

REACTION OF CARBONYL FLUORIDE WITH FLUORINE IN THE PRESENCE OF VARIOUS FLUORIDES AS CATALYSTS

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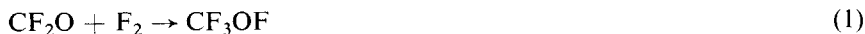
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SUMMARY

The fluorides KF, RbF and CsF have been known to serve as catalysts for the reaction $\text{CF}_2\text{O} + \text{F}_2 \rightarrow \text{CF}_3\text{OF}$. The list of catalysts for this process has now been enlarged to include NaF, MgF_2 , CaF_2 , SrF_2 , BaF_2 and LaF_3 . Lithium fluoride and thorium fluoride also give CF_3OF but are less active. Perhaps the substances $\text{CsF}\cdot\text{HF}$, KAgF_4 and NiF_2 should be included in this list. Silver fluoride, usually as a mixture of AgF_2 with AgF, has been known to catalyze the reaction of CF_2O with F_2 to give both CF_3OF and CF_3OOCF_3 . The proportion of the latter in the mixture of products increases with decreasing temperature. At 25° , the reaction is slow and the yield of CF_3OOCF_3 is very high. It has now been shown that TlF_3 behaves like silver fluoride. It has also been shown that many other fluorides of metals give higher yields of CF_3OOCF_3 than of CF_3OF but require higher temperatures than AgF_2 ($100\text{--}ca. 150^\circ$) to be effective. Various possible mechanisms for these catalytic processes are discussed.

INTRODUCTION

It is well known that CsF, RbF and KF serve as catalysts, and that the reaction



takes place readily at -78° when one of these salts is present¹. The catalytic behavior of cesium fluoride for this reaction was confirmed by Wechsberg and Cady² who also showed that silver fluoride (as a mixture of AgF with AgF_2) behaved as a catalyst at room temperature and above. With this catalyst, the yield of CF_3OF was low, while the yield of CF_3OOCF_3 was high.



Silver fluoride was also observed to act as a catalyst for reaction (3), but cesium fluoride was inactive.



The striking difference in behavior of the two types of catalyst must result from different mechanisms or from a marked difference in the relative importance of corresponding steps in one type of mechanism.

The principal objective of the present work was to observe the behavior of fluorides of many metals as catalysts for reactions (1) and (2). A secondary objective was to try to understand the mechanism of catalysis.

A brief summary of the history of catalytic fluorination has already been given².

EXPERIMENTAL

Materials

Fluorine was purchased from the Allied Chemical Co.. As a precaution (which may have been unnecessary), the gas was passed through a trap at -183° to remove condensable materials. Hydrogen fluoride was obtained from the Matheson Co.. When aqueous hydrofluoric acid was used it was of Baker Analyzed grade. At first, CF_2O was purchased from PCR Inc.. Later in the research, CF_2O was prepared in the laboratory by combining CO, in small excess, with F_2 in a flow reactor of copper tubing heated to 100° . The CF_2O was condensed in a trap at -183° and purified by pumping away the more volatile substances. The CF_2O was then stored before use in a stainless-steel vessel containing 20 g of dry KF. Neither the IR spectrum nor the graphical record made during fractional co-distillation of a sample revealed any contaminants.

In Table 1, the second column indicates by letters the method used to obtain each substance tested as a catalyst. The methods used were as follows:

- (a) These substances were commercial chemicals of good quality.
- (b) These fluorides were prepared by adding excess $\text{HF}(\text{aq.})$ to the corresponding metal carbonate³ in a Pt crucible and heating to dryness.
- (c) Silver(I) fluoride was prepared by the action of excess aqueous hydrofluoric acid upon freshly prepared silver carbonate³. A polyethylene container was used and the room was darkened. The solvent was evaporated away under vacuum produced by an aspirator at 25° .
- (d) These fluorides were prepared in 1951 by Jache⁴. They were produced by the action of liquid hydrogen fluoride upon the appropriate salt, *i.e.* NiCO_3 , ZnCO_3 or $\text{Zr}(\text{NO}_3)_4$.

