

Addition of Fluorine-18 Atoms to Acetylene¹

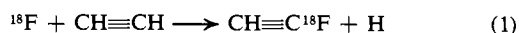
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Abstract: Energetic ¹⁸F atoms from the ¹⁹F(n,2n)¹⁸F nuclear reaction react with acetylene to form CH≡C¹⁸F in 2–3% yield. Both energetic and thermal ¹⁸F atoms form ·CH=CH¹⁸F* by addition to acetylene, and this radical can be observed as CH₂=CH¹⁸F after collisional stabilization followed by reaction with scavenger HI. In excess SF₆, the pressure for half stabilization of ·CH=CH¹⁸F* against ¹⁸F loss is ≤ 200 Torr (lifetime ≥ 5 × 10⁻¹⁰ sec). No evidence was found for pressure-dependent decomposition of ·CH=CH¹⁸F* by H atom loss. The combination of acetylene plus HI serves as an effective scavenger for near-thermal ¹⁸F atoms in various reaction systems.

The study of the reactions of atomic fluorine with acetylenic molecules has been severely limited in the past by the extreme reactivity of some reactants and products (*e.g.*, HF, F₂, etc.), as well as by the ready polymerization of the acetylenic molecules.² The development of radiochemical methods of studying the tracer reactions of ¹⁸F atoms has avoided some of these difficulties,^{3–9} and the particular success of experiments conducted in the presence of excess SF₆ has shown the feasibility of investigations of both translationally hot and of near-thermal ¹⁸F atoms with a wide variety of substrates.^{5–7} We have now applied these techniques to a detailed study of ¹⁸F atom reactions with acetylene.

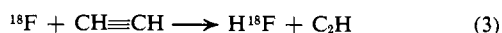
The most important reactions in this system are anticipated by analogy with olefinic systems³ to include (a) substitution of ¹⁸F for H



(b) addition to the π bond



and (c) abstraction of H



All three of these reactions can be initiated by translationally hot ¹⁸F atoms, and the addition of ¹⁸F to acetylene can also be initiated by thermal fluorine atoms. The abstraction process is exothermic by about 20 kcal/mol despite the high bond dissociation energy of C–H in acetylene and probably has a low enough activation energy that this reaction can also be initiated in reasonable yield by fluorine atoms in thermal equilibrium at 25°. ^{10–12}

The subsequent loss of an H atom from the excited fluorovinyl-¹⁸F radical of (2) leads to the same CH≡C¹⁸F product as the direct ¹⁸F/H substitution, while the loss

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

(2) See, for example, M. Hudlicky, "Chemistry of Organic Fluorine Compounds," Macmillan, New York, N. Y., 1962.

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

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

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

(6) T. Smail, R. S. Iyer, and F. S. Rowland, *ibid.*, **75**, 1324 (1971).

(7) T. Smail, R. S. Iyer, and F. S. Rowland, *J. Amer. Chem. Soc.*, **94**, 1041 (1972).

(8) C. McKnight and J. W. Root, *J. Phys. Chem.*, **73**, 4430 (1969).

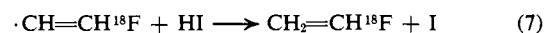
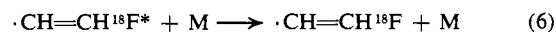
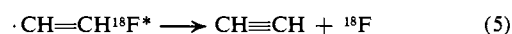
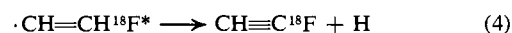
(9) C. McKnight, N. J. Parks, and J. W. Root, *ibid.*, **74**, 217 (1970).

(10) P. D. Mercer and H. O. Pritchard, *ibid.*, **63**, 1468 (1959).

(11) G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1064 (1960).

(12) G. C. Fettis and J. H. Knox, *Progr. React. Kinet.*, **2**, 1 (1964).

of ¹⁸F from this excited radical merely returns the ¹⁸F atom to the system for further reaction. These decomposition paths (4) and (5) compete with collisional stabilization of the excited radical, as in (6), followed in our system by reaction with HI to form the stable end product, CH₂=CH¹⁸F.



Although these ¹⁸F atoms are introduced into the system at energies in the 10⁵-eV range, no chemical reaction resulting in stable bond formation for ¹⁸F can occur until the atom has been reduced to <100 eV kinetic energy. In excess SF₆, most collisions at this energy are nonreactive scattering reactions and the great bulk of these ¹⁸F atoms are rapidly reduced to near-thermal energies. The experimental observations should thus be generally characteristic of those to be expected in true thermally equilibrated systems.

