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The gas-phase reactions of CF^+, CF_2^+, CF_3^+, $C_2F_3^+$, $C_2F_4^+$, $C_3F_5^+$, and $C_3F_7^+$ with tetrafluoroethylene, C_2F_4, have been studied using a variable temperature-selected ion flow tube (VT-SIFT) instrument at 300 and 496 K. In addition, reactions of CF_3^+ with the perfluorocarbons C_3F_6, 2-C_4F_8, and c-C_4F_8 have been studied at 300 and 496 K. Reaction rate constants and product branching fractions were measured. The reaction of CF^+ with C_2F_4 is fast and produces the ions CF_3^+, $C_3F_5^+$, and $C_2F_4^+$. The ion CF_2^+ reacts with C_2F_4 by nondissociative charge transfer at the collisional rate. The reaction of CF_3^+ with C_2F_4 proceeds slowly by association, forming $C_3F_7^+$ which reacts in a secondary reaction with C_2F_4 to regenerate CF_3^+. The neutral product of this secondary reaction is inferred to be C_4F_8; thus, dimerization of C_2F_4 is catalyzed by CF_3^+. For the reaction of $C_2F_3^+$ with C_2F_4, which is fast, $C_3F_5^+$ and a minor amount of $C_2F_4^+$ are produced. The reaction of $C_2F_4^+$ with C_2F_4 is slow, has a strong negative temperature dependence, and produces $C_3F_5^+$ which is itself unreactive with C_2F_4. While CF_3^+ does not measurably react with c-C_4F_8, CF_3^+ does react rapidly by F^- transfer with both C_3F_6 and 2-C_4F_8.

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Reactions of $C_nF_m^+$ Ions with C_2F_4 and Other Perfluorocarbons

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The gas-phase reactions of CF^+, CF_2^+, CF_3^+, $C_2F_3^+$, $C_2F_4^+$, $C_3F_5^+$, and $C_3F_7^+$ with tetrafluoroethylene, C_2F_4, have been studied using a variable temperature-selected ion flow tube (VT-SIFT) instrument at 300 and 496 K. In addition, reactions of CF_3^+ with the perfluorocarbons C_3F_6, 2-C_4F_8, and c-C_4F_8 have been studied at 300 and 496 K. Reaction rate constants and product branching fractions were measured. The reaction of CF^+ with C_2F_4 is fast and produces the ions CF_3^+, $C_3F_5^+$, and $C_2F_4^+$. The ion CF_2^+ reacts with C_2F_4 by nondissociative charge transfer at the collisional rate. The reaction of CF_3^+ with C_2F_4 proceeds slowly by association, forming $C_3F_7^+$ which reacts in a secondary reaction with C_2F_4 to regenerate CF_3^+. The neutral product of this secondary reaction is inferred to be C_4F_8; thus, dimerization of C_2F_4 is catalyzed by CF_3^+. For the reaction of $C_2F_3^+$ with C_2F_4, which is fast, $C_3F_5^+$ and a minor amount of $C_2F_4^+$ are produced. The reaction of $C_2F_4^+$ with C_2F_4 is slow, has a strong negative temperature dependence, and produces $C_3F_5^+$ which is itself unreactive with C_2F_4. While CF_3^+ does not measurably react with c-C_4F_8, CF_3^+ does react rapidly by F^- transfer with both C_3F_6 and 2-C_4F_8.

Introduction

A variety of processes, including polymerization and production of gaseous species, occur in discharges containing C_2F_4. Glow discharge polymerization of C_2F_4 has been used commercially to prepare and deposit thin dielectric films for capacitors.[1-5] The C_2F_4 glow discharge produces films which can have electrical properties superior to those of conventionally prepared poly(tetrafluoroethylene) (PTFE)[3] yet have IR spectra resembling spectra of conventional PTFE.[6-9] C_2F_4 is sometimes added to discharges of other halocarbons used in plasma etching in order to control the etching. Addition of C_2F_4 to a CF_4 plasma has the effect of reducing the fluorine-to-carbon ratio, which affects the Si-to-SiO_2 etch rate ratio.[10] When large amounts of C_2F_4 are added, deleterious polymerization occurs.[11] In addition, C_2F_4 is produced and acts as a recombinant in discharges of other halocarbon gases.[12,13]

