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PENTAFLUOROSULFUR CARBONYL FLUORIDE, PENTAFLUOROSULFUR FLUOROFORMATE AND PENTAFLUOROSULFUR PEROXOFLUOROFORMATE

by Ralph Czerepinski and George H. Cady

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34

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Pentafluorosulfur Carbonyl Fluoride, Pentafluorosulfur Fluoroformate and Pentafluorosulfur Peroxofluoroformate.

By Ralph Czerepinski and George H. Cady

The compounds SF_5CFO, SF_5OCFO and SF_5OOCFO are produced in low yields by ultraviolet irradiation of the following mixtures, respectively: (1) S_2F_{10} and $C_2O_2F_2$, (2) SF_5OF and $C_2O_2F_2$; (3) SF_5OOSF_5 with $C_2O_4F_2$. 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.

INTRODUCTION

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 $FCO\cdot$ and $FCO_2\cdot$ groups.

The fluorocarbonyl radical has been inferred as a chemical intermediate from the kinetics[1] and the products[2,3] of

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[1] J. Heras, A. Arvia, P. Aymonino, and H. Schumacher,

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 may be prepared easily,[5] this substance is a good material to use as a source for fluorocarbonyl radical.

Bis(fluorocarbonyl) peroxide [6] has been investigated as a potential source of $FCO_2\cdot$ 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)

Z. Physik. Chem. (Frankfurt) 28, 250 (1961).

[2] N. Fukuhara and L. A. Bigelow, J. Am. Chem. Soc. 63, 788 (1941).

[3] G. W. Fraser and J. M. Shreeve, Inorg. Chem. 4, 1497 (1965).

[4] D. E. Milligan, M. E. Jacox, A. M. Bass, J. J. Comeford, and D. E. Mann, J. Chem. Phys. 42, 3187 (1965).

[5] G. W. Tullock and D. D. Coffman, J. Org. Chem. 25, 2016 (1960).

[6] A. Arvia, P. Aymonino, C. Waldow, and H. J. Schumacher, Angew. Chem. 72, 169 (1960).

[7] W. B. Fox and G. Franz, Inorg. Chem. 5, 946 (1966).

[8] R. L. Cauble and G. H. Cady, J. Am. Chem. Soc. 89, 5161 (1967).

Disulfur decafluoride has been found to be a relatively poor source of $SF_5\cdot$ radicals for synthetic purposes.[9, 10, 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 SF_5CFO, SF_5OCFO and SF_5OOCFO have been found in relatively low yields among the products of the reactions of $C_2O_2F_2$ with S_2F_{10}, $C_2O_2F_2$ with SF_5OF; and $C_2O_4F_2$ with SF_5OOSF_5 or SF_5OF, respectively, under the influence

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[9] H. J. Emeleus and K. J. Packer, J. Chem. Soc. 771, (1962).

[10] H. L. Roberts, ibid, 3183 (1962).

[11] B. Cohen and A. G. MacDiarmid, Chem. Ind. 1866, (1962).

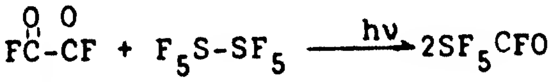
[12] F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., J. Am. Chem. Soc. 78, 1553 (1956).

[13] C. I. Merrill and G. H. Cady, J. Am. Chem. Soc. 83, 298 (1961).

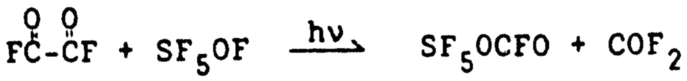
[14] S. M. Williamson and G. H. Cady, Inorg. Chem. 1, 673 (1963).

[15] C. I. Merrill and G. H. Cady, J. Am. Chem. Soc. 85, 909 (1963).

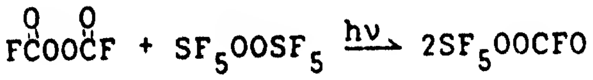
of ultraviolet irradiation.



$$F\overset{O}{C}-\overset{O}{C}F + F_5S-SF_5 \xrightarrow{h\nu} 2SF_5CFO \qquad (1)$$



$$F\overset{O}{C}-\overset{O}{C}F + SF_5OF \xrightarrow{h\nu} SF_5OCFO + COF_2 \qquad (2)$$



$$F\overset{O}{C}OO\overset{O}{C}F + SF_5OOSF_5 \xrightarrow{h\nu} 2SF_5OOCFO \qquad (3)$$

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

EXPERIMENTAL

Reagents.

Oxalyl fluoride was prepared by treating oxalyl chloride with sodium fluoride in acetonitile 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].

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16. G. H. Cady and D. P. Siegwarth, Anal. Chem., 31, 618 (1959).

Some of the oxalyl fluoride used was also prepared by treatment of oxalyl chloride with sodium fluoride at 100° for 24 hours in a 30cc brass cylinder. It was purified by fractional co-distillation.

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 millimole quantities to avoid possible harm from explosions. In a typical preparation, 10 mmol SOF_2 was condensed into a 50 cc brass cylinder (constructed from 3/16" wall, 3/4" brass pipe with a brass plug silver-soldered into the bottom, and a $\frac{1}{4}$" NPT brass female threaded fitting silver-soldered into the top. A brass body, stainless steel needle valve was sealed in place with Teflon tape.). The cylinder also contained 5 g. of dry cesium fluoride. Fluorine was condensed into the cylinder in 5 mmol quantities using liquid nitrogen, until a total of 30 mmol F_2 had been added. Between each addition of fluorine, the cylinder was closed and allowed to warm slowly to room temperature to 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,

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[17] J. K. Ruff and M. Lustig, Inorg. Chem. <u>3</u>, 1422 (1964).

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 byproduct 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]

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[18] A. Arvia, P. J. Aymonino and H. J. Schumacher, Z. Anorg. Allgem. Chem., <u>316</u>, 327 (1962).

One part carbon monoxide, six parts oxygen and two parts fluorine were allowed to flow into a 1 liter Pyrex glass flask with a total flow rate about 150 cc per minute. The $C_2O_4F_2$ 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 1mm, and the infrared spectrum[19] showed no impurities. During the course of investigation of the chemistry of oxalyl fluoride,

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[19] A. J. Arvia and P. J. Aymonino, Spectrochim Acta., <u>18</u>, 1299 (1962).

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 $C_2O_4F_2$ used in these studies was prepared in that manner.

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[20] R. Czerepinski and G. H. Cady, Inorg. Chem., 7, 0000 (1968).

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]

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[21] R. E. Dodd, L. A. Woodward and H. L. Roberts, Trans. Far. Soc., 53, 1545 (1957).