Experimental Section

A detailed discussion of many of the experimental aspects of ¹⁸F recoil chemistry as conducted in this laboratory has been recently presented.⁵ Our present experiments are basically quite similar, and only a brief summary of the procedures is given here.

The ¹⁸F atoms were formed by the ¹⁹F(n,2n)¹⁸F nuclear reaction on the fluorinated substrate SF₆ during irradiation with fast neutrons produced by a Kaman A711 fast neutron generator. The total ¹⁸F production in the gaseous contents of the ampoules was evaluated using the Teflon monitor system, with an accuracy for absolute yields of ±10%.⁴ Loss of ¹⁸F from the gas phase by recoil into the walls of the glass bulbs is unimportant (<5%) above about 400 Torr of SF₆ pressure.⁶

The chemicals used in these experiments were Research grade (Matheson Co.): acetylene, methane, HI (96%), SF₆ (98% stated purity). Experiments were carried out with no further purification of these gases except the removal of polymerization inhibitors by distillation from –78° baths, and by rigorous degassing *in vacuo*. Samples were prepared by standard procedures using a grease-free vacuum system. Hydrogen iodide pressures and low-pressure hydrocarbon components were measured in a mercury-free portion of the vacuum system using a spiral-gauge manometer. The pressure range available for experimentation was effectively limited on the high side by the characteristics of the glass vacuum line and the glass sample containers. The pressure range is limited on the low side by the irradiation geometry requirements of the neutron generator coupled with the increasing loss of ¹⁸F by recoil into the walls at lower pressures. For products with low percentage yields, the decrease in statistical accuracy is also significant at lower pressures.

The ¹⁸F-labeled products were analyzed by radio gas chromatography with an external flow proportional counter detector.^{5,13}

Table I. Typical Counting Data for ^{18}F Runs with Acetylene

Product	Retention time, ^a min		Observed counts			Correction ^a to $t = 0$	Corrected counts	Yield, % ^b
	Peak	Width	Gross	Bkgd	Net			
A. Mole Ratio $\text{SF}_6/\text{C}_2\text{H}_2/\text{HI} = 18.5/1.0/1.0$ (Total Pressure 3800 Torr)								
SF_5^{18}F	32	11	12,997	5,152	7,845	1.30	10,200	1.16 ± 0.03
$\text{CH}\equiv\text{C}^{18}\text{F}$	47	7	3,359	2,944	415	1.42	590	0.07 ± 0.03
CH_3^{18}F	61	5	3,026	2,256	770	1.55	1,190	0.15 ± 0.03
$\text{CH}_2=\text{CH}^{18}\text{F}$	69	21	303,750	10,272	293,478	1.63	478,000	59.3 ± 0.2
B. Mole Ratio $\text{SF}_6/\text{C}_2\text{H}_2/\text{HI} = 20/1.0/1.0$ (Total Pressure 300 Torr)								
SF_6^{18}F	31	8	4,163	3,772	391	1.31	513	0.77 ± 0.36
$\text{CH}\equiv\text{C}^{18}\text{F}$	47	6	2,705	2,760	-55			0.0 ± 0.35
CH_3^{18}F	61	6	2,696	2,668	28	1.58	44	0.06 ± 0.31
$\text{CH}_2=\text{CH}^{18}\text{F}$	68	18	31,215	8,648	22,567	1.65	37,200	56.9 ± 1.0

^a For experiment A, the time from the end of the irradiation to the injection of the sample into the gas chromatograph was 10 min. The listed retention times are the interval from injection to observation of the radioactivity in the flow counter. The time corrections on radioactivity have, however, been made to the end of the irradiation. For experiment B, the time between the end of the irradiation and sample injection was 13 min. ^b The error limits refer only to intra sample measurements. 2σ error limits = $2\sqrt{\sigma_{\text{gross}}^2 + \sigma_{\text{bkgd}}^2}/\text{net} \times \text{yield}$. For example, $2\sqrt{12,997 + 5,152/7,845} \times 1.16 = 0.03$.

Chromatographic separation of the products observed in these systems is routinely carried out with dimethylsulfolane or di-*n*-butyl phthalate columns 50 or 100 ft in length and with silicone oil columns either 25 or 50 ft in length.