The role of ion–molecule reactions in these plasmas is unclear. Kobayashi et al.[14] have discussed a radical-initiated mechanism for plasma-polymerized PTFE, and Vasile and Smolinsky[15] have reported that ion chemistry is not a dominant feature of the C_2F_4 discharge. However, Morris and Charlesby[16] have suggested that the glow discharge polymerization mechanism is dominated by positive ions. Weisz[17] observed the production of liquid olefinic compounds in a C_2F_4 glow discharge and attributed their formation to $C_2F_4^+$ ions. D'Agostino et al.[10] have suggested that the polymerization process is affected by charged particle densities in the plasma. A few kinetics studies of reactions of several fluorocarbocations with C_2F_4 have been reported in the literature,[18-21] and significant reaction rates were found. More recent experiments[22-24] have shown that the ions O^-, O_2^-, Ar^+, and H_2O^+ are very reactive with C_2F_4.

Despite the above examples, relatively few data are available for the gas-phase ionic reactions involved in C_2F_4 plasmas, especially under thermal conditions.[25] Previous studies include an ion source experiment,[18] which was used to measure rate constants under suprathermal conditions, and ion cyclotron resonance (ICR) experiments, in which several reactions of C_2F_4 were studied[19-21] but in which rate constants were only measured for the reaction of $C_2F_4^+$ with C_2F_4. Su et al. have studied selected reactions of negative ions with perfluoroolefins.[26] We report here a study of reactions of various fluorocarbocations with C_2F_4 and other selected perfluoroolefins. The present experiments were conducted under truly thermal conditions and in the absence of interfering ions. Rate constants and product branching fractions were measured at 300 and 496 K. These are the first thermal measurements of the rate constants for these reactions and the first temperature dependence studies thereof, and some of the reactions have not been studied previously by any technique.

Experimental Section

The measurements were made using a variable temperature-selected ion flow tube apparatus.[27] A detailed review of this type of instrument has been published,[28] and only those aspects important to the present study will be discussed here in detail.

CF^+, CF_2^+, and CF_3^+ ions were produced from CF_3Br by electron impact ionization in a moderate-pressure ion source (~0.1 Torr). The ions $C_2F_3^+$, $C_2F_4^+$, and $C_3F_5^+$ were produced from C_2F_4 in the source. $C_3F_7^+$ was formed from n-C_6F_{14}. The ion species of interest was then mass selected in a quadrupole mass spectrometer and injected into the flow tube through a Venturi inlet. The ions were thermalized upstream of the reaction region by thousands of collisions with the He buffer gas, which issues from the Venturi inlet. The reactant neutral was introduced downstream through one of two ring inlets and allowed to react with the ions for a known reaction time (~2 ms) in the fast flow (~10^4 cm s^{-1}) of He maintained at ~0.4 Torr. The total transit time from source to detector was on the order of a few milliseconds. The reactant and product ions were mass analyzed in a second quadrupole mass spectrometer and detected by a channel particle multiplier. Rate constants were extracted from least-squares fits of the logarithm of the reactant ion signal plotted versus the concentration of added reactant neutral. The reaction time was determined from ion time-of-flight measurements. For the experiments conducted at 496 K, the temperature of the flow tube was raised using electrical resistance heaters. The C_2F_4 had a stated purity of >99.5% and was used without further purification. The C_2F_4 contained approximately 0.01% limonene as an inhibitor, and no ions attributable to this impurity were detected in any of the experiments. The accuracy of the measured overall rate constants is ±25%, and the relative accuracy is ±15%.[27]

The product branching fractions were determined by recording the product ion count rates as a function of the flow rate of the reactant neutral. Because of secondary reactions of the product ions with the reactant neutral, the reported branching fractions

