Reaction of Atomic Carbon with Fluorocarbons

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Abstract: The reactions of atomic carbon with fluorocarbons and SF_6 have been studied using C^{11} recoiling from nuclear reactions. No convincing evidence was found for insertion into C–F bonds, in contrast to the situation with alkanes, for which C insertion into the C–H bond is the most prominent reaction. Nevertheless the reactivity of fluorocarbons is quite comparable to that of hydrocarbons. All data are consistent with the hypothesis that the favored reaction of atomic carbon with perfluoroalkenes and SF_6 is formation of CF. With perfluoroalkenes the spectrum of perfluorocarbons formed is consistent with the expectation that insertion into the double bond occurs as it does in alkenes. Both hot and thermal carbon atoms undergo these reactions but the thermalized species is less reactive. It is suggested that atomic carbon, as an electron deficient species, preferentially attacks at sterically accessible points where electrons are most readily available. This hypothesis naturally accounts for observed addition to double bonds, insertion into C–H bonds, abstraction from C–F linkages, and the relative inertness of C–C bonds.

The reactions of atomic carbon have been quite intensively studied over the past decade.[1-3] It has been established that carbon atoms insert into both C—H and C=C bonds. Adducts are thus formed which may be stabilized, or, because of their high internal energy, may rearrange, decompose, or otherwise react further. These primary insertion reactions are analogous to similar processes undergone by carbenes,[4] although the carbon atoms tend to be less specific, presumably reflecting their higher chemical potential.[5-7] Insertion into C—C bonds does not appear to be a prominent mode for either carbenes or carbon atoms.[1-4]

Most of the recent work on atomic carbon has been concerned with the subsequent reactions of the adducts formed by the primary reaction. This has left largely unanswered more fundamental questions regarding the nature of the initial reaction and the factors controlling it. Indeed these problems are incompletely understood not only in the case of carbon atoms but for electron-deficient species in general. The present work does not attempt to answer these questions definitively. We seek primarily to extend the range of available information by investigating the initial interaction of C with C–F bonds. It is known that carbenes do not insert into C–F bonds to any appreciable extent.[8] It is therefore of some interest to see whether the higher chemical potential and smaller size of the carbon atom enables it to do so, and if not, to study any alternative modes of reaction.

The prototypes of C atom insertion reactions were originally studied[6,9] in simple systems as, for instance

$$\begin{aligned} CH_4 + C^{11} \longrightarrow C_2H_4^* &\longrightarrow H_2C{=}C^{11}H_2 \\ &\longrightarrow HC{\equiv}C^{11}H \\ H_2C{=}CH_2 + C^{11} \longrightarrow C_3H_4^* &\longrightarrow H_2C{=}C^{11}{=}CH_2 \end{aligned}$$

(where the asterisk denotes the excited intermediate). Such insertion reactions have been shown to occur not only in hydrocarbons but also in halohydrocarbons.[10] Using the same source of atomic carbon, recoil C^{11} produced by nuclear processes, we have investigated analogous systems involving interaction with CF_4, CHF_3, C_2F_6, C_2F_4, other fluorocarbons, and SF_6.

Experimental Section

The general procedures employed in studies of carbon atom chemistry using C^{11} recoiling from nuclear reaction have been fully outlined elsewhere.[1,6] High kinetic C^{11} atoms are introduced into the reagents. They will undergo energy loss by successive collisions and may react while still translationally hot, or after thermalization. The probability of the latter is enhanced by addition of inert gases as moderators. Analysis of C^{11}-labeled products produced by hot or thermal reaction is by radiogas chromatography.[11,12] In the material below, only special points of technique involving these particular systems will be discussed.

Irradiation. Recoil C^{11} was produced by irradiations using the heavy ion and linear electron accelerators at Yale University. Both methods have been described previously.[1,7] Brass irradiation vessels with brass foils were used with the heavy ion accelerator for room-temperature experiments. The foil was reinforced with steel gauze outside for a few runs where pressures of several atmospheres were required (such vessels were calibrated for gauze transparency). Low-temperature experiments, all performed on the heavy ion accelerator, were done using a Pyrex vessel: a brass foil, sealed on with epoxy resin cement, formed the front wall of the chamber containing the substrate, as a gas, to be treated with C^{11}, and a vacuum-jacketed reservoir built onto the rear wall was filled with liquid nitrogen to form a condensed phase layer of the substrate. Teflon stopcocks sealed this and the cylindrical Pyrex vessels used on the electron accelerator.

The heavy ion accelerator was used for the great bulk of this work and is the source of the data reported in the tables. The electron accelerator was employed only for runs studying the effect of moderation on ethylene-scavenged CF_4 samples.

