with decarboxylated substrate, was observed for a number of the reactions. The effect was most pronounced where the catalyst was present to the extent of about 60–80% of the substrate. Figure 5 illustrates a reaction where this is occurring. Both manganese catalysts exhibited this behavior, but it was not observed for zinc, where the highest concentration of catalyst was only 20% of the substrate. It may be that the initial fast reaction was over before any measurements were made. Certainly when the manganese catalysts were at this concentration, the fast initial rate was difficult to see. The values given in Table I are for the slower part of the reaction. Initial rates were as much as five times this fast.

These complexes are the most like the enzyme, inasmuch as they are the most efficient catalysts and appear to have the same rate-determining step. The methoxy complexes at least do not derive their activation from the resonance effect, which does not occur for zinc and would be expected to deactivate the complex for manganese.

Other Catalysts. At low concentrations, some of the complexes showed deviations from the expected patterns of behavior. The corrections for these were large relative to the rate constant itself. Their observed rates are reported in Table I, but the corrected constants are omitted. These data were not used to compute intrinsic constants. The sodium salt of the sulfonated 4,7-diphenyl-1,10-phenanthroline complexes gave such erratic results that computations based on them are not meaningful.

Conclusions

It has been shown that when two ligands are coordinated to a single metal ion, changes in one can affect the reaction rate of the other, even when the changes in the first are remote from the second. Coordination of a manganese ion with a phenanthroline molecule greatly increases its ability to catalyze the decarboxylation of a β-keto acid. Catalysis by zinc, however, is unaffected by coordination with phenanthroline. Substitution of the phenanthroline at the 4 and 7 positions is also shown to change the rate. The resonance effect, which allows electron density from the acid to be delocalized into the system of the metal–phenanthroline complex, is suggested as a contributing influence. A second influence, the nature of which has not yet been determined, also affects the catalytic behavior of these compounds. The inductive effect is not usefully invoked to do this. Some very effective catalysts for decarboxylation have been found, and these are activated by the second influence. The data strongly suggest that they have the same rate-determining step as the decarboxylase enzyme. The enzyme protein does not activate the metal ion in the same way as phenanthroline itself does, but the second and unidentified influence, exerted for example by the methoxy phenanthrolines, may be a contributor to the activation by the enzyme.

Acknowledgment. This research was carried out under a grant from the National Institutes of Health, GM 11989.

Preparation and Characterization of New Fluoroxy Compounds. Bis(fluoroxy)perfluoroalkanes[1,2]

Phillip G. Thompson and Julianne H. Prager

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Abstract: The synthesis and characterization of $CF_3CF(OF)_2$ and $(CF_3)_2C(OF)_2$, representing the new class of geminal bisfluoroxy compounds, are reported. Their formation from $(CF_3)_2C(OH)ONa$ illustrates the unique behavior of salts in direct fluorination.

We have reported[3] the preparation and reactions of the monofluoroxy compounds: CF_3CF_2OF, $CF_3CF_2CF_2OF$, $(CF_3)_2CFOF$, $(CF_3)_3COF$, $NO_2CF_2CF_2OF$, $ClCF_2CF_2OF$, Cl_2CFCF_2OF, and Cl_3CCF_2OF, as well as[4] $FC(O)CF_2CF_2OF$ and $FOCF_2CF_2CF_2OF$. Cady and co-workers previously described the synthesis of CF_3OF[5] and several unstable acyl OF compounds.[6] In this paper the preparation of two members of a new class of compounds, the bis(fluoroxy)perfluoroalkanes, is reported. The characterization and certain reactions of these compounds, $CF_3CF(OF)_2$ and $(CF_3)_2C(OF)_2$, are also presented. In addition, an improved synthesis of C_2F_5OF[3] is reported.

Discussion

The direct fluorination of perfluoroacetone hydrate, $(CF_3)_2C(OH)_2$, yields $(CF_3)_2CFOF$.[3] We now report

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[1] (a) Some of the material in this paper was included in the review paper "Oxygen Fluorides and Hypofluorites" by P. G. Thompson at the Fluorine Symposium of the Inorganic Division of the American Chemical Society, Ann Arbor, Mich., June 27, 1966. (b) In accordance with the recommendations of the American Chemical Society Committee on Nomenclature of Highly Fluorinated Molecules, the term fluoroxy is used for the OF group.

