MASS SPECTRA AND PRIMARY PROCESSES OF THE RADIATION CHEMISTRY OF PARAFFINS

1961

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

M. V. GUR' EV

MASS SPECTRA AND PRIMARY PROCESSES OF THE RADIATION CHEMISTRY OF PARAFFINS

(Presented by Academician S. S. Medvedev, 23 VIII 1960)

The only attempt at a quantitative explanation of the mass spectra of complex molecules until recently remained the statistical theory, in which it is assumed that dissociation of the molecular ion in most cases occurs after a long time (up to $\simeq 10^{-6}$ sec) following ionization and excitation. According to this theory, during the indicated interval of time there is a complete redistribution and further migration of the excitation energy over the entire molecule, and dissociation is caused by a random concentration of energy on one bond or another (1,2).

It was shown earlier that any theory (including the one mentioned) which assumes that the excitation energy transferred by the electron is distributed over the entire molecule is inapplicable, at least for large molecules; and another hypothesis was proposed for the dissociation of large molecules under electron impact, which made it possible to explain qualitatively many regularities of mass spectra (3,4). In the present work we shall show that, even with the most primitive assumptions, the proposed theory makes it possible to calculate the mass spectra of practically all *n*-paraffins quantitatively without using any arbitrary quantities. We note that calculations of mass spectra according to the statistical theory include an arbitrary distribution function for the excitation energy, which is selected for each substance until the calculated mass spectrum agrees with the experimental one. Regardless of the initial premises and many simplifying assumptions, this deprives the theory of any practical value.

The basic premise of the "local" theory of mass spectra is that dissociation under electron impact occurs in the collision region without substantial redistribution of energy over the whole molecule; i.e., fragment ions are formed as a result of the "falling out" from the molecule of the region of collision with the electron.

Depending on the character of the collision, both the magnitude of this region and the probability of its "falling out" change (at the same electron energy). This is how the very fact of the mass spectrum is interpreted, i.e., the differences in the probability of formation of different fragments. From this point of view, the simplest is the mass spectrum of an infinitely large *n*-paraffin molecule, which is also taken as the basis for the calculations. Only group mass spectra are discussed, i.e., the total probabilities of formation of all ions with a given number of carbon atoms, independently of the number of hydrogen atoms. The mass spectrum of an infinitely large molecule may be considered known from experiment, since in practice it is sufficient to take the mass spectrum of an *n*-paraffin 2–3 times heavier in comparison with that whose mass spectrum is to be calculated.

The following assumptions were used in the calculation:

1. Formation of a fragment ion is a consequence of the "falling out" of the charged part of the molecule in the region of collision with the electron.
2. Cleavages of C—C bonds occur at equal distances from the "point" of collision.
3. The probability of formation of a fragment is determined by its size (the number of carbon atoms), but at every point of collision the complete set of probabilities of the mass spectrum of an infinitely large molecule is manifested, irrespective of whether, for the given dimensions of the finite molecule and the point of collision, the corresponding fragment can actually be formed or not. This means that if rupture of one of the bonds would have to occur outside the molecule, then only one bond is broken and, in the general case, a fragment smaller than that which should have been formed is produced. If ruptures of both bonds would have to occur outside the molecule, then the molecular ion is formed as a special case of the fragment ion.

Table 1

Substance	Number of C atoms in ion	Calculated, %	Found, %
Ethane	1	2.2	3
Ethane	2	100	100
Propane	1	4.5	4.5
Propane	2	75	100
Propane	3	100	50
n-Butane	1	3.2	4.2
n-Butane	2	64	75
n-Butane	3	100	100
n-Butane	4	50	13
n-Pentane	1	2.6	2.5
n-Pentane	2	53	31
n-Pentane	3	100	100
n-Pentane	4	63	9
n-Pentane	5	29	4.5
n-Hexane	1	2.7	4.0
n-Hexane	2	46	40
n-Hexane	3	100	100
n-Hexane	4	71	70
n-Hexane	5	32	3.1