Reagents. Air was a contaminant, up to 5%, of several fluorine compounds. All were purified further by first pumping on and then subliming the samples at low temperature and pressure. This procedure reduced oxygen, nitrogen, and argon contents to below 100 ppm, the detection limit. Only then was reproducibility of results obtained. The procedure also removed less volatile impurities, such as the 1% α-pirene stabilizer added to C_2F_4 to prevent formation of the perfluoroisobutylene dimer. CO_2 was reported or

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[1] C. MacKay and R. Wolfgang, *Science*, **148**, 899 (1965).

[2] R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 97 (1965).

[3] A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 201 (1964).

[4] W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

[5] C. MacKay, *et al.*, *J. Am. Chem. Soc.*, **84**, 308 (1962); see also ref 2, pp 115–117.

[6] J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4747 (1964).

[7] J. Dubrin, C. MacKay, M. Pandow, and R. Wolfgang, *J. Inorg. Nucl. Chem.*, **26**, 2113 (1964).

[8] B. A. Grzybowaka, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 746 (1963).

[9] M. Marshall, C. MacKay, and R. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4741 (1964).

[10] Reactions of C atoms with fluorohydrocarbons have been studied by H. J. Ache and A. P. Wolf, *Radiochim. Acta*, **10**, 41 (1968); *J. Am. Chem. Soc.*, **88**, 888 (1966). Only products resulting from the well-known interaction with C–H bonds were sought and found.

[11] R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).

[12] R. Wolfgang and C. MacKay, *Nucleonics*, **16**, 69 (1958).

found to be below 0.1%, and no correction for it was found to be necessary in chromatographic mass peak measurements of $C^{12}O_2$.

The sources and stated impurity levels of the reagents are as follows: CF_4, Matheson Co. ($H_2O < 15$ ppm, $HF < 1$ ppm); CF_4, Air Products and Chemicals Inc. ($CClF_3 + CCl_2F_2 + CO_2 <$ 0.1%, H_2O, 2–3 ppm); C_2F_4, C_2F_6, C_4F_{10}, Columbia Organic Chemicals Co.; SF_6, Air Products and Chemicals (CF_4, 675 ppm, $H_2O <$ 34 ppm); $CHFCF_2$, Peninsular Chemresearch; O_2 ($Ar < 45$ ppm, $N_2 < 500$ ppm), CO, CHF_3, Ar ($O_2 + N_2 + H_2O < 17$ ppm); Ne ("Research Grade"), and Xe ("Research Grade") all from Matheson Co.; C_2H_4, Phillips Petroleum ($\sim$500 ppm $CH_4 + C_2H_6$); $C^{14}O$, Tracerlab (1.3% $C^{14}O_2$ was removed by trapping at −196° and by gas chromatography).

Analyses. Separations of products were done by gas chromatography using various columns. The eluates, in a stream of helium carrier gas, first pass over a thermistor detector which produces a "mass" peak for more than $\sim 10^{16}$ molecules of a component, and then through a proportional counter, of a sandwich design,[12] which detects products labeled with radioisotopes. These products total less than 10^9 molecules. Enough inactive compound carrier to produce a mass peak was often added to the reaction mixture before analysis. This ensured that trace amounts of products were not lost and facilitated certain separations (*e.g.*, CO_2 and C_2F_4 on silica gel). The most important function of the carrier was, however, to establish the identities of trace products. If a radioactive peak had elution times identical with that of a carrier, on two or more columns having different separation characteristics, it was considered to have the chemical identity of the carrier. Lack of certain carriers, particularly fluorohydrocarbons, made definite identification of certain products impossible.

C_2F_2 was sought on a 10-ft silica gel column on which it has been reported[13] to elute after C_2F_4. Had COF_2 been formed in this work it would not have been detected, as it does not elute from alumina or molecular sieve columns, and is converted to CO_2 on silica gel and charcoal.

Columns were made of 0.25-in. copper tubing and operated at a helium flow from 50 to 100 cc/min, and at 25°. Listed below are the observed orders of elution for the several columns used.

A. 3.5 ft silica gel: air + CO; CF_4; $CO_2 + CF_2{=}CF_2$; C_2H_2 (tracer for C_2F_2).

B. 10 ft silica gel: air + CO; CF_4; CH_2F_2, C_2F_6; Xe; CO_2; $CF_2{=}CF_2$; C_2H_2 (v.s.).

C. 10 ft 40–60 mesh charcoal in stainless steel: air + C_2F_4; CO; CF_4; $C_2H_2 + CO_2$ (C_2F_6 retained).

D. 11 ft 15% w/w GE SF96 silicone: air + C_1's; C_3's; $CH_2{=}CHC{\equiv}CH$; $C_3H_7C{\equiv}CH$; $C_2H_5CH{=}C{=}CH_2$; Y; Z. (Retention volumes of Y and Z are 1.7 and 2.2 relative to pentyne-1.)

