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Abstract

Full Text

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ON THE MASS SPECTRA OF LARGE MOLECULES

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It is known that bombardment of polyatomic molecules by electrons with energies of 50–100 eV is accompanied by ionization and dissociation of these molecules. At present it is usually assumed that, in this process, the molecule dissociates by simple rupture of bonds [1]. Analysis of data on mass spectra [2], and especially on the formation of "rearrangement" ions [3,4], as well as our investigation of the mass spectrum of deuteriooctane [5], have led to the conclusion that this proposition is in general incorrect. This conclusion is confirmed, in particular, by the fact that in the mass spectrum of *n*-octane-2d_1 the ions $C_2H_5^+$ and $C_3H_7^+$ prove to be labeled not to 50%, as would be expected in the case of simple bond rupture, but to a substantially smaller extent—approximately 30%. To explain this result, the assumption was made that fragment ions are formed with approximately equal probability from any parts of the molecule, with capture of a hydrogen atom [5].

For an unambiguous judgment on the mechanism of dissociation, we synthesized *n*-nonane-5-C^{13} and studied its mass spectrum. For the synthesis, carbon monoxide containing 51% C^{13} was used. The synthesis was carried out according to the scheme:

$$C^{13}O \xrightarrow[H_2SO_4]{NaOH} HC^{13}OOH \xrightarrow{C_4H_9OH} HC^{13}(=O)OC_4H_9 \xrightarrow{C_4H_9MgBr} C_4H_9{-}C^{13}H(OH){-}C_4H_9 \longrightarrow$$

$$\xrightarrow{PBr_3} C_4H_9{-}C^{13}HBr{-}C_4H_9 \xrightarrow{Mg,H_2O} C_4H_9{-}C^{13}H_2{-}C_4H_9.$$

The mass spectra of *n*-nonane and *n*-nonane-5-C^{13}, corrected for the natural abundance of C^{13} and obtained under ordinary conditions on an MI-1303 instrument, are given in Table 1.

Table 2 gives, expressed as percentages, the fractions of ions containing C^{13} among ions of the given type.

If the molecule of *n*-nonane-5-C^{13} dissociated by simple bond rupture, then ions of the types $C_2H_5^+$, $C_3H_7^+$, $C_4H_9^+$ would not contain carbon C^{13}. However,

as is seen from Table 2, from 14 to 46% of these ions contain C^{13}. In the column "calculated" of Table 2 are given the percentages of ions of the given type containing C^{13}, calculated from the assumption that ions of the type $C^{+}_{nH_{2n+1}}$ ("head" ions) are formed with equal probability from any part of the molecule. From the middle parts of the molecule such ions, evidently, are formed with capture of a hydrogen atom. Fragment ions of other types $C_{nH}m^{+}$ ($m < 2n+1$), as we showed earlier [5], are formed mainly by detachment of hydrogen atoms from head ions.

Preliminary investigations of the mass spectrum of *n*-nonane-5-C^{13} as a function of electron energy showed that the mechanism of formation of head ions $C^{+}_{nH_{2n+1}}$ remains practically unchanged down to the appearance potential.

