

Figure 2.—Plot of $(k - k_0)^{-1}$ against $(\text{Cl}^-)^{-1}$ at 25° and ionic strength 1 M .

presence of $1.0 \times 10^{-1} M \text{Fe}^{2+}$ provided no evidence for the formation of an iron(II)–chloride complex of comparable stability to FeCl^{2+} . These observations suggest that K_1 is less than $0.5 M^{-1}$ at 25° and ionic strength 1.0 M and they are thus not consistent with the value of K_1 reported in ref 2.

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Some Reactions of Bis(fluoroxy)difluoromethane, $\text{CF}_2(\text{OF})_2$

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Several authors have recently reported the preparation and characterization of bis(fluoroxy)difluoromethane, $\text{CF}_2(\text{OF})_2$.^{1–3} It is conveniently prepared in high yield by the static, cesium fluoride catalyzed fluorination of carbon dioxide.^{1,3}

The longer known hypofluorite, trifluoromethyl hypofluorite, CF_3OF , undergoes a variety of interesting reactions, e.g., with SO_2 ,⁴ SO_3 ,⁴ SF_4 ,⁵ N_2F_4 ,⁶ C_2H_4 ,⁷ and C_2F_4 ⁸ to give the addition products $\text{CF}_3\text{OSO}_2\text{F}$, $\text{CF}_3\text{OOSO}_2\text{F}$, CF_3OSF_5 , CF_3ONF_2 , $\text{CF}_3\text{OCH}_2\text{CH}_2\text{F}$, and $\text{CF}_3\text{OCF}_2\text{CF}_3$, respectively. Because of the apparent similarity of $\text{CF}_2(\text{OF})_2$ and CF_3OF , it was of interest to examine the reactions of the former with a

variety of simple inorganic compounds and olefins to determine if analogous reaction products would be obtained. With C_2F_4 and *trans*- $\text{C}_2\text{H}_2\text{Cl}_2$ under appropriate reaction conditions, diethers of the form $(\text{RO})_2\text{CF}_2$, where $\text{R} = \text{C}_2\text{F}_5$ or $\text{C}_2\text{H}_2\text{Cl}_2\text{F}$, respectively, result. In this type of reaction, the two hypofluorites react identically. However, with inorganic compounds in which the central atom exists in a lower than maximum oxidation state, fluorination accompanied by the formation of oxygen and carbonyl fluoride is likely to occur. No conditions were found under which addition of the hypofluorite to the central atom by fissioning the OF bond would occur.

Reactions which proceeded at room temperature often did so with evolution of heat and light. Room-temperature reactions of $\text{CF}_2(\text{OF})_2$ with olefins without diluent usually resulted in explosions during which reaction vessels were completely demolished. *Caution!* Bis(fluoroxy)difluoromethane should not be allowed to contact organic or other easily oxidized material without adequate shielding.

Experimental Section

Materials.—Bis(fluoroxy)difluoromethane was prepared as previously described.¹ Sulfur trioxide was purchased as a stabilized form, "Sulfan" (Allied Chemical Corp.). Tetrafluoroethylene from the thermal decomposition of polytetrafluoroethylene was purified prior to use by fractional codistillation.⁹ All other compounds were standard commercial reagents.

General Methods.—Most work was done under high vacuum on a typical vacuum line. Infrared spectra were obtained by using a Beckman IR-5A spectrophotometer. Nuclear magnetic resonance spectra were recorded with instruments equipped with either 40- or 56.4-Mc oscillators for fluorine nuclei or 60-Mc oscillators for hydrogen nuclei using an external reference of CCl_3F or $\text{Si}(\text{CH}_3)_4$. Molecular weights were determined by the method of Regnault. Vapor pressures were obtained by the use of constant-temperature baths which surrounded the sample while the equilibrium vapor pressures were read on a mercury manometer. Elemental analyses were performed by Alfred Bernhardt Microanalytisches Laboratorium. Mass spectra were determined with a Consolidated Engineering Corp. Type 21-620 mass spectrometer at an ionizing potential of 100 V. Reaction vessels were of Pyrex glass (500 or 1000 ml), stainless steel (Hoke 75-ml cylinders), or nickel. Metal vessels were used whenever the reactions were heated. Identification of known compounds was made by infrared or molecular weight. Final purification of reaction products was attained by either fractional codistillation or gas chromatography with either QF-1 (fluorosilicone oil) or SE-60 (silicone gum rubber) on firebrick columns (F & M Scientific Corp.).

