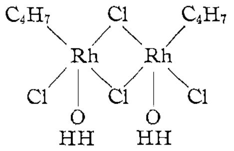
the 320- and 240-cm^{-1} absorptions found in their crotyl complex of rhodium, we assign the 330-cm^{-1} band to the terminal Rh–Cl stretch and the 280-cm^{-1} band to the bridged Rh–Cl–Rh stretching vibration. Recently Brookes and Shaw[14] investigated the low-frequency infrared spectra of a large number of rhodium chloride complexes and found Rh–Cl stretching vibrations in two ranges: 345–293 and 278–264 cm^{-1}.

The complex was insoluble in benzene, methanol, dimethylformamide, dimethyl sulfoxide, carbon tetrachloride, and water suggesting a binuclear or polymeric material. Because of the insolubility, molecular weight measurements and nmr studies could not be carried out.

Reaction of the complex with 10% KOH in ethylene glycol at 70° liberated a hydrocarbon gas mixture consisting of 51% *trans*-2-butene, 18% isobutane, 19% *cis*-2-butene, 5% 1-butene, and 7% lighter hydrocarbons. Reaction with concentrated HCl at 70° liberated a gaseous mixture consisting of 33% 1-butene, 31% *trans*-2-butene, 12.5% *cis*-2-butene, 2.5% butadiene, and 21% chlorinated hydrocarbons. The complex started to decompose at 240° upon heating in air at the rate of 1.8°/min. The weight loss amounted to approximately 32% of the sample weight. The hydrocarbon products obtained on decomposition were butenes, ethylbenzene, and ethylnaphthalene according to mass spectrographic analysis. Rhodium metal and an unidentified material were left in the tga cell as determined by X-ray diffraction.

Based on the elemental analyses and infrared data, it is believed that a π-crotylrhodium(III) complex and not a rhodium(I) complex has been formed. I and II are proposed as likely structures for the complex where the theoretical values of carbon, hydrogen, chlorine, and rhodium are 19.4, 3.6, 28.7, and 41.7% respectively. These values agree very well with the experimentally determined values. These structures are based mainly on a similar structure reported by Powell and Shaw[9] where butadiene is coordinated to the rhodium instead of the two water molecules. No evidence of coordinated butadiene was found in the complex reported in this paper, but very strong evidence for coordinated water has been obtained.



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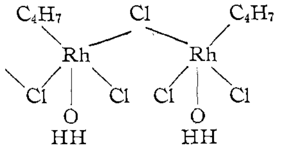

II

It is essential that metallic zinc be used in the preparation of this complex since it did not form when butadiene was added to ethanolic rhodium trichloride in the absence of zinc or when butadiene was added to an ethanolic rhodium trichloride–zinc chloride solution.

It is believed that a necessary step in preparing the complex is the reduction of Rh(III) with zinc to form a rhodium(I)–butadiene complex

$$RhCl_3 + C_4H_6 + Zn \longrightarrow [RhClC_4H_6] + ZnCl_2 \qquad (2)$$

Evidence of the reduction of rhodium with zinc was obtained by determining the zinc concentration under various conditions as shown in Table I. In the absence of butadiene there was a slow deposition of rhodium metal on the zinc granules with a corresponding oxidation of the zinc. In the presence of butadiene, the complex was formed and some rhodium metal deposited on the zinc. The calculated value of zinc ions in solution based on the amount of complex found and metal deposited agreed very well with the experimental value reported in Table I.

