Electron Spin Resonance Studies of Fluoroalkyl Radicals in Solution. III. Photolysis of Perfluoroketones and Adduct Formation

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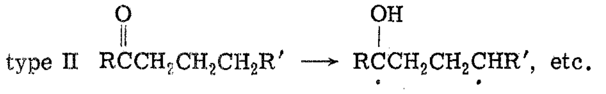
The esr spectra of paramagnetic species formed during the ultraviolet photolysis of various fluorinated ketones are examined directly in the cavity of the spectrometer. The production of fluoroalkyl radicals by Norrish type I photocleavage is observed in inert solvents. The fluoroalkyl and fluoroacyl radicals produced in the primary photochemical process add to the oxygen atom of the fluoroketones forming α-alkoxy- and α-acyloxyfluoroalkyl radicals. Fluoroacyl radicals have been detected by hydrogen atom abstraction from fluoroaldehydes. In cyclopropane solutions, α-hydroxyfluoroalkyl radicals resulting from hydrogen transfer from the solvent to the photoexcited ketone are observed, and their identity is verified by generating them by an independent procedure from the corresponding fluoroalcohol. The susceptibility of fluoroketones to addition of other radicals is also probed by the examination of the esr spectra of various adducts with silyl radicals. Addition of silyl radicals to sterically crowded perfluoroketones produces fluoroalkyl radicals of unusual stability. The esr spectrum of the carbonyl fluoride adduct $Et_3SiO\dot{C}F_2$ like other α,α-difluoroalkyl radicals shows a pronounced line width effect due to dipolar broadening, which is simulated by the relaxation matrix method assuming a correlation time in the region of 10^{-11} sec for the tumbling motion of the free radical in solution.

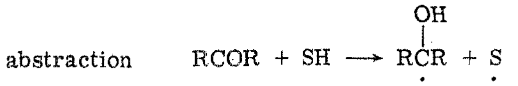
Introduction

The irradiation of the n–π^* band of ketones leads to a rich array of photochemical reactions including homolysis of the acyl carbon bonds and intramolecular and intermolecular hydrogen atom transfer reactions.[2a–d]

$$\text{type I}\qquad \text{RCOR}' \longrightarrow \text{R}\dot{\text{C}}\text{O} + \dot{\text{R}}' \qquad (1)$$



$$\text{type II}\quad \text{R}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_2\text{CH}_2\text{CH}_2\text{R}' \longrightarrow \text{R}\underset{\bullet}{\overset{\text{OH}}{\overset{|}{\text{C}}}}\text{CH}_2\text{CH}_2\underset{\bullet}{\text{C}}\text{HR}',\ \text{etc.} \qquad (2)$$



$$\text{abstraction}\qquad \text{RCOR} + \text{SH} \longrightarrow \text{R}\underset{\bullet}{\overset{\text{OH}}{\overset{|}{\text{C}}}}\text{R} + \underset{\bullet}{\text{S}} \qquad (3)$$

A variety of free-radical intermediates formed by such processes have been observed by esr techniques.[2e,f]

Perfluoroketones represent an interesting class of compounds with an exceptionally electron-deficient carbonyl function.[3,4] Their photochemical behavior has not been investigated as thoroughly as that of their hydrocarbon analogs, and there is uncertainty concerning the chemical processes following photoexcitation. Chemical studies indicate that the ultraviolet irradiation of hexafluoroacetone (HFA) in the gas phase affords principally carbon monoxide and perfluoroethane as the recombination product of two trifluoromethyl radicals.[5] The latter have been detected by esr as stabilized adsorbed species following the photolysis of HFA on zeolites at 77°K.[6] In one gas-phase study,[7] however, significant amounts of perfluoro-*tert*-butyl methyl ether were also found, particularly at higher vapor pressures, in addition to carbon monoxide and perfluoroethane. A reversible addition of the trifluoromethyl radicals to the oxygen atom of an HFA molecule was postulated followed by the coupling of the resulting α-trifluoromethoxy radical I with another trifluoromethyl radical to yield the perfluoro ether. Although this finding has been questioned,[5c] it is in harmony with the results of a recent investigation which shows that this perfluoro ether is in fact the major product (50–70% yield) obtained after prolonged exposure of liquid HFA to ultraviolet light.[8]

$$\text{CF}_3\text{COCF}_3 \xrightarrow{h\nu} [\text{CF}_3\dot{\text{C}}\text{O}\ \dot{\text{C}}\text{F}_3] \longrightarrow 2\dot{\text{C}}\text{F}_3 + \text{CO} \qquad (4)$$

$$\dot{\text{C}}\text{F}_3 + \text{CF}_3\text{COCF}_3 \rightleftarrows \underset{\text{I}}{(\text{CF}_3)_2\dot{\text{C}}\text{OCF}_3} \qquad (5)$$

$$(\text{CF}_3)_2\dot{\text{C}}\text{OCF}_3 + \dot{\text{C}}\text{F}_3 \longrightarrow (\text{CF}_3)_3\text{COCF}_3 \qquad (6)$$

The role and stability of trifluoroacetyl radicals during photolysis of HFA is also controversial. The notable absence of hexafluorobiacetyl among the products of photolysis has been taken to imply a direct dissociation of HFA into carbon monoxide and two trifluoromethyl radicals, or the kinetically equivalent formation of a "hot" trifluoroacetyl radical which dissociates spontaneously by virtue of its excess energy.[5b] The sole chemical indication extant so far of a stepwise decomposition consists in the observation of trifluoroacetyl halides from the photolysis of HFA in the presence of bromine or chlorine,[9] but it has been given alternative explanations.[3a,5b]

Chemical studies have also shown that HFA enters into a rich array of reactions *via* addition of various radicals to both the carbon and oxygen atoms of the carbonyl group.[3,10,11] The radical reactions of other perfluoro ketones have received much less attention so far. In this study, we examined the esr spectra of several types of fluorinated radical species in order to describe the paramagnetic intermediates in the photolysis of fluoroketones. The pertinent points we wish to describe are (a) radicals formed by uv photolysis of fluoroketones in inert fluorocarbon solvents with particular emphasis on hexafluoroacetone, (b) perfluoroacyl radicals obtained by hydrogen atom abstrac-

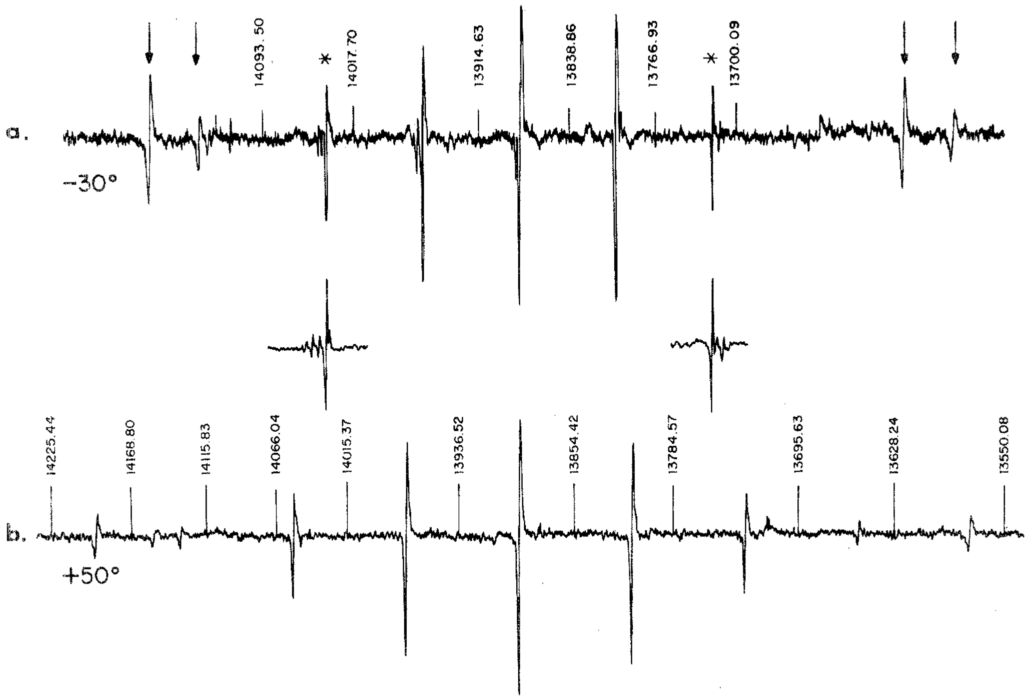


Figure 1. Esr spectra obtained during ultraviolet irradiation of hexafluoroacetone in dichlorodifluoromethane at −30° and in perfluoro-1,2-dimethylcyclobutane at +50°. The groups of lines denoted with asterisks are shown on an expanded scale in the inserts. The major septet spectrum belongs to $(CF_3)_2\dot{C}OCF_3$. The lines denoted with arrows are the $M_I = \pm\frac{1}{2}$ lines of the CF_3 radical. The proton nmr field markers are in kHz.

tion from perfluoroaldehydes, (c) α-hydroxyfluoroalkyl radicals derived by intermolecular photoreduction of fluoroketones as well as by independent methods, and (d) species formed by addition of silyl radicals to the electron-deficient carbonyl functions.

Results and Discussion

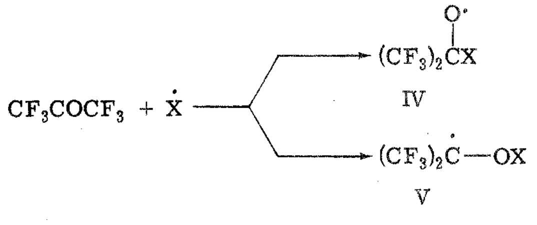
I. Photolysis of Fluoroketones in Inert Solvents. A. Photolysis of Hexafluoroacetone (HFA). Ultraviolet irradiation of a dilute solution of HFA in dichlorodifluoromethane (1:10 v/v) at −30° affords, at low microwave power levels and low modulation amplitudes, the esr spectrum shown in Figure 1a which indicates the presence of three radical species: (a) the trifluoromethyl radical[12-14] (only the $M_I^F = \pm\frac{1}{2}$ lines, denoted by arrows, are shown in Figure 1a), (b) a radical II giving rise to a septet spectrum (a = 18.74 G) with partially resolved second-order splittings, and (c) a third radical species III in lower concentration with a slightly larger septet splitting (19.30 G) and a small quartet splitting (0.84 G, see insets in Figure 1a). The same composite spectrum is obtained under similar conditions using a variety of inert fluorinated solvents such as 1,2-dichlorotetrafluoroethane, perfluorocyclobutane, and perfluoro-1,2-dimethylcyclobutane. The relative concentrations of the last two species are temperature dependent, with species III becoming less important at higher temperatures. Thus, photolysis of HFA in perfluoro-1,2-dimethylcyclobutane at +50° gives only the spectra of $\dot{C}F_3$ and of species II (Figure 1b). The major septet spectrum is not affected by any selective line broadening effects down to −120°.