(e) Potassium tetrafluoroargentate(III) was prepared by treating a finely ground equimolar mixture of AgNO_3 and KNO_3 with F_2 at 200° ⁵.

TABLE 1
CATALYSTS FOR THE REACTION OF CF_2O WITH F_2

Catalyst	Method of preparation	Temp. ($^{\circ}\text{C}$)	Approximate half-time of reaction (h)	% reacted CF_2O converted to CF_3OOCF_3	Line used
<i>Catalysts which lead almost exclusively to the formation of CF_3OF</i>					
NaF	a	-78	0.75	<5	Metal
KF	a	-78	<0.5	<5	Metal
RbF (ref. 1)		-78			
CsF	a	-78	<0.5	<5	Glass
CsCl	a	-78	<0.5	<5	Glass
NH_4F	g	-78	0.75	<5	Metal
MgF_2	a	-78	0.75	<5	Metal
CaF_2	b	-78	<0.5	<5	Metal
SrF_2	b	-78	<0.5	<5	Metal
BaF_2	b	-78	<0.5	<5	Metal
LaF_3	b	-78	<0.5	<5	Metal
$\text{CsF}\cdot\text{HF}$	f	25	<0.5	<5	Glass
		(not tried at -78°)			
KAgF_4	e	25	15	<5	Glass
ThF_4	o	25	20	<5	Glass
<i>Catalysts which lead to the formation of CF_3OOCF_3 as 15-30% of the final product</i>					
NiF_2	d	25	<0.5	20	Metal
LiF	b	100	4	20	Metal
	a	125	~10	85	Glass
<i>Catalysts which lead to the formation of CF_3OOCF_3 as 40-80% of the final product</i>					
CdF_2	b	100	30	65	Metal
BeF_2	h	100	10	50	Metal
AlF_3	d	150	6	70	Glass
	h	100	10	45	Metal
InF_3	h	100	3	50	Metal
MnF_3	a	100	7	70	Glass
FeF_3	a	100	4	50	Glass
CoF_3	a	100	6	55	Glass
CuF_2	k	100	9	70	Metal
ZnF_2	d	100	20	50	Glass
ZrF_4	d	100	20	80	Glass
PrF_3	b	100	27	65	Metal
NdF_3	m	100	10	75	Metal
UO_2F_2	a	100	35	70	Glass
<i>Catalysts which lead to the formation of CF_3OOCF_3 as over 80% of the final product</i>					
TlF_3	i	25	24	90	Glass
AgF	c	25	30	95	Glass
AgF_2	j	25	15	95	Glass
PbF_2	a	100	11	80	Glass
PbF_4	j	100	15	80	Glass
TbF_3	n	100	30	>95	Metal
BiF_3	i	150	12	>95	Metal
SnF_4	a	150	15	80	Metal
YF_3	n	150	10	>95	Metal

Table 1 (continued)

Catalyst	Method of preparation	Temp. (°C)	Approximate half-time of reaction (h)	% reacted CF ₂ O converted to CF ₃ OOCF ₃	Line used
AuF ₃	l	150	41	85	Glass
HgF ₂	a	150	10	85	Glass
CeF ₄	a	150	2	>90	Glass
GdF ₃	a	150	5	>95	Glass

(f) Cesium acid fluoride was prepared by adding 2.5 g CsF to an excess of HF(aq.). The salt was dried at 100° under vacuum produced by an aspirator. The product was probably CsF·HF as judged from known phase relationships.

(g) Ammonium fluoride resulted from passing an excess of NH₃ into several milliliters of HF(aq.)³. The solution was evaporated to dryness. Additional NH₃ was added and then removed at 25° by a stream of dry N₂.

(h) These were prepared by the thermal decomposition of the appropriate NH₄F complex³, *i.e.* (NH₄)₂BeF₄, (NH₄)₃AlF₆ or (NH₄)₃InF₆. The AlF₃ initially used had been previously prepared by dissolving Al in aqueous hydrofluoric acid⁴.

