Dissociation Lifetimes of Molecular Ions Produced by Charge Exchange *

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Ions of the benzonitrile, benzene and thiophene molecules were produced in well-defined states of excitation by charge exchange with Xe\(^+\), Kr\(^+\), Ar\(^+\), CO\(^+\), and N\(_2\)\(^+\). Their subsequent unimolecular decomposition was followed, as a function of time, by allowing the dissociations to take place within a strong homogeneous draw-out field and measuring the kinetic energy of the product ions. The decompositions were found to be purely exponential within experimental error, and the corresponding decay rate constants \(k\) (for \(2 \times 10^6\) sec\(^{-1} \leq k \leq 5 \times 10^8\) sec\(^{-1}\)) proved to be monotonically increasing functions of the excitation energy. These are the first unambiguous measurements of this function \(k(E)\) for any molecule. In the case of benzene, the reactions C\(_6\)H\(_6\)\(^+\) \(\rightarrow\) C\(_6\)H\(_5\)H\(^+\)+H and C\(_6\)H\(_6\)\(^+\) \(\rightarrow\) C\(_6\)H\(_5\)H\(^+\)+C\(_2\)H\(_4\) were found to be definitely not in competition with one another. Furthermore the dependence of the excitation energy on the impact energy was measured. A variation of the impact energy between 10 and 200 eV\(_{\text{c.m.}}\) only changes the internal energy \(E\) by about 0.1 eV. This value appears to be in qualitative agreement with calculations on near-resonant charge transfer by Gurnee and Magee.

I. Introduction

Unimolecular decompositions of excited polyatomic ions play an important role in many radiochemical and radiobiological systems as well as in organic mass spectrometry. An understanding of the host of possible concurrent and consecutive reactions has to be founded on a consistent picture of the time scale as well as the energetics of the unimolecular processes. Today still very little is known about the decomposition rate constant \(k\) of isolated excited ions, and even less about the dependence of \(k\) on the excitation energy \(E\). In principle the function \(k(E)\) can be calculated within the framework of the quasi-equilibrium theory, henceforth abbreviated as QET\(^1\). However, the great number of assumptions necessary for any such calculation makes an experimental determination of \(k(E)\) highly desirable. In previous communications\(^2,\ 3\) we have reported on a method for measuring, in a well-defined manner, the decomposition rate of ions produced by electron impact. Subsequently we have been able, by means of varying the electron energy, to extract from these measurements \(k(E)\) for a few decompositions of benzonitrile, butane and heptane ions\(^4,\ 5\). However, this

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derivation of \(k(E)\) was not quite unambiguous due to the fact that electron impact always produces ions possessing a wide and largely unknown spectrum of excitation energies. This disadvantage can be overcome by using charge exchange ionization. Lindholm has shown that charge exchange is capable of producing ions in monoenergetic levels of excitation. Combining Lindholm's method of well-defined excitation with our technique of measuring decomposition rates should therefore give definite information on \(k(E)\).

In the present work we report on experiments of this type on the benzonitrile, benzene and thiophene ions. They constitute, to our knowledge, the first direct measurements of \(k(E)\) for any ions. [For decomposition of neutrals, Rabinovitch has determined \(k(E)\) in a completely different way.] At the same time very accurate information was obtained on the amount of kinetic energy that is converted into excitation of the target in charge exchange processes. It is found to be small (though measurable), which a posteriori provides a sound basis for the "monoenergetic" excitation method. In a few cases the variation of the charge exchange cross section with initial kinetic energy was also measured.

### II. Principle of Measurement

The decomposition rate constant \(k\) was measured by relating it, or rather the mean parent ion lifetime \(\tau = 1/k\), to the fragment ion kinetic energy in the following way (for details see 3). Ionization takes place within a strong homogeneous draw-out field. The gas under investigation (e.g. benzonitrile) traverses this field in a very narrow molecular beam which coincides with an equipotential surface. Thus all ions are initially formed at the potential of this particular surface. An energy selector placed behind the exit of the ion source then records a kinetic energy distribution of the ions which simply reflects the gas density profile of the beam measured perpendicular to the ionization equipotential surface, with the draw-out field strength as a scale factor. However, this is only true for the parent ions \(M_0^+\) (of mass \(m_0\)) of the target gas. For any fragment mass \(m_1\) the kinetic energy distribution is distorted from that profile to the low-energy side. Figure 1 illustrates schematically this change of peak shape, shift of the peak center and the development of a "tail". A fragment ion which is formed from a parent ion with a delay \(t\) after the initial ionization, only retains the fraction \(m_1/m_0\) of the kinetic energy which the parent ion had at the instant of decomposition. This energy deficit increases proportionally to \(t^2\). Thus, the low energy component of the energy distribution of mass \(m_1\) ions is related to the distribution of lifetimes \(t\) and hence to the desired distribution \(\Pi(k)\). Of great practical importance is the draw-out field strength, \(F\). For small \(F\), only small values of \(k\) produce a noticeable peak distortion, while for the detection of contributions from large \(k\) high values of \(F\) are necessary. With our apparatus values of \(k\) ranging from \(2 \times 10^5\) to \(2 \times 10^8\) sec\(^{-1}\) can be measured.

In addition to the low energy tail on the beam profile peak, the energy distribution exhibits another, so-called satellite peak at still lower energy. It results from decompositions in the field-free region outside the ion source and is the analog on the energy scale of the classical "metastable peaks" on the mass scale. Both "main peak" distortion and relative satellite peak intensities were used in the analysis (see Sect. V).

### III. Experimental

The apparatus has been described in detail in 3. Figure 2 gives a schematic of the ion source. The essential element is a planar disc-shaped molecular beam of the target gas. It is defined by the concentric circu-
is applied. After retardation by the grid R the emerging ions are energy and mass analyzed. The experiments consist of scanning the kinetic energy distribution at a fixed mass.

Typical operating parameters were: electron current 30 mA, electron energy 120 eV. At a pressure of $5 \times 10^{-4}$ Torr in the primary ionization region a primary ion current of 0.5 μA was obtained through the charge exchange region, at an ion energy of 90 eV. The energy spread was between 1.5 and 5 eV. The target gas pressure in the center of the molecular beam disc was about $5 \times 10^{-5}$ Torr. The background pressure in the apparatus resulting from primary gas effusing through the grid AC+ amounted to $10^{-5}$ Torr. Great care was taken to keep the target gas background pressure in the primary ionization region as small as possible. Under the intense electron bombardment, even traces of target gas will yield considerable fragment ion intensities. Because the primary ionization region is at a more positive potential than the molecular beam region, fragments resulting from delayed decompositions can appear at and around the molecular beam potential, by virtue of an appropriate energy deficit as described above. These ions may seriously interfere with the measurement of the very small ion currents resulting from charge exchange. Efficient differential pumping of the primary ionization region is therefore extremely important.

The energy and mass selected ion current at the multiplier was, at the maximum of the beam profile, on the order of $10^{-16}$ A. This means an intensity loss of about two orders of magnitude compared with the earlier electron impact experiments.