Attempts to identify the esr spectrum of the trifluoroacetyl radical during the photolysis of HFA gave ambiguous results. Paul and Fischer[2e] had shown earlier that the esr spectra of acyl radicals can be observed during the photolysis of alkyl ketones at high microwave powers. Photolysis of HFA in various fluorinated solvents over a wide temperature range under conditions of high microwave power brings out additional broad lines which form a complex pattern and decay slowly upon shuttering the light. These lines cannot be attributed to the trifluoroacetyl radical, since they do not coincide with the esr spectrum of $CF_3\dot{C}O$ generated at low temperatures by hydrogen abstraction from trifluoroacetaldehyde (*vide infra*). Since the trifluoroacetyl radical is highly unstable, the observation of $\dot{C}F_3$ is not inconsistent with a stepwise decomposition of HFA by type I cleavage.

$$CF_3COCF_3 \xrightarrow{h\nu} CF_3\dot{C}O + \dot{C}F_3 \qquad (7)$$

$$CF_3\dot{C}O \longrightarrow \dot{C}F_3 + CO \qquad (8)$$

The unambiguous identification of radicals II and III poses several problems. The known propensity of HFA to enter into radical addition reactions[10,11] suggests that these species should be formed by addition of a radical X to the carbonyl function as shown in eq 9 and 10. Fluoroalkoxy radicals IV, resulting from the addition of X· to carbon, can


(9)
(10)

$$CF_3COCF_3 + \dot{X} \longrightarrow (CF_3)_2C(O\cdot)X \ \text{(IV)} \qquad (9)$$

$$CF_3COCF_3 + \dot{X} \longrightarrow (CF_3)_2\dot{C}{-}OX \ \text{(V)} \qquad (10)$$

almost certainly be excluded from consideration since the large g tensor anisotropy expected for such radicals is inconsistent with the unusually narrow line widths observed for radicals II and III (ΔH = 0.18 G for III at −30°). Indeed, it is doubtful that reactive alkoxy radicals can be detected in solution.[15] Esr studies cannot, therefore, evaluate

TABLE I: Esr Parameters of α-Hydroxy- and α-Fluoroalkoxyfluoroalkyl Radicals in Solution

Radical	T, °C	⟨g⟩	Proton and fluorine isotropic coupling constants, G				
$\dot{C}H_2OH^a$	−50	2.00336				α-H: 17.84	OH: 1.75
$CH_3\dot{C}H(OH)^a$	−33	2.00321		CH_3: 22.27		α-H: 15.50	OH: 0.98
$(CH_3)_2\dot{C}OH^a$	26	2.00317		CH_3: 19.66			OH: 0.70
$(CH_3)_2\dot{C}OH^a$	−23	2.00309		19.57			OH: 0.0
$CF_3\dot{C}H(OH)^b$	−44		CF_3: 29.82			α-H: 19.52	OH: 1.20
$CF_3\dot{C}(CH_3)OH^b$	−40		CF_3: 29.43	CH_3: 21.22			OH: c
$CF_3\dot{C}(CH_3)OH^b$	−109		29.00	21.38			
$(CF_3)_2\dot{C}OH^d$	−13		CF_3: 23.15				OH: 1.16
$(CF_3)_2\dot{C}OH^d$	−55	2.00284	CF_3: 23.94				OH: 1.72
$(CF_3)_2\dot{C}OH^d$	−130		$(CF_3)_a$: 26.49	$(CF_3)_b$: 22.28	$(CF_3)_{av}$: 24.39		OH: 2.41
$(CF_3)_2\dot{C}OCH(CF_3)_2{}^c$	−36		α-CF_3: 20.3			γ-CF_3: 2.2	
$(CF_3CF_2)_2\dot{C}OH^e$	−40		CF_2: 30.74		CF_3: 3.68		OH: 1.15
$(CF_3)_2CF\dot{C}(CF_3)OH^e$	−35		CF: 16.78	α-CF_3: 26.70	β-CF_3: 2.61		OH: c
$(CF_3)_2\dot{C}OCF_3{}^d$	50		α-CF_3: 18.81			β-CF_3: c	
$(CF_3)_2\dot{C}OCF_3{}^d$	−42	2.00257	α-CF_3: 18.74			β-CF_3: c	
$(CF_3)_2\dot{C}O_2CCF_3{}^d$	−42		α-CF_3: 19.30			γ-CF_3: 0.84	
$(CF_3)_2\dot{C}O_2CCH_3$	−48		α-CF_3: 21.23				
$(CF_3CF_2)_2\dot{C}OCF_2CF_3{}^d$	−70		α-CF_2: 24.00		β-CF_3: 3.20	OCF_2CF_3: 0.6^f	
$(n\text{-}Bu)_3SiCF_2\dot{C}F(OCF_3)$	−21	2.00397	α-CF_2: 12.23	α-F: 91.2	OCF_3: c		
$(n\text{-}Bu)_3SiCF_2\dot{C}F(OCF_2CF_3)$	−10		α-CF_2: 12.4	α-F: 89.9	OCF_2CF_3: 0.5^f		
$CF_3\dot{C}F_2{}^g$	−10	2.00386	CF_3: 11.43	α-F: 87.7			
$(CF_3)_2\dot{C}F$	+30	2.00321^h	CF_3: 19.75	α-F: 70.48			
$(CF_3)_2\dot{C}H^i$	−113	2.00221	CF_3: 22.64	α-H: 24.61			
$CF_3\dot{C}H_2{}^i$	−113	2.00234	CF_3: 29.61	α-H: 23.77			
$(CF_3)_3\dot{C}^j$	−60	2.0015	CF_3: 17.9				
$(CF_3)_2\dot{C}\text{-}O^{-k}$	25	2.00397	CF_3: 34.7				

[a] From R. Livingston and H. Zeldes, *J. Chem. Phys.*, **44,** 1245 (1966). In aqueous solution. [b] In alcohol as solvent. [c] Unresolved. [d] In dichlorodifluoromethane. [e] In cyclopropane. [f] Nearly equivalent CF_2 and CF_3 fluorines (sextet). [g] From ref 13. [h] Corrected for second-order shifts and for nmr probe placement. [i] From ref 14. [j] From ref 20. [k] From E. G. Janzen and J. L. Gerlock, *J. Phys. Chem.*, **71,** 4577 (1967).

the importance of such additions in the radical reactions of fluoroketones. Radical addition to oxygen to afford α-oxyperfluoroalkyl radicals V, on the other hand, is plausible. Indeed, the available evidence strongly supports the assignment of the major septet spectrum of Figure 1 to the α-trifluoromethoxyhexafluoroisopropyl radical V′ (X = CF_3, eq 10).[15a] The weaker spectrum consisting of a septet-of-quartets is attributed to the α-trifluoroacetoxyhexafluoroisopropyl radical V″ (X = CF_3CO, eq 10).

$$\underset{\text{V}'}{(CF_3)_2\dot{C}—OCF_3} \qquad \underset{\text{V}''}{(CF_3)_2\dot{C}—O_2CCF_3}$$

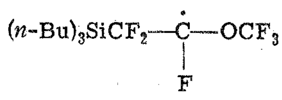
The formation of the ether radical V′ is in harmony with the chemical studies of Gordon[7] and Resnick,[8] since it is the direct precursor of perfluoro-*tert*-butyl methyl ether (eq 6) found by these authors among the products of photolysis of HFA at high vapor pressures and in the liquid phase, respectively. The septet hyperfine structure (Figure 1) is due to the six equivalent β fluorines. Their coupling constant ($A_\beta{}^F$ = 18.74 G) compares remarkably well with the β-fluorine coupling in the perfluoroisopropyl radical (19.75 G, Table I). The latter represents the proper comparison since α-fluoro and α-alkoxy groups exert similar out-of-plane bending influences on the trigonal carbon atom by virtue of the destabilizing interaction between the lone pairs of electrons on fluorine or oxygen and the adjacent half-filled p orbital on carbon.[14,16] The most remarkable feature of the spectrum of species V′, however, is the absence of any resolvable fluorine hyperfine structure due to the CF_3O group. For comparison, the methyl protons in methoxymethyl radical, $\dot{C}H_2OCH_3$, give rise to a splitting of about 2 G,[17] and one would assume that the analogous fluorine atoms would give rise to a comparable or larger interaction. We sought to confirm this unexpected effect by examining other α-perfluoroalkoxyalkyl radicals.

Indeed, the spectrum of radical VI, obtained by photolysis of a mixture of perfluorovinyl methyl ether, tri(*n*-butyl)silane, and di-*tert*-butyl peroxide in cyclopropane,[18] is also devoid of any resolvable structure (ΔH = 0.70 G) due to the ethereal CF_3 fluorines. The spectrum of radical VI (g = 2.00397, corrected for second-order effects) at −25° consists of a large doublet due to the α fluorine (91.20 G) further split into triplets by the two β fluorines (12.23 G). The magnitude of the doublet compares well with the α-fluorine coupling in $CF_3\dot{C}F_2$ (87.3 G), again demonstrating that $-\dot{C}FOR$ and $-\dot{C}F_2$ fragments have similar geometries at the radical sites. Analogous α-fluorine couplings in the region of 90 G have also been observed for a series of radicals VII formed by radical addition to perfluoroacyl fluorides.[19] The

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3CO\cdot$$

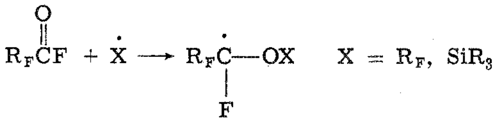
$$(CH_3)_3CO\cdot + (n\text{-}Bu)_3SiH \longrightarrow (n\text{-}Bu)_3Si\cdot + (CH_3)_3COH$$

$$(n\text{-}Bu)_3Si\cdot + CF_2{=\!=}CF—OCF_3 \longrightarrow$$



$$(n\text{-}Bu)_3SiCF_2—\underset{\displaystyle F}{\underset{|}{\dot{C}}}—OCF_3 \qquad (11)$$

VI



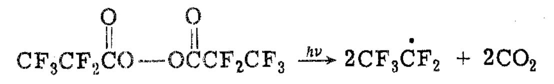
$$R_F\overset{\displaystyle O}{\overset{\|}{C}}F + \dot{X} \longrightarrow R_F\underset{\displaystyle F}{\underset{|}{\dot{C}}}—OX \qquad X = R_F,\ SiR_3 \qquad (12)$$

VII

triplets associated with the β protons in VI display a pronounced broadening of the central lines ($M_I = 0$ lines) below $-40°$, indicating hindered rotation about the C_α–C_β bond. This effect is also common for radicals such as VII and must be attributed to the strong pyramidality of a $-\dot{C}FOR$ radical site.[14]

The radical analogous to VI from perfluorovinyl ethyl ether and tri(n-butyl)silane ($a_\alpha{}^F = 89.9$ G; $a_\beta{}^F = 12.4$ G, $T = -10°$) is also interesting in that each line of the basic doublet-of-triplets is further split into an apparent sextet of 0.5 G. Thus, while the fluorines of an α-trifluoromethoxy groups in a fluoroalkyl radical give no resolvable hyperfine structure, the CF_2 fluorines of an α-pentafluoroethoxy group give a small splitting of nearly the same magnitude as the splitting of the CF_3 fluorines one carbon atom further removed from the radical site.