(i) Thallium or bismuth metal was heated in a Pt crucible with HF(aq.) to prepare TlF or BiF₃. TlF₃ was prepared in the reactor by adding TlF, evacuating the reactor and successively fluorinating at temperatures from 25° to 200°.

(j) Lead(II) fluoride⁶ or AgF was fluorinated in the reactor at 200° to form PbF₄ or AgF₂.

(k) To prepare CuF₂, fluorine was passed over CuCl₂ in a Pt tube at 300°³. The temperature was kept lower than that suggested in the literature³ because the Pt appeared to react with F₂ at 400°.

(l) The method of Sharpe⁷ was used to prepare AuF₃⁷. Metallic gold was allowed to react with BrF₃, formed *in situ*, to produce AuBrF₆. AuF₃ was then formed by heating to distil off the BrF₃.

(m) Neodymium oxide was dissolved in dilute HCl. The addition of HF(aq.) caused purple NdF₃ to precipitate. This was dried.

(n) Terbium oxide or yttrium oxide was added to a Pt crucible containing 15 M NH₄OH, and the mixture was heated. HF(aq.) was then added and the product was heated to dryness. The process of adding HF(aq.) followed by evaporation to dryness was repeated three times. Finally, 4 g of hydrogen fluoride was condensed into the reactor containing the TbF₃ and the bottom surface of the vessel was heated to 70–80° on a hot plate for 9 h before pumping away HF. For YF₃, 3 g of HF was used and allowed to stand 1 h at 50° before removing the HF. Prior to the final HF treatment, the TbF₃ had not exhibited catalytic activity at 150°.

(o) Excess HF(aq.) was added to a solution of Th(NO₃)₄ to form ThF₄. After being dried, the ThF₄ was placed in the reactor. The reactor was evacuated and 3 g of HF was added. The HF was removed after being in the reactor 12 h at 25°.

Apparatus

Two vacuum systems were used in the research. The first was of Pyrex glass. It had two manifolds, stopcocks lubricated with Kel-F 90 grease, mercury manometers in which the mercury was covered with a protective layer of Kel-F 3 oil and a system for fractional co-distillation. A metal system, constructed later, consisted of three 750 ml steel vessels joined by brass valves to a manifold made of copper tubing. Brass valves also connected the metal manifold to two brass standard-taper ground joints. The metal system was connected to the glass system and was evacuated through the latter.

Thirteen nearly identical reactors were constructed from stainless steel with welded seams. The volume of each cylindrical reactor was about 50 ml and the surface area of the flat bottom was 7 cm². A brass 0.635 cm pipe coupling was machine tooled to form a close overlap at the top of each reactor and was sealed to the reactor by silver solder. The coupling was threaded to a brass valve using Teflon tape to make a gas-tight seal. The valve was attached to a standard-taper ground joint so that the reactor could be connected to the manifold using Kel-F 90 grease on the joint.

Physical methods

Separations by co-distillation were performed as described by Cady and Siegwarth⁸. Infrared spectra were recorded on a Beckman Model IR 10 spectrophotometer. The samples were contained in a 10 cm Pyrex glass cell with AgCl windows attached by halocarbon wax.

Procedure

Before a new catalyst was added, the reaction vessel was cleaned thoroughly. It was later tested and considered suitable for use if a mixture of 3 mmole CF_2O with 3 mmole F_2 did not combine more than 5% (usually much less than 5%), based on CF_2O consumption, in 12 h or more at 100°. If the vessel were to be used at 150°, the test was made at 150°. Occasionally, replacement of the brass pipe coupling and valve was necessary when the reactor had previously been used.

After a reactor was found to be satisfactory, the desired catalyst was added to the vessel and the valve was replaced using a strip of Teflon tape around the valve threads. Most of the catalysts were added without the use of special conditions; however, those known to be highly hygroscopic were added in a glove bag containing dry nitrogen or were prepared in the reactors. Except for fluorides which were prepared in the reactors, each catalyst was ground to a fine powder using an agate mortar and pestle before being added to the reactor. Usually between 2 and 4 g of catalyst was added, and the amount was sufficient to cover the bottom of the vessel to a depth of several millimeters. Only 0.5 g PrF_3 was used, and the amounts of AuF_3 and PtF_4 were about 1.3 g each. For many of the experiments, the reactor containing catalyst was weighed before and after use.