TABLE I: Branching Fractions and Total Rate Constants for Reactions of Selected Positive Ions with Tetrafluoroethylene Measured at 300 and 496 K

reaction	branching fraction 300 K	branching fraction 496 K	total rate constant[a] (10^{-10} cm^3 s^{-1}) 300 K	total rate constant[a] (10^{-10} cm^3 s^{-1}) 496 K
$CF^+ + C_2F_4 \rightarrow CF_3^+ + C_2F_2$	0.65	0.67	6.1	2.3
$CF^+ + C_2F_4 \rightarrow C_2F_4^+ + CF$	0.04	0.14		
$CF^+ + C_2F_4 \rightarrow C_3F_5^+$	0.32	0.19		
$CF_2^+ + C_2F_4 \rightarrow C_2F_4^+ + CF_2$			11	9.9
$CF_3^+ + C_2F_4 \rightarrow C_3F_7^+$	≥0.94	>0.8[b]	0.28[d]	0.048[d]
$CF_3^+ + C_2F_4 \rightarrow C_3F_5^+$[c] $+ F_2$	≤0.04[c]	*b*		
$CF_3^+ + C_2F_4 \rightarrow C_2F_3^+$[c] $+ CF_4$	≤0.02[c]	*b*		
$C_2F_3^+ + C_2F_4 \rightarrow C_3F_5^+ + CF_2$	0.90	0.66	2.3	2.1
$C_2F_3^+ + C_2F_4 \rightarrow C_2F_4^+ + C_2F_3$	0.10	0.34		
$C_2F_4^+ + C_2F_4 \rightarrow C_3F_5^+ + CF_3$			0.20	0.033
$C_3F_5^+ + C_2F_4 \rightarrow$ no reaction			<0.03	<0.03
$C_3F_7^+ + C_2F_4 \rightarrow CF_3^+ + C_4F_8$	≥0.88	>0.8[b]	0.20[e]	0.082[e]
$C_3F_7^+ + C_2F_4 \rightarrow C_2F_5^+$[c] $+ C_3F_6$	≤0.07[c]	*b*		
$C_3F_7^+ + C_2F_4 \rightarrow C_4F_7^+$[c] $+ CF_4$	≤0.07[c]	*b*		

[a] The total pressure was 0.4 Torr at 300 K and 0.6 Torr at 496 K. [b] Accurate branching fractions were not measured at 496 K for this reaction. [c] These product ions may arise from impurities in the C_2F_4 and therefore should be regarded only as possible products as written—see text. [d] Rate constants derived from fit to curved kinetics plot. Curvature was due to the secondary reaction $C_3F_7^+ + C_2F_4 \rightarrow CF_3^+ + C_4F_8$. See text. [e] Rate constants derived from fit to curved kinetics plot. Curvature was due to the secondary reaction $CF_3^+ + C_2F_4 \rightarrow C_3F_7^+$. See text.

TABLE II: Total Rate Constants for Reactions of CF_3^+ with Perfluorocarbons Measured at 300 and 496 K

reaction	total rate constant (10^{-10} cm^3 s^{-1}) 300 K	total rate constant (10^{-10} cm^3 s^{-1}) 496 K
$CF_3^+ + CF_3CF{=}CFCF_3 \rightarrow C_4F_7^+ + CF_4$	6.8	3.2
$CF_3^+ + CF_2{=}CFCF_3 \rightarrow C_3F_5^+ + CF_4$	11	5.8
$CF_3^+ + c\text{-}C_4F_8 \rightarrow$ no reaction	<0.03	<0.03

were found by the usual technique of plotting the measured branching fractions versus reactant neutral flow rate and extrapolating the fractions to zero reactant flow. The loss of reactant ion signal with added reactant neutral was approximately equal to the sum of the product ion signals. Therefore, no attempt was made to account for the possible effects of either mass discrimination or differing rates of diffusion to the walls by the reactant and product ions. These two effects tend to cancel one another since they both depend generally on mass but in opposite senses.[29]

For the reaction of CF_3^+ with C_2F_4, which is a slow association reaction producing $C_3F_7^+$, the kinetics plots of logarithm of reactant ion signal versus reactant neutral flow rate exhibited upward curvature. The curvature was found to be caused by a secondary reaction in which the major product ion $C_3F_7^+$ reacted with the C_2F_4 neutral, regenerating the CF_3^+ primary ion. This was confirmed by studying this secondary reaction directly by producing $C_3F_7^+$ in the ion source from n-C_6F_{14} and reacting it with C_2F_4 in the flow tube. The rate constants for the individual reactions of CF_3^+ and $C_3F_7^+$ with C_2F_4 were obtained by fitting the integrated rate equation to the curved experimental data. Those kinetics results were confirmed in a separate set of conventional measurements made under conditions of low extent of reaction, where linear kinetics plots were obtained. The rate constants measured by this method were in good agreement with those obtained by fitting the curved data plots.