This observation is confirmed by additional experiments which also demonstrate the ready addition of perfluoroalkyl radicals to the oxygen atom of HFA. Photolysis of a solution of HFA and perfluoropropionyl peroxide in 1,2-bis(trifluoromethyl)perfluorocyclobutane at room temperature leads to a spectrum consisting of at least four species. The $\dot{C}F_3$ and $CF_3\dot{C}F_2$[13,20] radicals can be immediately recognized. The remaining two species, in comparable concentrations, give rise to overlapping septets of very similar splitting. Slow scans under conditions of low microwave power and modulation reveal that one septet has no additional resolved structure and is identical with the major septet of Figure 1, while the second septet is further split into apparent sextets of 0.7 G. This septet of small sextets must belong to the adduct VIII of a perfluoroethyl radical to the oxygen of HFA in which the five OCF_2CF_3 fluorines are again almost equally coupled to the unpaired electron despite their different positions. These small couplings to ethereal fluorines adjacent to the α-oxygen atom are surprising not only in view of the much larger coupling of the analogous ethereal protons, as was pointed out above, but also in comparison with radicals such as $CF_3OCH_2\dot{C}H_2$,[18] in which the fluorine splitting is 2.0 G despite the trifluoromethyl groups being one carbon further removed from the radical center. To add to the complexity of the situation, the radical $(CF_3)_2\dot{C}OCH(CF_3)_2$, obtained by hydrogen removal from bis(hexafluoroisopropyl) ether with $tert$-butoxy radicals in cyclopropane, shows no indication of a splitting by the ethereal proton. Its spectrum consists of a large septet of 20.3 G (α-CF_3 fluorines) further splitting into small septets of 2.2 G by six equivalent δ fluorines. Clearly, much remains to be learned about long-range fluorine hyperfine interactions.



$$CF_3CF_2\overset{O}{\overset{\|}{C}}O{-}O\overset{O}{\overset{\|}{C}}CF_2CF_3 \xrightarrow{h\nu} 2CF_3\dot{C}F_2 + 2CO_2$$

$$CF_3COCF_3 + CF_3\dot{C}F_2 \longrightarrow \underset{\text{VIII}}{(CF_3)_2\dot{C}{-}OCF_2CF_3} \quad (13)$$

$$CF_3COCF_3 + \dot{C}F_3 \longrightarrow \underset{\text{V}'}{(CF_3)\dot{C}OCF_3}$$

The trend displayed by the g factors for the series of radicals listed below (Table I) provides some insight into the possible causes for the small unresolvable hyperfine interaction to the OCF_3 fluorines in $(CF_3)_2\dot{C}OCF_3$. The smooth decrease in the g factors, from the highest value of 2.00336 for the hydroxymethyl radical to the lowest value of 2.00257 for the $(CF_3)_2\dot{C}OCF_3$ radical, indicates a steadily decreasing spin density on oxygen in this series. The latter is the major source for the increase in the g factors for α-hydroxyalkyl radicals over the values typical for alkyl radicals (2.0022–2.0026). Since the hyperfine interaction to the freely rotating CH_3 protons in $\dot{C}H_2OCH_3$ is determined by the spin density on oxygen through the combined effects of hyperconjugation and spin polarization, it is perhaps not surprising that the interaction to the ethereal CF_3 fluorines in $(CF_3)_2\dot{C}OCF_3$ will be small if the spin density on oxygen is greatly reduced as evidenced by the unusually low g factor for this radical. Another interesting deduction can be made by comparing the hydroxylic proton splittings for $(CH_3)_2\dot{C}OH$ and $(CF_3)_2\dot{C}OH$ (Table I). The small magnitudes of these splittings implies a more or less planar structure.[17] However, this splitting for the $(CH_3)_2\dot{C}OH$ radical must be *positive*, judging by the positive temperature coefficient of its absolute value (Table I), while the corresponding coupling in $(CF_3)_2\dot{C}OH$ must be *negative* since the temperature coefficient of its absolute value is negative in Table I (*cf.* ref 17).

$\dot{C}H_2OH$	$CH_3\dot{C}H(OH)$	$(CH_3)_2\dot{C}OH$	$(CF_3)_2\dot{C}OH$	$(CF_3)_2\dot{C}OCF_3$
(2.00336)	(2.00321)	(2.00309)	(2.00284)	(2.00257)

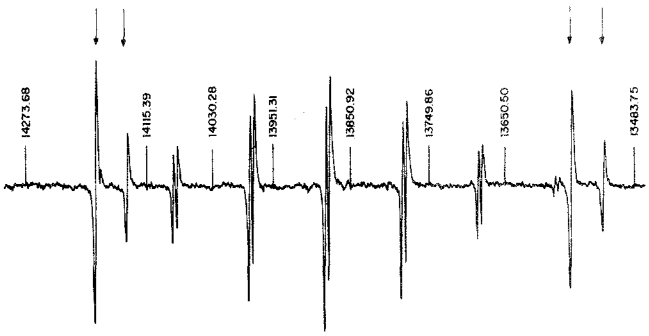
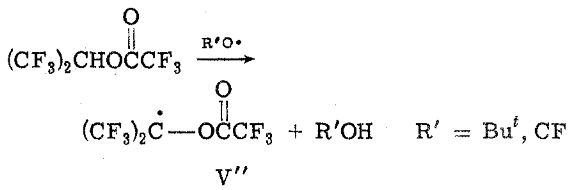


Figure 2. Esr spectrum of the $(CF_3)_2\dot{C}OH$ radical (0°) obtained by photolysis of a dichlorodifluoromethane solution containing hexafluoroacetone and trifluoroacetaldehyde. The lines denoted with arrows belong to the $\dot{C}F_3$ radical.

The identification of the minor radical species in the photolysis of HFA as radical V″ is less certain. Our direct attempts to prove the structure of V″ have been unsuccessful as yet. Thus, hydrogen atom abstraction from hexafluoroisopropyl trifluoroacetate (eq 15), under conditions well established to generate $tert$-butoxy or trifluoromethoxy radicals, afforded no esr spectrum of V″. Part of the difficulty is due to absorption of irradiation by the ester, even in dilute solutions.

$$CF_3\dot{C}O + CF_3COCF_3 \longrightarrow \underset{\text{V}''}{(CF_3)_2\dot{C}{-}O_2CCF_3} \quad (14)$$



$$(CF_3)_2CHO\overset{O}{\overset{\|}{C}}CF_3 \xrightarrow{R'O\cdot} \underset{\text{V}''}{(CF_3)_2\dot{C}{-}O\overset{O}{\overset{\|}{C}}CF_3} + R'OH \qquad R' = Bu^t, CF_3 \quad (15)$$

Another approach also failed to provide support for V″ but led to interesting information. It was hoped that photolysis of HFA in the presence of trifluoroacetaldehyde, which produces the trifluoroacetyl radical by loss of the hydrogen atom (*vide infra*), would lead to an enhanced spectrum of V″. The spectrum of Figure 2, obtained by photoly-

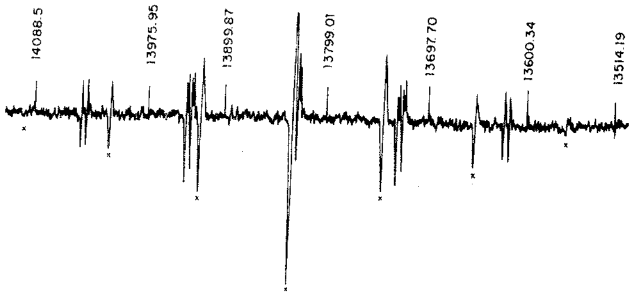


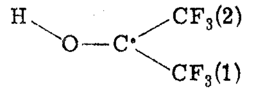
Figure 3. Esr spectrum obtained by photolysis of a mixture of hexafluoroacetone and acetaldehyde in a cyclopropane solution at −48°. Two radical species are present: the $(CF_3)_2\dot{C}OCOCH_3$ radical (septet*) and the $(CF_3)_2\dot{C}OH$ radical (septet-of-doublets).

sis of these substances in dichlorodifluoromethane at 0°, however, shows only the presence of the trifluoromethyl radical, produced by decarbonylation of the trifluoroacetyl radical, and of the hydroxyhexafluoroisopropyl radical IX clearly produced by photoreduction of HFA. Raising the

$$[CF_3COCF_3]^* + CF_3{-}CHO \longrightarrow \underset{\text{IX}}{(CF_3)_2\dot{C}{-}OH} + CF_3\dot{C}O \qquad (16)$$

$$CF_3\dot{C}O \longrightarrow \dot{C}F_3 + CO$$

temperature to 25° causes the appearance of an additional septet (18.81 G) identical with that of Figure 1, indicating that at higher temperatures radical V′ is also formed in sufficient concentration for detection. Lowering the temperature steadily decreases the importance of the $\dot{C}F_3$ radical and produces alternating line shape effects in the spectrum of $(CF_3)_2\dot{C}OH$ symptomatic of hindered rotation of the OH fragment.[17] At −140°, this rotation is slow on the esr time scale and the two CF_3 groups appear inequivalent ($a_1^{CF_3}$ = 26.49 G, $a_2^{CF_3}$ = 22.28 G, a^H = 2.41 G) indicating a more or less planar equilibrium structure X. This effect will be de-



X

scribed fully in another context.[21] The magnitudes of the fluorine and proton coupling constants are also notably temperature dependent. At the lowest temperature (−140°) and under conditions of high microwave power, the trifluoroacetyl radical can also be detected (*vide infra*). These experiments again underscore the low activation energy for decarbonylation of the trifluoroacetyl radical. Furthermore, the appearance of minor amounts of V′ only at relatively high temperatures is consistent with its formulation as $(CF_3)_2\dot{C}OCF_3$ rather than $(CF_3)_2\dot{C}{-}O_2CCF_3$, since the steady-state concentration of $\dot{C}F_3$ increases with temperature within the range studied while the concentration of $CF_3\dot{C}O$ decreases. The failure to observe V′ and V″ at lower temperatures is attributed to the high reactivity of the aldehydic proton toward abstraction and thus promoting an efficient radical chain reaction.

