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Study of the Gas Phase Reactions of Several Perfluorocarbons with Positive Ions of Atmospheric Interest

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The bimolecular rate coefficients and ion products for the reactions of H_3O^+, NO^+, O_2^+, H_2O^+, N_2O^+, O^+, CO_2^+, CO^+, N^+, and N_2^+ with three fluoroalkenes (C_2F_4, C_3F_6, and 2-C_4F_8) and three fully saturated perfluorocarbons (C_2F_6, C_3F_8, and n-C_4F_{10}) at 300 K are reported. All six perfluorocarbons are found to be unreactive with NO^+. C_2F_6 is also unreactive with O_2^+, H_2O^+, and N_2O^+, and C_3F_8 and n-C_4F_{10} are also unreactive with O_2^+. C_3F_6 is the only perfluorocarbon studied that reacts with H_3O^+ at a measurable rate. All the other reactions take place at or close to the collisional rate, the exceptions being the reactions of N_2O^+ with C_2F_4 and C_3F_8, and CO_2^+ with C_2F_4 and C_2F_6, for which the experimental rate coefficients show marked departures from the collisional values. It is proposed that most of the reactions proceed through a complex intermediate resulting in electrophilic attack by the ion on the perfluorocarbon. This mechanism generally takes precedent over "long-range" (formal) charge transfer. This work is of possible relevance to atmospheric ion-chemistry and plasma processes and may also be pertinent to the use of chemical ionization mass spectrometers for the trace detection of perflurocarbons in the environment.

Introduction

Atmospheric concentrations of perfluorocarbons (PFCs, C_xF_y) are increasing because of their use as substitutes for the ozone-depleting chlorofluorocarbons and because they are produced as byproducts in industrial processes.[1] This is of concern, since the coupling of the saturated PFCs' radiative properties, which make them efficient greenhouse gases,[2,3] and their estimated long residence times in the atmosphere[2] give them considerable potential for contributing to global warming. Saturated PFCs react very slowly, if at all, with atmospheric free radicals, are transparent to stratospheric UV radiation, and are water insoluble. The most likely degradation path proposed for the majority of these molecules is photolytic destruction in the mesosphere.[2]

Until recently, the effects of electron and ion reactions in the mesosphere on the atmospheric lifetimes of saturated PFCs have been ignored. However, new studies[4,5] have highlighted that such reactions can play a role in reducing the atmospheric lifetime of some PFCs, although the lifetimes are still large. In this paper we present new data on the thermal (300 K) reactions of a number of atmospheric positive ions (covering a range of recombination energies (6.37−15.58 eV)), including (in order of increasing recombination energy) H_3O^+, NO^+, O_2^+, H_2O^+, N_2O^+, O^+, CO_2^+, CO^+, N^+, and N_2^+, with three fully saturated PFCs (C_2F_6, C_3F_8, and n-C_4F_{10}). We have also performed studies of the reactions of the above ions with three fluoroalkenes (C_2F_4, C_3F_6, and 2-C_4F_8) to provide a useful comparison of the reaction kinetics and dynamics with the saturated molecules. Rate coefficients and product distributions for all the reactions are reported. Ultimately, this information may lead to a better understanding of the fate of saturated PFCs in the atmosphere and the role that ionic reactions play in industrial plasma etching using PFCs for the processing of microcircuits.

Two of the PFCs investigated here, tetrafluoroethylene (C_2F_4) and hexafluoropropene (C_3F_6), are industrially important monomers being used in the production of such fluorocarbon products as Teflon, Viton, etc.[1] C_2F_4 is also being used commercially to prepare and deposit thin dielectric films for capacitors. In addition, C_2F_4 and other PFCs are used in industrial plasmas mainly for etching processes. Large quantities of PFCs, particularly carbon tetrafluoride (CF_4) and hexafluoroethane (C_2F_6), are emitted each year in the production of aluminum.[3] Another PFC, the highly toxic perfluoroisobutene, has been identified as an atmospheric contaminant in industrial plants that produce and process polytetrafluoroethene and other perfluoropolymers[6] and has already been the subject of a number of recent studies by us.[7,8] There is obviously a need to develop convenient techniques to monitor PFCs in the environment, and gaseous ions can be used as powerful probes for this purpose.

Experimental Details

We have used a selected ion flow tube (SIFT) to measure the rate coefficients and to record ion products of the ionic reactions studied. The SIFT apparatus, experimental technique, and analysis of data have been extensively reviewed.[9] Therefore, only a few points specific to the present study are mentioned here. Ions were generated in an enclosed, high-pressure ion source containing appropriate gases as follows: NO^+ from NO, O_2^+ from an O_2/N_2 mixture, H_2O^+ and H_3O^+ from H_2O, N_2O^+ from N_2O, O^+ and CO_2^+ from CO_2, CO^+ from CO, and N^+ and N_2^+ from N_2. The ions were mass selected using a quadrupole mass filter and injected via a Venturi inlet into a fast flowing (~150 Torr L s^{-1}) He (99.997% purity) buffer gas that was maintained at a temperature and pressure of 300 K and 0.5 Torr, respectively. The ions were thus convected along the flow tube. Measured quantities of reactant gases were introduced into the carrier gas/ion stream downstream of the ion inlet. The reactant gases, C_2F_4, C_3F_6, and C_2F_6, and 2-C_4F_8, C_3F_8, and n-C_4F_{10} were obtained commercially, having stated purities of >99% and 97%, respectively, and were used without further purification. The sample of

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TABLE 1: Total Rate Coefficients, the Product Ions, and the Branching Percentages (in Parentheses) for the Reactions of O_2^+, H_2O^+, N_2O^+, O^+, CO_2^+, CO^+, N^+, and N_2^+ with Three Fluoroalkenes (C_2F_4, C_3F_6, and 2-C_4F_8)[a]

	ion (RE (eV))							
	O_2^+ (12.07) (v = 0, ~80%) (v = 1, ~10%) (v = 2, ~10%)	H_2O^+ (12.61)	N_2O^+ (12.87)	O^+ (13.62)	CO_2^+ (13.77)	CO^+ (14.01)	N^+ (14.54)	N_2^+ (15.58) (v = 0, ~60%) (v = 1, ~40%)
	Reaction with C_2F_4 (IP = 10.12 eV)							
k_{obs} (300 K)	1.1	1.3	0.33	1.5	0.21	1.1	1.6	1.1
k_{obs} (390 K)			0.23		0.14			
k_c (α = 4.2 Å^3)	0.98	1.2	0.87	1.3	0.87	1.0	1.4	1.0
ionic products	$C_2F_4^+$ (100%)	$C_2F_4^+$ (100%)	$C_2F_4^+$ (100%)	$C_2F_4^+$ (100%)	$C_2F_4^+$ (100%)	$C_2F_4^+$ (100%)	CF^+ (9%) CF_2^+ (1%) CF_3^+ (1%) $C_2F_3^+$ (4%) $C_2F_4^+$ (85%)	CF^+ (25%) CF_2^+ (11%) CF_3^+ (13%) $C_2F_3^+$ (5%) $C_2F_4^+$ (46%)
	Reaction with C_3F_6 (IP = 10.6 eV)							
k_{obs} (300 K)	1.6	1.6	1.0	2.2	1.3	1.7	1.9	1.3
k_c (α_{eff} = 9.7 ± 0.9 Å^3)	1.4	1.8	1.3	1.9	1.3	1.5	2.0	1.5
ionic products	$C_2F_4^+$ (13%) $C_3F_5^+$ (10%) $C_3F_6^+$ (77%)	$C_3F_5^+$ (6%) $C_3F_6^+$ (94%)	$C_3F_5^+$ (2%) $C_3F_6^+$ (98%)	$C_2F_4^+$ (15%) $C_3F_5^+$ (20%) $C_3F_6^+$ (65%)	$C_2F_4^+$ (18%) $C_3F_5^+$ (21%) $C_3F_6^+$ (61%)	$C_2F_4^+$ (28%) $C_3F_5^+$ (29%) $C_3F_6^+$ (43%)	$C_2F_4^+$ (50%) $C_3F_5^+$ (9%) $C_3F_6^+$ (41%)	CF_3^+ (3%) $C_2F_4^+$ (51%) $C_3F_5^+$ (46%)
	Reaction with 2-C_4F_8 (IP = 11.1 eV)							
k_{obs} (300 K)	1.8	2.2	1.3	2.0	1.6	1.8	2.2	1.8
k_c (α_{eff} = 13.7 ± 0.8 Å^3)	1.7	2.1	1.4	2.3	1.4	1.8	2.4	1.8
ionic products	$C_3F_5^+$ (5%) $C_3F_6^+$ (1%) $C_4F_7^+$ (3%) $C_4F_8^+$ (91%)	$C_3F_5^+$ (4%) $C_4F_7^+$ (11%) $C_4F_8^+$ (85%)	$C_3F_5^+$ (1%) $C_4F_8^+$ (99%)	$C_3F_5^+$ (33%) $C_3F_6^+$ (2%) $C_4F_7^+$ (12%) $C_4F_8^+$ (53%)	$C_3F_5^+$ (76%) $C_3F_6^+$ (2%) $C_4F_7^+$ (2%) $C_4F_8^+$ (20%)	$C_3F_5^+$ (27%) $C_3F_6^+$ (26%) $C_4F_7^+$ (39%) $C_4F_8^+$ (8%)	$C_3F_5^+$ (17%) $C_3F_6^+$ (4%) $C_4F_7^+$ (6%) $C_4F_8^+$ (73%)	$C_3F_5^+$ (23%) $C_3F_6^+$ (19%) $C_4F_7^+$ (58%)

