

**Table I.** Final Atomic Parameters<sup>a</sup> ( $B_{ij}$ 's  $\times 10^4$ )

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$B_{11}^b$	$\beta_{22}$	$B_{22}^b$	$\beta_{33}$	$B_{33}^b$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Mg	0	0	0.0282 (16)	54 (2)	3.90	54 (2)	3.90	129 (32)	4.85	0	0	0
Ox	0	0	0.2448 (22)	121 (10)	8.80	121 (10)	8.80	183 (28)	6.89	0	0	0
N	0.0355 (4)	0.1484 (4)	0	48 (4)	3.48	53 (4)	3.85	184 (10)	6.90	3 (3)	0	0
C <sub>1</sub>	-0.0294 (6)	0.2268 (5)	0	60 (5)	4.35	53 (5)	3.85	179 (13)	6.71	4 (4)	0	0
C <sub>2</sub>	0.0257 (7)	0.3183 (6)	0	70 (6)	5.04	58 (5)	4.23	252 (17)	9.48	-6 (5)	0	0
C <sub>3</sub>	0.1240 (6)	0.2950 (6)	0	60 (5)	4.35	56 (5)	4.09	197 (14)	7.39	1 (4)	0	0
C <sub>4</sub>	0.1296 (6)	0.1894 (6)	0	59 (5)	4.30	59 (5)	4.30	160 (12)	6.02	1 (4)	0	0
C <sub>5</sub>	0.2186 (5)	0.1333 (6)	0	52 (4)	3.77	67 (5)	4.87	160 (11)	6.02	-18 (4)	0	0
C <sub>6</sub>	0.1361 (6)	0.1932 (5)	0	55 (5)	3.96	62 (5)	4.47	185 (13)	6.96	2 (4)	0	0
C <sub>7</sub>	0.4906 (7)	0.2958 (6)	0	65 (6)	4.71	62 (6)	4.47	335 (24)	12.6	3 (5)	0	0
C <sub>8</sub>	0.3592 (5)	0.2181 (6)	0.1208 (8)	83 (5)	6.02	128 (6)	9.30	188 (11)	7.05	-34 (4)	-2 (6)	-43 (6)
C <sub>9</sub>	0.4490 (5)	0.2702 (6)	0.1228 (9)	88 (5)	6.36	121 (6)	8.76	245 (14)	9.19	-29 (4)	-12 (7)	-27 (7)

<sup>a</sup> Anisotropic temperature factor =  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . Standard errors are in parentheses. <sup>b</sup>  $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$ .

distinguished from our results: (a) a planar porphyrin with large  $B_{33}$ 's; (b) a nonplanar porphyrin with small deviations from planarity and normal  $B_{33}$ 's; (c) as in (b) but with larger  $B_{33}$ 's.

From Figure 1, it can be seen that the behavior of the TPP moiety is similar to that of other porphyrins and metalloporphyrins. There is the characteristically short C-C distance of the pyrrole ring (1.36 Å) and the abnormally long bridge-to-phenyl distance (1.54 Å). In the present instance, the latter seems to be somewhat enhanced and could be due to the phenyl ring being oriented at right angles to the porphyrin ring so that the phenyl groups cannot enter into conjugation with the  $\pi$ -bonding system of the porphyrin.

The magnesium atom approximates closely square-pyramidal coordination with the pyrrole nitrogen atoms and the hydrating water molecule. The major devia-

tion from square-pyramidal coordination comes from the magnesium being 0.273 Å (7.6°) out of the plane of the nitrogen atoms. It should be mentioned here that the water molecule is probably bound fairly firmly to the magnesium, since it was not introduced by us in the process of crystallization and must have been introduced at the time of preparation of the molecule.

Finally, in obtaining the bond distances and bond angles of the phenyl group, the atomic coordinates were corrected for a rigid body libration of the phenyl group in and perpendicular to its plane. The librations are clearly indicated by the  $B_{11}$ ,  $B_{22}$ ,  $\beta_{12}$ , and  $\beta_{23}$  parameters of C<sub>8</sub> and C<sub>9</sub> (plane of the phenyl  $\sim 30^\circ$  from the *a* axis). The corrections were of the order of 0.02 Å (root-mean-square angle of libration of about 10°), and the uncorrected bond distances are shown in Figure 1 in parentheses.