TABLE I

ZINC CONCENTRATION IN ETHANOLIC RHODIUM TRICHLORIDE

Reaction time, hr	Zinc concn, mg/ml	Conditions
1	0.20	Zinc metal added to ethanolic rhodium trichloride at 26° in the absence of butadiene; concentrations same as described in the Experimental Section
2	0.98	
3	2.30	
4	2.82	
3	1.36	Butadiene added; reaction conditions and concentrations same as discussed in the Experimental Section

To explain the formation of the π-crotylrhodium(III) complex, the rhodium(I) complex which is proposed in (2) would have to be oxidized with HCl[15] to form a dichlororhodium(III) hydrido complex. This complex would then react with the coordinated butadiene to form the crotyl complex.[16]

HCl was detected in solution and could be formed by a reaction between ethanol and rhodium trichloride as reported by Paiaro and coworkers.[17] The source of HCl and the mechanism for the formation of the crotyl complex will have to be established and work in this area is continuing.

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[14] P. R. Brookes and B. L. Shaw, *J. Chem. Soc., Sect. A*, 1079 (1967).

[15] R. Cramer, *J. Am. Chem. Soc.*, **87**, 4717 (1965).

[16] R. Cramer, *ibid.*, **89**, 1633 (1967).

[17] G. Paiaro, A. Musco, and G. Diana, *J. Organometal. Chem.* (Amsterdam), **4**, 466 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Stability Constant of the Monochloro Complex of Iron(II)[1]

BY HENRY N. PO AND NORMAN SUTIN

Received November 27, 1967

Recently Wells and Salam[2] reported that the rate of the iron(II)–hydrogen peroxide reaction was increased

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] C. F. Wells and M. A. Salam, *Trans. Faraday Soc.*, **63**, 620 (1967).

by halide ions. They ascribed this increase in rate to the formation of iron(II)–halide complexes with the complexes reacting faster than free ferrous ions with hydrogen peroxide. Wells and Salam also calculated the stability constants of the iron(II)–halide complexes from the magnitude of the catalysis and the "limiting rates" reached at high halide concentrations. This communication is concerned with the value of the equilibrium constant reported by Wells and Salam for the formation of the chloropentaaquoiron(II) complex. This value (5.54 M^{-1} at 25° and ionic strength 1.0 M) seems unreasonably high to us[3,4] and we have therefore reexamined the effect of chloride ions on the rate of oxidation of iron(II) by hydrogen peroxide.

Experimental Section

Iron(III) perchlorate (G. F. Smith Chemical Co.) was recrystallized twice from perchloric acid. Solutions of iron(II) perchlorate were prepared by electroreduction of perchloric acid solutions of iron(III) at a platinum electrode. The hydrogen peroxide (3%, Baker Analyzed reagent) contained 2.3 × 10^{-2}% acetophenetidin as a preservative. Distilled water was purified by redistillation from acid dichromate, followed by a distillation from alkaline permanganate and a final redistillation.

Iron(II) concentration was determined by complexation with 1,10-phenanthroline at pH 5 (ϵ 11,100 at 510 mμ). The hydrogen peroxide concentration was determined by the addition of excess cerium(IV) and measuring the remaining cerium(IV) spectrophotometrically (ϵ 5580 at 320 mμ).[5] Iron(III) concentration was determined spectrophotometrically (ϵ 4160 at 240 mμ).[6]

The reaction was studied under pseudo-first-order conditions on a Cary 14 spectrophotometer and on the stopped-flow apparatus which has been previously described.[7] The progress of the oxidation in the absence of chloride ion was followed at 240 and 280 mμ. The concentration ranges used in these runs were: $(Fe^{2+}) = 1.31 \times 10^{-4}$ to 1.02×10^{-2} M, $(H_2O_2) = 2.07 \times 10^{-5}$ to 5.25×10^{-3} M, and $(HClO_4) = 1.0$ M. In the presence of chloride ion, the reaction was followed at 280 mμ, which is an isosbestic point for Fe^{3+} and $FeCl^{2+}$. The concentration ranges used in these runs were: $(Fe^{2+}) = 2.06 \times 10^{-4}$ to 1.04×10^{-2} M, $(H_2O_2) = 2.07 \times 10^{-5}$ to 5.33×10^{-3} M, $(HCl) = 0.10$ to 0.90 M, and $[(HCl) + (HClO_4)] = 1.0$ M. All of the measurements were made at 25.0° and ionic strength 1.0 M.

