

# Gaseous ion–molecule reactions of $F^-$ , $CF_3^-$ , $C_2F_5^-$ , $CF_3^+$ and $C_2F_5^+$ with hexafluoropropene oxide

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Received 8 November 1994; accepted 8 February 1995

## Abstract

The gas-phase reactions of  $F^-$ ,  $CF_3^-$ ,  $C_2F_5^-$ ,  $CF_3^+$  and  $C_2F_5^+$  with hexafluoropropene oxide (HFPO,  $C_3F_6O$ ) have been studied using a selected ion flow tube (SIFT) instrument at 300 K. Reactions of  $C_4F_9^-$  and  $C_3F_7^+$  with HFPO have also been studied as secondary reactions. Reaction rate constants and product branching fractions were measured. The  $F^-$ ,  $CF_3^-$  and  $C_2F_5^-$  ions react rapidly with HFPO. The major reaction process is the formation of  $CF_2O$  and the corresponding negative product ions. A minor pathway is the production of the ion  $CF_3O^-$ . Another reaction channel of  $F^-$  and  $CF_3^-$  with HFPO is the formation of  $C_2F_4$  and the corresponding ions.  $C_4F_9^-$  ion reacts with HFPO by  $F^-$  transfer to produce  $C_3F_7O^-$ . The  $C_3F_7^+$  ion is the only product observed for the reaction of  $CF_3^+$  with HFPO. The  $C_2F_5^+$  ion reacts rapidly with HFPO. The major product is  $C_3F_7^+$  which, in turn, reacts with HFPO to regenerate  $C_2F_5^+$ , forming a cationic catalytic cycle for the formation of the inferred neutrals  $C_2F_4O$  and  $C_4F_8O$  from HFPO. Both  $C_2F_5^+$  and  $C_3F_7^+$  react with HFPO to produce neutral  $C_3F_8$  and the corresponding positive ions. A rather rapid association reaction was observed between  $C_3F_7^+$  and HFPO, forming the adduct  $C_6F_{13}O^+$ . A systematic estimation for the enthalpies of formation for a series of perfluorinated neutrals and ionic species is also presented.

**Keywords:** Ion–molecule reactions; Hexafluoropropene oxide; Fluorine ion; Trifluoromethyl ion; *F*-ethyl ion; Reaction kinetics

## 1. Introduction

Hexafluoropropene oxide (HFPO,  $C_3F_6O$ , 2,2,3-trifluoro-3-trifluoromethyloxirane) has been regarded as the most important member among fluorocarbon epoxides [1]. It is the starting material of many products which are of industrial importance [1]. Many reactions of HFPO have been studied in solution. The most common reactions are those with nucleophiles. For example, HFPO reacts readily with primary amines [2], secondary amines [3,4], tertiary amines [3,4] and enamines [5]. These reactions frequently result in the isomerization of HFPO to perfluoropropionyl fluoride. Numerical studies have been performed regarding the oligomerization of HFPO by anionic polymerization [6–15]. HFPO can react with fluorinated [16–19] and non-fluorinated [20–22] ethers and epoxides to form polyethers.

Reactions with water [3], alcohols [23–28], thiols [3,25] organometallic compounds [29,30] and many other nucle-

ophiles, including bifunctional nucleophiles [2], have also been observed. Some reactions of HFPO with electrophiles in solution (although rare) have been reported [31,32]. In these reactions, the oxirane ring is converted into a ketone functionality. HFPO has also been used as a source of difluorocarbene [33,34] which is obtained by heating HFPO to temperatures above 150 °C.

Although HFPO has been much studied in solution and has been the raw material for many products of important industrial and medical applications [1], gas-phase ionic reactions of HFPO have not been explored. Knowledge of the ion chemistry of HFPO in the gas phase may provide insight to its intrinsic properties, which may lead to new applications. We report here a study of reactions of several positive and negative ions with HFPO in the gas phase under thermal conditions at 300 K.

## 2. Experimental details

The experiments were performed at 300 K using the selected ion flow tube (SIFT) instrument at Phillips Labo-

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ratory. The technique has been fully described in the literature [35]. The following is a brief description of the details specific to the present study. Fluoride ions were generated by electron impact on SF<sub>6</sub> in a high-pressure (0.1–1 Torr) ion source. Similarly, CF<sub>3</sub><sup>−</sup> was generated from HFPO, and C<sub>2</sub>F<sub>5</sub><sup>−</sup>, CF<sub>3</sub><sup>+</sup> and C<sub>2</sub>F<sub>5</sub><sup>+</sup> were produced from C<sub>2</sub>F<sub>6</sub> or n-C<sub>8</sub>F<sub>18</sub>.

The ions were then mass-selected in a quadrupole mass spectrometer and injected through a Venturi inlet into a stainless-steel flow tube 1 m in length. Inside the flow tube the ions were entrained in the fast flow ( $\sim 10^4$  cm s<sup>−1</sup>) of He carrier gas which flowed from the Venturi inlet. The HFPO reactant neutral was introduced into the flow tube, and the reactant and product ions were sampled through a 0.2-mm diameter orifice in a truncated nose cone, mass analyzed in a second quadrupole mass spectrometer and detected by a channel particle multiplier.

Rate constants were calculated from the reaction times and the slopes of least-squares fits of the natural logarithm of the reactant ion signal plotted versus the added HFPO reactant gas concentration. The reaction time was obtained from the reaction distance and from direct ion time-of-flight measurements in the flow tube. The accuracy of the measured overall rate constants is  $\pm 25\%$ , and the experimental precision is  $\pm 15\%$ . Since the rate constant for an individual reaction channel is equal to the overall rate constant multiplied by the product branching fraction for that channel, the accuracy with which the branching fraction can be measured must be considered. We estimate the uncertainty in the channel-specific rate constants to be  $\pm 35\%$  with a precision of  $\pm 20\%$ .

Product ion branching fractions were measured by operating the downstream mass spectrometer at low resolution to avoid mass discrimination. For branching fraction determinations, the product ion signals were recorded as a function of reactant neutral flow rate at a low extent of reaction. Reported branching fractions are the result of extrapolating the branching fractions to zero reactant neutral flow rate in order to account for secondary reactions in the flow tube. The values reported are the averages of several runs.