Substance	Number of C atoms in ion	Calculated, %	Found, %
n-Hexane	6	21	7
n-Heptane	1	2.1	2.7
n-Heptane	2	42	48
n-Heptane	3	100	100
n-Heptane	4	77	45
n-Heptane	5	38	32
n-Heptane	6	17	1.1
n-Heptane	7	16	7
n-Octane	1	1.9	2
n-Octane	2	38	42
n-Octane	3	100	100
n-Octane	4	80	39
n-Octane	5	42	22
n-Octane	6	21	22
n-Octane	7	7	0.1
n-Octane	8	13	4.2
n-Nonane	1	1.8	2
n-Nonane	2	36	42
n-Nonane	3	100	100
n-Nonane	4	84	59
n-Nonane	5	45	20
n-Nonane	6	25	18
n-Nonane	7	8.8	4.6
n-Nonane	8	4.6	0.13
n-Nonane	9	11	3.9

x	$f(x)$
1	0.9
2	17
3	95
4	100
5	64
6	47
7	18
8	10.5
9	6.8
10	5.3
11	4.1
12	3.5
13	3.1
14	2.7
15	2.4

x	$f(x)$
16	2.0
17	1.8

4. The number of carbon atoms in the molecule, n, is sufficiently large that the molecule may be regarded as continuous. The dependence of the probability of fragment formation for a finite molecule, $\varphi_n(x)$, and for an infinitely large molecule, $f(x)$, is likewise regarded as a continuous function of the fragment length x.
5. We assume that molecules of any size differ only in their total length and that their ends do not differ from the middle parts.

All these assumptions, of course, greatly simplify the actual picture. Assumption 1 is the basic premise of the "local" theory of mass spectra, substantiated by us earlier ([3,4]), and is the most important of all. Assumptions 2 and 3 are justified only by the agreement of the results of the calculations with the experimental data.

Other assumptions were also considered, in particular concerning asymmetric (with respect to the collision point) formation of fragments, but all of them gave qualitative disagreement with experiment. The assumptions of continuity and of the absence of differences at the ends of the molecule are simplifications and are not necessary.

In the calculation, collisions of an electron with any point of the molecule are considered to be equally probable, and the probabilities of formation of each fragment are averaged over the entire molecule. The probability $\varphi(x,l)$ of formation, in one collision, of a fragment of a given length is a function of the fragment length x and of the distance l of the collision point from the end of the molecule. It is sufficient to consider one half of the molecule (in this case $0 \le l \le n/2$).

It follows from the assumptions that $\varphi(x,l) = f(x)$ for $x < 2l$, or $l > x/2$, i.e., when both bonds can in fact be broken. If, however, $l < x/2$, then the ion is formed from the end of the molecule, only one bond is broken, and a fragment $x = l + y/2$ is formed with probability $f(y)$, whence $y = 2x - 2l$. Hence

$$\begin{aligned} \varphi(x,l) &= f(x), & l &> \frac{x}{2}; \\ \varphi(x,l) &= f(2x-2l), & l &< \frac{x}{2}. \end{aligned} \tag{1}$$

The mass spectrum is the average probability over the whole molecule

$$\varphi_n(x) = \frac{2}{n}\int_0^{n/2} \varphi(x,l)\,dl.$$

Fig. 1

Figure 1: Fig. 1

Substituting the values of $\varphi(x, l)$ from (1), after transformations we have

$$\varphi_n(x) = \left(1 - \frac{x}{n}\right) f(x) + \frac{1}{n} \int_x^{2x} f(t)\, dt. \tag{2}$$

For molecular ions, an analogous method gives

$$\varphi_n(n) = \frac{1}{2n} \int_n^{2n} \int_t^{\infty} f(z)\, dz\, dt. \tag{3}$$

The results of calculations by equations (2) and (3), and the experimental data[5], are given in Table 1; there, with small corrections for the ends of the molecule according to equation (2), is also given the part of the mass spectrum of n-$C_{30}H_{62}$[5] used as the mass spectrum of an infinitely large molecule. As 100%, as usual, the maximum probability was taken. For light fragments ($x < n/2$) the discrepancy is within the errors of experiment. There is a large systematic discrepancy for ions close to the molecular ion, although the character of the mass spectrum in this region, especially for heavier molecules, is reproduced correctly*.