Results

The data gave excellent first-order plots. The second-order rate constants obtained in the absence of added chloride ions are presented in Table I. The constancy of k_0 over a wide range of ferrous and hydrogen peroxide concentrations confirmed the rate law

$$\frac{d[Fe(III)]}{dt} = 2k_0(Fe^{2+})(H_2O_2) \qquad (1)$$

The stoichiometry was checked in the presence of excess ferrous ions and found to be $2\Delta(H_2O_2) = \Delta(Fe^{2+})$ within the experimental error of the measurements (±2%). The rate constants obtained in the presence of chloride ions are presented in Table II. It will be seen that the reaction is first order with respect to the concentrations of iron(II) and hydrogen peroxide under the conditions used and that the rate constants show, at most, a modest chloride dependence.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE OXIDATION OF IRON(II) BY HYDROGEN PEROXIDE IN 1.0 M PERCHLORIC ACID AT 25.0°[a]

$10^3(Fe^{2+})$, M	$10^4(H_2O_2)$, M	No. of runs	k_0, M^{-1} sec^{-1}
10.2	2.07	6	57.1
10.2	1.04	8	58.9[b]
1.10	0.220	2	54.4[c]
1.03	0.207	2	54.5[c]
0.207	52.5	4	56.8
0.131	52.5	4	57.8
1.04	0.207	2	51.6[c,d]
10.3	2.00[f]	6	57.0

Av[e] $k_0 = 57.8 \pm 1.3$ M^{-1} sec^{-1}

[a] Reaction followed at 280 mμ unless otherwise noted. [b] Reaction followed at 240 mμ. [c] Reaction followed on Cary 14 spectrophotometer at 240 mμ and 24.7°. [d] Medium is 1.0 M $NaClO_4$ (recrystallized) containing 6.2×10^{-3} M $HClO_4$. [e] Average calculated from the rate constants for the individual runs (excluding the runs on the Cary 14). [f] Hydrogen peroxide (3%, Mallinckrodt Analytical Reagent) containing 2.0 × 10^{-2}% acetanilide as a preservative was used to prepare the reactant solution used in this series.

TABLE II

EFFECT OF CHLORIDE ION ON THE RATE OF OXIDATION OF IRON(II) BY HYDROGEN PEROXIDE IN 1.0 M [(HCl) + $(HClO_4)$] AT 25.0°

$10^3(Fe^{2+})$, M	$10^4(H_2O_2)$, M	(Cl^-), M	No. of runs	k, M^{-1} sec^{-1}
...	...	0		57.8 ± 1.3[a]
10.4	2.07	0.10	9	58.8 ± 1.0
10.3	2.07	0.20	6	59.8 ± 0.1
10.3	2.07	0.30	7	60.5 ± 1.3
10.3	2.06	0.40	7	61.5 ± 1.5
10.3	2.07	0.50	7	61.7 ± 0.1
1.02	0.207	0.50	2	58.8[b]
0.206	53.3	0.50	7	61.0 ± 0.4
1.03	0.207	0.50	2	54.0[b,c]
10.2	2.07	0.70	6	62.6 ± 0.8
10.2	2.07	0.90	4	64.0 ± 0.1

[a] From Table I. [b] Reaction followed on Cary 14 spectrophotometer at 24.7°. [c] Medium is 0.5 M $NaClO_4$ (recrystallized), 0.5 M NaCl, and 8.5×10^{-3} M $HClO_4$.

