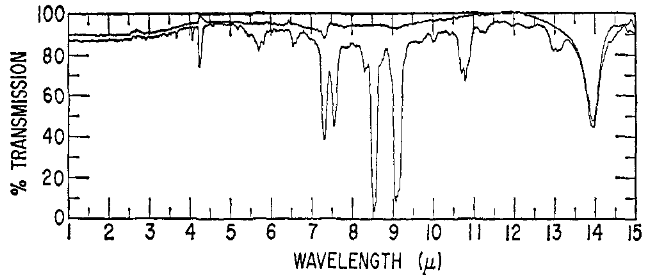

Figure 4. Infrared spectrum of perfluoromethylacetylene.

greater abundance of CF_3^+ is consistent with the presence of the CF_3 group in $CF_3C{\equiv}CF$. (2) The infrared spectrum (Figure 4) shows bands at 3.68, 4.07, 4.23, 5.7, 6.55, 7.31, 7.55, 8.51, 8.53, 9.07, 10.8, and 13.1 μ. The bands at 2457 and 2358 cm^{-1} (4.07 and 4.23 μ, respectively) correspond to the region associated with the triple-bond stretch. For comparison, similar bands were observed at 2342 and 2165 cm^{-1} in the infrared spectrum of $CF_3C{\equiv}CH$.[10] Typical values for the triple-bond stretch are from 2100 to 2250 cm^{-1}. One of the observed bands is presumably the triple-bond stretch and the other (probably the higher energy, lower intensity band) is an overtone or combination. No evidence of contribution from an allenic structure was seen from the perfluoromethylacetylene infrared spectrum.

Perfluoroallene

Perfluoroallene was observed from the mercury-sensitized decomposition of perfluorocyclopropene and perfluoromethylacetylene. The strong band observed at 2047 cm^{-1} closely corresponds to the band given by Jacobs and Bauer as 2065 cm^{-1} for perfluoroallene. Difficulties were encountered in attempts at purification so that a complete infrared or mass spectrum is not available. This product apparently underwent decomposition on the gas chromatographic column.

The mercury-sensitized decomposition of perfluoromethylacetylene, besides producing perfluoroallene, also gave other products which were not identified. After production of the allene from either reaction, the mixture was allowed to stand and the perfluoroallene decomposed slowly. The decomposition products were not identified but the products did show bands in the infrared region associated with the fluorinated double-bond stretch.

Acknowledgment. The authors wish to thank Mr. Vester Knight for help with the experimental work. Dr. Francis Wachi and Mr. Don Gilmartin recorded the mass spectrum of c-C_3F_4. The nmr spectrum of c-C_3F_4 was obtained through the courtesy of Professor Robert Taft. Financial support, under U. S. Air Force Contract No. 04(695)-1001, is gratefully acknowledged

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Pentafluorosulfur Carbonyl Fluoride, Pentafluorosulfur Fluoroformate, and Pentafluorosulfur Peroxofluoroformate

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Abstract: The compounds pentafluorosulfur carbonyl fluoride, $SF_5C(O)F$, pentafluorosulfur fluoroformate, $SF_5OC(O)F$, and pentafluorosulfur peroxofluoroformate, $SF_5OOC(O)F$, are produced in low yields by ultraviolet irradiation of the following mixtures, respectively: (1) S_2F_{10} and $FC(O)C(O)F$; (2) SF_5OF and $FC(O)C(O)F$; (3) SF_5OOSF_5 with $FC(O)OOC(O)F$. Each of the new compounds reacts readily with a solution of sodium hydroxide and has infrared and ^{19}F nmr spectra in keeping with its structure.

While many compounds containing the FC(O) group are known, nearly all have been prepared by fluorination of compounds already containing the carbonyl function, such as carboxylic acids, acid chlorides, and chloroformates. It would be of interest to produce similar compounds by direct addition of FC(O) groups to substrates. In order to test this possibility, $SF_5\cdot$ and $SF_5O\cdot$ radicals were used as substrates for addition of $FC(O)\cdot$ and $FC(O)O\cdot$ groups.

The fluorocarbonyl radical has been inferred as a chemical intermediate from the kinetics[1] and the products[2,3] of a number of reactions. The existence of the radical was clearly shown in the recent matrix isolation and identification by Milligan, *et al.*[4] Now that oxalyl fluoride, FC(O)C(O)F, may be prepared easily,[5] this substance is a good material to use as a source for fluorocarbonyl radical.

Bis(fluorocarbonyl) peroxide,[6] FC(O)OOC(O)F, has been investigated as a potential source of $FC(O)O\cdot$ radicals and has been found to give $FC(O)OSO_2F$ upon reaction with SO_2,[7] or to give FC(O)OF by reaction with fluorine.[8]

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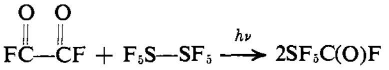
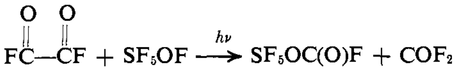
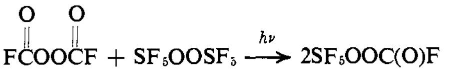
Disulfur decafluoride has been found to be a relatively poor source of $SF_5\cdot$ radicals for synthetic purposes.[9-11] In spite of this, the substance was successfully used in this research as a source of SF_5 radicals.