Direct measurement of H^{18}F yields has also been carried out on some typical samples by rinsing the fragments of the crushed sample vessel with $10^{-2} M \text{K}_2\text{CO}_3$ solution and assaying the resultant solution for ^{18}F . Root, *et al.*, have also shown that two separable inorganic components, tentatively identified as H^{18}F and a much smaller yield of F^{18}F , can be identified in similar systems.¹⁴ In our experiments, the H^{18}F yields determined directly are qualitatively consistent with the values inferred indirectly. However, the direct measurements showed more scatter, perhaps reflecting the uncertainty in subsequent reactions of H^{18}F in acetylenic mixtures contained in Pyrex glass.

The experimental radio gas chromatogram from a typical experiment with 3800 Torr total pressure ($\text{SF}_6 + \text{C}_2\text{H}_2 + \text{HI}$) is shown in Figure 1. The macroscopic peak of SF_6 is of course very large. The mass peaks of CH_3F and $\text{CH}_2=\text{CHF}$ are carriers added after

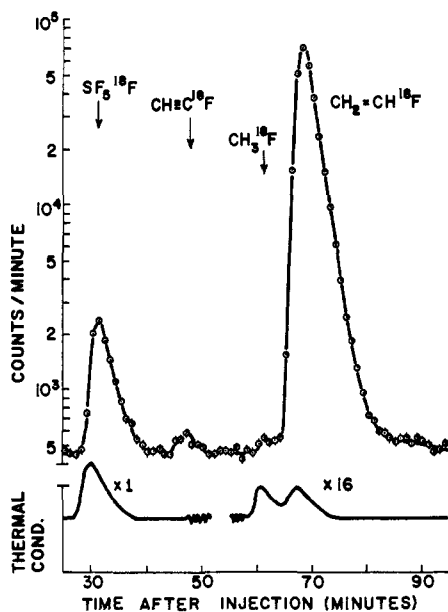


Figure 1. Radio gas chromatogram of volatile ^{18}F -labeled products from $^{19}\text{F}(n,2n)^{18}\text{F}$ reaction in $\text{SF}_6\text{-C}_2\text{H}_2\text{-HI}$ mixtures: upper plot, radioactivity; lower plot, macroscopic peaks (CH_3F and $\text{CH}_2=\text{CHF}$ added as carriers).

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

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

irradiation and prior to separation; radiation damage induced "natural" mass peaks are negligibly small.

The analytical details of this experiment are shown in Table I, together with a 300-Torr SF_6 experiment for comparison. The statistical errors shown in Table I are the counting errors applicable for intrasample comparisons. The actual absolute percentage yields are subject in addition to the statistical errors in measurement of the monitor yields (negligible because of the large numbers of observed counts) and to other random errors, of which the relative positioning of sample and monitor in the very inhomogeneous fast neutron flux is probably the dominant one. The limitations upon the statistical accuracy of most relative measurements and of absolute determinations for minor yield products are primarily those arising from the relatively small number of observed decays. The number of ^{18}F atoms formed in the system is linearly proportional to the pressure of the fluorinated source gas and to the number of F atoms in it. These factors are both near the maximum, at least for our standard glass vacuum line systems, with samples containing 3500 Torr SF_6 . Irradiations longer than about 1-2 hr do not offer worthwhile increments of ^{18}F activity because of its 110-min half-life, and our experiments have generally involved 15-30-min irradiations.

The reproducibility of measurement of high percentage yield products such as $\text{CH}_2=\text{CH}^{18}\text{F}$ is determined chiefly by the inaccuracies of the Teflon monitoring system used to determine the total fast neutron flux. Although the accuracy of this monitoring system is now about $\pm 10\%$, an accuracy of $\pm 3-4\%$ seems feasible in the near future.

Results

Formation of $\text{CH}_2=\text{CH}^{18}\text{F}$ in HI Systems. When acetylene alone is exposed to ^{18}F atoms in excess SF_6 , most of the radioactive ^{18}F is not observed as readily volatile products; about 1% is found as SF_5^{18}F and 0.1-0.5% (see Figure 2) as $\text{CH}\equiv\text{C}^{18}\text{F}$, with the remainder as nonvolatiles presumably formed by H^{18}F reactions with the wall or in radical polymerization reactions. However, when HI is also added to the system, the great majority of the ^{18}F radioactivity is now found as $\text{CH}_2=\text{CH}^{18}\text{F}$, as expected from the reaction sequence (2), (6), and (7). The other two products are unaffected by the addition of scavenger amounts of HI. As shown in Table II, a relatively small fraction of HI is sufficient for successful competition of reaction 7 with other possible routes for fluorovinyl- ^{18}F radicals, including, for example, $\text{CH}=\text{CH}^{18}\text{F} + \text{C}_2\text{H}_2 \rightarrow$ dimeric and/or polymeric materials.