## Comparative Studies of the Catalytic Fluorination of Carbon Monoxide with Elementary Fluorine

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**Abstract:** In spite of a lack of good understanding, the process called catalytic fluorination has been used in the past for synthesis of many volatile fluorides. The procedure involves mixing fluorine with a reactant in the presence of a mass of catalyst which may be a finely divided metal coated with a film of metal fluoride. By comparing the behavior of various "catalysts," it has now been shown that a film of silver fluoride(s) on copper truly is a catalyst for the reaction  $\text{CO} + \text{F}_2 = \text{CF}_2\text{O}$  (1) and for subsequent changes producing  $\text{CF}_3\text{OOCF}_3$  and  $\text{CF}_3\text{OF}$ . Copper alone is much less active, and aluminum appears not to be a catalyst for reaction 1. The behavior of cesium fluoride as a catalyst for the reaction  $\text{CF}_2\text{O} + \text{F}_2 = \text{CF}_3\text{OF}$  (2) has been confirmed and the salt has been shown not to help reaction 1. Possible mechanisms are discussed.

Although the process called catalytic fluorination has been used frequently in the past by many persons, including the senior author, little has been done to evaluate the relative activities of different catalysts or even in some cases to establish that without question catalysis occurs. The present paper answers some of the need for definite information.

Catalytic fluorination was first used by Fredenhagen and Cadenbach,<sup>1</sup> who allowed fluorine diluted by nitrogen to react with the vapors of several organic compounds. Fluorine contacted the organic material within the pores of a mass of copper gauze. The reaction proceeded smoothly without combustion or explo-

(1) K. Fredenhagen and G. Cadenbach, *Ber.*, 67, 928 (1934).

sion such as had been encountered by others who failed to use the gauze. During years since 1934, many people have used variations of this general method to fluorinate numerous organic and inorganic compounds.

One of the authors, together with his students, has made extensive use of a catalyst formed by (1) silver plating a tangled mass of fine copper ribbon and (2) converting the silver to fluoride(s) of the metal by action of fluorine. Only a few experiments have been run involving adequate controls to permit evaluation of the effectiveness of this or other catalysts formed from transition metals. The most extensive study was by Musgrave and Smith,<sup>2</sup> who converted benzene to perfluorocyclohexane by the action of fluorine in the presence of various catalysts, and obtained yields of  $C_6F_{12}$  decreasing in the order of listing of the catalysts as follows: (1) Au on Cu, (2) Co on Cu (3 to 6 about equal) Ni on Cu, brass only, Ag on Cu, Cu only, (7) Rh on Cu, (8) steel wool, (9) Hg on Cu, (10) Cr on Cu.

The reader who wishes to become familiar with some of the early work on catalytic fluorination may do so by consulting ref 3 to 16. While catalytic fluorination using copper or coated copper catalysts remains a rather obscure art, the use of alkali metal fluorides, especially cesium fluoride, as catalysts has developed rapidly since about 1960 and now is well established and rather well understood.<sup>17-21</sup>

The catalyst is considered to act by combination of fluoride ion with the reactant other than fluorine. This gives an anion which then reacts with fluorine. Thus,  $SOF_4$  combines with CsF, presumably to give the anion  $SF_5O^-$ , and this intermediate reacts with  $F_2$  to give  $SF_5OF$  and CsF.<sup>19</sup> Since the rate of exchange of fluorine in  $CF_3CF=CF_2$  with  $F^-$  in fluorides of alkali metals decreases in the order  $CsF > RbF > LiF > KF > NaF$ ,<sup>18</sup> one would expect these to decrease in activity as catalysts for reactions of  $CF_3CF=CF_2$ , in the same order. This has been demonstrated for the reaction of  $O_2$  with perfluoropropene.<sup>18</sup>

The mechanism of action of a copper catalyst whether coated with silver fluoride(s) or not is unclear. Fluoride ion may be involved. Also the metal fluoride cat-

alyst, for example  $AgF_2$ , may react more rapidly than  $F_2$  with the substance being fluorinated. The resulting metal or salt may then be quickly reconverted by the action of fluorine to the original metal fluoride.<sup>8,10</sup> Other beneficial effects of the catalyst which have been suggested<sup>7</sup> are (1) removal of heat from the reaction zone and (2) breaking of chains in free-radical-type reactions.

Catalytic fluorination is not carried out in the manner usually used in contact catalytic processes. Normally the reactants in a contact process are mixed and then passed over the catalyst where reaction occurs. In catalytic fluorination the reactants are mixed in the presence of the catalyst. The catalyst moderates the reaction, giving a greater yield of desired products than is obtained when reaction occurs in the absence of catalyst. In many cases the substances are capable of reacting very rapidly even in the absence of catalyst.