Only for the reactor containing NH_4F was a significant increase in weight (18 mg) observed.

Before use, the reactor containing the catalyst was evacuated at $100\text{--}500^\circ$. The temperature depended upon the substance being heated. Four millimoles of F_2 was then added to the reactor at room temperature and the vessel was held at 100° for several hours before the fluorine was removed. Exceptions were made to this procedure when it was thought that the catalysts could possibly be fluorinated at 100° . Thus, AgF , TlF , BiF_3 and PbF_2 were exposed to F_2 only at 25° prior to reaction while NH_4F and CsCl were not fluorinated prior to reaction.

The reactants were now added to the reactor. The usual procedure was to condense 3 mmole of CF_2O into the reactor at -196° and to also add 3 mmole of F_2 . The reactor was then detached from the vacuum line and placed in one of the following: (i) a Dry-Ice-trichloroethylene bath having a temperature of -78° , (ii) a water bath at room temperature or (iii) a steam bath for about 1 min, if the reaction was to proceed at or above 100° . Following this rapid rise to 100° , the reactor was held in an oven at the desired temperature (100° or above) for the desired length of time. Each catalyzed reaction was run at the lowest of the four temperatures which caused the reaction to proceed at a reasonable rate.

A run was terminated by placing the reactor in liquid oxygen. The amount of non-condensable gaseous product was then measured by observing its pressure when in a system of known volume. The reactor was then warmed to room temperature. The gaseous products were removed and separated by fractional co-distillation. The volume of each gas was measured. Products were identified by their distillation record and by their infrared spectra.

For each fluoride, several runs were made. The first objective was to find the lower of the four bath temperatures which would allow the reaction to take place at a suitable rate for study. Runs of different duration were then made at one temperature to determine the approximate length of time required for half of the CF_2O to be consumed. The best catalysts caused the reaction to be essentially complete within 30 min at -78° . For these the half-times were not determined.

Poisoning and reconditioning of catalysts

During the early part of this research, gaseous reactants were added to the catalytic reactors from the glass vacuum line. Inconsistent results were sometimes obtained, but the cause was not immediately recognized. Some catalysts exhibited a distinct reduction in activity with repeated use. There also seemed to be a difference in mechanism because the ratio of products often changed. Examples of obvious poisoning are apparent in the results shown in the next paragraph.

When freshly prepared LaF_3 was used, the reaction was complete within 30 min at -78° and gave only CF_3OF . A second and a third run gave the same

results as the first, but the catalyst was inactive at -78° for a fourth run. The poisoned catalyst gave a half-time for the reaction of about 4 h at 100° and a yield of CF_3OOCF_3 of about 65% based upon the amount of CF_2O consumed. Freshly prepared BaF_2 was active at -78° and gave a half-time for the reaction of less than 30 min. The product was CF_3OF . A second run was like the first but the third was much slower. At 100° , the half-time was somewhat over 30 h and about 55% of the consumed CF_2O was converted to CF_3OOCF_3 . Freshly prepared SrF_2 and CaF_2 were poisoned in the same way as BaF_2 .

Repeated experiments with LaF_3 showed that fresh catalyst was usually active at -78°C for three experiments with rapid formation of CF_3OF only. The catalyst became inactive for the fourth experiment. It was then discovered that the de-activated catalyst could be re-activated by heating at 300° for a short period while the reactor was being evacuated. In 16 runs, the above cycle was observed four times. A cold trap at -183° was used to collect any condensable material evacuated from the reactor while the catalyst was being re-activated. A small amount, between 0.05 and 0.10 mmole of material, demonstrated by its IR spectrum to be SiF_4 , was condensed in the cold trap. Later experiments showed that the intentional addition of small amounts of SiF_4 caused poisoning of some of the catalysts. The metal vacuum line was then constructed and after that the reactants were excluded from any contact with glass. When the metal system was used for adding reactants, SrF_2 , CaF_2 , BaF_2 and LaF_3 all exhibited activity at -78° with essentially 100% conversion of CF_2O to CF_3OF within 0.5 h. No deviation in activity was observed when the same catalyst samples were used for successive reactions. The effect of poisoning, presumed to be caused by formation of SiF_6^{2-} , was most pronounced with the alkaline earth metal fluorides and lanthanum fluoride.

