lithium alkyls, thereby effectively reducing the concentration of free lithium alkyl. Because of the rapid attainment of equilibrium between the associated and unassociated lithium alkyl, molecular weight is not affected.

The concentrations of lithium alkoxide considered here would correspond to 25 to 80% oxidation of lithium alkyl. This is above the range of oxidation to be expected on chance exposure of the catalyst to air. However, these experiments do emphasize the need for careful preparation and handling of lithium alkyls to prevent exposure to air if meaningful quantitative polymerization data are to be obtained.

Discussion

Compounds which are basic compared to the lithium alkyl increase the polarity of the lithium–carbon bond by coördination with the lithium atom in the sense that a greater negative charge is placed on carbon.[13]

$$\mathrm{R{-}Li} + 2\mathrm{B} \longrightarrow \mathrm{R}^{-}\ {}^{+}[\mathrm{Li{\cdot}2B}]$$

Therefore, in the presence of such basic compounds the reactivity of lithium alkyls is enhanced. The magnitude of rate of polymerization in the presence of excess base where all of the lithium alkyl is present as the complex is a measure of the degree of polarization of the lithium–carbon bone. This study indicates that all of the ethers examined induce the same degree of polarization in the lithium alkyl and ethers induce a greater degree of polarization than does triethylamine.

Acidic compounds also increase the degree of polarization of lithium alkyls. However, in this case the carbanion is associated with the coördinating acid so that the reactivity of the lithium alkyl is effectively neutralized.[13]

$$\mathrm{R{-}Li} + \mathrm{A} \longrightarrow \mathrm{Li}^{+}\ {}^{-}[\mathrm{AR}]$$

In the discussion of the results the nature of the group R in the lithium alkyl has been ignored. In the case of complexing with Lewis bases, both the complex and the free lithium alkyl add to monomer. Since the rate of propagation was used to indicate the degree of complex formation of the lithium alkyl, the group R must be the species present under these conditions. Therefore, the equilibrium which was studied was that involving the growing polymer chain, $\sim CH_2CH(C_6H_5)Li$.

This conclusion is probably not true in the case of complexing with the acidic metal alkyls. *n*-Butyllithium probably reacts faster with the metal alkyl than with styrene. Therefore, the complex forms rapidly and only unassociated lithium alkyl is available for addition to monomer. In this case then the equilibrium under consideration is that involving *n*-butyllithium. Since some exchange of lithium alkyl between complex and solution does occur during the polymerization, as evidenced by the data of Table VII, the group $\sim CH_2CH(C_6H_5)Li$ also must contribute to the equilibrium.

Acknowledgments.—The author wishes to express his appreciation to Dr. R. D. Lundberg and Dr. N. L. Zutty for their advice and helpful discussions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON]

The Reactions of Trifluoromethyl Hypofluorite with Sulfur Trioxide and Sulfur Dioxide

BY WAYNE P. VAN METER AND GEORGE H. CADY

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Trifluoromethyl hypofluorite reacts with sulfur trioxide in the temperature range 245 to 260° to form trifluoromethyl peroxyfluorosulfonate, CF_3OOSO_2F, a substance which melts at −117° and boils at 12.9°. Trifluoromethyl hypofluorite reacts with sulfur dioxide in the range 175 to 185° to yield many products, among them being the esters $F_3C{-}O{-}SO_2F$ (m.p. −121°, b.p. −4.2°), $F_3C{-}O{-}SO_2{-}O{-}CF_3$ (m.p. −99°, b.p. 31°), $F_3C{-}O{-}SO_2{-}O{-}SO_2F$ (b.p. 76°) and $F_3C{-}O{-}SO_2{-}O{-}SO_2{-}O{-}CF_3$ (m.p. −66°, b.p. 98°). The crude mixture of products has been separated into its components by fractional codistillation. Nuclear magnetic resonance, infrared, and mass spectra have been used to establish the structures of the new compounds. Differences in ease of hydrolysis by aqueous sodium hydroxide have been correlated with the proposed structures. Vapor pressure curves and gas and liquid densities have been measured for each of the substances.

