and $(CH_3)_2ClSnSO_3F$ have unexpectedly large Δ values. For the former it has been suggested[6] that the large splitting and the position of ν(Sn–Cl) may indicate the presence of weak chlorine bridging. For the latter, the occurrence of ν(Sn–Cl) in the same region as found for $(CH_3)_2ClSnF$ tempts us to suggest the possibility of some chlorine bridging here as well. If chlorine bridging *is* present in these compounds, leading to quasi-octahedral structures, there could well be a reorientation of the *z* axis of the field-gradient tensor. Thus, determination of the signs of the quadrupole coupling constants in these two derivatives would be of considerable interest, and we hope to report such measurements in the near future.

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The Reaction of Fluorosulfuric Acid with Xenon Fluorides. Synthesis of Pentafluoroxenon Fluorosulfate

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No evidence was obtained for a xenon(IV) fluorosulfate and only the previously reported xenon(II) fluorosulfates $FXeOSO_2F$ and $Xe(OSO_2F)_2$ are formed on reaction with XeF_4. Xenon hexafluoride forms only XeF_5OSO_2F on reaction with fluorosulfuric acid. Pentafluoroxenon fluorosulfate is a stable white solid at 22° which melts with decomposition above 73°. Raman and ^{19}F nmr spectra have been used to characterize the compound.

Introduction

The ability of xenon to form chemical compounds is now well established.[1] Until recently, the known compounds were of three general types: (1) fluorides formed by reaction of xenon with strong oxidative fluorinating reagents, (2) oxides and oxyfluorides formed from reactions of the xenon fluorides, and (3) a variety of complex compounds formed by the xenon fluorides and oxyfluorides with various fluoride donors and acceptors.

Recently several investigators have reported compounds of xenon(II) formed by substitution with xenon difluoride[2-6] and there have been two reports of xenon(IV) and -(VI) compounds formed by analogous reactions.[7,8] The latter claims have recently been questioned[9,10] and this work was undertaken to identify the species formed in reactions of xenon hexafluoride and xenon tetrafluoride with fluorosulfuric acid.

Experimental Section

General.—Volatile compounds were handled in a 316SS-Kel-F vacuum system or a glass system equipped with glass–Teflon valves. Pressures were measured with a precision Heise Bourdon gauge in the metal system and in a Wallace and Tiernan differential pressure gauge in the glass system. All-metal Kel-F, FEP, and Teflon equipment was preconditioned with ClF_3 before handling XeF_6 and XeF_4.

All reactions involving XeF_6 and XeF_4 were carried out in ∼6-ml Kel-F reactors fitted with 316 SS or Teflon diaphragm valves. Amounts of all reactants and products were determined by weight or *PVT* measurements. Molecular weights of gases were determined by *PVT* measurements employing a Wallace and Tiernan differential pressure gauge. Identification of volatile products was made by infrared spectra, physical properties, and vapor density molecular weight.

Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer with a 10-cm Monel or glass cell fitted with silver chloride windows. Raman spectra were taken on a Spex 4001 argon laser instrument using the 465.8 nm line for excitation. Samples were prepared and run in $^1/_4$ in. o.d. FEP tubes directly.

Fluorine nmr spectra were taken on a Varian XL-100 instrument using internal $HOSO_2F$ as a reference and proton lock source. Samples were contained in $^3/_8$ in. o.d. Kel-F tubes prepared as described above for the Raman spectra. The Kel-F sample tubes were inserted into standard glass nmr tubes to record the spectra.