One additional product is also found in a yield of about 0.1%, at the margin of detection, with the inclusion of HI in the irradiation system. This product has been identified as CH_3^{18}F from its chromatographic re-

Table II. Variation of Yields of Radioactive Products *vs.* HI Concentration for ^{18}F Atom Reactions in SF_6 -Moderated Acetylene

Pressure, Torr						
SF_6	1080	1070	1070	2830	2830	2830
C_2H_2	223	223	223	14	14	14
HI	0	4	46	14	43	72
Absolute yields of radioactive products, ^a %						
SF_6^{18}F	0.91 ± 0.10	0.96 ± 0.07	0.90 ± 0.08	1.24 ± 0.05	1.17 ± 0.04	1.15 ± 0.04
$\text{CH}\equiv\text{C}^{18}\text{F}$	0.46 ± 0.08	0.41 ± 0.06	0.33 ± 0.07	0.01 ± 0.03	0.00 ± 0.03	0.01 ± 0.03
$\text{CH}_2=\text{CH}^{18}\text{F}$	<0.2	67.6 ± 0.4	79.3 ± 0.4	72.1 ± 0.3	44.8 ± 0.3	31.0 ± 0.4

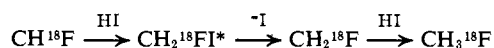
^a $\leq 0.07\%$ CH_3^{18}F also observed.

Table III. Yields of ^{18}F -Labeled Products in SF_6 - C_2H_2 Mixtures

Mole ratio ^b	Absolute yields, % ^a			
$\text{C}_2\text{H}_2/(\text{SF}_6 + \text{C}_2\text{H}_2)$	0.06	0.23	0.47	0.70
SF_6^{18}F	1.10 ± 0.07	0.93 ± 0.12	0.69 ± 0.10	0.53 ± 0.18
$\text{CH}\equiv\text{C}^{18}\text{F}$	0.18 ± 0.06	0.57 ± 0.15	0.87 ± 0.12	1.65 ± 0.23
$\text{C}_2\text{H}_3^{18}\text{F}$	75.0 ± 0.4	77.1 ± 0.7	73.2 ± 0.5	66.9 ± 0.7

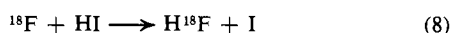
^a $\leq 0.2\%$ CH_3^{18}F also observed. ^b Total pressure, 1550 ± 50 Torr; HI, 50 Torr.

tention times on two separate columns. The mechanistic source of this compound has not been identified, and its yield is so low that variations with parameter changes are not accurately measurable. If CH^{18}F were formed in this system, then the successive reaction steps



would account for the formation of CH_3^{18}F as the final, observable product.¹³ However, the CH_3^{18}F yield does not vary with the mole fraction of C_2H_2 in SF_6 - C_2H_2 mixtures as expected for typical "hot" products of $^{18}\text{F} + \text{C}_2\text{H}_2$ (see Figure 2 below) and hence does not appear to be a "simple" high energy reaction product. It is possible that its method of formation involves an excited sulfur-containing species (*e.g.*, SF_4^{18}F), but our present information is insufficient to identify further the mechanistic source of this product.

A further increase of HI/ C_2H_2 ratios eventually leads to a decrease in the $\text{CH}_2=\text{CH}^{18}\text{F}$ yields, as abstraction of H from HI, as in (8), begins to compete with addition to C_2H_2 for the near-thermal ^{18}F atoms.