It was also found, as might have been expected, that the behavior of a fluoride as a catalyst was, at least in some cases, dependent upon the mode of preparation or upon surface conditioning of the sample. For example, lithium fluoride of reagent grade (J. T. Baker Chemical Co.) was not appreciably active at 100° . At 125° , the reaction was about two-thirds complete in 12 h and the consumed CF_2O was mostly converted to CF_3OOCF_3 . A sample of LiF , freshly prepared from the carbonate by method (b) above gave a half-time for the reaction of 4 h at 100° and about 80% of the consumed CF_2O was converted to CF_3OF . A similar difference was found between an old sample of AlF_3 and a freshly prepared sample (see Table 1). It has already been mentioned above under preparative method (n) that the activity of TbF_3 as a catalyst was increased by treatment with hydrogen fluoride.

During the preliminary investigations, CF_4 was sometimes obtained as a reaction product. Approximately 50% or more of the product was CF_4 in specific reactions with the following catalysts, temperatures and times: AlF_3 , 210° , 12 h; PbF_4 , 150° , 20 h; MnF_3 , 120° , 15 h; FeF_3 , 110° , 9 h; CoF_3 , 200° , 5 h;

NdF_3 , 230°, 1 h; NiF_2 , 25°, 13 h. Nickel fluoride was unique in that no other catalyzed system yielded CF_4 as a product at 25°. Experiments with PbF_4 suggest that the CF_4 was somehow formed by fluorination of CF_3OOCF_3 .

The following experiments were made with PbF_4 catalyst when the glass line was used. In 12 h at 125°, 3.0 mmole CF_2O and 3.0 mmole F_2 formed 0.6 mmole CF_4 , 1.1 mmole CF_3OF and 0.6 mmole CF_3OOCF_3 as condensable products. At 124° in 10 h, 7.0 mmole CF_3OF and 7.0 mmole F_2 did not react. At 120° in 10 h, 5.0 mmole CF_3OOCF_3 and 8.0 mmole F_2 formed 7.0 mmole CF_4 with 1.5 mmole CF_3OOCF_3 remaining. CF_4 was never observed as a product when the metal line was used.

Some of the catalysts, namely CdF_2 and NdF_3 , exhibited erratic behavior for which no explanation was found. However, most of the salts behaved in a reproducible manner.

RESULTS

The fluorination of CF_2O was negligible at 150° in clean and empty stainless-steel vessels and at the pressures used in this investigation. All salts used in the research, except some which react with F_2 below 150°, possessed some catalytic effect at or below 150°.

Table 1 summarizes the results obtained when 3 mmole of CF_2O was mixed with 3 mmole of F_2 and held in contact with catalyst. For each substance, enough runs were made to permit an estimation of the approximate length of time required for 1.5 mmole of CF_2O to react. For these runs the only recognized products were CF_3OF and CF_3OOCF_3 . Numbers given for reaction half-time and for percentage of reacted CF_2O converted to CF_3OOCF_3 should be regarded only as approximately correct. Details regarding the experimental runs are given in Kennedy's thesis⁹.