Reaction rate constants for secondary reactions were estimated by the method described elsewhere [36]. Taking into account the additional uncertainty, the overall uncertainty for the secondary rate constant is estimated to be  $\pm 50\%$ .

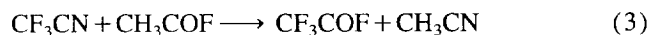
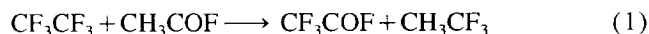
### 3. Thermochemical data

Reported thermochemical data are taken from the compilation of Lias et al. [37] except for those given in Table 1. Note that the thermochemical data in this report are for gas-phase species.

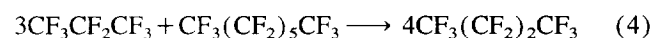
Enthalpies of formation were estimated for those species for which thermochemical data are not available in the literature. The estimation process presented in this section provides a systematic approach to estimating the enthalpies of formation of perfluorinated neutral or ionic species, although

some of the species being estimated may not be needed for the experimental results in this report. In the estimations below, all unreferenced thermochemical data have been taken from either the compilation of Lias et al. [37] or Pedley et al. [43].

The enthalpies of formation of the perfluoroacyl fluorides, C<sub>2</sub>F<sub>4</sub>O and the various isomers of C<sub>4</sub>F<sub>8</sub>O and C<sub>5</sub>F<sub>10</sub>O may be estimated as follows. Consider the following gas-phase isodesmic reactions [44] and tacitly assume that they are thermoneutral



The three predicted values for  $\Delta H_f$  of C<sub>2</sub>F<sub>4</sub>O are  $-1042 \pm 7$ ,  $-1041 \pm 4$  and  $-1014 \pm 4$  kJ mol<sup>−1</sup>, respectively. The first two results are consonant with each other as well as with the earlier suggested estimate of one of the authors [45]. The third result is not <sup>1</sup>. Admitting a rather large error bar, we suggest the  $\Delta H_f[\text{CF}_3\text{COF}, \text{g}]$  to be  $-1035 \pm 15$  kJ mol<sup>−1</sup>, where we find ourselves ‘preferring’ the enthalpy of formation values of hexafluoroethane and trifluoroacetic acid over that of trifluoroacetonitrile. To derive the enthalpies of formation of larger perfluoroacyl fluorides, a constant  $-\text{CF}_2-$  group increment should not be assumed <sup>2</sup>. Nonetheless, we will assume that the general  $-\text{CF}_2-$  group increment <sup>3</sup> is the difference of the enthalpies of formation of CF<sub>3</sub>CF<sub>2</sub>COF and CF<sub>3</sub>COF, which is  $-439 \pm 9$  kJ mol<sup>−1</sup>. Equating this value to the difference between the  $\Delta H_f$  values of CF<sub>3</sub>CF<sub>2</sub>CF<sub>3</sub> and CF<sub>3</sub>CF<sub>3</sub>,  $\Delta H_f[\text{CF}_3\text{CF}_2\text{COF}, \text{g}]$  was derived to be  $-1474$  kJ mol<sup>−1</sup>. To obtain  $\Delta H_f[\text{CF}_3(\text{CF}_2)_2\text{COF}, \text{g}]$ , we assume the difference between this quantity and that of CF<sub>3</sub>CF<sub>2</sub>COF to be equal to that between CF<sub>3</sub>(CF<sub>2</sub>)<sub>2</sub>CF<sub>3</sub> and CF<sub>3</sub>CF<sub>2</sub>CF<sub>3</sub>. There is no calorimetric measurement of the enthalpy of formation of perfluorobutane. However, let us assume that perfluoroalkanes become ‘normal’ (having an essentially constant difference of enthalpies of formation for successive  $-\text{CF}_2-$  group increment) as in the case of perfluoropropane <sup>4</sup> and that reaction (4) is thermoneutral.



Thus,  $\Delta H_f[\text{CF}_3(\text{CF}_2)_2\text{CF}_3, \text{g}]$  is deduced to be  $-2183$  kJ mol<sup>−1</sup> and  $\Delta H_f[\text{CF}_3(\text{CF}_2)_2\text{COF}, \text{g}]$  is derived to be  $-1874$  kJ mol<sup>−1</sup>.

We now turn to estimating  $\Delta H_f[(\text{CF}_3)_2\text{CFCOF}, \text{g}]$ . It is well established that the difference between the enthalpies of formation of the n-propyl and isopropyl species,

<sup>1</sup> The required enthalpy of formation of CH<sub>3</sub>CN has been taken from Ref. [46].

<sup>2</sup> For a recent discussion of the thermochemistry of fluorinated species, including the lack of constancy of various group increments, see Ref. [47].

<sup>3</sup> We mean by the  $-\text{CF}_2-$  group what is more properly written as C(F)<sub>2</sub>(CF<sub>2</sub>)<sub>2</sub> — see Ref. [48].

<sup>4</sup> For a discussion of the CH<sub>2</sub> group and ‘normalcy’ in the conceptually simpler series CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>, see Ref. [49].

Table I  
Enthalpies of formation at 298 K

| Gaseous species                                     | $\Delta H_f^\circ$ (kJ mol <sup>-1</sup> ) | Reference             |
|---|--|-----------------------|
| CF <sub>2</sub> O                                   | -606                                       | [38]                  |
| CF <sub>3</sub> <sup>+</sup>                        | 361  | [39]                  |
| iso-C <sub>3</sub> F <sub>7</sub> <sup>+</sup>      | -322                                       | [40]                  |
| sec-C <sub>4</sub> F <sub>9</sub> <sup>-</sup>      | -2067                                      | [41]                  |
| C <sub>3</sub> F <sub>6</sub> (perfluoropropene)    | -1152                                      | [42]                  |
| C <sub>4</sub> F <sub>8</sub>                       | -1552                                      | estimate <sup>a</sup> |
| HFPO (hexafluoropropene oxide,<br>                  | -1130                                      | estimate <sup>a</sup> |
| CF <sub>3</sub> COF                                 | -1035                                      | estimate <sup>a</sup> |
| CF <sub>3</sub> (CF <sub>2</sub> ) <sub>2</sub> COF | -1874                                      | estimate <sup>a</sup> |
|   | -1884                                      | estimate <sup>a</sup> |
|   | -1797                                      | estimate <sup>a</sup> |
| CF <sub>3</sub> (CF <sub>2</sub> ) <sub>3</sub> COF | -2274                                      | estimate <sup>a</sup> |
|   | -2284                                      | estimate <sup>a</sup> |
|   | -2197                                      | estimate <sup>a</sup> |
| CF <sub>3</sub> CO <sup>+</sup>                     | -322                                       | estimate <sup>a</sup> |
| CF <sub>3</sub> CF <sub>2</sub> CO <sup>+</sup>     | -289                                       | estimate <sup>a</sup> |
| CF <sub>3</sub> COCF <sub>2</sub> <sup>+</sup>      | -54  | estimate <sup>a</sup> |
|   | -2086                                      | estimate <sup>a</sup> |
|   | -2173                                      | estimate <sup>a</sup> |
|   | -2163                                      | estimate <sup>a</sup> |