Reagents.—Xenon hexafluoride was prepared by heating a 30:1 fluorine–xenon mixture at 230° for 5 days. The calculated pressure assuming ideal gas behavior was 300 atm. The XeF_6 was collected in a Monel–Kel-F U-trap cooled to −25°. The ir spectrum at 25 mm showed no $XeOF_4$. Under these conditions the amount of XeF_4 contamination was assumed to be small.[11]

Xenon tetrafluoride was obtained by heating a 7:1 ratio of fluorine to xenon in a 150 ml Monel reactor for 3 hr at 400°. The total pressure at 400° was calculated to be 7 atm assuming ideal gas behavior. The XeF_4 was collected at −5° in Monel–Kel-F U-trap. The ir at the equilibrium vapor pressure of XeF_4 at 28° showed only XeF_4.

Fluorosulfuric acid was doubly distilled in an all-glass apparatus and a middle fraction boiling at 163.0° was collected in a vessel fitted with a glass–Teflon valve. After collection the storage vessel was flamed off from the distillation setup and evacuated. Sulfur trioxide was obtained from the General

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TABLE I

REACTIONS OF XENON FLUORIDES

Reactants[a]	Conditions	Products[a,b]
XeF_6 1.44, $HOSO_2F$ 1.44	−22 to −5°, 3 days	F_5XeOSO_2F 1.44, HF 1.46
XeF_6 1.47, $HOSO_2F$ 2.99	−22 to −5°, 3 days	F_5XeOSO_2F,[c] $HOSO_2F$, HF–$S_2O_6F_2$ 0.064 g
XeF_6 1.22, $HOSO_2F$ 4.76	25°, 3 days	F_5XeOSO_2F, $HOSO_2F$, HF–$S_2O_6F_2$ 0.045 g
	45–50°, 5 days	F_5XeOSO_2F,[c] $HOSO_2F$, HF–$S_2O_6F_2$ 0.511 g, Xe 0.66
F_5XeOSO_2F 1.17	20–28°, 3 weeks	F_5XeOSO_2F 1.17
	80°, 30 min	XeF_6 0.90, Xe 0.23, $S_2O_6F_2$ 0.64
XeF_6 1.11, SO_3 1.53[d]	22°, 1 hr	XeF_6–SO_3 0.271 g, $S_2O_6F_2$ 0.53
	70°, 10 min	XeF_6 0.81, $S_2O_6F_2$ 0.80, Xe 0.29
XeF_4 2.01, $HOSO_2F$ 2.00	−22 to +5°, 3 days	XeF_4–$FXeOSO_2F$ 0.382 g, HF–$S_2O_6F_2$ 0.190 g, Xe 0.37
	80°, 15 min	XeF_4–XeF_2 0.315 g, HF–$S_2O_6F_2$ 0.236 g, Xe 0.49
XeF_4 1.30, $HOSO_2F$ 2.56	−22 to +5°, 3 days	XeF_4–$Xe(OSO_2F)_2$–$FXeOSO_2F$ 0.270 g, HF–$S_2O_6F_2$ 0.233 g, Xe 0.17
	20–28°, 5 days	XeF_4–XeF_2 0.164 g, $S_2O_6F_2$ 1.26, HF 2.6, Xe 0.47
XeF_4 1.50, $HOSO_2F$ 6.03	−22 to +5°, 2 days	$Xe(OSO_2F)_2$ 1.49, HF–$S_2O_6F_2$ 0.422 g
$Xe(OSO_2F)_2$ 1.49, XeF_4 0.74	20–25°, 3 days	XeF_4–XeF_2–$FXeOSO_2F$ 0.255 g, Xe 0.90, $S_2O_6F_2$ 1.39
	70°, 1 hr	XeF_4–XeF_2 0.230 g, Xe 1.01, $S_2O_6F_2$ 1.49

[a] Amounts are in millimoles except where grams are specified. [b] Small amounts of oxygen were observed in some instances but the amounts were too small to measure. Amounts of products in each reaction are cumulative. [c] Identified by ^{19}F nmr. [d] Similar results were obtained when a 3:1 mole ratio of $SO_3:XeF_6$ was used.

Chemical Division of Allied Chemical Corp. and used without further purification.