Discussion

The rate constant for the oxidation of iron(II) by hydrogen peroxide in the absence of added chloride ions determined in this work is compared with the values obtained in earlier studies in Table III.[7a] As a result of the use of the flow technique higher concentrations of the reactants could be used in this study and the order of the reaction could be checked over a larger concentration range than was possible in the earlier work.[2,8–10] It is evident from Table III that

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(3) The value of the formation constant of $FeCl^{2+}$ is 2.95 M^{-1} at 25° and ionic strength 1.0 M.[4]

(4) M. J. M. Woods, P. K. Gallagher, and E. L. King, *Inorg. Chem.*, **1**, 55 (1962); N. Sutin, J. K. Rowley, and R. W. Dodson, *J. Phys. Chem.*, **65**, 1248 (1961).

(5) A. I. Medalia and B. J. Byrne, *Anal. Chem.*, **23**, 453 (1951).

(6) R. Bastian, R. Weberling, and F. Palilla, *ibid.*, **28**, 429 (1956).

(7) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(7a) NOTE ADDED IN PROOF.—Measurements performed independently by J. R. Ward and A. Haim at the State University of New York, Stony Brook, N. Y., using their stopped-flow apparatus and different sources of the reagents and of the triple distilled water gave $k_0 = 57.5 \pm 1.9$ M^{-1} sec^{-1} (average of eight measurements) in 1.0 M $HClO_4$ at 25.0.°

(8) W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462 (1951).

(9) T. J. Hardwick, *Can. J. Chem.*, **35**, 428 (1957).

(10) Note that the k_0 values calculated from the Arrhenius equation $k_0 = A \exp(-E/RT)$, where $R = 1.987$ cal deg^{-1} mole^{-1} and $T = 298.2$°K, are 62.6,[2] 57.5,[8] and 63.0[9] M^{-1} sec^{-1}. These calculated values are significantly higher than those observed in the respective studies.

TABLE III

COMPARISON OF PUBLISHED RESULTS ON THE KINETICS OF THE OXIDATION OF IRON(II) BY HYDROGEN PEROXIDE IN PERCHLORIC ACID

k_0 (25.0°), M^{-1} sec^{-1}	E, kcal mole^{-1}	A, M^{-1} sec^{-1}	Medium	Ref
50.3 ± 1.4	7.30	1.4×10^7	4.0×10^{-3} M–1.00 M HClO$_4$^{c}	2
54.3 ± 0.7^a	9.40	4.45×10^8	2.5×10^{-3}–0.5 M HClO$_4$	8
56.0 ± 0.9^b	9.45	5.3×10^8	1.67×10^{-3}–1.00 M HClO$_4$	9
57.8 ± 1.3	...	...	1.0 M HClO$_4$	This work

[a] $k_0 = 53.0 \pm 0.7$ M^{-1} sec^{-1} at 24.6° corrected to 25.0° using $E = 9.40$ kcal mole^{-1}. [b] $k_0 = 42.7 \pm 0.9$ M^{-1} sec^{-1} at 20.0° corrected to 25.0° using $E = 9.45$ kcal mole^{-1}. [c] Ionic strength 1.0 M.

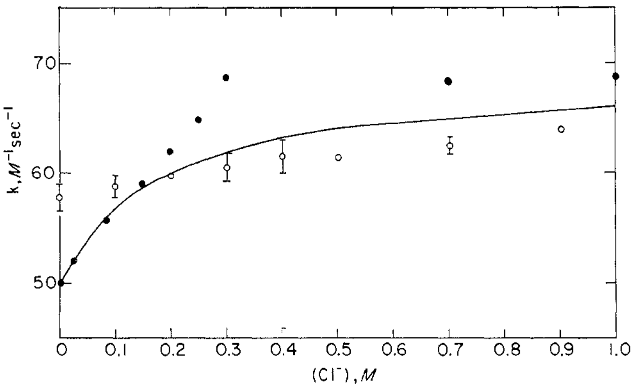

Figure 1.—Plot of k against chloride ion concentration at 25° and ionic strength 1 M: open circles, present work; closed circles, Wells and Salam.[2] The curve was calculated using eq 2 and the following parameters reported in ref 2: $k_0 = 50$ M^{-1} sec^{-1}, $k_1 = 68.4$ M^{-1} sec^{-1}, and $K_1 = 5.54$ M^{-1}.