IV. Possible Sources of Error

Proper operation of the apparatus was ascertained by the following tests.

a) As a check for possible collision-induced contributions to the decomposition the background pressure was raised from $10^{-5}$ to $10^{-4}$ Torr. For all processes studied (except Xe$^+$-benzonitrile, see below) the ratio of satellite to main peak remained constant within 1%. This remarkable insensitivity against pressure merely results from our choice of processes. In this work only decompositions were studied which have a very intense metastable peak to begin with, so that collisions, assuming reasonable cross sections, can make only minor contributions.

b) Possible distortion of the draw-out field by the space charge of the primary ions was checked using the process

$$\text{Xe}^+ + \text{C}_4\text{H}_4\text{S} \rightarrow \text{C}_2\text{H}_2\text{S}^+ + \text{C}_2\text{H}_2 + \text{Xe}.$$
Decreasing the Xe$^+$ current from $5 \cdot 10^{-7}$ to $5 \cdot 10^{-8}$ A did not change the satellite to main peak ratio within the error limits of $\pm 10\%$.

c) For the experiments with varying primary ion energy $eU_{ion}$ to be valid, the collection efficiency of the ions resulting from the charge transfer has to be independent of $U_{ion}$. This was ascertained for the reaction $Ar^+ + C_2H_2 \rightarrow C_2H_2^+ + Ar$ for which Maier has made reliable measurements of the cross section as a function of impact energy up to 50 eV$_{LAB}$\textsuperscript{10}. In the present apparatus, the variation of the $C_2H_2^+$ yield with the Ar$^+$ lab energy agreed with Maier’s data within $\pm 7\%$. Between 50 and 200 eV$_{LAB}$ similarly good agreement was found for the reaction $N_2^+ + O_2 \rightarrow O_2^+ + N_2$ with the results of STEBBINGS et al.\textsuperscript{11,12}. This indicates that any transverse momentum transfer associated with these particular charge exchange reactions is within the range that can be accepted by our apparatus. It is a plausible assumption that the same is true for all reactions studied here, which are also exothermic (see also Sect. VII, H).

d) Finally processes other than charge exchange which also could cause dissociative ionization had to be excluded. Ionization by secondary electrons produced at the electrodes AC$^+$ and AC$-$ or ionization by the impact of the primary ions could be discarded on the basis of the observed mass spectra (see below, Tables 3 and 4). These differ radically from the usual electron impact spectra and are, moreover, characteristically different for each primary ion species. Penning-Ionization by metastable neutral particles X$^*$\textsuperscript{13} effusing from the ion source certainly occurs\textsuperscript{14}. However, the energy available from a metastable X$^*$\textsuperscript{14} is always several volts less than RE(X$^*$), the energy liberated in charge exchanged with X$^*$\textsuperscript{6}. Therefore, if the latter lies in the range of interest just above some fragmentation threshold, the former will be insufficient to produce this fragmentation.

Table 1 gives the recombination energies RE of the primary ions used. The existence of several values of RE for the same ion is a complication which, however, can often usefully be exploited (see below). A further complication concerns the identity of the primary ions. Unlike in Lindholm’s work, a primary mass spectrometer could not be used for intensity reasons. This determined the choice of gases X. The mass spectra given in Table 2 also served to check the purity of the gases\textsuperscript{15}.

Table 1. Recombination energies RE of primary ions X$^+$.\textsuperscript{a}

<table>
<thead>
<tr>
<th>X$^+$</th>
<th>RE in eV (relative abundance in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe$^+$</td>
<td>12.13 (74—66); 13.44 (25—33); 12.5—16.5 (1)</td>
</tr>
<tr>
<td>Xe$^{++}$</td>
<td>12.5 (15); 18—20 (85)</td>
</tr>
<tr>
<td>Kr$^+$</td>
<td>14.0 (72—50); 14.67 (27—49); 16—18 (1)</td>
</tr>
<tr>
<td>Kr$^{++}$</td>
<td>21 (almost 100)</td>
</tr>
<tr>
<td>Ar$^+$</td>
<td>15.67, 15.94 (together 99); 18—20 (1)</td>
</tr>
<tr>
<td>Ar$^{++}$</td>
<td>11.5—12.5 (20); 24 (80)</td>
</tr>
<tr>
<td>Ne$^+$</td>
<td>21.56, 21.66 (together 100)</td>
</tr>
<tr>
<td>Ne$^{++}$</td>
<td>10.5—12.0 (almost 100)</td>
</tr>
<tr>
<td>He$^+$</td>
<td>24.58 (almost 100)</td>
</tr>
<tr>
<td>He$^{++}$</td>
<td>11.0—12.5 (7)</td>
</tr>
<tr>
<td>Ne$^+$</td>
<td>15.3—15.57 (almost 100)</td>
</tr>
<tr>
<td>N$^+$</td>
<td>10.97, 12.16, 14.54 (together 90); 15.03 (10)</td>
</tr>
<tr>
<td>CO$^+$</td>
<td>14.0 (almost 100)</td>
</tr>
<tr>
<td>C$^+$</td>
<td>8.58, 10.0, 11.26 (together 75—60); 12.40, 16.58 (together 24—40)</td>
</tr>
<tr>
<td>O$^+$</td>
<td>13.62 (33); 14.45, 14.98 (together 42); 16.67, 16.94, 18.64 (together 25)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Most of the data are taken from E. LINDEHOLM, in: Ion Molecule Reactions in the Gas Phase, Adv. in Chemistry Ser. No. 58, Amer. Chem. Soc., Washington 1966, p. 1. Data given there pertain to 100 eV electron energy and a time lapse of 1 usec after ionization. Additional Refs. see b–f.

b) B. TURNER, R. MATHIS, and J. RUTHERFORD, in: Proc. of the Conf. on Heavy Particle Coll. 1968, Univ. of Belfast, p. 126.

c) W. A. CHUPKA and E. LINDEHOLM, Ark. Fys. 25, 355 [1964].


f) P. WILMENIUS and E. LINDEHOLM, Ark. Fys. 21, 106 [1962].

Table 2. Mass spectra of primary ions X$^+$.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Primary gas$^{b,c}$</th>
<th>primary mass relative abundance in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe$^+$</td>
<td>Xe$^+$ (77.8), Xe$^{++}$ (16.7), Xe$^{+++}$ (5.5)</td>
</tr>
<tr>
<td>Kr$^+$</td>
<td>Kr$^+$ (80.6), Kr$^{++}$ (13.0), Kr$^{+++}$ (0.5)</td>
</tr>
<tr>
<td>Ar$^+$</td>
<td>Ar$^+$ (10.4)</td>
</tr>
<tr>
<td>Ne$^+$</td>
<td>Ne$^+$ (95.7), Ne$^{++}$ (2.5)</td>
</tr>
<tr>
<td>He$^+$</td>
<td>He$^+$ (99.9), He$^{++}$ (0.1)</td>
</tr>
<tr>
<td>N$_2$</td>
<td>N$_2^+$ (65—85), N$^+$ (35—15), N$_2^{++}$ (0.5—1.0)</td>
</tr>
<tr>
<td>CO$^+$</td>
<td>CO$^+$ (65—85), C$^+$ (18—8), O$^+$ (16—6), CO$^{++}$ (0.8—1.5)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Electron energy 120 eV.


\textsuperscript{c} For N$_2$ and CO the uncertainties of fragment ion abundance result from partial instrumental discrimination, cf. D. RAPP, P. ENGELANDER-GOLDEN, and D. BRIGLIA, J. Chem. Phys. 42, 4081 [1965]; C. E. BERRY, Phys. Rev. 78, 600 [1950]. In the present experiment the fragment abundance in the charge exchange region is probably in the upper part of the range given.
V. Method of Analysis

Let us consider charge exchange between an ion $X^+$ and a target molecule of mass $m_0$: $X^+ + M_0$ $\rightarrow$ X + M$_0^+$, which is followed by dissociation yielding a fragment $M_1^+$ of mass $m_1$. Let the overall rate of dissociation be described by a distribution $II(k)$ of individual rate constants $k$. Our aim is to deduce $II(k)$ from the experimental data. Of course we hope to find a fairly narrow distribution $II(k)$ centered around some mean $k_m$ which we will then associate with the recombination energy RE($X^+$). Note that in this approach we do not a priori postulate the existence of some small number of discrete rate constants. With a given target gas $M_0$, this analysis has to be performed for each species $X^+$ separately.

In the earlier electron impact work, the experimental information on $II(k)$ consisted mainly of the long tail that joined on to the $M_1^+$ peak on the energy scale towards the low-energy side. The $M_0^+$ peak had no tail on the low-energy side because the electron energy was chosen such that the electrons could only ionize $M_0$ in the beam, but not the $M_0$ background beyond the beam. Unfortunately, this is impossible with ion impact. The ions $X^+$ cannot be prevented from penetrating the beam and producing $M_0^+$ by charge exchange with $M_0$ background all the way down the draw-out field. Therefore, even the $M_0^+$ peak now has a low-energy tail. At any point the $M_1^+$ tail intensity is now the cumulative result from $M_0^+$ decompositions in the beam as well as in the low, but broad wings of the beam. Worse than that, the charge exchange cross section is energy dependent and changes along the tail. It is therefore impossible to obtain $II(k)$ from tail measurements. Instead we based the analysis on three other kinds of data:

I. The distortion of the $M_1^+$ main peak shape, compared to the $M_0^+$ peak. This distortion, which appears as a rounding-off to the low-energy side, is really the beginning of the tail formation. It is numerically described by beam profile readings on the recorder chart at selected sampling points $\Delta U$, $2\Delta U$, \ldots $n\Delta U$ along the energy axis.

