Submitted to Inorganic Chemistry

LBL-168
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March 1972

AEC Contract No. W-7405-eng-48

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Contribution from the Department of Chemistry, Princeton University, Princeton, N.J., 08540, The University of California, and the Lawrence Berkeley Laboratory, Berkeley, California, 94720.

FLUOROSULFATES AND PERCHLORATES OF XENON(II) AND THE SALT $[(FXe)_2O_2S(O)F]^+[AsF_6]^-$

by

M. Wechsberg, P. A. Bulliner, and F. O. Sladky

Department of Chemistry, Princeton University, Princeton, N.J., 08540

and

R. Mews and Neil Bartlett*

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and Department of Chemistry; University of California, Berkeley, California 94720

ABSTRACT

The fluorine ligands of xenon difluoride may be substituted, one at a time, by other electronegative species. Interaction of the difluoride with the appropriate molar quantity of anhydrous acid, below 0°, yields the monofluorosulfate, $FXeOSO_2F$, which is a colorless solid, m.p. 36.6°, the bis-fluorosulfate, $Xe(OSO_2F)_2$, which is a pale yellow solid, m.p. 43-45°, the monoperchlorate, $FXeOClO_3$, which is a colorless solid, m.p. 16.5° and a yellow solid, which decomposes below 0°, which is probably the bis-perchlorate, $Xe(OClO_3)_2$. All of these xenon difluoride derivatives are thermodynamically unstable and dismutate spontaneously above 0°, the

major products being as represented by the equations:

$$2FXeOSO_2F \rightarrow XeF_2 + Xe + S_2O_6F_2; \quad Xe(OSO_2F)_2 \rightarrow Xe + S_2O_6F_2;$$
$$2FXeOClO_3 \rightarrow XeF_2 + Cl_2O_7 + \tfrac{1}{2}O_2 + Xe; \quad Xe(OClO_3)_2 \rightarrow Xe + Cl_2O_6 + O_2.$$

Although solid products have been obtained from the interaction of XeF_2 with methyl- and trifluoromethyl-sulfuric acids, the stoichiometries of which suggest FXeOR species, they are explosive and have not been well characterized. $FXeOSO_2F$ can be vacuum sublimed at 20°. The bis-fluorosulfate, which is not volatileat 20°, is of lower thermal stability. Single crystals are primitive monoclinic with a = 7.8, b = 13.5, c = 6.7 Å (all ± 0.1 Å), β = 96°.

Vibrational spectroscopic evidence indicates that the xenon(II) atom is two coordinated in each of these compounds, the structural formulae being: $F{\cdot}Xe{\cdot}O{\cdot}S(O)_2{\cdot}F$; $F{\cdot}S(O)_2{\cdot}O{\cdot}Xe{\cdot}O{\cdot}S(O)_2{\cdot}F$ and $F{\cdot}Xe{\cdot}O{\cdot}ClO_3$. The vibrational spectra indicate that although the Xe atom in $Xe(OSO_2F)_2$ is symmetrically coordinated, the molecule is not centrosymmetric.

$FXeOSO_2F$ does not combine with excess XeF_2 to form a $[Xe_2F_3]^+$ salt, as do the $FXeMF_6$ compounds. The products of the reactions $XeF^+MF_6^-$ + FSO_2OH (M = Ru, As, Sb), in HF, may be $[XeOSO_2F]^+[MF_6]^-$ salts, but except for the Sb compound they are labile at room temperature. They have not been structurally characterized. The new salt, $[(FXe)_2SO_3F]^+[AsF_6]^-$ has been prepared and is sublimable without change. Vibrational spectra indicate that the cation is the symmetrical $[(FXe)_2O_2S(O)F]^+$ species. Efforts to prepare $[(FXe)_2O_2CCF_3]^+$ have led to immediate oxidation of the acid:

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

Hydrogen chloride is also readily oxidized:

$$[Xe_2F_3]^+[AsF_6]^- + HCl \rightarrow HF + \frac{1}{2}\,Cl_2 + \frac{1}{4}\,AsF_5 + \frac{3}{4}\,[Xe_2F_3]^+[AsF_6]^-$$

INTRODUCTION

The fluorides and substituted fluorides of xenon are thermodynamically stable[1], whereas the oxides are highly endothermic[2]. This difference is largely a consequence of the bond energy of molecular O_2 being greater than that of F_2 (110 versus 37 kcal mole^{-1}) although the bond energy for Xe-O is less than for Xe-F. 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 Pimentel and his coworkers[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[1,3] 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:

$$XeF_2 + HA \rightarrow FXeA + HF; \quad FXeA + HF \rightarrow XeA_2 + HF.$$

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.

Both the perchlorate and fluorosulfate ligands are strongly electron attracting and the generation of hydrogen fluoride (a very thermochemically favorable compound[8]), 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[9], and the crystal and molecular structure of $FXeOSO_2F$ is given in the accompanying paper[10]. The chemical and physical behavior 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 fluorosulfonating and perchloronating reagents, respectively.

The moderate thermal stability of the xenon fluorosulfates suggested that trifluomethyl 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 vibrational spectroscopic evidence indicates is CF_3SO_3XeF.

Since work in these laboratories[11] and independent work by Peacock and his coworkers[12], has established XeF_2 to be a fluoride ion donor we have tried to make the $(XeOSO_2F)^+$ salts by the interactions $FXeOSO_2F$ +

MF_5 (M = Ru, As, Sb). The 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 to be easy to generate and is relatively stable thermally.

Experimental Section

Materials.- Xenon difluoride was obtained by the method of Streng and Streng[13] and Holloway[14] as modified by Williamson[15]. Previous analytical, x-ray and spectroscopic examination in these laboratories has confirmed that this method yields high purity XeF_2[15]. Fluorosulfonic acid obtained from K and 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, b.p. 164°. Perchloric acid was prepared from commercial 70% perchloric acid, by adding a five-fold excess of conc. H_2SO_4 followed by distillation at 10 torr. Trifluormethyl sulfonic acid, obtained from The Chemical Division of the 3M Company, 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 the Ozark Chemical 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 difluroide were prepared in Kel-F tubes provided with Kel-F valves. The tubes were made by drilling approximately 3" lengths of 5/8" diameter Kel-F rod to preserve a 1/8" 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 Corporation Drilab. Manipulations involving volatile reactants or products were carried out on a vacuum line constructed of 1/3" nickel tubing linked by Monel Swagelock fittings and Monel Whitey valves and capable of a vacuum of 10^{-5} torr or better.

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 K_α radiation, on a G.E. Precission 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 conjection 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 fluorosulfonic 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 in a dynamic vacuum with the mixture held at 0°. A colorless solid, m.p. 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 was in accord with the overall reaction: $XeF_2 + HOSO_2F \rightarrow FXeOSO_2F + HF$. Typically, XeF_2 (0.728 g, 4.3 mM) plus $HOSO_2F$ (0.430 g, 4.3 mM) gave $FXeOSO_2F$ (1.040 g, 4.2 mM) of volatiles (0.125 g, mainly HF, but containing traces of Xe, $S_2O_5F_2$ and $S_2O_6F_2$, the latter being identified from infrared spectra[16,17]). In an experiment in which an excess of XeF_2 was employed, the same white solid, m.p. 36.6°, was obtained on removing excess XeF_2 in a dynamic vacuum (for 0.5 hr) at 20°: XeF_2 (4.95 mM) + $HOSO_2F$ (3.60 mM) → $FXeOSO_2F$ (3.60 mM) + HF (3.7 mM).

Some Properties of $FXeOSO_2F$.- A small sample at ~ 20° was completely transferred in 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 the accompanying paper[10]. 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.