Results and Discussion

Rate constants and branching fractions for the reactions of selected fluorocarbocations with C_2F_4 are presented in Table I. The results for reactions of CF_3^+ with the other reactant neutrals are given in Table II. Reported thermochemistry is taken from the compilation of Lias et al.[30] except for the following heats of formation (units of kJ mol^{-1}): 360.8 (CF_3^+),[31] ~0 ($C_3F_5^+$),[21] −308 (n-$C_3F_7^+$),[32] −322 (iso-$C_3F_7^+$), −184.9 (CF_2),[33,34] and −1505 (c-C_4F_8).[35]

Reactions of $C_nF_m^+$ with C_2F_4. *CF^+.* CF^+ reacts rapidly with C_2F_4, and several products are formed:

$$CF^+ + C_2F_4 \rightarrow CF_3^+ + FC{\equiv}CF; \quad \Delta H = -93.4 \text{ kJ mol}^{-1} \quad (1a)$$

$$CF^+ + C_2F_4 \rightarrow C_2F_4^+ + CF; \quad \Delta H = +96.0 \text{ kJ mol}^{-1} \quad (1b)$$

$$CF^+ + C_2F_4 \rightarrow C_3F_5^+; \quad \Delta H = -475 \text{ kJ mol}^{-1} \quad (1c)$$

The total rate constant k has a negative temperature dependence which can be represented as $k = CT^{-1.9}$, where C is a constant. The efficiency of the overall reaction drops from 62% at 300 K to 23% at 496 K. The reaction efficiency is defined as the ratio of the measured rate constant to the calculated[36,37] collisional rate constant. Some of the reduced efficiency at the higher temperature is a result of the expected strong negative temperature dependence of the association channel (reaction 1c) forming $C_3F_5^+$, discussed below. The rate constant for the channel producing CF_3^+ (i.e., the product of the branching fraction and the overall rate constant) also decreases with increasing temperature.

The observed charge-transfer channel is endothermic by 96 kJ mol^{-1} for CF^+ in its ground state. The charge transfer apparently arises from excited-state CF^+. There must be a sufficient population of excited states, with energies on the order of or greater than 96 kJ mol^{-1} (1 eV) above the CF^+ ground state, in order to account for the 3–4% efficiency of the observed charge-transfer channel. This would require vibrationally excited CF^+ in the $v = 5$ or higher level or would require an electronic CF^+ excited state. The present data cannot be used to distinguish between these possibilities. Evidence for some form of excited CF^+ produced in our ion source from electron impact on CF_3Br has been reported previously,[38] and it is well-known that both vibrationally and electronically excited NO^+ (isoelectronic with CF^+) can be produced by electron impact on NO. Given the experimental indication of excited CF^+ in the present experiment, the results on CF^+ reported here should be considered with this in mind.

The association channel producing $C_3F_5^+$ is exothermic, but the heat of formation of $C_3F_5^+$ has only been estimated.[21] The contribution by this channel, not surprisingly, decreases strongly with temperature, while the charge-transfer channel increases. The temperature dependence of the association channel is $T^{-3.0}$. While we refer to this channel as association, it is likely that the bond so formed is a chemical bond as distinguished from a weak cluster bond. If this is the case, it may be more appropriate to refer to this process as condensation, i.e., lengthening of the carbon chain. This point also applies to reaction 3, discussed later in this section.

Reaction 1 has been studied previously in an ion source experiment.[18] The rate constant measured in that experiment, 1.1×10^{-10} cm^3 s^{-1}, is consistent with the negative temperature dependence found in the present study since the ion source experiment was conducted at suprathermal energy. It was deduced[18] that reaction 1 forms the product ion CF_3^+, the major ionic product found in the present study. Anicich et al.,[19] using an ICR apparatus, also concluded that CF_3^+ is formed in this reaction, although the rate constant was not measured. While neither of these two previous studies noted the formation of the product ions $C_2F_4^+$ and $C_3F_5^+$, the $C_2F_4^+$ ion represents only 4% of the ionic products at 300 K, and the association channel would

not be expected to be observable under the low-pressure conditions of the ICR experiment.