Comments will now be made about the performance of some of the catalysts. In the case of CsCl , it is possible that some CsF may have been present on the surface and served as the catalyst. If so, the amount was very small. The material was not pre-treated with fluorine and it was kept at -78° while in contact with the reactants. Following its use as a catalyst, 14 mmole of F_2 was added to the reactor at -78° and allowed to stand for 12 h at this temperature. The gas was then pumped out through a trap at -183°. A small amount of white solid collected in the trap. This material was highly volatile and had an infrared spectrum corresponding to SiF_4 . Chlorine was absent. CsCl reacted with fluorine at 120° but apparently not at -78°. The sample of ammonium fluoride was also kept at -78° when in contact with the reactants. Since the vessel containing the salt increased in weight by only 18 mg as the result of containing the reactants and products, it appears that little or no reaction of F_2 with NH_4F occurred. The method of preparation of cesium acid fluoride should have given $\text{CsF}\cdot\text{HF}$ as

the product. This material was not analyzed, however, and it may have contained some CsF.

Table 2 reports the results of runs made with BaF₂, AlF₃, CuF₂, NdF₃, AgF₂ and PrF₃ using the metal vacuum line, and illustrates the nature of data obtained. For each of these runs, 3 mmole of CF₂O and 3 mmole of F₂ were used.

TABLE 2
TYPICAL RUNS USING 3 MMOLE QUANTITIES OF CF₂O AND F₂

Catalyst	Temp. (°C)	Duration of run (h)	Products (mmole)			% reacted CF ₂ O converted to CF ₃ OOCF ₃
			CF ₃ OF	CF ₂ O	CF ₃ OOCF ₃	
BaF ₂	25	0.5	3.0	0	0	0
	78	0.5	3.0	trace	0	0
	78	0.5	2.7	0.3	0	0
AlF ₃	100	24	1.2	0.8	0.7	55
	100	8.5	0.9	1.2	0.2	30
CuF ₂	100	2	0.3	1.8	0.4	75
	100	20	0.7	0.9	0.7	65
	100	20	0.7	0.8	0.8	70
	100	9	0.3	1.6	0.5	75
NdF ₃	25	16	0	3.0	0	no reaction
	150	4.5	2	0.4	0.2	15
	150	22	0.6	0	1.1	80
	110	21	0.6	0.2	1.0	75
	100	27	0.5	0.5	1.0	80
AgF ₂	25	24	0.1	1.0	0.8	95
	100	1.5	0.75	0.75	0.75	65
PrF ₃	100	27	0.5	1.5	0.5	65
	150	2	1.9	0.8	0.1	10

DISCUSSION

It is recognized that some of the catalysts behaved erratically. The study comprises a rather broad survey made to obtain a general idea of the types of activity shown by many different fluorides. A more detailed study with greater attention placed upon purity and method of preparation of the catalyst can be expected to give results differing from some of those reported here.

Table 1 does not list all of the fluorides which were studied. A sample of SmF₃ was found to be an active catalyst at 25° leading to the formation of CF₃OF. Since this behavior was radically different from that of the other lanthanide(III) fluorides, except for LaF₃, it seems likely that an impurity was present. AgSbF₆ and PtF₄ have been omitted because insufficient data were available to allow an estimation of the half-time. Both gave high yields of CF₃OOCF₃.

The rather high activity of KAgF₄ as a catalyst for the formation of CF₃OF, as shown in Table 1, could have been caused by an impurity. It seems possible

that KF was present. There is no apparent reason why NiF_2 should have been contaminated with an alkali metal fluoride and as far as is known it was of good quality; however, the high catalytic activity of this substance in the formation of CF_3OF does suggest the presence of an impurity. One would have expected NiF_2 to resemble CuF_2 which is not very active and gives a rather high yield of CF_3OOCF_3 .

The fluorides which have the most highly ionic character, *i.e.* NaF, KF, RbF, CsF, NH_4F , MgF_2 , CaF_2 , SrF_2 and BaF_2 , resemble each other by being active at -78° and by giving CF_3OF almost exclusively. LaF_3 and ThF_4 , and possibly NiF_2 and LiF , appear to be of the same type. Catalysts of this type are probably effective because of the presence of the F^- ion. They are poisoned by SiF_4 , probably because of combination with F^- to give the SiF_6^{2-} ion. The mode of action of cesium fluoride is thought to involve the reaction



(shown to occur by Redwood and Willis¹⁰) followed by reaction (5).