Reactions of XeF_6 and XeF_4 with $HOSO_2F$.—The reactions of XeF_6 and XeF_4 with $HOSO_2F$ were carried out in identical ways as follows. The xenon fluoride was condensed into a conditioned, preweighed Kel-F or FEP reactor at −196° and weighed. The $HOSO_2F$ was then added to a glass–Teflon vessel by vacuum transfer in an all-glass–Teflon–Kel-F vacuum line. After the desired amount of $HOSO_2F$ was obtained by trial and error, the contents of the vessel were condensed onto the xenon fluoride held it −196°. The reaction was then placed in an ice–salt bath at −22° and allowed to warm slowly.

After the reactor had reached the desired temperature it was warmed to room temperature and weighed. Oxygen was then checked for at −196°, followed by xenon at −111° and HF and $S_2O_6F_2$ at −10°. Xenon and O_2 were identified by their physical properties, by lack of any infrared absorptions and also in the case of Xe by vapor density molecular weight. Hydrogen fluoride was identified by its physical properties, by rapid formation of SiF_4 in a glass ir cell, and by its ir spectrum in a metal cell. The remaining products were identified where possible by their characteristic infrared spectra. Comparison was made in each case with a known sample run under similar conditions and with literature spectra (XeF_6,[12] XeF_4,[13,14] XeF_2,[15,16] and $S_2O_6F_2$[17]). The data for some representative reactions are given in Table I.

Results

Reaction of XeF_6 with $HOSO_2F$.—Xenon hexafluoride reacts rapidly at −22° with fluorosulfuric acid according to the equation

$$XeF_6 + HOSO_2F \longrightarrow F_5XeOSO_2F + HF$$

The reaction is quantitative when pure xenon hexafluoride is used and no further reaction of F_5XeOSO_2F occurs at this temperature. Even at 22°, the rate of reaction of F_5XeOSO_2F with fluorosulfuric acid is slow and only at temperatures above 40° does the rate become appreciable. At elevated temperatures reaction of F_5XeOSO_2F with fluorosulfuric acid forms xenon, hydrogen fluoride, and peroxydisulfuryl difluoride according to the equation

$$F_5XeOSO_2F + 5HOSO_2F \longrightarrow Xe + 5HF + 3S_2O_6F_2$$

No evidence was obtained for any other intermediate xenon compounds.

Pentafluoroxenon fluorosulfate is a white crystalline solid which melts with decomposition above 73°. The compound decomposes completely on heating at 80° as shown.

$$6F_5XeOSO_2F \longrightarrow Xe + 5XeF_6 + 3S_2O_6F_2$$

The Raman and ^{19}F mnr spectra for the compound are summarized in Table II and the ^{19}F nmr provides unequivocal proof for the presence of the pentafluoroxenon moiety. No S–F resonance other than that of the solvent was observed indicating the coincidence of the S–F resonance of F_5XeOSO_2F with that of fluorosulfuric acid. This is probably due to the complete ionization of XeF_5OSO_2F in fluorsulfuric acid to F_5Xe^+ and SO_3F^-.

TABLE II

RAMAN AND ^{19}F NMR OF F_5XeOSO_2F

Raman,[a] cm^{-1}	Rel intens	^{19}F nmr[b,c]
1250 br, $\nu_{as}(SO_3)$	29	$\mathit{F}\mathrm{XeF}_4^+$
1085, $\nu_s(SO_3)$	80	δ −188.0
795, $\nu(SF)$	9	Multiplicity 13
650 p, $\nu(Xe–F)$	160	J_{FF} = 178 Hz
595 p, $\nu_s(XeF_4)$	120	$J_{^{129}Xe-F}$ = 1377 Hz
564	~5	
543	~5	$\mathrm{FXe}\mathit{F}_4^+$
417	18	δ −68.9
375	3	Multiplicity 5
356	12	J_{FF} = 179 Hz
333	3	$J_{^{129}Xe-F}$ = 170 Hz
300	17	
250	3	
220	19	

[a] br = broad, p = polarized. [b] δ ppm relative to $HOSO_2\mathit{F}$ at 94.1 MHz and a temperature of −60°. [c] This spectrum is in agreement with that obtained by R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *Chem. Commun.*, 607 (1972).