the values of k_0 at 25.0° are in good agreement. However, to some extent this agreement is fortuitous since the experimental activation energies differ by about 2.1 kcal mole^{-1}. Moreover, these studies provide evidence for a small medium effect at constant ionic strength. Thus the rate constant in 1.0 M HClO$_4$ determined on the Cary 14 spectrophotometer at 24.7° (54.5 M^{-1} sec^{-1}) is significantly higher than the value in 1.0 M NaClO$_4$ and 6.2×10^{-3} M HClO$_4$ (51.6 M^{-1} sec^{-1}). The data reported in ref 2 also provide some evidence for a small medium effect at constant ionic strength; the value of k_0 in 1.0 M HClO$_4$ (54.2 M^{-1} sec^{-1}) being higher than the average value of k_0 in 1.0 M NaClO$_4$ and 4.0×10^{-3} M HClO$_4$ (49.7 M^{-1} sec^{-1}). Indeed the values of k_0 determined in this work are not too different from those determined at comparable acidities by Wells and Salam.[2]

On the other hand, the dependence of the rate constants on the chloride ion concentration obtained in this work is smaller than that reported by Wells and Salam.[2] The rate constants obtained by the latter authors are linearly dependent on (Cl$^-$) at low chloride concentrations and become independent of the chloride ion concentration at (Cl$^-$) ≈ 0.3 M. The results reported in ref 2 are presented in Figure 1 (closed circles) together with the results obtained in this study (open circles). The disagreement between the two sets of data appears to be outside the experimental error of the measurements. Moreover, the disagreement cannot be ascribed to a medium effect since it is evident from Tables I and II that the chloride effect is no larger at the lower acidities than it is in 1.0 M acid. The curve in Figure 1 was calculated from

$$k = \frac{k_0 + K_1k_1(\mathrm{Cl}^-)}{1 + K_1(\mathrm{Cl}^-)} \tag{2}$$

where K_1 is the equilibrium constant for the formation of monochloroiron(II), k_0 is the second-order rate constant for the oxidation of Fe^{2+} by H$_2$O$_2$, and k_1 is the second-order rate constant for the oxidation of FeCl$^+$ by H$_2$O$_2$. According to Wells and Salam,[2,11] $k_0 = 50$ M^{-1} sec^{-1}, $k_1 = 68.4$ M^{-1} sec^{-1}, and $K_0 = 5.54$ M^{-1} at 25° and ionic strength 1.0 M. By contrast, the chloride ion dependence of the rate constants obtained in this work is very small and does not lend itself to an unambiguous analysis. For purposes of comparison with the earlier work, we will assume that the mechanism proposed in ref 2 for the chloride dependence is correct. Equation 2 may be rearranged to give

$$\frac{1}{(k - k_0)} = \frac{1}{(k_1 - k_0)K_1(\mathrm{Cl}^-)} + \frac{1}{(k_1 - k_0)} \tag{3}$$

The plot suggested by eq 3 is made in Figure 2. From the slope and intercept of the plot in Figure 2 we estimate that $k_1 = 78 \pm 12$ M^{-1} sec^{-1} and $K_1 = 0.5 \pm 0.3$ M^{-1}. However, as mentioned above, other interpretations of the variation of the rate constants with the chloride ion concentration are also consistent with the data, and we therefore do not attach much significance to this estimate of K_1.[12]

