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Competitive Addition of Near-Thermal Fluorine-18 Atoms to Olefins[1]

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Abstract: Near-thermal ^{18}F atoms, produced by the $^{19}F(n,2n)^{18}F$ nuclear reaction and moderated in kinetic energy by collisions with excess SF_6, have been reacted with the fluorinated ethylenes. The radicals formed by ^{18}F addition are predominantly collisionally stabilized at 5 atm of pressure and are identified after abstraction of H from HI as the corresponding fluoroalkane-^{18}F. In intermolecular competition, the ^{18}F atoms react preferentially with less fluorinated positions. Intramolecularly, ^{18}F addition is also preferred at the less fluorinated end of the molecule. The competitive reaction ratios per molecule are generally independent of olefin/HI ratios, as well as of the ratios of two competing olefinic substrate molecules. The decomposition by CF_2 loss of $CHF^{18}FCF_2^*$ radicals from near-thermal addition of ^{18}F to $CHF{=}CF_2$ proceeds with a pressure for half stabilization of 45 ± 5 Torr in $CHF{=}CF_2$.

The energetic ^{18}F atoms formed by nuclear reactions on fluorine-containing compounds are well suited for many studies of fluorine atom reactions without some of the experimental difficulties associated with the handling of macroscopic amounts of F, HF, F_2, etc.[2-8] We have now used this technique for a study of the intermolecular and intramolecular competitions in F-atom addition to ethylene and several fluorinated ethylenes. The experimental conditions have been deliberately chosen to minimize the average kinetic energy of the ^{18}F atoms at the time of addition, and the observed reactions should be very similar in relative yields to those characteristic of true thermal F atom studies.

The ^{18}F atoms have been formed by the $^{19}F(n,2n)^{18}F$ nuclear reaction in gaseous SF_6[9] with which ^{18}F is quite unreactive.[5,6] Consequently, when SF_6 is present as the major component, most ^{18}F atoms lose much or all of their extra kinetic energy in elastic and inelastic collisions with SF_6 and react with minor components chiefly as thermal or near-thermal ^{18}F atoms.[10] When the minor components are olefins, the exothermic addition of ^{18}F leads to an excited fluoroalkyl-^{18}F radical which can be readily detected later after reaction with HI, through observation of the corresponding fluoroalkane-^{18}F. The chief complication in these experiments arises from the instability of the excited fluoroalkyl radicals toward secondary decomposition, and this decomposition can be minimized to some extent by conducting the experiments at higher pressures, thereby favoring rapid collisional stabilization of the excited radicals.[6] The important ^{18}F reactions with the olefins are illustrated in eq 1-6 for the specific example of vinyl fluoride:

$$^{18}F + CH_2{=}CHF \longrightarrow CH_2{}^{18}FCHF^* \quad (1)$$

$$^{18}F + CH_2{=}CHF \longrightarrow CH_2CHF^{18}F^* \quad (2)$$

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[1] This research was supported by AEC Contract No. AT-(04-3)-34, Agreement No. 126.

[2] N. Colebourne, J. F. J. Todd, and R. Wolfgang, "Chemical Effects of Nuclear Transformations," Vol. 1, International Atomic Energy Agency, Vienna, 1965, p 149.

[3] J. F. J. Todd, N. Colebourne, and R. Wolfgang, *J. Phys. Chem.*, 71, 2875 (1967).

[4] Y.-N. Tang, T. Smail, and F. S. Rowland, *J. Amer. Chem. Soc.*, 91, 2130 (1969).

[5] T. Smail and F. S. Rowland, *J. Phys. Chem.*, 74, 1866 (1970).

[6] T. Smail, G. Miller, and F. S. Rowland, *ibid.*, 74, 3464 (1970).

[7] C. McKnight and J. W. Root, *ibid.*, 73, 4430 (1969).

[8] C. McKnight, N. J. Parks, and J. W. Root, *ibid.*, 74, 217 (1970).

[9] The nuclear reaction also occurs with any other fluorine-containing species in direct proportion to the number density of F atoms per milliliter in the target bulb. The *molecular* site of the nuclear reaction is of no importance for ^{18}F formation, but a relatively inert molecule chemically is desirable as target in order to focus the subsequent ^{18}F chemistry upon the components of major interest, in this case, the olefin.

[10] The expression "near thermal" is necessarily somewhat vague. While a small fraction of ^{18}F atoms, varying with mole fraction of SF_6, certainly react while hot, the great bulk of the reacting ^{18}F atoms have made very many collisions without reaction and probably have a distribution of kinetic energies not very different from a Maxwellian distribution. Since we have not yet been able to vary target temperatures, we are unable to demonstrate experimentally that most of the ^{18}F atoms are reacting while in an essentially thermal distribution. We believe that the reacting distribution is very largely thermal with a few per cent higher energy tail and have used "near thermal" to describe this kind of distribution. Experiments are in progress which should clarify the characteristics implied by such terminology.