Two of the compounds that possess hypofluorite groups have been shown previously to form peroxides upon reaction with compounds having double-bonded oxygen atoms:[1,2]

$$CF_3OF + COF_2 = CF_3OOCF_3$$

$$FSO_2OF + SO_3 = FSO_2OOSO_2F$$

The reactions of trifluoromethyl hypofluorite with sulfur trioxide and with sulfur dioxide have been studied in the present research. In the case of sulfur trioxide, an unsymmetrical peroxide, analogous to the products shown above, has been prepared. The reaction with SO_2 has resulted in a series of four new esters which are not peroxides.

Reagents.—Trifluoromethyl hypofluorite was prepared[3] by mixing streams of carbon monoxide and fluorine in a ratio of somewhat more than two volumes of fluorine per volume of carbon monoxide. The gases passed through copper tubing held at about 400° where nearly all of the carbon monoxide was converted to trifluoromethyl hypofluorite. The unused fluorine remained in the stream of gases. Sulfur trioxide ("Sulfan B," General Chemical Division, Allied Chemical and Dye Corp.) and sulfur dioxide (in cylinder, Matheson Company, Inc.) were used as received.

Reaction of CF_3OF with SO_3.—Mixtures of trifluoromethyl hypofluorite and sulfur trioxide were allowed to react in a nickel vessel of 1.7 liter volume

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(1) R. S. Porter and G. H. Cady, THIS JOURNAL, **79**, 5628 (1957).

(2) F. B. Dudley and G. H. Cady, *ibid.*, **79**, 513 (1957).

(3) K. B. Kellogg and G. H. Cady, *ibid.*, **70**, 3986 (1948).

by slowly increasing the temperature while comparing the observed total pressure with that which one would expect of an ideal gas under the same conditions. Pressures significantly lower than ideal were observed when a reaction occurred. Using vacuum line techniques, a new compound having the formula CF_3OOSO_2F was isolated from the product. Carbonyl fluoride, sulfuryl fluoride and oxygen were also identified as products of the reaction. They may have been the result of a fluorination reaction on sulfur trioxide by trifluoromethyl hypofluorite, but it is more likely that they came from the decomposition of CF_3OOSO_2F. Thermal decomposition of a purified sample of CF_3OOSO_2F produced these three substances.

A larger sample of the product was obtained using a flow-reaction system. The mixture of trifluoromethyl hypofluorite and fluorine issuing from the preparation tube was treated to remove fluorine by allowing it to combine with sulfur trioxide. The fluorine fluorosulfonate so formed was condensed and the remaining stream of relatively pure trifluoromethyl hypofluorite was passed over liquid sulfur trioxide. The resulting mixture of gases entered the main reactor. This was held at 250°, the temperature which gave best results in the earlier experiments with the 1.7 liter nickel reactor. The main reactor was a copper cylinder 4 inches in diameter and 20 inches long containing nine brass baffle plates evenly spaced perpendicular to its long axis. During a 15 hr. run the flow of carbon monoxide was 1.3 liters per hour. The product which was collected in a trap at −78° had a liquid volume of about 15 ml. From this mixture about $1^1/_2$ ml. of CF_3OOSO_2F was isolated by fractional distillation. Most of the liquid product was peroxydisulfuryl difluoride, SO_2FOOSO_2F.

CF_3OOSO_2F was found to react at room temperature with aqueous iodide solutions to produce free iodine but not to react readily with water or concentrated sulfuric acid. The reaction with aqueous sodium hydroxide was slow, but complete within a few hours at 100°, according to the equation

$$CF_3OOSO_2F + 8OH^- = SO_4^{--} + CO_3^{--} + 4F^- + {}^1/_2O_2 + 4\ H_2O$$

Reaction of CF_3OF with SO_2.—Experiments with the 1.7 liter nickel reactor showed that trifluoromethyl hypofluorite and sulfur dioxide react with a net decrease in pressure at 170 to 185°. The crude product was more complex than that from the reaction with sulfur trioxide and contained COF_2, SO_2F_2, SOF_2 and SO_2 together with small amounts of several other substances of higher molecular weight. For the operation of a flow reaction train with sulfur dioxide a supply of pure trifluoromethyl hypofluorite was held in a small nickel cylinder. During a run lasting 18.5 hr. each of the reactant gases flowed at 0.9 liter/hr. About 65 ml. of liquid product was collected in a cold trap.