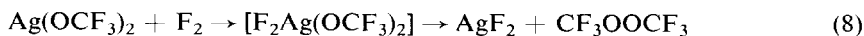
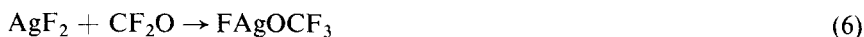


The latter reaction is known to occur at -78° . Even though this mechanism is both reasonable and attractive, Lustig, Pitochelli and Ruff¹ are cautious about claiming that the process involves these steps. They say, "It is probable that the metal fluoride either reacts directly with or polarizes the carbon-oxygen double bond to such an extent that a polar intermediate is formed, which is the active species in the fluorination.". One reason for caution is that some carbonyl compounds which are catalytically fluorinated do not appear to involve extensive combination with the metal fluoride. For example, CO_2 is not absorbed very much by CsF, but reacts with fluorine in the presence of CsF to give $\text{CF}_2(\text{OF})_2$ ^{11,12}.

In the present research, the substances $\text{CsF}\cdot\text{HF}$, KAgF_4 and CsCl could not have acted through the formation of CF_3O^- as an intermediate unless the salts contained alkali metal fluoride as an impurity. This situation increases the attractiveness of the "polar intermediate" mechanism. While this mechanism is not fully clear, it is in a better state of understanding than the mechanism for the type of catalytic reaction which leads largely to the formation of CF_3OOCF_3 .

Several of the catalysts which give high yields of CF_3OOCF_3 are strong fluorinating agents which one might expect to convert CF_2O to F_3CO , CF_3OOCF_3 or CF_3OF . None, not even AgF_2 nor CoF_3 , are capable of doing this, however. The initiating step in the catalysis, therefore, appears not to be fluorination of CF_2O by the fluoride of a metal.

Wechsberg, Kennedy and Cady have all been involved at the University of Washington with the study of the catalytic fluorination of CF_2O . Each of these three workers has had his own ideas about the mechanism of the process. Wechsberg² has proposed the following steps to account for the behavior of silver fluoride(s) as a catalyst.

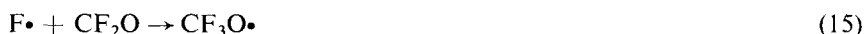


This proposal has the merit of placing two CF₃O groups close to each other in an intermediate from which they can be eliminated simultaneously as CF₃OOCF₃.

To Cady it has seemed that catalytic fluorination of CF₂O in the presence of silver fluoride(s) resembles the photochemical fluorination of SO₃ studied by Schumacher and his associates¹³. In this process, the mechanism is considered to be



The presence of a relatively large concentration of SO₃ causes much more of the atomic fluorine to react by (11) than by (13), and leads to the production of much more S₂O₆F₂ than SO₃F₂. Cady¹⁴ has proposed that silver fluoride(s) may catalyze the dissociation of the fluorine molecule to fluorine atoms and that the fluorination of carbonyl fluoride may involve the following steps:



If reaction (15) is fast, it is reasonable that the presence of a relatively high concentration of CF₂O would cause much more of the atomic fluorine to react by (15) than by (17) and to give a higher yield of CF₃OOCF₃ than of CF₃OF.

An alternative to this mechanism is that the first step involves "adsorption" of F₂ upon the catalyst. The adsorbed fluorine may then react with CF₂O to give the CF₃O• radical and (perhaps) F atoms. The "adsorbed" fluorine might be in the atomic condition. This could be followed by (16) and (17) or a reaction of CF₃O• with "adsorbed" fluorine.

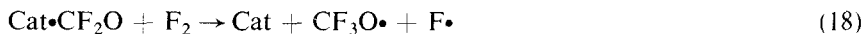
Kennedy, who undertook the experimental work for this paper in 1969–70, has favored a mechanism involving "adsorbed" CF₂O. Since that time, in association with Levy, he has, amongst other work, studied the kinetics of reaction (15).

The work on the kinetics will be reported elsewhere¹⁵. For reaction (15), the rate constant at 25° has been found to be 10^{3.5}.

