the smaller deviation from ideality. A smooth curve fits the data for the ternary mixtures except for mixtures 1 and 5, Table I. The calculated heats of solution for these solvents appear to be rather low. It should be noted that if the indicated error in solubility at the high temperature is in one direction and the error at the low end of the range has the opposite sign, a considerable change in the apparent heat of solution would result.

The values shown in Figure 7 for the heat of solution of CeF_3 in the two LiF–BeF_2 mixtures listed in Table I are higher than those calculated for LiF–BeF_2 solvents with higher BeF_2 concentrations[5] and are much greater than more recent values[10] for the heats of solution of NdF_3 and SmF_3 in LiF–BeF_2 (66–34 mol %), 11.5 and 10.5 kcal/mol, respectively. Consequently, the shape of the curve in the low-ThF_4 end of Figure 7 is not firmly established.

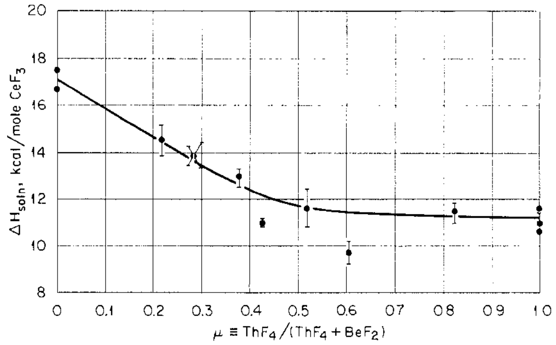

Figure 7.—Correlation of apparent heat of solution with solvent composition.

Acknowledgment.—The authors thank J. H. Shaffer and coworkers for supplying purified solvent compositions and members of the ORNL Analytical Chemistry Division under the supervision of W. R. Laing and L. J. Brady for performing wet chemical analyses.

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Chlorine Monofluoride. Reactions with Sulfur Oxides

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The reactions of ClF with SOF_2, SO_2, and SO_3 are reported. These reactions produce SOF_4, $ClSO_2F$, and $ClOSO_2F$, respectively, in excellent yields. New characterization data for $ClOSO_2F$ are presented and some of its reactions are described. The interaction of ClF with HSO_3F and HSO_3Cl is also reported.

Introduction

Chlorine monofluoride has been shown to react in a variety of ways. For example, it can function as either a Lewis acid[1] forming the ClF_2^- anion or a Lewis base[2] forming the Cl_2F^+ cation. In addition, it can act as a chlorinating agent,[3,4] a fluorinating agent,[5] or a chlorofluorinating material. The latter form of reaction can be either catalyzed[6,7] or uncatalyzed.[8] Our interest in the chemistry of ClF prompted an examination of the course of its reaction with a series of sulfur–oxygen-containing compounds.

Experimental Section

Apparatus.—Reactions were conducted in stainless steel cylinders and the products were separated and purified using a stainless steel–Teflon FEP (polyfluoroethylenepropylene) vacuum line. Pressures were measured by means of a Heise Bourdon-tube type pressure gauge. Infrared spectra were taken on Perkin-Elmer Infracords 137 and 337 using 5-cm path length stainless steel or Kel-F cells fitted with AgCl windows. The ^{19}F nmr spectra were obtained using a Varian Associates high-resolution nmr spectrometer operating at 56.4 Mc. Samples were sealed in Kel-F tubes and $CFCl_3$ was employed as the external standard. Mass spectral data were obtained with a CEC 21-103C mass spectrometer with the inlet system operating at room temperature and employing an ionization voltage of 70 V. A Hanovia 100-W utility lamp (Catalog No. 30620) was used for the photolysis.

Materials.—Chlorine monofluoride was prepared by heating an equimolar mixture of Cl_2 and ClF_3 to 150° for several hours in a stainless steel cylinder. Thionyl fluoride was made from thionyl chloride and NaF in acetonitrile.[9] Sulfur dioxide (Matheson Co.) and sulfur trioxide (Baker and Adamson) were commercial materials and were purified by removal of impurities not condensable at −196°. Fluorosulfonic (Baker and Adamson) and chlorosulfonic (Eastman) acids were used as received. Cesium fluoride and potassium fluoride were fused and then powdered in a drybox prior to use. In all cases the chlorine monofluoride was purified immediately before use by vacuum fractionation through a U trap cooled to −142°.

