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Fluorosulfates and Perchlorates of Xenon(II) and the Salt $[(FXeO)_2S(O)F]^+[AsF_6]^-$

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Each of the fluorine ligands of XeF_2 may be substituted by highly electronegative species. Interaction of XeF_2 with the appropriate molar quantity of anhydrous acid yields $FXeOSO_2F$ (colorless, mp 36.6°), $Xe(OSO_2F)_2$ (pale yellow, mp 43–45°), $FXeOClO_3$ (colorless, mp 16.5°), $Xe(OClO_3)_2$ (a yellow solid, which decomposes below 0°), and $FXeOSO_2CF_3$ and $FXeOSO_2CH_3$ (both of which are colorless solids). All of the compounds are thermodynamically unstable and the last three compounds are known to be detonators. Decomposition of the fluorosulfates provides for the synthesis of high-purity $S_2O_6F_2$. The acids HCl, $HOSO_2Cl$, and $HOC(CF_3)_3$ do not yield Xe derivatives and are oxidized. Vibrational spectroscopic evidence indicates that the xenon atom in the Xe(II) compounds is similarly coordinated to Xe in XeF_2 and $FXeOSO_2F$. Attempts to prepare $[XeOSO_2F]^+[MF_6]^-$ salts (M = Ru, As, Sb) have not been successful but the new cation $[(FXeO)_2S(O)F]^+$ has been isolated in the $[AsF_6]^-$ salt. Efforts to prepare $[(FXe)_2L]^+$ ($L^- = CF_3CO_2^-, Cl^-$) resulted in oxidation of L.

Introduction

The fluorides and substituted fluorides of xenon are thermodynamically stable, whereas the oxides are highly endothermic.[2] There is no indication that a neutral xenon chloride will be kinetically stable enough to persist at ordinary temperatures, although the matrix-isolation work of Nelson and Pimentel[3] has established that xenon dichloride can be made from the elements in a glow discharge. The bonding in chlorides and other halides is significantly weaker[2a,3] than in the fluorides.[4] The experimental evidence, therefore, suggests that only the most electronegative ligands can generate the bond strength essential to ensure the persistence of noble gas compounds under ordinary temperatures and pressures and this view is also supported by theoretical considerations.[5]

Earlier studies, in these laboratories, involving xenon difluoride as an oxidative fluorinator,[6] suggested that the fluorosulfate ligand could make an effective bond to xenon. We, therefore, sought xenon fluorosulfates and perchlorates, by metathesis from the difluoride: $XeF_2 + HA \rightarrow FXeA + HF$; $FXeA + HA \rightarrow XeA_2 + HF$. Independent investigation, by Musher,[7] into the possibility of xenon esters, $Xe(OR)_2$, demonstrated that acetates and trifluoroacetates could be prepared. Musher suggested that fluorosulfates and related compounds would also be preparable. Subsequent investigations of the XeF_2–CF_3COOH system by DesMarteau and Eisenberg[8] and independent ones by Sladky[9] have established the existence of xenon(II) trifluoroacetates.

Both the perchlorate and fluorosulfate ligands are strongly electron attracting and the generation of hydrogen fluoride (a very thermochemically favorable compound[10]) gave promise of a forward reaction. The syntheses are effective if the stoichiometry, temperature, and hydrogen fluoride removal are properly controlled. The monosubstituted compounds are more stable than the disubstituted and are, therefore, more easily made and handled than the latter. A brief description of the monosubstituted compounds has already been given,[11] and the crystal and molecular structure of $FXeOSO_2F$ has been given in a recent paper.[12] The chemical and physical behaviors of the fluorosulfates and perchlorates show that they are derivatives of bicovalent xenon(II) and the preliminary chemical evidence suggests that they will be effective sources of the fluorosulfate and perchlorate radicals, respectively.

The moderate thermal stability of the xenon fluorosulfates suggested that trifluoromethyl sulfates and even the methyl sulfates might be preparable. Although reactions to produce these compounds did proceed, under control, at temperatures of −20° or lower, the solid products usually detonated at or below room temperatures. The interaction of XeF_2 with a slight molar excess of $HOSO_2CF_3$ in HF has yielded a solid product which is indicated by vibrational spectroscopic evidence to be CF_3SO_3XeF.

Since work in these laboratories[13] and independent work by Peacock and his coworkers[14] have established XeF_2 to be a F^- donor, we have tried to make the $(XeOSO_2F)^+$ salts by the interactions $FXeOSO_2F + MF_5$ (M = Ru, As, Sb). Products of these reactions are (except for the Sb system) labile and remain ill defined, but the new complex cation $[(FXeO)_2S(O)F]^+$ has proved easy to generate and is relatively stable thermally.

Experimental Section

Materials.—**Xenon difluoride** was obtained by the method of Streng and Streng[15] and Holloway[16] as modified by Williamson.[17]

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(2) (a) This difference is largely a consequence of the bond energy of molecular O_2 being greater than that of F_2 (110 *vs.* 37 kcal mol^{-1}) although the bond energy for Xe–O is less tban for Xe–F: V. I. Pepekin, Y. A. Lekedev, and A. Y. Apin, *Zh. Fiz. Khim.*, **43**, 1564 (1969) (for $\Delta H_f°(XeF_2)$); L. Stein and P. L. Plurien in "Noble Gas Compounds," H. H. Hyman, Ed., Chicago University Press, Chicago, Ill., 1973, p 144 (for $\Delta H_f°(XeF_4)$ and $\Delta H_f°(XeF_6)$). (b) S. R. Gunn, *J. Amer. Chem. Soc.*, **87**, 2290 (1965).

(3) L. Y. Nelson and G. C. Pimentel, *Inorg. Chem.*, **6**, 1758 (1967).

(4) N. Bartlett, First Noranda Award Address, Toronto, June 8, 1963; *Chem. Can.*, **15** (8), 33 (1963); R. Hoppe, H. Mattauch, K. M. Rödder, and W. Dähne, *Z. Anorg. Allg. Chem.*, **324**, 214 (1963).

(5) (a) K. S. Pitzer, *Science*, **139**, 414 (1963); (b) C. A. Coulson, *J. Chem. Soc.*, 1442 (1964).

(6) N. Bartlett and F. O. Sladky, *Chem. Commun.*, 1046 (1968).

(7) J. I. Musher, *J. Amer. Chem. Soc.*, **90**, 7371 (1968).

(8) M. Eisenberg and D. D. DesMarteau, *Inorg. Nucl. Chem. Lett.*, **6**, 29 (1970).

(9) F. Sladky, *Monatsh. Chem.*, **101**, 1559 (1970).

(10) H. M. Feder, W. N. Hubbard, S. S. Wise, and J. L. Margrave, *J. Phys. Chem.*, **67**, 1148 (1963).

(11) N. Bartlett, M. Wechsberg, F. O. Sladky, P. A. Bulliner, G. R. Jones, and R. D. Burbank, *Chem. Commun.*, 703 (1969).

(12) N. Bartlett, M. Wechsberg, G. R. Jones, and R. D. Burbank, *Inorg. Chem.*, **11**, 1123 (1972).

(13) (a) F. O. Sladky, P. A. Bulliner, N. Bartlett, B. G. DeBoer, and A. Zalkin, *Chem. Commun.*, 1048 (1968); (b) F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc. A*, 2179 (1969).

(14) V. M. McRae, R. D. Peacock, and D. R. Russell, *Chem. Commun.*, 62 (1969).

(15) L. V. Streng and A. G. Streng, *Inorg. Chem.*, **4**, 1370 (1965).

(16) J. H. Holloway, *Chem. Commun.*, 22 (1966).

(17) S. M. Williamson, *Inorg. Syn.*, **11**, 147 (1968).

Previous analytical, X-ray, and spectroscopic examination in these laboratories has confirmed that this method yields high-purity XeF_2.[15] **Fluorosulfuric acid** obtained from K & K Laboratories, Inc., Plainview, N. Y., was purified by distillation under ordinary pressure followed by a high-vacuum distillation. The purified acid was a colorless liquid, bp 164°. **Perchloric acid** was prepared from commercial 70% perchloric acid, by adding a fivefold excess of concentrated H_2SO_4 followed by distillation at 10 Torr. **Trifluoromethylsulfuric acid**, obtained from the Chemical Division of the 3M Co., St. Paul, Minn., was distilled prior to use. **Methylsulfonic** acid was obtained from Eastern Chemical Corp., Paquannock, N. J., and was distilled prior to use. **Arsenic pentafluoride** was obtained from Ozark-Mahoning Co., and **antimony pentafluoride** was prepared by fluorination of antimony trioxide in an inclined glass tube. **Ruthenium pentafluoride** was prepared by fluorinating the metal in a Monel bomb at 200°.

