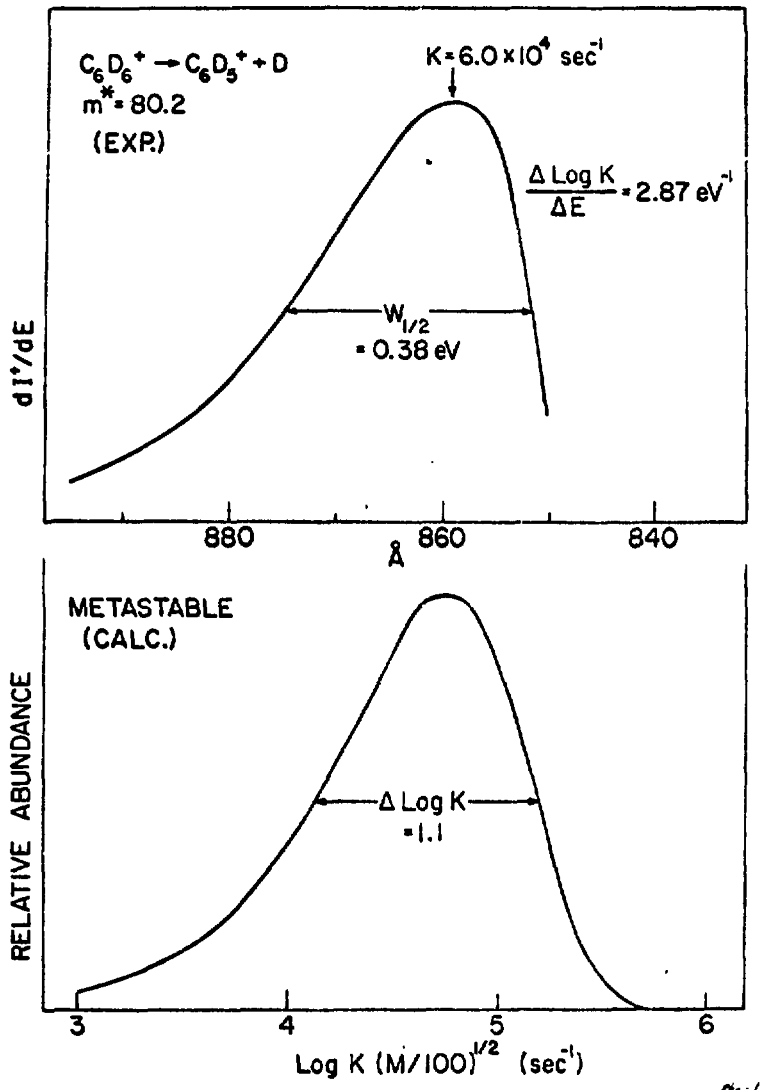

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Fig. 8. Comparison of experimental breakdown curve as a function of energy with calculated curve as a function of rate constant in order to determine dependence of log k on E^* for $C_6D_6^+$.

of Fig. 7, yet no significant deactivation by radiation is observed in 10^{-4} sec as shown by the presence of intense metastable ions. Several attempts have been made to observe fluorescence of the benzene ion without success. Studies(64,65) of isotopically substituted benzenes have shown that complete isotopic scrambling of all carbon and hydrogen atoms occurs independently prior to metastable decomposition and nearly complete scrambling before at least some of the faster fragmentations. The thermochemical threshold for the reaction producing $C_6H_5^+$ is independently known(62) to be at about 12.95 ev or $E_a = 3.70$ eV. Figures 6 and 7 show a large kinetic shift of about 1.9 eV which implies, in the framework of RRKM theory, a very high density of states for the active molecular ion which could only be attained in one or more of the lowest electronic states. The shift of metastable and fragment curves upward in energy by about 0.35 eV for C_6D_6 is approximately as expected from the increased density of states of the perdeuterated ion while the positions of the $^2E_{1u}$ and $^2B_{2u}$ states in the photoelectron spectrum remain very nearly unchanged. A very crude estimate of the radiationless transition rate from the $^2E_{1u}$ state to the $^2A_{2u}$ state just below at about 12.2 eV gives a value of 10^{10} - 10^{11} sec^{-1}. However, the larger gap (about 2.2 eV) between the ground and first excited states suggests that complete relaxation to the ground state may not occur. Indeed, Rosenstock et al.(62) interpret their data in terms of dissociation from the ground and first excited states independently.