[2] This research was supported by the Advanced Research Projects Agency under Contract NOrd 18688 and was monitored by the Bureau of Naval Weapons.

[3] J. H. Prager and P. G. Thompson, *J. Am. Chem. Soc.*, **87**, 230 (1965).

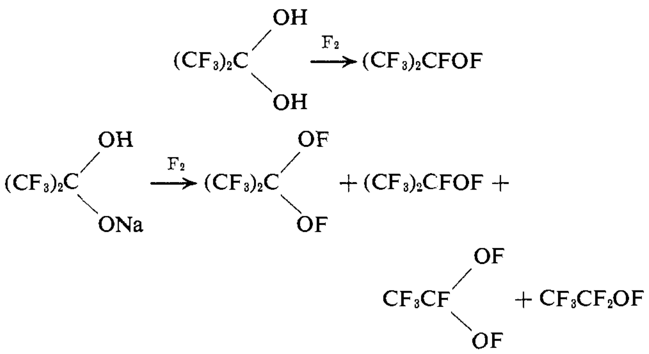
[4] J. H. Prager, *J. Org. Chem.*, **31**, 392 (1966).

[5] K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).

[6] (a) G. H. Cady and K. B. Kellogg, *ibid.*, **75**, 2501 (1953); (b) A. Menefee and G. H. Cady, *ibid.*, **76**, 2020 (1954).

the direct fluorination of the monosodium salt of perfluoroacetone hydrate, $(CF_3)_2C(OH)ONa$,[7] to give $(CF_3)_2C(OF)_2$ and $CF_3CF(OF)_2$ in addition to the previously reported[3] $(CF_3)_2CFOF$ and C_2F_5OF. The two compounds, 2,2-bis(fluoroxy)perfluoropropane and 1,1-bis(fluoroxy)perfluoroethane, represent the first examples of compounds containing two fluoroxy groups bonded to the same atom.[8]

The surprising difference in the products obtained from the direct fluorination of these two structurally similar materials illustrates the advantage of using salts to prepare fluoroxy compounds, particularly when bisfluoroxy structures are desired.



$$(CF_3)_2C(OH)_2 \xrightarrow{F_2} (CF_3)_2CFOF$$

$$(CF_3)_2C(OH)(ONa) \xrightarrow{F_2} (CF_3)_2C(OF)_2 + (CF_3)_2CFOF + CF_3CF(OF)_2 + CF_3CF_2OF$$

A further demonstration of this point is found in a comparison of the fluorination products of trifluoroacetic acid and its salts.[1,9] The acid affords rather low yields of the unstable hypofluorite, $CF_3C(O)OF$,[6a,10] whereas the salts give yields of up to 60% $CF_3CF(OF)_2$. The combined yield of OF compounds obtained from the perfluoroacetate salts can approach 95% of theory.[1,9]

It was earlier pointed out that OF-containing compounds are formed in best yield when starting materials low in C–H content are used.[3] The compound $(CF_3)_3COF$, for example, is obtained in excellent yield from $(CF_3)_3COH$. The fluorination of nitrosyl perfluoroacetate, $CF_3C(O)ONO$, described in this paper, gives CF_3CF_2OF in approximately 20% yield, while CF_3CH_2OH gives only about 10% of this product. The fluorination of a material high in C–H content, *i.e.*, $HOCH_2CH_2CH_2OC(O)CCl_3$, was shown to produce $FOCF_2CF_2CF_2OF$ only in very small amount.[4]

The direct fluorination of the monosodium salt of perfluoroacetone hydrate proceeds rapidly at room temperature. The products include CO_2, COF_2, and, in order of decreasing yield, the following OF-containing compounds: $(CF_3)_2CFOF$, $(CF_3)_2C(OF)_2$, CF_3CF_2OF, and $CF_3CF(OF)_2$. The combined yield of fluoroxy compounds obtained in this reaction is substantial, amounting to about 35% of the isolated product. It is interesting to note that under the conditions used in this fluorination reaction more of the three-carbon fluoroxy compounds were formed than of the two-carbon species. Although CO_2 and COF_2 were formed in rather large amounts, fluorination to CF_3OF apparently did not take place.