The colorless solid, on melting at 36.6°, produced a pale yellow-green liquid which evolved xenon and within an hour appeared to be completely decomposed according to the equation:

$2FXeOSO_2F \rightarrow XeF_2 + S_2O_6F_2 + Xe$. A ^{19}F n.m.r. 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 of xenon difluoride. The $S_2O_6F_2$ was identified by its characteristic infrared spectrum[17], with strong bands at 1490, 1246, 846 (PQR) and 752 cm^{-1}, and by its ready thermal dissociation to the colored OSO_2F radical. A preliminary survey of the chemical properties of $FXeOSO_2F$ show that it is a fluorosulfonating 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 $S_2O_6F_2$: $FXeOSO_2F + \underline{\gamma}SO_3 \rightarrow S_2O_6F_2 + Xe$; 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[16] 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 fluorosulfonic acid in a 1:2 mole ratio were transferred to a Kel-F reactor and maintained at -75° for 1/2 hour. 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 volatiles, removed in a dynamic vacuum at temperatures below 0°, were trapped and weighed. An infrared spectrum showed the volatiles to be

HF, with < 4 mole % $S_2O_5F_2$[16]. 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 mM) and $HOSO_2F$ (0.864 g, 8.64 mM) gave 1.371 g of yellow solid, (4.2 mM $Xe(OSO_2F)_2$) and 0.212 g of volatiles, which contained 8.7 mM 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 $Xe(OSO_2F)_2$ 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. Unlike $FXeOSO_2F$, $Xe(OSO_2F)_2$ appears to be involatile at room temperature. 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 $S_2O_6F_2$[17]. The infrared spectrum proved that other sulfur florides 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[17].

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 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 and $S_2O_6F_2$ 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.

Xe(II) fluoride perchlorate

Preparation.- Perchloric acid (0.294 g, 2.93 mM) was condensed into a Kel-F reactor containing XeF_2 (0.477 g, 2.82 mM) and allowed to warm first to -110° and after 10 minutes to -60°. The reaction was completed by warming to 0° at which temperature volatiles (0.091 g) were removed in a dynamic vacuum and trapped. The infrared spectrum of the volatiles showed them to consist mainly of 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 2.72 mM of $FXeOClO_3$. The colorless solid melted sharply at 16.5° decomposing simultaneously to yield a liquid which rapidly turned 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 $FClO_3$.[18] 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 is given in Table V. The vibrational spectra for $FXeOClO_3$ are given in Table VI.

Xe(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°, 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[19].

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 $O_2ClOXeOSO_2F$ was attempted both by adding perchloric acid to $FXeOSO_2F$ and fluorosulfonic 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-$OOSO_2F$). 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 at -78° 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:

$$XeF_2 + HCl \xrightarrow{(HF)} \tfrac{1}{2}XeF_2 + \tfrac{1}{2}Cl_2 + HF.$$

$\underline{CF_3SO_2OH}$ (CAUTION!). XeF_2 (4.73 mM) was condensed onto the acid which was in slight excess for a 1:1 reaction (5.52 mM). 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 (~ 1hr) brought to 0° and held at that temperature for 2 hours. Slight gas evolution occured 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 hours under dynamic vacuum, weighed 1.06 g (theoretical yield for $FXeOSO_2CF_3$, allowing for ready decomposition of the <u>bis</u> 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 up to room temperature.

$\underline{CH_3SO_2OH \cdot XeF_2}$ (9.45 mM) was condensed on to the acid (9.77 mM) 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 m mole XeF_2 and 6.69 mM CH_3SO_2OH in 4 ml 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 m mole min^{-1}). It detonated on warming to room temperature.