Reaction of ClF with Thionyl Fluoride.—Thionyl fluoride (102 cm³, 4.55 mmol) and ClF (211 cm³, 9.42 mmol) were successively condensed at −196° into a prepassivated 30-ml cylinder. The cylinder was then allowed to warm from −78° to

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TABLE I

MASS SPECTRUM OF $ClSO_2F$

m/e	Ion[a]	Rel intens	*m/e*	Ion	Rel intens
120	$^{37}ClSO_2F^+$ $Cl^{34}SO_2F^+$	15.54	64	SO_2^+	8.38
118	$ClSO_2F^+$	41.21	51	SF^+	2.43
101	$^{37}ClSO_2^+$	3.04	48	SO^+	11.89
99	$ClSO_2^+$	8.11	37	$^{37}Cl^+$	2.43
85	$^{34}SO_2F^+$	5.40	35	Cl^+	7.19
83	SO_2F^+	100.00	32	S^+	14.59
69	$^{34}SOF^+$ $^{37}ClS^+$	2.70	16	O^+	3.78
67	SOF^+ ClS^+	37.16			

[a] Sulfur-32 and chlorine-35 unless otherwise indicated.

ambient temperature over several hours and left at that temperature overnight. Subsequently the reaction products were separated by fractional condensation in U traps cooled at −126, −142 and −196°. The warmest trap contained Cl_2 and a trace of SO_2FCl while the coldest trap contained unreacted ClF and minor amounts of SOF_2, SOF_4, and SO_2F_2. The intermediate temperature fraction was found to be SOF_4 contaminated with a considerable amount of Cl_2. The latter was removed by reaction with mercury at ambient temperature and in this way pure SOF_4 (90.8 cm^3, 4.05 mmol) was obtained in 90% yields based on the amount of SOF_2 used. The purity and identity of the products were based on vapor pressure and infrared and mass spectral measurements.[10,11] Reactions using equimolar quantities of SOF_2 and ClF were also conducted at ambient temperature and at −78°. These experiments also resulted in the formation of SOF_4 in quite high yield based on one SOF_4 being formed from one SOF_2 and two ClF's.

Reaction of ClF with Sulfur Dioxide.—Sulfur dioxide (127 cm^3, 5.67 mmol) and ClF (162 cm^3, 7.23 mmol) were successively condensed into a 30-ml prepassivated cylinder cooled to −196°. The cylinder was then warmed from −78° to ambient temperature over several hours. Products of the reaction were separated by fractional condensation at −78, −112, −142, and −196°. No unreacted SO_2 was found and only small amounts of Cl_2 and SO_2F_2 were noted along with unreacted ClF. Sulfuryl chloride fluoride (125.3 cm^3, 5.59 mmol) was isolated in the trap cooled at −112° in 99% yield based on the amount of SO_2 used. The product was identified by its infrared[12] and mass spectra (Table I).

Reaction of ClF with Sulfur Trioxide.—In a typical reaction, SO_3 (191 cm^3, 8.53 mmol) and excess ClF were condensed into a prepassivated 30-ml cylinder at −196°. The cylinder was slowly warmed to room temperature (>2-hr warm-up) and fractionation was initiated through traps cooled to −78, −95, −142, and −196°. The −142 and −196° fractions consisted of unreacted ClF with small amounts of Cl_2 and SO_2F_2. The other fractions contained the pale yellow product $ClOSO_2F$ in 90+% yield based on the amount of SO_3 used. Continued pumping on the −78° fraction at that temperature resulted in the distillation of nearly all material from that fractionation. Measurements indicated the material to be pure $ClOSO_2F$: vapor density: obsd, 135.8 g/mol; theoret, 134.5 g/mol; ^{19}F nmr: lit.,[13] singlet at −33.9 ppm; obsd, singlet at −33.3 ppm with no other detectable resonances. In addition, the mass spectrum of the product agreed with that reported[13] for $ClOSO_2F$. The following temperature–vapor pressure data were observed (°C, mm): −31.0, 19; −23.8, 30; −10.0, 66; 0.0, 113; 5.9, 152; 12.7, 209; 20.8, 302. The vapor pressure–temperature relation is described by the equation $\log P_{mm} = 8.0951 - (1650.6/T°K)$. The normal boiling point calculated from the equation is 43.4°, with a heat of vaporization of 7.55 kcal/mol and a Trouton constant of 23.8.