Fig. 1

For heavy molecules (for $x > 13$) the calculation of the mass spectrum is performed on the basis of equation (3) and the experimentally known exponential dependence of the probability of formation of molecular ions on the number of carbon atoms in the molecule of n-paraffins[6]. The solution of the resulting simple functional equation is substituted into equation (2). The result of the calculation for n-$C_{30}H_{62}$ is shown as a curve in Fig. 1. The experimental data are shown by points. From Fig. 1 it is evident that the principal ratios of the mass spectrum are explained by the theory rather well. The deviations near the molecular ion are apparently connected with peculiarities of the process at the ends of the molecule.

This method was also applied to calculating the relative yields of neutral fragments under electron impact. It is assumed here that the parts of the molecule remaining after removal of the fragment ion are uncharged. A calculation completely analogous to that given above leads, for the distribution of neutral fragments $r(x)$, to the expression

$$r(x) = \frac{1}{n} \int_0^{2n-2x} f(t)\, dt. \tag{4}$$

From equations (2) and (4) one can calculate the distribution of primary dissociation products in radiolysis in the gas phase. Of course, under real radiolysis conditions this distribution may be changed beyond recognition as a result of secondary processes and of the different state of the molecules in the condensed phase. However, the yields of products involving rupture of a C—C bond are very close in the radiolysis of *n*-hexane both in the liquid and in the gas phase (^{7}). This may mean that, in the simplest case of paraffins, the role of distorting factors is not very great; therefore a direct comparison of the calculated distributions of the primary products with the final products is not meaningless. The results of the calculation and the experimental data on the radiolysis of *n*-hexane are given in Table 2 (the total yield is taken as 100%).

For the yield of methane in the radiolysis of various sufficiently heavy *n*-paraffins ($x = 1,\ n > 5$), equations (2) and (4) give $G = a/n + b$, where G is the yield (molecules/100 eV); a and b are constants ($b \ll a$). From Fig. 2 it is seen that the experimental data (^{8}) are indeed well described by a hyperbola.

Table 2

Number of C atoms in the product	Calc., %	Found (^{7}), %	Number of C atoms in the product	Calc., %	Found (^{7}), %
1	15	9	4	22	22
2	23	40	5	8	4
3	32	25			

From the theory one can estimate the relative yield of olefins in radiolysis. For hexane it turns out to be ~ 1.5 times smaller than the yield of paraffins with the same number of carbon atoms, which agrees with experiment (^{8,9}).

It should be noted that cleavage of C—C bonds during the radiolysis of paraffins is practically not subject to "protection" (^{7,9}). This agrees well with the fact that, according to the "local" theory, dissociation occurs in a time of the order of 10^{-13} sec. (^{3}). The influence of benzene on the yields of heavy products and hydrogen, however, may indicate another mechanism of the corresponding primary processes, different from the mechanism of mass spectra. It should be emphasized that the very fact of a correlation between mass spectra and

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* The mass spectra of "labeled" heavy *n*-paraffins, kindly communicated to us by J. H. Beynon (submitted to *J. Phys. Chem.*), can be calculated by this method more accurately than by the one used previously[3,4].

Fig. 2

Figure 2: Fig. 2

radiolysis products (see, for example, ([7,9])) can, in the general case, be explained only by the "local theory."

Fig. 2

The author expresses his gratitude to Prof. N. N. Tunitskii for assistance in the work and discussion of the results.

Physicochemical Institute
named after L. Ya. Karpov

Received
22 VIII 1960

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