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Abstract

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ON THE DISSOCIATION OF MOLECULAR IONS

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Data on collisions of electrons with molecules, obtained under the conditions of a mass spectrometer, form to a considerable extent the basis of the elementary processes of high-energy chemistry, in particular radiation chemistry. To describe the decomposition of large (tens of atoms) excited molecular ions, various hypotheses now exist, based on mutually exclusive assumptions. The statistical hypothesis assumes migration of the excitation over the molecular ion up to its decomposition over a time very large in comparison with the period of atomic vibrations (up to 10^{-6} sec) (^{1}). According to the local mechanism, decomposition occurs mainly in the region of collision of the electron with the molecule, in a time of the order of the period of one vibration ($\sim 10^{-13}$ sec) (^{2}).

The aim of the present work was, first, to obtain data on the occurrence of decompositions in a time of the order of 10^{-13} sec and, second, to estimate the possibility of charge migration over the molecular ion before its decomposition. This part of the problem is meaningful, of course, only for rapid decompositions (in a time of the order of 10^{-13} sec). To solve these questions we developed a special method and obtained data on the angular distribution of fragment ions.

It is known (^{4}) that fragment ions are always formed with excess kinetic energy above the thermal value. If, in the time before decomposition, the molecular ion has time to rotate several times (owing to thermal rotation), then the directions of emission of the fragment ions will be random, unrelated to the direction of the momentum of the ionizing electron, and the experimentally observed angular distribution of the ions will be isotropic. Any anisotropy in the angular distribution of fragments (^{3}) can be associated only with rapid decompositions, i.e., with decompositions in a time less than or of the order of one rotation of the molecule, which under our conditions averaged 10^{-13} sec. The second part of the problem is solved by analysis of the anisotropy obtained.

Following the local hypothesis (^{2}) on the interaction of the ionizing electron with a large molecule, one may expect anisotropy of velocities of a definite type, and it can be observed under the following conditions: 1) the electron, in the process leading to formation of the given ion, interacts with a limited part of the molecule; 2) there is a possibility of "screening" one part of the molecule from interaction with the electron by another part of it; 3) during the time in which the decomposition products (fragments) move apart, no exchange of charge between them has time to occur.

Conditions 1) and 3) essentially constitute the basis of the local mechanism of the processes of ionization and dissociation of large molecules (2). Fulfillment of these conditions means preferential ionization of precisely that part of the molecule with which the incident electron has collided, as well as preservation of the charge in this limited part of the molecule for a time $\sim 10^{-13}$ sec. Taking into account that during this time the molecule has not had time to change its orientation appreciably, it is easy to see that, despite the chaotic arrangement of the initial molecules, the emitted fragment will have an unaveraged component of velocity directed toward the electron impact, owing to the presence in the fragment of kinetic energy acquired upon decomposition.

Obviously, the shielding condition limits the possibility of observing fragments comparable in size to half the molecule, since a small part of the molecule cannot shield a large residue close to the molecular ion. Therefore, for study one should take a molecule that, even if only very roughly, can be represented as two opaque parts of approximately equal size. In such a case the process of formation of the given fragment ion may be regarded as ionization of that part with which the incident electron collided, followed by dissociation in a time $\sim 10^{-13}$ sec. The most effective orientation of the molecule in this sense will be that in which its axis is directed parallel to the electron impact. In this case the greatest shielding should be expected. With partial shielding there is a certain probability of ionization of the part of the molecule located in the "shadow," and the velocity of the corresponding fragment will have a component in the direction of the electron impact, i.e., will give a contribution of the opposite sign. If the molecule is oriented perpendicular to the direction of flight of the electrons, both parts may be ionized with equal probability, and the molecules give no contribution to the observed anisotropy.

It should be noted that fragment ions of one mass or another are formed from all parts of the molecule (5); however, one may expect that ions formed from the middle of the chain will not have a significant velocity anisotropy. Therefore the greatest contribution to the observed velocity anisotropy will be given by ions formed from the end parts of the molecule.