These various fluoroxy compounds present an interesting contrast in properties. The perfluoroethylidene compound, $CF_3CF(OF)_2$, is not especially susceptible to explosive decomposition, and it is considerably more stable thermally than CF_3CF_2OF. On the other hand, the perfluoropropylidene compound, $(CF_3)_2C(OF)_2$, is very prone to explode and, in fact, is more difficult to handle than any of the other fluoroxyperfluoroalkyl compounds investigated in our laboratory. The reason for this sensitivity is not understood. It does not appear to be due to steric crowding since no such difficulties were observed with $(CF_3)_3COF$.[3]

The tendency of $(CF_3)_2C(OF)_2$ to explode is so pronounced that a dilution technique was used in the work-up of these fluorination runs. The inert solvent, $CFCl_3$, was condensed into the trap containing the mixture of volatile fluorination products, and only then was the separation of the products attempted. In general, no difficulty was experienced in isolating and purifying CF_3CF_2OF, $(CF_3)_2CFOF$, and $CF_3CF(OF)_2$ by fractional distillation–condensation using vacuum-line techniques followed by gas chromatography. However, any operation which tended to concentrate $(CF_3)_2C(OF)_2$ was found to be difficult and, in fact, many attempts were necessary before the infrared and nmr spectra of this compound were successfully obtained on the same sample. Because of this great sensitivity little information was obtained on the reactions of this material.

Results

1,1-Bis(fluoroxy)perfluoroethane, $CF_3CF(OF)_2$. Isolation of pure $CF_3CF(OF)_2$ was accomplished by gas chromatography. 1,1-Bis(fluoroxy)perfluoroethane is a colorless gas boiling at approximately −35°. The melting point of a sample of $CF_3CF(OF)_2$ containing small amounts of SiF_4 and COF_2 was between −83 and −77°. The infrared spectrum of $CF_3CF(OF)_2$ contains absorptions at 7.44 (m), 7.79 (w), 8.06 (vs), 8.30 (s), 8.73 (s), 9.24 (s), 10.83 (w), 11.17 (m), and 13.58 μ (m).[11] The peak at 11.17 μ is attributed to the OF group.

The diagram in Figure 1 shows the analysis of the splittings observed in the F^{19} nmr spectrum of $CF_3CF(OF)_2$. The spectrum contains an absorption at ϕ^* −150.4 which is assigned to the OF group. The CF_3 group signal is at ϕ^* 77.4 and the CF at ϕ^* 111.9. The coupling constant between CF_3 and CF is less than 1 cps; that between OF and CF_3 is 10.3 cps and that between OF and CF is 26.2 cps. The absorption of the CF_3 group is split into a triplet by the two equivalent OF groups; additional splitting from the CF was not resolved with our instrument (40.0 Mc). The CF signal is likewise split into a triplet by the two OF groups. The absorption of the OF groups is split into a doublet by the CF and each mode further split into a quadruplet by the three equivalent fluorine nuclei of the CF_3 group. The peak areas were found to be in the ratio of 2.0:1.0:3.0.

1,1-Bis(fluoroxy)perfluoroethane shows much greater thermal stability than fluoroxyperfluoroethane.[3] Several samples, stored in sealed glass nmr tubes with

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[7] The preparation of this compound is described for the first time in this paper. Additional reactions will be published later by J. H. Prager and P. H. Ogden.

[8] There is a marked contrast between hypofluorites containing normal fluoroxy groups and the extremely unstable, low-temperature oxygen fluoride, O_3F_2, as discussed in ref 1.

[9] P. G. Thompson, to be published.

[10] G. L. Gard and G. H. Cady, *Inorg. Chem.*, 4, 594 (1965).

[11] The relative intensities of the absorptions are indicated by the symbols, vs, s, m, and w, standing for very strong, strong, medium, and weak, respectively.