[a] The measured rate coefficients (k_{obs}) and product distributions are considered to be accurate to ±20%. Adiabatic recombination energies (RE) and ionization potentials (IP) are given in parentheses for the ion and neutral species, respectively. The calculated 300 K collisional rate coefficient (k_c) for each reaction is also presented. The rate coefficients (experimental and calculated) are given in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. With the exception of C_2F_4, the collisional rate coefficients have been determined by using an estimate of the effective polarizabilities (α_{eff}) derived from plots of k_{obs} against reduced mass, as described in the text. It is only possible to give values of α_{eff} because the permanent dipole moments are, to our knowledge, unknown for C_3F_6 and 2-C_4F_8.

2-C_4F_8 used was a mixture of the *cis* and *trans* isomers. The precursor and product ions were focused through a Faraday plate, mass analyzed by a quadrupole mass filter downstream of the inlet, and detected by a channeltron electron multiplier. By correlation of the decrease of the primary (injected) ion count rate and the increase in the product ion count rates to the flow rate of the reactant gas, the rate coefficient and ion product distribution were obtained. The accuracy of the measured rate coefficients is ±20%. The product branching ratios were determined in the usual way by plotting product percentages against the flow rate of the reactant neutral and extrapolating to zero flow. Mass discrimination of the detection system was taken into account in the usual way.[10]

Results

The measured rate coefficients, the product ions, and their branching percentages for all the reactions included in this study are given in Table 1 for the perfluoroalkenes and in Table 2 for the perfluoroalkanes. The reactant molecules are listed (top to bottom) in increasing chain length, and the reactant ions are ordered (left to right) in increasing recombination energy. The ions NO^+ and H_3O^+ are not represented in the tables. NO^+ is unreactive with all the molecules studied in this work, presumably because there are no exothermic reaction channels available, and hence will not be discussed further. H_3O^+ is found to be reactive with only one of the PFCs: C_3F_6. That H_3O^+ is unreactive with C_2F_4 and the saturated PFCs studied can be explained by thermochemistry, i.e., all reaction pathways are endothermic. Thermochemistry probably also explains why H_3O^+ is unreactive with 2-C_4F_8, although we cannot say this with certainty because the enthalpy of the reaction leading to the most likely products ($C_4F_7^+$, HF, and H_2O) is unknown. H_3O^+ will therefore only be discussed again in the section of the paper dealing with C_3F_6. The results presented in the tables are self-explanatory, although prior to the discussion of these results some comments need to be made under three areas.

Determination of Collisional Rate Coefficients. Presented in the tables are the calculated collisional rate coefficients, k_c, which are useful for determining the efficiency of reactions by comparing them with the experimentally determined rate coefficients, k_{obs}. k_c can be determined according to the Langevin equation for nonpolar molecules,[11] where k_c may be written as

$$k_c = 2\pi q(\alpha/\mu)^{1/2} \tag{1}$$

q is the charge on the ion (in esu, one electron charge being 4.8032×10^{-10} esu), μ is the reduced mass of the colliding partners (in grams), and α is the polarizability of the molecule (in cm^3). The units of k_c are cm^3 molecule^{-1} s^{-1}.

For polar molecules several equations have been derived for k_c, the simplest being the average dipole orientation (ADO) theory,[12,13] where k_c may be written as

$$k_c = (2\pi q/\mu^{1/2})[\alpha^{1/2} + c\mu_D(2/(\pi k_B T))^{1/2}] \tag{2}$$

k_B is Boltzmann's constant (in units of ergs K^{-1}), μ_D is the dipole moment (in Fr cm), and c is the locking constant, which has been parametrized by Su and Bowers[12] over a range of temperatures and as a function of ($\mu_D/\alpha^{1/2}$). Note that eq 2 predicts that k_c is dependent on the temperature but reduces to the temperature-independent Langevin equation for molecules with no permanent dipole moment. A method using the parametrization of the collisional rate equation using trajectory calculations[14] is generally regarded as the most accurate method to calculate k_c, but independent values of both α and μ_D are needed.

TABLE 2: Total Rate Coefficients, the Product Ions, and the Branching Percentages (in Parentheses) for the Reactions of O_2^+, H_2O^+, N_2O^+, O^+, CO_2^+, CO^+, N^+, and N_2^+ with Three Fully Saturated PFCs (C_2F_6, C_3F_8, and C_4F_{10})^a