II. The change in $M_1^+$ integral peak intensity $A$, as a function of draw-out field strength $F$. With increasing $F$, more and more ions $M_1^+$ appear at energies appreciably below the $M_1^+$ peak potential (i.e. in the tail), so that the absolute integral peak intensity $A$ decreases. $A$ was measured planimetrically. To compensate for the concomitant intensity variation due to a change in focusing conditions with changing $F$, all peak areas $A_{M_1^+}(F)$ were normalized to the corresponding areas $A_{M_0^+}(F)$.

III. The ratio of satellite to main peak areas, SP/MP. The satellite peak results from decompositions in the field-free region. The ions $M_0^+$ enter and leave this region at times $\tau_1$ and $\tau_2$, respectively. The difference $\tau_2 - \tau_1$ does not depend on $F$, as in our apparatus the ion energy in the field-free region was always kept at 570 eV. However, the larger $F$ is, the smaller are both $\tau_1$ and $\tau_2$. Therefore, an increase in $F$ leads to an increase in satellite peak intensity.

At the same time, the $M_1^+$ main peak decreases [see (II)]. For the evaluation of the change of SP/MP with $F$ it is assumed that changes in focusing conditions affect SP and MP to the same extent. This is justified because of the general insensitivity of our apparatus to changes in $F$ (the absolute intensity variation between $F = 100$ and $F = 4000$ V/cm was only a factor of 3).

For any fixed $k$, the measurable quantities of type (I), (II) and (III) are calculable. The contributions to them of the individual values of $k$ are all additive, with relative weights, $II(k_1)$, $II(k_2)$, \ldots . The experimental results of type (I), (II) or (III) can therefore be described by linear equations with $II(k_i)$ as unknowns. The choice of the $k_i$ and the total number of unknowns are arbitrary to some extent; we worked with 20 equations.

The procedure we found most satisfactory is not to rely on data of type (I), (II) or (III) alone, but rather on a mixed set of equations. For example, for the reaction of benzonitrile with Kr$^+$, which gives a well-developed satellite peak, 5 equations of type (III) were used, for $F = 100$, 200, 400, 1000, 2000 V/cm; furthermore 3 equations of type (II), namely for the three pairs $F_1$, $F_2 = 200$, 1000; 1000, 4000; 200, 4000 V/cm. The remaining 12 equations were of type (I), based on, for example, three points on the beam profile ($A_U$, $2A_U$, $3A_U$), each for four values of $F$.

This initial step gives only the gross features of $II(k)$, but over a broad range of $k$. In subsequent refinements different sets of 20 equations each were used which, based on the results of the first step, were chosen so as to explore the details of $II(k)$ in various limited regions.
An important computational detail is the use of a least squares method described in 16. At the expense of trebling the number of equations (i.e., we actually solved 60 equations, on an IBM 7040) it guarantees a smooth solution $II (k)$.

Test runs were performed in which several known distributions $II (k)$ were backcalculated. For example, with a $\delta$-function as true $II (k)$, the result of the backcalculation was a broadened peak with a full width at half maximum (FWHM) of a factor of 2.8 on the $k$-scale. This factor represents therefore the upper limit on the resolution of all our measurements of $k$.

The complete analysis in terms of $II (k)$ as described above was only performed for the reactions of benzonitrile with krypton, argon, nitrogen, and carbon monoxide ions. For comparison, a much simpler analysis was also carried out for the reactions of $C_6H_5CN$ with $Kr^+$ and $Ar^+$. In this approach the existence of two discrete values $k_1$, $k_2$ for $Kr^+$ and one for $Ar^+$ was a priori postulated. Their values [and, for $Kr^+$, also their relative contributions $II (k_1)/II (k_2)$] could then be found easily from the correspondingly simplified linear equations mentioned above. The results from the complete and simplified methods agreed quite closely (see below), so that for all other reactions only the simplified method was used.

VI. Results

In order for a decomposition to be suitable for investigation with our method, it has to meet the following requirements:

a) It should have an intense metastable peak in the usual sense (e.g. as tabulated in electron impact mass spectra 17).

b) It has to be a decomposition of the parent ion itself. For secondary decompositions the energy content of the decomposing ion would not be accurately known because of energy fluctuation effects during the preceding dissociation 18.

c) The threshold energy of the process has to lie in the range of RE"s of Table 1.

These criteria led to the processes studied in this work. Further decompositions in cyclopentane, butadiene, pyridine and $H_2S$ were tried, but gave too little intensity or ($H_2S$) had too small ratios $Am/m_1$.

A) Charge Exchange Mass Spectra

The fragmentation patterns of benzonitrile and benzene resulting from dissociative ionization by charge exchange were measured at the "main peak" position on the energy scale. A weak draw-out field ($F = 100 \text{ V/cm}$) was employed in order to minimize effects due to the fragmentation kinetics. At $F = 100 \text{ V/cm}$, the main peak comprises all fragment ions formed with a delay up to 1 $\mu\text{sec}$ after the initial ionization.

The mass spectra obtained with various primary ions $X^+$ are given in Tables 3 and 4. The primary ion kinetic energy in the laboratory system was $U_{ion} = 20 \text{ V}$, for benzene three spectra taken with $U_{ion} = 200 \text{ V}$ are also given.

The striking differences between charge exchange mass spectra taken with different ions $X^+$ are already familiar from Lindholm's work on many molecules 6. The present two examples are shown here because, taken together with the RE"s from Table 1, they provide a good qualitative insight into the fragmentation energetics. The progressing fragmentation with increasing RE is evident. Note, in par-

<table>
<thead>
<tr>
<th>$m/e$</th>
<th>Xe</th>
<th>Kr</th>
<th>CO</th>
<th>Primary Gas</th>
<th>Ar</th>
<th>Ne</th>
<th>He</th>
<th>$e^-$</th>
</tr>
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<tbody>
<tr>
<td>103</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>75.0</td>
<td>4.2</td>
<td>22</td>
<td>12</td>
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<td>102</td>
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<td>0.7</td>
<td>0.8</td>
<td>3.0</td>
<td>2.7</td>
<td>6</td>
<td>?</td>
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<td>4.1</td>
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<td>17.8</td>
<td>5</td>
<td>1</td>
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<td>19.6</td>
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<td>—</td>
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<td>15</td>
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<td>51</td>
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<td>1.0</td>
<td>1.2</td>
<td>3.0</td>
<td>100</td>
<td>73</td>
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<tr>
<td>50</td>
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<td>1.5</td>
<td>0.9</td>
<td>100</td>
<td>100</td>
<td>18.1</td>
</tr>
</tbody>
</table>

*a* All intensities, uncorrected for isotopic contributions, are normalized to 100 for the most abundant fragment ion. They were recorded on the "main peak" (intersection of primary ion beam and molecular beam, see text) with a drawout field $F=100 \text{ V/cm}$ and primary ion energy $eU_{ion}=20 \text{ eV}$; the electron energy was 120 eV.

Table 4. Charge exchange mass spectra of Benzene.