Hot Reactions with Acetylene. The essentially "hot" nature of the reaction leading to $\text{CH}\equiv\text{C}^{18}\text{F}$ is illustrated in Table III and Figure 2, in which the various product yields are given as a function of the changing composition of SF_6 - C_2H_2 mixtures at constant total pressure. A linear increase in yield of $\text{CH}\equiv\text{C}^{18}\text{F}$ *vs.* C_2H_2 concentration is expected in the excess SF_6 regions, while the yield dependence at higher acetylene concentrations is dependent as well upon the relative moderating efficiencies of SF_6 and C_2H_2 and upon the total hot yield for all products.¹⁵ A small uncertainty in this respect is the unknown yield of "hot" H^{18}F in the high C_2H_2 systems, for which an upper limit can be estimated from the observation that two-thirds of the ^{18}F atoms still react with the formation of $\text{CH}_2=\text{CH}^{18}\text{F}$ in a system which is 73% C_2H_2 . The calculated dependence of $\text{CH}\equiv\text{C}^{18}\text{F}$ yield *vs.* C_2H_2 fraction is consistent with

(15) The moderating efficiencies are usually expressed in terms of the α values for each compound: see R. Wolfgang, *Progr. React. Kinet.*, **3**, 97 (1965).

$\alpha_{\text{C}_2\text{H}_2}/\alpha_{\text{SF}_6}$ in the range 0.5–1.0, as shown in Figure 3.¹⁶ The data plotted in Figure 3 include not only the 1550-Torr data of Table III, but many points measured at other pressures as well. Almost imperceptible changes occur as the assumed "hot" H^{18}F yield is varied from

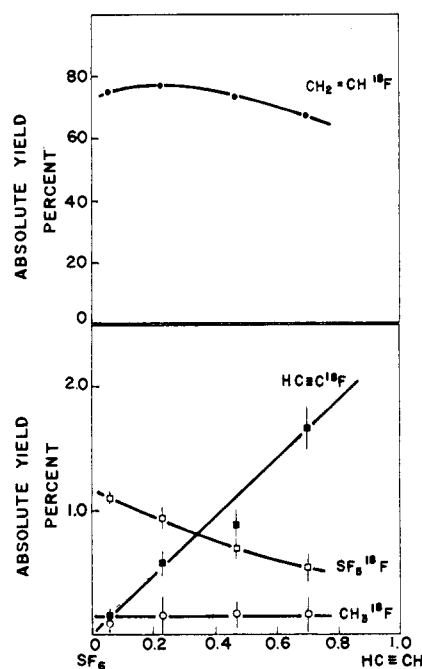


Figure 2. Absolute yields of ^{18}F -labeled products in SF_6 - C_2H_2 mixtures: (●) $\text{CH}_2=\text{CH}^{18}\text{F}$; (■) $\text{CH}\equiv\text{C}^{18}\text{F}$; (□) SF_6^{18}F ; (○) CH_3^{18}F .

0 to 40% in these calculations. For example, there is little difference between the curves for $x = 0.7$ with $k = 0$ (assumed hot H^{18}F yield = 0) and $k = 20$ (assumed hot H^{18}F yield = 40% in pure $\text{CH}\equiv\text{CH}$).

(16) These values have been calculated using the following parameters: (a) molecular diameters, SF_6 , 5.5 Å; C_2H_2 , 4.2 Å; F, 2.8 Å. Some of the ^{18}F activity not observed among the volatile products is presumably H^{18}F formed by thermal processes.

Table IV. Pressure Dependence of Product Yields from SF₆-Moderated ¹⁸F Atom Reactions with HI-Scavenged Acetylene

Total pressure, ^a Torr	3980	2360	1210	500	420	250
Absolute yield, %						
SF ₅ ¹⁸ F	1.04 ± 0.04	1.06 ± 0.06	0.90 ± 0.10	0.87 ± 0.17	0.90 ± 0.26	0.89 ± 0.32
CH≡C ¹⁸ F	0.52 ± 0.04	0.42 ± 0.05	0.50 ± 0.11	0.60 ± 0.16	0.43 ± 0.25	0.38 ± 0.29
CH ₂ =CH ¹⁸ F	76.8 ± 0.3	76.7 ± 0.3	71.5 ± 0.5	75.7 ± 0.8	65.9 ± 0.8	75.8 ± 1.2
Total pressure, ^b Torr	3800	690	300	250	100	
Absolute yield, %						
SF ₅ ¹⁸ F	1.16 ± 0.04	1.05 ± 0.15	0.77 ± 0.36	0.70 ± 0.22	1.0 ± 0.8	
CH≡C ¹⁸ F	0.07 ± 0.03	0.00 ± 0.15	0.00 ± 0.35	0.04 ± 0.23	0.6 ± 1.0	
CH ₂ =CH ¹⁸ F	59.3 ± 0.2	67.0 ± 0.6	56.9 ± 1.0	57.9 ± 0.9	48.2 ± 2.0	

^a Molar composition ratio, SF₆/C₂H₂/HI = 3.5/1.0/0.15. ^b Molar composition ratio, SF₆/C₂H₂/HI = 20/1.0/1.0.