$CFCl_3$, showed only minor decomposition after approximately 5 years at ambient temperatures. Differential thermal analysis indicated no decomposition up to 200°, at which temperature the sample underwent a very rapid exothermic reaction, probably exploding. In this case the $CF_3CF(OF)_2$ may have reacted with the metal cup in the dta apparatus; the products formed (as shown by infrared) were CF_4, COF_2, CO_2, and a trace of SiF_4. When $CF_3CF(OF)_2$ is flashed or ignited, quantitative analysis of the products formed indicates that thermal decomposition proceeds predominantly by

$$CF_3CF(OF)_2 \xrightarrow{\Delta} CF_4 + COF_2 + 0.5O_2$$

The results of additional stability tests (on rate of decomposition in glass) at elevated temperatures are given in Table I. An analysis of the products formed (SiF_4, CO_2, O_2, trace of BF_3, no CF_4) indicated that the OF compound was reacting with the Pyrex glass tube

$$CF_3CF(OF)_2 + 1.5SiO_2 \xrightarrow{\Delta} 1.5SiF_4 + 2CO_2 + 0.5O_2$$

rather than undergoing thermal decomposition (expected products: CF_4, COF_2, and O_2). The activation energy for the observed reaction with glass was calculated to be 38 kcal/mole.

Table I. Thermal Stability Tests of $CF_3CF(OF)_2$[a]

Temp, °C	Time, hr	% of $CF_3CF(OF)_2$ recovered
150	6.5	95
175	15	70
190	12	32

[a] Sealed in glass nmr tubes; 10–15 mole % solution in $CFCl_3$ as internal reference.

The polarographic half-wave potential of $CF_3CF(OF)_2$, measured by means of an indicating electrode *vs.* a saturated calomel electrode as reference, was found to be approximately 0.5 v, which is consistent with our earlier reported values[3] for CF_3OF and C_2F_5OF. Since the electrochemical reduction of these OF compounds is not reversible, oxidation potentials are not readily obtainable from the polarographic half-wave potential. However, as with other OF-containing compounds, 1,1-bis(fluoroxy)perfluoroethane is strongly oxidizing toward substances such as mercury, ferrocene, potassium iodide, and sodium hydroxide.

Reduction of $CF_3CF(OF)_2$ has been found to occur both by (1) normal reductive defluorination with a two-electron change per OF group, and by (2) reductive decomposition wherein oxidation–reduction occurs within the molecule *via* the fragmentation of $CF_3CF(OF)_2$, resulting in cleavage of the carbon–carbon bond. The mechanism for reductive decomposition is apparently not so straightforward as in the case of the monofluoroxy compounds discussed previously,[3] and it has not been determined whether a chain mechanism is involved.

The predominant mode of reduction appears to depend upon the effective contact of the OF compound with the reducing agent. With mercury, unless the reaction vessel is agitated, the film of mercurous fluoride hinders the reductive defluorination mode, and considerable CF_4 and CO_2 are formed, together with smaller amounts of CF_3CFO, $(CF_3CO_2)_2Hg$, and C_2F_6. The reaction with ferrocene also proceeds predominantly by the reductive decomposition path, CF_4 and CO_2 being the principal products in addition to ferricinium fluoride. With excess potassium iodide (in water or in acetonitrile–water media) the two-electron (per OF group) reductive defluorination mode takes place almost exclusively. The over-all reaction can be expressed by

$$CF_3CF(OF)_2 + 4KI \longrightarrow 2I_2 + CF_3CO_2K + 3KF$$

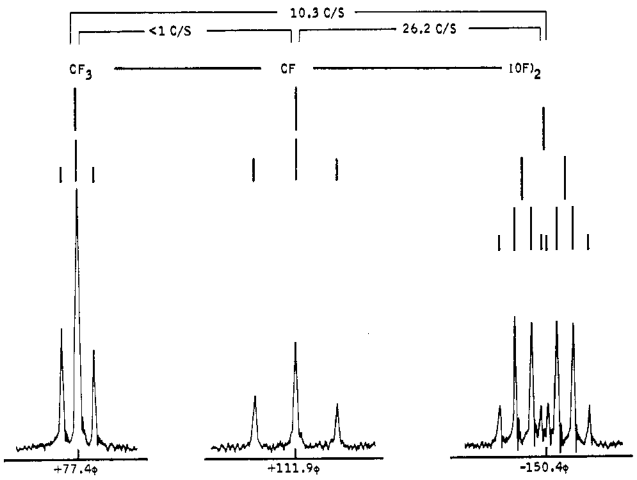

Figure 1. Nmr spectrum of $CF_3CF(OF)_2$.