<sup>a</sup> See text.

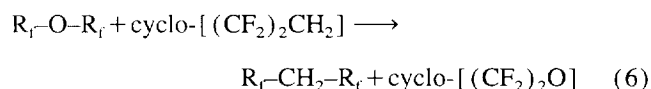
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>X and (CH<sub>3</sub>)<sub>2</sub>CHX, is some 8 kJ mol<sup>-1</sup> [50] regardless of the electronegativity of group X. It does not appear particularly unreasonable to assume a similar difference for their perfluoro derivatives. As such,  $\Delta H_f[(\text{CF}_3)_2\text{CFCOF}, \text{g}]$  equals -1884 kJ mol<sup>-1</sup>. Alternatively, Eq. (5) can be used to derive the most general -CF<sub>2</sub>- group enthalpy increment:

$$\Delta H_{\text{df}}[-\text{CF}_2-] = \Delta H_f[\text{CF}_3(\text{CF}_2)_2\text{CF}_3, \text{g}] - \Delta H_f[\text{CF}_3\text{CF}_2\text{CF}_3, \text{g}] \quad (5)$$

Numerically, the value is -400 kJ mol<sup>-1</sup>. This allows us to immediately derive  $\Delta H_f[\text{CF}_3\text{CF}_2\text{COCF}_3, \text{g}]$  to be equal to -1797 kJ mol<sup>-1</sup> by summing the enthalpy of formation of

gaseous hexafluoroacetone and that of the -CF<sub>2</sub>- increment. Relatedly,  $\Delta H_f[\text{CF}_3(\text{CF}_2)_3\text{COF}]$  equals -2274 kJ mol<sup>-1</sup>. Likewise,  $\Delta H_f[\text{CF}_3\text{CF}_2\text{CF}=\text{CF}_2]$  is derived from adding a -CF<sub>2</sub>- group increment to  $\Delta H_f[\text{CF}_3\text{CF}=\text{CF}_2]$  to be -1552 kJ mol<sup>-1</sup>. In this report, it is assumed that both 1-C<sub>4</sub>F<sub>8</sub> and 2-C<sub>4</sub>F<sub>8</sub> have the same enthalpy of formation.

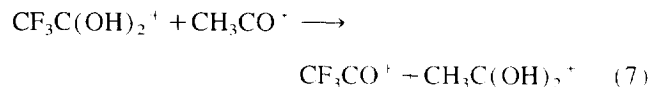
The enthalpy of formation of HFPO is estimated by assuming that cyclo-[(CF<sub>2</sub>)<sub>2</sub>O] has the same strain energy as cyclo-[(CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>] and that the following reaction is thermoneutral:



where  $R_f$  is a perfluoroalkyl group. That is, the difference in enthalpies of formation between cyclo-[(CF<sub>2</sub>)<sub>2</sub>O] and cyclo-[(CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>] is the same as that between the perfluoro ether  $R_f-O-R_f$  and the dihydrogen perfluoroalkane  $R_f-CH_2-R_f$ . Knowing that the enthalpies of formation for  $R_f-O-R_f$  with  $R_f = C_3F_7$ ,  $C_4F_9$  and  $C_5F_{11}$  are  $-3148$ ,  $-3979$  and  $-4806$  kJ mol<sup>-1</sup>, respectively,  $\Delta H_f[CF_3-O-CF_3]$  may be derived by  $-CF_2-$  group increments to be  $-1550$  kJ mol<sup>-1</sup>. The difference in enthalpy of formation between  $CF_3CH_2CF_3$  ( $-1406$  kJ mol<sup>-1</sup>) and  $CF_3-O-CF_3$ , and thus, that between cyclo-[(CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>] and cyclo-[(CF<sub>2</sub>)<sub>2</sub>O], is ca. 140 kJ mol<sup>-1</sup>. Taking the enthalpy of formation for cyclo-[(CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>] as  $-590 \pm 43$  kJ mol<sup>-1</sup> [51], the enthalpy of formation of cyclo-[(CF<sub>2</sub>)<sub>2</sub>O] is then  $(-590 - 140)$  kJ mol<sup>-1</sup> or  $-730$  kJ mol<sup>-1</sup>. The quantity  $\Delta H_f[HFPO]$  can be estimated by calculating the change of  $\Delta H_f$  when one of the F atoms in cyclo-[(CF<sub>2</sub>)<sub>2</sub>O] is replaced by a CF<sub>3</sub> group. Assuming that the difference between  $\Delta H_f[(CF_3)_2CFX]$  and  $\Delta H_f[CF_3CF_2X]$  is the same as that between  $\Delta H_f[CF_3CF_2CF_2X]$  and  $\Delta H_f[CF_3CF_2X]$  (i.e.  $-400$  kJ mol<sup>-1</sup>),  $\Delta H_f[HFPO]$  is then derived to be  $-1130$  kJ mol<sup>-1</sup>.

We now turn to the isomers  $CF_3CF_2CF(CF_3)COF$  and  $CF_3(CF_2)_2COCF_3$ . Following from the analysis of Liebman [50], we conclude that the difference between the enthalpies of formation of n- and sec-butyl derivatives is the same as that between n- and i-propyl derivatives, and from the above discussion we assert that perfluorination does not affect the result. Adding  $-400$  kJ mol<sup>-1</sup> to the enthalpies of formation of perfluoroisobutyl fluoride and perfluoro-2-butanone results in  $-2284$  and  $-2197$  kJ mol<sup>-1</sup> as predicted enthalpies of formation for these C<sub>5</sub>F<sub>10</sub>O isomers, respectively.