$$CH_2{}^{18}FCHF^* + M \longrightarrow CH_2{}^{18}FCHF + M \qquad (3)$$

$$CHF{}^{18}FCH_2{}^* + M \longrightarrow CHF{}^{18}FCH_2 + M \qquad (4)$$

$$CH_2{}^{18}FCHF + HI \longrightarrow CH_2{}^{18}FCH_2F + I \qquad (5)$$

$$CHF{}^{18}FCH_2 + HI \longrightarrow CHF{}^{16}FCH_3 + I \qquad (6)$$

Reactions 1 and 2 can both also be initiated by translationally "hot" ^{18}F atoms, with the result that the difluoroethyl radicals are excited to a higher energy representing both the exothermicity of the addition reaction plus the extra kinetic energy as well. The lifetimes of these radicals toward decomposition are consequently much shorter than those formed by the thermal addition of ^{18}F atoms to olefins. Rough estimates of radical lifetimes for fluoroethyl radicals, in analogy with ethyl radicals, suggest that kinetic energies of ^{18}F atoms of about 2-eV translational energy are large enough that only a small fraction survives long enough for reactions 3 or 4 to occur. The contribution of hot ^{18}F reactions to the final products of (5) and (6) is thus inherently limited to atoms possessing about 2 eV or less kinetic energy at the time of the initial addition reaction. After taking cognizance of these decomposition possibilities, the intramolecular competition between addition to the CHF and CH_2 ends of vinyl fluoride can be measured through the respective yields of $CHF{}^{18}FCH_3$ and $CH_2{}^{18}FCH_2F$. Similarly, the intermolecular competition between vinyl fluoride and ethylene can be studied with the determination of $C_2H_5{}^{18}F$ in addition to the two difluoroethylenes formed in (5) and (6).

Experimental Section

Formation of ^{18}F from (n,2n) Reaction in SF_6. The ^{18}F atoms were formed by the ^{19}F (n,2n) reaction with fast neutrons produced by a Kaman A711 fast neutron generator.[5,6] Total ^{18}F production was monitored with a Teflon-sleeve monitor described earlier.[6]

A small yield of $SF_5{}^{18}F$ was always observed from reaction 7. Presumably, since the S–F bond dissociation energy in SF_6 is only about 86 kcal/mol, appreciable unimolecular decomposition of excited $SF_5{}^{18}F^*$ could occur,[11] leading to the formation of other molecules containing both S and ^{18}F; no such products have yet been detected by our standard radio gas chromatographic analytical technique. In addition, some ^{18}F atoms react by H abstraction with hydrogeneous materials such as C_2H_4 or HI, as shown in (8)

$$^{18}F + SF_6 \longrightarrow SF_5{}^{18}F + F \qquad (7)$$

and (9), to form $H^{18}F$. The latter would also not be detected in our standard analysis because of its high reactivity with the sample

$$^{18}F + C_2H_4 \longrightarrow H^{18}F + C_2H_3 \qquad (8)$$

$$^{18}F + HI \longrightarrow H^{18}F + I \qquad (9)$$

bulb walls and with the components of the chromatographic system. Separate experiments to measure $H^{18}F$ have shown its presence in hydrogen-containing systems.[12] The observed absolute yields of ^{18}F do not sum to 100% in our experiments chiefly because of these losses to unmeasured $H^{18}F$ but do fall in the range from 40 to 75%.

Chemicals. Ethylene was Phillips Research Grade; *trans*-CHF=CHF was purified by gas chromatography from the cis/trans mixture supplied by Peninsular Chem Research. Vinyl fluoride, $CH_2{=}CF_2$ (both Matheson Co.), and $CHF{=}CF_2$ and C_2F_4 (both Peninsular Chem Research) were all degassed at −196°, and then distilled from −78° baths. This process removed any traces of polymerization inhibitor when present. The purity of the SF_6 (Matheson Co.) was stated as 98%; gas chromatographic purification of SF_6 did not seem to affect the product yields or distributions in some preliminary experiments, and most experiments were carried out without further purification of the SF_6, other than rigorous degassing.

Radio Gas Chromatography. The ^{18}F content of volatile products was determined by radio gas chromatography with an external flow proportional counter detector.[5,6] Since many of the partially fluorinated ethanes and other possible products were not commercially available, a number of compounds were synthesized in varying degrees of purity for calibration of the gas chromatographic columns. A sample of $CH{\equiv}CF$ was synthesized by the method of Middleton and Sharkey.[13] Several fluoroethanes (CHF_2CHF_2, CH_2FCH_2F, and CH_2FCF_3) were prepared by the photolysis at 130° of suitable mixtures of the ketones $(CHF_2)_2CO$, $(CH_2F)_2CO$, and $(CF_3)_2CO$.[14] An authentic sample of CH_3CF_3 was kindly furnished by Dr. Hal Jackson of the Du Pont laboratories. The retention times for these macroscopic fluoroethanes all agreed with those found for the ^{18}F-labeled carrier-free products expected from ^{18}F addition to an olefin, followed by H atom abstraction by the resultant radical, *e.g.*, from $CHF{=}CF_2$, only $CHF{}^{18}FCHF_2$ and $CH_2FCF_2{}^{18}F$ were observed. With this background information, the retention time for CH_2FCHF_2 was determined on each column solely from the location of the peak for the major volatile product (~40% of total ^{18}F) from ^{18}F reaction with CHF=CHF/HI mixtures.