The infrared spectrum of $ClOSO_2F$ has not been reported presumably because of the rapid attack of the compound on cell window materials. For example with AgCl an obscuring backgroup can form almost at once. This background has an infrared spectrum which is nearly identical with that reported[14] for $AgSO_3F$. However, $ClOSO_2F$ that had been fractionated as above resulted in only slow background formation. Furthermore samples that had been distilled at −95° resulted in almost no background buildup. This indicates that this reaction is catalyzed by an impurity. The infrared spectrum of $ClOSO_2F$ is shown in Figure 1 and the principal bands are at 1480 (s), 1248 (s), 855 (s), 832 (sh), 703 (m), 571 (m), and 529 (w) cm^{-1}.

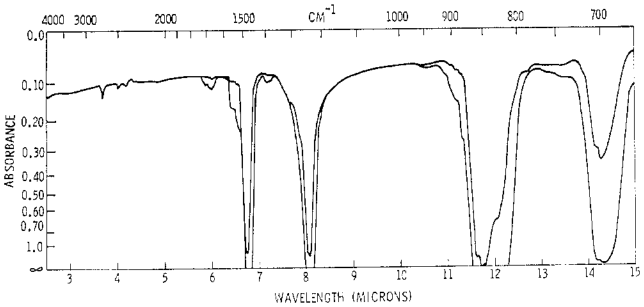

Figure 1.—Infrared spectrum of $ClSO_3F$ at 80 and 8 mm.

Reaction of $ClOSO_2F$ with CsF.—A 10-ml prepassivated cylinder was loaded with CsF (0.58 g, 3.82 mmol) and evacuated and then $ClOSO_2F$ (68.4 cm^3, 3.05 mmol) was added at −196°. The cylinder was allowed to warm to approximately 0° for 30 min before it was recooled to −142° and the material volatile at that temperature was pumped off and trapped at −196°. The volatiles were found by infrared examination to be pure ClF (16.8 cm^3). After rewarming to room temperature for 10 hr an additional 24.4 cm^3 of ClF was removed from the cylinder after recooling to −142°. A subsequent 3-day period at room temperature gave an additional 7.2 cm^3 of ClF and the unreacted $ClOSO_2F$ (20.2 cm^3, 0.90 mmol) was then recovered. The total amount of ClF formed (48.4 cm^3, 2.16 mmol) represented a 71% yield based on the amount of $ClOSO_2F$ used. The white solid left in the cylinder was weighed (0.75 g) and the weight gain was found to agree with that expected for a mixture of 2.16 mmol of $CsSO_3F$ and 1.66 mmol of CsF (0.75 g). The presence of $CsSO_3F$ in the solid was confirmed by comparing its infrared spectrum to that reported[14] for $CsSO_3F$. Potassium fluoride also reacted with $ClOSO_2F$ to generate ClF.

Photolysis of $ClOSO_2F$.—A 100-ml Pyrex bulb equipped with a Fisher–Porter Teflon needle valve was loaded with $ClOSO_2F$ (94 cm^3, 4.2 mmol). While maintaining the bulb at approximately −78°, the contents were irradiated for several hours with uv light. The products of the photolysis were separated by fractional condensation in traps cooled to −78 and −196°. The latter contained practically pure Cl_2 and the former had only $S_2O_6F_2$ (43 cm^3, 1.9 mmol) as determined by its infrared spectrum and vapor pressure.[15]

Reaction of ClF with HSO_3F and HSO_3Cl.—Quantitative data on the reaction of fluorosulfonic acid and ClF were not obtained. However, it was shown that the reaction was not particularly fast since an equimolar mixture of the two materials still had 15% unreacted ClF after 2 hr at room temperature. In addition, appreciable amounts of Cl_2, $FClO_2$, and Cl_2 were formed along with the expected HF. The formation of $ClOSO_2F$ by the reaction was indirectly determined by treating the fraction trapped at −78° with KF. This treatment resulted in a 30% yield of ClF based on the original HSO_3F used. An equimolar quantity of HSO_3Cl and ClF (6.30 mmol each) reacted at room

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temperature to form a nearly quantitative yield of Cl_2 (139 cm^3, 6.20 mmol). The relatively nonvolatile liquid product left was identified as HSO_3F with some unreacted HSO_3Cl by recording the infrared spectrum as a film between AgCl plates and comparing it to the literature spectra.[16]