	ion (RE (eV))							
	O_2^+ (12.07) ($v = 0$, ~80%) ($v = 1$, ~10%) ($v = 2$, ~10%)	H_2O^+ (12.61)	N_2O^+ (12.87)	O^+ (13.62)	CO_2^+ (13.77)	CO^+ (14.01)	N^+ (14.54)	N_2^+ (15.58) ($v = 0$, ~60%) ($v = 1$, ~40%)
Reaction with C_2F_6 (IP = 13.4 eV)								
k_{obs} (300 K)				1.3	0.84	1.1	1.6	1.2
k_c ($\alpha = 6.82$ Å^3)	1.2	1.5	1.1	1.6	1.1	1.3	1.7	1.3
ionic products				CF_3^+ (92%) $C_2F_5^+$ (8%)	CF_3^+ (100%)	CF_3^+ (41%) $C_2F_5^+$ (59%)	CF_3^+ (71%) $C_2F_5^+$ (29%)	CF_2^+ (2%) CF_3^+ (27%) $C_2F_5^+$ (71%)
Reaction with C_3F_8 (IP = 13.38 eV)								
k_{obs} (300 K)		1.3	0.77	1.5	1.2	1.5	1.8	1.2
k_c ($\alpha = 6.7 \pm 0.7$ Å$^{3)}$	1.2	1.5	1.0	1.6	1.0	1.2	1.7	1.2
ionic products		CF_3^+ (2%) $CF_3^+{\cdot}H_2O$ (72%) $C_2F_4^+$ (5%) $C_2F_5^+$ (1%) $C_2F_5^+{\cdot}H_2O$ (12%) $C_3F_7^+$ (8%)	CF_3^+ (21%) $C_2F_4^+$ (76%) $C_2F_5^+$ (2%) $C_3F_7^+$ (<1%)	CF_3^+ (44%) $C_2F_4^+$ (43%) $C_2F_5^+$ (2%) $C_3F_7^+$ (11%)	CF_3^+ (45%) $C_2F_4^+$ (48%) $C_2F_5^+$ (5%) $C_3F_7^+$ (2%)	CF_3^+ (73%) $C_2F_4^+$ (10%) $C_2F_5^+$ (12%) $C_3F_7^+$ (5%)	CF_3^+ (52%) $C_2F_4^+$ (14%) $C_2F_5^+$ (16%) $C_3F_7^+$ (18%)	CF_3^+ (37%) $C_2F_4^+$ (10%) $C_2F_5^+$ (24%) $C_3F_7^+$ (29%)
Reaction with *n*-C_4F_{10}								
k_{obs} (300 K)		1.9	1.1	2.0	1.3	1.5	2.2	1.7
k_c ($\alpha = 11.0 \pm 0.5$ Å$^{3)}$	1.5	1.9	1.3	2.0	1.3	1.6	2.1	1.6
ionic products		CF_3^+ (1%) $CF_3^+{\cdot}H_2O$ (32%) $C_2F_4^+$ (1%) $C_2F_5^+$ (2%) $C_2F_5^+{\cdot}H_2O$ (8%) $C_3F_6^+$ (28%) $C_4F_9^+$ (28%)	CF_3^+ (6%) $C_2F_4^+$ (3%) $C_3F_6^+$ (91%)	CF_3^+ (29%) $C_2F_4^+$ (15%) $C_2F_5^+$ (31%) $C_3F_6^+$ (17%) $C_4F_9^+$ (8%)	CF_3^+ (22%) $C_2F_4^+$ (12%) $C_2F_5^+$ (46%) $C_3F_6^+$ (17%) $C_3F_7^+$ (3%)	CF_3^+ (45%) $C_2F_4^+$ (8%) $C_2F_5^+$ (28%) $C_3F_6^+$ (11%) $C_3F_7^+$ (2%) $C_4F_9^+$ (6%)	CF_3^+ (33%) $C_2F_4^+$ (7%) $C_2F_5^+$ (30%) $C_3F_6^+$ (7%) $C_3F_7^+$ (3%) $C_4F_9^+$ (20%)	CF_3^+ (23%) $C_2F_4^+$ (4%) $C_2F_5^+$ (25%) $C_3F_6^+$ (2%) $C_3F_7^+$ (3%) $C_4F_9^+$ (43%)

[a] The measured rate coefficients (k_{obs}) and product distributions are considered to be accurate to ±20%. Adiabatic recombination energies (RE) and ionization potentials (IP) are given in parentheses for the ion and neutral species, respectively. The calculated 300 K collisional rate coefficient (k_c) for each reaction is also presented. The rate coefficients (experimental and calculated) are given in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. With the exception of C_2F_6, the collisional rate coefficients have been derived from an estimate of the polarizabilities determined from plots of k_{obs} against reduced mass, as described in the text. These polarizabilities are represented by α.

In this study, values for α are only available for C_2F_4 and C_2F_6 (both of which are nonpolar), and, in addition for the polar molecules, no dipole moments are known for the polar molecules. Nevertheless, since the reactions of each PFC have been studied at a constant temperature and with ions whose masses vary between 14 amu (N^+) and 44 amu (CO_2^+), it is still possible to use either the Langevin or ADO theory to estimate k_c and hence to determine whether reactions are proceeding below 100% efficiency. This can be done by plotting k_{obs} against $(2\pi q/\mu^{1/2})$. If the majority of reactions occur at the collisional rate, a straight line of slope $\alpha_{eff}^{1/2}$ passing through the origin will be obtained, where

$$\alpha_{eff} = [\alpha^{1/2} + c\mu_D(2/(\pi k_B T))^{1/2}]^2 \tag{3}$$

according to ADO theory. Reactions occurring at a rate below the collisional value will lie below this line. Figure 1 shows such a plot for the reactions of the polar molecule 2-C_4F_8, and, within experimental uncertainty, all the ions react at close to unit efficiency. If they did not, considerable scatter about the line would be observed. Obviously, a straight line fit would also be obtained if all the reactions were proceeding below the collisional rate with the same efficiency, and while this cannot be ruled out, it seems highly unlikely. Similar plots were obtained for C_3F_6, C_3F_8, and *n*-C_4F_{10} from whose slopes the collisional rate coefficients were determined. These values are shown in Tables 1 and 2.

We comment that the difference between modified ADO theory[14] and its simpler form[12,13] is not significant enough to warrant the use of the former method not only because rate coefficients are only measured to an accuracy of ±20% but also because ADO theory is only used here to derive an expression for α_{eff}.

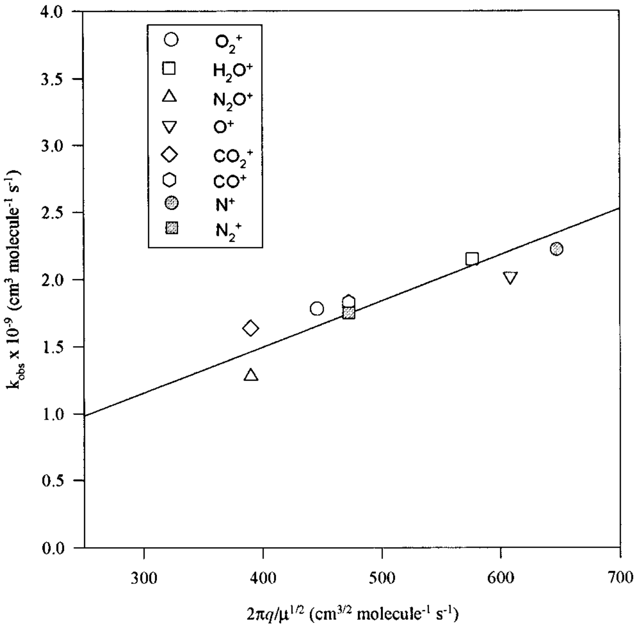


Figure 1. Plot of the measured rate coefficient, k_{obs}, against $(2\pi q/\mu)^{1/2}$ for the reactions with 2-C_4F_8, illustrating a near linear dependence from which the polarizability of 2-C_4F_8 can be estimated and hence collisional rate coefficients determined. Note that the line shown in the diagram has been constrained to pass through the origin. Similar plots were drawn and used to determine polarizabilities for all the other PFCs in this study, except for C_2F_4 and C_2F_6 whose polarizabilities are known.

Product Ions. For a number of the reactions some of the product ions have very small branching ratios (<2%) associated with them. Although it cannot be ruled out that for these values impurities in our samples reacting with the reactant ions with unit efficiencies could be forming these products, it is not obvious what impurities would produce such products.