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 two liter Pyrex glass flask equipped with an internal quartz finger containing a water-cooled Hanau 350 watt 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 3mm 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% $CFC\ell_3$ 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 5N 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 thymolphtalein endpoint, and a duplicate titration in the presence of excess barium chloride to the same endpoint, using standard $HC\ell$. The difference in endpoints was due to carbonate.

Preparations.

$(FCO)_2 + SF_4$. Ultraviolet irradiation of a mixture containing 2 mmol oxalyl fluoride and 2 mmol sulfur tetrafluoride was run for a period of 19 hours at ambient temperatures, in an attempt to produce $(FCO)_2SF_4$ and/or SF_5CFO.

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.

$(FCO)_2 + S_2F_{10}$. 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 was found among the products. The preferred conditions for maximizing the yield of SF_5CFO, while minimizing loss of reactants employed 10 mmol $(FCO)_2$ and 5 mmol S_2F_{10}, irradiated for a period of 3 hours at room temperature. Under such circumstances the yield of SF_5CFO 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 $(FCO)_2$ and S_2F_{10} combined, and about 0.5 mmol SOF_2. A quantity of gas which did not condense at -183°, assumed to be carbon monoxide, was disposed of without further identification. It was found that the yield of SF_5CFO was limited by a number of side reactions. Among these were the photochemical decompositions of oxalyl fluoride, disulfur decafluoride and pentafluorosulfur carbonyl fluoride. The apparent half life for decomposition of oxalyl fluoride by the reaction

$$(FCO)_2 \xrightarrow{h\nu} COF_2 + CO$$

under the conditions described above was about 2 to 3 hours. A similar irreversible photolysis of oxalyl chloride has been reported.[22] Disulfur decafluoride decomposes under the influence of ultraviolet light as shown in the equation.[23]

$$S_2F_{10} \xrightarrow{h\nu} SF_6 + SF_4$$

It was also observed that the yield of SF_5CFO reached a maximum, and decreased after long (e.g. 12 hours) irradiation, probably because of the reaction:

$$SF_5CFO \xrightarrow{h\nu} SF_5 + FCO$$

In an attempt to achieve thermal reaction, 0.6 mmol S_2F_{10} and 1.1 mmol $(FCO)_2$ were held in a 300 mℓ Pyrex glass flask for 8 days. Along with unreacted starting materials, small amounts of COF_2, CO_2 SiF_4, SF_6 and SOF_2 were found. No SF_5CFO was detected.

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[22] K. B. Krauskopf and G. K. Rollefson., J. Am. Chem. Soc., 58, 443 (1936).

[23] H. J. Emeléus and K. J. Packer, J. Chem. Soc., 771 (1962).

Liquid phase irradiation of a 3.4 to 1 molar ratio of S_2F_{10} and $(FCO)_2$ was attempted in a 0.7 mℓ Vycor glass finger attached to a 300 mℓ Pyrex flask. The water-cooled 350 watt ultraviolet lamp was placed next to the finger containing liquid S_2F_{10} and $(FCO)_2$. Irradiation was allowed to proceed for 9 hours at 10°C with about 0.5 cm water interposed between the lamp and finger. A small amount of SF_5CFO was detected along with larger amounts of COF_2, SiF_4, SF_6 and SOF_2, though the overall degree reaction was very small.

$\underline{S_2F_{10} + (FCO)_2 + O_2.}$ 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_5CFO was generally negligible, and in its place was found a new compound, SF_5OCFO, pentafluorosulfur fluoroformate. In one instance, 10 mmol $(FCO)_2$, 5 mmol S_2F_{10}, and an unknown amount of air were irradiated for 18 hours at ambient temperatures. Approximately 2 mmol unreacted S_2F_{10} was recovered, and about 1 mmol SF_5OCFO, along with approximately 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_5OCFO 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 S_2F_{10}, 3.6 mmol $(FCO)_2$, and 3.7 mmol O_2 was carried out for 11.5 hours. 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 $(FCO)_2$, SF_5OCFO, and relatively larger quantities of $C_2O_4F_2$ and S_2F_{10}; and another sample containing a total of 4.7 mmol $C_2O_4F_2$ and S_2F_{10}, combined. The large quantity of bis(fluorocarbonyl)peroxide obtained as a byproduct 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 occurence of the relatively large quantity of SF_5OCFO obtained as a product of the reaction involving air.

$\underline{(FCO_2)_2 + S_2F_{10}.}$ Disulfur decafluoride, 8.1 mmol and bis(fluorocarbonyl)peroxide, 8.6 mmol, were sealed in the ultraviolet irradiation flask, and irradiated for 3 hours. SiF_4, COF_2, CO_2, and SF_6 comprised 5.8 mmol of the products upon codistillation, $C_2O_4F_2$ and S_2F_{10} (impure with small amounts of SF_5OSF_5[24] 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 $C_2O_4F_2$, S_2F_{10} and SF_5OCFO. The yield of SF_5OCFO was not found to increase significantly after another 11 hours irradiation, though the reactants were diminished in quantity while their degradation products increased.

$\underline{SF_5OF + CO.}$ The success of photochemically adding CF_3OF to CO, producing CF_3OCFO[25], suggested that it might be possible to add SF_5OF to CO to produce SF_5OCFO. 13 mmol SF_5OF and

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[24] H. L. Roberts, J. Chem. Soc., 2774 (1960).

13 mmol CO were irradiated together for 4.5 hours. Less than 0.5 mmol SF_5OCFO was found amidst larger quantities of SiF_4, SF_6, CO_2, SOF_4[12], SF_5OF, S_2F_{10}, SF_5OSF_5, and SF_5OOSF_5.

$C_2O_2F_2$ + 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_5OCFO 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_5OCFO 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 $C_2O_2F_2$ and 8 mmol SF_5OF were irradiated for a period of 4 hours. Among the products were relatively large quantities of COF_2, CO_2, SF_5OCFO, SF_5OSF_5, and SF_5OOSF_5, along with smaller quantities of SiF_4, SF_6, SOF_4, SF_5OF, $(FCO)_2$, traces of several unidentified substances, and a very small amount of a new compound, which was tentatively identified as SF_5OOCFO, pentafluorosulfur peroxofluoroformate.

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25. P. J. Aymonino, Chem. Comm., 241 (1965).

$C_2O_4F_2$ + SF_5OF. Irradiation of a mixture of 3 mmol $C_2O_4F_2$ and 5 mmol SF_5OF for a period of 6.5 hours gave an estimated 1.5 mmol CO_2 and COF_2, 1 mmol SO_2F_2, 1 mmol SF_6, 2 mmol SF_5OF, 1 mmol $C_2O_4F_2$, 0.5 mmol SF_5OOCFO and 0.5 mmol SF_5OOSF_5, along with very small amounts of CF_3OOCFO,[26,27] CF_3OOSF_5[15], and traces of several unidentified substances.