A variety of chromatographic columns was used for the separation of the products observed from reaction with the various partially fluorinated ethylenes. Low-boiling products were separated either with a 50-ft propylene carbonate-on-alumina column or a 100-ft di-*n*-butyl phthalate column. Frequently, samples were also separated on a dimethylsulfolane column, either 25, 50, or 125 ft in length. The elution times for several fluorinated molecules with the 25-ft column at 25° and 0.5 ml/sec flow rate were (in minutes): air, 5; $CH{\equiv}CF$, 7.3; CH_3CF_3, 13.0; C_2H_5F, 21.0; CH_2FCF_3, 24.2; CH_3CHF_2, 29.4; CHF_2CHF_2, 71; CH_2FCHF_2, 120.

A separation of CH_2FCH_2F and CHF_2I was conveniently performed with a silicone oil column (either 25 or 50 ft) operated at 68°. With the 50-ft column at 68 ± 2° and a helium flow rate of 0.5 ml/sec, the following retention times were observed (in minutes): air, 9; CH_2FCH_2F, 37.4; CHF_2I, 83.

Various combinations of columns were used for "one aliquot" separations of all of the volatile, nonreactive products from particular samples, following the procedures described earlier.[5,6] No measurements were made of the yields of inorganic or nonvolatile ^{18}F-containing molecules.

Sample Preparation. The preparation of samples followed the standard procedures described earlier, using a grease-free vacuum system. The HI and olefin pressures were measured with a spiral-gauge manometer.

All intermolecular competition samples contained a large excess of SF_6 with a standard composition: SF_6, 3550 ± 90 Torr; total olefin, 170 ± 5 Torr; HI, 17 ± 2 Torr. The total pressure was effectively limited by the characteristics of the glass vacuum line used in handling the samples.

Results and Discussion

Reactions of Hot and Epithermal ^{18}F Atoms. The ^{18}F atoms formed at energies of 10^5 eV must be moderated through the high energy, "hot" range prior to reaction near thermal energies, and some reactions initiated at high energies (*e.g.*, 5–15 eV) must be statistically expected for those ^{18}F atoms which happen to collide with olefin instead of SF_6 while possessing kinetic energies in this range. These hot reactions are minimized by the usual 20/1 ratio of SF_6/Σ(olefins) in our experiments, and, in any event, most of the reactions do not interfere with the studies of lower energy ^{18}F atoms because they lead to different, chromatographically separable products. For example, hot ^{18}F atoms react

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[11] Approximately half of $CF_3{}^{18}F^*$ molecules formed by ^{18}F reaction with CF_4 have excitation energies ≥ 10 eV,[4] while about 90% of $CF_2{=}CF{}^{18}F^*$ molecules formed by ^{18}F reaction with $CF_2{=}CF_2$ decompose by C–C split (76 kcal/mol bond dissociation energy).[6] The average energy of excitation of $CH_3CF_2{}^{18}F^*$ from CH_3CF_3 has also been estimated to be > 10 eV.[8]

[12] N. J. Parks, K. A. Krohn, and J. W. Root, *J. Chem. Phys.*, **55**, 2690 (1971).

[13] W. J. Middleton and W. H. Sharkey, *J. Amer. Chem. Soc.*, **81**, 803 (1959). An intermediate for this synthesis was kindly supplied by Dr. Middleton of the Du Pont laboratories. $CH{\equiv}C{}^{18}F$ is found as a minor yield hot product from several fluoroethylenes.

[14] G. O. Pritchard and J. T. Bryant, *J. Phys. Chem.*, **70**, 1441 (1966); G. O. Pritchard, M. Venugopalan, and T. F. Graham, *ibid.*, **68**, 1786 (1964).

with $CF_2{=}CF_2$ to form $CF_2{=}CF^{18}F^*$, most of which decomposes to $CF_2 + CF^{18}F$, both of which are trapped by HI with the formation of the corresponding difluoroiodomethane. However, the $CHF^{18}FI$ product is readily separated and identified and does not interfere with the determination of the ^{18}F-labeled products from reaction by addition to the π-bond system of the olefin.