E. 30 ft alumina: air + CO + CF_4; CF_3CF_3; $CF_2{=}CF_2$ (CO_2 is retained).

F. 10 ft 30% HMP (hexamethylphosphoramide): air + CO + CO_2; $CHF{=}CF_2$; CHF_3.

G. 60 ft 30% silicone: $CHF{=}CF_2$.

Other columns used for identifying products from reaction with ethylene are as reported earlier.[6,14]

Radioassay. Assay by radiogas chromatography has been described previously.[6] Aliquots of irradiated samples were injected into various columns and the activity of the eluate measured by a flow-proportional counter.[11,12] In each case, one aliquot was directly passed through the counter in order to estimate the total volatile activity.

In using the electron accelerator, F^{18} is produced by the F^{19}-(γ,n)F^{18} reaction. The hot F^{18} tends to produce chemically different products than does C^{11} and so there is no ambiguity as to the origin of most products. However, analyses were repeated after a 1-hr interval. In view of the different half-lives involved (C^{11}, 20.4 min; F^{18}, 112 min), this allowed an estimate of the relative contribution, if any, of F^{18} to any given peak. Where necessary the appropriate simple correction was made.

Absolute Activities. Monitoring. The method of analysis detects only volatile products. It is, however, essential to know the total amount of C^{11} produced in order to be able to report yields on an absolute basis. Total C^{11} production was measured by irradiating appropriate monitors under conditions identical to the sample irradiations.[15,16] In the case of heavy-ion accelerator runs these consisted of standard vessels filled with O_2 to a pressure such that their stopping power was the same as that of the samples: all of the C^{11} stopped in oxygen appears in volatile form.[15] For electron accelerator runs, hydrocarbon samples containing an identical number of C^{12} atoms to that in the sample were used as monitors.[16] In the latter case, however, formation of large amounts of F^{18} activity complicated the estimation of absolute sample yields.

Radiation Effects. The energy dissipated by radiation amounts to less than 0.01 eV per molecule of sample.[15,16] Nevertheless, some radiation effects are noticeable. In particular, possible radiation oxidation of $C^{11}O$ to $C^{11}O_2$ was of importance in the interpretation. This was minimized by adding small amounts (<1 mol %) of $C^{12}O$ carrier to the sample. Oxidation still occurred to a small extent and was measured by the fraction of $C^{12}O$ which was converted to $C^{12}O_2$. Since $C^{11}O$ is only formed during the irradiation, the extent of its oxidation was taken to be half of that of the $C^{12}O$. The oxidation of $C^{14}O$ to $C^{14}O_2$ was also used to monitor this radiation-induced process.

Some radiation-induced conversion of $C^{11}F_2{=}CF_2$ product to $C^{11}F_3CF_3$ can also occur. This was suppressed by the addition of 1 mol % CF_2CF_2 or of 1 mol % ethylene.

State of the Reacting Carbon Atom. Considerations based on the adiabatic hypothesis of Mott and Massey[2,9,17] have led to the conclusion that carbon slowing to "chemical" energies (<100 eV) in hydrocarbons will be neutral and in any of the three low-lying electronic states (^3P, ^1D, ^1S).[18] Results obtained have been fully consistent with this expectation. Extending this analysis based on the adiabatic hypothesis to perfluorocarbons leads to the same prediction: the carbon will react as an atom in either the ground or one of the two lowest excited states.

The carbon atom is initially formed at high kinetic energy and is slowed by collision. In a system of pure reagent, it can thus react while translationally hot. Thermal reaction is favored by addition of a large excess of inert moderator—as was present in some of these experiments.[1,2]

Results and Discussion

C^{11} Reaction with Pure CF_4 and C_2F_6. The reaction of C^{11} with "pure" gaseous CF_4 gave erratic and irreproducible results. In a typical run in which a small amount (<0.1%) of air was present, about 90% of the total activity was recovered, most of which appeared as $C^{11}O_2$, with a lesser quantity of $C^{11}O$. The only other volatile compounds were so high boiling that they did not elute from a silicone column. From this, it appears that they contained at least five carbon atoms. On rigorous deaeration of the gas phase system, the $C^{11}O$ and $C^{11}O_2$ both drop by a large factor, and only a small amount of other volatile products appears in their place (see Table I). In solid CF_4 at −196°, a somewhat larger but quite irreproducible fraction of the C^{11} is recovered in gaseous form. This pattern of data suggests that observed yields from CF_4 are largely governed by the level of impurities, and reveals little about primary reactions of C atoms. Nor does the ratio of $C^{11}O$: $C^{11}O_2$ seem to have much significance. It increases considerably when $C^{12}O$ carrier is added, implying that most $C^{11}O_2$ is formed by oxidation of carbon monoxide.