Apparatus.—The derivatives of xenon difluoride were prepared in Kel-F tubes provided with Kel-F valves. The tubes were made by drilling approximately 3-in. lengths of $^5/_8$-in. diameter Kel-F rod to preserve a $^1/_8$-in. wall thickness. This tube was threaded at the neck and provided with a rounded lip to effect a tight ring seal when screwed into the valve. The valve was fashioned after a conventional V-stem, packed valve. The vacuum dried Kel-F tubes were loaded with XeF_2 in a Vacuum Atmospheres Corp. Drilab. Manipulations involving volatile reactants or products were carried out on a vacuum line constructed of $^1/_4$-in. nickel tubing linked by Monel Swagelock fittings and Monel Whitey valves and capable of a low pressure of 10^{-5} Torr or less.

X-Ray Powder Photographs.—Thin-walled 0.3-mm diameter quartz capillaries were dried under vacuum and loaded under dry nitrogen in a glove bag, this operation being carried out in a cold room at ~0°. The capillaries were sealed by drawing down in a small flame, the sample being kept cold at all times. X-Ray powder photographs were taken, using graphite "crystal" monochromatized Cu Kα radiation, on a GE Precision camera. The powder samples were maintained at ~0° by a stream of cold dry nitrogen.

Raman Spectra.—The microcrystalline solids and a sample of liquid $S_2O_6F_2$ were each contained in sealed thin walled 1-mm diameter Pyrex glass capillaries for Raman spectroscopy. The spectrometer employed a Spectra-Physics Model 125 He–Ne laser in conjunction with a Spex Model 1400 double monochromator.

Infrared Spectra.—A gas-tight Kel-F cell fitted with AgCl windows was used for all condensed-phase spectra. The powdered solids were dusted on to the inner surfaces of the windows, the same precautions being taken as for X-ray sample preparation. A Perkin-Elmer 137 Infracord was used over its full range of 4000–400 cm^{-1}.

Xenon(II) Fluoride Fluorosulfate, $FXeOSO_2F$. Preparation.—An equimolar amount of fluorosulfuric acid was added to a known weight of xenon difluoride contained in a Kel-F tube and valve assembly. The mixture, initially at −75°, rapidly yielded a colorless solution when warmed to 0°. Hydrogen fluoride was removed under a dynamic vacuum with the mixture held at 0°. A colorless solid, mp 36.6°, remained. The evolved hydrogen fluoride was trapped, weighed, and titrated with base. One mole of HF was evolved per mole of acid brought into interaction with XeF_2. Several syntheses were followed gravimetrically. In all cases the hydrogen fluoride evolution and the yield of product were in accord with the overall reaction $XeF_2 + HOSO_2F \rightarrow FXeOSO_2F + HF$. Typically, XeF_2 (0.728 g, 4.3 mmol) plus $HOSO_2F$ (0.430 g, 4.3 mmol) gave $FXeOSO_2F$ (1.040 g, 4.2 mmol) and volatiles (0.125 g, mainly HF, but containing traces of Xe, $S_2O_5F_2$, and $S_2O_6F_2$, the last being identified from infrared spectra[18]). In an experiment in which an excess of XeF_2 was employed, the same white solid, mp 36.6°, was obtained on removing excess XeF_2 under a dynamic vacuum (for 0.5 hr) at 20°: XeF_2 (4.95 mmol) + $HOSO_2F$ (3.60 mmol) → $FXeOSO_2F$ (3.60 mmol) + HF (3.7 mmol).

Some Properties of $FXeOSO_2F$.—A small sample at ~20° was completely transferred under a dynamic vacuum, after several hours, to a U tube cooled at −75°. Well-formed crystals were obtained in this way. This provided for the crystal structure determination reported in a recent paper.[12] That the single crystals were representative of the bulk material was proved by a complete indexing of the X-ray powder data given in Table I.[19]

The colorless solid, on melting at 36.6°, produced a pale yellow-green liquid which evolved xenon and within 1 hr decomposed completely according to the equation $2FXeOSO_2F \rightarrow XeF_2 + S_2O_6F_2 + Xe$. A ^{19}F nmr study of the melt confirmed this observation. Both the xenon difluoride and the peroxydisulfuryl difluoride produced in this decomposition were pure. This decomposition also occurs spontaneously in the solid at room temperature with a half-life of ~2 days at 20° and the transformation has been followed crystallographically, single crystals of the $FXeOSO_2F$ having decomposed, on X-irradiation at room temperature, to yield a colorless liquid ($S_2O_6F_2$) and well-formed crystals which were established by precession photography to be xenon difluoride. The $S_2O_6F_2$ was identified by its characteristic infrared spectrum[18b] with strong bands at 1490, 1246, 846 (PQR), and 752 cm^{-1} and by its ready thermal dissociation to the colored SO_3F radical. A preliminary survey of the chemical properties of $FXeOSO_2F$ show that it is a fluorosulfating agent, very like $S_2O_6F_2$. All reactions are accompanied by brisk evolution of xenon gas. Thus sulfur trioxide interacted with the solid to generate $S_2O_6F_2$: $FXeOSO_2F + \gamma SO_3 \rightarrow S_2O_6F_2 + Xe$; sulfur dioxide on the other hand yields $S_2O_5F_2$: $FXeOSO_2F + SO_2 \rightarrow S_2O_5F_2 + Xe$, as supported by the infrared spectrum[18a] of the gaseous product.

The vibrational spectra for $FXeOSO_2F$ are given in Table II.

Xenon(II) Bis(fluorosulfate), $Xe(OSO_2F)_2$. Preparation.—The preparation of $Xe(OSO_2F)_2$ was similar to that for $FXeOSO_2F$. Xenon difluoride and fluorosulfuric acid in a 1:2 mole ratio were transfered to a Kel-F reactor and maintained at −75° for 0.5 hr. To complete the reaction the yellow solution was allowed to warm to 0°. Traces of gaseous xenon were detected when the mixture was cooled to −75°. The volatile products were collected and shown by infrared spectroscopy to be HF, with <4 mol % $S_2O_5F_2$.[18a] Again, the number of moles of HF evolved corresponded to the number of moles of $HOSO_2F$ introduced and was in agreement with the overall reaction $XeF_2 + 2HOSO_2F = Xe(OSO_2F)_2 + 2HF$. In a representative preparation, XeF_2 (0.731 g, 4.3 mmol) and $HOSO_2F$ (0.864 g, 8.64 mmol) gave 1.371 g of yellow solid (4.2 mmol of $Xe(OSO_2F)_2$) and 0.212 g of volatile material containing 8.7 mmol of HF. When the molar ratio of the two reactants was between 1 and 2, a yellow liquid remained on removal of HF at 0°. This liquid (presumably a mixture of $FXeOSO_2F$ and $Xe(OSO_2F)_2$) slowly evolved xenon gas, even at 0°.

Some Properties of $Xe(OSO_2F)_2$.—The Raman spectrum is compared with those of $FXeOSO_2F$ and $S_2O_6F_2$ in Table III. Single crystals of $Xe(OSO_2F)_2$ were obtained by slow evaporation of a HF solution and fragmentary precession photograph data, from such a crystal, provided for the indexing of the X-ray powder data given in Table IV.[19] The unit cell is monoclinic with $a = 7.94$, $b = 13.7$, $c = 6.84$ Å, $\beta = 96°$. A small sample of $Xe(OSO_2F)_2$ under a dynamic vacuum at 20° slowly decomposed but none of the compound collected in the limbs of a U tube, cooled at −75°, provided to trap it.