Both SF_5OF[12] and SF_5OOSF_5[13] are sources of SF_5O radicals. Several derivatives have been reported.[14,15]

The compounds pentafluorosulfur carbonyl fluoride, $SF_5C(O)F$, pentafluorosulfur fluoroformate, $SF_5OC(O)F$, and pentafluorosulfur peroxofluoroformate, $SF_5OOC(O)F$, have been found in relatively low yields among the products of the reactions of $FC(O)C(O)F$ with S_2F_{10}, $FC(O)C(O)F$ with SF_5OF, and $FC(O)OOC(O)F$ with SF_5OOSF_5 or SF_5OF, respectively, under the influence of ultraviolet irradiation.


$$\mathrm{F}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{F} + F_5S-SF_5 \xrightarrow{h\nu} 2SF_5C(O)F \tag{1}$$


$$\mathrm{F}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{F} + SF_5OF \xrightarrow{h\nu} SF_5OC(O)F + COF_2 \tag{2}$$


$$\mathrm{F}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{F} + SF_5OOSF_5 \xrightarrow{h\nu} 2SF_5OOC(O)F \tag{3}$$

The latter two of these compounds were observed in trace quantities among the products of several other reactions which will be described below.

Experimental Section

Reagents. Oxalyl fluoride was prepared by treating oxalyl chloride with sodium fluoride in acetonitrile at reflux, employing essentially the method of Tullock and Coffman.[5] The crude product, contaminated with carbonyl fluoride, carbon dioxide, and acetonitrile, was collected at −183°. Pure oxalyl fluoride was obtained by first evaporating away that part of the crude mixture which was volatile at −78°, and then by repeatedly distilling from bulb to bulb under vacuum, discarding approximately the first 1% and last 5% with each operation. The product accepted for use was indicated to be pure by its infrared spectrum[4] and by fractional codistillation.[16] Some of the oxalyl fluoride used was also prepared by treatment of oxalyl chloride with sodium fluoride at 100° for 24 hr in a 30-cc brass cylinder. It was purified by fractional codistillation

Pentafluorosulfur hypofluorite[12] was prepared by treating thionyl fluoride with an excess of fluorine in the presence of cesium fluoride.[17] Since the fluorination of thionyl fluoride may proceed quite rapidly and exothermally, sample preparations were limited to 10-mmol quantities to avoid possible harm from explosions. Fluorine was condensed into the cylinder in 5-mmol quantities using liquid nitrogen, until a total of 30 mmol of F_2 had been added. Between each addition of fluorine, the cylinder was closed and allowed to warm slowly to room temperature and stand for about an hour, behind a safety shield. After the final addition of fluorine, the cylinder was again allowed to warm slowly to room temperature and let stand overnight. After completion of the reaction, the contents of the cylinder were bled slowly through a trap at −183° and pumped through a soda-lime tower to destroy remaining fluorine. Crude SF_5OF prepared in this manner was purified by fractional codistillation.

Bis(pentafluorosulfur) peroxide[13] was obtained incidentally as a by-product of a number of reactions employing SF_5OF and was isolated by fractional codistillation. The product was indicated to be pure by infrared spectroscopy.

Bis(fluorocarbonyl) peroxide was prepared by the method of Schumacher, *et al.*[18] One part carbon monoxide, six parts oxygen, and two parts fluorine were allowed to flow into a 1-l. Pyrex glass flask with a total flow rate about 150 cc/min. The $FC(O)OOC(O)F$ collected in a cold trap held at −183° was freed of CO_2, COF_2, and SiF_4 contamination by pumping on the entire sample at −78°, until the residual pressure of vapor at −78° fell significantly below 1 mm, and the infrared spectrum[19] showed no impurities. During the course of investigation of the chemistry of oxalyl fluoride, it was discovered that ultraviolet irradiation of oxalyl fluoride in the presence of excess oxygen produced bis(fluorocarbonyl) peroxide in yields approaching 50%.[20] Some of the $FC(O)OOC(O)F$ used in these studies was prepared in that manner.

Disulfur decafluoride was taken from a sample furnished by J. W. Dale. The material was shown to be pure by fractional codistillation and an infrared spectrum.[21]

All other chemicals used for these studies were obtained commercially and used without further purification.

General Methods. Reactions, except as noted, were carried out in a 2-l. Pyrex glass flask equipped with an internal quartz finger containing a water-cooled Hanau 350-W mercury arc lamp. Following irradiation, products usually were bled through a cold trap at −183°, and materials not condensed at that temperature were pumped away. The gases F_2, O_2, CO, and N_2, when present, were removed in this way. Following this, the condensed products were separated by fractional codistillation, and, when possible, identified by infrared spectroscopy, vapor pressure, molecular weight, nmr spectra, or reactions.

Infrared spectra were obtained using a Beckman IR-10 infrared spectrophotometer. Samples were contained in a 10-cm cell with 3-mm thick rolled silver chloride windows. Samples were identified by comparison with spectra taken of known samples, and by comparison with reported values and band envelopes.

Nmr spectra were obtained through the use of a Varian Model 4311B high-resolution spectrometer with a 40-Mc oscillator. Samples were sealed in 5-mm Pyrex glass tubes with approximately 50 mol % $CFCl_3$ as an internal reference.

Vapor densities were obtained using a 222-ml Pyrex glass flask and reported in molecular weight units, assuming ideal gas behavior for the vapor.

Analyses were obtained by hydrolysis of samples in excess 5 *N* sodium hydroxide solution. Fluorine was then determined by titration with thorium nitrate solution, buffered with chloroacetic acid. The titration was carried out potentiometrically, using an Orion Model 94-09 fluoride ion activity electrode. Sulfur was determined gravimetrically as barium sulfate. Carbon was determined as carbonate by titration of the basic hydrolysate to the thymolphthalein end point and a duplicate titration in the presence of excess barium chloride to the same end point, using standard HCl. The difference in end points was due to carbonate.