A careful search for possible C^{11}-labeled perfluoroacetylene and perfluoroethylene was made, since these products would be expected to appear if carbon atoms react with carbon tetrafluoride in a manner analogous to their reaction with methane. Neither was found. The yield of $C^{11}F_2{=}CF_2$ from gaseous CF_4 is less than 3% (see Table I). In some runs, a small amount of carrier C_2F_4 was present throughout the irradiation and recovered in the analysis, thus excluding the possibility that $C^{11}F_2CF_2$ was formed but decomposed before assay. No authentic sample of carrier difluoroacetylene

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(14) C. MacKay and R. Wolfgang, *Radiochim. Acta*, **1**, 42 (1962).

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(17) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, London, 1952, p 441.

(18) T. L. Rose, Ph.D. Thesis, Yale University, 1967.

Table I. Reaction of C^{11} with CF_4[a] and C_2F_4[b]

C^{11} labeled product	CF_4(g)[a]	CF_4(s)[a]	C_2F_4(g)
CO	5 ± 2	2	7
CO_2	<1.6	7	7
C_2F_2	<1.2	<0.3	7
C_2F_4	<2.5	<0.2	7
Other low boiling volatiles[c]	3.6 ± 1.5	36[e]	14[g]
High boiling volatiles[d]	10 ± 3	<1	33[h]
Polymeric[f]	79 ± 4	56	46

[a] Typical results for carefully deaerated CF_4 samples. Results for CF_4 depend sensitively on impurity levels. See text. [b] Yields given as per cent total C^{11} available. [c] Peaks observed eluting from alumina, charcoal, silica gel, or silicone columns before 1-pentyne, excluding products identified elsewhere in the table. CF_4 and C_2F_6 account for at least some of these yields. [d] These yields are activities measured by direct injection of aliquots of the irradiated samples through the counter, excluding activities accounted for by peaks eluting from silicon columns before 1-pentyne. [e] Saturated fluorocarbons, 20.4% CF_4, 10.6% C_2F_6, and an unidentified product, yield 4.7%, possibly C_3F_8. These yields are typical but irreproducible, and apparently reflect radiation damage and impurity level. See text. [f] Loosely defined as nonvolatile at room temperature. These compounds remained on the walls of the irradiation vessels when their contents were removed as gases at room temperature. [g] In three peaks. [h] Including two peaks.

was available. However it has been reported[13] to elute from a silica gel column near acetylene. Even in the presence of C_2H_2 carrier, the amount of recovered activity which could be attributed to $C^{11}FCF$ was less than 2%. With solid CF_4 (−196°) less than 0.3% of $C^{11}FCF$ and less than 0.2% $C^{11}F_2CF_2$ were found.

These results imply that either CF_4 is inert toward the atomic carbon, which then eventually reacts with impurities or products of radiation damage; or that, alternatively, it reacts to give a product which reacts further with impurities. In any case, CF_4 does not behave in a manner analogous to CH_4.

Runs on C^{11} with perfluoroethane gave similar results indicating that the presence of a C–C bond does not change the situation.

C^{11} Reaction with C_2F_4. Reaction of atomic carbon with tetrafluoroethylene yielded much more reproducible results. A summary of these is shown in Table I. Again no labeled C_2F_2 or C_2F_4 were found, but there was a substantial yield of a number of other low-boiling products. Due to lack of authentic carrier samples, these were not identified. However, from their elution times, it is likely that they contained from three to five carbon atoms. This yield pattern is what would be expected if reaction at the perfluoroethylene double bond proceeded similarly to reaction at the double bond in ethylene. It seems reasonable that perfluorination does not prevent the reaction of atomic carbon at multiple bonds.

Reaction of Atomic Carbon with Fluoroform. Returning now to the problem of reaction with saturated fluorocarbons, we consider the possibility that insertion into a C–F bond does occur, but that no rearrangement or further reaction analogous to that occurring in hydrocarbons is possible. Thus with methane, labeled ethylene is formed by the following mechanism.[6]

$$C^{11} + CH_4 \longrightarrow H_3CC^{11}H \xrightarrow{-H} H_2CC^{11}H \xrightarrow{CH_4} H_2C{=}C^{11}H_2$$

Perhaps with CF_4 an analogous $F_3CC^{11}F$ intermediate is formed which can neither eliminate F_2 to yield $FC{\equiv}C^{11}F$ nor react to give $F_2C{=}C^{11}F_2$.

To examine this possibility, we studied reaction with CHF_3. Typical results are shown in Table II. Small but probably significant yields of labeled $CHF{=}CF_2$ were found. These were presumably formed by insertion into the C–H bond to give $CF_3C^{11}H$ followed by further reaction. If this is the case, a similar further reaction should be possible for $CF_3C^{11}F$ intermediate. Since the corresponding product $CF_2{=}C^{11}F_2$ is not found, the implication is that such an intermediate is not formed with CF_4 because C–F bond insertion is not possible.