Since most of the former work has involved fluorination of hydrocarbons, it would seem logical first to make quantitative comparisons of the fluorination of methane or some other simple hydrocarbon. This course was not chosen, however, because the reaction would have produced hydrogen fluoride which would quickly have changed the nature of the cesium fluoride used as one of the catalysts. Instead of a hydrocarbon, the substance carbon monoxide was chosen as reactant. This is known to give an interesting variety of fluorination products, and catalysts are known to influence some of the reactions. Products identified and measured by infrared spectroscopy in this research were  $CF_2O$ ,  $CF_3OF$ ,  $CF_3OOCF_3$ , and  $FC(O)OO(O)CF$ .

## Experimental Section

**Apparatus.** The reactors were constructed to have the same size and geometry. They were fabricated from 203-mm lengths of commercially available 60.4-mm o.d. aluminum or copper pipe with 4.9-mm wall thickness. These were threaded and capped at the ends with aluminum or brass pipe caps, respectively. The vessels so formed had a volume of about 540 ml and a total interior length of about 244 mm. Those vessels which contained copper packing held about 460 g of the metal. One reactor contained 350 g of freshly machined aluminum turnings. Two tubes of 4.8-mm o.d. for use as gas inlets were connected by fittings at opposite sides of each pipe 59 mm from one end. An outlet tube of the same diameter was connected at the center of the opposite end of the reactor. This gave an active interior length for packed reactors from inlet to outlet of 185 mm. Connecting tubing was aluminum or copper and was the same metal as the reactor.

Copper packing consisted of a tangled mass of thin narrow ribbon. A commercial product called "Chore Girls" (woven copper net scouring pads) was used. The surface area of 460 g of this material was about 19,000  $cm^2$ . Before use the copper netting was washed with organic solvents and was then annealed in a reducing atmosphere at 400°. One reactor,  $R_{IV}$ , was packed tightly with this material. Another,  $R_{VI}$ , was packed with the same sort of material serving as a carrier for a film of cesium fluoride. Still another,  $R_V$ , was packed with the copper netting coated with a con-

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Table I. Flow Reactors

Reactor	Reactor material	Catalyst
$R_I$	Aluminum	None
$R_{II}$	Aluminum	Aluminum turnings
$R_{III}$	Copper	None
$R_{IV}$	Copper	Copper ribbon
$R_V$	Copper	Copper ribbon, silver plated, then fluorinated
$R_{VI}$	Copper	Copper ribbon coated with CsF

Table II. Reaction of CO with F<sub>2</sub> in Flow Reactors

Runs	Reactor	Temp, °C	Flow rates, l./hr at 25°			% yield based on initial CO			
			F <sub>2</sub>	CO	N <sub>2</sub>	CO	CF <sub>2</sub> O	CF <sub>3</sub> OF	CF <sub>3</sub> OOCF <sub>3</sub>
1	R <sub>I</sub>	25	0.5	0.25	8.6	>80	12	0	0
2	R <sub>II</sub>	25	0.5	0.25	8.6	>80	5	0	0
3	R <sub>III</sub>	25	0.5	0.25	8.6	>70	25	0	0
4	R <sub>IV</sub>	25	0.5	0.25	8.6	>70	15	0	0
5	R <sub>V</sub>	25	0.5	0.25	8.6	0	>95	0	0
6	R <sub>VI</sub>	25	1.0	0.5	16	80	14	4	0
7-9 <sup>a</sup>	R <sub>I</sub> , R <sub>II</sub> , R <sub>III</sub>	75	0.5	0.5	7	~0	>90	0	0
10	R <sub>IV</sub>	75	1.0	0.5	13	~0	>90	0	0
11	R <sub>V</sub>	75	1.0	0.5	7	0	70	20	4
12	R <sub>VI</sub>	75	1.0	0.5	16	~7	~5	~85	0
13	R <sub>V</sub>	100	1.0	1.0	11	0	92	3	3
14	R <sub>V</sub>	100	1.5	1.0	11	0	70	20	6
15	R <sub>V</sub>	100	1.0	0.5	11	0	57	35	6
16	R <sub>V</sub>	100	1.5	0.5	11	0	40	48	6
17-20 <sup>a</sup>	R <sub>I</sub> , R <sub>II</sub> , R <sub>III</sub> , R <sub>IV</sub>	160	1.5	0.5	18	0	>90	0	0
21	R <sub>V</sub>	160	1.5	0.5	18	0	26	64	6
22	R <sub>V</sub>	200	2	1	16	0	65	20	12
23	R <sub>VI</sub>	200	2	1	17	0	12	>75	6