$Xe(OSO_2F)_2$ is a yellow solid which gives a yellow melt at 43–45°. The melt decomposes slowly, but quantitatively: $Xe(OSO_2F)_2 \rightarrow Xe + S_2O_6F_2$. The solid decomposes similarly if kept at 20° for a few hours. In one experiment $Xe(OSO_2F)_2$ (0.5 g) was allowed to decompose in a Kel-F reactor and the xenon was pumped out at −75°. Vapor pressure measurements on the remaining liquid and the infrared spectrum, of a gaseous sample at 20°, corresponded to data given previously for $S_2O_6F_2$.[18b] The infrared spectrum proved that other sulfur fluorides and oxyfluorides were absent. Samples of $S_2O_6F_2$ obtained in this way melted sharply at −51.6°, a value 4° higher than that previously given.[18b]

The bis(fluorosulfate) dissolves in both IF_5 and BrF_3. These solutions decompose very slowly at room temperature, and even at 40° the xenon evolution is at a much lower rate than in the

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[18] (a) A. Simon and R. Lehmann, *Z. Anorg. Allg. Chem.*, **311**, 224 (1961); (b) F. B. Dudley and G. H. Cady, *J. Amer. Chem. Soc.*, **79**, 513 (1957).

[19] Tables I, IV, and V, listings of X-ray powder data, will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number INORG-72-3063. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE II

VIBRATIONAL SPECTRA AND ASSIGNMENTS FOR $FXeOSO_2F$[a] AND $FXeOSO_2CF_3$[d]

$FXeOSO_2F$		$FXeOSO_2CF_3$	
Bands, cm^{-1}	Assignments	Bands, cm^{-1}	Assignments
253 s R	δ(Xe–O–S)	236 vs R	δ(Xe–O–S)
243 m R		316 w R	δ(F–C–S) + δ(O–S–C)
395 mw R	ρ_w(S–F)	338 w R	
433 s R	ν(Xe–F) + ν(Xe–O–)	369 s R	ν(Xe–O)
518 vs ir		534 s R	ν(Xe–F)
521 vs R		539 w ir	
531 m R	δ(O–S–O)	505 sh R	δ(O–S–O) + δ(F–C–F)
536 m R		510 m ir	
540 s R		568 s R	
584 mw R		570 w ir	
597 w ir		582 s R	
614 m ir		595 m ir	
616 mw R		636 w R	
798 s ir	ν(S–F)	620 sh ir	
800 w R		771 w R	ν(S–C)
970 vs ir	ν(S–O–)	758 m ir	
970 w R		840 m, br ir	ν(C–F)
1197 w R	$\nu(S–O_{term})_{sym}$	922 m R	$\nu(S–O_{bridge})$
1210 vs ir		1143 w	ν(C–F)
1390 w R	$\nu(S–O_{term})_{asym}$	1120 m, br ir	
1393 s ir		1244 w R	$\nu(S–O_{term})_{sym}$
		1200 m, br ir	
		1390 w R	$\nu(S–O_{term})_{asym}$
		1390 w ir	

[a] The bands in the higher frequency range of 700–1400 cm^{-1} are assignable without much difficulty on the basis of comparisons with FSO_3^-, $Xe(OSO_2F)_2$, and $(SO_2F)_2$ as illustrated in Table III, but the assignments of the Xe–O and Xe–F stretchings were based on the assumption that the "symmetric" and "antisymmetric" F–Xe–O modes would be lower in frequency than 600 cm^{-1} (which characterizes the terminal XeF stretch in $[FXe][RuF_6]$ where the XeF bond length is 1.88 Å).[b,c] It was also assumed that the Xe–F and Xe–O stretching bands in the Raman spectra would be intense, as in the $Xe_2F_3^+$ salt spectra.[c] [b] N. Bartlett, D. Gibler, M. Gennis, and A. Zalkin, to be submitted for publication. [c] F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc. A*, 2179 (1969). [d] Assignments for $FXeOSO_2CF_3$ were made partly on the basis of comparison with $FXeOSO_2F$ but also with reference to the Raman spectra of KO_3SCF_3 and the hydrated acid. The potassium salt (which was prepared for us by Dr. C. J. Adams) and the acid both showed moderately strong bands at ~580 cm^{-1} (attributable to δ(O–S–O) or δ(F–C–F)) and an intense pair of bands at ~320 and 350 cm^{-1} (attributable to δ(F–C–S) or δ(O–S–C)). These assignments, in which we were assisted by Dr. Adams, were important to our assignment of ν(Xe–F) and ν(Xe–O), respectively.

TABLE III

RAMAN FREQUENCIES AND ASSIGNMENTS[a] FOR $FXeOSO_2F$, $Xe(OSO_2F)_2$, AND $S_2O_6F_2$

FSO_3^-[b]	1287 $\nu(S–O_{term})_{asym}$	1082 $\nu(S–O_{term})_{sym}$		786 ν(S–F)		592 δ(O–S–O)	566		409 ρ_w(S–F)	
$FXeOSO_2F$	1390 w	1197 w	970 w	800 w		616 mw 584 mw 540 s	536 m 531 m	433 s 521 vs ν(Xe–F) + ν(Xe–O)	395 mw	253 s 243 m
$Xe(OSO_2F)_2$	1425 w 1417 w	1238 mw 1219 mw	959 mw 946 mw	823 w 815 w		601 s	541 w	436 s ν(Xe–O)	386 mw	257 vs 253 δ(Xe–O–S)
FO_2SOOSO_2F	1497 mw	1251 vs	880 m $\nu(S–O_{bridge})$	824 s	798 vs ν(O–O)[e]	598 mw	527 mw 485 mw		392 mw	299 s ?

[a] Key: w, weak; m, medium; s, strong; v, very; ν, stretching; δ, deformation; ρ_w, wagging (ρ_w(S–F) can also be written as $\rho_r(SO_3)$). For bands occurring at frequencies >700 cm^{-1} the assignments were straightforward, as the table itself indicates, but the ν(Xe–O) + ν(Xe–F) bands were chosen for $FXeOSO_2F$ largely on the basis of their appreciable Raman intensity (bands in the region 600–400 cm^{-1} having been indicated by the structural features). For ν(Xe–O) of $Xe(OSO_2F)_2$ there was more difficulty, the choice being between 601 and 436 cm^{-1}. The latter was chosen on the basis of a comparison with Sladky's findings[c] for $Xe(OTeF_5)_2$ and Aubke and Carter's findings[d] for $I(OSO_2F)_4$. [b] From K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963. [c] F. O. Sladky, *Angew. Chem., Int. Ed. Engl.*, **8**, 523 (1969). [d] F. Aubke, H. A. Carter, and S. P. L. Jones, *Inorg. Chem.*, **9**, 11, 2485 (1970). [e] It should be noted that the stretching frequency of the peroxide bond, ν(O–O) 798 cm^{-1}, is low and is compatible with the ready dissociation of $S_2O_6F_2$: $FS(O)_2\dot{O}–OS(O)_2–F \rightarrow 2FSO_3\cdot$.[19] This may be associated with the high electron-withdrawing capability of the $-OSO_2F$ group, which presumably prevents the location of appreciable electron density in the peroxide bond.

case of pure $Xe(OSO_2F)_2$. The solution in IF_5 decomposed according to the equation $Xe(OSO_2F)_2 \rightarrow Xe + S_2O_6F_2$. The BrF_3 solution yielded SO_2F_2 as well as Xe, $S_2O_6F_2$, and a viscous residue. Raman spectroscopy showed the last to be similar to the product of irradiation of a BrF_3–$S_2O_6F_2$ mixture and demonstrated the presence of SO_3F groups in the product.

Xenon(II) Fluoride Perchlorate. Preparation.—Perchloric acid (0.294 g, 2.93 mmol) was condensed into a Kel-F reactor containing XeF_2 (0.477 g, 2.82 mmol) and was allowed to warm first to −110° and after 10 min to −60°. The reaction was completed by warming to 0° at which temperature volatile material (0.091 g) was removed and collected. The infrared spectrum of the volatile material showed it to be mainly HF with traces of Cl_2O_7, ClO_2, and ClO_3F, the last being in smallest concentration. The solid residue (0.680 g) corresponded to $FXeOClO_3$ (2.72 mmol). The colorless solid melted sharply at 16.5° decomposing simultaneously to yield a liquid which rapidly changed from yellow to red. The infrared spectrum of the gaseous products of decomposition was accounted for completely assuming the main product to be Cl_2O_7, with some ClO_2

and traces of $FClO_3$.[20] Xenon and oxygen were also present.