$C_2O_4F_2$ + SF_5OOSF_5. In a typical run, SF_5OOSF_5, (about 2.5 mmol) and about 2.5 mmol $C_2O_4F_2$ were irradiated for two hours. The products, separated by codistillation, were collected in four fractions: (1) Four mmol of a mixture of CO_2, COF_2, SiF_4, SF_6, SO_2F_2 and SOF_4, (2) 0.5 mmol $C_2O_4F_2$ containing some SF_5OOCFO, (3) 1 mmol SF_5OOCFO of SF_5OOCFO 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_5OOCFO.

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 hours, as prolonged irradiation failed to increase the yield of pentafluorosulfur peroxofluoroformate.

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[26] R. L. Talbott, Private communication.

[27] R. L. Cauble, Private communication.

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. Additonal 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 pentafluorosulfur carboxylic acid, SF_5COOH.

The boiling point of SF_5CFO 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_5CFO 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:

$$SF_5CFO + 10\ OH^- \longrightarrow 6F^- + SO_4^{--} + CO_3^{--} + 5H_2O$$

Found for SF_5CFO: mol wt. 171; F 64.8%; S 18.0%; C 6.4%; 10.2 mmol OH^- consumed/ mmol sample. Calculated: mol wt. 174; F 65.5%; S 18.4%, C 6.9%, 10.0 mmol OH^- consumed/ mmol sample.

The infrared spectrum of pentaluorosulfur carbonyl fluoride is presented in Table I and illustrated in Fig. 1.

Some of the features in Table I are more readily observed at higher pressures than that in Fig. 1. The infrared spectrum is consistent with the formulation SF_5CFO.

TABLE I

INFRARED ABSORPTIONS OF PENTAFLUOROSULFUR CARBONYL FLUORIDE

Frequency cm^{-1}		Intensity*	Tentative assignment	Comparable values
1899		s	C=O stretch	1868 COClF[28]
1871		m	unassigned	
1159		s	C-F stretch	1095 COClF
937		w	S-F stretch	904 CF_3SF_5[29]
898		vvs	S-F stretch	885 CF_3SF_5
723	PQR	m	S-F stretch	692 CF_3SF_5
687	PQR	w	CFO out of plane	667 COClF
612	PQR	m	S-F deformation	614 CF_3SF_5
579		w	S-F deformation	593 CF_3SF_5

* s-strong, m-medium, w-weak, v [illegible] ery.

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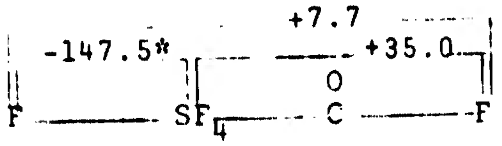
28. A. H. Nielson,T. G. Burke, P. J. H. Woltz and E. A. Jones J. Chem. Phys., 20, 596 (1952).

29. D. F. Eggers, Jr. and H. E. Wright, J. Chem. Phys., 35, 1045 (1961).

Supporting evidence that this compound was indeed SF_5CFO was provided by its ^{19}F NMR spectrum, which was found to be very closely matched by one calculated using an AB_4C model (Fig. 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.[30] Details of the NMR analysis and a tabulation of observed and calculated data are presented elsewhere.[31]



			coupling constants, cps
-60.16ϕ	-48.62ϕ	-10.83ϕ	chemical shifts, ppm relative to internal $CFCl_3$
(1.0)	(3.8)	(1.0)	relative areas

Fig. 2. Nuclear magnetic resonance data calculated for SF_5CFO.

* Note: signs of the coupling constants are relative to one another, and not necessarily absolute.

Pentafluorosulfur fluoroformate. This compound was estimated to boil at about 5°C by the position of its

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

[31] R. Czerepinski, Ph.D. Thesis, University of Washington, 1967.

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_5OCFO 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. Found for SF_5OCFO: mol wt 188; F 59.4%; S 16.5%; C 5.9%; 10.46 equivalents OH^- consumed per mole. Calculated: mol wt 190; F 60.0; S 16.8; C 6.3; 10.00 equiv. base.

The infrared spectrum of pentafluorosulfur fluoroformate (Table II, Fig. 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 Fig. 4. The observed spectrum is consistent with the formulation SF_5OCFO.

TABLE II

INFRARED ABSORPTIONS OF PENTAFLUOROSULFUR FLUOROFORMATE

Frequency (cm^{-1})	Intensity*	Tentative assignment	Comparable values	
1959	w	unassigned		
1900	s	C=O stretch	1902	$C_2O_4F_2$[19]
1201	s	C-F stretch	1221	$C_2O_4F_2$
1022	m	C-O stretch	1016	$C_2O_4F_2$
941	vs	SF_5O stretch	934	CF_3OSF_5[32]
878	vs	SF_5O stretch	854	CF_3OSF_5
755	w	FCO_2 out-of-plane	749	$C_2O_4F_2$
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

* s-strong, m-medium, w-weak, v-very.

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32. L. C. Duncan and G. H. Cady, Inorg. Chem., 3, 850 (1964).

The ^{19}F nuclear magnetic resonance spectrum of SF_5OCFO was analyzed in a manner similar to that employed for SF_5CFO, beginning with Merrill's approach.[30,31]

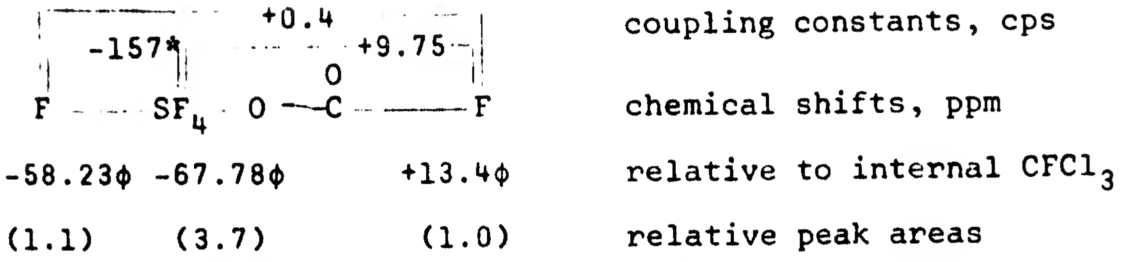

Fig.5. Nuclear magnetic resonance data calculated for SF_5OCFO.

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* Note: signs of the coupling constants are relative to one another, and not necessarily absolute.

<u>Pentafluorosulfur peroxofluoroformate.</u> 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 potassium iodide, and displayed an apparent boiling point of about 25°, as it codistilled between $C_2O_4F_2$ (bp 16°) and bis(pentafluorosulfur)peroxide (bp 49°).