Reactions of $\text{CF}_2(\text{OF})_2$ with Inorganic Compounds

The reaction data are summarized in Table I. In every case, carbonyl fluoride is observed as one of the products and in no case does the bis(hypofluorite) react to give a final product which would arise from addition of FOCF_2O or OCF_2O fragments to the central atom.

Reactions of $\text{CF}_2(\text{OF})_2$ with Olefins

Tetrafluoroethylene.—In an attempt to add $\text{CF}_2(\text{OF})_2$ across the double bond in C_2F_4 , a procedure analogous to that used in the preparation of $\text{CF}_3\text{OCF}_2\text{CF}_3$ ⁸

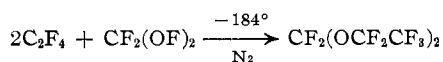
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TABLE I
 REACTIONS OF $\text{CF}_2(\text{OF})_2$ WITH INORGANIC COMPOUNDS

Reactants, $\text{CF}_2(\text{OF})_2 +$	Conditions	Products
SO_2	25°	No reaction
SO_2	60°	SO_2F_2 , COF_2 , O_2
SO_2	Uv, Pyrex	$\text{S}_2\text{O}_5\text{F}_2$, COF_2
SO_3	185-190°, 10 hr	SO_2F_2 , COF_2 , O_2
SO_3	Uv, Pyrex	$\text{S}_2\text{O}_5\text{F}_2$, COF_2 , O_2
SF_4	25°	No reaction
SF_4	70°, 3 hr	SF_6 , COF_2 , O_2
N_2F_4	25°	COF_2 , NO_2 , SiF_4 , $(\text{NO})_2\text{SiF}_6$
N_2F_4	0°, N_2 dilution	COF_2 , NO_2 , SiF_4 , $(\text{NO})_2\text{SiF}_6$
NO	25°	COF_2 , NO_2 , SiF_4
PF_3	-79°	COF_2 , OPF_3 , PF_5

was employed. Typically, 1.08 mmol of C_2F_4 was diluted in a 12-l. Pyrex glass bulb with at least a 400-fold excess of dry nitrogen. The bulb was connected to a Pyrex tube at -184° in which 0.53 mmol of $\text{CF}_2(\text{OF})_2$ had been condensed. A 1.25-mm Teflon needle valve (Fischer and Porter Co.) between the bulb and the tube was used to control the flow rate of the N_2 - C_2F_4 mixture over the $\text{CF}_2(\text{OF})_2$ as the system was subjected to dynamic vacuum. The product from the reaction



is obtained in 80-90% yield with only COF_2 , C_2F_4 , and C_3F_6 as contaminants condensable at -184° . These are easily removed by fractional codistillation.⁹ If these reactants are mixed in the presence of nitrogen at 25°, COF_2 is the main product.

Perfluorodiethoxymethane was also prepared by condensing $\text{CF}_2(\text{OF})_2$ on C_2F_4 in a 50-ml Pyrex glass tube at -184° which had been filled two-thirds full with 2-mm glass beads. The vessel was warmed very slowly in a cold dewar. This method gives about the same yields and has been used for only very small quantities of reactants (1 mmol or less).

Great care must be taken to see that unreacted starting materials are not warmed rapidly together in either method. Violent explosions then occur.

Perfluorodiethoxymethane is a colorless liquid at room temperature which forms a glass when cooled to -184° . The molecular weight as obtained from vapor density measurements is 320 (calcd 320). The infrared spectrum is given in Table II. The peaks in the 1200-cm^{-1} region are the result of CF stretching while those at 750-cm^{-1} are attributable to CF bending. The one at 900-cm^{-1} may be assigned to CO stretch, and the one at 850-cm^{-1} to CC stretch.