For an understanding of reaction mechanisms, it is important to know if excited state reactant ions are present in the flow tube. If such ions are present, then ground state thermochemistry cannot be used to determine if certain ion products are thermodynamically allowed. This is particularly serious for vibrationally excited molecular ions because of the inefficiency of vibrational−translational energy transfer in the helium buffer gas. The high pressure of the source gases in the ionization chamber, used to produce the ions in this investigation, is known to significantly quench (metastable) electronically and vibrationally excited states of many ions prior to their injection into the flow tube. Nevertheless, in this study a number of independent checks were made for excited state reactant ions. Excited states of N^+ (i.e., ^1D at 1.90 eV and ^1S at 4.05 eV above the $^3P_0$ ground state[15]) and O^+ (i.e., ^2D at 3.3 eV above the ^4S ground state[15]) were not present. This was shown by the absence of reaction of either ion with N_2 (ionization potential = 15.58 eV). However, a significant fraction of the N_2^+ and O_2^+ ions were vibrationally excited, but such ions react with the PFCs with the same rate coefficients as the ground state ($v = 0$) ions, i.e., no curvature was observed in the pseudo-first-order kinetic plots (logarithm of the reactant ion signal vs the reactant neutral concentration). By study of the reaction of N_2^+ with Ar, it was found that the excited state N_2^+ ions amounted to about 40% of the total ion signal, and it was impossible to quench such ions in the ionization source. Independent studies have shown that this signal is essentially all due to N_2^+ ($v = 1$).[16,17] For the O_2^+ ion, reactions with Xe and SO_2 indicated that approximately 20% of the O_2^+ was present in the $v = 1$ and 2 levels, and the lack of reaction with H_2O showed that the $v \geq 3$ levels were unpopulated. For the product ions consideration of the vibrationally excited states may be required to determine whether a particular reaction pathway is exothermic or not. However, this turns out to be necessary only for one of the reactions in this study, that of N_2^+ with C_2F_4, and this is discussed further below. For the other PFCs, the exothermicities of the reaction pathways are so high that the ion products observed are energetically possible for the $v = 0$ and $v > 0$ vibrational levels of O_2^+ and N_2^+. Therefore, with the exception of the N_2^+ reaction with C_2F_4, no attempt was made to quench the vibrational levels of the O_2^+ and N_2^+ ions, and the product ion distributions presented in the tables for the O_2^+ and N_2^+ ions are those resulting from reactions with O_2^+ ($v = 0$) (80%) and O_2^+ ($v > 0$) (20%) and from N_2^+ ($v = 0$) (60%) and N_2^+ ($v = 1$) (40%). Although this may affect the values of the branching ratios, the arguments for the formation of the product ions as discussed individually below are not affected.

Reactions of H_2O^+. In the H_2O^+ study a significant amount of H_3O^+ was injected with H_2O^+ into the flow tube, and in order to maintain a satisfactory H_2O^+ signal, it was not possible for the first quadrupole mass spectrometer to resolve these two ions. Specifically, when tuned to H_2O^+, the signal from this quadrupole at $m/e = 19$ was ca. 40% of the signal at $m/e = 18$. However, because H_3O^+ was found to be unreactive with all the molecules except for one, C_3F_6, no attempt was made to improve the problem of the poor resolution at the injection end of the instrument. To determine the products from H_2O^+ reacting with C_3F_6, a separate study was performed with the injection quadrupole tuned to H_3O^+. For this the signals at $m/e = 19$ and 18 were in the ratio ca. 95:5. No OH^+ ions were detected in the flow tube for the studies involving either H_2O^+ or H_3O^+. For collection of the rate data for the H_2O^+ reactions, the detection quadrupole mass spectrometer was set at high enough resolution to separate H_2O^+ from H_3O^+. However, except for the C_3F_6 reaction, the product ion data were taken at the lowest possible mass resolution both to minimize mass discrimination effects and to detect very weak product channels. High mass resolution was needed for the C_3F_6 reaction in order to differentiate one of the products of the H_3O^+ reaction, $C_3F_5{\cdot}H_2O^+$ m/e=149, from the main product of the H_2O^+ reaction, $C_3F_6^+$ m/e=150 (see the Discussion for further details).

It should be noted that because of water contamination in the flow tube, some charge transfer from H_2O occurred for those injected ions whose recombination energies are greater than the ionization potential of H_2O. The resulting H_2O^+ and H_3O^+ signals were always less than 5% of the parent ion signal, but the effects of this were taken account of in the determination of the product distributions.

Discussion

In the following discussion, most of the thermochemical data used to determine the enthalpy of the reactions presented are taken from the compilation by Lias et al.[18] The heat of formation of $C_3F_5^+$ (<126 kJ mol^{-1}) is taken from Anicich and Bowers[19] and that of $C_3F_7^+$ (−314 kJ mol^{-1}) from Su et al.[20] The heats of formation of $C_4F_7^+$ and n-C_4F_{10} are, to the best of our knowledge, not known. Note also that, for convenience, the reactant ion will generally be referred to as M^+.

Charge transfer is one of the general mechanisms by which the reactions studied occur. Two different pathways for charge transfer have been proposed. One is the long-range electron jump mechanism, where “long-range” is used to imply that charge transfer occurs at impact parameters considerably larger than those predicted from the classical orbiting limit.[21] We will refer to this process as formal charge transfer, and it can be either nondissociative (i.e., $M^+ + RF \rightarrow RF^+ + M$, where RF is a general alkyl fluoride) or dissociative, i.e., where an unstable excited intermediate is formed following the charge transfer (e.g., $M^+ + RF \rightarrow (RF^+)^* + M \rightarrow R^+ + F + M$). Either way, the charge transfer involves a nonorbiting collision for which reactions proceed via vertical transitions because electron transfer is fast relative to nuclear motion. The efficiency of such a reaction therefore depends upon favorable Franck−Condon factors connecting the ground state of the neutral molecule to an appropriate ionic state.[21−23] Distortion of Franck−Condon factors upon the approach of an ion to a neutral molecule has been included in this model to explain why certain charge transfer reactions are still facile, although small Franck−Condon factors are involved.[21,24,25] Presumably, with molecular reactant ions the efficiency of long-range charge transfer will also depend on favorable Franck−Condon factors connecting the molecular ion to its neutral ground state; we believe that this is the first time this point has been made in the literature. The second ion−molecule charge transfer mechanism initially involves the formation of a reaction complex. Now neither good Franck−Condon factors nor energy resonances are of great importance, and the nuclei have sufficient time to adjust their spatial configuration prior to charge transfer. Furthermore, under these circumstances other energetically allowed reaction pathways (e.g., $M^+ + RF \rightarrow [R{\cdots}F{\cdots}M^+]^* \rightarrow R^+ + FM$) can compete with this charge transfer mechanism. Note that products such as FM cannot form if formal charge transfer takes place.

Despite several studies investigating charge transfer processes,[26−29] including one that suggests that electron correlation effects can be important,[30] the physical properties of the reactant ion and molecule that determine the efficiency of this process and whether it will be long-range or short-range still have to be definitively established.[27,28] However, if both long-range and short-range pathways are energetically available, the former pathway is generally preferred provided that other factors, such as energy barriers or steric effects, have no influence on the reaction pathway. When Franck−Condon factors are small or some other physical effect reduces the efficiency of formal charge transfer, then charge transfer can only take place via complex formation. With the large number of fast reactions studied using ions with significantly different recombination energies, it is doubtful that Franck−Condon factors will be large for all of the reactions, and formal charge transfer is therefore unlikely for many of them. Coupled to the requirement that for a significant number of the observed (dissociative) ion products an M−F bond must be formed to make the overall reaction exothermic, this implies that the majority of the charge transfer products are produced after a reaction complex is formed. This forms a unifying theme throughout this discussion.