Since this oxidation of iodide to iodine occurs rapidly and without appreciable side reactions, the process can be used for a quantitative measure of the oxidizing power of the fluoroxy compound. Determination of the oxidizing power of a sample of chromatographed $CF_3CF(OF)_2$[12] by this reaction gave a value of 22.0 mequiv of iodine per gram of sample (calculated for two-electron change per OF group, 23.0).

An attempt to follow the mode of decomposition in an infrared gas cell equipped with NaCl windows led to the formation of considerable CF_3CO_2Na on the windows after several days. The products detected indicate that the following reaction, analogous to that above with KI, occurred.

$$CF_3CF(OF)_2 + 4NaCl \longrightarrow 2Cl_2 + CF_3CO_2Na + 3NaF$$

1,1-Bis(fluoroxy)perfluoroethane reacts only very slowly with water or acidic media, but rapidly oxidizes aqueous base, liberating oxygen[3] according to the following equation.

$$CF_3CF(OF)_2 + 4NaOH \longrightarrow O_2 + CF_3CO_2Na + 3NaF + 2H_2O$$

The reaction is essentially stoichiometric. Oxygen was determined by gas chromatographic analysis, fluoride by conventional thorium nitrate titration, and sodium trifluoroacetate by infrared analysis of the solids. It should be noted that the reaction between the fluoroxy compound and aqueous base is a redox reaction, also analogous to the reaction of $CF_3CF(OF)_2$ with aqueous potassium iodide, and does not involve

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(12) A value of 21.1 mequiv of I_2/g was initially obtained; upon standing overnight a value of 22.0 mequiv of I_2/g (after possible air oxidation was corrected by a blank) was obtained. Apparently approximately 4% of the $CF_3CF(OF)_2$ undergoes side reactions under the conditions employed.

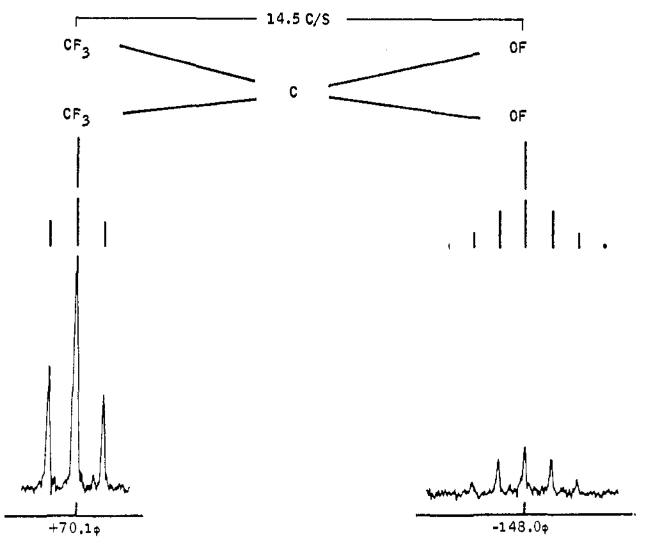

Figure 2. Nmr spectrum of $(CF_3)_2C(OF)_2$.

hydrolysis. Thus, the oxygen formed in this reaction would be expected to come from the NaOH and not from the OF compound.

2,2-Bis(fluoroxy)perfluoropropane, $(CF_3)_2C(OF)_2$. 2,2-Bis(fluoroxy)perfluoropropane is a colorless gas which is strongly oxidizing and shows a pronounced tendency to explode. After considerable difficulty, infrared and nmr spectra were successfully obtained on the same sample of this material. The infrared spectrum shows peaks at 7.77 (vs), 7.92 (vs), 8.14 (sh), 8.89 (s), 9.28 (s), 9.79 (s), 11.26 (m), and 13.50 μ (m).[11] It is interesting to observe how closely the spectrum of $(CF_3)_2C(OF)_2$ resembles the spectra of $(CF_3)_2CFOF$[3] and $(CF_3)_2CF_2$.[13] However, C_3F_8 shows no absorption in the 11-μ region, whereas the spectrum of $(CF_3)_2CFOF$ shows medium intensity absorption at 11.3 μ and $(CF_3)_2C(OF)_2$ shows a relatively stronger absorption at 11.26 μ. Infrared spectra of fluoroxy compounds have been shown to have absorption in this region.[3,14] Thus the infrared spectrum of this compound is reasonable for $(CF_3)_2C(OF)_2$.