Ordinary fractional distillation at one atmosphere pressure was only partially successful as a means for separating the mixture into its pure components. The technique of fractional codistillation[4] was successful, however. This technique resembles gas-chromatography, the distillation being conducted in a stream of inert carrier gas. The column used for this separation was of $^5/_{16}$ inch o.d. copper tubing 24 inches long bent into a U shape and filled with 40- to 60-mesh magnesium granules. Good separations were obtained using 0.5 to 0.7 ml. of liquid sample. Only one case of interference between compounds was noticed; SO_2F_2 and CO_2 were not well separated. It is probably significant that their vapor pressure curves cross at about −123°. The following compounds were identified as components of the product mixture: CF_4, CF_3OF, SiF_4, CO_2, SO_2F_2, SO_2, and $S_2O_2F_2$. Four new materials were also found: CF_3SO_3F, $(CF_3)_2SO_4$, $CF_3S_2O_6F$ and $(CF_3)_2S_2O_7$. Small amounts of four other substances with boiling points greater than room temperature were detected but the compounds were not identified.

Analytical.—Analyses of the new substances were accomplished or attempted by hydrolyzing purified samples in aqueous sodium hydroxide, producing sulfate, carbonate and fluoride ions and, in one case, free oxygen. Sulfur was determined gravimetrically as $BaSO_4$. Fluorine was determined either by the precipitation and separation of PbClF, followed by a Volhard titration of the chloride[5,6] or by the precipitation as triphenyltin fluoride.[7] The carbonate content was determined, approximately, by adding barium chloride to the basic solution after hydrolysis. This gave a precipitate of barium sulfate and barium carbonate. The precipitate was washed and was then titrated with hydrochloric acid to the phenolphthalein end-point and then to the methyl orange end-point. The difference gave the amount of carbonate. One of the samples, $(CF_3)_2SO_4$, did not hydrolyze completely; therefore, it was not analyzed. The fluoride determinations were not all satisfactory, probably because of a lack of experience by the analyst.

Analytical data are presented in Table I. They are not as good as would be desired but they, together with the observed molecular weights given in Table III, indicate the correct formulas for the compounds.

TABLE I

ANALYTICAL DATA

	Sulfur, wt. %		Fluorine, wt. %		Carbon, wt. %	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
CF_3OOSO_2F	16.5	17.42	41.9	41.29	5.8	6.53
CF_3SO_3F	19.0	19.09	47.6	45.25	6.2	7.15
$CF_3S_2O_6F$	25.8	25.80	30.7	30.63	4.6	4.84
$(CF_3)_2S_2O_7$	19.6	20.41	40.1	36.29	7.1	7.65

Fluorine was also determined quantitatively by nuclear magnetic resonance. To determine the amount of fluorine attached to carbon in a compound, it was necessary to have a known reference sample containing fluorine bonded to carbon. The reference material was perfluorocyclopentane, C_5F_{10}. This substance gave a single n.m.r. resonance for fluorine, the strength of the signal being proportional to the number of fluorine atoms per ml. in the sample. Immediately after or before taking

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(4) G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

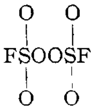
(5) F. G. Hawley, *Ind. and Eng. Chem.*, **18**, 573 (1926).

(6) J. F. Miller, H. Hunt and E. T. McBee, *Anal. Chem.*, **19**, 148 (1947).

(7) N. Allen and N. H. Furman, THIS JOURNAL, **54**, 4625 (1932).

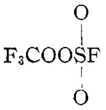
this spectrum, a sample of unknown was used under identical conditions. From the area of its resonance peak(s) for fluorine attached to carbon (and from the reference peak) it was possible to calculate the number of such fluorine atoms per ml. in the liquid unknown. From this and the molar volume of the unknown (obtained from molecular weight and density), the number of atoms of fluorine (attached to carbon) per molecule could be calculated.