CF_2^+. The reaction of CF_2^+ with C_2F_4 proceeds at the collisional rate by charge transfer at both 300 and 496 K:

$$CF_2^+ + C_2F_4 \rightarrow C_2F_4^+ + CF_2; \quad \Delta H = -107 \text{ kJ mol}^{-1} \quad (2)$$

This reaction has been studied previously in both the ion source[18] and ICR[19] studies mentioned previously. In the ion source experiment, a rate constant of 1.05×10^{-9} cm^3 s^{-1} was measured for reaction 2, and $C_2F_4^+$ was identified as the ionic product. This rate constant value is in agreement with the present values, which are collisional, showing essentially no temperature dependence from 300 to 496 K; the rate constant measured at suprathermal energy in the ion source is expected to be approximately the same as the temperature-independent thermal rate constants. The ICR study revealed the occurrence of reaction 2, but the rate constant was not measured.

CF_3^+. The reaction of CF_3^+ with C_2F_4 is a slow association reaction and has not been reported previously:

$$CF_3^+ + C_2F_4 \rightarrow C_3F_7^+; \quad \Delta H = -9.7 \text{ kJ mol}^{-1} \ (n\text{-}C_3F_7^+)$$

$$CF_3^+ + C_2F_4 \rightarrow C_3F_7^+; \quad \Delta H = -23.6 \text{ kJ mol}^{-1} \ (iso\text{-}C_3F_7^+) \quad (3)$$

The exothermicity of reaction 3 depends upon the isomeric form of the $C_3F_7^+$ product; the more stable form of $C_3F_7^+$ is that with the positive charge on the central carbon, iso-$C_3F_7^+$. However, migration of a fluorine atom would be required in order for this isomer to be formed. The less stable isomer, with the charge on a terminal carbon, would result from simple addition of CF_3^+ to C_2F_4.

The ions $C_3F_5^+$ and $C_2F_3^+$ appeared in the product ion spectra, and branching fractions of 4% and 2% were derived for these ions, respectively, at 300 K. However, the small abundances of these ions, the slow rate of the primary reaction (reaction 3), and the 0.5% expected impurity levels in the C_2F_4 lead to the conclusion that these ions could arise solely from reactions of impurities in the C_2F_4. Therefore, the identification of these ions as products of reaction 3 should be viewed as questionable.

As discussed in the Experimental Section, the product ion $C_3F_7^+$ was found to undergo a secondary reaction which regenerates the primary CF_3^+ ion. The rate constant for reaction 3 was found by fitting the integrated rate expression to the CF_3^+ decay data, which exhibited upward curvature with increasing C_2F_4 flow rate as a result of the regeneration of the primary ion in the reaction region of the flow tube. The rate constant derived by this method was essentially the same as that measured in the conventional manner at low extent of reaction.

The rate constant for reaction 3 has a strong negative temperature dependence, as expected for an association reaction. The temperature dependence is $T^{-3.5}$. The rate constant for this reaction has not been reported previously. In their ion source experiment, Derwish et al.[18] could not associate the formation of any product ion with the disappearance of CF_3^+ and discarded the possibility that $C_3F_7^+$ is formed in the reaction of CF_3^+ with C_2F_4.

$C_2F_3^+$. The reaction of $C_2F_3^+$ with C_2F_4 produces mainly $C_3F_5^+$, with a minor amount of nondissociative charge transfer occurring:

$$C_2F_3^+ + C_2F_4 \rightarrow C_3F_5^+ + CF_2; \quad \Delta H = -317 \text{ kJ mol}^{-1}$$

$$C_2F_3^+ + C_2F_4 \rightarrow C_2F_4^+ + C_2F_3; \quad \Delta H = -8 \text{ kJ mol}^{-1} \quad (4)$$