The substance was found to attack mercury rapidly, forming a grey 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:

$$SF_5OOCFO + 10\ OH^- \longrightarrow 6F^- + SO_4^{--} + CO_3^{--} + 5H_2O + \tfrac{1}{2}O_2$$

Found for SF_5OOCFO: F 52.7%; S 13.8; C 6.0; O_2 liberation 0.56 mmol/mmol; OH^- consumption 10.6 equiv/mol. Calculated: F 55.4; S 15.5; C 5.8; O_2 liberation 0.50 mmol/mmol; OH^- consumption 10.0 equiv/mol. Molecular weight found: 206.5, calc: 206.1.

The infrared spectrum was consistent with the formula SF_5OOCFO. The spectrum reported in Table III includes features observed at higher pressures than that used for the illustration in Fig. 7.

TABLE III

INFRARED ABSORPTIONS OF PENTAFLUOROSULFUR PEROXOFLUOROFORMATE

Frequency (cm^{-1})	Intensity*	Tentative assignment	Comparable values	
1922	vs	C=O stretch	1902	$C_2O_4F_2$[19]
1239	ms	2(611)=1222	1221	$C_2O_4F_2$
1196	vvs	C-F stretch	1178	$C_2O_4F_2$
998	w	C-O stretch	1016	$C_2O_4F_2$
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	749 740	$C_2O_4F_2$, SF_5OOSF_5
692	w	SF_5O deformation	695	SF_5OOSF_5
611	s	FCO_2 deformation	586	$C_2O_4F_2$
569	w	SF_5O deformation	585	SF_5OF[12]

* 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.[33] The envelope of the SF_5 spectrum is similar to that observed for other $OOSF_5$ compounds.[30] (Fig. 9). The observed chemical shift of the fluorocarbonyl group is close to that of $C_2O_4F_2$(34.4φ)[7] and CF_3OOCFO(32.3φ).[26, 27] The SF_5 chemical shift is within the normal range observed for OSF_5 compounds.

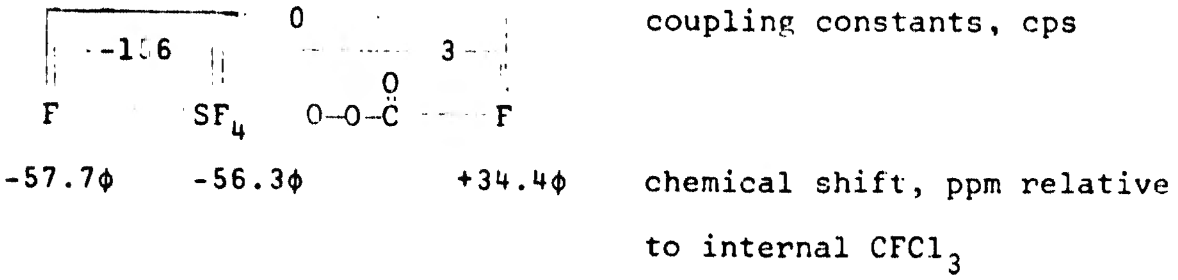

Fig. 8. Nuclear magnetic resonance data calculated for SF_5OOCFO.

DISCUSSION

The above reactions must have involved formation and subsequent reaction of free radicals. A reasonable explanation for production of SF_5CFO is combination of SF_5 with CFO derived respectively from S_2F_{10} and $C_2O_2F_2$. Synthesis of SF_5OCFO

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[33] N. Boden, J. W. Emsley, J. Feeney and L. H. Sutcliffe, Trans. Far. Soc., 59, 620 (1963).

from S_2F_{10} and $C_2O_4F_2$ indicates strongly that irradiation of $C_2O_4F_2$ gave FCO_2. This conclusion is confirmed by the formation of SF_5OOCFO from $C_2O_4F_2$ and SF_5OF or SF_5OOSF_5. Apparently the latter two compounds yielded SF_5O when irradiated. Behavior of the systems while subjected to $\mu\nu$ radiation showed that the products SF_5CFO, SF_5OCFO and SF_5OOCFO decomposed photochemically.

Various byproducts, which increased in amount with time, indicated that each of the radicals, $SF_5\cdot$, $SF_5O\cdot$, $CFO\cdot$, $FCO_2\cdot$, 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 $SF_5\cdot$, $FCO\cdot$, SF_4, CO, COF_2, or glass, resulting in the formation of SF_6, COF_2, $SF_5\cdot$, $CFO\cdot$, $CF_3O\cdot$, or SiF_4, respectively. The $SF_5O\cdot$ and $FCO_2\cdot$ radicals might similarly oxygenate species such as CO, SF_4, $FCO\cdot$ for $SF_5\cdot$ 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 byproducts S_2F_{10}, SF_5OSF_5, SF_5OOSF_5, $C_2O_4F_2$, CF_3OOSF_5 and CF_3OOCFO 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 byproducts: CO, COF_2, CO_2, SF_6, SOF_4, SO_2F_2 and SiF_4.

The photochemical reaction of SF_5OF with $C_2O_2F_2$ gave a higher yield of SF_5OCFO than did the reaction of SF_5OF with CO or the reaction of S_2F_{10} with $C_2O_4F_2$ under similar conditions. This indicates a greater rate of formation of SF_5OCFO 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 FCO· and FCO_2· radicals, respectively.