Table 1

m/e	Substance	Substance	m/e	Substance	Substance	m/e	Substance	Substance
	n-nonane	*n*-nonane-5 C^{13}		*n*-nonane	*n*-nonane-5 C^{13}		*n*-nonane	*n*-nonane-5 C^{13}
13	0,034	0,043	48	0,003	0,002	77,7	–	0,085
14	0,081	0,089	49	0,012	0,007	79	0,038	0,026
15	0,383	0,406	50	0,085	0,049	80	0,008	0,036
15,5	0,006	0,002	51	0,175	0,127	81	0,028	0,075
16	0,070	0,102	52	0,085	0,143	82	0,017	0,045
21,7	0,044	0,002	53	0,593	0,316	83	0,063	0,038
22,7	–	0,024	54	0,308	0,513	84	1,335	0,112
24	0,025	0,026	55	3,053	1,424	85	4,85	1,310
25	0,090	0,082	56	3,55	4,44	86	–	4,74
26	0,786	0,666	57	15,20	9,02	91	0,013	0,012
27	6,71	5,98	58	–	6,55	92	0,003	0,012
28	1,534	2,23	61	0,002	0,001	93	0,004	–
29	8,51	7,73	62	0,009	0,004	94	0,002	0,005
29,5	0,014	0,06	63	0,029	0,014	95	0,008	0,028
30	0,026	1,173	64	0,007	0,027	96	0,009	0,044
32,8	0,14	0,02	65	0,076	0,049	97	0,025	0,009
33,8	–	0,086	66	0,034	0,079	98	0,577	0,056
36	0,013	0,014	67	0,162	0,093	99	1,132	0,498
37	0,088	0,073	68	0,067	0,208	100	0,010	1,163
38	0,162	0,163	69	0,589	0,144	112	0,008	0,011
39	3,66	2,449	70	2,47	0,567	113	0,013	0,006
40	0,606	1,62	71	4,04	2,544	114	–	0,017
41	11,30	7,95	72	–	3,81	126	0,013	0,004
42	3,45	5,67				127	–	0,014
43	22,37	12,95	76,6	0,070	0,016	128	1,026	–
44	–	10,24				129	–	1,045
							100,000	100,000

Thus, in general, the dissociation of large molecules under electron impact proceeds as follows: at first, with approximately equal probability, "head" ions with an even number of electrons are formed from any part of the molecule with capture of a hydrogen atom; then some of these ions decompose with the detachment of hydrogen atoms and form the complete mass spectrum of the substance.

For example, for one of the variants of the formation of an ion of the type $C_3H_7^+$ we have:

$$H{-}C{-}C{-}C{-}C{-}C{-}C{-}C{-}C{-}C{-}H \longrightarrow C_3H_7^+$$

These facts agree with those conclusions that can be obtained from consideration of the mass spectra of large molecules.

At the present time it is accepted that, after electron impact, the excitation energy is redistributed over the entire molecule, which then dissociates in a random manner. Let us consider from this point of view two molecules of normal structure, for example, *n*-hexane C_6H_{14} and *n*-tetratetracontane $C_{44}H_{90}$. It is reasonable to assume that the electron strikes, with approximately equal probability, any part of the molecule. The molecules under consideration consist mainly of CH_2 groups, whose chemical and physical properties are practically identical. Therefore one may think that the average excitation energies transferred to these molecules under electron impact differ insignificantly. Hence one could expect that

Table 2

Ion	$C_2H_5^+$	$C_3H_7^+$	$C_4H_9^+$
Found	14	46	44
Calculated	25	43	67

molecular ions will be represented much more strongly in the mass spectrum of $C_{44}H_{90}$ than in that of C_6H_{14}. Experience, however, shows that the larger the molecule (for the same structure), the smaller the fraction of molecular ions in its mass spectrum (6).

Thus, in order to explain the very fact of the existence of mass spectra of large molecules, one must make the opposite assumption, namely that the energy transferred by the electron does not have time to be redistributed over the whole molecule before its dissociation. This assumption is consistent with data from the study of the initial portions of ionization curves (7) and makes it possible to explain readily the experimental results obtained by us. Indeed, if an electron strikes any part of the molecule with equal probability and the energy it transfers before dissociation is distributed only in a small part of the molecule, then it is evidently precisely this part of the molecule that "falls out"

in the form of a fragment ion. The ions formed in this way carry the major part of the excitation energy and therefore subsequently dissociate readily with the loss of hydrogen atoms.

It follows from this, in particular, that molecules whose structure permits excitation to be transmitted along a chain of bonds will dissociate under electron impact only to a small extent. In the mass spectra of such molecules the fractions of molecular ions will be large. Such, for example, is the mass spectrum of benzene.

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Note: Figure translations are in progress. See original paper for figures.