The adduct of acetyl radicals to HFA, however, can be observed together with $(CF_3)_2\dot{C}OH$ in the photolysis of a mixture of HFA and acetaldehyde in Freon 12 or cyclopropane (Figure 3). The septet of doublets is readily assigned to $(CF_3)_2\dot{C}OH$. The broader septet lines (starred, a^F = 21.23 G) are associated with the acetyl adduct $(CF_3)_2\dot{C}O_2CCH_3$ in eq 17 (R = CH_3). Indeed, chemical studies[11] have shown that 1:1 adducts XI can be isolated in high yields during the free-radical chain reaction of aldehydes and hexafluoroacetone, *e.g.*

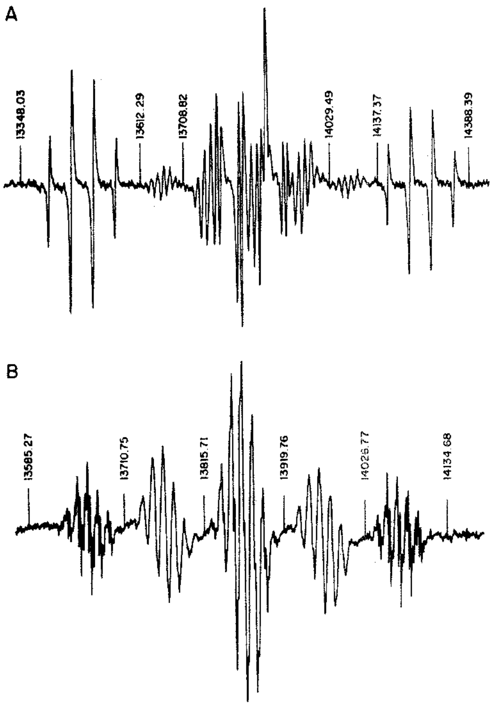
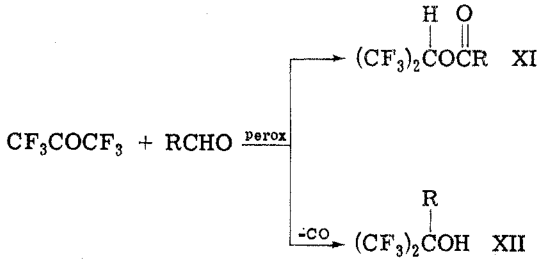


Figure 4. Esr spectra recorded during photolysis of perfluoroethyl ketone in dichlorodifluoromethane: (A) −30°, wide scan at relatively high microwave power showing the perfluoroethyl radical (note the unencumbered outer quartets) and radical XIII, (B) −70°, radical XIII at low microwave power and low modulation amplitude (expanded scale) showing selective line broadening.



$$CF_3COCF_3 + RCHO \xrightarrow{\text{perox}} (CF_3)_2\overset{H}{\overset{|}{C}}O\overset{O}{\overset{\|}{C}}R \quad \text{XI}; \qquad \xrightarrow{-CO} (CF_3)_2\overset{R}{\overset{|}{C}}OH \quad \text{XII}$$

In addition, carbon monoxide and tertiary alcohols XII are formed. The structures of XI and XII suggest that acyl radicals as intermediates add to the perfluoroketones at the oxygen terminus, whereas alkyl radicals resulting from de-

$$R\dot{C}O + CF_3COCF_3 \longrightarrow (CF_3)_2\dot{C}O_2CR \qquad (17)$$

$$(CF_3)_2\dot{C}O_2CR + RCHO \longrightarrow \text{XI} + R\dot{C}O \qquad (18)$$

$$R\dot{C}O \longrightarrow R\cdot + CO \qquad (19)$$

$$R\cdot + (CF_3)_2C{=}O \rightleftarrows (CF_3)_2(R)CO\cdot \qquad (20)$$

$$(CF_3)_2(R)CO\cdot + RCHO \longrightarrow \text{XII} + R\dot{C}O, \text{ etc.} \qquad (21)$$

carbonylation add to carbon. The quantitative delineation of these processes is made difficult by the reversibility in the latter instance. The ready observation of the acetyl adduct contrasts with our inability to observe the trifluoroacetyl adduct under similar conditions. One of the factors responsible for the contrasting behavior is no doubt ascribable to the longer lifetime of the acetyl radical prior to decarboxylation compared to the trifluoroacetyl radical.

B. Photolysis of Higher Fluoroketones. Type I cleavage (eq 1) followed by addition of the resulting fluoroalkyl radical to the carbonyl oxygen appears to be a general sequence of events in the photochemistry of fluoroketones in inert fluorocarbon solvents. Photolysis of a dilute solution of perfluoroethyl ketone in dichlorodifluoromethane (1:10 v/v) at −30° leads to the spectrum of Figure 4A in which two radical species are apparent: the $CF_3\dot{C}F_2$ radical, recognized by the outer quartets and by their separation, and a second species giving rise to a quintet of small septets. The latter spectrum can be recorded without interference from the $CF_3\dot{C}F_2$ radical using low microwave powers, low modulation amplitudes, and slow scans. Under these conditions the spectrum of this species at −70° (Figure 4B) reveals additional hyperfine structure and the presence of selective line broadening affecting the $M_I = \pm 1$ lines and, to a lesser extent, the $M_I = 0$ lines of the major quintet. This spectrum is assigned to radical XIII resulting from the addition of a $CF_3\dot{C}F_2$ radical to the oxygen of perfluoroethyl ketone.

$$C_2F_5COC_2F_5 + CF_3\dot{C}F_2 \longrightarrow \underset{\text{XIII}}{(CF_3CF_2)_2\dot{C}{-}OCF_2CF_3} \quad (22)$$

The quintet structure (24.00 G) is associated with the four β fluorines and the septets (3.20 G) with the six equivalent γ fluorines. The additional partially resolved hyperfine structure (0.6 G) is believed to consist of sextets associated with five nearly equivalent OCF_2CF_3 fluorines. Although the wing lines of the sextets are too weak to be clearly discerned and are also obscured by overlap, this interpretation is consistent with similar results for the α-perfluoroethoxyalkyl radicals discussed above. The observed line width effect affecting the inner lines of major quintet indicates that the rotation about the two C_α–C_β bonds is hindered and that each α-$\dot{C}F_2$ group exists in a preferred conformation relative to the axis of the central trigonal carbon atom in which the two β fluorines are nonequivalent. Unfortunately better quality spectra could not be obtained at sufficiently low temperatures to observe the spectrum in the slow exchange limit where the four β fluorines would presumably appear nonequivalent in pairs and give rise to a triplet-of-triplets spectrum.

Photolysis of a dilute solution of perfluoroisopropyl ketone in perfluoro-1,2-dimethylcyclobutane at room temperature produces an intense spectrum of the perfluoroisopropyl radical[20] formed by a type I cleavage ($a^F(CF_3) = 19.75$ G, $a_\alpha{}^F = 70.48$ G, $g = 2.00321$ corrected for second-order shift), together with the spectrum of a second radical species (Figure 5A) which can be best recorded under conditions of low microwave power (Figure 5B). By analogy with the simpler fluoroketones, we believe that this spectrum is also associated with an adduct radical such as XIV,

$$(CF_3)_2CFCOCF(CF_3)_2 + (CF_3)_2\dot{C}F \longrightarrow$$

$$\underset{\text{XIV}}{[(CF_3)_2CF]_2\dot{C}{-}OCF(CF_3)_2} \quad (23)$$

although we have been unable to analyze it in detail. A doublet splitting of about 20 G, however, is definitely part of this spectrum and constitutes the largest splitting, indicating that the two α-perfluoroisopropyl groups cannot be conformationally equivalent. Examination of molecular models also suggests that these groups should be locked in nonequivalent orientations with respect to the axis of the central trigonal carbon by the steric requirements of the bulky CF_3 groups. The steric crowding around the carbon radical center is also responsible, no doubt, for the unusually long life of this radical. Additional examples of extraordinarily stable fluoroalkyl radicals with bulky substituents will be mentioned below.

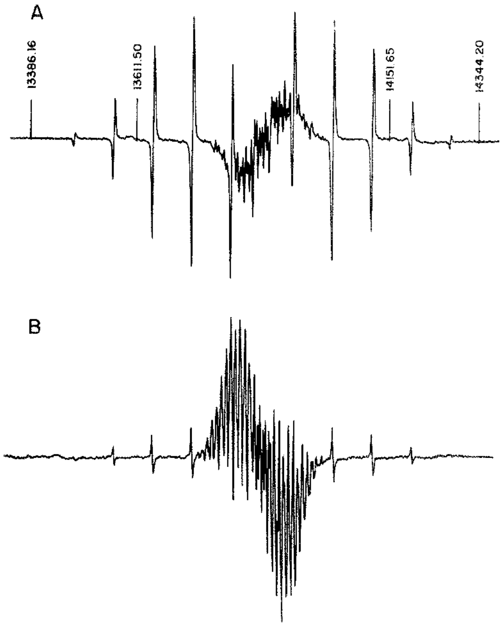
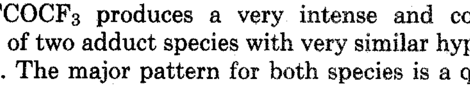
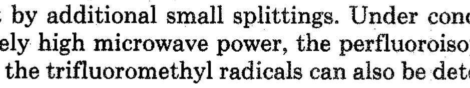


Figure 5. Esr spectra at high (A) and low microwave power levels (B) resulting by photolysis of a dilute solution of perfluoroisopropyl ketone in perfluoro-1,2-dimethylcyclobutane showing the spectra of the perfluoroisopropyl radical (doublet-of-septets) and of the adduct radical XIV (room temperature).

