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Formation of CF_3^+ Ions in Photoionization of Hexafluoroethane

By I. G. Simm† and C. J. Danby*

Physical Chemistry Laboratory, South Parks Road, Oxford

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A detailed study of the formation of CF_3^+ ions from C_2F_6 has been undertaken by photoelectron-photoion coincidence spectrometry. The distributions of kinetic energy released in CF_3^+ production have been measured over a range of internal energies of the parent ion. All the CF_3^+ ions observed are apparently formed by primary dissociation of the molecular ions; fission of the C—C bond in highly excited $C_2F_6^+$ ions probably occurs before internal conversion to the ground electronic state. The distributions of kinetic energy released in formation of CF_3^+ from ground state $C_2F_6^+$, and the rate of change of the average kinetic energy release with the ionization energy, are consistent with predictions made on the basis of statistical theories of reaction. The distributions of kinetic energy released in dissociation of highly excited $C_2F_6^+$ ions are broader, and also change unexpectedly slowly with internal energy.

The technique of photoelectron-photoion coincidence spectrometry [1, 2] has been used to investigate the mechanisms of several ion dissociations.[3-6] Here we report a detailed study of the formation of CF_3^+ ions in the photoionization of hexafluoroethane, and discuss the results in the light of theories of unimolecular decomposition. The distribution of kinetic energy released in dissociation can be determined from the experimental time of flight peaks for fragment ions,[2, 7, 8] and has been measured for CF_3^+ formation over a range of internal energy of the molecular ion.

EXPERIMENTAL RESULTS

The experimental method has already been described,[3, 5, 6] as has the method by which kinetic energy distributions are derived from the time-of-flight peaks.[7, 8] Accounts of the general features of the dissociation of $C_2F_6^+$ have already been published.[3, 7] Significant proportions of CF_3^+ are produced in decompositions of molecular ions in their ground state, and at ionization energies above about 17 eV, but not at intermediate energies.[3] We have calculated the distributions of kinetic energy released, assuming primary dissociation of $C_2F_6^+$, which best fit the experimental time-of-flight peak shapes for CF_3^+. The distributions are obtained as sets of discrete energy releases, each with a characteristic weight. The significance of the individual values in the set is small [5] and the distributions are best regarded as approximations to continuous functions. The peaks cannot be fitted by reasonable analytic forms of distribution, such as maxwellian functions or decreasing exponentials.

THE ORIGIN OF THE CF_3^+ IONS

The CF_3^+ ions may be formed from $C_2F_6^+$ by simple C—C bond fission, or by loss of a fluorine atom followed by secondary dissociation of $C_2F_5^+$:

$$C_2F_6^+ \rightarrow CF_3^+ + CF_3 \quad (1)$$

$$C_2F_6^+ \rightarrow C_2F_5^+ + F \rightarrow CF_3^+ + CF_2 + F. \quad (2)$$

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† present address: Dept. of Theoretical Chemistry, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW.

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Su and Kevan[8] have detected, in electron impact experiments, a metastable peak corresponding to the second stage of process (2), indicating a secondary origin for at least some of the CF_3^+ ions observed in the electron impact mass spectrum. Because of the different states populated in ionization by electron and photon impact, the observation of a metastable peak is not necessarily a reliable guide to the processes occurring in the particular electronic states populated in our experiments. We may assume that the CF_3^+ ions observed as decomposition products of ground state $C_2F_6^+$ are formed as primary fragments by the lower energy process (1), since the threshold of observation of $C_2F_5^+$ lies above the ground state of the molecular ion. The CF_3^+ ions observed at higher ionization energies may be secondary products of decompositions of $C_2F_5^+$.

If this were the case, the initial velocity distribution of the CF_3^+ ions would depend on that of the $C_2F_5^+$ ions. A secondary fragment ion must inherit the velocity of its precursor, plus a contribution from the kinetic energy released in its own formation. This places a lower limit on the average kinetic energy of the secondary fragments, provided that high kinetic energy primary fragments retain sufficient internal energy to decompose. At an ionization energy of 17.52 eV, where the intensities of both CF_3^+ and $C_2F_5^+$ are high enough for their velocity distributions to be compared, the CF_3^+ ions have sufficiently large an average kinetic energy for them to be products of decomposition of $C_2F_5^+$.