Reactions with the Perfluoroalkenes. *C_2F_4.* With the exception of H_3O^+, NO^+, N_2O^+, and CO_2^+, the ions studied in this investigation react, within experimental uncertainty, at the collisional rate with C_2F_4. The dominant process is nondissociative charge transfer, i.e.,

$$M^+ + C_2F_4 \rightarrow C_2F_4^{\ +} + M$$

which is highly exothermic; the enthalpies of this reaction for $M^+ = O_2^+$, H_2O^+, N_2O^+, O^+, CO_2^+, CO^+, N^+, and N_2^+ are −190, −242, −268, −329, −354, −377, −423, and −528 kJ mol^{-1}, respectively. Such a process could either be long-range or short-range. With the possible exception of N_2^+ ($v = 1$), there are negligible Franck−Condon factors connecting C_2F_4 with vibronic states of $C_2F_4^+$ at the recombination energies of the ions involved.[31] Thus, we suggest that the long-range interaction is not important and that charge transfer is taking place through a short-range process. Furthermore, among the fragment ions produced in the reaction with N^+ is $C_2F_3^+$. Since N^+ is only present in the flow tube in its ground ($^3P_{0,1,2}$) electronic states and since the energy separations between the $J = 0$ and $J = 1$ and $J = 0$ and $J = 2$ levels are only 0.6 and 1.5 kJ mol^{-1}, respectively,[15] the formation of $C_2F_3^+$ by formal dissociative charge transfer is endothermic by about 127 kJ mol^{-1}. The small branching ratio associated with $C_2F_3^+$ (4%) is too large to be accounted for by a Boltzmann thermal distribution. Therefore, $C_2F_3^+$ can only be produced from the N^+ reaction if chemical bonds are formed, i.e., if NF is the neutral product. This product is only possible if a short-range collision complex between N^+ and C_2F_4 initially forms. For the three other dissociative ion products associated with the N^+ reaction, namely CF^+, CF_2^+, and CF_3^+, the thermochemistry of formal dissociative charge transfer can explain their presence provided the neutral products are CF_3, CF_2, and CF, respectively. Nevertheless, taking all the other evidence into account (i.e., products containing atoms from both interacting particles and poor Franck−Condon factors), we suggest that most of the products in the ionic reactions with C_2F_4 are formed through reactions taking place in short-range collision complexes.

We now turn to the special case of N_2^+. At the recombination energy of N_2^+ (v =1), good Franck−Condon factors connect the ground state of C_2F_4 to the first excited state of $C_2F_4^+$.[31] Therefore, the reaction products from N_2^+ ($v = 1$) may be produced by long-range formal charge transfer. This mechanism may also be valid for the reactions with N_2^+ ($v = 0$), providing distortion of the ground state potential surface of C_2F_4 is sufficient to alter significantly the Franck−Condon factors to make electron transfer efficient. However, one of the products, namely $C_2F_3^+$ (5%), is energetically not allowed by dissociative charge transfer if N_2^+ is in the $v = 0$ level ($\Delta H = +26$ kJ mol^{-1}) but is possible for reaction with N_2^+ ($v = 1$), providing the neutral N_2 is formed in the $v = 0$ level. It could therefore be assumed that the $C_2F_3^+$ ion is produced only via the N_2^+ ($v = 1$) reaction. However, by introducing small quantities of N_2 into the flow tube, we found that we could remove all the N_2^+ ($v = 1$) by the reaction $N_2^+ (v = 1) + N_2 \rightarrow N_2 (v = 1) + N_2^+ (v = 0)$. Surprisingly, under these circumstances the product $C_2F_3^+$ was still present. Note that the production of this ion from N_2^+ ($v = 0$) is only possible if an intimate interaction between N_2^+ and C_2F_4 occurs, resulting in the neutral product N_2F. For N_2^+ (v=1) the reaction can proceed either through a long-range or through a short-range mechanism. However, it is of note that there are only small Franck−Condon factors connecting N_2^+ ($v = 1$) to N_2 ($v = 0$) and this may inhibit the vertical transition leading to dissociative charge transfer of C_2F_4 to $C_2F_3^+$ + F. Therefore, it is possible that N_2^+ ($v = 1$) also reacts with C_2F_4 via an intimate interaction.

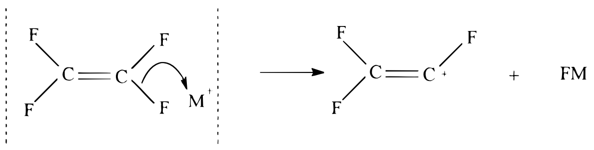
Further evidence for complex formation comes from the reactions of the isoelectronic ions N_2O^+ and CO_2^+, which at 300 K, are only 38% and 28% efficient, respectively. Note that at the recombination energies of N_2O^+ (12.87 eV) and CO_2^+ (13.77 eV) no vibronic states of $C_2F_4^+$ exist.[31] However, zero Franck−Condon factors cannot explain the inefficiency of these reactions because other ions in our study with similar recombination energies to N_2O^+ and CO_2^+ do react with C_2F_4 at or close to the collisional value. Note also that there are very favorable Franck−Condon factors connecting the reactant ions to their ground neutral states, i.e., the (000) transition dominates the first photoelectron band for both N_2O and CO_2.

To explain how the short-range interaction can account for the above observations and the product ions, the following mechanisms are proposed. Initially, a loosely bound collision complex is formed, i.e.,

$$C_2F_4 + M^+ \rightarrow |C_2F_4\cdots M^+|^*$$

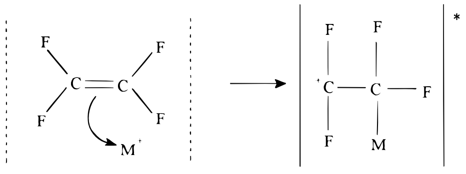
Then for M = N^+ or N_2^+ ($v = 0$) two possible reaction pathways could follow:

Electrophilic attack by the ion invoking the breaking of a σ-bond



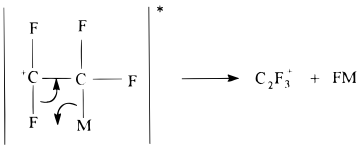
If N^+ or N_2^+ attacks a fluorine, an electron is removed from the σ-bond (i.e., this mechanism can only produce dissociative products such as $C_2F_3^+$), but if enough energy is available, $C_2F_3^+$ may dissociate to form the other observed ions. The N_2^+ ($v = 1$) reaction may also result in the formation of $C_2F_3^+$ through this route, or formal dissociative charge transfer may occur, or there may be competition between the two mechanisms.

Electrophilic attack by the ion on the carbon-carbon double bond to form a chemically bound transition state



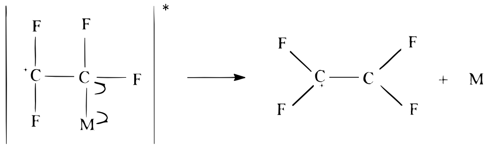
We believe this second mechanism will probably be favored, since the double bond is electron rich and will readily combine with the electrophilic ion. The chemically bound transition state can react further via the following two processes illustrated below.

Formation of dissociative type products



Again, if enough energy is available after reaction, $C_2F_3^+$ could dissociate to the other observed ion products.

Formation of 'charge transfer' type products

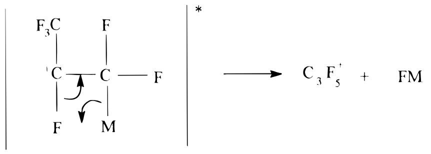


This latter mechanism can also explain the production of the nondissociative charge transfer product for the reactions with O_2^+, H_2O^+, N_2O^+, O^+, CO_2^+, and CO^+. That $C_2F_3^+$ is not observed for the reactions with these ions is probably because the M−F bond strength is insufficient to make this exit channel energetically accessible. The only possible exception is that the enthalpy of the reaction $O^+ + C_2F_4 \rightarrow [C_2F_4{\cdots}O^+] \rightarrow C_2F_3^+ + FO$ is 4.1 kJ mol^{-1} exothermic. However, there is enough uncertainty in the heat of formation of $C_2F_3^+$ to render this reaction channel endothermic.