Several asymmetric fluoroketones were also irradiated in inert fluorocarbon solvents, and in all cases adduct formation appeared to be an important radical process attending photolysis. Unfortunately, the resulting spectra were complicated by the presence of more than one radical species. The occurrence of at least two adducts in the photolysis of an asymmetric fluoroketone R_FCOR_F' is, of course, expected since either $\dot{R}_F$ or $\dot{R}_F'$, resulting by type I cleavage, can add to the oxygen of a ground-state ketone molecule (eq 24 and 25). Indeed, the superposed spectra are often quite



$$R_FCOR_F' + \dot{R}_F \longrightarrow \begin{matrix} R_F' \\ \diagdown \\ \dot{C}{-}OR_F \\ \diagup \\ R_F \end{matrix} \quad (24)$$



$$R_FCOR_F' + \dot{R}_F' \longrightarrow \begin{matrix} R_F' \\ \diagdown \\ \dot{C}{-}OR_F' \\ \diagup \\ R_F \end{matrix} \quad (25)$$

similar with regard to the major splitting pattern which is determined by the nature of the fluoroalkyl groups directly attached to the central carbon atom. Thus, photolysis of $(CF_3)_2CFCOCF_3$ produces a very intense and complex spectrum of two adduct species with very similar hyperfine splittings. The major pattern for both species is a quartet of doublet of septets (approximately 20, 10, and 3 G, respectively), as required by the structure of the ketone, further split by additional small splittings. Under conditions of relatively high microwave power, the perfluoroisopropyl as well as the trifluoromethyl radicals can also be detected.

An intense spectrum of a relatively stable radical species can also be obtained after a short irradiation of a dilute so-

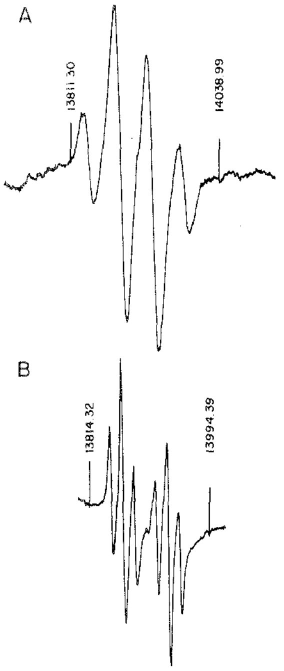
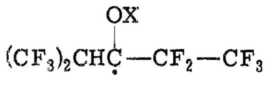


Figure 6. Esr spectra of the trifluoroacetyl radical (A, −97°) and of the perfluoropropionyl radical (B, −135°) obtained by photolysis of cyclopropane solutions containing di-*tert*-butyl peroxide and trifluoroacetaldehyde and pentafluoropropionaldehyde, respectively.

lution of $(CF_3)_2CHCOCF_2CF_3$ in dichlorodifluoromethane at room temperature. It consists of a well-separated triplet of 26.46 G further split into a complex pattern of many lines. Interestingly, the central pattern appears with reduced amplitude relative to the wing multiplets (selective line broadening) indicating a pair of exchanging spins of ½. We believe this stable species to be radical XV in which X may be the $(CF_3)_2CH$ or the CF_3CF_2 group. The triplet is

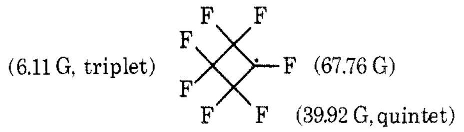


$$(CF_3)_2CH\overset{OX}{\dot{C}}-CF_2-CF_3$$

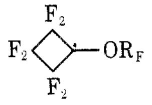
XV

clearly associated with the two β-CF_2 fluorines which undergo exchange between two conformational positions.

We have also briefly examined the photolysis of perfluorocyclobutanone. This ketone is interesting since previous photochemical product studies[22] have shown the formation of perfluorocyclopropane as well as tetrafluoroethylene. Photolysis in the esr cavity of this ketone dissolved in dichlorodifluoromethane at −30° produces an intense spectrum which clearly represents the superposition of two similar quintets of triplets of different intensities (approximately 2:1). For the major species the couplings are a^F(quintet) = 50.91 G and a^F(triplet) = 11.22 G, while for the minor species they are a^F(quintet) = 49.06 G and a^F(triplet) = 10.32 G (ΔH = 1.0 G). Because of their large magnitudes, the quintets show second-order splittings for the $M_I = \pm 1$ and $M_I = 0$ lines. Product studies now in progress will be needed to identify these radicals. Our results are nevertheless noteworthy, since they show that the photolysis of perfluorocyclobutanone solutions at low temperatures afford radicals which retain the integrity of the cyclic carbon framework. This conclusion is reached by comparison with the fluorine couplings in the perfluorocyclobutyl radical[23] at −60°.



We propose that two types of adduct radicals such as XVI are involved with different R_F groups.



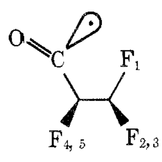
XVI

II. Perfluoroacyl Radicals. The stability of the trifluoroacetyl radical is a subject of considerable controversy.[5,9] Our attempts to identify this radical in the low-temperature photolysis of HFA were hampered by the presence of other radical species. The esr spectrum of this radical can be obtained, however, by photolysis of a cyclopropane solution containing di-*tert*-butyl peroxide and trifluoroacetaldehyde below −80° and at high microwave powers (Figure 6A). The spectrum consists of a broad (ΔH = 4 G) quartet of 11.54-G splitting with the unusually low g factor of 2.00104. Such low g factors are typical for acyl radicals[2e,f] as well as for other σ radicals.[24] Above −80°, this spectra is replaced by that of the $\dot{C}F_3$ radical which becomes progressively more intense as the temperature is raised. Gas evolution can also be observed at higher temperatures. These observations are consistent with abstraction of the aldehydic hydrogen atom to give the trifluoroacetyl radical which readily decarbonylates above −80°.

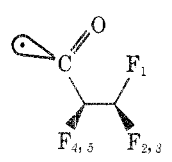
$$CF_3CHO + (CH_3)_3CO\cdot \longrightarrow CF_3\dot{C}O + (CH_3)_3COH \quad (26)$$

$$CF_3\dot{C}O \longrightarrow \dot{C}F_3 + CO \quad (27)$$

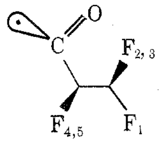
The perfluoropropionyl radical can similarly be generated from perfluoropropionaldehyde in cyclopropane solutions below −100°. Above this temperature the spectrum is replaced by that of the $CF_3\dot{C}F_2$ radical formed from the acyl radical by loss of CO (bubbling accompanies experiments above −100°). The spectrum of the perfluoropropionyl radical (Figure 6B) is quite unusual in that it consists of a doublet of 16.1 G further split into triplets of 4.44 G (−124°). The low g factor of 2.00075 leaves little doubt that this spectrum indeed belongs to $CF_3CF_2\dot{C}O$. The doublet splitting could imply a CF_3 group "locked" in such a conformation as to allow only one of the three γ fluorines to interact appreciably with the unpaired electron localized in an sp^2-hybrid orbital. Four conformations consistent with the equivalence of the β fluorines are depicted in projection below. Conformation XVII′ can almost certainly be



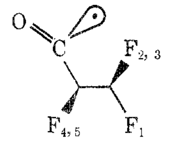
XVII



XVII′



XVIII



XVIII′

excluded from consideration since space-filling models in-

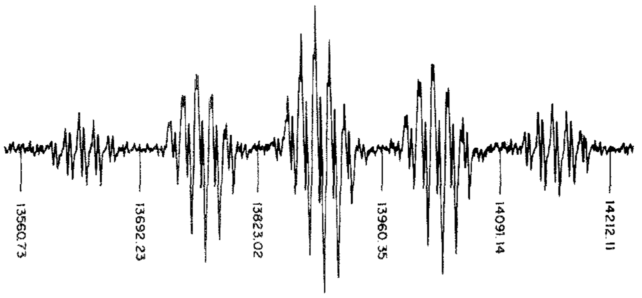
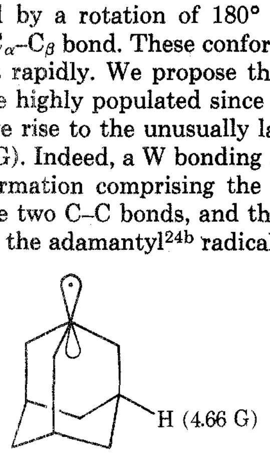


Figure 7. Esr spectrum of the radical $(CF_3CF_2)_2\dot{C}OH$ obtained by photolysis of perfluoroethyl ketone in cyclopropane at −40°.

dicate a severe steric interaction between the oxygen and the F_1 atom. Furthermore, the eclipsing of the two β fluorines with two of the γ fluorines in this conformation, as well as in conformation XVII, must surely represent an endoenergetic situation. The most likely equilibrium conformations for the radical appear to be XVIII and XVIII′, which are related by a rotation of 180° of the carbonyl group about the C_α–C_β bond. These conformations may indeed interconvert rapidly. We propose that conformation XVIII is the more highly populated since this structure is more likely to give rise to the unusually large γ-hyperfine interaction (16.1 G). Indeed, a W bonding arrangement exists in this conformation comprising the axis of the sp^2-hybrid orbital, the two C–C bonds, and the C–F_1 bond. In another σ radical, the adamantyl[24b] radical shown below, a



similar W bonding arrangement also led to a large γ hyperfine interactions. Molecular orbital calculations are now underway to clarify this unusual effect. Interestingly, the magnitude of the β-fluorine coupling is temperature dependent, varying smoothly from 4.15 G at −135° to 4.71 G at −108°, while the doublet splitting is essentially constant (16.10 and 16.02 G, respectively). Torsional motions about the C_α–C_β bond must be responsible for this dependence. The positive sign of the temperature coefficient is also consistent with the magnitude of the fluorine coupling in $CF_3\dot{C}O$ (11.54 G), which could be taken as the high-temperature limit for a freely rotating β-CF_2 group in $CF_3CF_2\dot{C}O$.

It should be noted that the perfluoropropionyl radical could not be detected above −100°, while the trifluoroacetyl radical under identical experimental conditions, gave a rather good spectrum up to −80°. We believe that this observation implies a lower activation energy for decarbonylation in the perfluoropropionyl radical.