Some complication is expected from chemical reactions initiated by epithermal ^{18}F atoms (*e.g.*, 0.5–3 eV), for these atoms can be expected also to add to olefins to form highly excited fluoroalkyl-^{18}F radicals, which in turn exhibit a high decomposition/stabilization (D/S) ratio reflecting this additional excitation energy. These changes can be indicated through measurement of the (D/S) ratio *vs.* SF_6 concentration; for example, with $CF_2{}^{18}FCF_2{}^*$, the minimum energy decomposition path is C–C bond break with the formation of $CF_2{}^{18}F$ $(+CF_2)$, and (D/S) is directly measured by the ratio of $CHF_2{}^{18}F/CF_2{}^{18}FCHF_2$ in the presence of HI. In pure $CF_2{=}CF_2$, this (D/S) is about 0.42 at 5 atm of pressure and can be split rather cleanly into about 70% thermal ^{18}F addition and about 30% energetic ^{18}F addition to the olefin.[6] Under our present conditions of about 3800 Torr total pressure and a 20/1 ratio of SF_6 olefin, the fraction of ^{18}F additions occurring while the ^{18}F carries substantial excess kinetic energy is suppressed somewhat below the value found in pure C_2F_4. Nevertheless, the excited $C_2F_4{}^{18}F^*$ radicals formed by essentially thermal ^{18}F addition contribute a measurable yield of $CF_2{}^{18}F$ (about 0.28 times the yield of stabilized $CF_2{}^{18}FCF_2$) at the 5 atm of pressure used in our experiments.

An estimate of 0.03–0.04 can similarly be made for the fractional decomposition of $CH_2{}^{18}FCH_2{}^*$ radicals at 3800 Torr from the pressure dependence data of Wolfgang *et al.*,[2,3] for ^{18}F reactions with C_2H_4 in an I_2-scavenged system; our observed ratio with HI as scavenger was 0.02–0.03. The excellent agreement between these two high-pressure $CH_2{=}CH^{18}F$ measurements indicates that (a) very few hot ^{18}F reactions with C_2H_4 are found under our experimental conditions; and (b) the relatively small $CH_2{=}CH^{18}F$ yield would only amount to a 2–3% correction to the measured yield of $C_2H_5{}^{18}F$ as an estimate of the original primary yield of $CH_2{}^{18}FCH_2{}^*$.

Decomposition of Other Excited Radicals. Among the products from ^{18}F addition to $CHF{=}CF_2$ is the excited radical $CHF^{18}FCF_2{}^*$, as in (10), which can then undergo either decomposition by one of the three possible paths (11–13), or collisional stabilization (14). The competition between decomposition and stabilization can be monitored by measurement of the D/S

$$^{18}F + CHF{=}CF_2 \longrightarrow CHF^{18}FCF_2{}^* \qquad (10)$$

$$CHF^{18}FCF_2{}^* \longrightarrow CHF^{18}F + CF_2 \qquad (11)$$

$$CHF^{18}FCF_2{}^* \longrightarrow CH^{18}F{=}CF_2 + F \qquad (12)$$

$$CHF^{18}FCF_2{}^* \longrightarrow CF^{18}F{=}CF_2 + H \qquad (13)$$

$$CHF^{18}FCF_2{}^* + M \longrightarrow CHF^{18}FCF_2 + M \qquad (14)$$

ratio: the ratio of the sum of the yields of $[CH_2F^{18}F + CH^{18}F{=}CF_2 + CF^{18}F{=}CF_2]$ *vs.* that of $CHF^{18}FCHF_2$. The first and last of these are formed by abstraction of H from HI by the respective radicals of (11) and (14), while the $CH^{18}F{=}CF_2$ yield must be doubled to correct for formation of $CHF{=}CF_2$ with loss of ^{18}F.

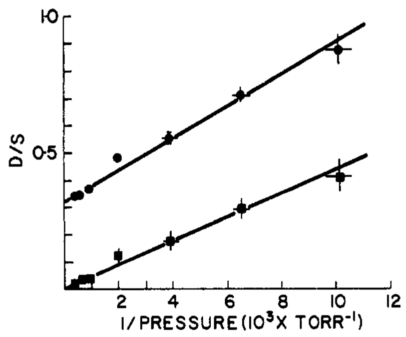

Figure 1. Pressure stabilization of $CHF^{18}FCF_2$ radicals produced by ^{18}F addition to $CHF{=}CF_2$: (●) experimental values; (■) corrected data after subtraction of yield from hot reactions.

Although each of reactions 11–13 is approximately thermoneutral, appreciable decomposition is found only by the C–C split of (11). The pressure dependence of the (D/S) ratio $(CH_2F^{18}F/CHF^{18}FCHF_2)$ measured in pure $CHF{=}CF_2$ shows a nonzero intercept, and yet a linear slope for the plot of (D/S) *vs.* $1/P$ (Figure 1). A linear slope signifies a substantial group of radicals with essentially the same excitation energy, as expected for the addition of thermal F atoms to the olefin. However, if all of the radicals were formed in this manner, a zero intercept is predicted at infinite pressure. The nonzero intercept indicates a second group of reacting radicals, those with sufficient energy to undergo decomposition at the highest experimental pressures used here. A third group of radicals is presumably also present, with excitation energies larger than those of the radicals formed by thermal F atoms and yet insufficient to cause complete decomposition at the highest experimental pressure. However, the absence of appreciable curvature in the plot of (D/S) *vs.* $1/P$ indicates that this third group is quite small relative to the first two.