Preparations. $FC(O)C(O)F + SF_4$. Ultraviolet irradiation of a mixture containing 2 mmol of oxalyl fluoride and 2 mmol of sulfur tetrafluoride was run for a period of 19 hr at ambient temperature, in an attempt to produce $[FC(O)]_2SF_4$ and/or $SF_5C(O)F$.

The products trapped at −183° and identified by infrared spectroscopy following separation by fractional codistillation were found to consist primarily of COF_2, SOF_2, SiF_4, and SF_6, and 0.3 mmol of S_2F_{10}. The disulfur decafluoride was identified by comparison of its infrared spectrum with that of a known sample.

$FC(O)C(O)F + S_2F_{10}$. The photochemical reaction of oxalyl fluoride with disulfur decafluoride was run at a variety of pressures, relative ratios of reactants, and for varying lengths of time. A new compound, identified as pentafluorosulfur carbonyl fluoride, $SF_5C(O)F$, was found among the products. The preferred conditions for maximizing the yield of $SF_5C(O)F$, while minimizing loss of reactants, employed 10 mmol of $FC(O)C(O)F$ and 5 mmol of S_2F_{10}, irradiated for a period of 3 hr at room temperature. Under such circumstances the yield of $SF_5C(O)F$ was approximately 2 mmol. The resulting mixture also contained approximately 8 mmol of COF_2, CO_2, SF_6, and SiF_4 combined, about 5 mmol of unreacted $FC(O)C(O)F$ and S_2F_{10} combined, and about 0.5 mmol of SOF_2. A quantity of gas which did not condense at −183°, as-

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sumed to be carbon monoxide, was disposed of without further identification.

In an attempt to achieve thermal reaction, 0.6 mmol of S_2F_{10} and 1.1 mmol of FC(O)C(O)F were held in a 300-ml Pyrex glass flask. Along with unreacted starting materials, small amounts of COF_2, CO_2, SiF_4, SF_6, and SOF_2 were found. No $SF_5C(O)F$ was detected after 8 days at 100°.

Liquid-phase irradiation of a 3.4:1 molar ratio of S_2F_{10} and FC(O)C(O)F was attempted in a 0.7-ml Vycor glass finger attached to a 300-ml Pyrex flask. The water-cooled 350-W ultraviolet lamp was placed next to the finger containing liquid S_2F_{10} and FC(O)C(O)F. Irradiation was allowed to proceed for 9 hr at 10° with about 0.5 cm of water interposed between the lamp and finger. A small amount of $SF_5C(O)F$ was detected along with larger amounts of COF_2, SiF_4, SF_6, and SOF_2, though the over-all degree of reaction was very small.

S_2F_{10} + FC(O)C(O)F + O_2. In some instances, while irradiation of gaseous mixtures of oxalyl fluoride and disulfur decafluoride were in progress, air accidentally leaked into the reaction flask. In these cases, the yield of $SF_5C(O)F$ was generally negligible, and in its place was found a new compound, $SF_5OC(O)F$, pentafluorosulfur fluoroformate. In one instance, 10 mmol of FC(O)C(O)F, 5 mmol of S_2F_{10}, and an unknown amount of air were irradiated for 18 hr at ambient temperatures. Approximately 2 mmol of unreacted S_2F_{10} was recovered, and about 1 mmol of $SF_5OC(O)F$, along with approximately a 12-mmol total of more volatile materials, including CO_2, COF_2, SiF_4, SF_6, SO_2F_2, SO_2, SOF_2, and traces of several unidentified substances. $SF_5OC(O)F$ obtained in this manner was contaminated with S_2F_{10}, which was removed by several repetitive codistillations.

Irradiation of an intentionally produced mixture containing 3.5 mmol of S_2F_{10}, 3.6 mmol of FC(O)C(O)F, and 3.7 mmol of O_2 was carried out for 11.5 hr. Found were 4.3 mmol of a mixture of COF_2, SiF_4, CO_2, SOF_2, and SF_6, a 0.1-mmol sample containing FC(O)C(O)F, $SF_5OC(O)F$, and relatively larger quantities of FC(O)OOC(O)F and S_2F_{10}, and another sample containing a total of 4.7 mmol of FC(O)OOC(O)F and S_2F_{10}, combined. The large quantity of bis(fluorocarbonyl) peroxide obtained as a by-product of this reaction was not actually anticipated, and it prompted an investigation into the reaction of oxalyl fluoride with oxygen.[20] At this point, no good explanation is available for the occurrence of the relatively large quantity of $SF_5OC(O)F$ obtained as a product of the reaction involving air.

FC(O)OOC(O)F + S_2F_{10}. Disulfur decafluoride, 8.1 mmol, and bis(fluorocarbonyl) peroxide, 8.6 mmol, were sealed in the ultraviolet irradiation flask and irradiated for 3 hr. SiF_4, COF_2, CO_2, and SF_6 comprised 5.8 mmol of the products upon codistillation, FC(O)OOC(O)F and S_2F_{10} (impure with small amounts of SF_5OSF_5[22] and SF_5OOSF_5[13]) comprised 14.4 mmol, and boiling between these two large fractions was about 0.2 mmol of a mixture of FC(O)OOC(O)F, S_2F_{10}, and $SF_5OC(O)F$. The yield of $SF_5OC(O)F$ was not found to increase significantly after another 11 hr of irradiation, though the reactants were diminished in quantity while their degradation products increased.