Table II. Reaction of C^{11} with CHF_3[a]

C^{11} labeled product	CHF_3, gas, 25°	CHF_3, solid, −196°
$CO + CO_2$	10.4	5.8 ± 1.0
$CHF{=}CF_2$	0.5	2.6 ± 0.3
CHF_3	0.8	7.9 ± 0.2

[a] Yields given as per cent total C^{11} available.

The relatively high yield of $C^{11}HF_3$ is interesting, but was not studied further.

Reaction of Atomic Carbon with CF_4–O_2 Mixtures. Although atomic carbon apparently does not insert into C–F bonds, it does appear to undergo reaction with CF_4. This is shown by results on CF_4–O_2 mixtures, as given in Figure 1. With pure O_2, C^{11} reacts to form $C^{11}O$ and very little $C^{11}O_2$, as is already known.[19,20] But as the proportion of CF_4 mixed with the O_2 increases, there is a rising yield of $C^{11}O_2$. This yield is not due to oxidation of $C^{11}O$, as is shown by experiments in which a small amount of $C^{12}O$ or $C^{14}O$ is added to the reaction mixture. Generally, little of this is oxidized, and since the average $C^{11}O$ molecule is only formed in the middle of the irradiation, the extent of its oxidation will only be about half that of the $C^{12}O$ or $C^{14}O$. The values in Figure 1 have been corrected for this small amount of oxidation.

Evidently the carbon atoms react with CF_4 to form an intermediate which reacts further with O_2 to form $C^{11}O_2$ as well as $C^{11}O$. On partial thermalization of the carbon atoms, by addition of 95% Ar moderator to CF_4–O_2 mixtures, similar effects are observed (see Figure 1). However, the amount of $C^{11}O_2$ is diminished, indicating that relative to O_2, reaction with CF_4 is more efficient for hot than for thermal atomic carbon.

Extrapolation of the data to 100% CF_4, where there is no direct reaction with O_2, implies that the intermediate reacts with O_2 to yield ~27% $C^{11}O_2$ and ~73% $C^{11}O$.

Reaction of atomic carbon with SF_6–O_2 mixtures yields results which are quite similar to those given above for CF_4–O_2 systems.

Reaction of Atomic Carbon with CF_4–C_2H_4 Mixtures. Results of reaction of C^{11} with CF_4–C_2H_4 mixtures, shown in Table III, confirm the conclusion reached above. Upon addition of CF_4 to C_2H_4, products are observed which are found with neither of the pure compounds. In particular, large yields are found for two compounds, named Y and Z. These have not been identified. However, their elution times are what

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(19) C. MacKay, M. Pandow, P. Polak, and R. Wolfgang, "Chemical Effects of Nuclear Transformations, Vol. II," I.A.E.A., Vienna, 1961, pp 17–26.

(20) J. Dubrin, *et al.*, *J. Inorg. Nucl. Chem.*, 26, 2113 (1964).

Table III. Reaction of C^{11} with Various Mixtures Containing C_2H_4[a]

C^{11} labeled products	Elution[b] vol, cc of He	C_2H_4 pure	4% C_2H_4– 96% Ne	97.5% CF_4– 2.5% C_2H_4	91% CF_4– 9% C_2H_4	87% C_2F_6– 13% C_2H_4	80% n-C_4F_{10}– 20% C_2H_4	87% SF_6– 13% C_2H_4
Acetylene (+ other C_1 + C_2's)	170	26	12	9.8	6.4	6.0	9.5	15.7
C_3H_4 (+ other C_3's)	200	18	9.5	3.2	4.7	4.8	3.9	
C_4's	275	7	4.1	4	4.7	3.6	2.9	2.6
C_5's (excluding C_5H_8's)	425	0.7	<1.0	2	1.7	1.4	1.7	3.0
1-Pentyne	575	4.3	15	11	11.8	10.9	9.4	10.6
Ethylallene	670	2.1	7.4	5.2	2.5	3.0	2.2	12.8[c]
Sum of eluted products found with pure C_2H_4		58	48	33	32	30	30	35
Compound Y	970	<0.7	n.d.[e]	12	11.0	11.4	17.9[c]	19.0[c]
Compound Z	1,260	<0.6	n.d.	5	5.4	7.4	6.3	5.0
Other products not found with pure C_2H_4[d]		0	0	3	6.4	14.6	24	14
Volatile activity not eluted	>10,000	7	7	11	8.2	6.2	13	8
"Polymer"[f]		35	45	36	37	31	10	20

[a] All reagents are gases at 25°, 1 atm total pressure. Yields given as per cent of total C^{11} available. [b] Volume of 11 ft 15% silicone column plus half counter volume = 170 cc. [c] Peak includes activity due to other products. [d] Eluting at volume >1260 cc. [e] n.d.: not determined. [f] "Polymer": not volatile at 25°, very approximately determined by difference between estimated available C^{11} (from monitor) and total volatile activity.

would be expected for a monofluorohydrocarbon containing about five or six carbon atoms. Furthermore, they are oxidized by $KMnO_4$, indicating that they are unsaturated. Figure 2 shows the dependence of the yield of products Y and Z on the relative amount of CF_4 and C_2H_4.