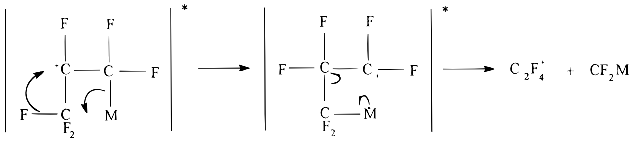
To the best of our knowledge, only two of the reactions with C_2F_4 presented in this paper have previously been investigated. The reaction of $CO^+ + C_2F_4$ leading to $C_2F_4^+$ has been reported to be "fast" by Bowers and Chau,[32] but no rate coefficient is quoted. The H_2O^+ reaction has been studied by Morris et al.,[33] and the agreement in the results between their study and ours is very good.

C_3F_6. Apart from that of NO^+, all reactions with C_3F_6 investigated in this study are fast, with the rate coefficients being at or close to the collisional values within the limits of experimental error. Except for the reactions with H_3O^+ and N_2^+, nondissociative charge transfer is a major or dominant reaction mechanism. For N_2^+, dissociative charge transfer (either by a formal or complex mechanism) can account for all the products. Products other than $C_3F_6^+$ are also observed for the other reactions but generally to a lesser extent. This is as expected because the amount of dissociation should decrease as the recombination energies of the reactant ions (and hence exothermicities of the reactions) decrease. Note that this trend is not obeyed for the O_2^+ and H_2O^+ ions. For O_2^+ this can be explained in terms of the energetics. Formation of $C_2F_4^+$ ($+ CF_2 + O_2$) by dissociative charge transfer is endothermic by 71, 48, and 27 kJ mol^{-1} for the $v = 0$, 1, and 2 vibrational levels of O_2^+, respectively. Dissociative charge transfer is also endothermic for the production of $C_3F_5^+$ from the reaction with O_2^+ ($v = 0$, 1, and 2). O_2^+ must therefore react with C_3F_6 to form these products by bond breakage and formation. (For example the reaction with O_2^+ leading to $C_2F_4^+$ is exothermic if $CF_2O + O$ are formed.) Indeed, the production of $C_3F_5^+$ is endothermic by formal dissociative charge transfer if the recombination energy of the reactant ion is less than 13.8 eV (although there is some uncertainty in this value due to the uncertainty in the heat of formation of $C_3F_5^+$). For example, the reaction of H_2O^+ yielding $C_3F_5^+$ (6%) is only possible if FH and OH are formed as neutrals. For ions whose recombination energies are greater than 13.8 eV formal dissociative charge transfer may explain the presence of $C_3F_5^+$ as well as all the other ion products. However, only at the recombination energies of the N^+ and N_2^+ ions are there good Franck−Condon factors connecting C_3F_6 to its ionic states,[34−36] and for these ions formal charge transfer may indeed be occurring. Poor or zero Franck−Condon factors exist at the recombination energies of all the other ions. This implies that formal nondissociative charge transfer probably cannot occur from any of these ions. Taking this into account, and the observation of the ion products $C_2F_4^+$ from the O_2^+ reaction, and $C_3F_5^+$ from the reactions with O_2^+, H_2O^+, N_2O^+, and O^+, none of which can energetically be formed by formal dissociative charge transfer, we suggest that, as with C_2F_4, chemical reaction involving a short-range complex is competing with charge transfer. This indicates that for the majority of the reactions a complex must first be formed before an electron can be donated from the PFC neutral.

The nondissociative charge transfer products ($C_3F_6^+ + M$) can be formed via the transition state in a similar way as illustrated for C_2F_4. Two possible intimate mechanisms, identical with those discussed and illustrated for C_2F_4, are suggested for reactions forming the dissociative ion products. However, for the reactions with C_3F_6, energetics are such that all the reactant ions can participate in the reaction leading to dissociative channels. Electrophilic attack by the ion on the PFC results in the breaking of a C−F σ-bond, and/or electrophilic attack occurs on the carbon−carbon double bond. The chemically bound transition state resulting from the second process can rearrange to form dissociative products $C_3F_5^+$ and $C_2F_4^+$ as illustrated below:



and



Note that in the former case, F + M could be the neutral products for reactant ions whose recombination energies are greater than about 13.8 eV, although as mentioned earlier, uncertainty in the heat of formation of $C_3F_5^+$ makes a definite choice of the neutral products impossible. In the latter case, CF_2M needs only to be formed for the O_2^+ reaction; the products $CF_2 + M$ are energetically allowed for the other reactant ions for which $C_2F_4^+$ is an observed product from the reaction.

For the N_2^+ reaction, the $C_3F_5^+$ and $C_2F_4^+$ could dissociate to CF_3^+ if enough energy is available, providing the neutral products are not CF_2, CF, and N_2 (the endothermicity of this reaction being 71 kJ mol^{-1}), i.e., N_2 would have to be incorporated into one of the neutral products. Alternatively, the CF_3^+ product could be formed through some other mechanism, resulting in the neutral products C_2F_3 and N_2 (this reaction is exothermic by 171 kJ mol^{-1}). If a complex does not form with N_2^+, formal dissociative charge transfer can account for all the ion products. This is also true for the N^+ and (perhaps) the CO^+ reactant ions.

C_3F_6 is the only PFC in this study that is found to react with H_3O^+ at a measurable rate. The rate coefficient is 0.9×10^{-9} cm^3 $molecule^{-1}$ s^{-1}, being about 50% of the collisional value, with the ion products being $C_3F_5{\cdot}H_2O^+$ (~2%) and $C_3F_5^+$

(~98%). The observation of $C_3F_5{\cdot}H_2O^+$ (149 amu) clearly demonstrates that a collision complex initially forms, with the subsequent production of HF driving the reaction. Note that charge transfer is highly endothermic, and proton transfer cannot occur. The most likely mechanism to produce $C_3F_5^+$ is similar to that shown above for other ion reactions. That is, a collision complex is initially formed. However, for this reaction there is likely to be attack of the acidic H^+ from H_3O^+ on the carbon–carbon double bond, which is immediately followed by loss of HF to produce H_2O and $C_3F_5^+$. Within the lifetime of the collision complex H_2O may bond to the outgoing $C_3F_5^+$ with the resulting ion being collisionally stabilized by the helium buffer gas. This mechanism can explain the presence of the weak but definite signal at 149 amu. A small enhancement of the $C_3F_5^+$ signal relative to the $C_3F_5{\cdot}H_2O^+$ signal was observed as the voltage on the Faraday plate was increased. This indicates that some of the $C_3F_5^+$ signal could have arisen through collisions of the weakly bound $C_3F_5{\cdot}H_2O^+$ with helium as the ion is accelerated through the orifice in the Faraday plate. To determine the true branching ratios, the Faraday plate voltage was reduced until the ratio of the $C_3F_5^+$ and $C_3F_5{\cdot}H_2O^+$ signals remained constant. Thus, the branching ratios presented above should represent the true values for this reaction.

2-C_4F_8. Nondissociative charge transfer is the dominant mechanism for the O_2^+, H_2O^+, N_2O^+, O^+, and N^+ reactions, is a major mechanism for the CO_2^+ and CO^+ reactions, and does not occur for the N_2^+ reaction. Dissociative channels are also observed for these reactions, with products $C_3F_5^+$, $C_3F_6^+$ (except for the reactions with H_2O^+ and N_2O^+), and $C_4F_7^+$ (except for the reaction with N_2O^+). The heat of formation of $C_4F_7^+$ is unknown, and therefore, little can be said about the reaction channel forming it. However, the $C_3F_5^+$ ion cannot be produced by dissociative charge transfer for the reactions with O_2^+ and H_2O^+, implying that, for this channel at least, an intimate interaction occurs between these ions and 2-C_4F_8. It may be argued that the observation of one reaction channel that requires an intimate interaction does not necessarily rule out long-range charge transfer for the other channels, i.e., different product channels could result from different types of encounter. Thus, for the other dissociative channels resulting from reactions with O_2^+ and H_2O^+ formal dissociative charge transfer could indeed be occurring. However, it is unlikely that good Franck–Condon factors exist at the recombination energies of all the ions involved. Thus, the most likely type of interaction is intimate for the majority of the observed product channels.