SF_5OF + CO. The success of photochemically adding CF_3OF to CO, producing $CF_3OC(O)F$,[23] suggested that it might be possible to add SF_5OF to CO to produce $SF_5OC(O)F$. A mixture of 13 mmol of SF_5OF and 13 mmol of CO was irradiated for 4.5 hr. Less than 0.5 mmol of $SF_5OC(O)F$ was found among larger quantities of SiF_4, SF_6, CO_2, SOF_4,[12] SF_5OF, S_2F_{10}, SF_5OSF_5, and SF_5OOSF_5.

FC(O)C(O)F + SF_5OF. The reaction of oxalyl fluoride with pentafluorosulfur hypofluorite was investigated as another possible route to pentafluorosulfur fluoroformate. This process was, in fact, the best found in terms of gross yield (about 15%) and availability and ease of handling of reactants even though the crude $SF_5OC(O)F$ was contaminated with both oxalyl fluoride and bis(pentafluorosulfur) oxide. The resulting mixture was distilled away from oxalyl fluoride by evaporation from a trap held between −78 and −95°. At this temperature oxalyl fluoride is a solid of low volatility, while $SF_5OC(O)F$ and SF_5OSF_5 are liquid and more volatile. Pentafluorosulfur fluoroformate was then separated from SF_5OSF_5 contamination by repetitive fractional codistillations.

In a typical run, 7 mmol of FC(O)C(O)F and 8 mmol of SF_5OF were irradiated for a period of 4 hr. Among the products were relatively large quantities of COF_2, CO_2, $SF_5OC(O)F$, SF_5OSF_5, and SF_5OOSF_5, along with smaller quantities of SiF_4, SF_6, SOF_4, SF_5OF, FC(O)C(O)F, traces of several unidentified substances, and a very small amount of a new compound, which was tentatively identified as $SF_5OOC(O)F$, pentafluorosulfur peroxofluoroformate.

FC(O)OOC(O)F + SF_5OF. Irradiation of a mixture of 3 mmol of FC(O)OOC(O)F and 5 mmol of SF_5OF for a period of 6.5 hr gave an estimated 1.5 mmol of CO_2 and COF_2, 1 mmol of SO_2F_2, 1 mmol of SF_6, 2 mmol of SF_6OF, 1 mmol of FC(O)OOC(O)F, 0.5 mmol of $SF_5OOC(O)F$, and 0.5 mmol of SF_5OOSF_5, along with very small amounts of $CF_3OOC(O)F$,[24,25] CF_3OOSF_5,[15] and traces of several unidentified substances.

FC(O)OOC(O)F + SF_5OOSF_5. In a typical run, SF_5OOSF_5 (about 2.5 mmol) and about 2.5 mmol of FC(O)OOC(O)F were irradiated for 2 hr. The products, separated by codistillation, were collected in four fractions: (1) 4 mmol of a mixture of CO_2, COF_2, SiF_4, SF_6, SO_2F_2, and SOF_4; (2) 0.5 mmol of FC(O)OOC(O)F containing some $SF_5OOC(O)F$; (3) 1 mmol of $SF_5OOC(O)F$ containing some SF_5OOSF_5; and (4) 1.5 mmol of SF_5OOSF_5. Fractions 2 and 4 were recycled to produce additional quantities of products. Several portions of fraction 3 were eventually combined and subjected to repetitive codistillations to give pure pentafluorosulfur peroxofluoroformate, $SF_5OOC(O)F$.

Runs such as these indicated SF_5OOSF_5 to be a cleaner, but more sluggish, source of SF_5O radicals than SF_5OF.

There was some indication that the reaction approached photolytic equilibrium after approximately 2 hr, as prolonged irradiation failed to increase the yield of pentafluorosulfur peroxofluoroformate.

Properties. Pentafluorosulfur Carbonyl Fluoride. This compound was tentatively recognized by its infrared spectrum, which showed absorptions reasonable for a fluorocarbonyl group and a pentafluorosulfur group. Additional support was given to this identification by the vapor-phase hydrolysis, which in the infrared cell proceeded to give SOF_2, CO_2, and SiF_4. No absorption bands were observed for the hoped for but unknown pentafluorosulfurcarboxylic acid, SF_5COOH.

The boiling point of $SF_5C(O)F$ was estimated to be about −10°, based upon its position between thionyl fluoride (bp −35°) and oxalyl fluoride (bp 0°) during fractional codistillation. During handling, $SF_5C(O)F$ was found to be sensitive to traces of water in the vacuum system, but showed no other tendencies toward reaction. Clean mercury was not affected over several minutes' exposure.

Chemical analysis was carried out as described above, sulfite having been oxidized to sulfate using a 10% excess of hydrogen peroxide before gravimetric determination as barium sulfate. The hydrolysis equation was found to be

$$SF_5C(O)F + 10OH^- \longrightarrow 6F^- + SO_4^{2-} + CO_3^{2-} + 5H_2O$$

Anal. Calcd for $SF_5C(O)F$: F, 65.5; S, 18.4; C, 6.9; mol wt, 174; 10.0 mmol of OH^- consumed/mmol of sample. Found: F, 64.8; S, 18.0; C, 6.4; mol wt, 171; 10.2 mmol of OH^- consumed/mmol of sample.

The infrared spectrum of pentafluorosulfur carbonyl fluoride is presented in Table I and illustrated in Figure 1. Some of the features in Table I are more readily observed at higher pressures than

Table I. Infrared Absorptions of Pentafluorosulfur Carbonyl Fluoride

Frequency, cm^{-1}	Intensity[a]	Tentative assignment	Comparable values, cm^{-1}
1899	s	C=O stretch	1868 C(O)ClF[b]
1871	m	Unassigned	
1159	s	C—F stretch	1095 C(O)ClF
937	w	S—F stretch	904 CF_3SF_5[c]
898	vvs	S—F stretch	885 CF_3SF_5
723 PQR	m	S—F stretch	692 CF_3SF_5
687 PQR	w	C(O)F out-of-plane	667 C(O)ClF
612 PQR	m	S—F deformation	614 CF_3SF_5
579	w	S—F deformation	593 CF_3SF_5

[a] s = strong, m = medium, w = weak, v = very. [b] A. H. Nielson, T. G. Burke, P. J. H. Woltz, and E. A. Jones, *J. Chem. Phys.*, **20**, 596 (1952). [c] D. F. Eggers, Jr., and H. E. Wright, *ibid.*, **35**, 1045 (1961).