X-Ray powder photographs of $FXeOClO_3$ showed some similarity to those of $FXeOSO_2F$ but indicated that the compounds were not isomorphous. The powder data are given in Table V.[19] The vibrational spectra for $FXeOClO_3$ are given in Table VI.

TABLE VI

VIBRATIONAL SPECTRA AND ASSIGNMENTS FOR $FXeOClO_3$

$FXeOClO_3$		ClO_4^- [a]	
Bands, cm^{-1}	Assignments[b]	Bands, cm^{-1}	Assignments
202 m R	δ(F–Xe–O)		
258 s R	δ(Xe–O–Cl)		
505 vs ir	ν(Xe–F) + ν(Xe–O–)		
507 vs R			
520 sh ir			
530 sh ir			
525 ms R			
586 s ir	$\delta(ClO_3)$ + $\rho_r(ClO_3)$ + ν(Cl–O–)	465	$\delta(ClO_2)$
593 w R		632	$\delta(ClO_2)$
614 R			
620 vs ir			
628 vs ir			
638 R			
722 vs ir			
726 w R			
758 sh ir			
754 w R			
770 w R			
1014 mw R	$\nu(Cl\text{–}O_{term})_{sym}$	938	$\nu(Cl\text{–}O)_{sym}$
1018 vs ir			
1032 vw R			
1048 sh ir			
1202 mw R	$\nu(Cl\text{–}O_{term})_{asym}$	1119	$\nu(Cl\text{–}O)_{asym}$
1215 vs ir			
1243 vw R			
1295 w ir			

[a] Assignments are those given by R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 769 (1964). The quoted frequencies are averages of those quoted by Hester and Plane. [b] The four frequencies between 1000 and 1250 cm^{-1} must arise from terminal Cl–O stretching, although only three stretching fundamentals are expected in this region for a single $FXeOClO_3$ unit. Similarly the bands in the 590–770-cm^{-1} region can be assigned to deformation and rocking vibrations of the ClO_3 group. In addition, the Cl–O– bridging stretch is expected to occur in this region. The remaining bands at lower frequency may be confidently assigned to motions involving significant displacement of the xenon atom. The appreciable intensity of these low-frequency bands in the Raman spectrum is consistent with our experience that such motions give rise to intense Raman features. In view of the similar masses of oxygen and fluorine and the closeness of the frequencies assignable to Xe–F and Xe–O– stretch (507, 525 cm^{-1}) it is meaningless to assign one to Xe–F and the other to Xe–O. It is better to describe the modes as "symmetric" and "antisymmetric" F–Xe–O stretching, with the higher frequency attributable to the latter.

Xenon(II) Bis(perchlorate).—In an attempt to prepare $Xe(OClO_3)_2$ a small amount of $FXeClO_4$ was transferred to a Kel-F reactor and an equimolar amount of $HClO_4$ condensed on to it. This mixture which was shaken initially at −11° and then at −60° for several minutes generated a yellow solid and HF. The latter was largely removed at −50°. On warming to 0° the yellow solid rapidly changed to a red liquid. Xe, O_2, Cl_2O_7, and traces of ClO_2 and $FClO_3$ were liberated as the gaseous products of decomposition. The residual red liquid detonates when heated and corresponds to the description of the chlorine oxide described as Cl_2O_6.[21]

Although on those occasions when care has been taken to carry out the $HClO_4$–XeF_2 interaction at low temperatures and HF has been removed at low temperatures, there have been no explosions; on other occasions, when rapid warm-up of the reactants has been permitted, very strong detonations have occurred.

Attempted Preparation of Xenon(II) Perchlorate Fluorosulfate, $O_3ClOXeOSO_2F$.—The synthesis of $O_3ClOXeOSO_2F$ was attempted by adding both perchloric acid to $FXeOSO_2F$ and fluorosulfuric acid to $FXeOClO_3$ in a manner similar to that used for the bis(perchlorate) preparation. Although the products of the interactions showed no gas evolution at −60° and yielded a colorless solution in anhydrous HF, removal of volatiles produced a yellow solid which rapidly yielded a red liquid and simultaneously evolved xenon and oxygen, even below 0°. Infrared spectra of the vapor from this product showed $S_2O_6F_2$ and various chlorine oxides to be present. There was no indication of mixed oxides or peroxide (*e.g.*, $O_3Cl\text{–}OOSO_2F$). The product indeed behaved like a mixture of $Xe(OSO_2F)_2$ and $Xe(OClO_3)_2$.

Interaction of XeF_2 with Some Other Protonic Acids. HCl.—Xenon difluoride did not interact with pure HCl (1:1) at −58° but addition of anhydrous HF produced a red-brown coloration at ∼−100°. Xenon was evolved even at −100° and quantitative recovery of the Xe was obtained at −50°. The interaction proceeded according to the equation

$$2XeF_2 + 2HCl \xrightarrow{HF} XeF_2 + Cl_2 + 2HF + Xe$$

CF_3SO_2OH (*Caution!*).—XeF_2 (4.73 mmol) was condensed onto the acid which was in slight excess for a 1:1 reaction (5.52 mmol). The mixture was contained in the usual Kel-F reactor. Anhydrous HF (6 ml) was added by vacuum distillation and the stirred mixture was slowly (∼1 hr) brought to 0° and held at that temperature for 2 hr. Slight gas evolution occurred in this time and infrared spectroscopy, of the gas, indicated the presence of C_2F_6. The solvent was removed between −40 and −30°. The remaining solid was colorless at −80° but yellow at 0°. The residue, after 3 hr under dynamic vacuum, weighed 1.06 g (theoretical yield for $FXeOSO_2CF_3$, allowing for ready decomposition of the bis compound, 1.18 g). The Raman spectrum given in Table II is compatible with the formulation $FXeOSO_2CF_3$. The solid decomposed slowly at 0° and rapidly between 40 and 60° (no melting up to 60°). The major gaseous products were CF_4 and Xe.

Efforts to prepare $FXeOSO_2CF_3$ with XeF_2-rich or exact 1:1 mixtures of the reactants yielded very unstable solid products, which decomposed slowly at 0° to yield the gaseous products SO_2F_2, CF_4, and Xe. In all cases the solids *detonated* on warming to room temperature.

CH_3SO_2OH.—XeF_2 (9.45 mmol) was condensed on to the acid (9.77 mmol) and the neat mixture was warmed slowly to −15°, at which temperature a yellow color developed at the interface between the two solids. Gas slowly evolved at −15° and on warming the mixture to 0°, to hasten the interaction of the two solids, very fast gas evolution occurred, which was not arrested by cooling in liquid nitrogen. *Detonation occurred!* A similar reaction, carried out in HF, generated a colorless clear solution at −65° (6.74 mmol of XeF_2 and 6.69 mmol of CH_3SO_2OH in 4 ml of HF). Slight gas evolution occurred on warm-up to ∼−40°, at which point a faint yellow color also developed. The solvent was removed between −50 and −20°. The solid which remained was pale yellow at 0° and slowly yielded gaseous products (∼0.02 mmol min^{-1}). It *detonated* on warming to room temperature.

$ClSO_2OH$.—Addition of XeF_2 (3.0 mmol) to the acid (3.0 mmol) followed by warm-up to −78° led to a vigorous reaction to yield a pale yellow solution and much gas, which contained 3 mmol of Xe. Chlorine gas was the other identifiable gaseous product. Similar interaction of acid with XeF_2, but in a 2:1 molar ratio (4.18 mmol of $ClSO_2OH$, 2.09 mmol of XeF_2), generated Xe (2.1 mmol) and Cl_2 (2.15 mmol), even at −95°. The less volatile liquid residue proved to be HSO_3F, thus indicating the overall reaction to be $XeF_2 + 2ClSO_2H \rightarrow Xe + Cl_2 + 2FSO_2OH$.

$(CF_3)_3COH$.—XeF_2 (4.3 mmol) interacted, with gas evolution, with the acid (4.33 mmol) at 0°. (No reaction occurred below that temperature.) The reaction accelerated with time and gave a colorless solution and quantitative evolution of xenon (4.3 mmol).