Anal. Calcd for $\text{C}_5\text{F}_{12}\text{O}_2$: C, 18.77; F, 71.23. Found: C, 19.20; F, 71.08.

The nmr spectrum was determined at 56.4 Mc. Resonances are found at 51.3 (quintet, $J = 10$ cps), 86.0 (singlet), and 89.2 (triplet, $J = 10$ cps) ppm with CCl_3F as the internal reference. These peaks are in the ratio of 1.0:3.1:1.9 and have been assigned to the OCF_2O , the CF_3C , and the OCF_2C fluorines, respec-

 TABLE II
 INFRARED SPECTRA

$\text{CF}_2(\text{OCF}_2\text{CF}_3)_2$
2611 vw, 2445 vw, 2364 vw, 2128 vw, 2070 vw, 1980 vw, 1927 vw, 1698 vw, 1661 vw, 1621 vw, 1605 vw, 1541 vw, 1475 vw, 1404 m, 1258 sh, 1242 vs, 1200 s, 1175 s, 1116 vs, 1099 vs, 901 m, 849 m, 839 sh, 833 sh, 801 sh, 756 sh, 746 s, 685 m
$\text{CF}_2(\text{OCHClCHClF})_2$
2941 w, 2421 vw, 2083 vw, 1368 m, 1346 m, 1323 sh, 1312 m, 1279 s, 1198 vs, 1139 vs, 1040 s, 984 m, 961 m, 936 w, 810 s, 753 s

tively. Apparently no interaction occurs between the CF_2 groups and the CF_3 groups.

Vapor pressure measurements were taken on carefully purified samples and recorded in Table III. From these data, the following physical constants have been determined: $T_b = 313.0^\circ\text{K}$ (39.8°); $\Delta\bar{H}_{\text{vap}} = 7536$ cal/mol; $\Delta\bar{S}_{\text{vap}} = 24.0$ cal/mol deg. The temperature-pressure dependence for perfluorodiethoxymethane may be expressed by the equation $\log P_{\text{mm}} = -1645/T_{\text{K}} + 8.138$.

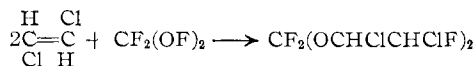
TABLE III

VAPOR PRESSURE OF PERFLUORODIETHOXYMETHANE			
Pressure, mm	Temp, °K	Pressure, mm	Temp, °K
28.9	246.4	54.1	256.7
29.6	247.7	136.6	273.2
36.8	250.0	402.1	297.4
41.6	252.0	413.2	297.7
46.5	254.0	434.6	299.0

No parent peak was noted in the mass spectrum. Peaks attributed to the following species (with mass number and relative abundance, respectively) were observed: C^+ , 12, 0.2; CO^+ , 28, 1.0; CF^+ , 31, 9.8; COF^+ , 47, 4.2; CF_2^+ , 50, 5.7; CF_2O^+ , 66, 0.5; CF_3^+ , 69, 41.5; $^{13}\text{CF}_3^+$, 70, 0.5; $\text{C}_2\text{F}_3\text{O}^+$, 97, 0.2; C_2F_4^+ , 100, 0.7; C_2F_5^+ , 119, 100; $^{13}\text{CCF}_3^+$, 120, 2.3; $\text{C}_2\text{F}_5\text{OCF}_2$, 185, 8.4.

trans-1,2-Dichloroethylene.—The reaction of *trans*- $\text{C}_2\text{H}_2\text{Cl}_2$ with $\text{CF}_2(\text{OF})_2$ was studied with the aid of an inert solvent to moderate the reaction. Typically, 14 mmol of the olefin and 10 ml (about 100 mmol) of CCl_3F were condensed into a 50-ml Pyrex-glass tube at -184° and then permitted to warm and mix. The tube was cooled again to -184° and 7 mmol of $\text{CF}_2(\text{OF})_2$ was condensed into it. The vessel was sealed and permitted to stand for several days at room temperature. It was then opened and all volatile materials were pumped out. A small amount of non-volatile material, about 0.25 g, remained. This was injected into a gas chromatograph having a 21-ft QF-1 column at 170° which showed that about 80% of this material was a single compound. The latter was collected and passed through a 12-ft SE-30 column at 120° . Again a single peak was obtained which indicated the compound had a purity in excess of 99%.