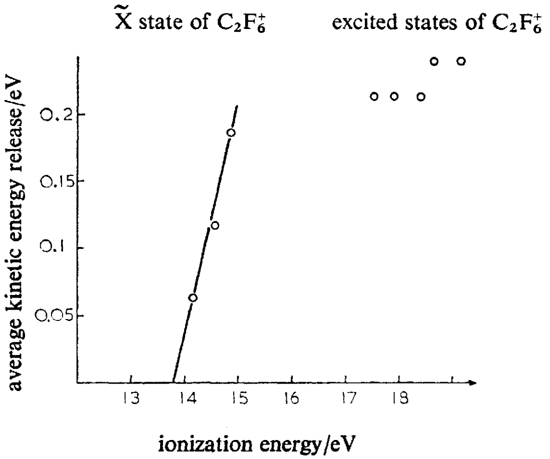

FIG. 1.—Average kinetic energy released in formation of CF_3^+ ions from $C_2F_6^+$, as a function of the ionization energy.

Thermodynamic evidence, however, argues against secondary decompositions of $C_2F_5^+$. From published heats of formation,[9-11] and the ionization potential of CF_3,[12] the threshold energies for processes (1) and (2) are found to be 13.33±0.08 and 17.34±0.15 eV respectively. In formation of $C_2F_5^+$ at an ionization energy of 17.52 eV, high kinetic energy releases ($\geqslant$ 0.75 eV) predominate,[5] and very few $C_2F_5^+$ ions will have sufficient internal energy to decompose. The distributions of kinetic energy released in $C_2F_5^+$ formation remain very similar across a wide range of ionization energy, showing no depletion of low kinetic energy ions as the threshold for further dissociation to CF_3^+ is passed. The $C_2F_5^+$ ions abruptly disappear from the coincidence spectra above an ionization energy of 17.52 eV, even though the predominant high kinetic energy ions will still have insufficient internal energy to decompose.

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If, as appears most probable, all the CF_3^+ ions are formed directly from $C_2F_6^+$, the calculated distributions of kinetic energy released are those arising from the dissociations of $C_2F_6^+$ ions. In fig. 1, the average kinetic energy released is shown as a function of the ionization energy. It can be seen that the values obtained for dissociations of highly excited molecular ions lie well below those expected from extrapolation of the ground state results. The average kinetic energy released changes very slowly with internal energy in measurements on the excited states, compared with the variation in the ground state. Both these observations suggest that molecular ions in highly excited states dissociate without prior internal conversion to the ground state. We have already shown [3] that if $C_2F_6^+$ ions in excited states undergo C—C bond fission, symmetry considerations require that one or both of the products be formed in an excited state.* This would lower the excess energy available to the reaction, and tend to produce lower kinetic energy releases than might otherwise be expected.

AVERAGE KINETIC ENERGY RELEASE

It is only recently that distributions of kinetic energy released, $P(\varepsilon_t)$, in ion dissociations have become experimentally measurable, and mass spectrometrists have concentrated more on the average kinetic energy release, $\bar{\varepsilon}_t$. Taking the values in fig. 1 for the dissociations of ground state $C_2F_6^+$, we find a linear relationship, within experimental error, between $\bar{\varepsilon}_t$ and the ionization energy E_I, as predicted by Haney and Franklin.[13] If the results are extrapolated to zero kinetic energy, we find a "threshold energy" of 13.8±0.1 eV, which is well above the calculated thermodynamic limit, above the photoionization appearance potential obtained by Noutary,[14] and above the onset of the $\tilde{X}^2A_{1g}$ photoelectron band. Since no parent ions are observed either in coincidence spectra [3] or photoionization,[14] $C_2F_6^+$ ions formed in the $\tilde{X}^2A_{1g}$ state must be completely dissociated to $CF_3^+ + CF_3$; the extrapolation in fig. 1 is, therefore, faulty. This may be because of discontinuities near threshold, or because the graph of E_I against $\bar{\varepsilon}_t$ is concave to the E_I-axis, for which there is some slight evidence in the experimental results. Non-linear relationships between $\bar{\varepsilon}_t$ and excitation energy E ($E = E_I - E_0$, where E_0 is the thermodynamic threshold) are predicted by Klots [15] on the basis of a statistical theory of reactions, but these curves are convex to the E-axis. The experimental value of $dE/d\bar{\varepsilon}_t$, is 5.6±0.8, which is consistent with statistical reaction models for $C_2F_6^+$, a system with 18 oscillators.