<u>$ClSO_2OH$</u>.- Addition of XeF_2 (3.0 mM) to the acid (3.0 mM) followed by warm-up to -78° led to a vigorous reaction to yield a pale yellow solution and much gas, which contained 3 mM 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 mM $ClSO_2OH$, 2.09 mM XeF_2) generated Xe (2.1 mM) and Cl_2 (2.15 mM), even at -95°. The less volatile liquid residue proved to be HSO_3F, this indicating the overall reaction to be:

$$XeF_2 + 2ClSO_2OH \rightarrow Xe + Cl_2 + FSO_2OH.$$

<u>$(CF_3)_3COH$</u>.- XeF_2 (4.3 mM), interacted with gas evolution, with the acid (4.33 mM) at 0°. (No reaction occurred below that temperature.) The reaction accelerated with time and gave a colorless solution. Xenon was removed under vacuum at -130° and amounted to (4.33 mM).

<u>Attempts to Prepare $[XeOSO_2F]^+MF_6^-$ Salts.</u>

<u>$[XeF]^+[SbF_6]^-$</u> was prepared by adding XeF_2 (42.2 mM) to a solution of SbF_5 (40.7 mM) in HF (10 ml). This mixture was stirred for 4 hours at 0°, by which time a clear pale yellow solution had formed. The HF was removed in a dynamic vacuum at 0° to leave a pale yellow solid. The powder photograph indicated isomorphisum with $[FXe]^+[RuF_6]^-$ and was indexed[20] on the basis of an orthorhombic unit cell of dimensions: a = 11.2, b = 8.0, c = 7.5 Å

(all ± 0.1 Å). The Raman spectrum showed the presence of $Xe_2F_3^+SbF_6^-$ (as anticipaged 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[11] of $XeF^+MF_6^-$ salts:

668(13, νSb-F), 651(3,νSb-F), 643(6,νSb-F), 624(3,νSb-F), 612(25, νXe-F), 607(sh,νXe-F), 596(sh,νSb-F), 591(sh,$\nu Xe_2F_3^+$ impurity), 581(sh,$\nu Xe_2F_3^+$ impurity), 470(2 broad,νSb-F), 290(5,δSb-F), 270(4, δSb-F).

<u>$[XeF]^+[SbF_6]^-$ and FSO_2OH</u> (5.44 mM and 6.1 mM respectively) were dissolved in HF (10 ml) with stirring at 0° for 4 hours to give a yellow-green solution. The solvent was removed in a dynamic vacuum, at -30° to leave a yellow-green solid. Xenon evolution during all manipulations to this point amounted to < 0.5 mM. 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 towards 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 hours.

<u>$[XeF]^+[RuF_6]^-$</u>, (1.36 mM) prepared as previously described,[11] was mixed with HSO_3F (1.41 mM) in HF (2 ml) with stirring, at o°, for 5 hours. 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.

<u>$[XeF]^+[AsF_6]^-$</u> was prepared by dissolving AsF_5 (10.87 mM) and XeF_2(10.4 mM) in HF (5 ml) and FSO_2OH (10.6 mM) was condensed into this mixture which was allowed to warm to 0°. It was maintained with vigorous stirring at 0° for 2 hours then for a further 2 hours 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 in a dynamic vacuum. The greenish solid, which remained, rapidly become 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 and $S_2O_6F_2$), under dynamic vacuum, a residue of 1.84 g of $[(FXe)_2O_2\ S(O)F]^+[AsF_6]^-$ (see below) remained.

<u>The preparation of $[(FXe)_2O_2S(O)F]^+[AsF_6]^-$</u>.- XeF_2 (7.8 mM) and FSO_2OH (4.38 mM) were condensed in HF (6 ml) and stirred at 0° for 4 hours. AsF_5 (4.2 mM) 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°C, 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 $[(XeF)_2O_2S(O)F]^+[AsF_6]^-$ with some $[Xe_2F_3]^+[AsF_6]^-$ impurity. This composition is entirely consistent with the stoichiometry of the starting materials since the XeF_2 concentration was less than required for the ideal interaction:

$$FXeOSO_2F + XeF_2 + AsF_5 \rightarrow [(FXe)_2O_2S(O)F]^+[AsF_6]^- \quad .$$

A purer product was obtained from the $[FXe]^+[AsF_6]^-$ - $HFSO_2OH$ 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 hours at -40°, to yield a colorless solid, which Raman spectroscopy proved to be a mixture of $Xe(OSO_2F)_2$ and $[(FXe)_2O_2S(O)F]^+[AsF_6]^-$. Warming this mixture to 40° destroyed the former but not the latter.