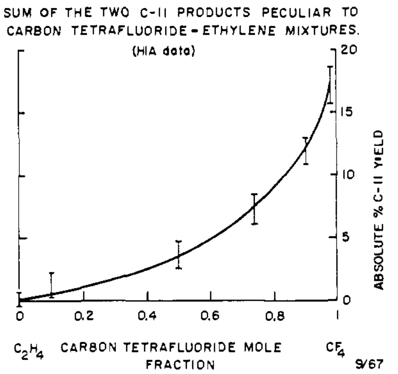


Figure 1. Yield of $C^{11}O_2$ from reaction of C^{11} with O_2–CF_4 mixtures (corrected for radiation oxidation of $C^{11}O$).

Upon moderation by neon of a 40:1 CF_4–C_2H_4 mixture, the yields of Y and Z decline considerably, to 6 ± 6% at the limit of a complete thermalization. This indicates that relative to reaction with C_2H_4 carbon atoms attack CF_4 to form the reactive intermediate more readily when they are hot than when they are thermal. A similar conclusion was found from results on moderation of CF_4–O_2 mixtures.

Reactions with Various Mixtures of Fluorine Compounds and Ethylene. We have now established that atomic carbon reacts with CF_4 to form some kind of reactive intermediate and seek to identify this. It could be an adduct of the type $CC^{11}F_4$. Alternatively, it might be a product of fluorine abstraction, $C^{11}F$. $C^{11}F_2$ seems unlikely because its presumed addition products to ethylene, $C_2C^{11}H_4F_2$, are not found. However, the well-known low reactivity of CF_2 might cause it to react otherwise, and we thus cannot exclude possible participation by this species. CF_3 is also improbable because, in analogy to the reaction of CH_3 with ethylene, it would be expected eventually to yield saturated products. However, the major products of the reaction of the intermediate with ethylene, Y and Z, appear to be unsaturated.

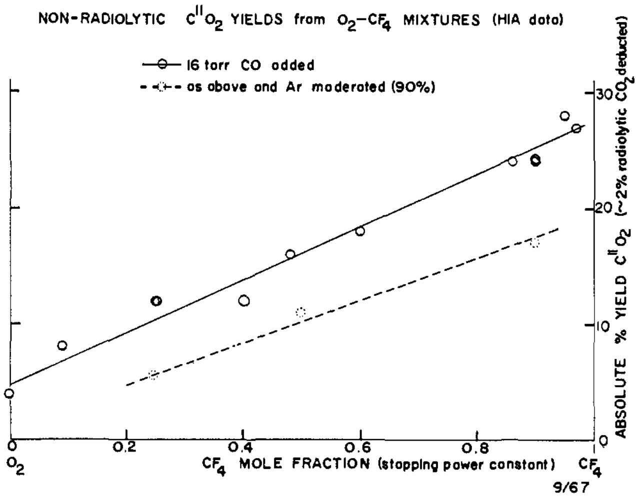


Figure 2. Yields of products Y and Z from reaction of C^{11} with CF_4–C_2H_4 mixtures.

If the intermediate is an adduct, then both it and the final products it yields on reaction with C_2H_4 might be expected to change when the initial fluorine compound is changed. This would not be the case for an intermediate such as $C^{11}F$, or possibly $C^{11}F_2$, as formed by abstraction.

Table III shows results obtained with mixtures of CF_4, C_2F_6, n-C_4F_{10}, and SF_6 with ethylene. The product spectra obtained are very similar to that found with CF_4–C_2H_4. This strongly implies that the immediate product of reaction of atomic carbon with fluorine compounds is an abstraction product, probably C–F. (It does not exclude the possibility that the intermediates are adducts of a type where the C atom is not intimately incorporated. If the C^{11} remains peripheral to the reagent molecules, perhaps weakly bound to one or two of the fluorine atoms, then all such adducts could plausibly be expected to undergo similar reactions. In this case, however, the adduct might well react simply by donating the "loose" carbon atoms, without the transfer of fluorine.)