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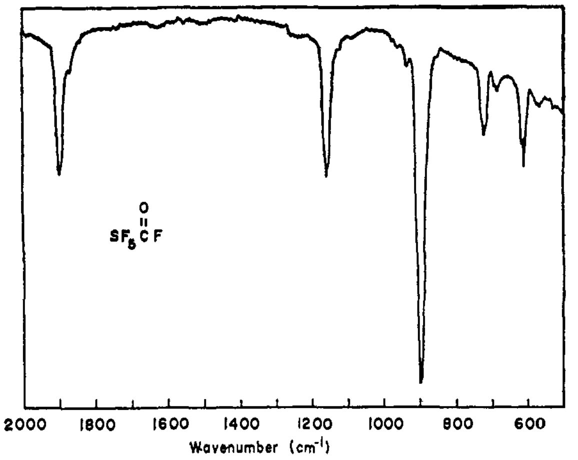

Figure 1. Infrared spectrum of pentafluorosulfur carbonyl fluoride (2 mm).

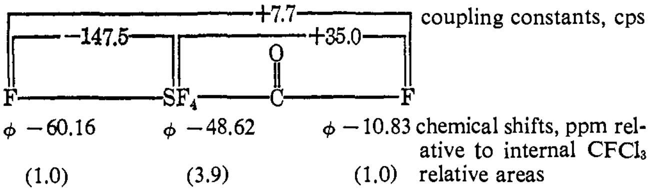

Figure 2. Nuclear magnetic resonance data calculated for $SF_6C(O)F$ The signs of the coupling constants are relative to one another and not necessarily absolute.

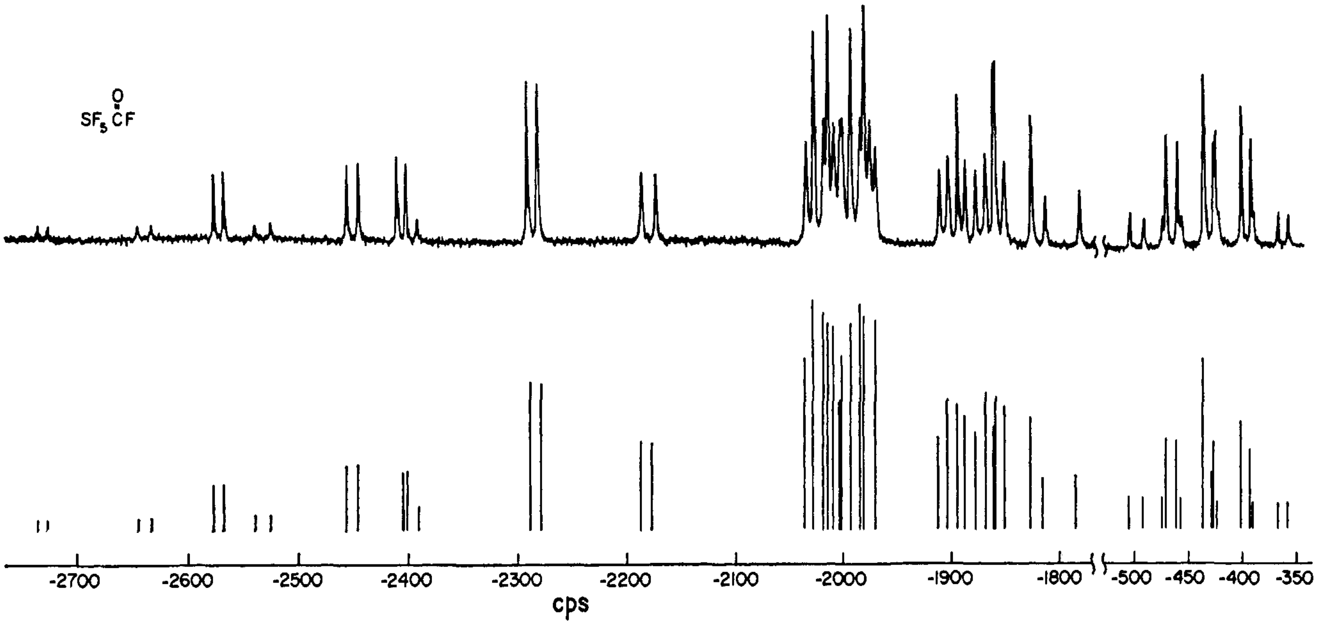

Figure 3. Nuclear magnetic resonance spectrum of pentafluorosulfur carbonyl fluoride taken at 40 Mc. Peaks between −2750 and −2150 cps are due to the unique fluorine atom on sulfur. Peaks between −2050 and 1750 cps are due to the SF_4 fluorine atoms, and peaks between −520 and −350 cps are due to the fluorine atom bonded to carbon.

that in Figure 1. The infrared spectrum is consistent with the formulation $SF_5C(O)F$; see Figure 2 for nmr data.