<table>
<thead>
<tr>
<th>m/e</th>
<th>Primary Xe</th>
<th>Kr</th>
<th>Kr</th>
<th>CO</th>
<th>N₂</th>
<th>N₂</th>
<th>Ar</th>
<th>Ar</th>
<th>Ne</th>
<th>e⁻</th>
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<tbody>
<tr>
<td></td>
<td>Gas</td>
<td>Uion (V)</td>
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<td>(100.0)</td>
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<td>1.2</td>
<td>1.0</td>
<td>2.0</td>
<td>0.7</td>
<td>3.6</td>
<td>5.9</td>
<td>2.3</td>
<td>7.2</td>
<td>100</td>
<td>20.1</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>0.4</td>
<td>0.6</td>
<td>0.3</td>
<td>2.2</td>
<td>2.9</td>
<td>2.5</td>
<td>3.7</td>
<td>38</td>
<td>16.8</td>
</tr>
<tr>
<td>39</td>
<td>?</td>
<td>2.9</td>
<td>5.1</td>
<td>2.2</td>
<td>27.2</td>
<td>20.4</td>
<td>34.9</td>
<td>36.8</td>
<td>20</td>
<td>13.5</td>
</tr>
</tbody>
</table>

a For legend, see Table 3. Here data for \( U_{\text{ion}} = 200 \text{ eV} \) have been included. Some relative intensities, marked by parentheses, are at variance with results by B.-Ö. Jonsson and E. Lindholm, Ark. Fys. 39, 65 [1969]. They probably contain contributions from Penning ionization (see Sect. IV, d).


ticular, that both in \( \text{C}_6\text{H}_5\text{CN} \) and in \( \text{C}_6\text{H}_6 \) the overall fragmentation is less with CO than with Kr. With Kr, the 33% Kr\(^{33+} \) in the \( ^3\text{P}_{1/2} \) level, \( \text{RE} = 14.67 \text{ eV} \), raises the mean \( \text{RE} \) appreciably above 14.0 eV, the \( \text{RE} \) of Kr\(^{33+} \) (\( ^3\text{P}_{3/2} \)), while with CO the \( \text{C}^+ \) and O\(^+ \) admixtures are of such low abundance (Table 2) that, in spite of their high \( \text{RE} \) (around 16.8 eV), the \( \text{RE} \) (CO\(^+ \)) = 14.0 eV remains dominant.

B) Measurements of Dissociation Rate Constants

1) Benzonitrile

The rate constant distributions \( \Pi (k) \) the process \( \text{C}_6\text{H}_5\text{CN}^+ \rightarrow \text{C}_6\text{H}_4^+ + \text{HCN} \) were measured using the primary ions Kr\(^+ \), Ar\(^+ \), CO\(^+ \) (accompanied by C\(^+ \) and O\(^+ \)) and N\(_2\)\(^+ \) (with N\(^+ \)) to produce \( \text{C}_6\text{H}_5\text{CN}^+ \) by charge exchange. Fragmentation by collision with Xe\(^+ \) was also observed, but appears to be an endothermic process (see below). As a qualitative illustration, Fig. 3 shows the M\(_1^+ \) beam profile, in this case for \( X^+ = \text{CO}^+ \) impact, and the various M\(_2^+ \) beam profiles. The steadily increasing distortion in going from Ar\(^+ \) to Kr\(^+ \) is obvious. It must be emphasized that the final results are derived from many runs under varying conditions and are therefore much more accurate than an individual example such as in Fig. 3 would seem to warrant. The Ar\(^+ \), N\(_2\)\(^+ \) and CO\(^+ \) curves in Fig. 3 are all rather similar. Nevertheless, the corresponding satellite peaks have very different intensity; the ratio of satellite to main peak (at \( F = 100 \text{ V/cm}, U_{\text{ion}} = 90 \text{ V} \)) is in the order Kr\(^+ \), CO\(^+ \), N\(_2\)\(^+ \), Ar\(^+ \): SP/MP = 0.47; 0.24; 0.028; <0.003. This indicates components of \( \Pi (k) \) at low \( k \) for the first two reactions, which are almost absent for the third and completely missing for the fourth.

These qualitative expectations are borne out by detailed analysis. Each curve of the type shown in Fig. 3 was scanned at least 10 times and averaged. The entire amount of experimental data gathered for charge exchange between benzonitrile and any one primary ion species \( X^+ \) was simultaneously processed by the analytical method described above. It yielded automatically the complete rate constant distribution \( \Pi (k) \) for each \( X^+ \) species between about \( k = 5 \cdot 10^4 \) and \( 10^9 \text{ sec}^{-1} \).

The resulting four distributions \( \Pi (k) \) for \( X = \text{Kr}, \text{CO}, \text{N}_2 \) and Ar are given in Figure 4. They differ dramatically in shape. Moreover, their structure can be closely correlated with the \( \text{RE} \)'s in Table 1: Each \( \text{RE} \) is represented by a peak in \( \Pi (k) \), whose location on the \( k \)-axis is a monotonic function of \( \text{RE} \) (cf. the peak labeling in Fig. 4).

The three peaks in Fig. 4 a can be attributed to three different ionic species. The big CO\(^+ \) peak at low \( k \) explains the previously mentioned satellite peak for this reaction. In Fig. 4 b the two peaks are due to the \( ^3\text{P}_{3/2} \) and \( ^3\text{P}_{1/2} \) states of Kr\(^+ \). In Fig. 4 d, the same two states of Ar\(^+ \) are not resolved. Note the position of the Ar\(^+ \) peak on the \( k \)-axis: in contrast to the Kr\(^+ \) peak, it covers the range of large \( k \) only, which explains the absence of a satellite peak in the Ar\(^+ \) experiments. In Fig. 4 c the N\(_2\)\(^+ \) peak is again composite. It comprises several values of \( k \), corresponding to recombination of N\(_2\)\(^+ \) into N\(_2\)X\(^1\) \( \Sigma^+ \) \((v' = 1 \text{ and } v' = 0) \).

The desired dependence \( k(E) \) can now be obtained by combining Figs. 4 a–d into one figure.
Fig. 3. Typical results for C₆H₅CN₊X⁺→C₆H₅CN⁺₊X (top trace) and C₆H₅CN₊X⁺→C₆H₄⁺+HCN+X (with X+=sum of all ions formed from CO in top trace and from Ar, N₂, CO, Kr in the lower traces). Draw-out field F=1000 V/cm. Compare the schematic Fig. 1: The progressing peak distortion indicates an increase of mean parent ion lifetime. Satellite peaks are not shown.

As a prerequisite, the zero point on the E-scale has to be fixed. According to the principle of charge exchange ionization, \( E = R - I.P. + \Delta E \), where I.P. = adiabatic ionization potential of benzonitrile. \( \Delta E \) represents the sum of the initial average thermal energy and the average energy transferred in the collision. The former is estimated to be about 0.1 eV (taken over from butane¹⁸, which has a similar number of degrees of freedom). The latter can be assessed by observing the effect of a change of the bombarding ion energy \( eU_{\text{ion}} \) in our experiment. Results presented below lead to a value of about 0.15 eV. Thus \( \Delta E \) is taken as 0.25 eV.

In Fig. 5 the positions of all maxima of the four distributions \( \Pi(k) \) from Fig. 4 a–d are plotted

Fig. 4. Probability distributions \( \Pi(k) \) of rate constants \( k \) for unimolecular decomposition of C₆H₅CN⁺, produced by charge exchange with ions from four different primary gases. \( \Pi(k) \) was obtained from curves like those shown in Fig. 3 by a mathematical procedure explained in the text. The pairs of symbols (○, x) and (●, +) give a measure of the uncertainty of the calculation; for ○ and ● the set of selected values \( k_i \) (see Sect. V) was displaced as a whole towards lower \( k \), as compared to x and + by a factor of 2. Negative values of \( \Pi(k) \) are also a computational artifact.
versus $E$, which was calculated using $I.P. = 9.705$ eV\textsuperscript{20} and the RE's from Table 1. The smooth variation of $\log k$ with $E$ which is obtained is extremely gratifying. It gives strong support to our procedure of analysis and to the thesis that this curve truly represents the function $k(E)$.

The error bars in Fig. 5 indicate the 90\% width of the $II(k)$ peaks. This was preferred to FWHM because of the incomplete peak resolution in Fig. 4b and 4c. Where several RE contribute to the same peak ($N_2^+$, $Ar^+$, $C^+/O^+$), the presumably predominant component is marked with a heavier dot.