Relative Reactivites. The relative reactivities of CF_4 and O_2 may be evaluated as follows. In accordance with the above discussion, we write the reactions

$$C + CF_4 \xrightarrow{k_1} X$$

$$X + O_2 \xrightarrow{k_2} C^{11}O_2$$

$$X + O_2 \xrightarrow{k_3} C^{11}O$$

$$C + O_2 \xrightarrow{k_4} C^{11}O$$

The reactive intermediate, X, is probably $C^{11}F$. Then

$$\frac{\text{yield of } C^{11}O_2}{\text{yield of } C^{11}O} = \frac{k_1[CF_4]\dfrac{k_2}{k_2 + k_3}}{k_4[O_2] + k_1[CF_4]\dfrac{k_3}{k_2 + k_3}} \qquad (1)$$

When $[O_2] = 0$

$$\frac{\text{yield } C^{11}O_2}{\text{yield } C^{11}O} = \frac{k_2}{k_3} \qquad (2)$$

Using eq 2 and the extrapolated data from Figure 1, $k_2/k_3 = 0.38$. The straight line in Figure 1 can then be well fitted if $k_1 = k_4$. This implies that the reactivity of hot C^{11} toward O_2 to form $C^{11}O$, and toward CF_4 to form the reactive intermediate ($C^{11}F$), is about equal. It is possible to apply the same analysis to the moderated, partially thermalized systems, but these data (see Figure 1) seem too imprecise to make this worthwhile. However, as has already been remarked, it is qualitatively obvious that k_1/k_4 will be lower for thermal carbon atoms.

For the reaction in CF_4–C_2H_4 systems, we can write

$$C + CF_4 \xrightarrow{k_1} X$$

$$X + C_2H_4 \xrightarrow{k_5} \text{Y and Z}$$

$$X + C_2H_4 \xrightarrow{k_6} \text{unobserved products}$$

$$C + C_2H_4 \xrightarrow{k_7} C^{11}\text{-acetylene, allene, etc.}$$

Then

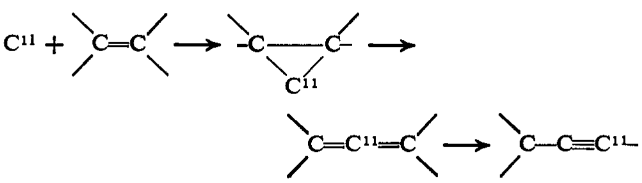
$$\frac{\text{yield of Y and Z}}{\text{total of } C^{11} \text{ available}} = \frac{k_1k_5[CF_4]/(k_5 + k_6)}{k_1[CF_4] + k_7[C_2H_4]} \qquad (3)$$

If $k_1/k_7 = 0.28 \pm 0.15$ and $k_5/k_6 = 0.25 \pm 0.05$ the curve of Figure 2 is obtained, satisfactorily describing the data. The analyses also yield a ratio $k_4/k_7 = 0.3$ which is in reasonable agreement with that measured directly.[21] The important conclusion is again that the reactivity of C atoms toward CF_4 and C_2H_4 is comparable.

Results from CF_4–C_2H_4 mixtures, moderated by excess neon, again indicate that the relative reactivity of CF_4 compared with C_2H_4 is lower toward thermal than toward hot carbon atoms. On the basis of the very rough data available, it appears that k_1/k_7 drops to the vicinity of 0.1 with thermalized atomic carbon.

Summary

The Nature of Attack by Atomic Carbon. This work indicates that carbon atoms react with perfluorinated carbon–carbon double bonds in a manner apparently analogous to that previously established[1,3,9,22] for the reaction with alkenes.



On the other hand, we find no evidence for reactions with CF_4 and perfluoroalkanes which are analogous to the well-known reaction with alkanes.

$$C^{11} + CF_4 \longrightarrow F_3CC^{11}F \longrightarrow FC{\equiv}C^{11}F + F_2$$
$$\longrightarrow F_2C{=}C^{11}F_2$$

Instead there is good circumstantial evidence for formation of CF, not only with fluorocarbons, but with SF_6 as well. This does not exclude the possibility of insertion into a C–F bond; indeed were an intermediate such as $F_3CC^{11}F$ formed, decomposition to CF_3 and $C^{11}F$ would probably be an energetically more favorable mode of decomposition than would decomposition of $H_3CC^{11}H$ to CH_3 and $C^{11}H$. However, the fact that other possible products of insertion into a C–F bond are not formed, even with hot carbon atoms, and the similar behavior of SF_6 and fluorocarbons encourages the simpler hypothesis that abstraction occurs directly rather than by initial insertion.

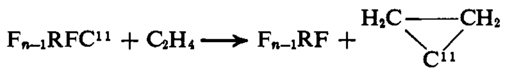
$$C^{11} + RF_n \longrightarrow F_{n-1}RFC^{11} \longrightarrow F_{n-1}R + C^{11}F$$

Again we do not know whether the intermediate in this abstraction has a transient existence of only one vibration, or whether it has a longer life.