Extensive photoionization mass spectrometric measurements of fragmentation of the phenyl halides have been made.(63) The lowest energy process for the chloride, bromide and iodide is the simple bond fission forming $C_6H_5^+$. No other fragmentation process occurs until much higher energies. In all cases, intense metastable ions are seen and measurements of k vs. E^* similar to the dashed line of Fig. 6 were made. The parent ions at threshold are in all cases initially prepared in highly excited electronic states but the energy dependence of k and the values of the kinetic shift which increase with activation energy all indicate extensive and possibly complete electronic relaxation at the fragmentation threshold. The photoelectron spectra in all cases show energy gaps which are smaller than the larger ones in benzene.

Kinetic energy release in fragmentation

Early measurements (66,67) of kinetic energy release in fragmentation of polyatomic ions were made for ions prepared with a rather large and inaccurately known internal energy distribution. The experimental kinetic energy distributions were found to be predominantly quasi-Maxwellian and approximately as predicted by application of QET. The application of QET requires an additional assumption regarding disposition of kinetic energy in the decomposition of the activated complex. It has been assumed(68) that the kinetic energy distribution is equal to that along the reaction coordinate plus any due to activation energy for the reverse reaction. Other formulations(44) have employed microscopic reversibility and the assumption of a Langevin cross section (centrifugal barrier only) for the reverse reaction which is thus assumed to have no activation energy. Fortunately, many decompositions (e.g. practically all simple bond fission) are expected to have zero reverse activation energy and measured kinetic energies of such decompositions have usually been in reasonable agreement with theory. This agreement has encouraged the use of measured kinetic energies in a semi-empirical method of correction for excess internal energy in the calculation of thermochemical thersholds from measured values.(69) More important as test of the applicability of QET to the calculation of kinetic energy distributions are measurements on metastable ions which are produced from parent ions with a narrow range of internal energies and which have kinetic energy distributions measurable with very high precision. Such high precision measurements are only recently being made.(8) Together with precise determinations of E^* by photoionization techniques, such data should provide excellent tests of the applicability of QET to simple bond fission processes and may give valuable information on the characteristics of activated complexes for those rearrangement decompositions which occur with excess activation energy.

CONCLUSION

Fragmentation processes of diatomic and small polyatomic ions are fairly well understood in principle and a fruitful interplay of experiment and theory is in progress. For larger polyatomic molecules, progress requires much more experimental information on the degree of electronic and vibrational relaxation and the validity of RRKM theory for preparations of varying randomness, particularly at the higher interval energies (up to about 10 eV or so) produced in valence shell ionization. Nevertheless, QET has provided a fairly successful description of a wide range of phenomena enencountered and there is reasonable hope that tractable extensions or completely new theoretical treatments which specifically include the effects of incomplete electronic and vibrational relaxation can be developed. The latter types of approach are being developed particularly in connection with studies of photochemical decompositions(70) which are formally the same as the dissociation processes considered here, although a few significant differences exist. The energy gaps between electronic states, particularly that between the ground and first excited state, are generally much smaller for ions and hence electronic relaxation should be more rapid. The polyatomic ions are practically always doublet radicals characterized by unusual lability and subject to a wide variety of rearrangements. Simple bond dissociation nearly always occurs without excess activation energy and the long range ion-induced-dipole potential for the departing fragments yields a well known rotational barrier for the reaction. Most of these factors support the expectation that simple statistical theories will be valid more generally for ionic decompositions than for photochemical ones. A serious disadvantage in the case of polyatomic ions is the relative lack of knowledge of the geometry and other properties of parent and fragment ions. This gap in knowledge is slowly being filled by a variety of techniques but at present remains a significant difficulty.

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