Charge exchange with $Xe^+$ also gave a measurable satellite peak. It would, by extrapolation, correspond to a point at $k = 3 \cdot 10^4$ sec$^{-1}$, $RE = 13.4$ eV. However, this point was not included in Fig. 5 because of the incomplete peak resolution in Fig. 7, was derived as follows. For $Ar^+$ a common $k$ value was attributed to the two RE's of $15.76$ and $15.94$ eV. This $k$ can then be calculated immediately from the experimental SP/MP ratio. For $Kr^+$ two values of $k$ (at $14.0$ and $14.7$ eV) combine to give the observed SP/MP ratio. From this experiment alone $k_{14.0}$ and $k_{14.7}$ can only be determined if one makes an assumption about

$Xe^+ + C_6H_5CN \rightarrow C_6H_4^+ + HCN + Xe$

is most likely endothermic. This follows from the appearance potential of $C_6H_4^+$ of 13.9 eV\textsuperscript{21}. More convincing, in view of the uncertainties of all appearance potential measurements, is the unusual dependence of the satellite peak intensity\textsuperscript{22} on the primary ion kinetic energy $eU_{ion}$. Compared to the “ordinary” increase of intensity towards lower $U_{ion}$ which was observed in several other cases (see Sect. VI, C2), the rise was here 4 times steeper. This suggests transverse momentum transfer leading to ion loss at large $U_{ion}$ (see\textsuperscript{23}). The intensity of $C_6H_5CN^+$ from charge exchange with $Xe^+$ was very much lower than with the other gases X. This also points to a different mechanism, i. e. an endothermic process.

The well-established $k(E)$ for the benzonitrile decomposition was used as a test for the simplified method of analysis which presupposes discrete values of $k_m$ (see above). The result for $k_m(E)$, deduced from experiments with $Kr^+$ and $Ar^+$ only, is compared in Fig. 6 with the more accurate $k(E)$ from Figure 5. The good agreement obtained was taken as justification to use only the simplified method for the determination of $k(E)$ of benzene and thiophene.

2) Benzene

Of the four important primary decompositions $C_6H_6^+ \rightarrow C_6H_5^+, C_6H_4^+, C_4H_4^+$ and $C_3H_3^+$ only the first and third could be used to derive a $k_m(E)$. The second and fourth were masked by background on mass 76$^+$ (benzonitrile residue) and 39$^+$ (K$^+$ from surfaces), qualitatively they appeared to behave similarly to the first and third process, respectively. The function $k_m(E)$ for $C_6H_6^+ \rightarrow C_6H_4^+$, as determined from charge exchange with $Kr^+$, is given in Figure 7. It is seen that the two $Kr^+$ states yield two widely different $k_m$. $Ar^+$ with its relatively high RE gave already a practically undistorted peak, so that here only a lower limit for $k_m$ could be stated.

The important process $C_6H_6^+ \rightarrow C_6H_5^+$ presented special difficulties. The energy deficit associated with the delayed loss of one mass unit is very small. Consequently peak distortion and tail are negligible. The only measurable quantity is the satellite peak, which is here located very close to the main peak. It is extremely intense, as is shown in Fig. 8 a and b. From its intensity (relative to the main peak) the $k_m(E)$ for this process, as given in Fig. 7, was derived as follows. For $Ar^+$ a common $k$ value was attributed to the two RE's of 15.76 and 15.94 eV. This $k$ can then be calculated immediately from the experimental SP/MP ratio. For $Kr^+$ two values of $k$ (at 14.0 and 14.7 eV) combine to give the observed SP/MP ratio. From this experiment alone $k_{14.0}$ and $k_{14.7}$ can only be determined if one makes an assumption about

![Figure 6](image-url)

*Fig. 6. Comparison of $k(E)$ for $C_6H_5CN^+ \rightarrow C_6H_4^+ + HCN$ as obtained by the complete (solid curve) and a simplified (dashed curve) mathematical procedure.*
with the $k$ value for Ar$^+$, they lie on a straight line in a log $k(E)$ plot. The resulting functions $k(E)$ are shown in Fig. 7 for the assumed ratios $Q_{14.0}/Q_{14.7} = 3.0; 1.0; 0.33$ (curves a, b, c respectively). The value of $k$ for the limiting, but quite unlikely cases $Q_{14.0} = 0$ or $Q_{14.7} = 0$, $k = 3.6 \cdot 10^5$ sec$^{-1}$, is also shown.

An alternative method of finding $k_{11.0}$ and $k_{14.7}$ was also used. Instead of the assumptions about $Q_{14.0}/Q_{14.7}$ and the straight line conditions, the experimental data from CO$^+$ charge exchange were adduced. The rather involved analysis yielded points also shown in Fig. 7, in good agreement with the first method.

The $k(E)$ obtained in this way is also in accord with the SP/MP ratio measured with N$_2^+$ (and N$^+$) primary ions.

3) Thiophene

The primary decomposition $C_4H_4S^+ \rightarrow C_2H_2S^+ + C_2H_2$ occurred with a measurable delay only after charge exchange with Xe$^+$. Xe$^+$ has RE's of 12.13 and 13.44 eV. The simplified method of analysis, as described above, yielded corresponding values of $k$ differing by 2.4 orders of magnitude. Between these, $k(E)$ was interpolated as shown in Figure 9.
C) Charge Exchange at varying Ion Impact Energy

1) Translational Energy Transfer

All experiments discussed so far were done with 90 eV primary ions. By varying the ion impact energy the amount of energy transferred from kinetic to excitation energy can be measured.

The ratio SP/MP is a sensitive indicator for the amount of energy transferred. A spectacular qualitative example is given in Figure 8. Here the kinetic energy in the c.m. system changes by a factor of 30, from 0.6 to 18 times the recombination energy. The ratio SP/MP, however, only changes by a factor of 1.4. Therefore the amount of kinetic energy transferred in this charge exchange collision is very small. This is true in all cases studied. Figure 10 gives two other examples. Since the kinetic energy plays only such a minor role, the curves \( k(E) \) obtained above (with \( U_{ion} = 90 \) eV) can now serve as gauges to measure quantitatively the amount of translational energy transfer.

\[
\begin{align*}
\text{Fig. 10. Variation of the intensity ratio satellite peak : main peak with } U_{ion} \text{ (see Fig. 8) } (F=100 \text{ V/cm}).
\end{align*}
\]

Fig. 11. Kinetic to internal energy transfer for three charge exchange processes, obtained from data such as in Fig. 10 via the \( k(E) \) curves of Figs. 5 and 7.

Measurements were made for ion energies \( eU_{ion} \) between 8 and 250 eV (LAB system). The ratio SP/MP of satellite to main peak intensity was determined for different field strengths \( F \). The results for each energy \( eU_{ion} \) were analyzed as above (using the "simplified method") and yielded values of \( k \) which, at each \( RE \), increased monotonically with \( U_{ion} \). This variation of \( k \) was converted via the known \( k(E) \) to yield the change of internal energy \( E \). The result is shown in Figure 11. It can be seen that less than 0.1% of the c.m. kinetic energy is transferred in these charge exchange processes.

2) Charge Exchange Cross Section

The relative cross section, as a function of \( U_{ion} \), for formation of a secondary ion by charge exchange cannot, in general, be obtained directly from a measurement of the main peak intensity as a function of \( U_{ion} \). The reason is the transfer of kinetic into excitation energy as discussed in Sect. VI, Cl, which causes \( k \) and hence the fraction of the total ion yield collected within the peak to change with \( U_{ion} \). Among the cases studied, this effect was negligible only for

\[
\text{C}_6\text{H}_5\text{CN} + \text{Ar} \rightarrow \text{C}_6\text{H}_4^+ + \text{HCN} + \text{Ar},
\]

because here \( k \) is so large (see Figs. 4 and 5) that a small variation is insignificant. The main peak intensity for this process, normalized to the \( \text{Ar}^+ \) current, is shown in Fig. 12 [curve (d)].