Hardly any dissociative products are observed with N_2O^+ compared to O_2^+ and H_2O^+, both of which have lower recombination energies than N_2O^+. This may indicate that N_2O^+ has some difficulty in forming a complex with 2-C_4F_8 without considerable rearrangement of its bonds. It is also slightly surprising that in comparison to the reaction with O^+ and CO_2^+, the N^+ reaction does not cause as much fragmentation.

As described earlier for C_2F_4 and C_3F_6, two possible intimate reaction pathways, electrophilic attack by the ion on one of the fluorines and electrophilic attack by the ion on the double bond, can be used to explain all the observed ion products. Although the formation of a collision complex can explain the ion products, formal charge transfer cannot be ruled out for ions whose recombination energies are such that good Franck–Condon factors connect the neutral species to its ionic states. However, to the best of our knowledge the valence photoelectron spectrum of 2-C_4F_8 has not been recorded.

Reactions with the Perfluoroalkanes. *C_2F_6*. No reaction is observed with H_3O^+, NO^+, O_2^+, H_2O^+, and N_2O^+. For these ions charge transfer is endothermic, as are reactions involving a complex intermediate leading to products containing atoms from both interacting particles. Charge transfer, however, is energetically possible for all the other reactant ions, although $C_2F_6^+$ is not observed as a product. CF_3^+, a major ion observed in all the reactions, can be produced from both formal dissociative charge transfer or through a complex mechanism, whereas $C_2F_5^+$, observed in the reactions with O^+, CO^+, and N^+, can only be produced if M is incorporated into the neutral fragments of the reaction. For example, the reaction of O^+ to form $C_2F_5^+$ is exothermic only if FO is produced as the neutral. One possibility why $C_2F_5^+$ is not observed for the reaction with CO_2^+ may be that the CO_2–F bond strength is not sufficient to make the exit channel exothermic. At the recombination energies of the O^+, CO_2^+, and CO^+ ions, the Franck–Condon factors connecting C_2F_6 to the ground state of the parent ion are poor,[32,37] and significant distortion of the C_2F_6 potential surface would be required to make the reaction viable via formal charge transfer. Although this cannot be ruled out, the observation of the $C_2F_5^+$ product for the O^+ and CO^+ reactions implies that formal charge transfer does not occur. At the recombination energy of N^+ there are good Franck–Condon factors, and this should mean that the reaction takes place via a long-range interaction. However, the 29% branching percentage associated with the $C_2F_5^+$ product from the reaction channel

$$N^+ + C_2F_6 \rightarrow C_2F_5^+ + NF \quad \Delta H = -300\ \text{kJ mol}^{-1}$$

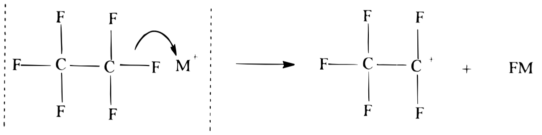
indicates that an intimate interaction is taking place in direct competition with, or instead of, the nonintimate process. At the recombination energy of N_2^+ good Franck–Condon factors also exist, but now there is no need to involve an intimate interaction because all the products can be explained by formal dissociative charge transfer.

We conclude, as for the unsaturated PFCs, that, again with the possible exception of N^+ and N_2^+, the ion–molecule reactions leading to the observed products most likely proceed through a collision complex as illustrated below.

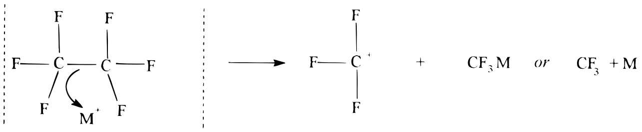
Initially, a collision complex is formed:

$$C_2F_6 + M^+ \rightarrow |C_2F_6{\cdots}M^+|^*$$

Electrophilic attack by the ion on a fluorine atom can then result in the production of $C_2F_5^+$



and/or electrophilic attack on the C–C bond of the PFC results in the formation of CF_3^+



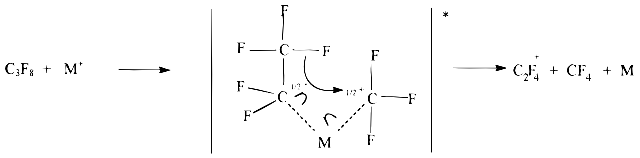
The product CF_2^+ from the N_2^+ reaction cannot be explained by the above schemes, and therefore, if complex formation does occur, a different pathway is required to form this product. However, the CF_2^+ product can also be explained by formal dissociative charge transfer if CF_4 is the resulting neutral product.

The main difference from the unsaturated PFCs is that the absence of a π-bond requires that electrophilic attack on the PFC breaks either a C–C or a C–F σ-bond, meaning that nondissociative charge transfer cannot occur. We comment that formal charge transfer may be another route to produce CF_3^+ for ions with recombination energies in the range 13.4−15.6 eV, the Franck−Condon zone of the ground state of $C_2F_6^+$.[37] Unlike the unsaturated PFCs, the ground state of $C_2F_6^+$ is repulsive in the Franck−Condon region and dissociates nonstatistically, probably on a sub-picosecond time scale to $CF_3^+ + CF_3$.[37,38] However, this mechanism cannot explain the presence of the $C_2F_5^+$ or CF_2^+ products, implying once again that short-range interactions are in direct competition with, or taking place instead of, long-range interactions.

The reactions of CO^+ and CO_2^+ with C_2F_6 have previously been studied using an ion cyclotron resonance apparatus by Bowers and Chau.[32] They also conclude that a complex mechanism reaction is the only feasible explanation for the formation of $C_2F_5^+$ from the CO^+ reaction. The rate coefficients from their study are ca. 30% smaller than those reported here. In addition, there is some disagreement about the product branching ratios in the $CO^+ + C_2F_6$ reaction; we find that the major product is $C_2F_5^+$ (59%) whereas Bowers and Chau favor the CF_3^+ product (66%). The reactions of O^+ and O_2^+ with C_2F_6 have been studied both by Morris et al.[4,5] and by Fisher et al.,[39] and our results are in excellent agreement with theirs.

C_3F_8. H_3O^+, NO^+, and O_2^+ are found to be unreactive, whereas the other ions, except for N_2O^+, react with a rate coefficient close to or at the collisional value. Note that $C_3F_8^+$ is not formed as a product of any of the reactions. That both H_2O^+ and N_2O^+, whose recombination energies are less than the ionization potential of C_3F_8 (13.38 eV), react means that formal charge transfer and dissociation of the resulting ion cannot occur at thermal energies. For N_2O^+, the major product is $C_2F_4^+$, which can only be formed through an intermediate complex if CF_4 is also produced as a neutral. The other main product for N_2O^+, CF_3^+ (21%), can be explained if CF_3, CF_2O, and N_2 are produced as neutrals—this being the only exothermic route. Thus again, an intimate interaction is implied. For the H_2O^+ reaction, the major ion products incorporate the H_2O^+ reactant ion ($CF_3{\cdot}H_2O^+$ (72%) and $C_2F_5{\cdot}H_2O^+$ (12%)), also illustrating that an intimate complex must be formed.