The presumed abstraction reaction becomes relatively less efficient if the carbon atom is thermal instead of hot. There could be two reasons for this finding. The attack of thermal C^{11} on the fluorine compound may then be less effective. Alternatively the initial reaction with RF_n may be equally efficient for both fast and slow carbon atoms, but the intermediate $F_{n-1}RFC^{11}$ may have a longer lifetime at lower energies. If this is the case, instead of decomposing to $C^{11}F$, it may act as a carbon atom donor and lose its carbon atom to the other reagent. For example

$$F_{n-1}RFC^{11} + O_2 \longrightarrow F_{n-1}RF + C^{11}O + O$$

or



In summary, atomic carbon seems to share with carbenes the property that it will insert into carbon double bonds somewhat more readily than into C–H bonds.[4] Like carbenes, it probably does not insert into C–F bonds to any appreciable extent. However, it can probably abstract fluorine atoms (there is no evidence or expectation that carbenes are able to do this). These

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(21) R. F. Peterson, unpublished results, indicating $k_4/k_7 \sim 0.5$. The difference may be partially due to a different mean energy of C atoms moderated by CF_4 in the CF_4 mixtures.

(22) R. T. Mullen and A. P. Wolf, *J. Am. Chem. Soc.*, **84**, 3214 (1962).

general properties of such electron-deficient species may be rationalized as follows. The species involved are electron deficient and will therefore seek the site where electrons are most readily available. This is to be found at multiple π bonds, and these are therefore preferentially attacked. With C–H bonds, the highest electron density is present between the carbon and the hydrogen and accordingly insertion will occur. In the case of C–F bonds, however, the unbonded side of the fluorine atom presents a high electron density due to nonbonding electrons. It is quite plausible that the incoming carbon atom finds this side to be a more readily available source of electrons than the C–F bond itself. Steric factors may also contribute to making insertion to give a C–C–F transition state less favorable than simple attachment to give a C–F–C configuration. The CF_4 molecule presents mostly the electron-rich unbonded "backside" of the fluorine atom to an impinging C atom, while with CH_4 there is relatively little peripheral electron density to prevent an approach to the C–H bond. The hypothesis that at C–F bonds abstraction is favored over insertion thus becomes reasonable. The same consideration can also account for the apparent unreactivity of single C–C bonds toward electron-deficient species.[1,4]

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Monomeric Oxygen Adducts of N,N′-Ethylenebis(acetylacetoniminato)ligandcobalt(II). Preparation and Properties[1]

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Abstract: A series of monomeric molecular oxygen carriers of the general formula $Co(acacen)(B)O_2$ (acacen = $(CH_3C(O^-){=}CHC(CH_3){=}NCH_2\text{-})_2$; B = N,N-dimethylformamide, pyridine, 4-aminopyridine, 4-methylpyridine, and 4-cyanopyridine) were prepared in nonaqueous solvents. These adducts are reversibly formed in solution and are shown to be monomeric by oxygen uptake and molecular weight experiments. The equilibrium constant for the reaction in N,N-dimethylformamide was measured at $-10°$ and found to be $\log K_{eq} = 2.11 \pm 0.10$. Crystalline adducts were isolated and characterized by means of elemental analysis, oxygen evolution measurements, molecular weight, magnetic measurements, and electronic and infrared spectra. These oxygen adducts are formulated as monomeric octahedral complexes of low-spin cobalt(III), because epr measurements[3] show that the unpaired electron is largely associated with the coordinated oxygen.

Schiff base complexes of cobalt(II) have long been known to bind molecular oxygen.[4] Following the discovery of Tsumaki[5] that crystals of N,N′-ethylenebis(salicylideneiminato)cobalt(II) darken when exposed to the atmosphere, Calvin and his coworkers[6] conducted an exhaustive study of the oxygen-carrying capabilities of this complex and some of its ring-substituted derivatives in the solid state. They discovered that reversible coordination with oxygen was only possible with an "active" crystalline modification of the solid complex.

Solution oxygenation reactions of these complexes would preclude the necessity of preparing an active form of the crystal. Calvin makes only a brief reference to the oxygenation of N,N′-ethylenebis(salicylideneiminato)cobalt(II) in pyridine solution.[7] This reaction in pyridine and other solvents has recently been investigated by Calderazzo and coworkers.[8,9] Fritz and Gretner[10] have investigated the reaction of oxygen with a pentadentate cobalt(II) Schiff base complex, N,N′-dipropylenaminebis(salicylideneiminato)cobalt(II).

Although the initial formation of a monomeric 1:1 oxygen adduct in solution has been postulated on the basis of kinetic evidence,[11] thus far practically all of the oxygen adducts of cobalt(II) complexes have been dimeric oxygen-bridged species. The first well-defined example of a monomeric oxygen adduct of cobalt(II) prepared in solution and isolated as a crystalline solid was recently reported by Floriani and Calderazzo.[9] We wish to report here in detail results given in an earlier communication[12] on the reaction of molecular oxy-

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(1) Abstracted from the Ph.D. Thesis of A. L. Crumbliss, Northwestern University, 1968.

(2) National Institutes of Health Predoctoral Fellow, 1965–1968.

(3) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Am. Chem. Soc.*, **92**, 61 (1970).

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(12) A. L. Crumbliss and F. Basolo, *Science*, **164**, 1168 (1969).