Attempts to Prepare $[XeOSO_2F]^+[MF_6]^-$ Salts. $[XeF]^+[SbF_6]^-$ was prepared by adding XeF_2 (42.2 mmol) to a solution of SbF_5 (40.7 mmol) in HF (10 ml). This mixture was stirred for 4 hr at 0°, by which time a clear pale yellow solution had formed.

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(20) R. S. Savoie and P. A. Giguere, *Can. J. Chem.*, **40**, 991 (1962).

(21) Gmelin, "Handbuch der anorganischen Chemie," Vol. 6 (Chlorine), Supplement B, 1968, p 227.

The HF was removed under a dynamic vacuum at 0° to leave a pale yellow solid. The powder photograph indicated isomorphism with $[FXe]^+[RuF_6]^-$ and was indexed[22] on the basis of an orthorhombic unit cell of dimensions $a = 11.2$, $b = 8.0$, and $c = 7.5$ Å (all ±0.1 Å). The Raman spectrum showed the presence of $[Xe_2F_3]^+[SbF_6]^-$ (as anticipated from the slight excess of XeF_2 over the 1:1 stoichiometry) but the other bands were entirely attributable to $[XeF]^+[SbF_6]^-$. The Raman bands (in cm^{-1}), with relative intensities and assignments in parentheses, are as expected on the basis of previous studies[13] of $[XeF]^+[MF_6]^-$ salts: 668 (13, ν(Sb–F)), 651 (3, ν(Sb–F)), 643 (6, ν(Sb–F)), 624 (3, ν(Sb–F)), 612 (25, ν(Xe–F)), 607 (sh, ν(Xe–F)), 596 (sh, ν(Sb–F)), 591 (sh, $\nu(Xe_2F_3^+$ impurity)), 581 (sh, $\nu(Xe_2F_3^+$ impurity)), 470 (2 broad, ν(Sb–F)), 290 (5, δ(Sb–F)), 270 (4, δ(Sb–F)).

$[XeF]^+[SbF_6]^-$ and FSO_2OH (5.44 and 6.1 mmol, respectively) were dissolved in HF (10 ml) with stirring at 0° for 4 hr to give a yellow-green solution. The solvent was removed under a dynamic vacuum, at −30°, to leave a yellow-green solid. Xenon evolution during all manipulations to this point was <0.5 mmol. The weight of residue amounted to 2.4 g, whereas that anticipated for $[XeSO_3F]^+[SbF_6]^-$ is 2.5 g. The solid gave a unique powder photograph but the Raman spectrum was of poor quality and the great reactivity of the compound toward the AgCl plates rendered the infrared spectra valueless. A similar solid, having an identical X-ray powder pattern, was prepared by mixing equimolar proportions of the neat reactants at 48° for 48 hr.

$[XeF]^+[RuF_6]^-$ (1.36 mmol), prepared as previously described,[13] was mixed with HSO_3F (1.41 mmol) in HF (2 ml) with stirring, at 0°, for 5 hr. The $[XeF]^+[RuF_6]^-$ appeared to dissolve and a second crystalline phase appeared at the surface of the solution, which assumed a yellow tint. Removal of the HF at 0° yielded a yellow solid, which rapidly turned red-brown and rapidly decomposed with gas evolution, xenon and sulfur oxyfluorides being formed.

$[XeF]^+[AsF_6]^-$ was prepared by dissolving AsF_5 (10.87 mmol) and XeF_2 (10.4 mmol) in HF (5 ml) and $HOSO_2F$ (10.6 mmol) was condensed into this mixture which was allowed to warm to 0°. It was maintained with vigorous stirring at 0° for 2 hr and then for a further 2 hr at ~20°. The solution became greenish but some colorless solid remained out of solution. More solid precipitated on cooling to −40°, at which temperature the HF was removed under a dynamic vacuum. The greenish solid, which remained, rapidly became brown on warm-up to −30°, at which point the solid melted and evolved gas. Eventually, with removal of volatiles (AsF_5, Xe, SO_2F_2, $S_2O_6F_2$), under dynamic vacuum, a residue of 1.84 g of $[(FXe_2O)_2S(O)F]^+[AsF_6]^-$ (see below) remained.

The Preparation of $[(FXeO)_2S(O)F]^+[AsF_6]^-$.—$XeF_2$ (7.8 mmol) and FSO_2OH (4.38 mmol) were condensed in HF (6 ml) and stirred at 0° for 4 hr. AsF_5 (4.2 mmol) was added to the solution, which was held at −78°. This HF solution was almost colorless, although a second yellowish phase was observed at the bottom of the Kel-F container. The HF was removed between −30 and 0°, to leave a pale yellow solid (2.14 g). Traces of SO_2F_2 were present in the gaseous products. Under vacuum, at room temperature, the solid became colorless. The Raman spectrum showed the materials to be mainly $[(FXeO)_2S(O)F]^+[AsF_6]^-$ with some $[Xe_2F_3]^+[AsF_6]^-$ impurity. This composition is consistent with the loss of some fluorosulfate in SO_2F_2 formation since the XeF_2 concentration was less than required for the ideal interaction $FXeOSO_2F + XeF_2 + AsF_5 \rightarrow [(FXeO)_2S(O)F]^+[AsF_6]^-$. A purer product was obtained from the $[FXe]^+[AsF_6]^-$–$HOSO_2F$ interaction described above and from the interaction of equimolar quantities of $Xe(OSO_2F)_2$ and AsF_5 in HF. This latter reaction generated a colorless crystalline solid at 0°, but removal of HF between −40 and −50° yielded a dark brown liquid which evolved SO_2F_2, AsF_5, and HF, under a dynamic vacuum, for 15 hr at −40°, to yield a colorless solid, which Raman spectroscopy proved to be a mixture of $Xe(OSO_2F)_2$ and $[(FXeO)_2S(O)F]^+[AsF_6]^-$. Warming this mixture to 40° destroyed the former but not the latter.

TABLE VII

ASSIGNMENT OF THE RAMAN SPECTRUM OF $[(FXe)_2O_2S(O)F]^+[AsF_6]^-$ (BANDS IN CM^{-1}, RELATIVE INTENSITIES IN PARENTHESES)

$[(FXe)_2F]^+[AsF_6]^-$ [a]	$[(FXe)_2O_2S(O)F]^+$-$[AsF_6]^-$	$[SO_3F]^-$ [b]
369 (7) $\nu_5(AsF_6^-)$	372 (6)	
	410 (8)	409 ρ(S–F)
	551 sh	566
588 (94) $\nu(XeF)_{sym}$	563 (88)	
575 sh $\nu_2(AsF_6^-)$	573 sh	
600 (100) $\nu(XeF)_{asym}$	581 (100)	
	588 (23)	592
	633 (12.5)	
683 (19) $\nu_1(AsF_6^-)$	685 (13.5)	
	875 (2)	786 ν(S–F)
	1035 (9)	1082 $\nu(S–O)_{sym}$
	1090 (3)	
	1350 (5)	1287 $\nu(S–O)_{asym}$

[a] F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc.*, 2179 (1969). [b] K. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., and London, 1970, p 114.

The Raman spectrum (Table VII) and the effectiveness of the stoichiometry $2XeF_2 + HOSO_2F + AsF_5$ in forming the product, together, provide strong support for the formulation $[(FXeO)_2S(O)F]^+[AsF_6]^-$.

Analysis.—Several samples from different preparations were analyzed for xenon. This was accomplished by sealing samples of the solid in preweighed quartz X-ray capillaries, which were then inserted into a conventional combustion tube of a Dumas nitrometer. The nitrometer was previously purged with xenon. *Anal.* Calcd for $O_3AsSF_9Xe_2$: Xe, 44.6. Found: Xe, sample a, 45.8, 45.4; Xe, sample b, 45.4, 45.5. Unfortunately, the sample capillaries could not be evacuated prior to closing and therefore contained small, but imprecisely known, volumes of nitrogen. Thus the xenon analysis by this method should be high. The greatest possible error (if the capillary volume of nitrogen were present) would introduce a 3% excess to the xenon analysis. Since the samples, in each case, occupied approximately half the capillary volume, it is probable that the analyses were high by approximately half this amount. On this basis, the xenon analysis, by the Dumas nitrogen method, gives findings in excellent accord with expectations.