The heats of reaction for reaction 4 are not well known because the published heats of formation of $C_2F_3^+$ and $C_3F_5^+$ are only approximate values. The charge-transfer channel may in fact be slightly endothermic. The observation of charge transfer with rate constants of 2.3×10^{-11} and 7.1×10^{-11} cm^3 s^{-1} at 300 and 496 K, respectively, can be used to derive a lower limit to the heat of formation of $C_2F_3^+$ using the relation $k = k_c \exp(-\Delta H/kT)$ where k_c is the collisional rate constant and ΔH is the heat of reaction. This derivation yields a heat of reaction of $< +10$ kJ mol^{-1} for the charge-transfer channel which, combined with the published heats of formation of the other species involved in the reaction, places a limit of >772 kJ mol^{-1} on the heat of formation of $C_2F_3^+$. The positive temperature dependences of the branching fraction and rate constant for the charge-transfer channel are consistent with this pathway being slightly endothermic. Using the Arrhenius equation, an activation energy of 7 kJ mol^{-1} is derived for the charge-transfer channel.

Reaction 4 is fast but proceeds more slowly than the collisional rate. The rate constants are in agreement with the value of 2.9×10^{-10} cm^3 s^{-1} measured for the disappearance of $C_2F_3^+$ in C_2F_4 in the ion source experiment,[18] although the reaction products were not identified in that study. The production of $C_3F_5^+$ in this reaction was noted in the ICR study,[19] but the rate constant was not measured.

$C_2F_4^+$. The reaction of $C_2F_4^+$ with C_2F_4 is slow and produces $C_3F_5^+$:

$$C_2F_4^+ + C_2F_4 \rightarrow C_3F_5^+ + CF_3; \quad \Delta H = -117 \text{ kJ mol}^{-1} \quad (5)$$

As mentioned above, the heat of formation of $C_3F_5^+$ is not known reliably, and thus the heat of reaction given for reaction 5 is only approximate. The rate constant for this reaction displayed a strong negative temperature dependence of $T^{-3.6}$. Negative temperature dependences of slow ion–molecule reactions are commonplace and are often explained in terms of a double-well potential surface for the reaction.[39]

Reaction 5 has been studied previously using ICR[19-21] and ion source[18] techniques. As in the present study, $C_3F_5^+$ product was observed in both ICR and ion source experiments. The rate constants from the previous studies are in reasonable agreement with the present values. Evidence for excited $C_2F_4^+$ reactant ion, produced by electron impact, was found in the ICR experiments. However, no curvature was seen in the pseudo-first-order kinetics plots in the present experiment, which suggests that any excited $C_2F_4^+$ was quenched by the He buffer gas.

In the ion source experiment, it was suspected that the reaction of $C_2F_4^+$ with C_2F_4 formed $C_3F_7^+$ as an additional product. The present SIFT study gave no evidence for this at either 300 or 496 K. However, the suprathermal energies which obtain in the ion source environment could be the reason for this discrepancy.

$C_3F_5^+$. $C_3F_5^+$ was found to be unreactive with C_2F_4 within experimental sensitivity. Upper limits to the rate constant of $<3 \times 10^{-12}$ cm^3 s^{-1} are reported for 300 and 496 K. The lack of reactivity of $C_3F_5^+$ with C_2F_4 has been noted previously.[18,19]

$C_3F_7^+$. The reaction of $C_3F_7^+$ with C_2F_4 is slow and produces CF_3^+:

$$C_3F_7^+ + C_2F_4 \rightarrow CF_3^+ + C_4F_8; \quad \Delta H \text{ depends on isomers} \quad (6)$$

The thermochemistry for reaction 6 cannot be specified because the isomeric forms of the $C_3F_7^+$ reactant ion and the neutral product C_4F_8 are not known. The following isomers of C_4F_8 (listed with resulting exothermicities of reaction 6 for iso-$C_3F_7^+$ reactant ion) are possible neutral products: c-C_4F_8 (–163 kJ mol^{-1}), *Z*-2-C_4F_8 (–255), *E*-2-C_4F_8 (–259), iso-C_4F_8 (?), and 1-C_4F_8 (?). The neutral product(s) must be some isomeric form(s) of C_4F_8 since it is endothermic for reaction 6 to form, along with CF_3^+, any combination of fragments of C_4F_8, e.g., $2CF_3 + C_2F_2$. The rate constant for this reaction has not been reported previously.