The observed yields can be divided into two radical groups formed by the addition of hot and of thermal ^{18}F atoms through extrapolation of the experimental straight line to $1/P$ = zero. The intercept then measures the yield of radicals formed by addition of hot ^{18}F atoms. Subtraction of this hot yield at each pressure leaves the residual straight line passing through zero shown in Figure 1. The thermal decomposition step for this excited radical clearly involves C–C bond rupture, in analogy with the decomposition path observed for $CF_2{}^{18}FCF_2{}^*$. The half pressure for stabilization of the thermal component of $CHF^{18}FCF_2{}^*$ can be evaluated as 45 ± 5 Torr from the slope of the plot of Figure 1; the corresponding value for $C_2F_4{}^{18}F^*$ is 218 ± 15 Torr.[6]

The effects of moderator SF_6 upon several of the product yields from ^{18}F reaction with $CHF{=}CF_2$ are illustrated in Figure 2. These data on $CH_2F^{18}F$ yields are combined with the stabilized yield of $CHF^{18}FCF_2$ radicals (measured as $CHF^{18}FCHF_2$ and not shown in Figure 2) to give the D/S ratio *vs.* moderator in Table I. Even at the highest SF_6 mole fraction, some of the $CHF^{18}FCF_2{}^*$ radicals still decompose to $CHF^{18}F + CF_2$, as anticipated from the thermal component plot of Figure 1. The contribution of hot additions to this yield could probably be reduced somewhat by utilizing a higher ratio of SF_6/olefin, perhaps 100/1 or 1000/1,

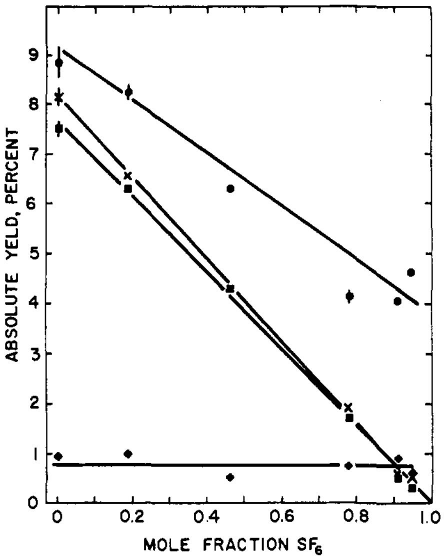

Figure 2. Effect of SF$_6$ moderator upon product yields from ^{18}F reactions with $CHF{=}CF_2$: (●) $CH_2F^{18}F$; (×) $CHF^{18}FI$; (◆) $CHF_2{}^{18}F$; (■) $CH^{18}F{=}CF_2$ + $CHF{=}CF^{18}F$; total pressure, 2500 Torr; ratio ($CHF{=}CF_2$)/HI) = 10.0 ± 0.2.

but this procedural alteration would have only a minor effect on the relative yields measured in competition between olefins while complicating our sample handling procedures.

Table I. Effect of Added SF$_6$ Moderator upon Decomposition/Stabilization Ratios for $CHF^{18}FCF_2$ Radicals

Mole fraction,[a] SF$_6$	D/S = $CH_2F^{18}F$/ $CHF^{18}FCHF_2$
0.0	0.34 ± 0.02
0.19	0.26 ± 0.01
0.46	0.16 ± 0.01
0.78	0.09 ± 0.01
0.91	0.10 ± 0.02

[a] Total pressure: 2500 ± 100 Torr; $CHF{=}CF_2$/HI = 10.

Radical Decomposition by Carbene Loss. The decomposition of $C_2F_4{}^{18}F^*$ by loss of CF$_2$ is calculated to be exothermic by 17 kcal/mol (see Table II) and therefore energetically favored over the loss of F (either ^{18}F or one of the others) from the excited radical. Similarly, the loss of CF$_2$ from the excited $CHF^{18}FCF_2{}^*$ radical of Figures 1 and 2 is approximately thermoneutral and can be reasonably expected from radicals excited by near-thermal ^{18}F atom addition. On the other hand, the loss of CH$_2$ from excited $CH_2{}^{18}FCH_2{}^*$ is a highly endothermic pathway (ΔH = +52 kcal/mol) and gives at most a very minor reaction yield, initiated entirely by hot ^{18}F atoms. The very high average bond energy of C–F bonds in CF$_2$ (about 125 kcal/mol) relative to ethylenic C–F bonds (about 110 kcal/mol) is the chief source for the steady trends in ΔH for C–C bond rupture shown in Table II. The experimental measurements of D/S in this table confirm that the only radicals undergoing appreciable C–C bond rupture with carbene formation are those in which the carbene fragment is CF$_2$.