Properties of $[(FXeO)_2S(O)F]^+[AsF_6]^-$.—The Raman spectrum of the colorless solid is represented in Table VII. It is remarkably similar to that of $[Xe_2F_3]^+[AsF_6]^-$. The solid is sublimable, at ~20°, *in vacuo*, and the Raman spectrum of the sublimate shows only traces of $[Xe_2F_3]^+[AsF_6]^-$. The solid decomposes above 64° at ordinary pressures and yields $S_2O_6F_2$, Xe, and $Xe_2F_3^+AsF_6^-$ in accord with the equation

$$4[(FXeO)_2S(O)F]^+[AsF_6]^- \longrightarrow 3[Xe_2F_3]^+[AsF_6]^- + AsF_5 + 2Xe + 2S_2O_6F_2$$

The solid interacts rapidly with dry CH_3CN.

The Attempted Preparation of $[(FXeO)_2CCF_3]^+[AsF_6]^-$ and $[(FXe)_2Cl]^+[AsF_6]^-$.—**CF_3COOH** (2.25 mmol) was added at −196° to a solution of $Xe_2F_3^+AsF_6^-$ (2.22 mmol) in HF (5 ml). As soon as the mixture melted on warm-up, a vigorous interaction occurred and was complete within 1 or 2 min. The volatile products, which were removed under vacuum at 20°, proved to be CF_4, CO_2, and Xe. The residue proved to be pure $[Xe_2F_3]^+[AsF_6]^-$ (0.63 mmol). If allowance is made for the volatility of $[Xe_2F_3]^+[AsF_6]^-$, these observations are in accord with the overall reaction

$$[Xe_2F_3]^+[AsF_6]^- + 2CF_3COOH \longrightarrow 2CF_4 + 2CO_2 + 2HF + AsF_5 + 2Xe$$

HCl (2.26 mmol) was added to a solution of $[Xe_2F_3]^+[AsF_6]^-$ (2.26 mmol) in HF (5 ml) at −80°. Evolution of Xe and Cl_2 gas occurred above −40° and removal of the volatiles at this temperature left only a residue of $[Xe_2F_3]^+[AsF_6]^-$. Evidently the decomposition proceeded according to the equation

$$[Xe_2F_3]^+[AsF_6]^- + 4HCl \xrightarrow{HF} 4HF + 2Cl_2 + 2Xe + AsF_5$$

Discussion

Preparative.—Our studies have demonstrated that

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[22] Although $[XeF]^+[RuF_6]^-$ is monoclinic, with $a = 7.991$, $b = 11.086$, $c = 7.250$ Å (all ±0.006 Å), $\beta = 90.68 \pm 0.05°$, and space group $P2_1/n$, the departure from orthorhombic symmetry is not revealed by our Debye–Scherrer photographs. It is probable that the true unit cell of $[XeF]^+[SbF_6]^-$ is also monoclinic.

the F ligands of XeF_2 may be substituted, one at a time by highly electronegative ligands. At least for the $-OSO_2F$ and $-OClO_3$ ligands there is no dismutation of the monosubstituted derivatives (*i.e.*, $2FXeOR \not\rightarrow XeF_2 + Xe(OR)_2$), and the FXeOR compounds may be obtained pure by mixing the reactants in a 1:1 molar ratio: $XeF_2 + HOR \rightarrow FXeOR + HF$. On the other hand, we have failed to generate the unsymmetrical compounds: $FXeOR + HOR' \rightarrow {}^1/_2Xe(OR)_2 + {}^1/_2Xe(OR')_2$. It is not known whether the production of an equimolecular mixture of $Xe(OSO_2F)_2$ and $Xe(OClO_3)_2$ is a consequence of lower solubility, of one or both of the symmetrical compounds, relative to the unsymmetrical compound, or whether the symmetrical compounds are energetically more favorable (perhaps from greater resonance stabilization) than the unsymmetrical. Presumably the intermolecular ligand exchange is provided for by some solvolysis by the hydrogen fluoride.

Failure to prepare FXeCl or $XeCl_2$ by substitution of the F ligands of XeF_2

$$HCl + XeF_2 \longrightarrow {}^1/_2XeF_2 + HF + {}^1/_2Cl_2$$

or of $Xe_2F_3{}^+$

$$[Xe_2F_3]^+[AsF_6]^- + HCl \longrightarrow HF + {}^1/_2Cl_2 + {}^1/_2Xe + {}^1/_4AsF_5 + {}^3/_4[Xe_2F_3]^+[AsF_6]^-$$

indicates that the chlorine ligand is too readily oxidized to molecular chlorine, for Xe–Cl compounds to be preserved under normal conditions of temperature and pressure. It is of interest, here, that chlorine is also liberated in the interaction of chlorsulfuric acid with XeF_2: $XeF_2 + 2HOSO_2Cl \rightarrow Xe + Cl_2 + 2HOSO_2F$.

The difficulties experienced in preparing Xe(II) derivatives of the trifluoromethyl and methyl sulfates show, that even when bound species are generated, it is not always possible to preserve what are frequently thermodynamically unstable compounds at room temperature. The gaseous decomposition products of the mono(trifluoromethyl) sulfate $FXeOSO_2CF_3$ are mainly carbon tetrafluoride and xenon, which suggests the overall change: $FXeOSO_2CF_3 \rightarrow Xe + CF_4 + SO_3$. In our one successful preparation, slight excess of acid was employed and the reaction was accompanied by evolution of a gas which contained C_2F_6 (no CF_4). This is consistent with the formation of an unstable bis compound, $Xe(OSO_2CF_3)_2$. If this material were to decompose similarly to $Xe(OSO_2F)_2$, the peroxide $CF_3O_2S{-}O{-}O{-}SO_2CF_3$ would be the product. The latter, however, has been reported by Noftle and Cady[23] to undergo exothermic decomposition to perfluoroethane, sulfur trioxide, and trifluoromethanesulfonate. It may be that the explosive decomposition of samples from our other acid-rich preparations were triggered by this decomposition. The appearance of CF_4 and the absence of C_2F_6 in the thermal decomposition of $FXeOSO_2CF_3$ suggest that the $SO_3CF_3\cdot$ radical is not an important decomposition species but indicate that there is either fluorine attack at the S–C bond or (less likely) SO_3 elimination with transient $FXeCF_3$ formation. Evidently much the same kind of change occurs in the system XeF_2–CF_3COOH (1:1 molar ratio in HF), which liberates gases (including CF_4) even at −25°. The trifluoroacetate group is very effectively fluorinated when attempts are made to substitute into the $Xe_2F_3{}^+$ ion

$$Xe_2F_3{}^+AsF_6{}^- + CF_3COOH \xrightarrow{HF} ([(XeF)_2CO_2CF_3]^+[AsF_6]^-) \longrightarrow [XeF]^+[AsF_6]^- + Xe + CF_4 + CO_2 + HF$$

Curiously, the decomposition of $FXeCO_2CF_3$ is reported by Eisenberg and DesMarteau[8] to yield C_2F_6 and not CF_4.

The fluorosulfate decompositions proceed quantitatively as

$$\begin{aligned} 2FXeOSO_2F &\longrightarrow XeF_2 + S_2O_6F_2 + Xe \\ Xe(OSO_2F)_2 &\longrightarrow Xe + (SO_3F)_2 \end{aligned} \qquad (1)$$

The perchlorate decompositions are much more complex and although it is possible that $(ClO_4)_2$ or $ClO_4\cdot$ may be initial products of the decomposition, there is presently no evidence to support the existence of either species in the products of the reactions. The clean nature of the fluorosulfate dismutations may in part rest on the high stability of the $SO_3F\cdot$ radical.[18b] It is reasonable to postulate the $XeF\cdot$ radical as the other initial product of decomposition. If this radical occurs, it must be stable toward either dissociation into atoms or mutual annihilation, *i.e.*

$$2XeF\cdot \not\rightarrow 2Xe + F_2 \qquad (2)$$

since neither fluorine nor $FOSO_2F$ is detected in the decomposition products. The thermochemical bond energy of $XeF\cdot$ must not exceed that in XeF_2, however, if the XeF radical is to disproportionate spontaneously

$$2XeF\cdot \longrightarrow Xe + XeF_2 \qquad (3)$$

since the entropy change is slightly unfavorable for XeF_2 formation in this reaction.[24] Therefore, if the $XeF\cdot$ radical is an intermediate in the $FXeOSO_2F$ decomposition, the bond energy must be <32 kcal mol^{-1} to be compatible[2a] with process 3 and >18 kcal mol^{-1} to account for the absence of fluorine[25] (eq 2). It is pertinent that the $XeF\cdot$ radical has also been postulated[13] as an intermediate, which disproportionates, in the redox reaction $3XeF^+OsF_6{}^- \rightarrow Xe_2F_3{}^+OsF_6{}^- + 2OsF_6 + Xe$.