The ions $C_2F_5^+$ and $C_4F_7^+$ appeared in the product ion spectra, and branching fractions of 7% were derived for each of the channels

producing these ions at 300 K. However, the small abundances of these ions, the slow rate of the primary reaction (reaction 6), and the 0.5% expected impurity levels in the C_2F_4 lead to the conclusion that these ions could arise solely from reactions of impurities in the C_2F_4. Therefore, the identification of these ions as products of reaction 6 should be viewed as questionable.

Reactions 3 and 6 together constitute a catalytic cycle, i.e., dimerization of C_2F_4 catalyzed by CF_3^+:

$$CF_3^+ + C_2F_4 \rightarrow C_3F_7^+ \quad (3)$$

$$C_3F_7^+ + C_2F_4 \rightarrow CF_3^+ + C_4F_8 \quad (6)$$

$$\text{net: } 2C_2F_4 \rightarrow C_4F_8$$

This ion-catalyzed scheme has not been reported previously. However, other ion-catalyzed neutral recombinations have been reported; e.g., $C_2H_2^+$ and C_3H^+ catalyze the recombination of H atoms.[40] C_{60}^+ may also catalyze the recombination of H.[41] Ion-catalyzed polymerization of olefins is a well-known process in the liquid phase.[42]

Reactions of CF_3^+ with Other Perfluorocarbons. *$CF_3^+ + C_3F_6$.* The reaction of CF_3^+ with C_3F_6 ($CF_3CF{=}CF_2$) proceeds rapidly by F^- abstraction:

$$CF_3^+ + C_3F_6 \rightarrow C_3F_5^+ + CF_4; \quad \Delta H = -170 \text{ kJ mol}^{-1} \quad (7)$$

Because the heat of formation of $C_3F_5^+$ is not known reliably, this reported heat of reaction is only approximate. Reaction 7 has been studied previously by the ICR technique[43] and the $C_3F_5^+$ product noted, but the rate constant was not measured.

$CF_3^+ + 2\text{-}C_4F_8$. The reaction of CF_3^+ with 2-C_4F_8 (CF_3-$CF{=}CFCF_3$) proceeds rapidly by F^- abstraction:

$$CF_3^+ + 2\text{-}C_4F_8 \rightarrow C_4F_7^+ + CF_4; \quad \Delta H = ? \quad (8)$$

The heat of formation of $C_4F_7^+$ is not known.

$CF_3^+ + c\text{-}C_4F_8$. CF_3^+ was found to be unreactive with c-C_4F_8. An upper limit to the rate constant of $<3 \times 10^{-12}$ cm^3 s^{-1} at 300 and 496 K is reported.

Summary and Conclusions

A variety of types of reactions with C_2F_4, including charge transfer, fluoride transfer, and association, occur for the small positive fluorocarbon ions studied. Many of the reactions proceed rapidly, and several have significant temperature dependences. Neutral reaction products include the free radical species CF, CF_2, CF_3, and C_2F_3. For these reasons, ion–molecule reactions should be included in chemical modeling of gaseous plasmas containing C_2F_4.

The association reaction of CF_3^+ with C_2F_4 features an interesting complication in that the $C_3F_7^+$ product ion undergoes secondary reaction with C_2F_4 to regenerate CF_3^+. This two-step sequence constitutes dimerization of C_2F_4 catalyzed by CF_3^+. The reaction rates for the two steps were measured at 300 and 496 K. The isomeric form of the resulting C_4F_8 was not determined.

Some generalizations appear to apply to the reactivity of CF_3^+ toward perfluorocarbons. For those perfluorocarbons studied (previous and present work), CF_3^+ abstracts fluoride when a CF_3 group is present in the reactant neutral, regardless of whether the neutral is fully saturated. Examples are the neutrals C_2F_6,[38,43-46] C_3F_6, C_3F_8,[32] and 2-C_4F_8. If the neutral contains no CF_3 groups but does contain an unsaturation, as in the case of C_2F_4, then CF_3^+ reacts by association. The neutral c-C_4F_8, which contains no CF_3 groups and no unsaturations, does not measurably react with CF_3^+.

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