Although it is more precarious to estimate the enthalpies of formation for ions<sup>5</sup>, a reasonable estimation for the series of ions  $CF_3CO^+$ ,  $CF_3CF_2CO^+$  and  $CF_3(CF_2)_2CO^+$  can be made as follows. It is not unreasonable to assume that reactions (7) and (8) are essentially thermoneutral:



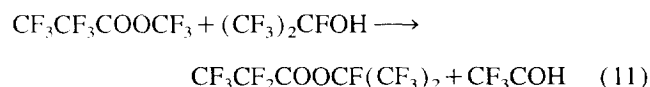
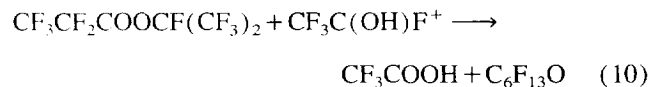
From reactions (7) and (8), the discordant values of 143 and 179 kJ mol<sup>-1</sup>, respectively, are derived for  $\Delta H_f[CF_3CO^+]$ , g]. Much of the discrepancy of the energetics of reactions (7) and (8) is shared by the neutral species of reactions (1) or (2), and (3). Having favored reaction (1) and (2) over (3), we again prefer results from trifluoroacetic acid over those from trifluoroacetonitrile and so suggest  $\Delta H_f[CF_3CO^+]$ , g] to be ca. 150 kJ mol<sup>-1</sup>. Were size effects<sup>5</sup> irrelevant, then the difference between the enthalpies of formation of  $CF_3CF_2CO^+$  and  $CF_3CO^+$  is the same as the dif-

ference between  $CF_3CF_2CF_3$  and  $CF_3CF_3$ . Also, the difference between  $CF_3(CF_2)_2CO^+$  and  $CF_3CF_2CO^+$  is the same as that of  $CF_3(CF_2)_2CF_3$  and  $CF_3CF_2CF_3$ . Ignoring size effects,  $\Delta H_f[CF_3CF_2CO^+]$ , g] would equal  $-289$  kJ mol<sup>-1</sup> and  $\Delta H_f[CF_3(CF_2)_2CO^+]$ , g] would equal  $-689$  kJ mol<sup>-1</sup>. From Ref. [45], we find the proton affinities of  $CF_3CN$ ,  $CF_3CF_2CN$  and  $CF_3(CF_2)_2CN$  are 695, 699 and 700 kJ mol<sup>-1</sup>, respectively, suggesting that size effects may well be negligible for highly fluorinated species<sup>6</sup>, and they will in fact be neglected here. Intuitively, using hydrocarbon analogies,  $CF_3CF_2CO^+$  should be more stable than its isomer  $CF_3COCF_2^+$  (after all, acyl cations are more stable than  $\beta$ -ketoalkyl cations). Yet, it is not unambiguous here at first glance that the two  $\alpha$ -fluorines destabilize the acyl cation in the former species while the two  $\alpha$ -fluorines stabilize the latter. For lack of other information, we approximate  $\Delta H_f[CF_3COCF_2^+]$ , g] by assuming thermoneutrality for

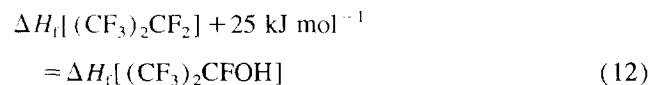


The result is  $-54$  kJ mol<sup>-1</sup> with an error bar of  $>60$  kJ mol<sup>-1</sup> because of huge uncertainties in the experimental measurements of  $\Delta H_f[CF_3CF_2^+]$ , g].

The enthalpy of formation for  $C_6F_{13}O^+$  with the structure  $CF_3CF_2-C^+(F)-O-CF(CF_3)_2$  may be estimated by assuming reactions (10) and (11) to be thermoneutral:



and that



based on other organic F, OH replacements (see Refs. [52–54] and the studies cited therein). This gives  $\Delta H_f[CF_3CF_2-C^+(F)-O-CF(CF_3)_2] = -2135$  kJ mol<sup>-1</sup>. A more accurate value can be obtained by considering (1) the effect of the  $CF_3CF_2$  group on the stability of the cation compared to the  $CF_3$  group in  $CF_3C(OH)F^+$  and (2) the effect of  $(CF_3)_2CF$  on the stability of the cation compared to that of H. Since the proton affinity of  $CF_3CF_2CN$  is 4 kJ mol<sup>-1</sup> higher than that of  $CF_3CN$ , replacing the  $CF_3$  group by the  $CF_3CF_2$  group would stabilize the cation by 4 kJ mol<sup>-1</sup>. Looking at a collection of oxygen bases, ketones, esters, alcohols and ethers, the proton affinity of RH is some 43 kJ mol<sup>-1</sup> higher than that of  $RCF_3$  [52]. But the functional group of interest is

<sup>5</sup> By size effects we lump together the awareness that the ionization potentials and proton affinities for the series  $CH_3(CH_2)_nX$  respectively decrease and increase with  $n$ , i.e. a charge center is stabilized by larger affixed groups (For example, see the introduction to Ref. [37].)

<sup>6</sup> By contrast, the proton affinities of their all-hydrogen analogs  $CH_3CN$ ,  $CH_3CH_2CN$  and  $CH_3CH_2CH_2CN$  are 788, 806 and 810 kJ mol<sup>-1</sup>. It is a moot point whether the difference is because of 'more stuff' even for smaller perfluoroalkyl chains and so saturation is achieved earlier or that there is increasing electron withdrawal as the perfluoro chain gets longer which cancels the size effect.