The Raman spectrum (Table VII) and the effectiveness of the stoichiometry $2XeF_2 + FSO_2OH + AsF_5$ in forming the product, together, provide strong support for the formulation $[(FXe)_2O_2S(O)F]^+[AsF_6]^-$.

Analysis.- Several samples from different preparations were analysed 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. Found: Xe, sample (a): 45.8; 45.4; sample (b) 45.4; 45.5%. Required for $O_3AsSF_9Xe_2$: Xe, 44.6%. 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 $[(FXe)_2O_2S(O)F]^+[AsF_6]^-$.- The Raman spectrum of the colorless

solid is represented in Table VII. It is remarkably similar to that of $[Xe_2F_3]^+[AsF_6]^-$. Surprizingly, the solid is sublimable, at ~ 20°, in a dynamic vacuum. The Raman spectrum 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:

$$[(FXe)_2O_2S(O)F]^+[AsF_6]^- \rightarrow \frac{3}{4}[Xe_2F_3]^+[AsF_6]^- + \frac{1}{4}AsF_5 + \frac{1}{2}Xe + \frac{1}{2}S_2O_6F_2$$

The solid interacts rapidly with dry CH_3CN.

<u>The attempted preparation of $[(FXe)_2O_2CCF_3]^+[AsF_6]^-$ and $[(FXe)_2Cl]^+[AsF_6]^-$.-</u>

<u>CF_3COOH</u> (2.25 mM) was added at -196° to a solution of $Xe_2F_3{}^+AsF_6{}^-$ (2.22 mM) in HF (5 ml). As soon as the mixture melted on warm up, a vigorous interaction occured and was complete within 1 or 2 minutes. 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 $[Xe_2F_3]^+[AsF_6]^-$ (0.32 g). If allowance is made for the volatility of $[Xe_2F_3]^+[AsF_6]^-$, these observations are in accord with the overall reaction:

$$[Xe_2F_3]^+[AsF_6]^- + CF_3COOH \rightarrow CF_4 + CO_2 + HF + \frac{1}{2}AsF_5 + Xe + \frac{1}{2}[Xe_2F_3]^+[AsF_6]^-.$$

<u>HCl</u> (2.26 mM) was added to a solution of $[Xe_2F_3]^+[AsF_6]^-$ (2.26 mM) in HF (5 ml) at -80°. Evolution of Xe and Cl_2 gas occured 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:

$$[Xe_2F_3]^+[AsF_6]^- + HCl \xrightarrow{(HF)} HF + \frac{1}{2}Cl_2 + \frac{1}{2}Xe + \frac{1}{4}AsF_5 + \frac{3}{4}[Xe_2F_3]^+[AsF_6]^- .$$

DISCUSSION

Preparative.- Our studies have demonstrated that 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 tendancy for the mono-substituted derivatives to dismutate (i.e., $2FXeOR \not\rightarrow XeF_2 + Xe(OR)_2$), since the FXeOR compounds may be obtained pure by mixing the reactants in 1:1 molar ratio:

$$XeF_2^+ \; HOR \rightarrow FXeOR + HF.$$

On the other hand, we have failed to generate the unsymmetrical compounds:

$$FXeOR + HOR' \rightarrow \frac{1}{2}Xe(OR)_2 + \frac{1}{2}Xe(OR')_2.$$

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:

$$HCl + XeF_2 \rightarrow \frac{1}{2}XeF_2 + HF + \frac{1}{2}Cl_2$$

or of $Xe_2F_3^+$:

