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IONIZATION AND DISSOCIATION OF HEXAFLUOROPROPYLENE BY ELECTRONS OF VARIOUS ENERGIES

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A comparative study of the dependence of the character of the dissociative ionization of ethylene and tetrafluoroethylene on the energy of the ionizing electrons made it possible, in the case of tetrafluoroethylene, to establish a number of features that do not agree with data on the strength of bonds in the stable molecule. On the basis of a study of the curves of relative ionization efficiency, a mechanism was proposed based on the assumption of the preferential formation of molecular ions with an asymmetric charge distribution as a result of ionization in the region of one of the C–F bonds (1).

In the present communication we give the results of an investigation of the dissociative ionization of hexafluoropropylene. The samples used in the work were purified by repeated distillation. The measurements were carried out on an MS-2 mass spectrometer. The accelerating voltage was 2500 V, the emission current 0.8 mA. The energy of the ionizing electrons was varied in the range 10–70 eV. Correction of the electron-energy scale was carried out from the ionization potential of xenon. The appearance potentials of the principal ions were measured by the method of extrapolating the straight-line portions of the ionization curves (2).

Table 1

Appearance potentials and activation energies

Ion	Appearance potential, eV	Activation energy in formation from the molecular ion, eV
$C_3F_6^+$	10.3 ± 0.2	–
$C_3F_5^+$	14.8 ± 0.3	4.5
$C_2F_4^+$	12.5 ± 0.1	2.2
$C_2F_3^+$	16.1 ± 0.2	–
CF_3^+	15.0 ± 0.1	7.7

Figure 1

Figure 1: Figure 1

The obtained appearance potentials and the values of the activation energies of certain dissociative processes in molecular ions are given in Table 1. The activation energy was determined as the difference between the appearance potentials of the corresponding fragment and molecular ions. Table 2 presents data relating to several metastable transitions identified at 70 eV. The main experimental results are given in Fig. 1 in the form of the dependence of the intensity of the molecular and certain fragment ions (expressed as percentages of the total ionization) on the energy of the ionizing electrons.

Table 2

Metastable ionic transitions at 70 eV

Process	Effective mass number	Total ionization, %
$C_3F_6^+ \rightarrow C_2F_4^+ + [CF_2]$	66,67	0,013
$C_3F_5^+ \rightarrow CF_3^+ + [C_2F_2]$	36,37	0,250
$C_2F_4^+ \rightarrow CF_3^+ + [CF]$	47,61	0,015

As is seen from Fig. 1, the first fragment ions to appear as the electron energy is increased are $C_2F_4^+$ ions. The activation energy is 2.2 eV. The intensive formation of these ions with only a slight increase in the electron energy above the ionization potential of hexafluoropropylene is quite unusual, if one proceeds from the known ideas about the structure and bond strengths in the molecule, reflected by the formula $CF_3—CF = CF_2$. Indeed, the formation of $C_2F_4^+$ ions in this case could be caused only by rupture of the relatively strong double bond $C = C$ while the weaker single bond $C—C$ is retained. Such a mechanism, of course, cannot be energetically favorable.

Let us consider another mechanism of this process, based on the ideas proposed for explaining the dissociative ionization of tetrafluoroethylene ([1]). Proceeding from this analogy, let us suppose that ionization of the hexafluoropropylene molecule occurs predominantly in the region of one of the C—F bonds of the trifluoromethyl group. This character of ionization leads to weakening of the C—F bond. In this case the fluorine atom, as in tetrafluoroethylene, migrates to the difluoromethylene group. It must also be assumed that the fluorine atom migrates in the form of a positive ion, which possibly accounts for such a rearrangement. Then, by analogy with the transition ionic complex $CF = CF_2(F^+)$ in tetrafluoroethylene, the corresponding complex for hexafluoropropylene will have the structure $CF_2—CF = CF_2(F^+)$. In this case the predominant formation of $C_2F_4^+$ ions is quite natural, since the process leading to their appearance corresponds to rupture of the weakest C—C bond.

Fig. 1. Relative ionization efficiency of hexafluoropropylene. Ions: 1–$C_3F_5^+$, 2 –CF_3^+, 3–CF^+, 4–$C_2F_4^+$, 5–C_2F_3, 6–$C_3F_6^+$. For curves 1—5, $n = 1$; for curve 6, $n = 3.3$.

The subsequent dissociative processes are consistent with rupture of stronger bonds in the transition complex. Indeed, as can be seen from the figure, with a further increase in the electron energy, $C_3F_5^+$ and CF_3^+ ions appear with very close activation-energy values (4.5 and 4.7 eV, respectively), which also corresponds to the closeness of the energies of the C—F and C = C bonds that dissociate in these processes (3).

The mechanism of formation of $C_2F_4^+$, $C_3F_5^+$, and CF_3^+ ions is further identified by the observed metastable ionic transitions. As can be seen from the data of Table 2, $C_2F_4^+$ ions are formed from molecular ions, which, as shown above, is observed in the region of low electron energies. The fact that the metastable transitions were determined at 70 eV confirms that the indicated process also occurs at higher energy. The intense metastable transition shows that CF_3^+ ions are formed not only from molecular ions but also during the dissociation of fragment ions $C_3F_5^+$. A certain contribution to the intensity of CF_3^+ ions is also made by decomposition of $C_2F_4^+$ ions, likewise identified by a metastable transition.

Let us note two other dissociative processes that begin with a further increase in the electron energy. As follows from the figure, the formation of CF^+ ions can to a considerable extent be attributed to secondary decomposition of $C_2F_4^+$ ions, since these ions appear and their intensity increases in the energy range for which the reverse

phenomenon in the case of $C_2F_4^+$ ions. For $C_2F_3^+$ ions, we note that the high appearance potential of these ions additionally confirms the impossibility of applying the concept of a non-rearranged structure of the molecular ion, from which $C_2F_3^+$ ions could readily be formed upon rupture of the C–C bond.

Consideration of the experimental results obtained has shown that the assumption of the existence of a transitional ionic complex made it possible to explain the mechanism of dissociative ionization of hexafluoropropylene and to establish, for the processes of primary decomposition of molecular ions, a quantitative relation with the energies of the corresponding bonds. It is important to note that the regularities obtained are characteristic precisely of fluorocarbon molecules. In our particular case, comparison with data obtained in an analogous study of propylene (4) shows a difference in the mechanisms of dissociative ionization, as was also noted in comparing tetrafluoroethylene and ethylene (1).

Analysis of the mass spectra of fluorocarbon compounds known from the literature (5), recorded at the generally accepted electron energy of 70 eV, leads to the conclusion that the C–C bond in the molecular ion is extremely weak, which contradicts data on the high strength of this bond in the stable molecule (3) and, in general, the known ideas concerning the chemical inertness of these compounds. Such a difference is not observed, however, in the case of analogous hydrocarbon molecules, where the C—C bonds under electron impact exhibit sufficient strength. As is known, the first ionization potentials of paraffin and olefin molecules are due to removal of σ- and π-electrons, respectively, from the carbon-carbon bond (^{6}). The high specificity of the character of dissociative ionization of the entire class of fluorocarbons permits the assumption that the supposition of predominant ionization in the region of one of the C—F bonds, proposed for tetrafluoroethylene and hexafluoropropylene, is sufficiently general.

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