A similar procedure was used to determine the number of fluorine atoms attached to sulfur atoms in the molecule. For this the reference substance was peroxydisulfuryl difluoride



$$F\overset{O}{\underset{O}{S}}OO\overset{O}{\underset{O}{S}}F$$

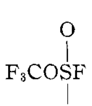
CF_3OOSO_2F.—The n.m.r. peak areas corresponded to 3.3 atoms of fluorine attached to carbon in the molecule and to 0.90 atoms of fluorine attached to sulfur. The strongest peak in the mass-spectrum was for COF^+ with COF_2^+ being second at a relative intensity of 48%. Rupture of the peroxide bond apparently was important in the distribution of the resulting ions. This is the only one of the five new compounds which liberated iodine from a solution containing I^- or which gave oxygen upon hydrolysis. The probable structure is



$$F_3COO\overset{O}{\underset{O}{S}}F$$

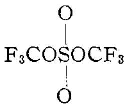
The proposed name is trifluoromethyl peroxyfluorosulfonate.

CF_3SO_3F.—Analysis by n.m.r. indicated 3.3 atoms of fluorine attached to carbon in the molecule and 1.0 atom of fluorine attached to sulfur. The strongest peak in the mass spectrum was for CF_3^+. This was followed by SO_2F^+ at a relative intensity of 25%—definite evidence for fluorine bound to sulfur. The compound required several hours for complete hydrolysis in aqueous sodium hydroxide solution at 100°. The name, trifluoromethyl fluorosulfonate, corresponds to the probable structure



$$F_3CO\overset{O}{\underset{O}{S}}F$$

$(CF_3)_2SO_4$.—The n.m.r. spectrum indicated 6.3 atoms of fluorine attached to carbon in the molecule and no fluorine attached to sulfur. The strongest peak in the mass-spectrum was for CF_3^+ and the next strongest, at relative intensity 6.5%, was for SO^+. This compound was only partially hydrolyzed upon contact with 5 M NaOH at 100° for 39 hr. The name, bis-(trifluoromethyl) sulfate corresponds to the probable structure



$$F_3CO\overset{O}{\underset{O}{S}}OCF_3$$

$CF_3S_2O_6F$.—The n.m.r. spectrum indicated 3.0 and 1.0 atoms of fluorine per molecule attached to carbon and to sulfur, respectively. The strongest peak in the mass-spectrum was due to CF_3^+ and the next smaller ones were SO_2F^+ (21% relative intensity) and SO^+ (16% relative intensity). This substance hydrolyzed immediately upon contact with 5 M NaOH at room temperature. The

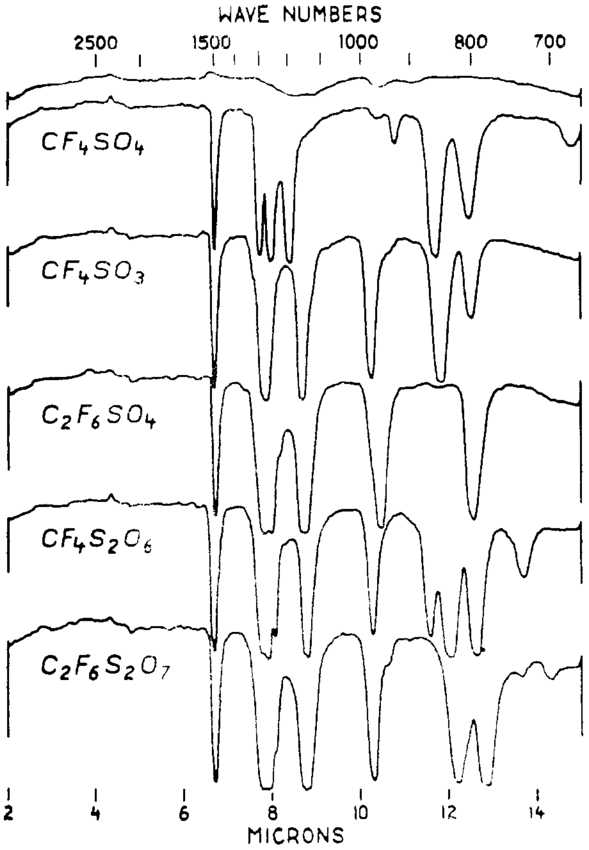


Fig. 1.