Formal dissociative charge transfer to produce $C_2F_4^+$, CF_3, F, and M is endothermic for all the ion reactions studied. The formation of CF_4 may therefore be the driving force behind the reaction channel leading to the $C_2F_4^+$ product. For all reactant ions other than H_2O^+ and N_2O^+ formal dissociative charge transfer could lead to $C_2F_4^+$. However, a collision complex as shown below can also explain this product and is indeed necessary for the H_2O^+ and N_2O^+ reactions:



The lack of reactivity of O_2^+ through this channel may imply that the reaction is endothermic. (The dissociative energy required to form $C_2F_4^+ + CF_4$ from C_3F_8 is 12.1 ± 0.1 eV, compared to the recombination energy of O^+ at 12.07 eV.) Formal charge transfer cannot be ruled out for ions whose recombination energies are greater than the ionization potential of C_3F_8 because reasonable Franck−Condon factors apply at the energies 13.5−15.5 eV.[38] However, this mechanism can only explain the CF_3^+ product and not the $C_3F_7^+$ product because very recent photoelectron−photoion coincidence experiments[38] show that the ground state of $C_3F_8^+$ dissociates to CF_3^+ by C−C bond cleavage and not to $C_3F_7^+$ by C−F bond cleavage. Note also that this mechanism will not explain the presence of $C_2F_5^+$ in the reactions with CO_2^+, CO^+, N^+, and N_2^+. For the O^+ reaction producing $C_2F_5^+$, dissociative charge transfer is endothermic with $\Delta H = +9$ kJ mol^{-1}, although at such small endothermicities reactions of ions with thermal energies in the tail of the Boltzmann energy distribution could account for the small branching ratio observed.

Bowers and Chau[32] report the reactions of CO^+ and CO_2^+ with C_3F_8. The agreement between our results and theirs is good, although, as found for the C_2F_6 molecule, our rate coefficients are ca. 30% higher than their values and the branching ratios are slightly different. CO^+ reaction leads to the following products CF_3^+, $C_2F_4^+$, $C_2F_5^+$, and $C_3F_7^+$ with branching ratios given by us to be 73%, 10%, 12%, and 5%, respectively, compared to Bowers and Chau values of 64.8%, 17.6%, 8.7%, and 8.9%, respectively. Bowers and Chau also conclude from the thermodynamics that $C_3F_7^+$ can only be produced via a reaction complex. For the CO_2^+ reaction we observe the same four products as in the CO^+ reaction with branching percentages of 45% for CF_3^+, 48% for $C_2F_4^+$, 5% for $C_2F_5^+$, and 2% for $C_3F_7^+$, to be compared with values from Bowers and Chau of 71.5%, 24.2%, 4.3%, and 0%, respectively.

n-C_4F_{10}. With the exception of H_3O^+, NO^+, and O_2^+, all ions react with *n*-C_4F_{10} at or near the collisional rate. O_2^+ is found to be unreactive, which suggests that the ionization potential of *n*-C_4F_{10} (as yet unknown) is greater than 12.07 eV. However, this is not conclusive because there are many examples of exothermic reactions that are very inefficient. The heat of formation of *n*-C_4F_{10}, to our knowledge, is also unknown, and therefore, we cannot determine whether most of the products observed are a result of formal dissociative charge transfer or a chemical reaction. However, because of the low probability of good Franck−Condon factors existing at all the recombination energies of the reactant ions, it is likely that most of the products do result from charge transfer driven through a complex intermediate. To support the complex mechanism, and as observed for the C_3F_8 molecule, for the H_2O^+ reaction the reactant ion is incorporated into two ion products, namely $CF_3{\cdot}H_2O^+$ (32%) and $C_2F_5{\cdot}H_2O^+$ (8%). For none of the reactions is the product $C_4F_{10}^+$ observed. We conclude that if charge transfer does occur, either formally or through a complex, the ground state of $C_4F_{10}^+$ is repulsive and fragments probably to CF_3^+ through C−C bond cleavage.

Summary

There are compelling reasons for undertaking fundamental and comprehensive investigations of the ion chemistry of PFCs. These include an application of ion reactions to plasma processing and pollutant monitors and an understanding of their role in atmospheric chemistry. In this paper a detailed study of the reactions of several cations, H_3O^+, NO^+, O_2^+, H_2O^+, N_2O^+, O^+, CO_2^+, CO^+, N^+, and N_2^+, with six PFCs, C_2F_4, C_2F_6, C_3F_6, C_3F_8, 2-C_4F_8, and *n*-C_4F_{10}, has been presented. Most of these reactions have not been studied previously.

NO^+ does not react with any of the unsaturated PFCs, whereas H_3O^+ reacts only with C_3F_6 with a rate coefficient of about half the collisional value. Apart from these reactions and the anomalous reactions of N_2O^+ and CO_2^+ with C_2F_4, the three unsaturated PFCs react with the other ions at the collisional rate. It is difficult to find a satisfactory explanation of why C_2F_4 reacts with N_2O^+ and CO_2^+ with rate coefficients substantially below the collisional value, whereas reactions of these ions with C_3F_6 and 2-C_4F_8 proceed with a rate coefficient close to or at the collisional value. N_2O^+ and CO_2^+ are the largest cations we have studied, but if there is steric hindrance to the formation of the collision complex, this should occur to a greater extent with the larger PFCs and not with C_2F_4. Similarly, the stability of the complexed cation is expected to be greater if fluorine atoms are attached directly to the positively charged carbon atom, C^+ (i.e., in the α position), and to a lesser extent if one or more CF_3 groups are attached to C^+ (i.e., the fluorine atoms are in the β position). In other words, these two effects both predict that C_2F_4 should react with these ions with a greater efficiency than observed. For the three saturated PFCs studied, H_3O^+, NO^+, and $O_2{}^+$ are all unreactive, and H_2O^+ and N_2O^+ are also unreactive with C_2F_6. All the other ions react with the three saturated PFCs with a rate coefficient at or close to the collisional value, the only exception being the reaction of N_2O^+ with C_3F_8.

Perhaps the most important conclusions from this work concern the mechanism of how the ion−molecule reactions proceed. For many of the reactions ion products are observed that could result from a long-range electron jump, but for the same reactions some of the products can only result from an intimate collision. As mentioned earlier, it may be argued that the two reaction processes are not incompatible, i.e., a short-range intimate interaction can compete with a long-range interaction. Thus, different product channels could result from different encounters (e.g., different trajectories, steric effects, etc.). This may indeed be the case for some of the reactions we have studied, and we have no evidence to support or reject this suggestion. However, a long-range charge transfer requires favorable Franck−Condon factors connecting the ground state of the neutral molecule to an appropriate ionic state. Furthermore, good Franck−Condon factors connecting the ground state reactant ion to its neutral ground state may also be required. If these criteria are met, then we suggest that the long-range interactions are likely to dominate. However, for many of the reactions studied, these criteria are not met. In addition, many of the observed products can only be formed following charge transfer and bond formation within an interacting complex. Only for a small number of reactions studied (e.g., $N^+ + C_2F_6$) does it appear that there can be direct competition between short-range and long-range processes. This raises the question of why does competition occur for such reactions when the long-range process is expected to dominate. A possible solution is that some other physical property of the reacting system (other than poor Franck−Condon factors) inhibits formal charge transfer, and a short-range process leads to all of the observed products. We therefore believe that long-range charge transfer does not take place for most of the reactions studied and that short-range processes dominate. We note that the large polarizabilites associated with the molecules in this study may promote the formation of the collision complex.[30]

Finally, with the increasing concentrations of PFCs in the atmosphere, there is a clear need to develop convenient techniques for their detection, identification, and monitoring in the environment. However, since the atmosphere contains many trace gases at varying concentrations, monitors used to detect and distinguish one pollutant from another in this complex chemical environment rely heavily on their sensitivity and selectivity. Ion−molecule reactions provide such factors because of the ion's ability to act as a powerful probe of neutral trace gases. For example, the reactions of $N_2{}^+$ could be used to distinguish each of the six PFCs we have studied, since each produces a range of different product ions. This fundamental work may therefore help in the development of trace gas analysis of PFCs, for example, by determining suitable ions for detection of specific PFCs.

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