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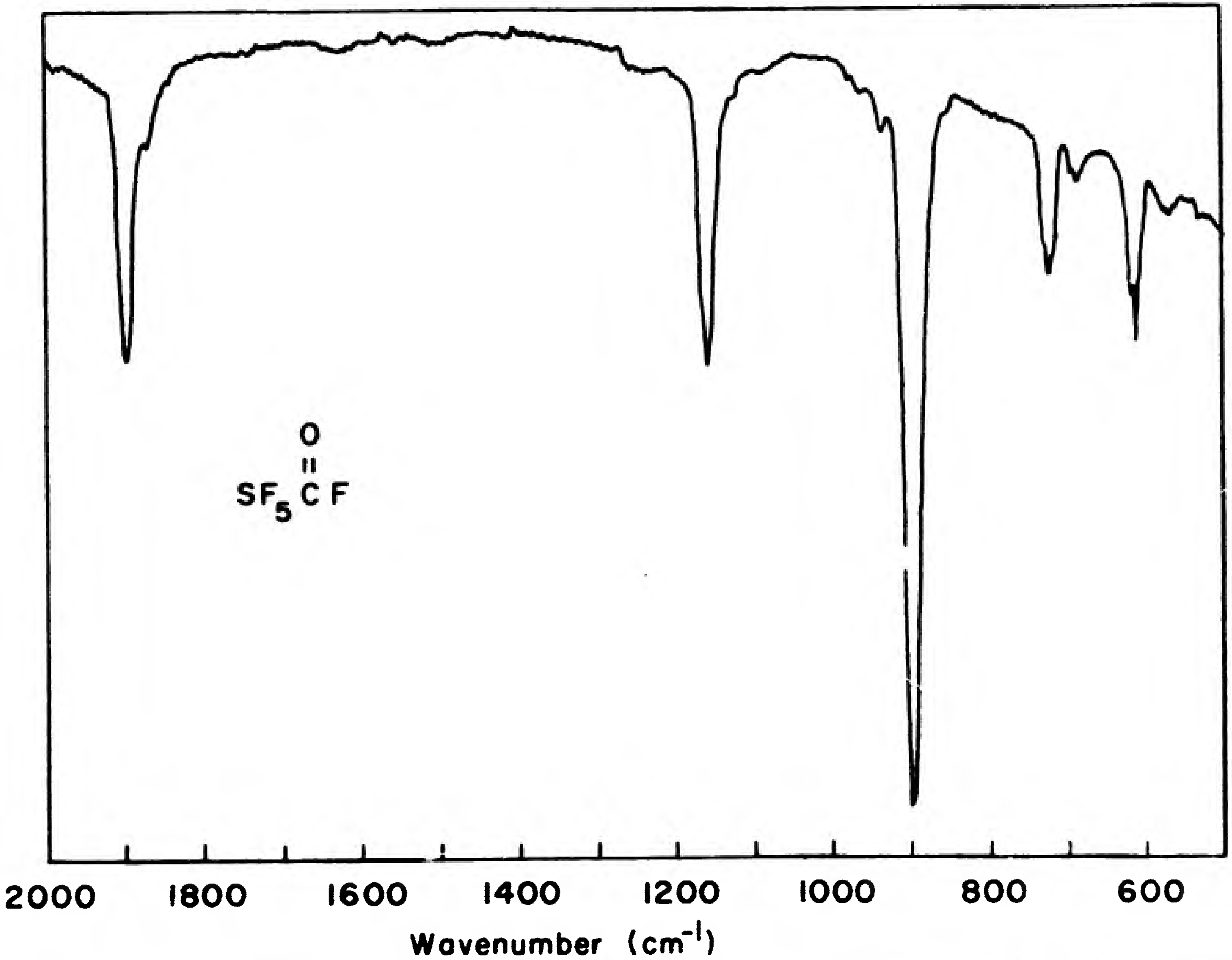

Fig. 1 Infrared spectrum of pentafluorosulfur carbonyl fluoride (2mm).

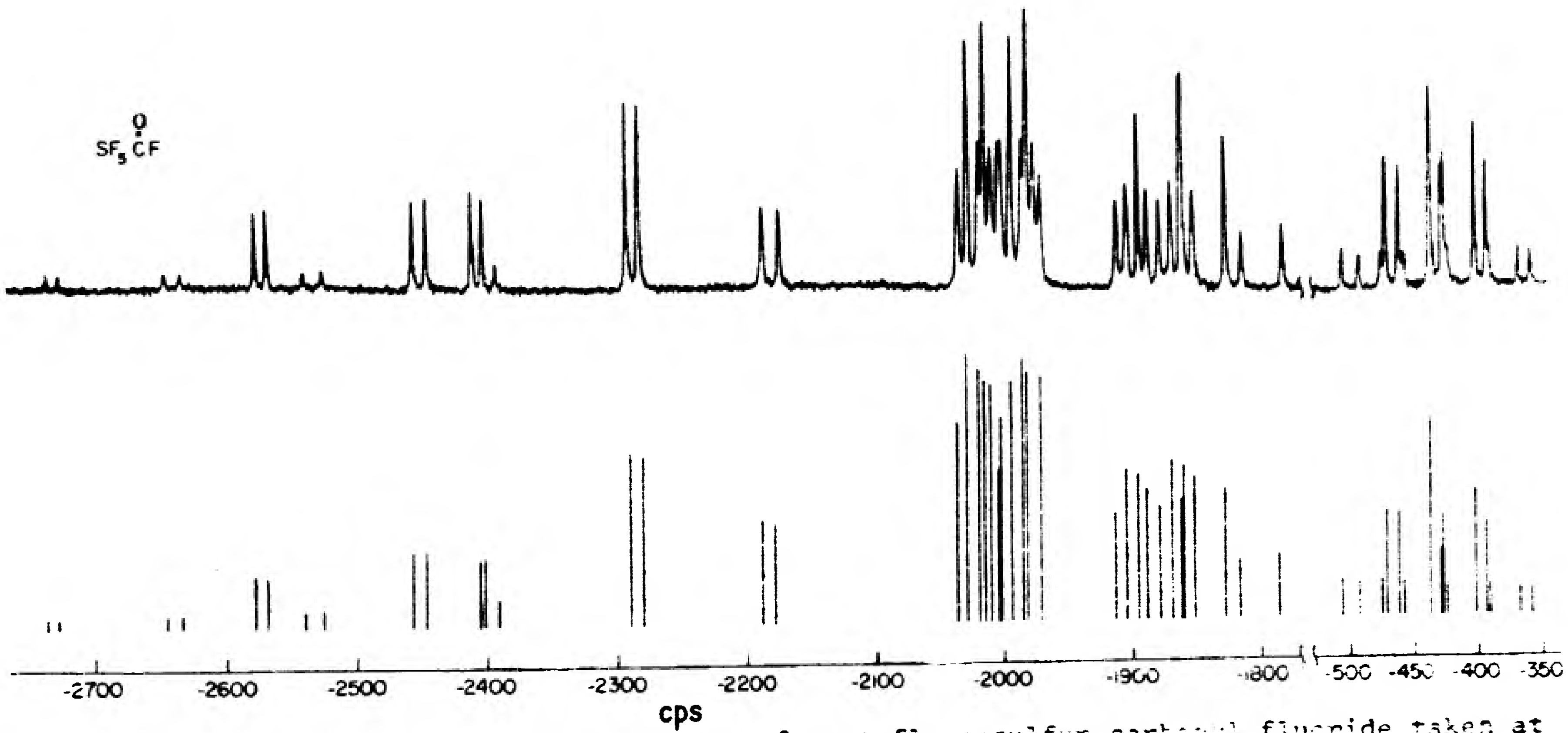

Fig. 3. Nuclear magnetic resonance spectrum of pentafluorosulfur carbonyl fluoride taken at 40 mc. Peaks between -2750 and -2150 cps are due to the unique fluorine atom on sulfur. Peaks between -2050 and -1750 cps are due to the SF_4 fluorine atoms, and peaks between -520 and -350 cps are due to the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