TABLE II

VAPOR PRESSURE DATA

CF_3OOSO_2F	
T, °C.	p, mm.
−40.1	51.9
−25 3	126.2
−16.5	201.0
− 7.5	315.5
− 2.0	401.1
+ 5.4	562
6.4	584
12.1	736
12.9	762

$(CF_3)_2SO_4$	
T, °C.	p, mm.
−54.3	5.6
−29.1	39.3
− 9.1	126.7
+ 3.9	246.8
12.6	357.8
16.6	432
21.3	511
25.0	597
30.1	731
31.6	761

CF_3SO_3F			
T, °C.	p, mm.	T, °C.	p, mm.
−79.0	9.4	−28 3	245.7
−70.0	16.6	−24.9	291.1
−65.0	26.0	−21.1	351.8
−57.0	47.8	−20.4	381
−52.0	63.9	−18.3	403
−46.0	92.3	−16.7	442
−43.6	103.4	−16.2	465
−41 0	127.8	−13.8	500
−39.5	134.7	−11.5	549
−34.0	179.1	−11.2	563
−32.4	195.3	− 9.1	626
−30.7	227 3	− 9.0	612
		− 6.7	687
		− 6.5	690
		− 5.2	726
		− 3.8	768

$CF_3S_2O_6F$	
T, °C.	p, mm.
+19.6	70.5
34.8	147.4
49.4	277.6
54.5	345.9
63.3	485
72.1	651
73 2	685.2
78.5	803

$(CF_3)_2S_2O_7$	
T, °C.	p, mm.
+55.0	143.0
70.7	277.4
83.9	453.6

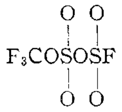
TABLE III

PHYSICAL CONSTANTS

	CF_3OOSO_2F	CF_3SO_3F	$(CF_3)_2SO_4$	$CF_3S_2O_6F$	$(CF_3)_2S_2O_7$
M.p., °C.	−117	−121	−99	.....[a]	−66
B.p., °C.	12.9	− 4.2	31	76	98
ΔH_{vap}, kcal./mole	6.61	6.11	6.86	8.21	9.15
Trouton constant	23.1	22.7	22.5	23.5	24.6
Vapor density, g./GMV					
Exptl.	184	167	234	250	317
Calcd.	184.1	168.1	234.1	248.1	314.1
Liquid density, g./ml. (t, °C.)	1.98 (−117)	1.78 (−42)	1.890 (−74.9)	1.916 (−32.4)	1.72 (27)
	1.56 (25)	1.63 (0)	1.839 (−57.7)	1.761 (22.5)	
		1.60 (5)	1.740 (−25.5)		
		1.58 (10)	1.592 (18.1)		

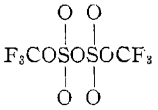
[a] $CF_3S_2O_6F$ formed a glass: no crystalline phase was observed.

name, trifluoromethyl fluorodisulfate, corresponds to the probable structure



$F_3CO\overset{O}{\underset{O}{S}}O\overset{O}{\underset{O}{S}}F$

$(CF_3)_2S_2O_7$.—The n.m.r. spectrum indicated 5.8 atoms of fluorine attached to carbon in the molecule but no fluorine attached to sulfur. The principal peak in the mass-spectrum was for CF_3^+ and this was followed by COF^+ at 10% relative intensity. The hydrolysis was complete only after several hours of contact with 5 *M* NaOH at 100°. The name bis-(trifluoromethyl) disulfate corresponds to the structure



$F_3CO\overset{O}{\underset{O}{S}}O\overset{O}{\underset{O}{S}}OCF_3$

Tables II and III give physical properties of the five new compounds. Values for ΔH vap. have been calculated from the vapor pressure curves with the aid of the Clausius-Clapeyron equation. The vapor densities are average values for several samples as measured at room temperature using a glass flask. Table IV gives the observed absorption frequencies in the infrared and Fig. 1 shows the spectra.

TABLE IV

MAJOR ABSORPTION BANDS OF THE INFRARED SPECTRA (VALUES IN WAVE NUMBERS, CM.$^{-1}$)[a]

CF_3OOSO_2F	CF_3SO_3F	$(CF_3)_2SO_4$	$CF_3S_2O_6F$	$(CF_3)_2S_2O_7$
1490s	1493s	1490s	1491s	1483s
1300s	1269s	1280s	1283s	1284s
1250s	1149s	1249s	1261s	1252s
1190s	976s	1143s	1238s	1235s
927m	843s	953s	1133s	1137s
855s	799m	795s	971s	968s
805s			863s	778s
680m			830s	733s
			791s	698m
			730m	

[a] s = strong; m = moderate.

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