The F^{19} nmr spectrum (Figure 2) shows an absorption at ϕ^* -148.0, which is assigned to the OF groups; it is split into a sevenfold peak[15] by the six equivalent fluorine nuclei of the two CF_3 groups. The absorption at ϕ^* 70.1 is a triplet assigned to the CF_3 groups. The coupling constant is 14.5 cps. The peak areas were found to be in the ratio of 1.0:3.2.

Because of the extreme tendency to explode exhibited by the samples of undiluted 2,2-bis(fluoroxy)perfluoropropane prepared in this work, additional characterization of this compound was not done. Although some may feel that the structure of 2,2-bis(fluoroxy)perfluoropropane is thus tentative, it is the opinion of the authors that the identity of this compound is firmly established on the basis of straightforward analysis of the F^{19} nmr spectrum and additionally supported by the infrared spectrum, oxidizing properties, gas chromatography retention time, synthesis route, and identity of the other products formed.

It is well known that nuclear magnetic resonance spectroscopy is a very useful method for determining molecular structures. For fluoroxyperfluoroalkanes it should be noted that F^{19} nmr spectroscopy is an exceptionally definitive method. There are two features of the spectra of both mono- and bis(fluoroxy)perfluoroalkanes which make them particularly valuable for structure assignment. (1) The values of the chemical shift for the fluorine of a fluoroxy group lie within a narrow range (approximately ϕ^* -140 to -160) and are well outside the range of most other fluorine absorptions. (2) Furthermore, the OF group as well as other types of F in fluoroxyperfluoroalkanes give unusually clear, sharp, and well-resolved spectra (although for OF compounds containing longer perfluoroalkyl chains, the resolution becomes poorer because of the many rather similar coupling constants involved). Thus, consideration of the chemical shifts together with simple first-order analysis of the fine structure caused by spin–spin interaction as well as the relative area ratios permit an unequivocal assignment of structure to the OF compound in many instances. An extensive file of nmr spectra of related compounds has aided greatly in assigning specific positions to specific groups, of course. For all fluoroxy compounds reported by us to date, additional analytical data have merely served to confirm the structure as assigned from nmr data.

Obviously, molecular weight and elemental composition data, although useful, do not distinguish between compounds having the same molecular formula. Since F^{19} nmr spectra of simple molecules such as the fluoroxyperfluoroalkanes reported by us can often yield molecular structures directly, elemental composition and molecular weight of the compound are also indirectly obtained. Moreover, nmr has the extremely valuable advantage (especially for very reactive or unstable compounds) of not requiring completely pure samples. In a number of cases, only nmr spectroscopy has allowed a definite structure determination for several new compounds having the same molecular formula.[1a,9]

Experimental Section

General Procedures. The direct fluorination reactions were carried out by a static bed procedure similar to that described previously.[3] Fluorine (General Chemical Division, Allied Chemical Corp., about 95% pure), diluted with nitrogen to the desired concentration (mole per cent), was passed over the sample to be fluorinated, and the volatile products were condensed in a trap at −183° from the effluent gas stream. Because fluorination reactions occasionally proceed explosively, adequate shields were provided and safety equipment was worn.

Volatile fluorination products were worked up by slightly modified standard vacuum-line techniques; contact of the fluoroxy compounds with reducing agents such as mercury and hydrocarbon vacuum grease was avoided.

Gas chromatographic analyses were carried out with a Perkin-Elmer vapor fractometer (Model 154-D), which had been equipped with 3M Co. linear-type gas sampling and backflush valves. Perfluorotributylamine[16] (33% on 30–60 mesh acid-washed Celite)[17] gave the best results of all the stationary phases examined. The column temperature was usually maintained at −30°. For preparative scale separations 0.5-in. diameter columns of 10-ft and 8 ft, 7-in. length were employed. Helium, dried by passing through

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[13] D. G. Weiblen, "The Infrared Spectra of Fluorocarbons and Related Compounds," "Fluorine Chemistry," Vol. II, J. H. Simons, Ed., Academic Press Inc., New York, N. Y., 1954, p 469.