The concentration of fluorine atoms which can exist in equilibrium with F₂ molecules at a concentration of 0.06 mole l⁻¹, the value corresponding to 3 mmole F₂ in a 50 ml reactor, is¹⁶ only about 8 × 10⁻¹³ mole l⁻¹. The initial rate of production of CF₃• from this concentration of F• at 25° would be about 1.5 × 10⁻¹⁰ mole l⁻¹ s⁻¹. The observed rate of production of CF₃OOCF₃ in the presence of silver fluoride(s) or thallium(III) fluoride is about 10⁴ times as great as expected from the above rate. Hence steps (14) and (15) cannot give enough CF₃O• to account for the catalytic production of CF₃OOCF₃ and CF₃OF.

Kennedy's proposition will now be considered, *i.e.* that the catalysts reported here function primarily by physical adsorption and distortion of the CF₂O molecules. The carbon-oxygen π-bond dissociation energy is probably the most important barrier to fluorination of gaseous CF₂O at ambient temperature. It is suggested that the adsorbed species, Cat•CF₂O, may be distorted from the planar configuration of gaseous CF₂O and exhibit π-bond orbitals which are more susceptible to reaction with F₂. This model for the catalysis is similar in principle to the "orbital steering" mechanism advanced by Storm and Koshland¹⁷ to explain the fast rates of enzyme catalysis.

The adsorbed CF₂O may be fluorinated in two different ways.



If the carbonyl π bond of "adsorbed" CF₂O is considered analogous to an olefin π bond for the purposes of F₂ addition, there are known indirect precedents for both proposed reactions (18) and (19)^{18,19}. Although it is suggested that reaction (19) may be a one-step addition of F₂ to a polar molecular intermediate, there is no evidence to disprove the existence of the ionic intermediate shown in equations (4) and (5).

Important reactions forming products subsequent to reaction (18) would then be:



The rate constants for reactions (15), (17) and (16) have been determined¹⁵. Reaction (15) has an activation energy of 8.1 kcal mole⁻¹. From the present considerations, reaction (20) will have an activation energy less than 8.1 kcal mole⁻¹, possibly close to zero. Free-radical reactions (17) and (16) are assumed to proceed with zero activation energy.

The most apparent trends in the results of Tables 1 and 2 are: (a) that catalysts active at the lower temperatures are generally the more highly ionic salts, (b) that catalysts active at -78° mostly catalyze the formation of CF₃OF, (c) that catalysts which are initially active at 25° to 150° cause the production of relatively high yields of CF₃OOCF₃ and (d) that the percentage of CF₃OF in the product apparently increases with reaction temperature when the same catalyst is used (see Table 2 for NdF₃, AgF₂ and PrF₃). The experimental observations are consistent with Kennedy's proposed mechanism in the following ways:

(i) Many metal fluoride salts adsorb CF₂O at 25° sufficiently to be detected by IR spectroscopy²⁰; therefore, one can expect heterogeneous reactions involving adsorbed CF₂O to be important.

(ii) Carbonyl fluoride is not held tightly by the catalyst (even CsOCF₃, considered to be the most stable compound formed from a metal fluoride and carbonyl fluoride, dissociates to CsF + CF₂O at 80° ¹⁰); therefore, homogeneous reactions in the gaseous phase can be expected to increase in importance in relation to heterogeneous reactions when the temperature rises.

(iii) The product distribution of each catalyzed reaction will be determined largely by which of the competitive reactions (18) or (19) predominates.

(iv) The product distribution of reaction (18) will be determined by the relative rates of the subsequent reactions ((15)-(17) and (20)). Rate constants for reactions (16) and (17) are independent of temperature. The rate constant for reaction (15) increases with temperature. Reaction (20) is postulated to be less important at the higher temperatures because fewer Cat•CF₂O sites exist.

Even though the question of mechanism has not been settled, the topic has been discussed here at some length because the Authors feel that it is interesting and deserves further attention. Since the Authors have discontinued their work on the topic, they consider it desirable to report rather fully now.

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