<sup>a</sup> These runs are condensed into one line because the data are identical.

tinuous film of silver plated from solution containing Ag(CN)<sub>2</sub><sup>-</sup>. Copper reactors were made gas-tight by winding Teflon tape around the threads before screwing the parts together. Aluminum reactors had to be additionally sealed with a high-temperature cement containing aluminum powder. The reactors were evacuated while hot to remove water. A stream of fluorine diluted by nitrogen was then passed through each reactor until absorption of fluorine at temperatures up to 200° was judged to be complete. Thereafter care was taken to keep the vessels closed when not in use to prevent entry by air or other unwanted gases. Table I describes and identifies the various flow reactors.

The completed reactors were assembled in an oven which could be held constantly near any desired temperature between 25 and 200°. To permit measurement of temperature, a thermocouple was attached on the wall of each reactor at a spot about 25 mm downstream from the inlet tubes. In the various runs only a small rise in temperature (not over 5°) was found to result from the reaction.

The metal used in copper tubing, pipe, and packing was about 99.9% pure. Brass pipe caps contained 85% Cu and 15% Zn. Aluminum pipe was made from an alloy containing 0.25% Cu, 1.0% Mg, 0.6% Si, and 0.25% Cr. The turnings had a higher content of aluminum than this but the cast metal in pipe caps must have had a lower content.

By means of a manifold of metal tubing and valves, it was possible to use any one of the reactors and to change quickly from one to another. Gas from the reactor passed through copper or aluminum tubing and within 8 sec or less entered an infrared cell at 25° made of aluminum. The length of the cell was 10 cm and the internal diameter was 24 mm. Windows were of silver chloride. A Beckman IR 10 spectrophotometer was used to observe the spectrum of the gas within the range 400-4000 cm<sup>-1</sup> wave numbers. This served as a means for identifying and measuring the products. The intensities of well-resolved absorption bands of the various products permitted estimation of relative yields by comparison with spectra of the pure compounds at known pressures. In most cases the band lengths were highly reproducible; however, the estimated yields should be regarded as only approximately correct. Yields of 0% given below mean that infrared absorption bands for the substance were not observed.

To measure the flow of F<sub>2</sub>, a flowmeter was used in which the gas passed through a tiny pinhole in a piece of platinum foil. The pressure difference across this orifice was measured using a manometer of Teflon tubing containing as liquid some Kel-F No. 3 oil (a polymer of trifluorochloroethylene obtained from the 3 M Co.). The relationship between pressure differential and rate of flow of fluorine was established by calibration. Flowmeters for measuring N<sub>2</sub>, CO, and O<sub>2</sub> flow rates employed the principle of measuring the drop in pressure, by means of a manometer, as the gas passed through a piece of capillary glass tubing. These meters were calibrated using known rates of flow of N<sub>2</sub>, CO, and O<sub>2</sub>, respectively. During runs, carbon monoxide and oxygen were used directly

from cylinders of the dry commercial gases. The streams of N<sub>2</sub> and F<sub>2</sub> were passed through traps cooled by liquid oxygen before going to the flowmeters. This removed possible contaminants such as H<sub>2</sub>O, HF, and SiF<sub>4</sub>.

As the work progressed, it became desirable to test the behavior of certain combinations of reactants under prolonged contact. To do this, two copper reactors of about 33-ml volume were constructed as bombs which could be closed with brass valves. One, called S<sub>I</sub>, was empty; the other, S<sub>II</sub>, was packed with 20 g of silver-plated copper ribbon like that for R<sub>V</sub>. Both were well treated with fluorine at temperatures up to about 200° before use. A run was made by introducing the reactants and then holding the temperature of the reactor approximately constant for a measured duration. The reactor was then chilled in a bath of liquid nitrogen while volatile materials (F<sub>2</sub> and perhaps O<sub>2</sub>) were pumped away. After the reactor then returned to room temperature its contents were expanded into the infrared cell and the gases were measured by intensities of characteristic bands.

## Results

The experimental conditions and yields of products obtained in various runs in which carbon monoxide was allowed to react with fluorine are summarized in Table II. In these runs half of the total flow of nitrogen entered the reactor as diluent for the stream of carbon monoxide and half entered as diluent for fluorine. Numerous other runs were made with results similar to those of Table II.

Data for runs made in the static reactors are given in Table III.