Table 2  
Branching fractions and total rate constants for reactions of selected negative ions with HFPO measured at 300 K

| Reaction  | Branching fraction | Total rate constant<br>( $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ) |
|---|--------------------|---|
| $F^- + C_3F_6O \longrightarrow C_2F_5^- + CF_2O$  | 0.65               | 11  |
| $\longrightarrow CF_3^- + C_2F_4O$  | 0.30               |   |
| $\longrightarrow CF_3O^- + C_2F_4$  | 0.05               |   |
| $CF_3^- + C_3F_6O \longrightarrow C_3F_7^- + CF_2O$   | 0.61               | 11  |
| $\longrightarrow C_2F_5^- + C_2F_4O$  | 0.22               |   |
| $\longrightarrow CF_3O^- + C_3F_6$  | 0.17               |   |
| $C_2F_5^- + C_3F_6O \longrightarrow C_4F_6^- + CF_2O$   | 0.75               | 7.3   |
| $\begin{array}{l} \begin{array}{l} \text{C}_3\text{F}_6\text{O} \\ \longrightarrow \text{C}_3\text{F}_7\text{O}^- + \text{C}_4\text{F}_8 \end{array} \end{array}$ |                    |   |
| $\longrightarrow CF_3O^- + C_4F_8$  | 0.17               |   |
| $\longrightarrow F^- + C_5F_{10}O$  | 0.07               |   |
| $\longrightarrow CF_3^- + C_4F_8O$  | 0.01               |   |

Table 3  
Branching fractions and total rate constants for reactions of selected positive ions with HFPO measured at 300 K<sup>a</sup>

| Reaction   | Branching fraction | Total rate constant<br>( $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ) |
|--|--------------------|---|
| $CF_3^+ + C_3F_6O \longrightarrow C_3F_7^+ + CF_2O$  | 1.00               | 7.2   |
| $\begin{array}{l} \text{C}_3\text{F}_6\text{O} \\ \longrightarrow \text{C}_2\text{F}_5^+ + \text{C}_4\text{F}_8\text{O} \\ \longrightarrow \text{C}_3\text{F}_5\text{O}^+ + \text{C}_3\text{F}_8 \\ \longrightarrow \text{C}_6\text{F}_{11}\text{O}^+ \end{array}$ |                    | 2.2   |
|  |                    | 1.4   |
|  |                    | 5.4   |
| $C_2F_5^+ + C_3F_6O \longrightarrow C_3F_7^+ + C_2F_4O$  | 0.83               | 7.6   |
| $\longrightarrow C_2F_5O^+ + C_3F_8$   | 0.17               |   |

<sup>a</sup> Rate constant for secondary reactions are individual reaction rate constants.

$(CF_3)_2CF$ , where two F atoms are replaced by  $CF_3$  groups. It was shown earlier that changing F to  $CF_3$  decreases the proton affinity by ca.  $5 \text{ kJ mol}^{-1}$ . Assuming additivity and no saturation, a decrease in proton affinity is equivalent to an increase in enthalpy of formation; we therefore conclude that  $\Delta H_f[CF_3CF_2-C^+(F)-O-CF(CF_3)_2] = -2135 - 4 + 43 + 2 \times 5 = -2086 \text{ kJ mol}^{-1}$ .

We now turn to the ions  $(CF_3)_2C^+-O-CF(CF_3)_2$  and  $(CF_3)_2C^+-O-CF_2CF_2CF_3$ . Let us assume that the difference between the enthalpies of formation of  $(CF_3)_2COR^+$  and  $CF_3CF_2CFOR^+$  is independent of the affixed group R: as such, take  $R=H$  for our estimates. The first new cation is recognized as protonated hexafluoroacetone and has a suggested enthalpy of formation of  $-495 \text{ kJ mol}^{-1}$ . Ignoring size effects as suggested earlier in this text,  $\Delta H_f[CF_3CF_2CFOH^+, g]$  equals the sum of  $\Delta H_f[CF_3CFOH^+, g]$  and that of the universal  $-CF_2-$  increment. This new enthalpy of formation is  $-582 \text{ kJ mol}^{-1}$ , resulting in a difference of ion enthalpies of formation of  $87 \text{ kJ mol}^{-1}$  favoring the latter cation. As such, the enthalpy of formation of  $(CF_3)_2C^+-O-CF(CF_3)_2$  is predicted to be  $(-2086 - 87) \text{ kJ mol}^{-1} = -2173 \text{ kJ mol}^{-1}$ . From the difference of enthal-

pies of formation between n-propyl and isopropyl species mentioned above, the  $\Delta H_f$  value of  $(CF_3)_2C^+-O-CF_2CF_2CF_3$  is estimated to be  $-2163 \text{ kJ mol}^{-1}$ .

## 4. Results and discussion

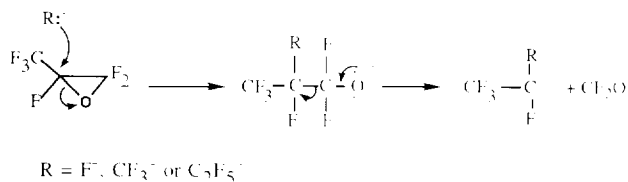
Rate constants and branching fractions for the reactions of selected negative ions and positive ions with HFPO are presented in Table 2 and Table 3, respectively.

### 4.1. Reactions of negative ions ( $F^-$ , $CF_3^-$ and $C_2F_5^-$ ) with HFPO

HFPO reacts rapidly with  $F^-$ ,  $CF_3^-$  and  $C_2F_5^-$ . In all three cases, the major reaction channel is the formation of  $CF_2O$  and the corresponding negative ions.

| Reaction  | $\Delta H$<br>(kJ mol <sup>-1</sup> ) | Rate<br>constant<br>(10 <sup>-10</sup> cm <sup>3</sup><br>s <sup>-1</sup> ) | Equation<br>No. |
|---|---------------------------------------|---|-----------------|
| $F^- + C_3F_6O \rightarrow C_2F_5^- + CF_2O$      | -294                                  | 7.2   | (13)            |
| $CF_3^- + C_3F_6O \rightarrow C_3F_7^- + CF_2O$   | -410                                  | 6.7   | (14)            |
| $C_2F_5^- + C_3F_6O \rightarrow C_4F_9^- + CF_2O$ | -476                                  | 5.5   | (15)            |

It appears that these reactions take place by nucleophilic attack at the more substituted carbon of the epoxide with concomitant ring-opening as shown below:



The presence of  $CF_3O^-$  was also observed, being formed at relatively slower rates as a product of the reactions of  $F^-$ ,  $CF_3^-$  and  $C_2F_5^-$  with HFPO:

| Reaction  | $\Delta H$<br>(kJ mol <sup>-1</sup> ) | Rate<br>constant<br>(10 <sup>-10</sup> cm <sup>3</sup><br>s <sup>-1</sup> ) | Equation<br>No. |
|---|---------------------------------------|---|-----------------|
| $F^- + C_3F_6O \rightarrow CF_3O^- + C_2F_4$      | -342                                  | 0.5   | (16)            |
| $CF_3^- + C_3F_6O \rightarrow CF_3O^- + C_3F_6$   | -436                                  | 1.9   | (17)            |
| $C_2F_5^- + C_3F_6O \rightarrow CF_3O^- + C_4F_8$ | -417                                  | 1.2   | (18)            |

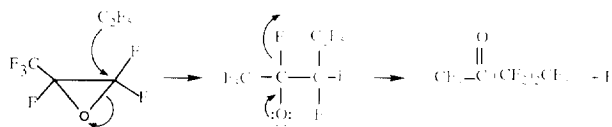
The formation of  $CF_3O^-$  in these reactions probably originates from reactions (13)–(15) immediately followed by  $F^-$  transfer from  $(RCFCF_3)^-$  to  $CF_2O$ .

Fluoride ion was also observed (7%) in the reaction of  $C_2F_5^-$  with HFPO. A small amount of  $F^-$  formation arises from the collision-induced dissociation [55] of  $C_2F_5^-$  (< 1%). The remaining fluoride ion is produced in the reaction of  $C_2F_5^-$  with HFPO (19):

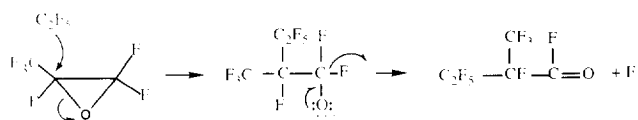
| Reaction  | $\Delta H$<br>(kJ mol <sup>-1</sup> ) | Rate<br>constant<br>(10 <sup>-10</sup> cm <sup>3</sup><br>s <sup>-1</sup> ) | Equation<br>No. |
|---|---------------------------------------|---|-----------------|
| $C_2F_5^- + C_3F_6O \rightarrow F^- + C_5F_{10}O$ | -249 or -336                          | 0.5   | (19)            |

The reaction may occur via a nucleophilic ring-opening on either end of the epoxide, yielding different isomers of  $C_5F_{10}O$ :

Mechanism I:  $\Delta H = -249$  kJ mol<sup>-1</sup>



Mechanism II:  $\Delta H = -336$  kJ mol<sup>-1</sup>

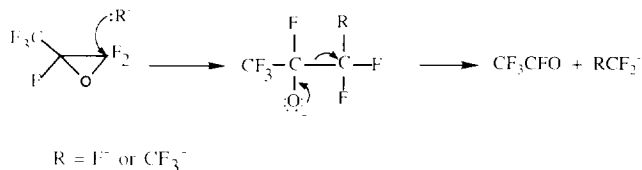


In mechanism I,  $C_2F_5^-$  attacks the terminal carbon resulting in the formation of  $F^-$  and the  $CF_3COCF_2CF_2CF_3$  isomer. In mechanism II, on the other hand, the ion attacks the more substituted carbon, leading to a more stable isomer  $CF_3CF_2CF(CF_3)COF$  (see Table 1) as a product. Furthermore, in mechanism II, the negative charge on the O atom of the intermediate is stabilized by two electron-withdrawing F atoms attached to the nearest carbon, whereas in mechanism I, the negative charge is stabilized by only one nearest F atom. In the light of the above reasoning, the reaction most likely proceeded via mechanism II.

The presence of  $C_2F_4O$  was also inferred as a product of the reactions of  $F^-$  and  $CF_3^-$  with HFPO:

| Reaction  | $\Delta H$<br>(kJ mol <sup>-1</sup> ) | Rate<br>constant<br>(10 <sup>-10</sup><br>cm <sup>3</sup><br>s <sup>-1</sup> ) | Equation<br>No. |
|---|---------------------------------------|--|-----------------|
| $F^- + C_3F_6O \rightarrow CF_3^- + C_2F_4O$      | -304                                  | 3.3  | (20)            |
| $CF_3^- + C_3F_6O \rightarrow C_2F_5^- + C_2F_4O$ | -324                                  | 2.4  | (21)            |

These reactions probably occur by an attack at the terminal carbon:



Although this reaction mechanism is similar to that proposed for reactions (13)–(15), the attack on the terminal carbon leads to a less stable intermediate [see discussion of reaction (19)] and, consequently, a lower reaction rate.

As a secondary reaction in the study of the  $C_2F_5^-$  reactions with HFPO,  $C_4F_9^-$  was observed to react with HFPO forming  $C_3F_7O^-$  via a fluoride ion transfer process:

| Reaction  | $\Delta H$<br>(kJ mol <sup>-1</sup> ) | Rate<br>constant<br>(10 <sup>-10</sup> cm <sup>3</sup><br>s <sup>-1</sup> ) | Equation<br>No. |
|---|---------------------------------------|---|-----------------|
| $C_4F_9^- + C_3F_6O \rightarrow C_3F_7O^- + C_4F_8$ | -209                                  | 3.0   | (22)            |

The association reaction of  $F^-$  and HFPO was not observed, however. It should be noted that in the study of the  $F^-$  reactions,  $C_4F_9^-$  was observed as a secondary ion and  $C_3F_7O^-$  as a tertiary ion. In fact,  $C_3F_7O^-$  is the most abundant product

ion at high pressures. Traces of  $\text{CF}_3^-$  were also detected. We believe that this product is a result of impurities in the system.