Finally there is other evidence indicating that K_1 is smaller than 5.54 M^{-1} at 25°. Woods, Gallagher, and King[4] have used both electromotive force and spectrophotometric measurements to determine the equilibrium constant for the formation of FeCl^{2+}. The results obtained by the two methods agree well and give 2.95 M^{-1} for the stability constant of FeCl^{2+} at 25° and 1.0 M perchloric acid. Since the solutions used in the electromotive force method contained comparable amounts of iron(II) and iron(III), while those used in the spectrophotometric method contained only iron(III), the two methods would not have agreed unless $K_1 \ll 2.95$ M^{-1}. Moreover, spectrophotometric measurements at 336 mμ (an absorption maximum of FeCl^{2+}) of iron(III) solutions (2.0×10^{-2} M Fe^{3+}, 4.0×10^{-3} M Cl$^-$, and 1.0 M HClO$_4$) in the absence and in the

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(11) Two values of K_1, 5.54 and 9.80 M^{-1}, are given in Table II of ref 2 under the entry "chloride ion" at 25° and ionic strength 1.0 M. We have assumed that the entry $K_1 = 9.80$ M^{-1} at ionic strength 1 M is a result of a typographical error since $K_1 = 9.80$ M^{-1} at ionic strength 4 M. Moreover the authors have used $K_1 = 5.54$ M^{-1} at ionic strength 1 M in constructing the Arrhenius plot presented in Figure 5 of ref 2.

(12) If it is assumed that the rate constants obtained in this study are linearly dependent on the chloride ion concentration, *i.e.*, $k = k_0 + K_1k_1(\mathrm{Cl}^-)$, then we estimate from the slope of the plot of our data in Figure 1 (together with $k_1 > k_0$ for chloride catalysis to be observed) that $K_1 \leq 0.2$ M^{-1} at 25°.

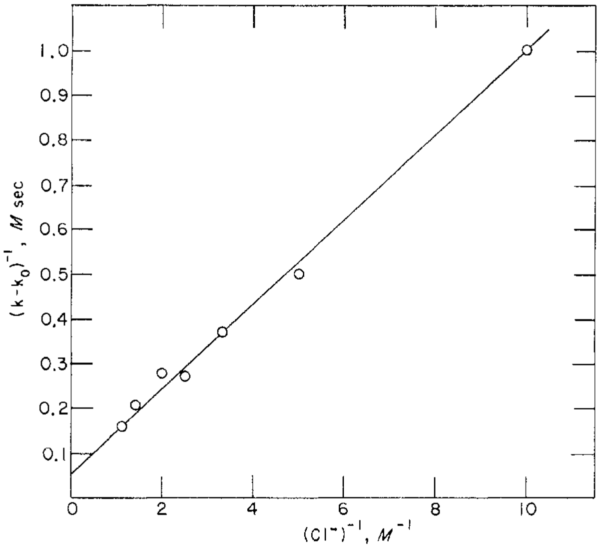

Figure 2.—Plot of $(k - k_0)^{-1}$ against $(Cl^-)^{-1}$ at 25° and ionic strength 1 *M*.

presence of 1.0×10^{-1} *M* 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, $CF_2(OF)_2$

By Frederick A. Hohorst and Jean'ne M. Shreeve

Received December 1, 1967

Several authors have recently reported the preparation and characterization of bis(fluoroxy)difluoromethane, $CF_2(OF)_2$.[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 CF_3OSO_2F, CF_3OOSO_2F, CF_3OSF_5, CF_3ONF_2, $CF_3OCH_2CH_2F$, and $CF_3OCF_2CF_3$, respectively. Because of the apparent similarity of $CF_2(OF)_2$ 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*-$C_2H_2Cl_2$ under appropriate reaction conditions, diethers of the form $(RO)_2CF_2$, where R = C_2F_5 or $C_2H_2Cl_2F$, 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 $CF_2(OF)_2$ 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 stablized 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 $Si(CH_3)_4$. 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 $CF_2(OF)_2$ 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 $CF_2(OF)_2$ with Olefins

Tetrafluoroethylene.—In an attempt to add $CF_2(OF)_2$ across the double bond in C_2F_4, a procedure analogous to that used in the preparation of $CF_3OCF_2CF_3$[8]

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