Results and Discussion

The reaction of thionyl fluoride and ClF

$$SOF_2 + 2ClF \longrightarrow SOF_4 + Cl_2$$

occurred readily to give thionyl tetrafluoride in high yield and provides a useful alternate synthesis of that compound when F_2 is not available. Variation of the reactant ratios and the reaction temperatures (−78 to 25°) did not alter the course of the reaction. The observed, facile oxidative fluorination of thionyl fluoride using ClF is somewhat surprising when compared to the more stringent conditions described[10,17] where elemental fluorine is the fluorinating agent. It is possible that an initial chlorofluorination occurs to give a product such as SOF_3Cl which then is rapidly fluorinated to SOF_4. However, efforts to verify the formation of such an intermediate by using lower temperatures and limited amounts of ClF were not successful. Additional fluorination or chlorofluorination of SOF_4 was not expected or encountered since it does not occur except in the presence of certain alkali metal fluorides.[7]

Sulfur dioxide and chlorine monofluoride react rapidly and completely to give a nearly quantitative yield of sulfuryl chloride fluoride. Additional ClF did not react with $ClSO_2F$ under the present conditions. The reaction

$$SO_2 + ClF \longrightarrow ClSO_2F$$

represents a more convenient synthesis of this material since previous preparations, using SbF_3,[18] NH_4F,[19] or KF in CH_3CN[20] to fluorinate SO_2Cl_2, give lower yields and are more tedious. The exclusive chlorofluorination observed with SO_2 is markedly different from the exclusive fluorination noted with SOF_2 and ClF. No obvious explanation for this difference in reactivity is apparent.

Sulfur trioxide and ClF reacted readily to form chlorine fluorosulfate in high yield

$$SO_3 + ClF \longrightarrow ClOSO_2F$$

Only one other method of preparing $ClOSO_2F$ has been reported[13] and that involved the reaction of Cl_2 and peroxydisulfuryl difluoride. The present reaction offers an attractive alternate since the use of $S_2O_6F_2$ may be hazardous if the potentially explosive impurity, fluorine fluorosulfate,[21] is not completely removed.

While the ClF reactions with SOF_2 or SO_2 involved only attack on the sulfur central atom, in the case of SO_3 addition across one of the S=O double bonds occurred. This is the first example of the uncatalyzed addition of ClF to an S=O group. A previously reported addition[7] to an S=O group (*i.e.*, the conversion of SOF_4 to SF_5OCl) required a catalyst. However, both additions produce compounds containing the ClOSF grouping as would be expected from a consideration of the polarity of the starting materials. Here too no additional fluorination occurred with excess ClF, a result which appears to be typical of high-valent chloroxy-substituted species such as CF_3OCl[6] and SF_5OCl.[7]

Measurements of several properties of $ClOSO_2F$ (vapor density, ^{19}F nmr, and mass spectra) agreed well with the values originally reported.[13] However, all the samples we prepared differed with regard to vapor pressure, our measured values being somewhat higher at all temperatures. This discrepancy may be due to the fact that the original work was carried out in glass with which $ClOSO_2F$ reacts slowly whereas the present work was conducted in a stainless steel–Teflon FEP system with which $ClOSO_2F$ did not show any sign of reaction after proper passivation.

The infrared spectrum of $ClOSO_2F$ which has not been reported previously is shown in Figure 1. The absorptions found were quite similar to those of other covalent fluorosulfates[15,22] and showed the characteristic absorptions for SO_2 (1480, 1248, and 571 cm^{-1}) and SF (855 cm^{-1}) groups. The band observed at 703 cm^{-1} occurs in the range[6,7] characteristic for a Cl–O stretching vibration. A detailed analysis of the vibrational spectrum of $ClOSO_2F$ is in progress.[23]

Chlorine fluorosulfate reacted with KF and CsF as shown by

$$ClOSO_2F + MF \longrightarrow MSO_3F + ClF \qquad (M = K, Cs)$$

This reaction represents the first example of the generation of a chlorine fluoride from a covalent noninterhalogen compound. The liberation of only ClF indicates a preferred attack of the fluoride ion on the positively polarized chlorine atom resulting in the rupture of the Cl–O bond. Comparably substituted compounds such as CF_3OCl and SF_5OCl do not react with alkali metal fluorides under similar conditions.[6,7] Thus, it appears that the stability of the anion formed on breaking the Cl–O bond (SO_3F^- *vs.* CF_3O^- or SF_5O^-) is important in determining whether these compounds are readily susceptible to fluoride ion attack.[24] The related reaction of fluorine fluorosulfate[25] follows a different stoichiometry and has been interpreted as proceeding through a primary attack on the sulfur. This leads to the generation of SO_2F_2 by cleavage of the S–O bond.