For \( \text{Kr}^+ \) the main peak intensity, normalized to the primary ion current, was corrected to obtain the true relative cross section \( Q(U_{ion}) \) using the results of Sect. Cl. In that analysis, for each \( U_{ion} \) both \( k(RE=14.0) \) and \( k(RE=14.67) \) as well as their relative contributions were obtained. This information was used here to convert the main peak intensity at mass 76 into the total ion yield, \( I_{76}^+(U_{ion}) \). The two contributions from \( \text{Kr}^+(2\text{P}_{1/2}) \) and \( \text{Kr}^+(2\text{P}_{3/2}) \), \( I_{76}^+(1/2)(U_{ion}) \) and \( I_{76}^+(3/2)(U_{ion}) \), were obtained separately, see Fig. 12, curves (b) and (c). The main peak intensity raw data [curve (a)] are also given. A comparison of curves (b) and (c) with (a) illustrates the effect of the correction for the \( k \) variation \( ^{27} \). Figure 13 shows the analogous curves for charge exchange of \( \text{Kr}^+ \) with benzene, forming mass 52 ions; curve (a) is the uncorrected main peak intensity, curve (b) and (c) give the true \( Q(U_{ion}) \) for the \( \text{Kr}^+(2\text{P}_{1/2}) \) and \( \text{Kr}^+(2\text{P}_{3/2}) \) species, respectively.
Fig. 12. Dependence of dissociative charge exchange cross section on relative kinetic energy, for Kr\(^+\) + C\(_6\)H\(_5\)CN -> C\(_6\)H\(_4\)\(^+\) + HCN + Kr (curves a–c) and Ar\(^+\) + C\(_6\)H\(_5\)CN -> C\(_6\)H\(_4\)\(^+\) + HCN + Ar (curve d); (a) gives the uncorrected normalized main peak intensity, (b) and (c) the true separate contributions, as derived from (a), from Kr\(^+\)(\(^2\)P\(_1/2\)) and Kr\(^+\)(\(^2\)P\(_3/2\)) respectively. Unlike (a), the normalized main peak data of curve (d) need not be corrected for kinetic effects.

VII. Discussion

A) Is the decay law for C\(_6\)H\(_5\)CN\(^+\) -> C\(_6\)H\(_4\)\(^+\) + HCN an exponential?

The benzonitrile ion now is the first system whose decomposition behaviour is known in considerable detail. Previous studies of unimolecular decompositions gave only average rate constants \(k\) or at best indicated some structure or changes in the broad distributions \(\Pi(k)\). The results depicted in Fig. 4 show that in the present experiment benzonitrile ions were prepared in states with narrow distributions \(\Pi(k)\).

These distributions are remarkably sharply peaked, considering the various factors contributing to their width:

a) The limited resolution of the unfolding process, resulting in an uncertainty of a factor of 2.8 on the \(k\)-scale;

b) the broadening from experimental noise;

c) the spread of thermal energy (0.1 eV, corresponding to an uncertainty of \(k\) within a factor of 1.4, cf. Fig. 5);

d) the spread of RE’s (0.16 eV for Ar\(^+\), 0.29 eV for N\(_2\)\(^+\), corresponding to \(k\) values differing by a factor of 1.8 and 2.8, respectively).

e) The spread of energy transferred from kinetic energy.

The observed widths (FWHM) of the \(\Pi(k)\) peaks are a factor of 4 for Ar\(^+\) and a factor of 5 for N\(_2\)\(^+\). Thus the true \(\Pi(k)\) may well be a \(\delta\)-function for each RE; a generously estimated upper limit to its width is a factor of 2.

MIES and Krauss\(^{28}\) as well as Bunker\(^{29}\) have discussed the possibility of non-exponential unimolecular decay. Bunker performed classical trajectory calculations on molecules dissociating after collisional activation in a heat bath. This is appropriate to the usual chemical unimolecular decomposition, but less so to the present, rather specific mode of excitation. Mies and Krauss considered individual quantum mechanical resonance states (corresponding to the activated ion states) with overlapping level widths. It was shown that departures from exponential decay can occur through the interaction of the resonance states with the dissociation continuum.

If a non-exponential decay existed, it would in our experiment show up as a more or less broadened distribution \(\Pi(k)\). We conclude, therefore, that in the present cases the conditions for non-exponential decay (specified in \(^{28}\) in terms of level width
and spacing distributions, in $^{29}$ in terms of hindrance of intramolecular energy flow) probably do not obtain. In particular, Mies and Krauss point out the possibility that metastable (i.e. long-lived) ions with excitation energies well above the dissociation threshold may exist. For benzonitrile, Fig. 5 shows clearly that the lifetime is monotonically shortened as the excitation energy increases.

B) Comparison with $k(E)$ from electron impact experiments

The earlier electron impact work$^4$ also gave the dependence $k(E)$ for $\text{C}_6\text{H}_5\text{CN}^+ \rightarrow \text{C}_6\text{H}_4^+ + \text{HCN}$, though only with some assumptions on the density of states and the threshold law for excitation of each state. Justification of these assumptions was at that time given by the excellent agreement of calculated and measured ion yield, as a function of electron energy for "normal" and "metastable" fragment ions. The $k(E)$ obtained in that work was a linear dependence of $\log k$ on $E$ with slope $1.54/\text{eV}^{20}$. This function is shown in Fig. 5 by the dashed line. The position on the $E$-axis was fixed by means of the measured appearance potential of the "normal" fragment $\text{C}_6\text{H}_4^+$, $\text{AP}(76^+) = 15.2 \pm 0.2 \text{ eV}^{4,21}$. "Normal" fragments in our apparatus are those with $k \geq 10^7 \text{ sec}^{-1}$. Therefore the dashed line in Fig. 5 is positioned such that $k = 10^7$ is reached at $E = 15.2 - 9.705 + 0.1 = 5.6 \text{ eV}$ (9.705 eV = I.P. of benzonitrile$^{20}$, 0.1 eV = average thermal excitation energy). It is seen that the functions $k(E)$ as obtained from electron impact and charge exchange are in excellent agreement in the lower part. At high $k$, the latter curve is certainly more reliable. The deviation of the former curve is not unexpected in view of the assumptions made in its derivation.

The reassuring agreement between both sets of data also lends strong support to the $k(E)$ curves for butane and heptane derived from electron impact experiments$^5$. In those cases the same assumptions as for benzonitrile were made, though under somewhat less favourable circumstances. Unfortunately, a check with the present method is impossible because of the lack of suitable charge exchange partners.

C) The concurrent reaction

$\text{C}_6\text{H}_5\text{CN}^+ \rightarrow \text{C}_6\text{H}_5^+ + \text{CN}$

According to the mass spectrum (Table 3), the mass 77 intensity is only about 15 – 20% of the 76+ intensity, for Kr+ through Ar+. Correction for the $^{13}\text{C}^2\text{H}_4^+$ contribution reduces it further by a factor of about 0.6. With this low abundance and the $^{13}\text{C}^2\text{H}_4^+$ background it was not possible to measure $k(E)$ directly in the same way as for mass 76. This is unfortunate since such a measurement would have resolved unambiguously the problem of whether the losses of CN and HCN from the benzonitrile ion are in competition with one another or not. In the first case, which conforms to the usual ideas of the QET, at each RE the value of $k$ measured for the two processes would have been exactly the same, namely equal to the overall decomposition rate of the parent ion. The ion yields measured at mass 76 and mass 77 would in this case have been in the ratio $k_{76}/k_{77}$, with $k = k_{77} + k_{76}$. (Note that in this case $k_{76}$ and $k_{77}$ cannot be measured directly, but only inferred from the relative ion yields and the value of $k$.) The ratio $k_{76}/k_{77}$ could, of course, have been different for each RE. For the case of isolated, non-competing decompositions to form 76+ and 77+ ions, one would in general at each RE measure different values of $k$ for the two fragments. Also, these would not be related to the relative ion yields.

We adopt the assumption of competing processes as the more likely one. This means that the $k(E)$ given in Fig. 5 is to be interpreted as $k_{77} + k_{76}$. $k_{76}$ alone would be about 10% smaller at all energies, $k_{77}$ would be smaller by a factor of 10. If, on the other hand, the mass 77 formation is not in competition with mass 76 formation, Fig. 5 gives the true $k_{76}$ (which is thus not very sensitive as to which of the two assumptions is made), and $k_{77}$ is then completely unknown.