## Discussion

From the above experiments one sees that some of the tested solids behave as true catalysts. Information is given about the following reactions in which the equations are not intended to express mechanism.



Table III. Reactions in "Static Reactors"

Run	Reactor	Temp, °C	Duration of run, hr	Amounts of reactants, mmoles				Products, mole % of total condensable product		
				F <sub>2</sub>	CF <sub>2</sub> O	CF <sub>3</sub> OF	CF <sub>3</sub> OOCF <sub>3</sub>	CF <sub>2</sub> O	CF <sub>3</sub> OF	CF <sub>3</sub> OOCF <sub>3</sub>
A	S <sub>I</sub>	25	24	1.1	0.55	0	0	>95	0	0
B	S <sub>I</sub>	200	1.5	1.1	0.55	0	0	>95	0	0
C	S <sub>II</sub>	25	24	1.1	0.55	0	0	0	5	90
D	S <sub>I</sub>	25	24	0	0.55	0.55	0	50	50	0
E	S <sub>I</sub>	200	1.5	0	0.55	0.55	0	45	45	5
F	S <sub>II</sub>	25	24	0	0.55	0.55	0	50	45	Trace
G	S <sub>II</sub>	200	1	0	0.55	0.55	0	75	5	<15
H	S <sub>II</sub>	25	24	0	0.30	0	0	>90	0	0
I	S <sub>II</sub>	200	1	0	0.30	0	0	>90	0	0
J	S <sub>II</sub>	25	20	0.4	0	0	0.2	0	0	>95
K	S <sub>II</sub>	200	1	0.4	0	0	0.2	0	0	>95

**Reaction 1.** There is good basis for considering reaction 1 in an aluminum vessel to be homogeneous and not catalyzed by the walls. Support for this point of view is provided by work of Heras, Arvia, Aymonino, and Schumacher,<sup>22</sup> who studied kinetics of the reaction  $2\text{CO} + \text{F}_2 + \text{O}_2 \rightarrow \text{FC(O)OO(O)CF}$  and found it to be homogeneous in an aluminum vessel, the initiating step being  $\text{CO} + \text{F}_2 \rightarrow \text{CFO} \cdot + \text{F} \cdot$ . Probably this reaction is also the first step of the combining of CO with F<sub>2</sub> to give CF<sub>2</sub>O. Since mixing of reactants would be retarded by the packing in a reactor, it is understandable that run 2 gave a lower yield of CF<sub>2</sub>O than run 1. While a similar retardation occurred for copper packing in a copper vessel, as shown by runs 3 and 4, the effect was less strong than for aluminum reactors. This fact, together with the somewhat greater rate in copper vessels than in aluminum, indicates some catalysis of reaction 1 by fluorine-treated copper. By contrast, a comparison of runs 2, 4, 5, and 6 shows copper coated with silver fluoride(s) to be an excellent catalyst while CsF apparently is not a catalyst for reaction 1.

Since the film of catalyst formed by fluorination of silver may contain the metal in both oxidation states I and II, the material is described in this paper as silver fluoride(s).

A few runs at 25° similar to runs 1 to 5 were made, in which oxygen was added to the reactants in an amount equal in moles to the carbon monoxide. Oxygen caused a decrease in yield of CF<sub>2</sub>O in all reactors except R<sub>V</sub>. The main product formed in the aluminum vessels, R<sub>I</sub> and R<sub>II</sub>, was FC(O)OO(O)CF,<sup>22</sup> but this substance was not found in the products from the other reactors. In an additional experiment, a sample of FC(O)OO(O)CF was stored in the copper vessel S<sub>I</sub> for a day at 25°. The peroxide was then found to be completely decomposed into CF<sub>2</sub>O, CO<sub>2</sub>, CO, and O<sub>2</sub>. The latter two were identified by mass spectrometry using the part of the product which did not condense at -183°. It was also shown that a film of silver fluoride(s) acted upon FC(O)OO(O)CF very rapidly to cause decomposition to CF<sub>2</sub>O, CO<sub>2</sub>, and O<sub>2</sub>. All of the peroxide, if formed in the flow reactors other than R<sub>I</sub> and R<sub>II</sub>, decomposed before reaching the infrared cell.

**Reaction 2.** In this discussion it is assumed that the CF<sub>3</sub>OF in the various products was formed by the successive two steps, reactions 1 and 2.

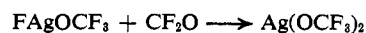
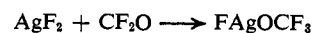


This assumption is probably correct.