Although the heats of formation of many of these fluorinated species are relatively uncertain, the replacement of H by ^{18}F is calculated to be exothermic throughout, and the replacement of F by ^{18}F is thermoneutral. Thus, the loss of H atom from an excited radical is certainly the energetically preferred mechanism of decay for $CH_2{}^{18}F$-$CH_2{}^*$[2,3,15] and could be an important outlet for decomposition of some of the other radicals. Furthermore, the loss of a fluorine atom from the excited radical must always be considered as a possible decay mode. Nevertheless, the yield of $CH_2{}^{18}F$ (observed as $CH_3{}^{18}F$) is much higher in pure $CH_2{=}CF_2$ systems than is the yield from the exothermic loss of H; when moderated in excess SF$_6$, the endothermic CF$_2$ loss is effectively suppressed. This apparent preference for the more endothermic route in hot reactions suggests that some other factor is outweighing the normal energetic preferences. The necessity for motion for *all* four substituent atoms of $CH_2{=}CF_2$ in attaining the near-tetrahedral configurations of both $CH_2{}^{18}F$ and CF$_2$ in ground-state $CH_2{}^{18}FCF_2$ may act as a dynamic drag on the completion of this radical-forming reaction;[16] the C–C bond rupture can then be the path favored by this inertial resistance. In contrast, a radical such as $CH_2{}^{18}FCH_2$ would be tetrahedral only on the methyl carbon, with planar C–H's on the methylene end,[17] requiring no change from the position in the original olefin.

After addition to a CH$_2$ position to form $CH_2{}^{18}F$, the subsequent loss of ^{18}F is the observational equivalent in our experiments to a highly inelastic scattering of the original ^{18}F atom. After addition to CHF or CF$_2$ positions, however, the loss of F can leave the ^{18}F-labeled parent molecule as a product. Since the hot ^{18}F-for-H and ^{18}F-for-F substitution reactions occur readily at C–H and C–F positions not involving π-bond systems,[2–5] the separate identification of reactions involving hot, direct substitutions from those occurring with H or F atom loss from radical intermediates requires detailed study of each molecular system. Our experiments indicate that decomposition of excited radicals by H or F atom loss accounts for only a minor fraction of the radicals with any of these substrates at these pressures.[18] The near absence of the ^{18}F/H products indicates not only that decomposition of a radical by H loss is quite unlikely but also that the direct substitution reaction does not often leave a stable product. Radical decomposition (10%) at 3800 Torr by these atomic loss pathways may be quite possible for some of the radicals. In our competitive studies reported below, these corrections are not important except for relative measurements requiring an accuracy better than ±20–30%.

Efficiency of HI as a Radical Scavenger. These experiments rely heavily on the high efficiency of reacaction 15 for conversion of all of the fluoroalkyl-^{18}*F*

$$R + HI \longrightarrow RH + I \tag{15}$$

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(15) R. L. Williams and F. S. Rowland, unpublished results.

(16) The nonplanarity of CF$_3$ and CHF$_2$ radicals should carry over to $\geqslant CCF_2$ radicals: see R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 43, 2704 (1965); D. E. Milligan and M. E. Jacob, *ibid.*, 48, 2265 (1968).

(17) See L. Andrews and G. Pimentel, *ibid.*, 47, 3637 (1967), for calculations concerning the planarity of CH$_3$.

(18) For all of the radicals containing both F and H, the loss of HF with the formation of a vinyl radical is also an exothermic process (*e.g.*, $CH_2FCH_2 \rightarrow CH_2{=}CH + HF$; ΔH = −30 kcal/mol) and might possibly occur. Small yields of vinylic radicals are observed in some of these systems.

Table II. Energetics and Yields for Decomposition Pathways for Fluoroethyl Radicals Formed by Addition of ^{18}F to Olefins

Olefin	Radical	Decomposition products	ΔH, kcal/mol	D/S	
				Olefin[a] alone	SF_8/olefin[b]
$CF_2{=}CF_2$	$CF_2{}^{18}FCF_2$	$CF_2{}^{18}F + CF_2$	−17	0.42 ± 0.04	0.28
		$CF^{18}F{=}CF_2 + F$	0	<0.02	<0.01
$CHF{=}CF_2$	$CHF^{18}FCF_2$	$CHF^{18}F + CF_2$	+2	0.34 ± 0.02	0.12
		$CH^{18}F{=}CF_2 + F$	0	<0.1	<0.02
		$CF^{18}F{=}CF_2 + H$	−5	<0.02	<0.01
	$CF_2{}^{18}FCHF$	$CF_2{}^{18}F + CHF$	+9	0.07 ± 0.02	<0.2[c]
		$CF^{18}F{=}CHF + F$	0	<0.2[f]	<0.05
$CH_2{=}CF_2$	$CH_2{}^{18}FCF_2$	$CH_2{}^{18}F + CF_2$	+18	0.29 ± 0.02	0.01
		$CH^{18}F{=}CF_2 + H$	−3	0.05 ± 0.01[d]	<0.01
	$CF_2{}^{18}FCH_2$	$CF_2{}^{18}F + CH_2$	+38	0.04 ± 0.01	<0.01
		$CF^{18}F{=}CH_2 + F$	0	<0.2[f]	<0.01
$CHF{=}CHF$ (trans)	$CHF^{18}FCHF$	$CHF^{18}F + CHF$	+13	0.05 ± 0.01	~0.05
		$CH^{18}F{=}CHF + F$	0	<0.15	<0.03
		$CF^{18}F{=}CHF + H$	−20	<0.12[d]	<0.02
$CH_2{=}CHF$	$CH_2{}^{18}FCHF$	$CH_2{}^{18}F + CHF$	+27	0.06 ± 0.03[e]	<0.1[c]
		$CH^{18}F{=}CHF + H$	−5	<0.05	<0.01
	$CHF^{18}FCH_2$	$CHF^{18}F + CH_2$	+40	0.03 ± 0.02	<0.01
		$CH^{18}F{=}CH_2 + F$	0	<0.1[f]	<0.03
		$CF^{18}F{=}CH_2 + H$	−21	<0.05	<0.01
$CH_2{=}CH_2$	$CH_2{}^{18}FCH_2$	$CH_2{}^{18}F + CH_2$	+52	No ^{18}F source	~0.02
		$CH^{18}F{=}CH_2 + H$	−7		~0.05