III. Photoreduction of Fluoroketones and α-Hydroxyfluoroalkyl Radicals. The formation of the α-hydroxyhexafluoroisopropyl radical IX (eq 16) during photolysis of HFA and trifluoroacetaldehyde has been discussed above. The intense esr spectra (Figure 2) obtained by this photochemical reaction no doubt reflect the ease with which the aldehydic hydrogen can be abstracted by the photoexcited HFA molecule. Much less reactive hydrogen atoms can also be abstracted by photoexcited HFA. Thus, photolysis of HFA in cyclopropane also produces the esr spectrum of the

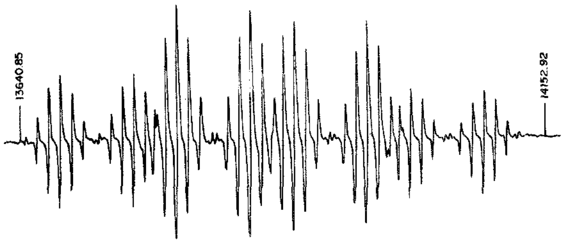


Figure 8. Esr spectrum of radical XX formed during irradiation of perfluoroisopropyl trifluoromethyl ketone in cyclopropane at −35°.

α-hydroxyperfluoroisopropyl radical (Table I) over a broad temperature range. No spectral evidence for the cyclopropyl radical was obtained, however, although it is necessarily formed in these experiments. Spectra of adducts formed by radical addition to the oxygen atom of ground-state HFA were also absent. The spectrum of the α-hydroxyperfluoroisopropyl radical can also be obtained by photolysis of HFA and hexafluoroisopropyl alcohol (HFIP) in Freon solvents, or by hydrogen abstraction from the same alcohol with trifluoromethoxy radicals generated photochemically from bis(trifluoromethyl) peroxide.

$$[CF_3COCF_3]^* + (CF_3)_2CHOH \longrightarrow 2(CF_3)_2\dot{C}OH \qquad (28)$$

The α-hydroxytrifluoroisopropyl radical (Table I) can similarly be generated from 1,1,1-trifluoroisopropyl alcohol.

$$(CF_3)_2CHOH + CF_3O\cdot \longrightarrow (CF_3)_2\dot{C}OH + CF_3OH \qquad (29)$$

Interestingly, *tert*-butoxy radicals are not capable of abstracting efficiently the two hydrogen atoms from HFIP, indicating that this alcohol is a poor hydrogen donor. Thus, photolysis of dilute solutions of HFIP and di-*tert*-butyl peroxide in dichlorodifluoromethane gives rise only to the spectrum of the methyl radical even at very low temperatures (−100°). With more concentrated solutions, a very weak spectrum of IX can be observed but the major radical species remains the $\dot{C}H_3$ radical. The latter can also be observed by irradiating di-*tert*-butyl peroxide alone in dichlorodifluoromethane. These observations are unusual since they imply β scission of *tert*-butoxy radicals which we have never observed directly in hydrocarbon solvents, including cyclopropane.

$$(CH_3)_3CO\cdot \longrightarrow \dot{C}H_3 + CH_3COCH_3 \qquad (30)$$

We conclude that the absence of abstractable hydrogens in inert fluorocarbon solvents promotes β scission of *tert*-butoxy radicals as a favorable alternative to their recombination to regenerate the peroxide.

Photolysis of other fluoroketones in cyclopropane produces the corresponding α-hydroxyfluoroalkyl radicals by photoreduction.

$$[CF_3CF_2COCF_2CF_3]^* \xrightarrow{C_3H_6} \underset{\text{XIX}}{(CF_3CF_2)_2\dot{C}OH}$$

Thus, photolysis of a dilute solution of perfluoroethyl ketone in cyclopropane at −40° yields the spectrum of radical XIX (Figure 7) as the sole observable radical species, consisting of a quintet (30.74 G), from four α fluorines, of septets (3.68 G), from six CF_3 fluorines, further split into small doublets (1.15 G) by the hydroxylic proton. Similarly, photolysis of a dilute cyclopropane solution of perfluoroisopropyl trifluoromethyl ketone at −35° gives a particularly intense spectrum of radical XX (Figure 8) showing a quartet ($a_\alpha{}^{CF_3} = 26.70$ G) of doublets ($a^{CF} = 16.78$ G) of septets ($a_\gamma{}^{CF_3} = 2.61$ G). No observable splitting for the hydroxylic proton is observed in this case. It is

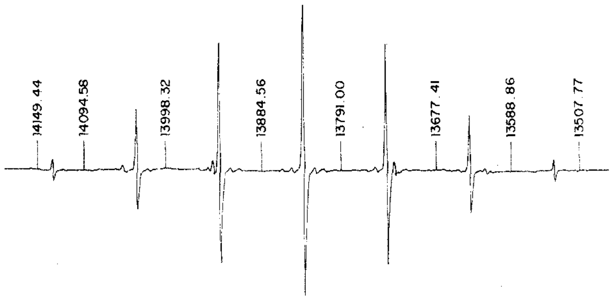
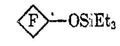
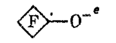
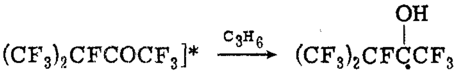


Figure 9. Esr spectrum (septet) of the $(CF_3)_2\dot{C}OSiEt_3$ radical resulting by addition of triethylsilyl radicals to hexafluoroacetone at −40° in a cyclopropane solution. Some of the minor peaks are due to hyperfine interaction with ^{29}Si.

TABLE II: Esr Parameters of Silyl Adducts to Fluoroketones and Related Radicals

Radical	T, °C	Proton and fluorine isotropic coupling constants, G	
$(CF_3)_2\dot{C}OSiEt_3$	−118	CF_3: 23.24	
$(CF_3)_2\dot{C}OSiEt_3$	−47	23.28	
$CF_3\dot{C}(CH_3)OSiEt_3$[a]	b	CF_3: 28.8	CH_3: 21.5
$(CH_3)_2\dot{C}OSiEt_3$	−121		CH_3: 19.95
$(CF_3)_2\dot{C}OH$	−55	CF_3: 23.94	
$(CH_3)_2\dot{C}OH$[c]	26		CH_3: 19.66
$F_2\dot{C}OSiEt_3$	−86	α-F: 147.6	^{29}Si: 1.9
$(CF_3CF_2)_2\dot{C}OSi(n\text{-}Bu)_3$	−60	CF_2: 30.31	CF_3: 3.65
	−63	β-F: 51.53	γ-F: 10.98
 [d]	−60	β-F: 39.92 α-F: 67.76	γ-F: 6.11
 [e]	+25	β-F: 82.9	γ-F: 37.33

[a] From ref 26a. [b] Not given in ref 26a. [c] From R. Livingston and H. Zeldes, *J. Chem. Phys.*, **44**, 1245 (1966). [d] From ref 23. [e] J. L. Gerlock and E. G. Janzen, *J. Phys. Chem.*, **72**, 1832 (1968).

 (31)

$$[(CF_3)_2CFCOCF_3]^* \xrightarrow{C_3H_6} (CF_3)_2CF\dot{C}(OH)CF_3 \quad (31)$$

XX

also noteworthy that radical XX decays after shuttering the light. A lifetime of about 6 sec for this radical underscores the already mentiond stabilizing effect of α-perfluoroisopropyl groups on fluoroalkyl radicals.

IV. Homolytic Additions to Fluoroketones. Silyl radicals generated from silanes and *tert*-butoxy radicals[25] add efficiently to fluoroketones at the oxygen site.[10,26] The esr spectrum of the adduct XXI (Figure 9) is obtained on photolysis of a dilute cyclopropane solution containing HFA, triethylsilane, and di-*tert*-butyl peroxide. The septet splitting (a^{CF_3} = 23.28 G at −47°) is relatively temperature independent as shown in Table II, and no line width effects were observed down to −120°.

$$Et_3SiH + (CH_3)_3CO\cdot \longrightarrow Et_3Si\cdot + (CH_3)_3COH \quad (32)$$

$$Et_3Si\cdot + CF_3COCF_3 \longrightarrow (CF_3)_2\dot{C}\text{—}OSiEt_3 \quad (33)$$

XXI

Related α-siloxyfluoroalkyl radicals were also obtained in a similar manner from perfluoroethyl ketone and perfluorocyclobutanone with or without added di-*tert*-butyl peroxide (Table II). In the latter case, the photoexcited fluoroketone must abstract the hydrogen attached to silicon in the initial radical process. The resulting α-hydroxyfluoroalkyl radicals could not be observed, presumably because of their participation in a chain reaction. These spectra are unusually intense as seen in Figure 10 for radical XXII. No indication of resolvable structure due to the protons of the siloxy groups was obtained for these radicals.

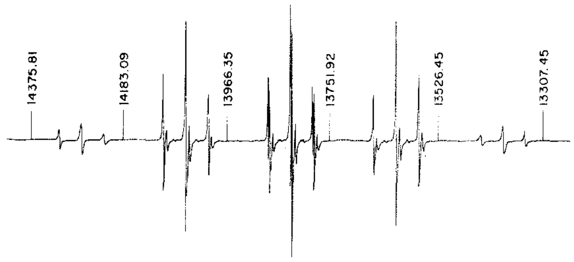


Figure 10. Esr spectrum of the radical resulting by addition of triethylsilyl radicals to perfluorocyclobutanone in a cyclopropane solution at −55°. The additional splittings of the inner triplets are due to second-order effects.

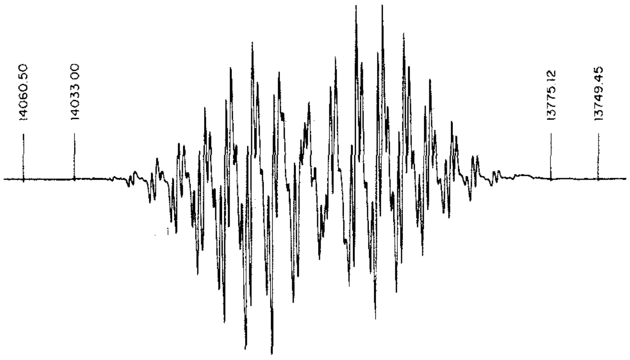
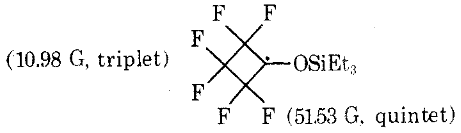
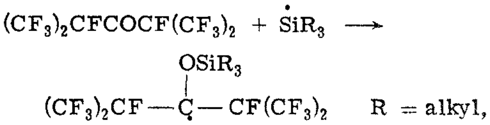


Figure 11. Esr spectrum of radical XXIII obtained by addition of tri-*n*-butylsilyl radicals to perfluoroisopropyl ketone at −28° in a cyclopropane solution.