D) Two clearly non-competing decompositions of $\text{C}_6\text{H}_6^+$

The two concurrent decomposition paths of $\text{C}_6\text{H}_6^+$, leading to $\text{C}_6\text{H}_5^+$ and $\text{C}_5\text{H}_4^+$, respectively, constitute a clear-cut example of the existence of reactions that are not in competition with one another. Here, in contrast to the two $\text{C}_6\text{H}_5\text{CN}^+$ decompositions discussed in the preceding paragraph, we did measure separately the rate constants for
the two decomposition paths. Figure 8 shows that for them the functions \( k(E) \) are completely different. It is to be emphasized that at each RE the two values of \( k \) were obtained quite independently. For example, with Ar\(^+\) as primary ion the mass 52 main peak was identical in shape to the mass 78 main peak, indicating an unmeasurably large \( k_{78} \rightarrow 52 \), while at mass 77 a considerable main peak distortion and a satellite peak were observed, leading to \( k_{77} \rightarrow 77 = 1.56 \cdot 10^6 \text{sec}^{-1} \). For competing reactions, the fast \( 78^+ \rightarrow 52^+ \) process would have suppressed any slow mass 77 formation. Thus, Fig. 8 does not simply mean that a fast and a slow decomposition of \( C_6H_6^+ \) exist side by side (which would, of course, be entirely compatible with the QET), but gives proof, because of the principle of our measurement, that these processes are non-competing.

The same seems to be true for the pair of processes \( C_6H_6^+ \rightarrow C_3H_3^+ + C_3H_3 \) [steep \( k(E) \)] and \( C_6H_6^+ \rightarrow C_6H_4^+ + H_2 \) [slow \( k(E) \) rise], which unfortunately could not be measured accurately (see above). Thus, it seems that processes involving breakage of a C–C bond and those involving hydrogen loss originate from different types of excited states, between which energy randomization is not possible within the time (\( \approx 10^{-6} \text{sec} \)) available for decay.

**E) Comparison of \( k(E) \) for \( C_6H_6^+ \rightarrow C_6H_5^+ + H \)**

with electron impact metastables

The uncertainties of the \( k(E) \) for \( 77^+ \), resulting from the complications with the two RE values of Kr\(^+\), cannot possibly invalidate the above conclusion. Furthermore, there is additional support for this \( k(E) \) from a comparison with the electron impact experiments. In those experiments (see, e.g., Fig. 1 in \(^{32}\)) large satellite:main peak intensity ratios were found. They can be predicted by an extrapolation of \( k(E) \) for \( 77^+ \) in Figure 7. The lower part of \( k(E) \) will produce the satellite peak, while the upper part contributes predominantly to the main peak. The extrapolation has to be terminated at the onset of the first secondary decomposition, presumably \( C_6H_5^+ \rightarrow C_3H_3^+ + C_3H_2 \). The appearance potential of \( C_3H_3^+ \) is 17.6 ± 0.1 eV.\(^{33}\) Also, the distribution \( P(E) \) of the states excited by 70 eV electrons and leading to \( C_6H_5^+ \) formation has to be known. For lack of electron impact data, a rough estimate for \( P(E) \) for the present charge exchange excitation was used; \( P(E) \) seems to drop by a factor of about 2 between 14 and 17 eV.\(^{26}\) With this \( P(E) \) the SP/MP ratio measured with electron impact is obtained, if \( k(E) \) in Fig. 7 is extrapolated such that \( k = 3 \cdot 10^8 \text{sec}^{-1} \) at the "cutoff" energy of 17.6 eV.\(^{34}\)

Thus an additional, though rather uncertain "point" of \( k(E) \) for \( C_6H_6^+ \rightarrow C_6H_5^+ + H \) is obtained. It again supports the extraordinarily slow rise of this function: Over an \( E \)-interval of 3 eV \( k(E) \) increases by only one order of magnitude. This unusual behavior of the simplest of all \( C_6H_6^+ \) dissociations can certainly not be explained by the unmodified QET. Its elucidation, probably in terms of forbidden transitions between electronic states, remains an interesting problem.

**F) Appearance potentials**

Jonsson and Lindholm have recently measured the breakdown diagram of benzene with charge exchange.\(^{35}\) From it they obtained appearance potentials for \( C_6H_5^+ \) and \( C_4H_4^+ \) ions. The former one, 13.8 eV, agrees well with our \( k(E) \) in Fig. 7; it is also in agreement with a value from photoionization, 13.8 ± 0.2 eV.\(^{36}\) For \( C_4H_4^+ \) the lowest appearance potential reported for electron impact is 14.5 ± 0.2 eV.\(^{33}\) Jonsson and Lindholm find about 14.0 eV, by a somewhat uncertain extrapolation. From our \( k(E) \) it appears that an even lower value, about the same as for \( C_6H_5^+ \) (13.8 ± 0.2 eV), might be better still. In 1963, Rosenstock and Krauss cited the large differences between the appearance potentials of various fragments formed from \( C_6H_6^+ \) as evidence for dissociation paths without effective competition. For the case of \( C_6H_5^+ / C_4H_4^+ \) this argument has now been invalidated by the similar onsets of the corresponding \( k(E) \) curves. However, ironically, the conclusion remains unaltered by virtue of the different slopes of these very same curves.

**G) Kinetic energy transfer**

A fundamental problem with charge exchange processes \( X^+ + A \rightarrow A^+ + X \) is the question of how much kinetic energy is transferred from the \( X^+ \) ions into excitation energy of \( A^+ \). Only if this energy transfer is negligible has the excitation energy \( E_1 \) of \( A^+ \) the well-defined value

\[ E_1 = \text{RE}(X^+) - \text{I.P.}(A) + E_{\text{th}}(A) \]
(cf. abscissa of Fig. 5). Lindholm's experiments were designed so as to circumvent this problem:
By extracting the ions A+ at right angles ("perpendicular geometry") to the X+ beam, only those ions A+ should be observed which are formed with little or no transfer of kinetic energy. By the same token, though, Lindholm cannot make any statement about the extent to which kinetic energy can be transformed into excitation energy.

In fact it is known from experiments with the "longitudinal" type of apparatus, where X+ and A+ ions have parallel paths (like in our instrument) that the kinetic energy of X+ can be converted into electronic energy of A+. An example is the endothermic process Kr+ + D2 → D2+ + Kr. Because the reaction Kr+ + H2 → H2+ + Kr has been found by Gustafsson and Lindholm to occur with large cross section, Maier argues that in this case the perpendicular geometry employed in cannot have discriminated effectively against detection of the H2+ product. Nevertheless, the general success of Lindholm's numerous measurements of ionic breakdown patterns, which are all based on the assumption of monoenergetic excitation by charge exchange, lends strong support to his method.

The majority of Lindholm's investigations were concerned with exothermic reactions, like ours. For these the above relation for E1 may well be fulfilled in spite of incomplete discrimination against processes with momentum transfer. Exothermic charge exchange of X+ with a complex molecule A will usually be nearly resonant with some excited level of A+. Near-resonant charge exchange is expected to occur with a large cross section, so that glancing collisions will predominate which transfer very little momentum and kinetic energy.

Accurate measurements of the extent of kinetic to excitation energy transfer are thus highly desirable in order to assess the importance of the discrimination effect of the perpendicular geometry.

The occurrence of some kinetic energy transfer even for exothermic reactions with complex molecules may be inferred from the variation of charge exchange mass spectra with the X+ kinetic energy eUion. If the energy content of an ion A+ is changed by some amount δE, the branching ratio of its decomposition products B1+, B2+, ..., i.e. the mass spectrum, will also change. However, a quantitative evaluation of δE as a function of Uion is extremely difficult. It would require not only detailed knowledge of the decomposition kinetics but also of the discrimination characteristics of the apparatus. In fact, longitudinal and perpendicular instruments can give quite dissimilar mass spectra, depending on Uion. Our measurements of δE (see Sect. VI, CI) is also based on the evaluation of kinetic effects, but in a straightforward manner. Also, as was shown in Sect. IVc, our data are insensitive to transfer of transverse momentum. This is particularly true for the present problem of kinetic energy transfer: The results of Sect. VI CI are derived from measurements of the satellite peak to main peak ratio, as a function of Uion. Should there be some ion los due to transverse momentum transfer, it would affect both peaks similarly and would cancel out in their intensity ratio.