The number of ligands which will satisfy the high electronegativity requirements for bonding to a xenon atom and yet be capable of withstanding fluorine atom attack must be small. Fluorosulfate and perchlorate evidently are good ligands but the pentafluoroorthotellurate ligand $-O-TeF_5$, as demonstrated by Sladky, appears to be the best so far.[26]

Structure and Properties.—The vibrational spectroscopic data, given in Tables II, III, and VI, indicate that the binding of the xenon atom to its ligands, in the FXeOR or $Xe(OR)_2$ compounds, is comparable to that in XeF_2. The stretching modes ν(Xe–F) and ν(Xe–O–) are mixed in $FXeOSO_2F$ and $FXeOClO_3$. They appear at 521 and 433 cm^{-1} in the fluorosulfate and at 525 and 505 cm^{-1} in the perchlorate. It seems from these frequencies that in neither case is the bonding very different from that in XeF_2 where ν_{sym} is 495 and

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(23) R. E. Noftle and G. H. Cady, *Inorg. Chem.*, **4**, 1010 (1965).

(24) The standard entropies for gaseous Xe ($S° = 40.5$ eu) and XeF_2 ($S° = 62.0$ eu) are known and that for $XeF\cdot$ can be taken to be essentially the same as for IF ($S° = 56.5$ eu).[25]

(25) *Nat. Bur. Stand.* (*U. S.*), *Tech. Note*, **No. 270-3** (1968); **No. 270-4** (1969).

(26) F. Sladky, *Monatsh. Chem.*, **101**, 1559 (1970).

ν_{asym} is 555 cm^{-1}.[27] Furthermore, the observed Xe–O stretching frequency in $Xe(OSO_2F)_2$ (ν(Xe–O)$_{sym}$ 436 cm^{-1}) is not only comparable to the XeF and XeO stretching frequencies in $FXeOSO_2F$ but is remarkably similar to the ν(I–O)$_{sym}$ 441 cm^{-1} observed recently by Aubke and his coworkers for $I(OSO_2F)_4^-$.[28]

The preference of the $XeF_2 \cdot 2MF_5$ derivatives for the structure $[FXe]^+[F_5M\text{–}F\text{–}MF_5]^-$ [13,14] raised the possibility of the bis(fluorosulfate) being $[FXe]^+[O_3S\text{–}OSO_2F]^-$ but the vibrational spectroscopic evidence does not support this formulation. As the data in Table III demonstrate, the fluorosulfate group in $Xe(OSO_2F)_2$ is similar in character to that in $FXeOSO_2F$, although less anion-like. It is seen, however, that each $-SO_3F$ band of the $FXeOSO_2F$ spectrum is represented in the spectrum of $Xe(OSO_2F)_2$ by a close doublet. This is consistent with a structure in which the xenon atom is bound to two $-OSO_2F$ groups in a noncentrosymmetric assembly. As in all other known Xe(II) structures (see ref 12), the xenon atom is probably coordinated linearly, –O–Xe–O–, but the spectra require that the molecule, at least in the solid state, have a gauche or cis configuration. The comparison of the $Xe(OSO_2F)$ spectrum with that of $S_2O_6F_2$ is also of interest. The singularity of the $-SO_3F$ modes in the Raman show it to be a centrosymmetric molecule. Evidently the $-SO_3F$ groups in this molecule are less SO_3F^--like than in $Xe(OSO_2F)_2$.

Bonding.—In the valence-bond description of XeF_2, Coulson[5b] has emphasized the dominance of the canonical forms $(F\text{–}Xe)^+F^-$ and $F^-(Xe\text{–}F)^-$ in the resonance hybrid. This representation accounts well for the polarity $^{1/2-}FXe^+F^{1/2-}$, indicated by nmr,[29] Mössbauer,[30] ESCA,[31] and thermodynamic data.[32] It is particularly impressive that the enthalpy of sublimination derived for the XeF_2 case, by Rice and his coworkers[32] in 1963, on the basis of the charge distribution $^{1/2-}FXe^+F^{1/2-}$, is 13.3 kcal mol^{-1}, whereas the experimental value reported[33] in 1968 is 13.2 kcal mol^{-1}. It should be recognized that the Coulson valence-bond model is not, in the final analysis, significantly different from the Rundle[34] and Pimentel[35] three-center molecular orbital description or the Bilham and Linnett one-electron-bond description,[36] but it does provide for a more straightforward estimation of thermodynamic stabilities of compounds than the other approaches do.

We can appreciate from Figure 1 that the ionization potential of the noble gas atom is a key indicator of bonding prospects. Size and electron affinity of the ligand are also important. The lower the ionization potential, the less energy is required from the steps ΔH(electron pair) ($G^+ + L \rightarrow GL^+$), ΔH(electrostatic) ($G\text{–}L^+ + L^- \rightarrow L\text{–}G^+L^-$(g)), and R (resonance energy) to ensure a bound species GL . If L is sufficiently electronegative (G–L)– will be stable with respect to G and L^+ and ΔH(electron-pair bond) will be an exothermic term. Again if L is sufficiently electronegative $(L\text{–}G)^+L^-$ will be stable with respect to L–G and L (note that electrostatic energy is lost in this change) but it is also clear that the smaller L is, the more exothermic will be ΔH(electrostatic) and the more favorable will be the conditions for bonding. The instability of $XeCl_2$ can now be appreciated in terms of this model. It should first be noted that chlorine electron-pair bonds, with typical elements, are energetically less favorable than fluorine bonds[25,37] (thus the bond energies for ICl and I–F are 58 and 67 kcal mol^{-1}, respectively). Furthermore, the chlorine atom and ion are much bigger than their fluorine counterparts.[37] The energy of ion-pair formation, ΔH(electrostatic), is therefore less exothermic than in the fluoride case. If we take the observed interatomic distance of 2.0 Å in XeF_2, as a measure of the interionic distance in the ion pair, we would estimate the interionic distance in $XeCl_2$ to be ~2.4 Å. The attraction energies associated with these distances are 166 and 138 kcal mol^{-1}, respectively. Although the electron affinity of chlorine is 3 kcal mol^{-1} greater than for fluorine,[25] this is the only term in the cycle which is more favorable for the chlorine case and the summation indicates[37a] that the enthalpy of formation of $XeCl_2$(g) from the gaseous atoms would be less favorable than for XeF_2, by 34 kcal mol^{-1}, with $\Delta H_{at}(XeF_2) = 65$ and $\Delta H_{at}(XeCl_2) \approx 31$ kcal mol^{-1}. These values are in harmony with the stretching force constants given[3] by Nelson and Pimentel, which are $k_r = 1.32$ mdyn/Å for $XeCl_2$ and $k_r = 2.6$ mdyn/Å for XeF_2. Since the strong-acid anions are highly electronegative, it seemed likely that they would be good ligands for the heavier noble gases.

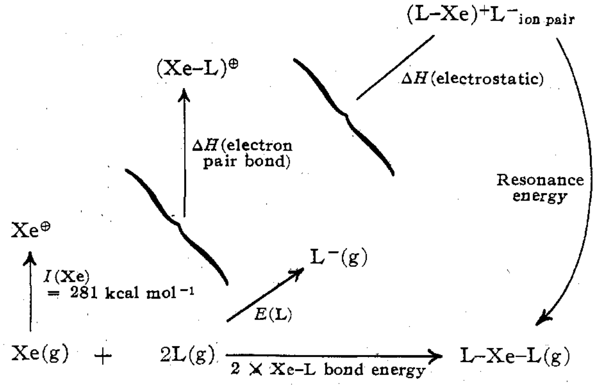

Figure 1.—A thermochemical cycle for XeL_2. In the case of XeF_2, E(F) is −80 (ref 39), ΔH(electron pair bond) is −48 (J. Berkowitz and W. A. Chupka, *Chem. Phys. Lett.*, **7**, 447 (1970)), and the total bond energy (ref 1a) is −65 kcal mol^{-1}. Thus $\Sigma(\Delta H$(electrostatic) + reasonance energy) = −218 kcal mol^{-1}.