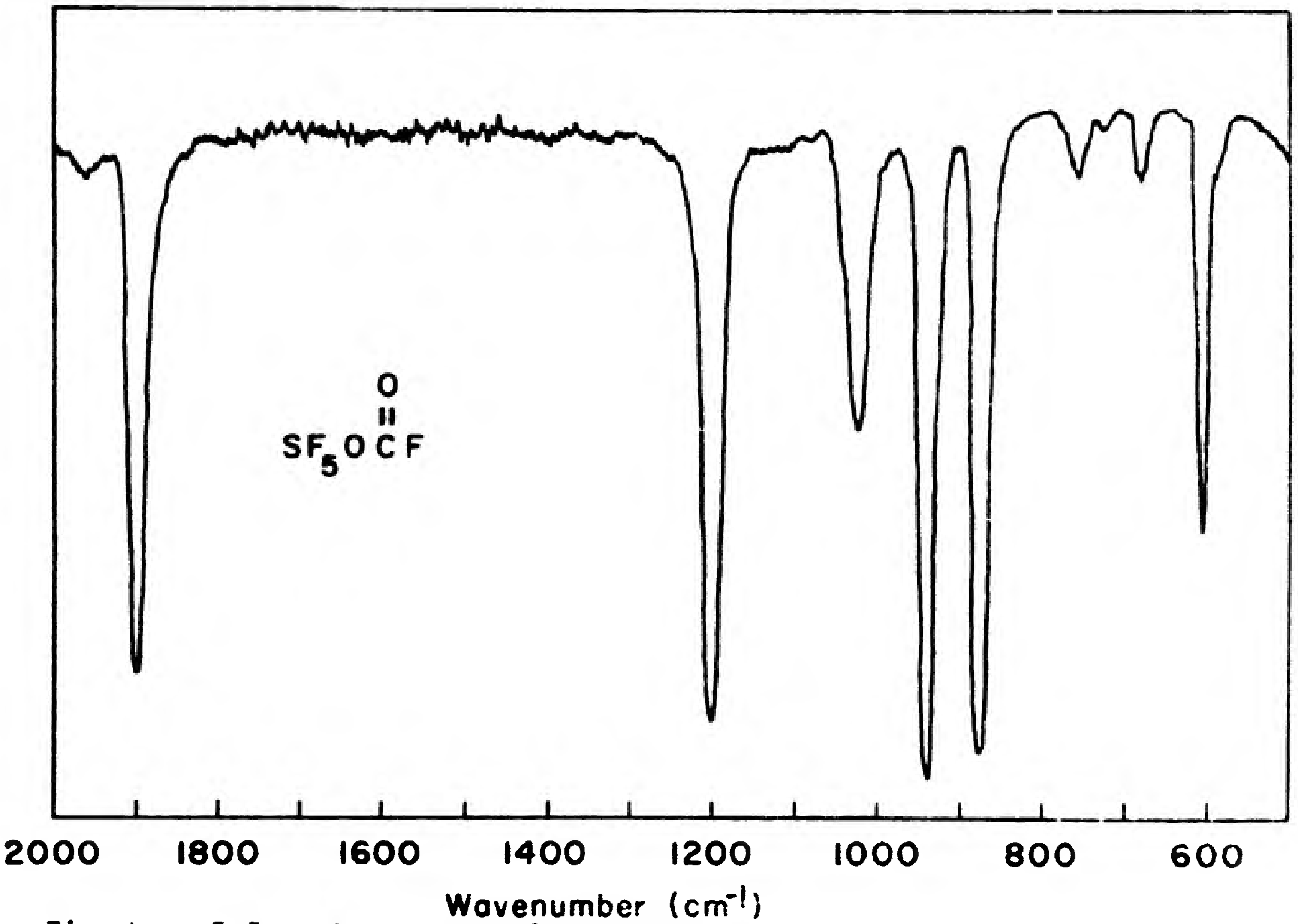

Fig. 4. Infrared spectrum of pentafluorosulfur fluoroformate (3mm).

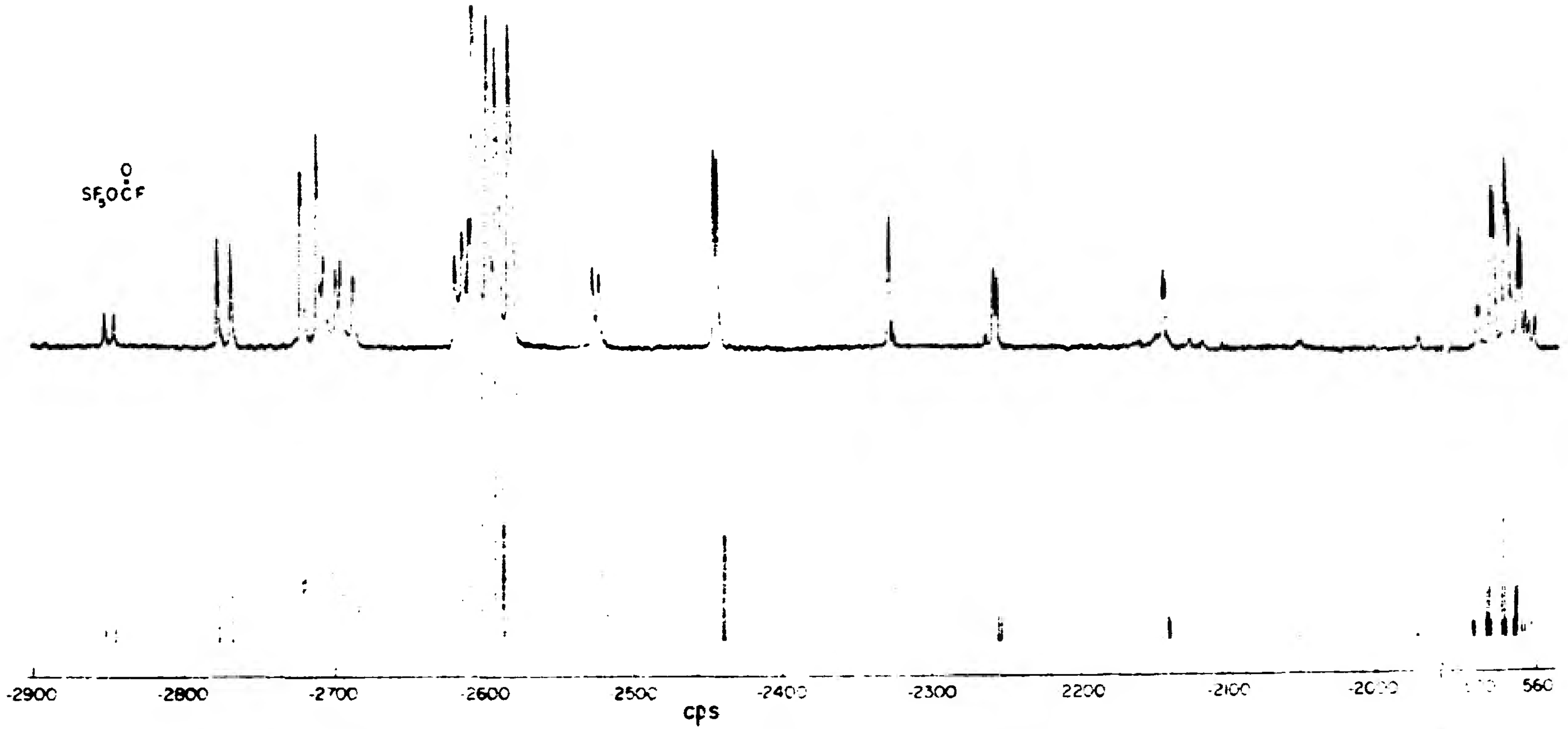

Fig. 6. Nuclear magnetic resonance spectrum of pentafluorosulfur fluoroformate taken at 40 mc. Peaks between -2900 and -2550 cps are due to the SF_4 fluorine atoms. Peaks between -2550 and -1950 cps are due to the unique fluorine atom on sulfur. Peaks in the vicinity near +540 cps are due to the fluorine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