Heats of Formation, kcal/mol

		Ref			Ref			Ref
H	52.1	*g*	CH_2	+90	*h*	CH_2CHF	−28	*i*
F	18.9	*j*	CF_3	−116	*k*	CH_2CF_2	−82.5	*l*
HF	−64.8	*g*	CHF_2	−59 ± 4	*m*	CHFCHF	−66	*n*
CF_2	−39 ± 3	*k*	CH_2F	−7 ± 4	*m*	$CHFCF_2$	−119	*l*
CHF	+25	*n*	CH_2CH_2	+12.5	*g*	CF_2CF_2	−157	*l*

[a] Measured from the yield of the corresponding fluoroalkanes, after reaction of the radicals with HI. Total pressure, 2500 Torr. [b] All samples contained: SF_6, 3550 Torr; olefin, 170 Torr; HI, 17 Torr. [c] Upper limit; not completely resolved from other products. [d] Including direct ^{18}F for H with no radical intermediate, if this mechanism is present. [e] A rough correction has been estimated for $CH_3{}^{18}F$ from $CH^{18}F$, another reaction product in this system. [f] Including direct ^{18}F for F, which is known to be present in nontrivial yield. [g] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965). [h] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [i] P. G. Maslov and Yu. P. Maslov, *Khim. Tekhnol. Topl. Masel*, **13**, 50 (1968). [j] We continue to use the "old" value of 18.9 (*g*). A value of 15.5 has been given by V. H. Dibeler, J. A. Walker, and K. E. McCulloh, *J. Chem. Phys.*, **50**, 4592 (1969). [k] K. F. Zmbov, O. M. Uy, and J. L. Margrave, *J. Amer. Chem. Soc.*, **90**, 5090 (1968). [l] J. R. Lacher and H. A. Skinner, *J. Chem. Soc. A*, 1034 (1968). [m] Based on ΔH_f for CH_3F (−55.9 ± 0.8) and CH_2F_2 (−108.2 ± 0.2) from *l* combined with assumed C–H bond dissociation energies of 101 ± 4 from *h*. [n] Estimated by group additivity.

Table III. Effect of HI Concentration on ^{18}F Atom Addition to Olefins[a]

$\frac{C_2H_4 + C_2HF_3}{HI}$	Yields, % total ^{18}F			Ratios	
	$C_2H_5{}^{18}F$	$CHF^{18}FCHF_2$	$CF_2{}^{18}FCH_2F$	$\frac{CHF^{18}FCHF_2}{CF_2{}^{18}FCH_2F}$	$\frac{^{18}F + CHFCF_2}{^{18}F + C_2H_4}$
28.0	51.9 ± 0.5	10.6 ± 0.2	3.34 ± 0.13	3.2	0.27
10.0	53.5 ± 0.5	11.3 ± 0.2	2.63 ± 0.10	4.3	0.26
4.5	43.8 ± 0.4	10.3 ± 0.2	3.03 ± 0.06	3.4	0.30
2.0	40.0 ± 0.4	10.0 ± 0.2	3.50 ± 0.14	2.9	0.34

[a] All samples contained (Torr): 3580 ± 60 SF_6; 85 ± 4 C_2H_4; 85 ± 4 C_2HF_3; HI as indicated.

radicals formed from the various olefins into the corresponding fluoroalkanes-^{18}F. The change in yield of $C_2H_5{}^{18}F$ with varying HI concentration is shown in Table III, suggesting a competition between ^{18}F addition to the ethylene and direct reaction of ^{18}F with HI, favoring the former by about a factor of 4. In the same system, however, the yield of the products from reaction of ^{18}F with $CHF{=}CF_2$ does not appear to be sensitive to the olefin/HI ratio. These variations in behavior, while not large, appear to be significant and may indicate that the energy ranges for reaction with ^{18}F are sufficiently different that the "competition" is effectively averaged over not quite the same energy range for each molecule. Over a 14-fold change in HI concentration, however, there is no doubt that ^{18}F reacts (a) more readily by a factor of 3–4 with $CH_2{=}CH_2$ than with $CHF{=}CF_2$ in intermolecular competition; and (b) that ^{18}F reacts preferentially with the CHF end of the $CHF{=}CF_2$ molecule in intramolecular competition with the CF_2 end.