Supporting evidence that this compound was indeed $SF_5C(O)F$ was provided by its ^{19}F nmr spectrum, which was found to be very closely matched by one calculated using an AB_4C model (Figure 3). The SF_5 spectrum was similar to that observed for other SF_5 compounds and fell in the same portion of the spectrum. The peaks due to fluorine on carbon fell in a region typical for fluorocarbonyl groups. The spectrum was analyzed using the method of Merrill, *et al.*[26] Details of the analysis and a tabulation of observed and calculated data are presented elsewhere.[27]

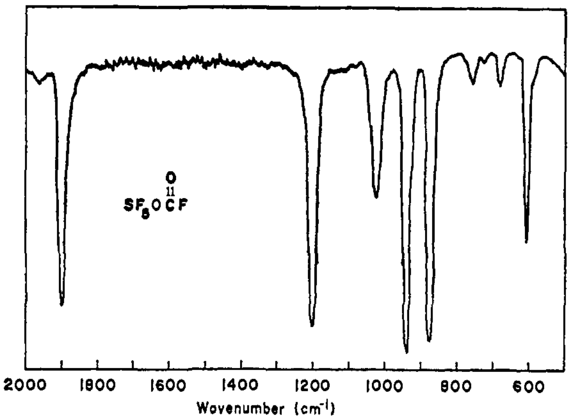

Figure 4. Infrared spectrum of pentafluorosulfur fluoroformate (3 mm).

Pentafluorosulfur Fluoroformate. This compound was estimated to boil at about 5° by the position of its codistillation peak between oxalyl fluoride (bp 0°) and bis(pentafluorosulfur) peroxide (bp 31°). The substance is a white solid at low temperatures and was observed to melt in the range −79 to −77.6°, giving a colorless liquid which did not attack glass. It was easily handled as a gas in vacuum apparatus. Hydrolysis of $SF_5OC(O)F$ in a Pyrex glass infrared cell proceeded slowly to give SO_2F_2, CO_2, and SiF_4, with no detected intermediates.

Chemical analysis of pentafluorosulfur fluoroformate was carried out as described. *Anal.* Calcd for $SF_5OC(O)F$: F, 60.0; S, 16.8; C, 6.3; mol wt, 190; 10.00 equiv of OH^- consumed per mole. Found: F, 59.4; S, 16.5; C, 5.9; mol wt, 188; 10.46 equiv of OH^- consumed per mole.

The infrared spectrum of pentafluorosulfur fluoroformate (Table II, Figure 4) showed absorptions characteristic of SF_5O groups and FCO_2 groups. The assignments in Table II are tentative. Some of the features listed in the table are observed at pressures greater than that for the spectrum shown in Figure 4. The observed spectrum is consistent with the formulation $SF_5OC(O)F$.

The ^{19}F nuclear magnetic resonance spectrum of $SF_5OC(O)F$ was analyzed in a manner similar to that employed for $SF_5C(O)F$, beginning with Merrill's approach;[26, 27] see Figure 5.

Pentafluorosulfur Peroxofluoroformate. Tentative recognition of this compound came from its infrared spectrum, which showed absorptions due to an FCO_2 group and bands attributable to an SF_5O group. The compound liberated iodine from aqueous potas-

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(26) C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, Jr., *Inorg. Chem.*, 1, 215 (1962).

(27) R. Czerepinski, Ph.D. Thesis, University of Washington, 1967.

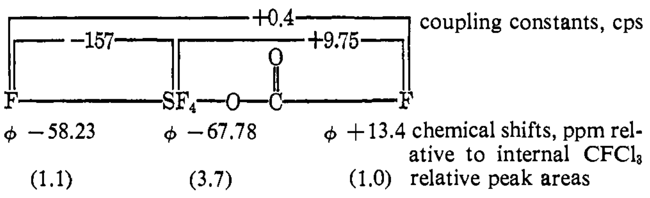

Figure 5. Nuclear magnetic resonance data calculated for $SF_5OC(O)F$. The signs of the coupling constants are relative to one another and not necessarily absolute.