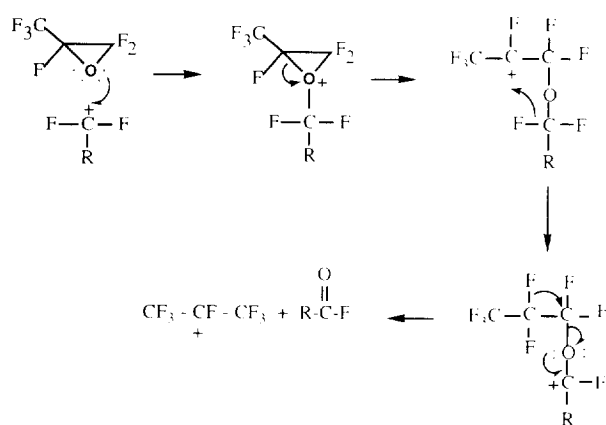
In solution, most nucleophiles react with HFPO by attacking the more substituted carbon [2–5,24,25,30,56]. Our results indicate that the reactions in the gas phase have the same preference. Attack at the terminal carbon was also observed in solution for nucleophiles exhibiting large steric hindrance [57]. In the gas phase however, small nucleophiles ( $\text{F}^-$ ,  $\text{CF}_3^-$ ) attack HFPO at the terminal carbon quite readily [see reactions (20) and (21)]. However,  $\text{C}_2\text{F}_5^-$  does not follow this trend. This is probably not an effect of steric hindrance. The heat of reaction for the process  $\text{C}_2\text{F}_5^- + \text{C}_3\text{F}_6\text{O} \rightarrow \text{C}_3\text{F}_7^- + \text{C}_2\text{F}_4\text{O}$  is  $-420 \text{ kJ mol}^{-1}$  which is more exothermic than both reactions (20) and (21). The reason why this reaction was not observed is yet unclear.

#### 4.2. Reactions of positive ions ( $\text{CF}_3^+$ and $\text{C}_2\text{F}_5^+$ ) with HFPO

Although reactions of HFPO with electrophiles in solution are rare, HFPO appears to react quite readily with  $\text{CF}_3^+$  and  $\text{C}_2\text{F}_5^+$  in the gas phase with rate constants comparable to those for the reactions with the corresponding negative ions. The  $\text{C}_3\text{F}_7^+$  ion is the only product of the reaction between HFPO and  $\text{CF}_3^+$ , and it is the major product in the reaction between HFPO and  $\text{C}_2\text{F}_5^+$ .

| Reaction  | $\Delta H$<br>( $\text{kJ mol}^{-1}$ ) | Rate constant<br>( $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ) | Equation No. |
|---|--|---|--------------|
| $\text{CF}_3^+ + \text{C}_3\text{F}_6\text{O} \rightarrow \text{C}_3\text{F}_7^+ + \text{CF}_2\text{O}$                   | -159                                   | 7.2   | (23)         |
| $\text{C}_2\text{F}_5^+ + \text{C}_3\text{F}_6\text{O} \rightarrow \text{C}_3\text{F}_7^+ + \text{C}_2\text{F}_4\text{O}$ | -227                                   | 6.3   | (24)         |

In both cases the formation of  $\text{C}_3\text{F}_7^+$  occurs with similar rates, suggesting a common mechanism. The reactions are probably initiated by the positive ion attacking the oxygen atom:



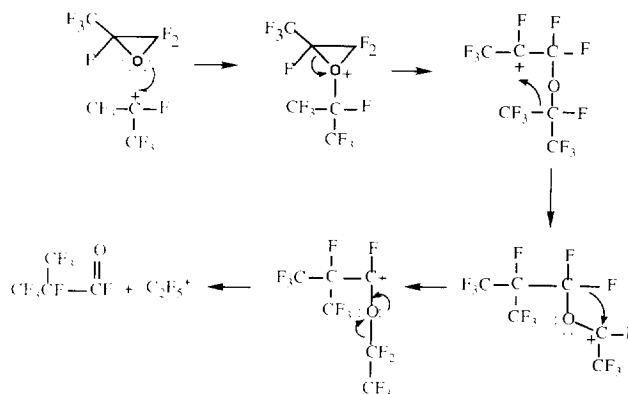
Reaction of  $\text{C}_2\text{F}_5^+$  with HFPO also produces  $\text{C}_2\text{F}_3\text{O}^+$ .

| Reaction  | $\Delta H$<br>( $\text{kJ mol}^{-1}$ ) | Rate constant<br>( $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ) | Equation No. |
|---|--|---|--------------|
| $\text{C}_2\text{F}_5^+ + \text{C}_3\text{F}_6\text{O} \rightarrow \text{C}_2\text{F}_3\text{O}^+ + \text{C}_3\text{F}_8$ | -503                                   | 1.3   | (25)         |

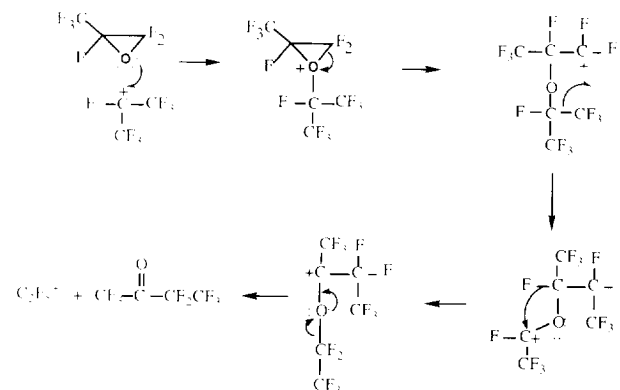
As secondary processes in the study of the  $\text{CF}_3^+$  reaction with HFPO,  $\text{C}_3\text{F}_7^+$  was observed to react with HFPO producing  $\text{C}_2\text{F}_5^+$ ,  $\text{C}_3\text{F}_5\text{O}^+$  and  $\text{C}_6\text{F}_{13}\text{O}^+$ :

| Reaction  | $\Delta H$<br>( $\text{kJ mol}^{-1}$ ) | Rate constant<br>( $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ) | Equation No. |
|---|--|---|--------------|
| $\text{C}_3\text{F}_7^+ + \text{C}_3\text{F}_6\text{O} \rightarrow \text{C}_2\text{F}_5^+ + \text{C}_4\text{F}_8\text{O}$ | -422 or<br>-345                        | 2.2   | (26)         |
| $\quad \rightarrow \text{C}_3\text{F}_5\text{O}^+ + \text{C}_3\text{F}_8$   | -385                                   | 1.4   | (27)         |
| $\quad \rightarrow \text{C}_6\text{F}_{13}\text{O}^+$   | < -634                                 | 5.4   | (28)         |