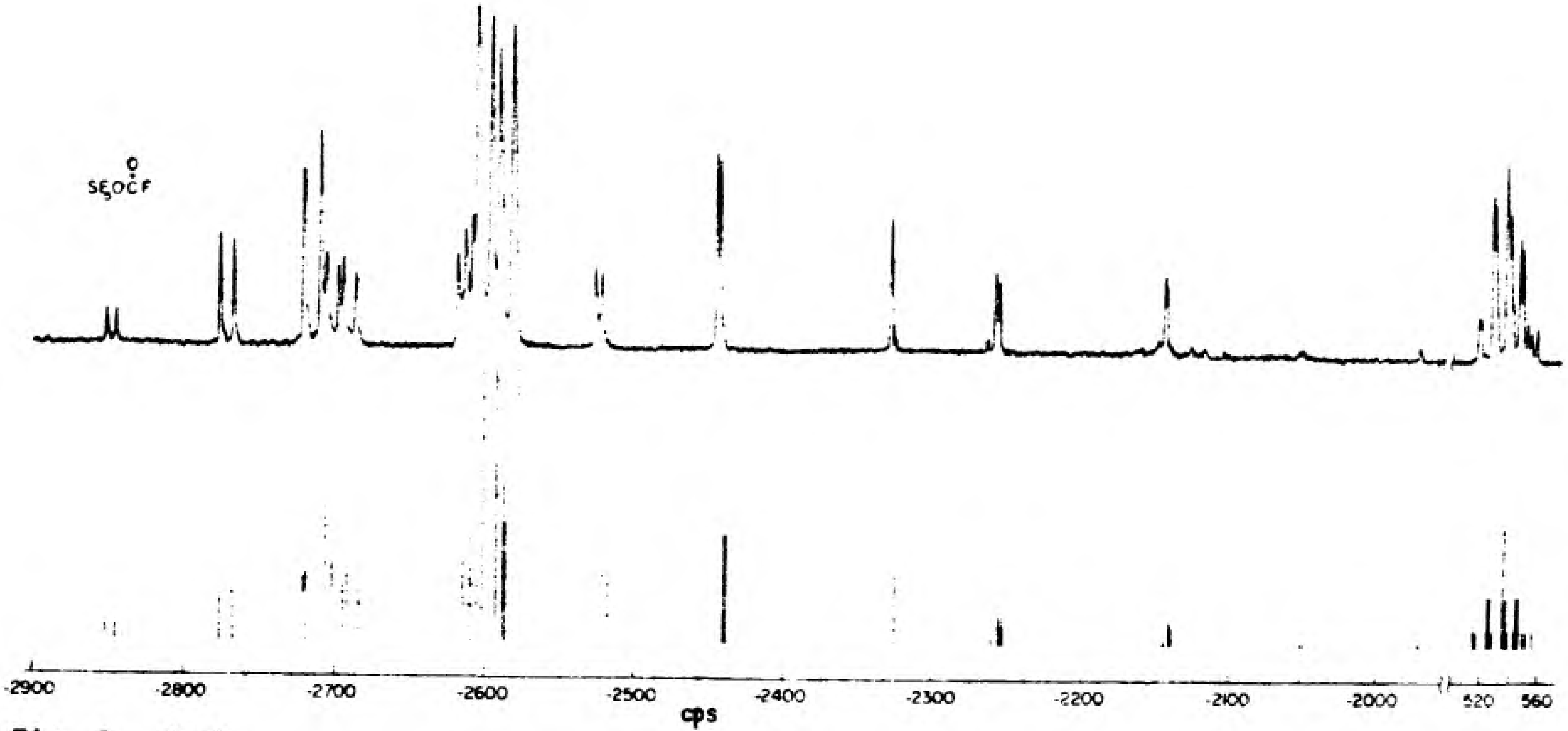

Fig. 6. Nuclear magnetic resonance spectrum of pentafluorosulfur fluoroformate taken at 40 mc. Peaks between -2900 and -2550 cps are due to the SF_4 fluorine atoms. Peaks between -2550 and -1950 cps are due to the unique fluorine atom on sulfur. Peaks in the vicinity near +540 cps are due to the fluorine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