Pressure Dependence of ·CH=CH¹⁸F and SF₅¹⁸F Yields. The relative lack of variation of ¹⁸F yields with total pressure in a system of fixed ratio of substrates is shown in Table IV for two different SF₆/

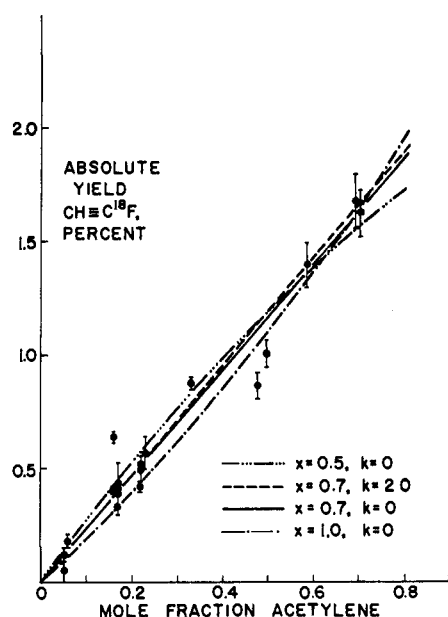


Figure 3. Absolute yields of CH≡C¹⁸F vs. mole fraction of acetylene. Curves correspond to various assumptions about the values of $x = \alpha_{C_2H_2}/\alpha_{SF_6}$ and $k = (\text{hot yield of } H^{18}F)/(\text{hot yield of } CH\equiv C^{18}F)$.

C₂H₂/HI composition ratios. If the chief route of decomposition of ·CH=CH¹⁸F* were the loss of H, then one would anticipate an increase at lower pressures in the yield of CH≡C¹⁸F. The absence of such an increase puts rather a stringent upper limit (<0.2% in Table IV) upon the fractional decomposition of ·CH=CH¹⁸F by H atom loss.

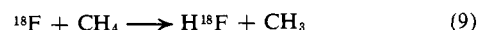
This system by itself is not very sensitive to the decomposition of ·CH=CH¹⁸F* by the alternate route of ¹⁸F loss, for such ¹⁸F atoms are then free to react again with the components of the system and will once again predominantly add to acetylene with the re-formation of the fluorovinyl-¹⁸F radical. Only by repetition of this process several times will an appreciable fraction of the ¹⁸F atoms be diverted into another reaction path such as the abstraction of H from acetylene. This other possible competitive pathway for such ¹⁸F atoms can account for no more than one-fifth as much yield as the addition reaction, since no more than 20% of the ¹⁸F

atoms are present finally as H¹⁸F at the higher pressures. A measurement of the lifetime of the ·CH=CH¹⁸F* radical against ¹⁸F loss has been obtained, however, by study of C₂H₂-CH₄ competition for reactions of near-thermal ¹⁸F atoms, as shown below.

The yield of SF₅¹⁸F slowly decreases with decreasing pressure, consistent with the secondary decomposition of some excited SF₅¹⁸F* molecules. By analogy with the extensive decomposition of CF₃¹⁸F* found in CF₄ systems,¹⁷ appreciable decomposition of SF₅¹⁸F* is not unexpected. However, no products attributable to decomposition fragments (e.g., SF₄¹⁸F) have yet been definitely identified.

The additional data in the lower half of Table IV show a pressure dependence study under conditions of higher SF₆ and HI concentrations. The competition of HI for the available ¹⁸F atoms is evidenced by the reduced yield (77 → 59%) for CH₂=CH¹⁸F at high pressure. At the lowest absolute pressures (100–250 Torr), the total yields are diminished by recoil loss of ¹⁸F into the ampoule walls.

Acetylene-Methane Competition. The ¹⁸F atoms which would otherwise have reacted with acetylene to form ·CH=CH¹⁸F* can be deflected from this route by prior reaction with some other substrate molecule, such as by abstraction of H from HI or from CH₄ as in (9).