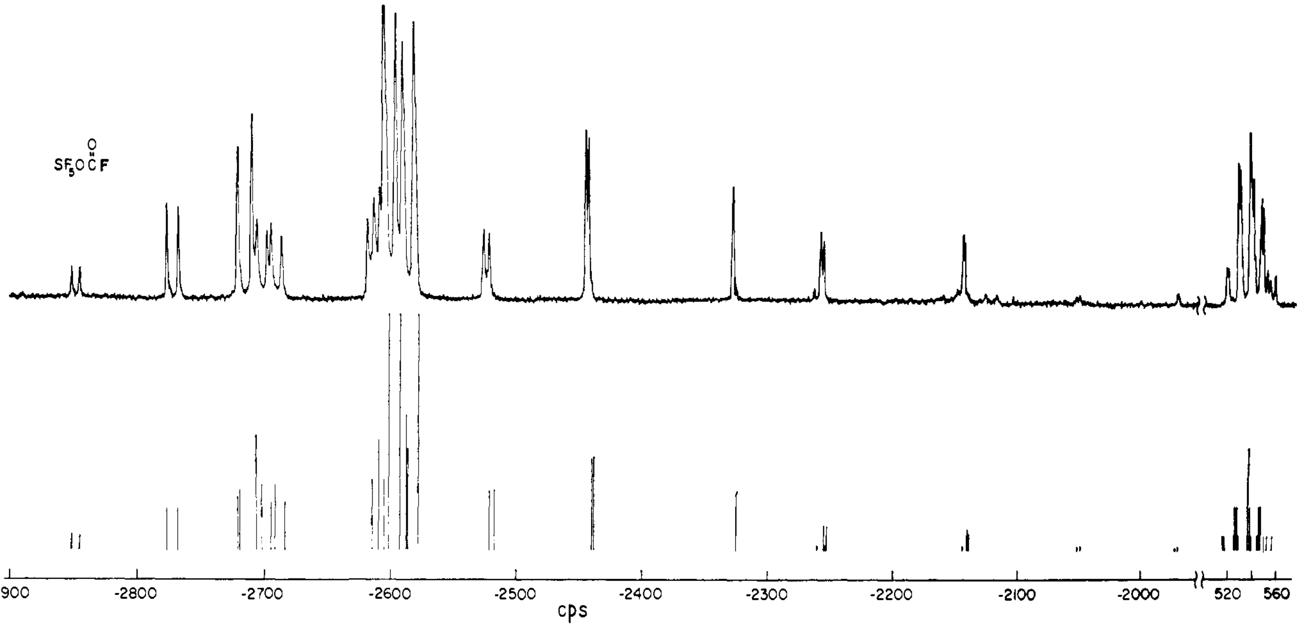

Figure 6. Nuclear magnetic resonance spectrum of pentafluorosulfur fluoroformate taken at 40 Mc. Peaks between −2900 and −2550 cps are due to the SF_4 fluorine atoms. Peaks between −2550 and −1950 cps are due to the unique fluorine atom on sulfur. Peaks in the vicinity of +540 cps are due to the fluorine atom bonded to carbon.

Table II. Infrared Absorptions of Pentafluorosulfur Fluoroformate

Frequency, cm^{-1}	Intensity[a]	Tentative assignment	Comparable values, cm^{-1}
1959	w	Unassigned	
1900	s	C=O stretch	1902 FC(O)OOC(O)F[19]
1201	s	C—F stretch	1221 FC(O)OOC(O)F
1022	m	C—O stretch	1016 FC(O)OOC(O)F
941	vs	SF_5O stretch	934 CF_3OSF_5[b]
878	vs	SF_5O stretch	854 CF_3OSF_5
755	w	FCO_2 out-of-plane	749 FC(O)OOC(O)F
680	w	SF_5O stretch	698 CF_3OSF_5
605	s	SF_5O deformation	614 SF_5OF
560	w	SF_5O deformation	585 SF_5OF

[a] s = strong, m = medium, w = weak, v = very. [b] L. C. Duncan and G. H. Cady, *Inorg. Chem.*, **3**, 850 (1964).

sium iodide and displayed an apparent boiling point of about 25°, as it codistilled between FC(O)OOC(O)F (bp 16°) and bis(pentafluorosulfur)peroxide (bp 49°).

The substance was found to attack mercury rapidly, forming a gray film. It also dissolved readily in the Kel-F oil protecting mercury manometers, again attacking mercury to a considerable degree.

Chemical analysis of pentafluorosulfur peroxofluoroformate was carried out as for the other compounds. The amount of oxygen liberated during hydrolysis was determined by weight. (The weighed hydrolysis flask was chilled to −183°, pumped to remove O_2, allowed to warm, and weighed again.) The initial hydrolysis reaction occurred quite vigorously at low temperatures and was accompanied by a transient yellow color in both the surface of the liquid and the vapor above. The net hydrolysis reaction was

$$SF_5OOC(O)F + 10OH^- \longrightarrow 6F^- + SO_4^{2-} + CO_3^{2-} + 5H_2O + 0.5O_2$$

Anal. Calcd for $SF_5OOC(O)F$: F, 55.4; S, 15.5; C, 5.8; O_2 liberation, 0.50 mmol/mmol; OH^- consumption, 10.0 equiv/mol; mol wt, 206.1. Found: F, 52.7; S, 13.8; C, 6.0; mol wt, 206.5; O_2 liberation, 0.56 mmol/mmol; OH^- consumption, 10.6 equiv/mol.

The nmr resonance spectrum is shown in Figure 6. The infrared spectrum was consistent with the formula $SF_5OOC(O)F$. The spectrum reported in Table III includes features observed at higher pressures than that used for the illustration in Figure 7.

Table III. Infrared Absorptions of Pentafluorosulfur Peroxofluoroformate

Frequency, cm^{-1}	Intensity[a]	Tentative assignment	Comparable values, cm^{-1}
1922	vs	C=O stretch	1902 FC(O)OOC(O)F[19]
1239	ms	2(611) = 1222	1221 FC(O)OOC(O)F
1196	vvs	C—F stretch	1178 (FC(O)OOC(O)F
998	w	C—O stretch	1016 FC(O)OOC(O)F
937	vvs	SF_5O stretch	950 SF_5OOSF_5[13]
889	vvs	SF_5O stretch	862 SF_5OOSF_5
751	m	FCO_2 out-of-plane	749 FC(O)OOC(O)F 740 SF_5OOSF_5
692	w	SF_5O deformation	695 SF_5OOSF_5
611	s	FCO_2 deformation	586 FC(O)OOC(O)F
569	w	SF_5O deformation	585 SF_5OF[12]

[a] s = strong, m = medium, w = weak, v = very.

The nuclear magnetic resonance spectrum of pentafluorosulfur peroxofluoroformate was taken at 40 Mc with $CFCl_3$ as an internal reference. It was not found possible to resolve the spectrum completely; therefore, only approximate values were obtained for the various constants. The spectrum was treated as an AB_4X case, using equations worked out for AB_4 spin systems.[28] The en-

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(28) N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Trans. Faraday Soc.*, **59**, 620 (1963).