DISTRIBUTIONS OF KINETIC ENERGY RELEASED

In fig. 2, the distributions of kinetic energy released in dissociations of ground state $C_2F_6^+$ ions are shown as continuous functions; similar curves for excited states appear in fig. 3. It will be noted that several of the excited state peak shapes are identical within experimental error, implying that the distributions of kinetic energy released do not change significantly over a range of internal energy. This rather unexpected behaviour has been observed for a number of other fluorinated ions.[5, 16] Phenomenologically, it implies that the vibrational modes excited in photoionization do not affect the extension of the reaction co-ordinate, and that the excited ion does not visit all accessible areas of its phase space before dissociation. The width of the kinetic energy release distribution implies, however, that there must be many states populated before dissociation. Previous observations of similar

*There is an error in ref. (3). The minimum symmetry which must be conserved in the dissociation is not C_{3v}, as stated there, but C_3, with irreducible representations A and E. The substance of the argument is unaffected.

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behaviour suggest that the kinetic energy release distributions are dependent on the electronic state of the molecular ion. It may be, therefore, that in the appropriate energy region, $C_2F_6^+$ ions in only two electronic states give CF_3^+ as a dissociation product.

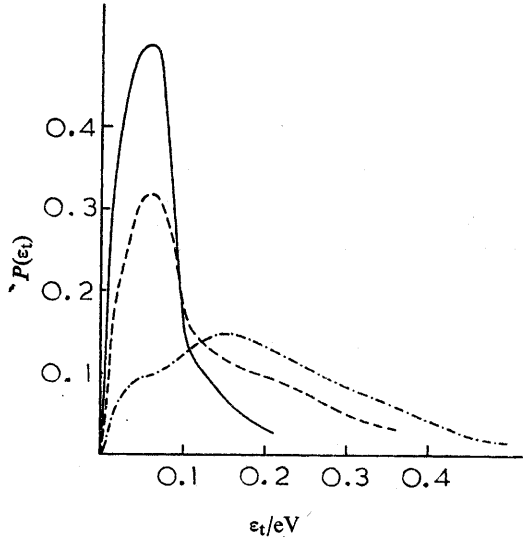

Fig. 2.—Distributions of kinetic energy released in formation of CF_3^+ in the ground state, at ionization energies: 14.14 eV —; 14.54 eV ----; 14.84 eV -·-·-.

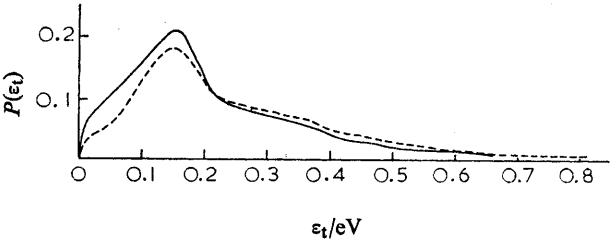

Fig. 3.—Distributions of kinetic energy released in formation of CF_3^+ ions from $C_2F_6^+$ in excited states, at ionization energies: 17.52, 17.89, 18.39 eV —; 18.64, 19.14 eV ----.

The shapes of the kinetic energy release distributions for dissociations of ground state $C_2F_6^+$ are consistent with those predicted on the basis of statistical theories of dissociation in which conservation of angular momentum is included.[17, 18] Other predictions based on the quasi-equilibrium theory of mass spectra [15, 19] give kinetic energy distributions which peak at $\varepsilon_t = 0$. These are physically unrealistic; the limit of zero translational energy release implies no separation of the products, and therefore no dissociation at all.[20] Because of the disagreement between the precise forms of kinetic energy distribution predicted by the various statistical models, no detailed calculations have been made for $C_2F_6^+$.

It is perhaps rather surprising that dissociation of ground state $C_2F_6^+$ ions is described quite well by the statistical model. The photoelectron band is diffuse, and lies wholly above the calculated dissociation limit for CF_3^+ formation. The $^2A_{1g}$ ground state of $C_2F_6^+$ corresponds to loss of a C—C bonding electron from the molecule, which should lead to the excitation of the principal C—C stretching

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vibration. Such excitation must contribute substantially to the extension of the reaction coordinate for C—C bond fission, even if other geometrical factors affect the reaction. Excitation of the ion above the dissocation limit might, therefore, be expected to lead to direct, or at least fast, dissociation. The forms of the kinetic energy release distributions suggest that the ions visit many regions of their phase space before dissociating, and seem to rule out direct dissociation within a vibrational period. This is also true of the dissociations of excited $C_2F_6^+$, but in these cases the very slow change in kinetic energy release with internal energy is clearly incompatible with the statistical models.

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