The inclusion of an amount of CH₄ 1.4 times that of C₂H₂ is sufficient to reduce the CH₂=CH¹⁸F yield almost in half, as shown in Table V. (The measurable increase in the yield of CH₃¹⁸F results from direct substitution of ¹⁸F for H in CH₄.) With this addition of CH₄, reasonable estimates can be made of the fractional decomposition of ·CH=CH¹⁸F* by loss of ¹⁸F or H and thereby of the importance of multiple exposure of ¹⁸F atoms to capture by C₂H₂. If loss of ¹⁸F were a probable occurrence, then the ¹⁸F atoms would again be able to react either by addition (2) or by abstraction from C₂H₂, HI, or CH₄, and the competition might occur several times for each ¹⁸F atom. Since the collisional stabilization of ·CH=CH¹⁸F* should be less likely at lower pressures and decomposition by ¹⁸F loss more likely, any such multiple decomposition processes could be identified by a progressive diminution in observed CH₂=CH¹⁸F yield at the lowest pressures. The inclusion of a substantial amount of CH₄ ensures that the sum of the abstraction processes competes quite well with addition by (2), thereby increasing the

(17) Y.-N. Tang, T. Smail, and F. S. Rowland, *J. Amer. Chem. Soc.*, 71, 2130 (1969).

Table V. Pressure Dependence of Yields of ^{18}F Products in $\text{C}_2\text{H}_2\text{-CH}_4$ Competition

Total pressure, ^a Torr	3840	2490	690	380	300	250
Absolute yield, %						
SF_6^{18}F	1.12 ± 0.05	1.06 ± 0.04	0.94 ± 0.18	0.90 ± 0.25	0.8 ± 0.4	0.8 ± 0.3
$\text{CH}\equiv\text{C}^{18}\text{F}$	0.06 ± 0.03	0.04 ± 0.03	0.09 ± 0.18	0.14 ± 0.2	0.4 ± 0.4	0.0 ± 0.3
$\text{CH}_2=\text{CH}^{18}\text{F}$	43.3 ± 0.2	42.2 ± 0.2	39.9 ± 0.5	38.0 ± 0.8	39.7 ± 0.9	32.8 ± 0.8
CH_3^{18}F	0.59 ± 0.03	0.59 ± 0.04	0.52 ± 0.16	0.6 ± 0.3	0.7 ± 0.4	0.4 ± 0.3

^a Molar composition ratio, $\text{SF}_6/\text{C}_2\text{H}_2/\text{CH}_4/\text{HI} = 20/1.0/1.4/1.0$.

magnitude of the anticipated diminution in $\text{CH}_2=\text{CH}^{18}\text{F}$ yield if ^{18}F loss is important at these pressures.¹⁸

The $\text{CH}_2=\text{CH}^{18}\text{F}$ yield in Table V is approximately constant with pressure for this fixed composition ratio of the four components, indicating that at most a small fraction of $\cdot\text{CH}=\text{CH}^{18}\text{F}^*$ radicals decomposes by this pathway even at the lower pressures. The expected pressure dependence of $\cdot\text{CH}=\text{CH}^{18}\text{F}^*$ has been calculated for various pressures for half stabilization of excited $\cdot\text{CH}=\text{CH}^{18}\text{F}^*$ radicals, fitting the experimental data at 4000 Torr as shown in Figure 4. The pressure for half stabilization is certainly less than 200 Torr and could be much less when the statistical uncertainties from the monitoring process are taken into account. The combination of both lower statistical accuracy and increasing recoil loss at lower pressures makes it uncertain whether any decomposition by ^{18}F loss is shown by the data of Figure 4. While similar calculations can also be performed for the $\text{C}_2\text{H}_2\text{-HI}$ mixtures of Table IV and Figure 4, the expected curvature at low pressure is steadily lessened from that shown for the CH_4 competitions as the fraction of ^{18}F reacting by abstraction is decreased. The predicted curvatures for a half-stabilization pressure of 200 Torr are much less than the scatter of the data and have not been shown on Figure 4. (The 100-Torr point for the lower half of Table IV has been omitted because the correction for recoil loss is large, and uncertain, at such a low pressure.)