Reaction (26) could occur by any of the following mechanisms:

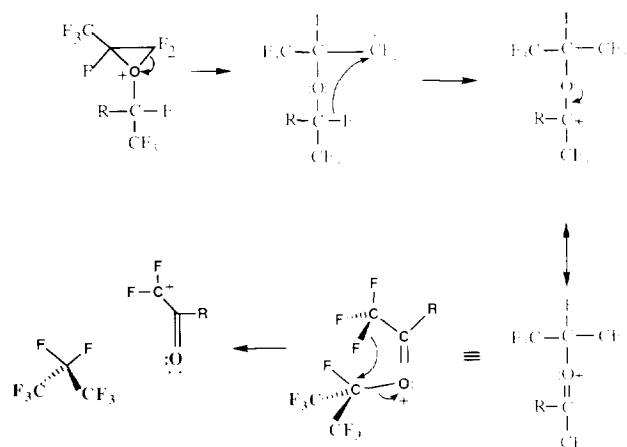


or

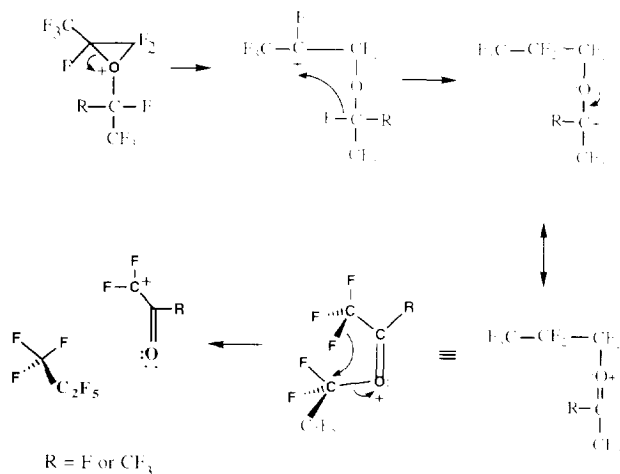


The first mechanism, which results in a more stable isomer of  $\text{C}_4\text{F}_8\text{O}$  (see Table 1) as a product, is the more probable reaction process. A small portion of  $\text{C}_2\text{F}_5^+$  could be produced by collision-induced dissociation [40].

Reactions (25) and (27) yield  $C_3F_8$  with similar rates. This result suggests that they proceed via a similar mechanism:



This mechanism involves two  $F^-$  shifts. Alternatively, ring-opening can take place between oxygen and the more substituted carbon:



Both of the above mechanisms yield the same products. The latter however proceeds via a more stable (secondary) carbonium ion as an intermediate and is therefore considered to be the more likely process. The ionic product ( $C_2F_3O^+$ ) in reaction (25) possibly rearranges itself via an  $F^-$  shift to form the isomer  $CF_3CO^+$  which is believed to be more stable than the isomer  $\dot{C}F_2CFO$  based on a similar argument as that for the  $C_3F_5O^+$  ion discussed in Section 3.

It is possible that reaction (27) occurs by a simple one-step  $F^-$  transfer:



This mechanism is less likely since  $F^-$  transfer was not observed in the reactions of  $CF_3^+$  and  $C_2F_5^+$  with HFPO.

An association reaction (28) was observed. This adduct is probably a stabilized intermediate of reaction (27). While the structure of  $C_6F_{13}O^+$  is not clear, an estimation of the enthalpies of formation of a few possible isomers of  $C_6F_{13}O^+$  (see Table 1) suggests that reaction (28) is highly exothermic.

Reactions (24) and (26) together constitute a catalytic cycle, i.e., the formation of  $C_2F_4O$  and  $C_4F_8O$  from  $C_3F_6O$  catalyzed by either  $C_2F_5^+$  or  $C_3F_7^+$ :



A similar ion-catalyzed scheme has been reported for the reaction of  $CF_3^+$  with  $C_2F_4$  [58]. Combination of reactions (13) and (19) have a similar catalytic property. However, because reaction (19) is much slower than reaction (13), this catalytic cycle is not considered to be important.

## 5. Summary and conclusions

Several types of reactions were observed for the interactions of selected positive and negative fluorocarbon ions with HFPO in the gas phase. Many of these reactions proceed rapidly. Negative ions prefer the attack at the more substituted carbon of the epoxide. The major channel for all three negative ions studied is the transfer of  $C_2F_4$  from HFPO to form the neutral product  $CF_2O$  and the corresponding ions. A minor channel is the formation of the  $CF_3O^-$  ion by a  $C_2F_3^+$  transfer from HFPO. Attack at the terminal carbon of HFPO by  $F^-$  and  $CF_3^-$  to produce  $C_2F_4O$  via a  $CF_2$  transfer was also observed with lower reactivities compared to the attack at the more substituted carbon.

HFPO reacts with  $CF_3^+$ ,  $C_2F_5^+$  and  $C_3F_7^+$  quite rapidly, with rate constants comparable to the negative ion reactions studied. These ions attack the oxygen atom of HFPO with a subsequent ring-opening. Most of the positive ion reactions occur with multiple steps. While negative ions favor a transfer of an ion or a neutral species with HFPO, positive ions prefer a formal exchange reaction. The major reaction of both  $CF_3^+$  and  $C_2F_5^+$  with HFPO is a formal exchange of an  $F^-$  ion from the positive ion with an  $O^{2-}$  ion derived from HFPO to form  $C_3F_7^+$ . Reactions of  $C_2F_5^+$  and  $C_3F_7^+$  with HFPO also occur via a formal exchange of two  $F^-$  ions from the positive ion with an  $O^{2-}$  ion from HFPO to form  $C_3F_8$ .

The reaction of  $C_2F_5^+$  with HFPO features an interesting complication in that the  $C_3F_7^+$  product ion also reacts with HFPO to regenerate  $C_2F_5^+$  with a comparable rate. This two-step sequence leads to the formation of  $C_2F_4O$  and  $C_4F_8O$  catalyzed by  $C_2F_5^+$ .

## Acknowledgments

Part of this work was supported by a contract between E.I. duPont de Nemours and Company and T. Su through the



University of Massachusetts, Dartmouth. Financial support from the National Science Foundation (CHE-9122304) to G. Hammond is acknowledged with gratitude.

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