Reaction of XeF_4 with $HOSO_2F$.—Xenon tetra-

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fluoride reacts slowly with fluorosulfuric acid at −22 to +5° forming hydrogen fluoride, peroxydisulfuryl difluoride, and apparently mixtures of $FXeOSO_2F$, $Xe(OSO_2F)_2$, and unreacted XeF_4 depending on the stoichiometry used. With a 1:4 stoichiometry the reaction is quantitative as shown

$$XeF_4 + 4HOSO_2F \longrightarrow Xe(OSO_2F)_2 + S_2O_6F_2 + 4HF$$

At higher ratios of XeF_4 to $HOSO_2F$, hydrogen fluoride and peroxydisulfuryl difluoride are formed in amounts that indicate complete reaction of fluorosulfuric acid and reduction of part of the Xe(IV):Xe(II). The xenon products formed under these conditions are liquids or low-melting solids. They decompose on standing at ambient temperature forming xenon and peroxydisulfuryl difluoride in a 1:1 mole ratio. After complete decomposition to yield the theoretical amount of peroxydisulfuryl difluoride, a crystalline solid remains that is a mixture of XeF_4 and XeF_2. These results are consistent with the presence of $Xe(OSO_2F)_2$ and $FXeOSO_2F$ which decompose according to the equations[2,3]

$$Xe(OSO_2F)_2 \longrightarrow Xe + S_2O_6F_2$$
$$2FXeOSO_2F \longrightarrow Xe + XeF_2 + S_2O_6F_2$$

In order to further clarify these mixtures a sample of $Xe(OSO_2F)_2$ was allowed to react with XeF_4. On standing at room temperature the mixture rapidly formed a pale yellow liquid. This liquid decomposed over several days to a crystalline solid and a colorless liquid which were shown to be XeF_4, XeF_2, Xe, and $S_2O_6F_2$. The relative amounts of XeF_2 and XeF_4 were not determined but there is little doubt that some of the $Xe(OSO_2F)_2$ and XeF_4 were converted to XeF_2. These observations also indicate that the liquid or low-melting xenon products noted earlier are mixtures of XeF_4, XeF_2, $FXeOSO_2F$, and probably $Xe(OSO_2F)_2$.

Discussion

The results presented here indicate that the earlier report[7] of a xenon(VI) fluorosulfate, $F_4Xe(OSO_2F)_2$, and xenon(IV) fluorosulfate, $F_2Xe(OSO_2F)_2$, was incorrect.[18] No evidence is obtained for these compounds when pure xenon hexafluoride and xenon tetrafluoride are allowed to react under similar conditions. At present there is evidence for only three xenon fluorosulfates, $Xe(OSO_2F)_2$, $FXeOSO_2F$, and F_5XeOSO_2F. The latter compound is the most stable of the three and many other pentafluoroxenon derivatives are likely.

The Raman spectrum of pentafluoroxenon fluorosulfate is consistent with formulation of the compounds as $F_5Xe^+SO_3F^-$. Presumably F_5Xe^+ has C_{4v} symmetry as has been shown for other isoelectronic species[19–22] and SO_3F^- has C_{3v} symmetry. The Raman lines at 1250 and 1085 cm^{-1} are assigned to $\nu_{as}(SO_3)$ and $\nu_s(SO_3)$, respectively. These values are in good agreement with those of ionic fluorosulfates[23–25] and are rather inconsistent with the S–O stretches expected for a covolent OSO_2F group.[26] However, the broad 1250 cm^{-1} frequency may be due in part to an unresolved splitting of this E mode by covalent interaction with F_5Xe^+. The very strong Raman lines at 650 and 595 cm^{-1} are assigned to $\nu(XeF)$ axial and $\nu_s(XeF_4)$ of F_5Xe^+. Similar strong lines occur in the spectrum of $F_5Xe^+AsF_6^-$[27] and the fact that these lines are polarized is consistent with this assignment. Both of these Raman bands shift to higher frequencies by about 20 cm^{-1} when the spectrum is taken of a fluorosulfuric acid solution. Assignment of the other Raman bands are complicated by the overlap of SO_3F^- and F_5Xe^+ frequencies.