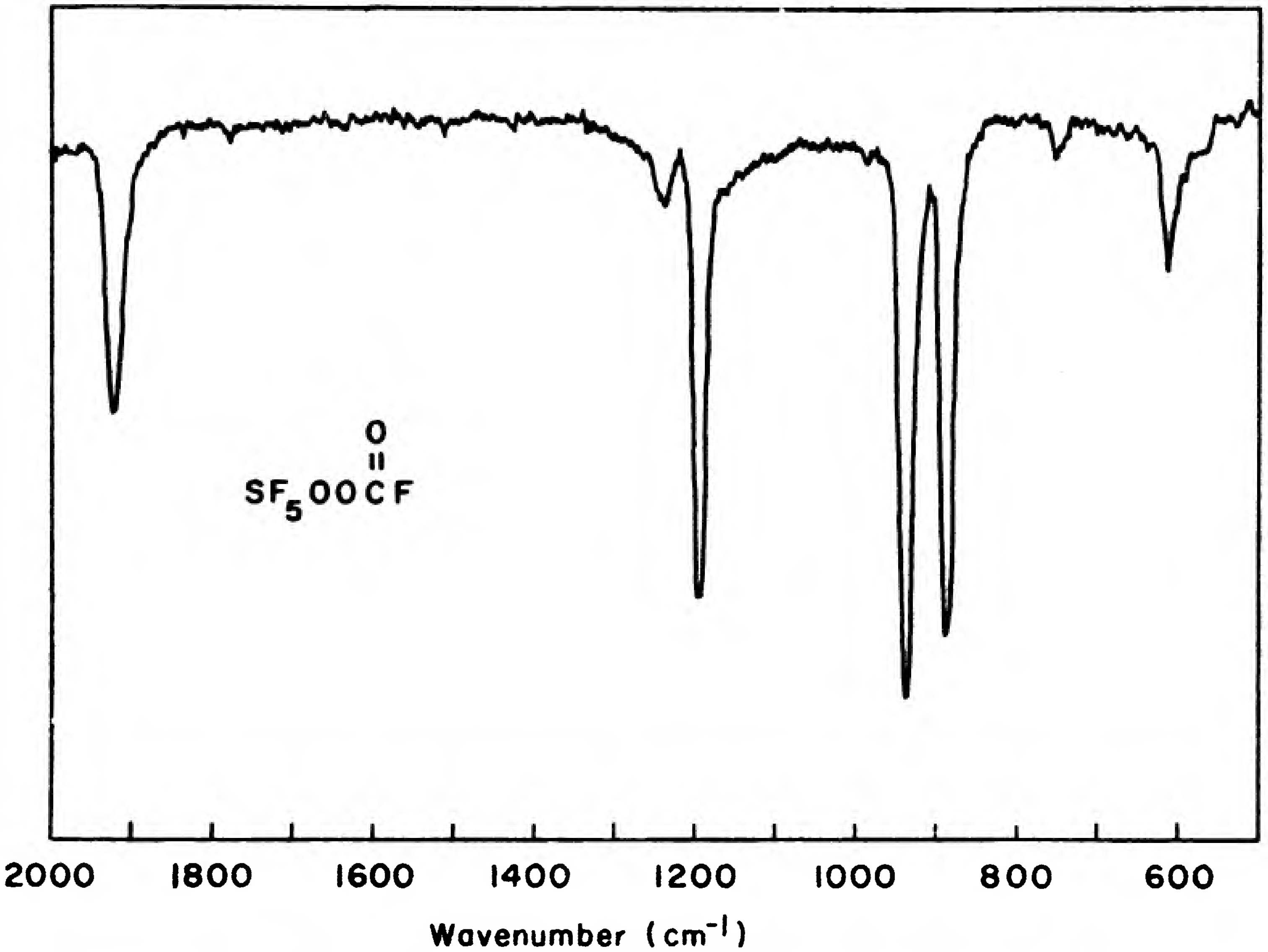

Fig. 7. Infrared spectrum of pentafluorosulfur peroxofluoroformate (2mm).

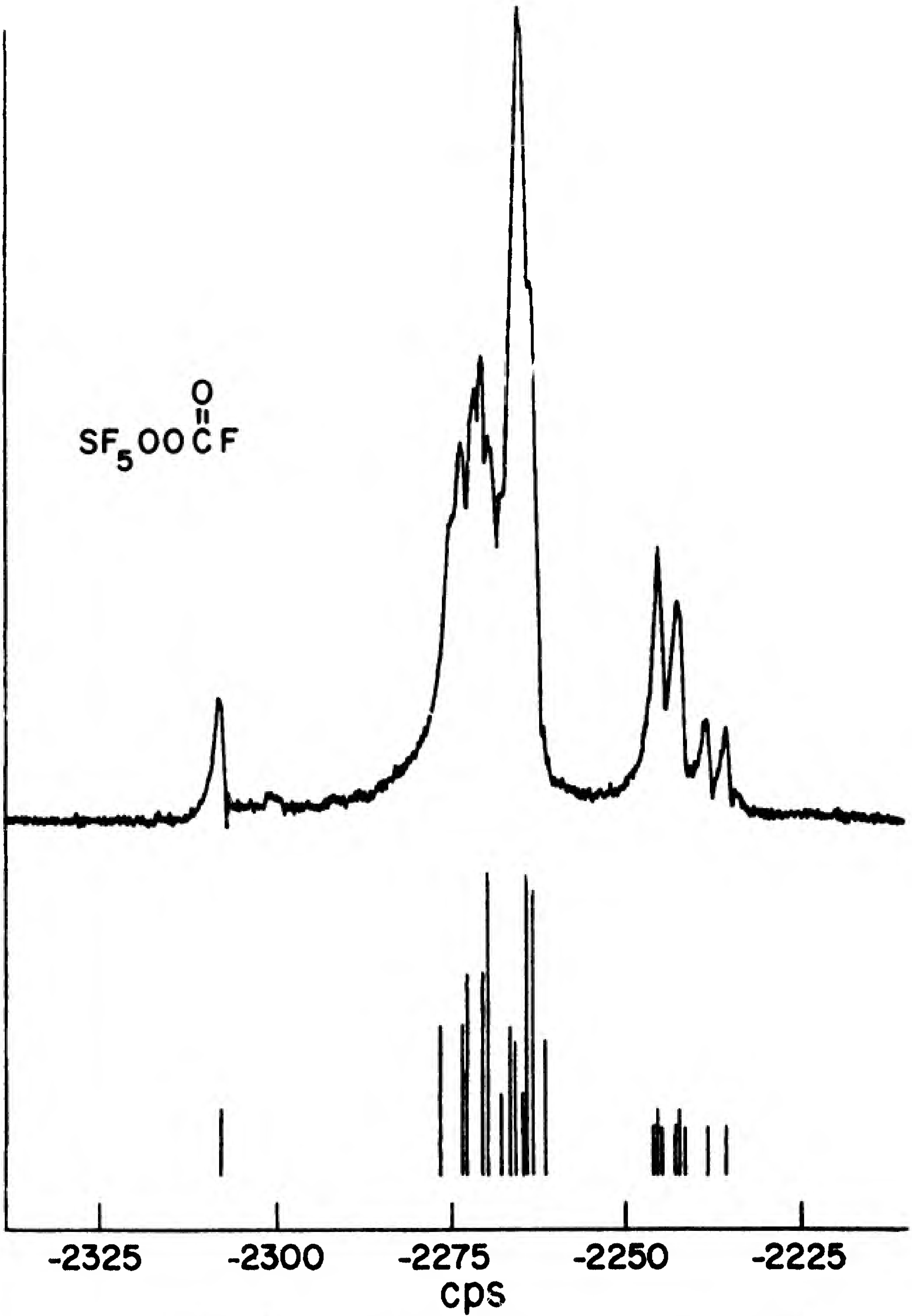

Fig. 9. Nuclear magnetic resonance spectrum of the SF_5 region of pentafluorosulfur peroxofluoroformate taken at 40 mc.

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The compounds SF_5CFO, SF_5OCFO and SF_5OOCFO are produced in low yields by ultraviolet irradiation of the following mixtures, respectively: (1) S_2F_{10} and $C_2O_2F_2$; (2) SF_5OF and $C_2O_2F_2$; (3) SF_5OOSF_5 and $C_2O_4F_2$. 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.

None

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Pentafluorosulfur Peroxofluoroformate					

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