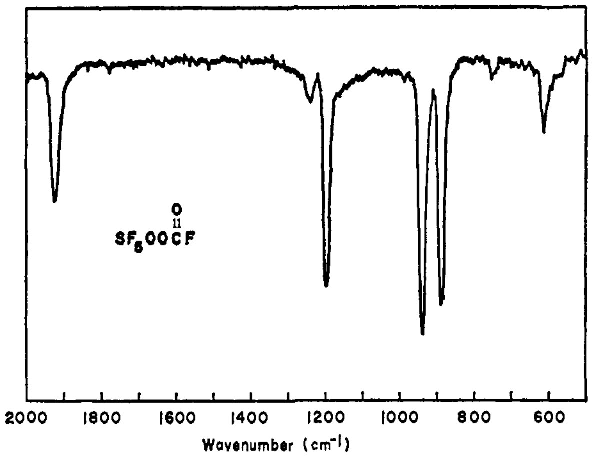

Figure 7. Infrared spectrum of pentafluorosulfur peroxofluoroformate (2 mm).

velope of the SF_5 spectrum is similar to that observed for other $OOSF_5$ compounds[28] (Figure 8). The observed chemical shift of the fluorocarbonyl group is close to that of FC(O)OOC(O)F (ϕ 34.4)[7] and $CF_3OOC(O)F$ (ϕ 32.3).[24,25] The SF_5 chemical shift is within the normal range observed for OSF_5 compounds; see Figure 9.

Discussion

The above reactions must have involved formation and subsequent reaction of the free radicals. A reasonable explanation for production of $SF_5C(O)F$ is combination of SF_5 with FC(O) derived respectively from S_2F_{10} and FC(O)C(O)F. Synthesis of $SF_5OC(O)F$ from S_2F_{10} and FC(O)OOC(O)F indicates strongly that irradiation of FC(O)OOC(O)F gave FCO_2. This conclusion is confirmed by the formation of $SF_5OOC(O)F$ from FC(O)OOC(O)F and SF_5OF or SF_5OOSF_5. Apparently the latter two compounds yielded SF_5O when irradiated. Behavior of the systems while subjected to uv radiation showed that the products $SF_5C(O)F$, $SF_5OC(O)F$, and $SF_5OOC(O)F$ decomposed photochemically.

Various by-products, which increased in amount with time, indicated that each of the radicals, $SF_5\cdot$, $SF_5O\cdot$, FC(O)·, FC(O)O·, and fluorine atoms entered into reactions other than simple combination with one another. Each of these radicals might undergo reaction by transfer of a fluorine atom to another species such as $SF_5\cdot$, FC(O)·, SF_4, CO, COF_2, or glass, resulting in the formation of SF_6, COF_2, $SF_5\cdot$, FC(O)·, $CF_3O\cdot$, or SiF_4, respectively. The $SF_5O\cdot$ and FC(O)O· radicals might similarly oxygenate species such as CO, SF_4, FC(O)·, or $SF_5\cdot$ to give CO_2, SF_4O, FCO_2, or $SF_5O\cdot$, respectively. In addition to the fluorine atom sources above, the compounds SF_4, OSF_4, and COF_2 may attack glass giving $SiF_4\cdot$ along with SOF_2, SO_2F_2, and CO_2, respectively.

The by-products S_2F_{10}, SF_5OSF_5, SF_5OOSF_5, FC(O)OOC(O)F, CF_3OOSF_5, and $CF_3OOC(O)F$ are reasonably accounted for as products of combination of free radicals in the irradiated systems. Similarly, other reactions of radicals discussed in the preceding paragraph account for other observed by-products: CO, COF_2, CO_2, SF_6, SOF_4, SO_2F_2, and SiF_4.

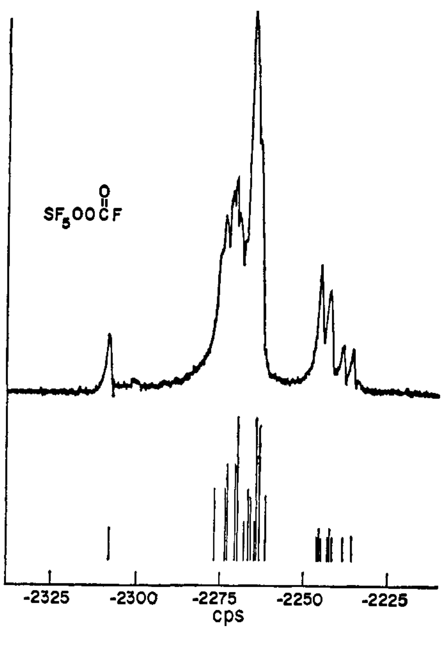

Figure 8. Nuclear magnetic resonance spectrum of the SF_5 region of pentafluorosulfur peroxofluoroformate taken at 40 Mc.

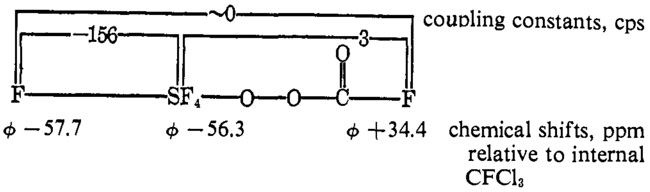

Figure 9. Nuclear magnetic resonance data calculated for $SF_5OOC(O)F$.

The photochemical reaction of SF_5OF with FC(O)C(O)F gave a higher yield of $SF_5OC(O)F$ than did the reaction of SF_5OF with CO or the reaction of S_2F_{10} with FC(O)OOC(O)F under similar conditions. This indicates a greater rate of formation of $SF_5OC(O)F$ in the first case than in the latter two, since the rate of photolysis of the product probably should be the same in all three.

This research gives additional evidence that oxalyl fluoride and bis(fluorocarbonyl) peroxide are useful sources of C(O)F· and OC(O)F· radicals, respectively.

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