The ^{19}F nmr of F_5XeOSO_2F in fluorosulfuric acid provides unequivocal proof for the presence of F_5Xe^+. The axial fluorine shows 13 of the expected 15 lines (a quintet with ^{129}Xe doublets for each line of the multiplet and $^1/_2$ of each doublet of the outermost lines overlapping with these) and the equatorial fluorines show the expected five-line multiplet. The spectra are temperature dependent, which is probably due to intermolecular exchange caused by the presence of hydrogen fluoride. The rate of exchange varied between the different samples providing further support for the above rationale.

The decomposition of pentafluoroxenon fluorosulfate may occur *via* the intermediate formation of xenon hexafluoride and sulfur trioxide. This mode of decomposition for fluorosulfates is well known[28–30] and, in support of this, it was found that XeF_6 reacts with SO_3 according to the equation

$$XeF_6 + 6SO_3 \longrightarrow Xe + 3S_2O_6F_2$$

No lower fluorides of xenon were observed and it appeared that some F_5XeOSO_2F may have been formed initially. The alternative to the above would be the formation of SO_3F radicals directly but there is no proof that any known fluorosulfates actually decompose in this way.[31]

From the reaction of XeF_6, XeF_4, XeF_2, $FXeOSO_2F$, and F_5XeOSO_2F with fluorosulfuric acid, a relative ordering of stabilities in fluorosulfuric acid can be established as follows: $F_5Xe^+ \gg XeF_4 \geq FXe^+ > XeF_6 \geq XeF_2$. This ordering is based on the following observations: (1) XeF_6 and XeF_2 react with $HOSO_2F$ at lower temperatures than XeF_4, and XeF_2 appears to react at an even lower temperature than XeF_6; (2) the nmr of FXe^+ has been observed in $HOSO_2F$ at low temperatures but $FXeOSO_2F$ will react with HO-

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(18) The author wishes to express his gratitude to Professor R. J. Gillespie for pointing out the possible discrepancies in this work. In repeating the earlier work it was obvious that mixtures of xenon fluorides had been used and not pure XeF_6 and XeF_4. In fact the two compounds reported, $F_4Xe(OSO_2F)_2$ and $F_2Xe(OSO_2F)_2$, both contained a high percentage of F_5XeOSO_2F. The latter compound was also obtained previously (M. Eisenberg, Ph.D. Thesis, Northeastern University, 1971), but the properties reported for it indicate that it was not obtained very pure.

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SO_2F at −75° to form $Xe(OSO_2F)_2$;[32,33] and (3) F_5Xe-OSO_2F reacts very slowly with $HOSO_2F$ at 22°. In conclusion it seems likely that a variety of pentafluoroxenon compounds are possible where the very stable XeF_5^+ could exist in combination with anions resistant to oxidation and fluorination.

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Electrochemical Reduction of Sulfur Dioxide in Dimethylformamide

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The reduction of sulfur dioxide in dimethylformamide has been investigated by means of cyclic voltammetry, chronopotentiometry, and controlled-potential electrolysis. At a gold electrode SO_2 is reduced by a one-electron process to a product which is complexed by SO_2 to give a blue species (580 nm). The reduction product also dimerizes to dithionite, $S_2O_4^{2-}$, which is complexed at low SO_2 concentrations to give a red species (485 nm). On the basis of the electrochemical and spectroscopic data, mechanisms are proposed for the reduction of SO_2 and the subsequent equilibration reactions. The equilibrium constants for the dimerization reaction and the complexation reaction of SO_2 with dithionite have been determined.