Photolysis of $ClOSO_2F$ at low temperature was found to give peroxydisulfuryl difluoride readily

$$2ClOSO_2F \xrightarrow{h\nu} Cl_2 + FSO_2OOSO_2F$$

This reaction is the reverse of the original synthesis[13] of

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$ClOSO_2F$. Cleavage of the Cl–O bond by ultraviolet radiation has been generally observed[6,7] to produce the respective peroxide in good yield.

The reactions of HNO_3 or HNF_2 with ClF have been demonstrated[3,4] to be fast and efficient methods of forming the respective chlorine-substituted compounds $ClNO_3$ and $ClNF_2$. However, fluorosulfonic acid and ClF reacted more slowly and with appreciable formation of the by-products Cl_2, $FClO_2$, and ClO_2. These compounds are indicative of a ClF–H_2O reaction,[26] the latter being an impurity in the commercial HSO_3F used. Nevertheless, $ClOSO_2F$ was obtained in at least 30% yield. Chlorosulfonic acid and an equivalent amount of ClF reacted as shown by

$$HSO_3Cl + ClF \longrightarrow HSO_3F + Cl_2$$

rather than giving the unknown compound, chlorine chlorosulfate. Thus, only fluorination occurred through halogen exchange and no evidence for chlorination of the OH group was obtained.

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Hydrogen Elimination in Dimethylamine–Borane

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The elimination of hydrogen from dimethylamine–borane was studied at 100° by observing the hydrogen isotope distribution in the products resulting from reactants with different hydrogen isotopes on nitrogen and/or boron. The results clearly eliminate the possibility of a unimolecular elimination and favor a bimolecular reaction. Different deuterium isotope effects on the elimination rates were deduced, depending on whether the nitrogen atom or the boron atom was substituted ($k_{N-H}/k_{N-D} = 3.5$; $k_{B-H}/k_{B-D} = 1.2$). Various possible isotopic exchange reactions which could have complicated the study were investigated.

Introduction

Dimethylamine–borane and other borane adducts of primary and secondary amines have been reported to lose hydrogen at elevated temperature to yield aminoboranes, borazine, and redistribution products or substituted boranes.[1–3]

The first step in these reactions has been demonstrated to follow the stoichiometry expressed by

$$R_2NHBH_3 \longrightarrow R_2NBH_2 + H_2 \qquad (1)$$

It would be of interest to determine whether this reaction proceeds *via* a unimolecular elimination, as is the case in a number of organic systems, or whether elimination occurs between more than one molecule. The normal experimental approach, where the rate law would be established from concentration measurements, seemed inappropriate since the amine–boranes are not very volatile nor are they, as mixtures of the products, readily susceptible to quantitative analysis. Moreover, the aminoborane products may dimerize, trimerize, or redistribute to give bis(aminoboranes) and aminodiboranes.[3] Therefore, the problem was approached by labeling boron and/or nitrogen bonds with deuterium and following the reaction by isotopic analysis of the noncondensable products.

Discussion

It was proposed to answer two basic questions in this study. (1) Is the hydrogen elimination reaction in dimethylamine–borane unimolecular or not? (2) What is the magnitude of the hydrogen isotope effect?

The first question was answered by the first two experiments in Table I, where mixtures of about equal proportions of undeuterated and completely deuterated compounds were heated or where mixtures of $(CH_3)_2NHBD_3$ and $(CH_3)_3NDBH_3$ were heated. Intramolecular hydrogen elimination should, in the first instance, produce only H_2 and D_2, whereas in the second instance, only HD should be formed. Incomplete deuteration might in either set introduce a small quantity of the missing isotopic variety of molecular hydrogen. On the other hand, intermolecular hydrogen elimination should produce all three hydrogen species in propor-

Table I

Decomposition of Deuterated Dimethylamine–Boranes

Isotopic species	Amt of species, mmol	% reaction	% products		
			D_2	HD	H_2
$(CH_3)_2NDBD_3$	0.82	31.3	11.0	47.7	41.3
$(CH_3)_2NHBH_3$	0.77				
$(CH_3)_2NDBH_3$	0.50	32.8	12.9	46.5	40.6
$(CH_3)_2NHBD_3$	0.48				
$(CH_3)_2NDBD_3$	1.05	38	83.1	16.9	...
$(CH_3)_2NDBD_3$	1.47	3.9	60.5	39.5	...

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