Intermolecular Competition. One further possible problem in studying olefinic competitions has been tested with a 25-fold range of mole fraction ratios for mixtures of C_2H_4 and $CHF{=}CF_2$. The results of Table IV show that both the intermolecular and intramolecular competition ratios are reasonably independent of the mole fractions of the olefins present during the experiment and, hence, that the numerical ratios *per molecule* have general validity within roughly 20% error limits.

A series of competitions were then carried out at 5/5/1 ratios of ethylene/competing olefin/HI in order to determine the reactivities of each olefin relative to C_2H_4 as the standard. The trends have been calculated

Table IV. Relative Reactivity of C_2H_4 and $CHF{=}CF_2$ *vs.* Mole Ratio toward Addition of ^{18}F

Target ratio[a] $\frac{CH_2{=}CH_2}{CHF{=}CF_2}$	Product yields, % total ^{18}F			Competitive rates	
	$C_2H_5{}^{18}F$	$CHF^{18}FCHF_2$	$CF_2{}^{18}FCH_2F$	Intermolecular $\frac{(^{18}F + CHF{=}CF_2)}{(^{18}F + CH_2{=}CH_2)}$	Intramolecular $\frac{(CHF^{18}FCF_2)}{(CF_2{}^{18}FCH_2)}$
5.0	59.4 ± 0.6	2.37 ± 0.04	0.69 ± 0.05	0.26 ± 0.01	3.4 ± 0.3
1.0	53.5 ± 0.5	11.3 ± 0.2	2.63 ± 0.10	0.26 ± 0.01	4.3 ± 0.2
0.2	24.0 ± 0.4	24.1 ± 0.2	5.41 ± 0.05	0.25 ± 0.01	4.5 ± 0.1

[a] Samples contained (Torr): 3580 ± 100 SF_6; 170 ± 5 olefin; 17 ± 2 HI.

on the basis of the stabilized fluoroethyl radicals, observed as the corresponding fluoroethanes, without correction for any decomposition of excited radicals. In these comparisons, then, the relative ^{18}F reactivities are being averaged over ^{18}F atoms of thermal or near-thermal energies, with the relative yields summarized in Table V. For convenience, the reactivity per CH_2 group in ethylene has been given the value of 1.0, and both the intermolecular and intramolecular competitions have been expressed in comparison to this standard. Approximate corrections for radical decomposition by CF_2 loss have been made as indicated by the numbers in parentheses in Table V.

Table V. Intermolecular and Intramolecular Selectivity in ^{18}F Atom Addition to Olefins in Excess SF_6

Olefin	Normalized yield per olefinic carbon atom[a] CH_2	CHF	CF_2
$CH_2{=}CH_2$	1.0		
$CHF{=}CH_2$	0.7 (0.8)	0.6	
$CF_2{=}CH_2$	0.8 (1.1)		0.2
trans-CHF=CHF		0.3	
$CHF{=}CF_2$		0.4	0.1
$CF_2{=}CF_2$			0.14 (0.2)

[a] Yield per carbon atom of the stabilized radical formed by addition of ^{18}F to the listed group, relative to CH_2 in ethylene as 1.0. Numbers in parentheses are the yields after approximate correction for decomposition of excited radicals.

The addition of ^{18}F to ethylenes containing C-H or C-F bonds consistently favors, on both an intermolecular and intramolecular basis, addition to the less fluorinated positions. This result is consistent with earlier observations that attack by other radicals proceeds at the molecular end with the greater electron density in the π system, *i.e.*, usually the end with fewer highly electronegative substituents. This simple interpretation is quite satisfactory for reactions with partially fluorinated olefins by electrophilic radicals such as F, CF_3, and Br.[19] However, questions have been raised about the corollary that nucleophilic radicals should differ from electrophiles in their preferences for attack on unsymmetrical olefins.[20] While heats of formation of sufficient accuracy seem to be lacking, it seems also quite probable that the radicals formed by F-atom addition are thermodynamically more stable when the addition is made at the less fluorinated end of a fluorinated ethylene.

The present experimental limitation that the reactions must be carried out in the vicinity of 10° prevents a determination of the role of activation energies in the observed reaction selectivity. More precise measurements of the *thermal* competition between various olefins for ^{18}F atoms require detailed mechanistic studies of each olefin, following the pattern established for C_2F_4,[6] thereby furnishing the necessary corrections for the hot ^{18}F reactions in the same system. Such a study with acetylene is described in the accompanying paper,[21] while several others are now being carried out with various olefinic and acetylenic molecules.

(19) N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 2800 (1957).

(20) See, for example, the reports of entirely terminal attack by both CF_3 and CH_3 upon allene: H. G. Meunier and P. I. Abell, *J. Phys. Chem.*, **71**, 1430 (1967).

(21) R. L. Williams and F. S. Rowland, *J. Amer. Chem. Soc.*, **94**, 1047 (1972).