An electrolyzed solution of SO_2 in dimethylformamide (DMF) exhibits esr lines which have been assigned to two postulated reduction products of SO_2, an anion radical and its complex (eq 1, 2).[1] On the basis

$$SO_2 + e^- \rightleftarrows SO_2^- \qquad (1)$$

$$xSO_2 + SO_2^- \rightleftarrows (SO_2)_xSO_2^- \qquad K \qquad (2)$$

of a temperature study of the esr data the value of K was found to be 1.86×10^6 at 0° with x assumed to be 2.

Rinker and Lynn[2,3] reduced sulfur dioxide with sodium amalgam to produce a blue radical in dimethylformamide. On the basis of spectroscopic studies the blue species was concluded to be $(SO_2)SO_2^-$. Upon standing $Na_2S_2O_4$ was found to precipitate out of solution.

More recently[4] the electrochemical reduction of SO_2 in dimethyl sulfoxide was reported with dithionite ($S_2O_4^{2-}$) and SO_2^- as the primary products. The present paper summarizes the results of an electrochemical and spectroscopic study of sulfur dioxide reduction in dimethylformamide and the chemistry of the several product species that are formed in solution.

Experimental Section

Electrochemical measurements were made with an instrument based on Philbrick operational amplifiers[5] or one constructed from solid-state components.[6] A Moseley Model 7030A X-Y recorder and a Sargent Model SR recorder were used with the above instruments.

A three-electrode system was employed for all measurements with the platinum counterelectrode isolated by a fine-porosity glass frit from the working electrode compartment. The reference electrode was an aqueous silver–silver chloride electrode corrected to 0.000 V *vs.* sce by adjustment of the tetramethylammonium chloride concentration. Connection to the sample solution was by means of a cracked glass-bead tip immersed into a Luggin capillary filled with the supporting electrolyte solution. Three types of working electrode were used: a gold-foil electrode for coulometry, a gold-inlay electrode (made by sealing a gold rod in a polyethylene tube), and a platinum-inlay electrode (Beckman No. 39273).

Controlled-potential coulometry was performed in a Dry-Lab glove box with a large gold-foil electrode. For cyclic voltammetry and chronopotentiometry air was excluded by first bubbling the solution with nitrogen and then maintaining a steady stream of nitrogen over the surface.

Spectroscopic measurements were made with a Cary Model 14 spectrophotometer. Solutions were transferred to the cells and stoppered with ground-glass stoppers under a dry nitrogen atmosphere. The supporting electrolyte concentration was adjusted to 0.25 *F* for all of the spectroscopic studies.

Mallenckrodt reagent grade dimethylformamide was dried over calcium hydride and distilled at 50 Torr. The supporting electrolyte, tetraethylammonium perchlorate (TEAP), was prepared from Matheson Coleman and Bell tetraethylammonium bromide (99%) and Mallenckrodt perchloric acid (70%), reagent grade, and was recrystallized from water three times.

Matheson anhydrous sulfur dioxide was used without purification. Stock solutions were prepared by dissolving sulfur dioxide in previously degassed dimethylformamide. Analysis of SO_2 in the stock solution was performed by adding an aliquot to a known concentration of iodine solution and back-titrating with thiosulfate. Sulfur dioxide concentrations also were determined by titration with standardized base.

Results

Reduction of sulfur dioxide in dimethylformamide yields a well-defined cyclic voltammogram, as illustrated in Figure 1, with a cathodic peak at −0.84 V *vs.* sce and an anodic peak at −0.74 V *vs.* sce. This is in close agreement with the observations of Bonnaterre and Cauquis[4] for dimethyl sulfoxide solutions. In ad-

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