XXII

The most dramatic demonstration of the attenuation of radical reactivity by bulky fluoroalkyl substituents attached to a carbon radical center is afforded by the photochemical reaction between perfluoroisopropyl ketone and a variety of silanes. Thus, the intense spectrum of Figure 11 is obtained at −28° when a dilute cyclopropane solution containing perfluoroisopropyl ketone and tri-*n*-butylsilane (10:1:1 v/v) is briefly irradiated with uv light. The radical species giving rise to this spectrum is stable indefinitely in the original sealed tube. The doublet splitting of 16.5 G is the only feature of the spectrum which can be immediately recognized. By analogy with the simpler fluoroketones, we attribute this spectrum to the siloxy radical XXIII (R = *n*-butyl). The observation of only one doublet as the largest fluorine hyperfine splitting for the series of radicals XXIII,

 (34)

$$(CF_3)_2CFCOCF(CF_3)_2 + \dot{S}iR_3 \longrightarrow (CF_3)_2CF\text{—}\dot{C}(OSiR_3)\text{—}CF(CF_3)_2 \qquad R = \text{alkyl, phenyl} \quad (34)$$

XXIII

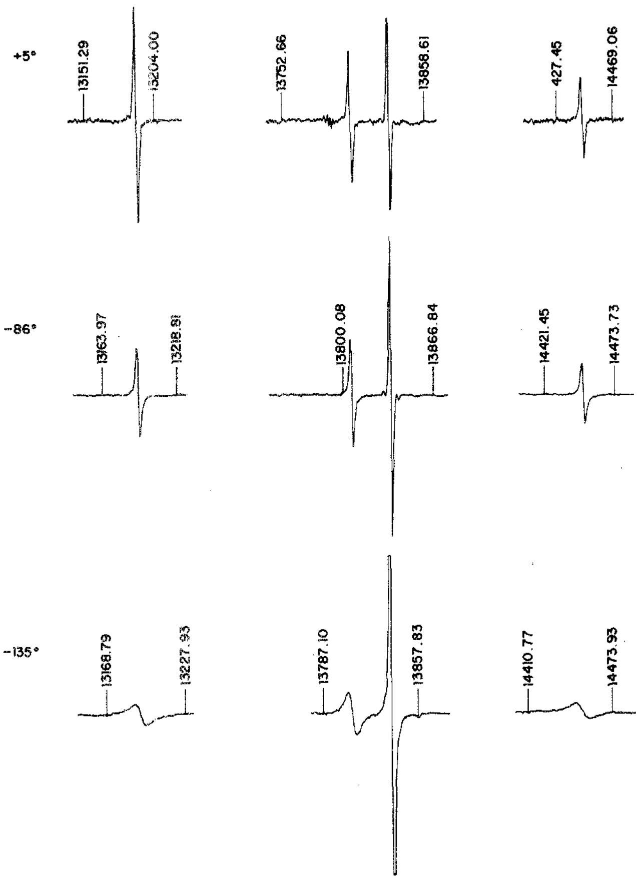


Figure 12. Temperature dependence of the line shapes in the esr spectrum of the $\dot{C}F_2OSiEt_3$ radical.

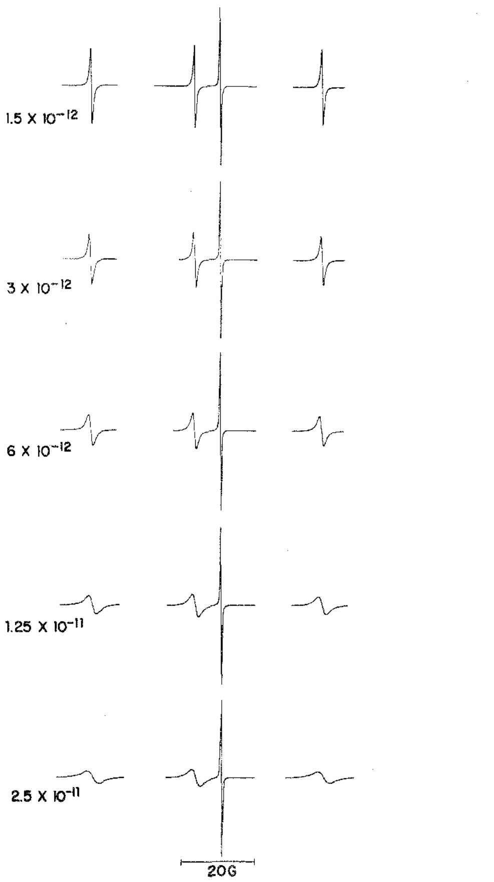


Figure 13. Calculated line shapes for the radical $\dot{C}F_2OSiEt_3$ as a function of the rotational correlation time in sec (see text).

indicates two conformationally nonequivalent perfluoroisopropyl groups. The two β fluorines are therefore locked in specific orientations relative to the half-occupied p orbital on the central carbon in such a manner that only one fluorine interacts appreciably (16.5 G) with the unpaired electron. A more complete account of the esr spectra of these uniquely stable fluoroalkyl radicals will be reported elsewhere.[27]

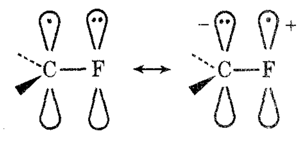
Triethylsilyl radicals add to carbonyl fluoride in cyclopropane solutions to afford the α,α-difluoromethyl adduct XXIV shown in Figure 12. The hyperfine pattern at +5°

$$\mathrm{Et_3Si\cdot} + \mathrm{F_2C{=}O} \longrightarrow \underset{\text{XXIV}}{\mathrm{F_2\dot{C}{-}OSiEt_3}} \qquad (35)$$

consists of a triplet of 147.5 G, in which the $M_I = 0$ line shows a large second-order splitting. The triplet splitting is essentially independent of temperature, being 147.6 G at −135°. It should be noted that this splitting is larger than the fluorine splitting in the trifluoromethyl radical[12-14] (144.1 G at −90°) indicating that the siloxydifluoromethyl radical is slightly more pyramidal than the trifluoromethyl radical. At −86° satellite lines due to splitting by ^{29}Si can be seen flanking the narrowest line of the spectrum and separated by 1.9 G.

As the temperature is lowered, the two $M_I = \pm 1$ lines are selectively broadened together with only the low-field $M_I = 0$ line. Below −135° this broadening is so severe as to make these lines undetectable. In the absence of unusual relaxation effects, the four lines of the spectrum in Figure 12 should be of equal amplitude. Unfortunately, the steady-state concentration of $F_2\dot{C}OSiEt_2$ diminished rapidly at the highest temperature studied (+5°) and the true intensities were difficult to record in the entire spectrum. This problem was less severe at lower temperatures and fairly accurate relative line intensities could be obtained. The spectra at −86 and −135° clearly show that the outer lines and the low-field second-order line become progressively broader as the temperature is lowered. The relatively small temperature dependence and the strong solvent (viscosity) dependence of this selective line broadening indicate a relaxation process which is dependent on the tumbling motion of the radical in solution as previously presented for $\dot{C}F_3$, $CH_3\dot{C}F_2$, and $CF_3\dot{C}F_2$.[13,14,28]

Experimental studies on fluorinated radicals in single crystals and theoretical considerations indicate that the anisotropic component (dipolar component) of the hyperfine coupling tensor in α-fluoroalkyl radicals is very large relative to the anisotropy of the coupling to α protons.[29] The origin of this large dipolar interaction in α-fluoroalkyl radicals can be attributed to the presence of substantial unpaired spin density in nonbonding p orbitals on fluorine arising through the p–π interaction which confers to the trivalent carbon at the radical center some of the properties of carbanions including the pyramidal configuration typical of α-fluoroalkyl radicals.[14] Modulation of this elec-

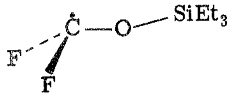


tron spin–nuclear spin dipolar interaction by the tumbling of the radical in solution provides an efficient relaxation mechanism.

A relaxation-matrix analysis of a spin system undergoing dipolar relaxation was carried out by assuming that the two fluorine nuclei in a CF_2 fragment are completely equivalent (that is, that the anisotropic part of the hyperfine tensor has the same orientation for both fluorine nuclei) and that they have an axially symmetric hyperfine tensor. The dipolar contributions to the line widths of the wing lines ($M_I = \pm1$) and of the second-order line was given previously.[13,14,30]

As can be seen from Figures 12 and 13, the calculated and observed spectra are in good qualitative agreement for this model. In these calculations the anisotropic component of the A tensor in $\dot{C}F_2OSiEt_3$ was represented by $A_{\parallel} = 108$ G and $A_{\perp} = -54$ G. These values were obtained for the $\dot{C}F_3$ radical in a single crystal study.[31]

The temperature-dependent line width effect in the spectrum of $F_2\dot{C}OSiEt_3$, thus, can be attributed solely to dipolar broadening. The absence of other dynamic processes (in particular, modulation of the fluorine hyperfine splitting due to a mutual exchange process) suggests that the radical exists in a stable symmetric conformation such as XXV. Furthermore, the small γ-^{29}Si splitting of 2 G contrasts with that observed in the alkyl analog, $Et_3SiCH_2\dot{C}H_2$ ($a^{Si} = 37.4$ G),[32] and it may be due to the highly pyramidal radical center or an expanded C_{α}-O-Si angle [compare also ref 18].