The reaction



apparently occurred in about 9% yield. The more volatile products were not identified.

Bis(1,2-dichloro-2-fluoroethoxy)difluoromethane is a liquid at 25° with a density of 1.63 g/ml at 24°. The infrared spectrum is given in Table II. The peak at 2941 cm⁻¹ is the result of CH stretch. Those near 1100 and 1200 cm⁻¹ are probably CF stretch or CH bend. The two at about 800 cm⁻¹ are the result of CCl stretch.

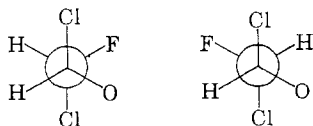
Anal. Calcd for C₅H₄Cl₄F₄O₂: C, 19.13; H, 1.28; Cl, 45.18; F, 24.21. Found: C, 19.15; H, 1.02; Cl, 44.42; F, 24.81.

The ¹⁹F nmr spectrum shows absorptions at +60.7 ppm, assigned to CF₂, and at +142.4, 143.7, 145.4, and 146.7 ppm, assigned to CF. These have relative areas of 4:1:1:1, respectively. The separation between the first and second and between the third and fourth CF peaks is about 52 cps. This is the magnitude of the coupling expected for hydrogen and fluorine attached to the same carbon atom.

The proton nmr spectrum has peaks at 5.91, 6.18, and 6.72 ppm which are in the ratio of 1.00:2.05:1.01, respectively. The separation of the first and third peaks is 49 cps. This suggests that two types of hydrogens are present, one of which is coupling with a fluorine attached to the same carbon.

The peaks in both the proton and ¹⁹F nmr spectra which have been described above show further splitting of 5–10 cps under high resolution. This has made complete analysis of the spectrum impossible. Part of the difficulty may arise from a spin-spin coupling constant between the two nonequivalent protons and the chemical shift between them of about the same value (about 8 cps).

These nmr data suggest that more than one isomer of the CHClCHClF group is present—one corresponding to the *cis*-addition product and one to the *trans*-addition product as shown by the two conformations



Even with free rotation about all bonds, the atoms in the two configurations are not equivalent.

Heating the sample to +60° and cooling it to -40° did not change the spectrum.

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Infrared and Raman Spectra of the Hexafluoroiodine(V) Anion, IF₆⁻

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In the course of a systematic investigation of the halogen fluoride ions, the structure of and the type of bonding in ClF₂⁻,²⁻⁴ ClF₂⁺,^{5,6} ClF₄⁻,^{7,8} and IF₆⁺⁹ have recently been established. In particular, ClF₂⁻⁴ and ClF₄⁻⁸ appear to be, as far as structure and bonding are concerned, closely related to isoelectronic (considering only valence electrons) XeF₂ and XeF₄, respectively. The existence of representatives of the hexafluorohalogenate(V) anions, IF₆⁻¹⁰⁻¹⁵ and BrF₆⁻,¹⁶ is well known; however, no data on their structure and bonding have been reported. These compounds are of special interest since they are isoelectronic and probably also isostructural with XeF₆. The latter seems to have a unique structure and for the past 3 years numerous efforts to establish its structure have been unsuccessful. Furthermore, a hexafluorohalogenate(V) salt with respect to structural investigation offers several advantages over XeF₆. For example, its preparation is easier, its reactivity is lower, and the anions are probably separated by relatively large cations, thus rendering polymeric structures rather unlikely. However, the lattice interactions can be expected to be greater for ionic structures. This paper is concerned with data obtained for CsIF₆.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a standard Pyrex-glass high-vacuum system which had stopcocks and joints lubricated with Halocarbon grease (high-temperature grade). Iodine pentafluoride (Allied Chemical) was purified by distillation. Cesium fluoride (99.9% from K & K Laboratories, Inc.) was dried for 48 hr at 500°. Outside of the vacuum system the materials (owing to their hygroscopic nature) were handled in the dry nitrogen atmosphere of a glove box.

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