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[27] P. A. Agron G. M. Begun, H. A. Levy, A. A. Mason, G. Jones, and D. F. Smith, *Science*, **139**, 842 (1963); H. H. Hyman, Ed., "Noble-Gas Compounds," Chicago University Press, 1963, pp 101, 295, 304.

[28] F. Aubke, H. A. Carter, and S. P. L. Jones, *Inorg. Chem.*, **9**, 2485 (1970).

[29] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, **40**, 2285 (1964); D. K. Hindermann and W. E. Falconer, *ibid.*, **50**, 1203 (1969).

[30] C. L. Chernick, C. E. Johnson, J. G. Malm, G. J. Perlow, and M. R. Perlow, *Phys. Lett.*, **5**, 103 (1963).

[31] S.-E. Karlsson, K. Siegbahn, and N. Bartlett, Report 18,502, University of California Research Laboratory, Berkeley, Calif., 1969.

[32] J. Jortner, E. G. Wilson, and S. A. Rice, *J. Amer. Chem. Soc.*, **85**, 814 (1963).

[33] F. Schreiner, G. N. McDonald, and C. L. Chernick, *J. Phys. Chem.*, **72**, 1162 (1968).

[34] R. E. Rundle, *J. Amer. Chem. Soc.*, **85**, 112 (1963).

[35] G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

[36] J. Bilham and J. W. Linnett, *Nature (London)*, **201**, 1323 (1964).

[37] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

[37a] In order to complete the cycle for $XeCl_2$ it is necessary to estimate the resonance energy (R). This may be equated with the difference between the (measurable) electron affinity of one ligand atom, appropriate for $(L\text{–}Xe)^+L^-$, and the sum of the two *half-electron affinities*, appropriate for the formulation $L^{1/2-}Xe^+L^{1/2-}$. Since the electron affinity of the Cl atom is similar to that of the F atom, it is reasonable to suppose that the "half-electron affinities" would be similar. On this basis $R(XeCl_2)$ has been assumed to be the same as $R(XeF_2)$.

However, these multiatom ligands, while conferring advantages from their high electron affinities, are nevertheless sizable species. The ion-pair energy ΔH(electrostatic) for species such as $FXe^+ClO_4^-$ or $FXe^+SO_3F^-$ could be as much as 40 kcal mol^{-1} less than for $F\text{-}Xe^+F^-$, since the lattice energies of Rb and Cs perchlorates are ~40 kcal mol^{-1} less than for the corresponding fluorides.[38] Therefore, even though the electron affinity of ClO_4(g) is greater[39] than for F(g) and even though the electron-pair bond in $(XeOClO_3)^+$ may be as favorable as in $(Xe\text{-}F)^+$, the overall energetics could well be less favorable than for XeF_2, simply because of the large ligand size. This may account for the disappointing thermal stability of the fluorosulfates and perchlorates.

The dominance of the $(F\text{-}Xe)^+(SO_3F)^-$ canonical form over the $(FO_2SO\text{-}Xe)^+F^-$ form in the resonance hybrid, indicated by the crystal structure,[12] calls for comment. At the outset it should be noted that the first canonical form alone is less appropriate than in the case of the $XeF_2\text{-}RuF_5$ compound, where $(F\text{-}Xe)^+(RuF_6)^-$ is judged to be of overwhelming importance compared with $F^-(Xe\text{-}F\text{-}RuF_5)^+$ or $F^-(Xe\text{-}F)^+\text{-}RuF_5$.[40] The ability of the hexafluororuthenate(V) to form a $Xe_2F_3^+$ salt,[11] $FXe^+RuF_6^- + XeF_2 \rightarrow (Xe_2F_3)^+(RuF_6)^-$, and the failure of $FXeOSO_2$ to do likewise give a chemical justification for this differentiation of the compound types. The $(FO_2S\text{-}O\text{-}Xe)^+F^-$ canonical form is therefore judged to be significant. It is a fair assumption that the ion-pair attraction and repulsion energies of this form are approximately the same as for $(F\text{-}Xe)^+(SO_3F)^-$. The high electron affinity[38] of SO_3F relative to F will tend to favor the latter canonical form. Evidently, the electron-pair-bond energy in $(FO_2SO\text{-}Xe)^+$, of the $(FO_2SO\text{-}Xe)^+F^-$ form, would need to exceed the $(Xe\text{-}F)^+$ bond energy, in the $(FXe)^+(OSO_2F)^-$ form, by the difference in the SO_3F and F electron affinities, for the two forms to have comparable weight in the resonance hybrid.

Similar considerations provide for an understanding of the low thermal stability of the $(Xe\text{-}OSO_2F)^+(MF_6)^-$ and related salts. Clearly the lattice energy for such salts will be less favorable than for $(Xe\text{-}F)^+(MF_6)^-$ where U has been estimated to be approximately −115 kcal mol^{-1}.[13b] Electron or F^- transfer will occur if the cation has high electron affinity and the lattice energy is sufficiently low. Previous work[13] has shown that the compound $(FXe)^+(AsF_6)^-$ is thermally unstable with respect to F^- abstraction from the anion: $2FXe^+AsF_6^- \rightarrow Xe_2F_3^+AsF_6^- + AsF_5$. It may be that the fate of the xenon fluorosulfate cation in the hexafluoroarsenate is similar: $2(XeOSO_2F)^+AsF_6^- \rightarrow [(FXeO)_2S(O)F]^+[AsF_6]^- + Xe(OSO_2F)_2AsF_5$. The close similarity of the vibrational spectra of $[(FXeO)_2S(O)F]^+[AsF_6]^-$ and $((FXe)_2F)^+(AsF_6)^-$, compared in Table VII, indicates that the F–Xe bond is similar in the two cations. The higher electron affinity of the SO_3F group, relative to F, favors its location in the bridging position of the cation, the $(F\text{-}Xe)^+(SO_3F)^-\text{-}(Xe\text{-}F)^+$ canonical form therefore being the anticipated dominant one.

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(38) The perchlorates and fluorosulfates of the alkali metals are usually isostructural (all usually in space group *Pnma*). Thus for $KClO_4$, a = 8.83, b = 5.65, c = 7.24 Å (N. V. Mani, *Proc. Indian Acad. Sci., Sect. A*, **46**, 143 (1957)); for KSO_3F, a = 8.62, b = 5.84, c = 7.35 Å (K. O'Sullivan, R. C. Thompson, and J. Trotter, *J. Chem. Soc. A*, 2026 (1967)); and for KBF_4, a = 8.66, b = 5.48, c = 7.03 Å (G. Brunton, *Acta Crystallogr., Sect. B*, **25**, 2161 (1969)). A thermochemical radius of 2.1 Å has been advocated (A. H. Sharpe, *Halogen Chem.*, **1**, 1 (1971)) for BF_4^- in lattice energy calculations, using the second Kapustinskii equation, from which $U(RbBH_4)$ = 149 and $U(CsBH_4)$ = 144 kcal mol^{-1}. It is probable, in view of the slightly greater size of ClO_4^- and SO_3F^- relative to BF_4^-, that the lattice energies for the Rb and Cs salts of these anions will be a little less than the values quoted for BF_4^-. The lattice energies, quoted by Sharpe, for RbF and CsF are 186 and 179 kcal mol^{-1}, respectively.

(39) The electron affinity of ClO_4 has been estimated from a Born–Haber cycle, employing a lattice energy calculation, to be 134 kcal mol^{-1} (V. I. Medeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," St. Martin's Press, New York, N. Y., 1966), whereas the electron affinity of the F atom has been determined spectroscopically to be 79.5 ± 0.1 kcal mol^{-1} (R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, **38**, 1540 (1963)).

(40) N. Bartlett, M. Gennis, D. D. Gibler, B. K. Morrell, and A. Zalkin, to be submitted for publication.