A comparison of runs 7, 10, and 12 shows CsF to be a catalyst for reaction 2. This confirms work of Lustig, Pitochelli, and Ruff.<sup>21</sup> A good explanation for this catalysis is that CF<sub>2</sub>O combines with CsF to give CF<sub>3</sub>O<sup>-</sup> anion<sup>20</sup> which in turn reacts with fluorine to give CsF and CF<sub>3</sub>OF.<sup>21</sup>

At 75° and above, reaction 1 went substantially to completion in reactors R<sub>I</sub>, R<sub>II</sub>, R<sub>III</sub>, and R<sub>IV</sub>, but even up to 200° little if any CF<sub>3</sub>OF or CF<sub>3</sub>OOCF<sub>3</sub> was formed. By contrast R<sub>V</sub> gave substantial yields of these products. A film of silver fluoride(s) served as a catalyst for reaction 2 but was not as good a catalyst as CsF.

**Reactions 3 and 4.** The moderate yields of CF<sub>3</sub>OOCF<sub>3</sub> obtained in runs 11, 13-16, 21, and 22 together with the high yield from run C show a film of silver fluoride(s) to be a catalyst for reaction 3, in which fluorine converts CF<sub>2</sub>O to CF<sub>3</sub>OOCF<sub>3</sub>. It has been shown by Porter and Cady<sup>23</sup> that at temperatures near 240° carbonyl fluoride combines with CF<sub>3</sub>OF to form CF<sub>3</sub>OOCF<sub>3</sub>, eq 4. Below about 237° the reaction is slow, but high yields of CF<sub>3</sub>OOCF<sub>3</sub> obtained by the catalytic fluorination of carbon monoxide below 180°<sup>23</sup> have been interpreted to result from catalysis of reaction 4 by silver fluoride(s) on copper.<sup>24</sup> Apparently this interpretation is not correct. Runs D, E, F, and G in Table III indicate that neither silver fluoride(s) nor copper is a good catalyst for reaction 4. It follows that the CF<sub>3</sub>OOCF<sub>3</sub> produced by fluorination of carbon monoxide or CF<sub>2</sub>O in reactor R<sub>V</sub> or S<sub>II</sub> was mostly formed by a process other than reaction 4. Perhaps an intermediate was involved which contained two CF<sub>3</sub>O groups attached to the same silver atom. These groups could have come off together as CF<sub>3</sub>OOCF<sub>3</sub>. Such a route is indicated by the following speculative equations which are not intended to show all possible steps.



(23) R. S. Porter and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 5628 (1957).

(24) G. Cady, XVIIth Congress of Pure and Applied Chemistry, Vol. I (Inorganic Chemistry), Butterworth & Co., Ltd., London, 1960, p 205.

(22) J. M. Heras, A. J. Arvia, P. J. Aymonino, and H. J. Schumacher, *Z. Physik. Chem. (Frankfurt)*, **28**, 250 (1961).

$\text{CF}_3\text{OF}$ , which is also produced, could be obtained by the reaction of  $\text{F}_2$  with  $\text{F}\text{Ag}\text{OCF}_3$ .

Since the formation of  $\text{CF}_3\text{OOCF}_3$  by the fluorination of carbon monoxide over fluorinated silver catalyst appears not to require  $\text{CF}_3\text{OF}$  as an intermediate, one may wonder whether part or all of the  $\text{CF}_3\text{OF}$  produced in runs 11, 13-16, 21, 22, and C resulted from reaction 5 rather than reaction 2. This is shown not to be the



case by runs J and K in which fluorine failed to react substantially with  $\text{CF}_3\text{OOCF}_3$ .

It is interesting to compare the fluorination of carbon monoxide with the action of  $\text{F}_2$  upon  $\text{SO}_3$ , which also is catalyzed by silver fluoride(s).<sup>15</sup> Peroxydisulfuryl difluoride (1)



is obtained at about  $165^\circ$  over silver fluoride(s) with some 2 as a side product.<sup>15</sup> At higher temperatures the yield of  $\text{SO}_3\text{F}_2$  increases. This process can be described in terms of the above mechanism. The side product,  $\text{SO}_3\text{F}_2$ , corresponds to  $\text{CF}_3\text{OF}$  in the  $\text{CF}_2\text{O}-\text{F}_2$  system. In both systems the catalyst is apparently capable, in the presence of fluorine, of linking the two oxygen atoms together and aiding the fluorination of the more electropositive partner of a  $\text{M}=\text{O}$  bond ( $\text{M} = \text{C}, \text{S},$  and possibly other elements).

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