The half-stabilization pressure of ≤ 200 Torr implies a lifetime for $\cdot\text{CH}=\text{CH}^{18}\text{F}^*$ of $\geq 5 \times 10^{-10}$ sec. Experimental measurements of the addition of thermal D atoms to acetylene at 298°K show a pressure for half stabilization of $\cdot\text{CH}=\text{CHD}^*$ radicals against H atom loss of about 2 Torr.¹⁹ The lifetime of the excited fluorovinyl- ^{18}F radicals, while not as long as that of $\cdot\text{CH}=\text{CHD}^*$, implies that the typical addition of ^{18}F to acetylene does not involve very much excess kinetic energy for the ^{18}F atom. At 100-Torr pressure, the observed limit on the loss of H from $\cdot\text{CH}=\text{CH}^{18}\text{F}^*$ ($<0.2\%$) indicates that the lifetime against H loss is $\geq 10^{-8}$ sec. However, since crossed molecular beam studies of thermal F atom reactions with acetylene have failed to show an F/H replacement reaction,²⁰ H atom loss is at most a minor path for the decomposition of $\cdot\text{CH}=\text{CH}^{18}\text{F}$ radicals under those collision-free conditions.

(18) The competition among (2), (8), and (9) for ^{18}F atoms is dependent to some extent upon the energy of the ^{18}F atom. Detailed experiments, however, indicate that the reactions are roughly competitive (changes of factors of 2) over a wide range of energies (unpublished experiments by R. L. Williams and F. S. Rowland).

(19) Unpublished results of B. Thrush, P. B. Davies, and F. C. James.

(20) Unpublished result of Y. T. Lee and J. M. Parson.

Relative Yields of the Hydrogen Abstraction Reactions. The observed competition among abstraction reactions (3), (8), (9) and addition (2) suggests that more detailed studies of the variation in H^{18}F yield, or in diminution of the $\text{CH}_2=\text{CH}^{18}\text{F}$ yield, can lead to a measurement of the relative rates of these reactions. The substitution of other RH molecules for CH_4 can then permit the extension of such relative rates to many molecules. A preliminary report of some estimated relative rates of abstraction has been prepared.²¹

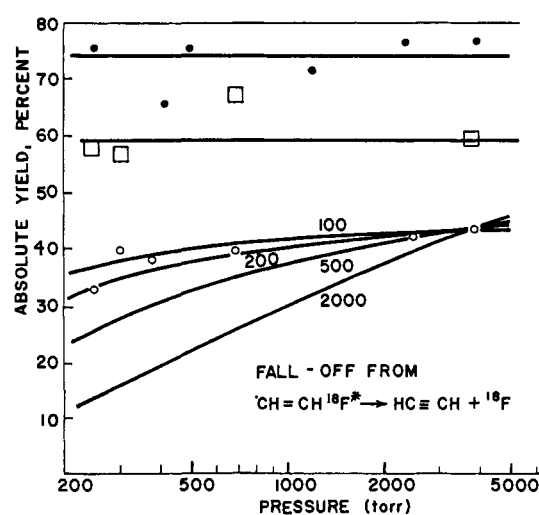


Figure 4. Absolute yield of $\text{CH}_2=\text{CH}^{18}\text{F}$ vs. pressure in methane-acetylene compositions: (●) $(\text{SF}_6/\text{C}_2\text{H}_2/\text{HI}) = 3.5/1.0/0.15$; (□) $(\text{SF}_6/\text{C}_2\text{H}_2/\text{HI}) = 20/1.0/1.0$; (○) $(\text{SF}_6/\text{C}_2\text{H}_2/\text{CH}_4/\text{HI}) = 20/1.0/1.4/1.0$. Curves labeled 100, 200, 500, and 2000 correspond to expected pressure dependence for decomposition of $\cdot\text{CH}=\text{CH}^{18}\text{F}^*$ by loss of ^{18}F with these half pressures (in Torr).

Acetylene as a Scavenger for ^{18}F Atom Systems. The observed reactions of ^{18}F atoms indicate that acetylene has several characteristics that make it especially useful as a scavenger for ^{18}F atom reaction systems. (a) The molecule has a relatively low cross section for hot ^{18}F reactions, even when acetylene is the major constituent of the system, and gives only 0.18% $\text{CH}\equiv\text{C}^{18}\text{F}$ in 95% SF_6 . (b) The efficiency of reaction with thermal ^{18}F atoms is quite satisfactory, being competitive with the fastest other known reactions of ^{18}F atoms. (c) The scavenged yield of ^{18}F can be readily converted into an easily measured volatile product through the inclusion of a small concentration of HI in the system. (d) The product spectrum is very simple (only $\text{CH}_2=\text{CH}^{18}\text{F}$) over the entire range of pressures from 200 to 4000 Torr.

(21) R. Williams and F. S. Rowland, *J. Phys. Chem.*, 75, 2709 (1971).