[14] P. G. Thompson, *J. Am. Chem. Soc.*, 89, 1811 (1967).

[15] Although Figure 2 only shows five peaks which are observed with certainty for the OF absorption, subsequent spectra at higher concentrations clearly show sevenfold splitting for the OF absorption. The intensity ratio for the splittings also indicates that the pattern is sevenfold rather than fivefold.

[16] FC-43 (3M Co.).

[17] Chromosorb P (Johns-Manville).

50 mesh 4A Linde Molecular Sieves cooled in liquid nitrogen, was used as the carrier gas at flow rates of 150 to 320 cc/min.

Infrared spectra were obtained on a Perkin-Elmer Model 21 double-beam instrument with a 2.5-cm gas cell with sodium chloride windows. Fluorine nuclear magnetic resonance spectra were measured with a Varian V-4300-2 instrument operating at 40.0 Mc. Trichlorofluoromethane was used as an internal standard for the determination of shielding values. The shielding values are reported in ϕ^{*}[18] units at dilutions of about 15–30%, negative values for low field. All precision measurements (chemical shifts and spin-spin splittings) were made according to techniques described by Tiers.[19] Side bands were produced by amplitude modulation of the radiofrequency[20] for reasons discussed previously.[3]

Reactions of $CF_3CF(OF)_2$ have been carried out for the most part using vacuum-line techniques. The course of reactions has been followed by appropriate methods such as infrared, nmr, and mass spectroscopy, powder X-ray, gas chromatography, and *P–V–T* measurements, as well as conventional volumetric analyses. Elemental analyses for carbon and fluorine were conducted according to the standard microcombustion procedure for highly fluorinated compounds.[21] Differential thermal analyses were carried out using the apparatus and procedures developed in these laboratories for potentially explosive, fluorine-containing compounds.[22]

Safety Precautions. It should be noted that the OF-containing compounds described in this paper are potentially hazardous, although they have been handled, with the exception of 2,2-bis(fluoroxy)perfluoropropane, without great difficulty. However, explosions have occurred in the course of this work, and it is recommended that suitable protective equipment[23] be used when preparing, treating, or storing these compounds. No detailed toxicity studies have been carried out on these substances, but it would appear advisable to avoid exposure to any OF-containing compound in view of the known toxicity of OF_2.[24]

Preparation of the Monosodium Salt of Perfluoroacetone Hydrate. To 6.9 g (0.038 mole) of perfluoroacetone hydrate was added with stirring enough 1 *N* NaOH to bring the pH to 8.8. The amount required (38 ml) was close to the stoichiometric equivalent. The resulting solution was evaporated to dryness in air and then *in vacuo* at room temperature. The white, crystalline solid thus obtained was found to be soluble in ether.

Anal. Calcd for $C_3F_6HO_2Na$: C, 17.5; Na, 11.2. Found: C, 18.0; Na, 11.2.

Elemental analysis and infrared spectrum are consistent with the molecular formula $(CF_3)_2C(OH)ONa$. Absorptions at 4.1 and 5.4 μ appear to be due to a strongly associated OH structure. The infrared spectrum shows practically no carbonyl-type absorption.