XXV

Conclusions

The esr study presented in this paper serves primarily to identify and characterize some of the transient paramagnetic species formed during ultraviolet irradiation of fluoroketones. We surmise that photolysis of perfluoroketones is similar to that of their hydrocarbon analogs with several outstanding exceptions. Thus, products of type I cleavage (eq 1) are observed in inert fluorocarbon solvents, and intermolecular processes (eq 3) are observed in protiated solvents. However, the formation of adducts, such as V′ from hexafluoroacetone and the analogous species from higher perfluoroketones as the principal radical species in inert solvents, suggests that radical addition to perfluoroketones is a significantly more facile process than it is with alkyl ketones. Another major difference pertains to the greater thermal instability of perfluoroacyl radicals derived by type I scission of fluoroketones which lose carbon monoxide much more readily than their hydrocarbon analogs. Chemical studies have indicated that addition can occur at both the C and O termini of the carbonyl function. The observation of α-perfluoroalkyoxyfluoroalkyl radicals is consistent with addition to oxygen. Esr studies in solution are unable to evaluate the importance of radical addition to C, since the fluoroalkoxy radicals so formed cannot be detected by esr. Photoexcited fluoroketones in their triplet states are powerful hydrogen abstracting agents as evidenced by their photoreduction in the presence of even poor hydrogen donors such as cyclopropane. Silicon-centered radicals are particularly prone toward addition to the oxygen terminus of fluoroketones. Addition of silyl radicals to sterically crowded ketones results in the formation of extraordinarily stable fluoroalkyl radicals. Additional chemical studies would be highly desirable to elucidate further the apparent diversity of radical processes in the photochemistry of fluoroketones in solution.

Experimental Section

The fluoroketones in this study were kindly supplied by Drs. D. C. England, E. G. Howard, W. J. Middleton, and J. E. Nottke. Bis(hexafluoroisopropyl) ether was donated by W. J. Middleton. 1,2-Bis(trifluoromethyl)perfluorocyclobutane was a gift from Dr. P. R. Resnick. The remaining fluoroorganic compounds were either Du Pont materials or were obtained from P.C.R. Inc. and the Aldrich Chemical Co.

Hexafluoroisopropyl trifluoroacetate was prepared by adding a 10% excess of trifluoroacetic anhydride dropwise to hexafluoroisopropyl alcohol at 0° followed by a similar addition of pyridine (10% excess). The mixture was allowed to stand for 1 day and worked up by diluting with ice water, washing the upper phase with water, and drying it over anhydrous magnesium sulfate. Distillation afforded 30% of hexafluoroisopropyl trifluoroacetate boiling at 44.5°. The proton nmr spectrum consisted of a binomial septet at δ 5.77 ppm.

Trifluoroacetaldehyde was generated by dropwise addition of trifluoroacetaldehyde methyl hemiacetal (P.C.R. Inc.) to polyphosphoric acid at 150°. Essentially pure trifluoroacetaldehyde distilled off and was used immediately. Perfluoropropionaldehyde was similarly prepared from the corresponding hemiacetal.

The technique for sample preparation and the esr instrumentation were described previously.[18a]

Acknowledgments. We are grateful to Drs. D. C. England, E. G. Howard, W. Mahler, W. J. Middleton, J. E. Nottke, W. A. Sheppard, and P. R. Resnick (Du Pont) for many samples and useful discussions and to Mr. B. F. Gordon for technical assistance. K. S. C. wishes to thank the National Science Foundation for financial support.

References and Notes

(1) (a) E. I. du Pont de Nemours and Company. (b) Department of Chemistry, Indiana University. (c) Contribution No. 2135 from E. I. du Pont de Nemours and Co. (d) Contribution No. 2392 from the Department of Chemistry, Indiana University.

(2) (a) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5,** 21 (1968); (b) P. J. Wagner, *Accounts Chem. Res.*, **4,** 168 (1971); (c) D. Bryce-Smith, "Special Periodical Reports on Photochemistry," Vol. I, II, III, Chemical Society, London, 1970, 1971, 1972; (d) J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21,** 499 (1970); (e) H. Paul and H. Fischer, *J. Chem. Soc., Chem. Commun,* 1038 (1971); *Helv. Chim. Acta,* **56,** 1575 (1973); (f) H. E. Chen, S. P. Vaish, and M. Cocivera, *J. Amer. Chem. Soc.*, **95,** 7586 (1973).

(3) (a) C. G. Krespan and W. J. Middleton, *Fluorine Chem. Rev.*, **1,** 145 (1967); (b) H. P. Braendlin and E. T. McBee, *Advan. Fluorine Chem.*, **3,** 1 (1963); (c) J. Heicklen, *Advan. Photochem.*, **7,** 57 (1969).

(4) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, p 437 *ff.*

(5) (a) P. S. Ayscough and E. W. R. Steacie, *Proc. Roy. Soc., Ser. A,* **234,** 476 (1956); (b) J. S. McIntosh and G. B. Porter, *Trans. Faraday Soc.*, **64,** 119 (1968); (c) S. L. Chong and S. Toby, *J. Phys. Chem.*, **74,** 2801 (1970).

(6) P. Svejda, *J. Phys. Chem.*, **76,** 2690 (1972).

(7) A. S. Gordon, *J. Chem. Phys.*, **36,** 1330 (1962).

(8) P. R. Resnick, personal communication.

(9) B. G. Tucker and E. Whittle, *Proc. Chem. Soc.*, 93 (1963); *Trans. Faraday Soc.*, **61,** 484 (1965).

(10) E. G. Howard, P. B. Sargeant, and C. G. Krespan, *J. Amer. Chem. Soc.*, **89,** 1422 (1967).

(11) W. H. Urry, A. Nishihara, and J. H. Y. Niu, *J. Org. Chem.*, **32,** 347 (1967).

(12) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43,** 2704 (1965).

(13) P. Meakin and P. J. Krusic, *J. Amer. Chem. Soc.*, **95**, 8185 (1973).
(14) K. S. Chen, P. J. Krusic, P. Meakin, and J. K. Kochi, *J. Phys. Chem.*, **78**, 2014 (1974).
(15) M. C. R. Symon, *J. Amer. Chem. Soc.*, **91**, 5924 (1969).
(15a) *Note Added in Proof.* This assignment has recently been confirmed by the detection of radical V′ formed by type I cleavage during the photolysis of $CF_3OC(CF_3)_2COF$ in inert fluorocarbon solvents.

$$CF_3COC(CF_3)_2COF \xrightarrow{h\nu} CF_3O\dot{C}(CF_3)_2 + \dot{C}OF$$

We thank Dr. P. R. Resnick for suggesting this experiment and a sample of the fluoroacyl fluoride. Esr studies of the radicals involved in the photolysis of fluoroacyl halides are in progress.
(16) R. C. Bingham and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **95**, 7182 (1973); *cf.* also A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc. A*, 124 (1971).
(17) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971).
(18) (a) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971); (b) K. S. Chen, P. J. Krusic, and J. K. Kochi, *J. Phys. Chem.*, **78**, 2030 (1974).
(19) P. J. Krusic, manuscript in preparation.
(20) R. B. Lloyd and M. T. Rogers, *J. Amer. Chem. Soc.*, **95**, 1512 (1973).
(21) P. J. Krusic and P. Meakin, manuscript in preparation.
(22) (a) D. England, *J. Amer. Chem. Soc.*, **83**, 2205 (1961); (b) D. Phillips, *J. Phys. Chem.*, **70**, 1235 (1966).
(23) B. S. Smart and P. J. Krusic, manuscript in preparation.
(24) (a) P. J. Krusic and T. A. Rettig, *J. Amer. Chem. Soc.*, **92**, 722 (1970); (b) P. J. Krusic, T. A. Rettig, and P. v. R. Schleyer, *ibid.*, **94**, 995 (1972).
(25) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 3938 (1969).
(26) A. J. Bowles, A. Hudson, and R. A. Jackson, *J. Chem. Soc. B*, 1947 (1971); J. Cooper, A. Hudson, and R. A. Jackson, *J. Chem. Soc., Perkin Trans. 2*, 1933 (1973).
(27) P. J. Krusic, manuscript in preparation.
(28) K. S. Chen and J. K. Kochi, *Chem. Phys. Lett.*, **23**, 233 (1973); *J. Amer. Chem. Soc.*, **96**, 794 (1974).
(29) (a) M. Iwasaki, *Fluorine Chem. Rev.*, **5**, 1 (1971); (b) A. Hudson and K. D. J. Root, *Advan. Mag. Resonance*, **5**, 1 (1971).
(30) J. Cooper, A. Hudson, R. A. Jackson, and M. Townson, *Mol. Phys.*, **23**, 1155 (1972).
(31) M. T. Rogers and L. D. Kispert, *J. Chem. Phys.*, **46**, 3193 (1967).
(32) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 6161 (1969).

Electron Spin Resonance Measurement of Ammonia Condensed at 77°K after Reaction with Discharge Products and after High-Frequency Discharge

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Amino radicals are condensed at 77°K from the vapor of a fast flow system. The esr spectra are somewhat different for the discharge (where their shape depends on HF discharge energy and pressure) and for the reaction of discharge products from N_2, H_2, and Ar with ammonia, added through an inlet between the discharge and the detection system. The differences can be caused by the environment of the radicals and by signals from other radicals.

Introduction

Electron impact excitation of ammonia at 2×10^{-5} to 5×10^{-3} Torr yield NH radicals as primary products.[2a] Above 10^{-2} Torr is a small contribution of NH_2 radicals, visible by emission of the α bands of ammonia ($^2A_1$). In gas-phase photolysis,[2b] pulse radiolysis,[3] and in reaction of atoms with ammonia[4] NH radicals have been found as well as NH_2 radicals. By condensation of the radicals from a fast flow system and subsequent esr measurement it was possible to obtain further information on this system. For better identification deuterated ammonia is used as well.

Esr spectra of ammonia at 77°K have been measured after γ-irradiation,[5-9] photolysis,[5,6,10] and electron impact.[5,11] The spectra have been ascribed to amino radicals with one exception, which has been corrected by private communication. NH radicals have been observed only by their uv spectra[12] and the lack of esr spectra is explained by broadening of the resonance lines even at 4°K. The present investigation deals with the measurement of amino radicals at 77°K and the variation of the esr spectra found for different experimental conditions.

Experimental Section

The apparatus is shown in Figure 1. Radicals are produced in a fast flow system by a microwave discharge (Microtron 200, 2.45 GC) and condensed on a cold finger at 77°K inside the esr cavity. The position of the discharge and the substrate inlet can be varied along the flow tube. The distance between cold finger and discharge varied from 50 to 100 cm and between substrate inlet and cold finger from 5 to 25 cm. That corresponds at the linear flow velocity of 1000 cm/sec (at the pressure used for most experiments and measured by the disappearance of esr signals in the gas phase with different positions of the discharge) to a time of 0.05–0.1 sec for the discharge products to reach the cold finger and for the added materials 0.005–0.025-sec flow time until they are condensed. The total pressure was varied between 5×10^{-3} and 1 Torr and the discharge energy between 15 and 150 W. The deposit was collected for a constant time of 10 min for all experiments, after checking the linear dependence of esr signal intensity with time of deposition.

The discharge in flowing ammonia is a very complex sys-