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Abstract

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REVERSAL OF THE TEMPERATURE DEPENDENCE OF THE INTENSITY OF FRAGMENT LINES IN A MOLECULAR MASS SPECTRUM

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It is known that the degree of dissociation of molecules upon ionization by electrons increases with increasing gas temperature (see, for example, [1,2]). This phenomenon is connected, in particular, with the necessity of stabilizing the temperature of the ion source in mass-spectrometric analysis of mixtures of polyatomic gases.

At present there are only the first attempts at creating a theory of dissociative ionization of molecules, and no quantitative relations exist for the dependence of the intensity distribution in a molecular mass spectrum on temperature, although the reasons leading to the existence of such a dependence are qualitatively clear. In particular, in the light of the statistical theory of the decay of an intermediate molecular ion [3], it is clear why the mass spectra of more polyatomic molecules, in which the probability is higher of concentrating energy sufficient to rupture some bond on this bond, should be subject to a greater influence of temperature.

All known measurements of the dependence of the intensity distribution in mass spectra on temperature have been carried out in the electron-energy region of 50–90 eV, where this distribution already depends very little on electron energy. Meanwhile, for the construction of a theory of dissociative ionization, apparently the temperature dependences in mass spectra at low electron energies, near the appearance potentials of fragment ions, should be of greatest interest.

The authors carried out such measurements using n-heptane as an example. The choice of the object was determined by the fact that the greatest temperature dependences are observed in the mass spectra of heavy hydrocarbons.

The experiments were carried out on an MS-1a mass spectrometer [4], equipped with a system for measuring and stabilizing the temperature in the ion source [5]. It had been shown previously [6] that the temperature measured by a thermocouple in the ion source corresponds to the true temperature of the gas being ionized.

Fig. 1. Dependence of the relative intensity of fragment lines in the mass spectrum of *n*-heptane on temperature at different electron energies

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The intensity distribution among lines in the mass spectrum was measured at different electron energies. The results of these measurements for the lines of the ions $C_5H_{11}^+$ (71 a.m.u.), $C_4H_9^+$ (57 a.m.u.) and $C_3H_7^+$ (43 a.m.u.) are given in Fig. 1.

Along the abscissa is plotted the gas temperature in °C in the ionization region; along the ordinate, the ratio of the intensity I of the given line to the total intensity ΣI of the lines of the mass spectrum (in percent of the value at a temperature of 300°). In these experiments the electrons were not monochromatized; the energy spread was approximately ±1 eV. Curves 1 were recorded at an electron energy of 30 eV, curves 2 at 17 eV, and curves 3 at 13 eV.

In all the cases considered, the temperature dependence of $I/\Sigma I$ proves to be approximately linear. A decrease in the electron energy leads to a shift in the temperature coefficient of the quantity $I/\Sigma I$ for the consid-

of the lines under consideration toward more positive values; moreover, for the lines of the ions $C_4H_9^+$ and $C_5H_{11}^+$ there are values of the electron energy at which the magnitude of the temperature coefficient passes through zero—an "inversion effect" is observed (these electron-energy values could be called the "potentials of inversion of the temperature dependence").

The observed phenomena can apparently be interpreted by assuming that the decomposition of the initial molecular ion (in our case $C_7H_{16}^+$), formed immediately after the collision of the molecule with an electron, does not proceed at once to all possible fragment ions, but in stages. For example, decompositions along C—C bonds occur first, and then the resulting fragment ions decompose along C—C and C—H bonds. From this point of view, the observed change in the temperature coefficient of the yield of the ions $C_nH_{2n+1}^+$ when the electron energy is decreased can be explained as the result of a decrease in the depth of decomposition of the initial molecular ion: at low electron energies the ions $C_nH_{2n+1}^+$ simply have fewer possible paths for further decomposition. In this case an increase in temperature already affects the decomposition processes of the initial molecular ion to a greater extent than the processes of subsequent decomposition of the ions $C_nH_{2n+1}^+$. Of special theoretical interest, apparently, should be the "inversion potential," at which, in accordance with the scheme presented, the temperature dependences of the processes of formation of the ions $C_nH_{2n+1}^+$ and the processes of decomposition of these ions should become equal.

Fig. 1. Dependence of the relative intensity of fragment lines in the mass spectrum of *n*-heptane on temperature at different electron energies

For a transition to quantitative use of the observed effect, it will be necessary to measure the temperature dependences and the exact appearance potentials of all ions in the mass spectrum of the molecule under study near the appearance potentials, using, for example, the method of quasi-monochromatization of electrons ([7,8]).

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