Fluorination of the Monosodium Salt of Perfluoroacetone Hydrate. A 1.5-g (7.3 mmoles) sample of the sodium salt of perfluoroacetone hydrate was treated with 0.42 mole of fluorine under the following conditions: 3% fluorine, 1 hr, −20°; 15% fluorine, 1 hr, −20°; and 15% fluorine, 4 hr, temperature gradually increased from −20 to 20°. The residual material in the reactor was found to weigh 0.47 g. The contents of the liquid oxygen trap were worked up as follows. The noncondensable gases were removed from the trap at liquid nitrogen temperatures under vacuum, and about 0.5 ml of $CFCl_3$ was condensed into the trap. (This dilution technique was found to eliminate explosions during this part of the work-up.) The mixed condensate was then allowed to warm gradually and was passed at about 40 mm pressure through traps at −78, −119, and −196°. The −119° fraction contained $(CF_3)_2CFOF$ in major amount and $(CF_3)_2C(OF)_2$, C_2F_5OF, and $CF_3CF(OF)_2$ in smaller amounts. The −196° fraction also contained small amounts of the latter two compounds. Because of the large incidence of explosions in these runs, little reliable data regarding yields are available. In a run carried out before the dilution technique was used, a total of 4.05 mmoles of volatile products was isolated from 7.3 mmoles of starting material. It was estimated that 1.5 mmoles or about 35% of the isolated product consisted of OF-containing compounds. A typical product distribution was estimated by means of F^{19} nmr and infrared spectroscopy to consist of approximately 20–25% $(CF_3)_2CFOF$, 5% $(CF_3)_2C(OF)_2$, 5% C_2F_5OF, and 3% $CF_3CF(OF)_2$. The major by-products were generally CO_2 and COF_2.

Fluorination of Nitrosyl Trifluoroacetate. Nitrosyl perfluoroacetate was kindly supplied by Dr. C. W. Taylor of our Central Research Laboratories. It was prepared by treating silver perfluoroacetate with excess nitrosyl chloride.[25,26] A 1-g (7.0 mmoles) sample of this compound, contained in a stainless-steel boat in the reactor, was treated with 0.16 mole of fluorine (2%) at −15° over a 6-hr period. The trapped gases were fractionated on the vacuum line through traps at −111 and −196°. The lower boiling fraction consisted of 2.1 mmoles of products, which included C_2F_5OF. The over-all yield of this compound was 19%. Perfluoroacetyl fluoride, COF_2, and NO_2OF were the major by-products.

1,1-Bis(fluoroxy)perfluoroethane. 1,1-Bis(fluoroxy)perfluoroethane was purified by gas chromatography at −30°. Its retention time was found to be 92 relative to fluorotrichloromethane. It is a colorless gas with an estimated boiling point of −35°; its melting point lies between −83 and −77°. Elemental analyses were obtained on a sample of chromatographed $CF_3CF(OF)_2$. A molecular weight determination (vapor density) on this material gave a value of 164 (calculated 170).

Anal. Calcd for $C_2F_6O_2$: C, 14.1; F, 67.0. Found: C, 14.1; F, 65.5.

2,2-Bis(fluoroxy)perfluoropropane. 2,2-Bis(fluoroxy)perfluoropropane was purified by gas chromatography at −30°. Its retention time was found to be 217 relative to fluorotrichloromethane. It is a colorless gas, which is rather prone to explode.

Acknowledgments. The authors are indebted to Dr. Robert L. Bohon for dta measurements, to Dr. Robert L. Rebertus for checking the stoichiometry of several reactions, and to Dr. John J. McBrady and Mr. Rudd A. Meiklejohn for their help and counsel in regard to the interpretation of the nmr spectra. We also wish to thank the Analytical Section of our Central Research Laboratories for their expert support, and Mr. Richard B. Castle and Mr. Larry A. Fletcher for their fine experimental assistance.

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(18) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

(19) G. V. D. Tiers, *ibid.*, **62**, 1151 (1958).

(20) G. V. D. Tiers, *ibid.*, **67**, 928 (1963).

(21) H. E. Freier, B. W. Nippoldt, P. B. Olson, and D. G. Weiblen, *Anal. Chem.*, **27**, 146 (1955).

(22) R. L. Bohon, *ibid.*, **33**, 1451 (1961).

(23) We have operated without injury within a quantity limit of 1 g, using 0.25-in. poly(methyl methacrylate) shielding and wearing heavy-duty face shields, leather coats, and leather gloves. Nonflammable slush baths are, of course, preferred.

(24) D. Lester and W. R. Adams, *Am. Ind. Hyg. Assoc. J.*, **26**, 562 (1962).

(25) R. E. Banks, R. N. Haszeldine, and M. K. McCreath, *Proc. Chem. Soc.*, 33 (1961).

(26) C. W. Taylor, T. J. Brice, and R. L. Wear, *J. Org. Chem.*, **27**, 1064 (1962).