The results presented in Fig. 11 appear to be the first data of this kind. The very small increase of internal excitation energy with a large variation in relative translational energy is consistent with the picture of near-resonant, large impact parameter collisions.

This finding at the same time supports the value of the recombination energies RE assumed in this work (Table 1), which were derived by Lindholm from spectroscopic data. As he has pointed out, in very close collisions the optical selection rules would break down, and different RE's would obtain.

Gurnee and Magee have treated near-resonant charge exchange processes semi-quantitatively. In their calculation, using the impact parameter method, they compute the probability for near-resonant charge transfer, relative to the case of exact resonance, as a function of the energy deficit ε. Their result is a Gauss function, centered around ε = 0 (i.e. exact resonance), whose width increases with the relative velocity v (see 43, Fig. 9). Another parameter entering into the width is the screening factor of the Slater type wave functions used, which was chosen rather arbitrarily.

In our experiment, for Kr+ + C6H5CN, the relative velocities range from v = 6.5·105 cm/sec to 2.5·106 cm/sec. According to 43, at our lowest velocity only C6H5CN+ states in very close resonance with RE(Kr+) could be excited (within about 0.02 eV), whereas for the highest velocity states lying up to about 0.15 eV off resonance would be accessible. The sign of ε does not enter, so that the excited energy band widens up symmetrically around
exact resonance as the impact velocity is increased. However, for large molecules the density of states increases very rapidly with energy $^{44-46}$, so that the net result will be an upward shift of the mean excitation energy of $C_6H_5CN^+$. We believe, therefore, that our results shown in Fig. 11 can, as far as the order of magnitude is concerned, be explained by the theory of Gurnee and Magee. A quantitative comparison would require an adaptation of their calculation to our specific cases as well as a calculation of the density distribution of excited states of the organic ions around the RE values in question.

H) Charge exchange cross section

In Figs. 12 and 13 we find a decrease of the cross section for our particular dissociative charge transfer processes by a factor of 3 in going from about 5 to 150 V c.m. This is more than the variation calculated by Gurnee and Magee $^{43}$, which, over the same energy interval, amounts to a decrease by about 1/3 for atomic and a factor of 2 for diatomic systems. The corresponding experiments $^{40}$ also show this slower fall-off. However, we believe it unlikely that our steep decrease is an artifact caused by transverse momentum transfer (see IV, C). This is supported by the fact that the cross sections for charge exchange of $Ar^+$, $Kr^+$ and $CO^+$ with $C_6H_5CN$ fall off in a very similar manner, despite the differing masses of the reactant ions. Thus, charge exchange with aromatic molecules really seems to depend more strongly on the relative velocity than with smaller systems. A rough measure of the relative cross sections, at a fixed impact energy, of various ions $X^+$ can be obtained from the $II(k)$ distributions in Fig. 4 by dividing the relative peak heights by the relative abundances in the ion beam. For example the ratio of the peak heights at $RE = 14.0$ and $RE = 14.7$ in Fig. 4 is $2.2 \pm 20\%$. The intensity ratio of $Kr^+(3P_{3/2}) : Kr^+(3P_{1/2})$ is probably 2:1 (see $^6$), which indicates a similar cross section for the two species in agreement with Fig. 12.

I) Double ionization by charge exchange

As a product of charge exchange between $H^+$ and benzonitrile the ion $C_6H_5CN^{++}$ ($m/e = 51.5$) was observed. It is attributed to autoionization of an intermediary $C_6H_5CN^+$. With $Ne^+$, no $C_6H_5CN^{++}$ is found, so that the appearance potential of $C_6H_5CN^{++}$ must lie between 21.6 eV and 24.58 eV. For comparison, the appearance potentials of doubly ionized benzene, toluene and naphthalene all have the rather low values 26.0; 24.5 and 22.8 eV, respectively $^{46}$.

This appears to be the first known example of a charge exchange process $X^+ + A \rightarrow A^{++} + X + e$. Much less surprising is the occurrence of processes of the type $X^{++} + A \rightarrow A^{++} + X$, as reported, for example, in Ref. $^{34}$.

VIII. Conclusion

The present experiment constitutes a novel and direct way of measuring the dependence $k(E)$ of the unimolecular decomposition rate constant on the excitation energy. Conceivably, by employing primary mass selection and more sophisticated detection techniques like signal averaging, this method could be applied to a much larger variety of substances. This would open up the most direct experimental approach to unravel the dissociation kinetics of complex systems.

Acknowledgments

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2 O. Osberghaus and Ch. Ottinger, Phys. Lett. 16, 121 [1965].
7 A brief account of the present work has been given: B. Andlauer and Ch. Ottinger, J. Chem. Phys. 55, 1471 [1971].
9 In contrast, some very weak metastable peaks in acetylene double their intensity at a pressure of only $2 \times 10^{-7}$ Torr, see U. Löhle and Ch. Ottinger, Int. J. Mass Spectrom. and Ion Physics 5, 265 [1970].
Table 4 contains a few examples of ions suspected to originate from Penning ionization. As a test, in that case all primary ions were blocked off by changing the ion source potentials appropriately. Although this did suppress the secondary ions in question, it is not a proof against Penning processes taking place, because changing the ion source conditions might also have reduced the yield of excited neutrals.

This is, for example, very important for the reaction $\text{Kr}^+ + \text{C}_6\text{H}_4\text{CN}$, where a small impurity of air in the krypton would lead to a spuriously small satellite: main peak intensity ratio (see Figs. 4 and 5).

E. E. Muschitz, Science 159, 599 [1968]; V. Cermák, J. Chem. Phys. 44, 1318 [1965]. Other long-lived states with excitation energies close to the I. P. are also unlikely to contribute (H. Hotop, private communication).

The main peak could not be used for this experiment because it was largely due to charge exchange with Xe$^+$. Furthermore, the large excess of parent ion in the Xe$^+ + \text{C}_6\text{H}_4\text{CN}$ mass spectrum caused a contribution to the satellite peak on mass 76 from collision-induced dissociation, which had to be subtracted.

Of course, for an endothermic process the ion yield must eventually tend to zero with decreasing impact energy. For the very small endothermicity in the present case this portion is below the accessible energy range.

A measurement of SP/MP at a higher value of the drawout-field $F$ would obviate these assumptions by providing additional experimental information, but is not feasible because of the broadening of both peaks with increasing $F$.

In addition to these factors, the relative contributions from $RE=14.0$ and 14.7 eV were multiplied by the abundance ratio $\text{Kr}^+ (P_{2/3})/\text{Kr}^+ (P_{1/2})=2:1$ (see Ref. 4 and Table 1).


See Eq. (1) in 4; the additive term $-21.7$ merely results from the uncorrected $U_{el}$ scale used in that paper.

Similar, but much less direct evidence for incomplete energy randomization can be found in: U. Löhrle and Ch. Ottinger, Int. J. Mass Spectrom. and Ion Physics 5, 265 [1970].


Similar considerations concerning the influence of the $k(E)$ cutoff position on the ratio metastable: normal fragment ions were already presented in Refs. 4 and 5.


The possible observation that $\text{C}_6\text{H}_4^+$ might be formed by endothermic charge exchange with Kr$^+ (P_{2/3})$, RE=14.0 eV, was disproved by measuring the relative yields $I(14.0)$ and $I(14.7)$ at RE=14.0 and 14.7 eV, respectively, as a function of the Kr$^+$ translational energy $eU_{ion}$. Between $U_{ion}=20$ and 250 V the ratio $I(14.0)/I(14.7)$ increased by only 5%.


E. Gustafsson and E. Lindholm, Ark. Fysik 18, 219 [1960].


V. L. Talrose, Pure and Appl. Chem. 5, 455 [1962].