As examples, $C_4H_9^+$ ions from 2,2,4-trimethylpentane, *n*-octane, and *n*-hexane were chosen; these are the most intense in the corresponding mass spectra. Such a dissociation process is one of the most probable for all paraffins heavier than C_5, and also for many other organic molecules (6).

Our measurements were carried out on an MV-2302 type mass spectrometer with a specially designed ion source at an electron energy of 70 eV. The ion source had deflecting plates for analysis of ions by velocity projections, analogous to (7), and two cathodes arranged so that the direction of the electron beam from one of them was parallel, and from the other perpendicular, to the direction of deflection in the plates. The distribution of ions by velocity projections along the lines of force of the analyzer magnetic field was recorded when a sawtooth voltage was applied to the deflecting plates. Measures were also taken to eliminate inhomogeneities of the electric and magnetic fields in the ion source and differences in the density and arrangement of the electron beams.

The anisotropy of the velocities of fragment ions in rapid dissociations appears as a change in the distribution upon transition from a perpendicular to a parallel orientation of the electron beam relative to the direction under study. This change is characterized, in particular, by a shift of the maximum of the distribution function along the velocity scale. It was precisely this shift that was measured experimentally.

To increase accuracy, relative measurements were made for the molecular and fragment ions and for the two directions of the electron beam. In this way all distortions introduced by the ion source that could not be eliminated by its design alone were removed. The correction for the momentum transferred by the electron to the ion was introduced by the method described in (8), taking into account that the fragment ion carries only part of the momentum received by the molecular ion. The excitation energy (together with the ionization potential) was taken to be 13 eV both for the fragment and for the molecular ion. The magnitude of this correction was about 15% of the observed value of the anisotropy. Table 1 gives the values of the mean velocity for ions from different molecules and the values of the anisotropy. The anisotropy is defined as $v_{01} - v_{\mathrm{M1}} - (v_{02} - v_{\mathrm{M2}})$, where v is the magnitude of the velocity projection at the maximum of the distribution function for frag-

cular and molecular ions (subscripts 0 and m) and for the parallel and perpendicular directions of the electron beam (subscripts 1 and 2, respectively).

The fraction of fast processes among all other processes of formation of a given ion can be estimated by comparing the experimental data obtained with those that can be calculated on the basis of one or another model. Such calculations were carried out for the simplest model, consisting of two opaque spheres, using the value of the kinetic energy

Table 1

Ion	Parent molecule	Mean velocity, $\mathrm{eV}^{1/2}$	Anisotropy, $\mathrm{eV}^{1/2}$
$C_4H_9^+$	*n*-Hexane	0.27	0.004 ± 0.001
$C_6H_{14}^+$	*n*-Hexane	0.25	
$C_4H_9^+$	*n*-Octane	0.27	0.005 ± 0.001
$C_4H_9^+$	2,2,4-Trimethylpentane	0.27	0.005 ± 0.001
$C_6D_4^+$	Benzene-d_6	0.27	0.000 ± 0.002
$*C_4H_9^+*$	*n*-Hexane	0.27	0.001 ± 0.001

of the ion $C_4H_9^+$, and gave for the anisotropy the value 0.01 $eV^{1/2}$. From this it may be concluded that the principal mass of $C_4H_9^+$ ions is formed by a local mechanism. Differences in the anisotropy values for different paraffin molecules may be associated with differences in their structure. The small anisotropy value for the $C_6D_4^+$ ion from deuteriobenzene, apart from considerations of shielding, may be connected with the fact that the anisotropy must be (all other conditions being equal) proportional to the mean velocity of the ion in the system of the center of inertia, and not to the total mean velocity, which is the mean quadratic thermal velocity of the parent molecule and the velocity obtained upon decay. The latter, for the $C_6D_4^+$ ion, is considerably smaller than for the $C_4H_9^+$ ion, which leads to a decrease in the numerical value of the anisotropy.

Electrons of high energies must pass through the entire molecule without appreciable shielding. In this case anisotropy should be absent. The corresponding result is marked in Table 1 by an asterisk (electron energy 1000 eV).

The results obtained definitely testify in favor of the local mechanism and cannot be explained in any other way.

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