$$[Xe_2F_3]^+[AsF_6]^- + HCl \rightarrow HF + \frac{1}{2}Cl_2 + \frac{1}{2}Xe + \frac{1}{4}AsF_5 + \frac{3}{4}[Xe_2F_3]^+[AsF_6]^-$$

indicate that the chlorine ligand is too readily oxidized to molecular chlorine, for Xe-Cl compounds to be preserved under normal conditions of termperature and pressure. It is of interest, here, that chlorine is also liberated in the interaction of chlorsulfonic acid with XeF_2:

$$XeF_2 + 2HOSO_2Cl \rightarrow Xe + Cl_2 + 2HOSO_2F.$$

This may simply be a consequence of HCl generation:

$$HF + HOSO_2Cl \rightarrow HOSO_2F + HCl.$$

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-trifluoromethylsulfate, $FXeOSO_2CF_3$, 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 $CF_3O_2S\text{-}O\text{-}O\text{-}SO_2CF_3$ would be the product. The latter however, has been reported by Noftle and Cady[21], 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 $FXeOSO_2CF_3$ suggests that the $SO_3CF_3^{\cdot}$ radical is not an important decomposition species but indicates rather that there is fluorine attack at the S-C bond, perhaps intra-molecularly. Evidently much the same kind of attack 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:

$$Xe_2F_3^+ AsF_6^- + CF_3COOH \xrightarrow{HF} ([(XeF)_2CO_2CF_3]^+[AsF_6]^-) \rightarrow$$

$$[XeF]^+[AsF_6]^- + Xe + CF_4 + CO_2 \quad .$$

The work of Eisenberg and DesMarteaux[22] and Sladky[23] has already established the instability of the trifluoroacetates.

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.[24]

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 $\underline{\nu}$(Xe-F)and $\underline{\nu}$(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 $\underline{\nu}_{sym}$ = 495 and

ν_{asym} = 555 cm^{-1}.[25] Furthermore, the observed Xe-O stretching frequency in $Xe(OSO_2F)_2$, $\nu(Xe\text{-}O)_{sym}$ = 436 cm^{-1}, is not only comparable to the XeF and XeO stretching frequencies in $FXeOSO_2F$, but is remarkably similar to the $\nu(I\text{-}O)_{sym}$ = 441 cm^{-1} observed recently by Aubke and his coworkers for $I(OSO_2F)_4^-$.[26]

The preference of the $XeF_2 \cdot 2MF_5$ derivatives for the structure $FXe^+[F_5M\text{-}F\text{-}MF_5]^-$ [11,12], raised the possibility of the bisfluorosulfate 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 non-centrosymmetric assembly. If, in keeping with all known Xe(II) structures (See Reference 10), the xenon atom is linearly coordinated in oxygen, -O-Xe-O-, the spectra required that the molecule, at least in the solid state, have a gauche or cis configuration. The comparison of the $Xe(OSO_2F)_2$ 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 $Xe(OSO_2F)_2$. Incidentally, it should also be noted that the stretching frequency of the peroxide bond $\nu(O\text{-}O)$ = 798 cm^{-1}, is low and is compatible with the ready dissociation of $S_2O_6F_2$:

$$FS(O)_2 \cdot O\text{-}OS(O)_2\text{-}F \rightarrow 2FSO_3^{\cdot}$$.[17]

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.

The fluorosulfate decompositions proceed quantitatively as follows:

$$2FXeOSO_2F \rightarrow XeF_2 + S_2O_6F_2 + Xe$$
$$Xe(OSO_2F)_2 \rightarrow Xe + (SO_3F)_2 \quad . \qquad (1)$$

The perchlorate decompositions are much more complex and although it is possible that $(ClO_4)_2$ or $ClO_4^{\bullet}$ 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 radical.[17] It is reasonable to postulate the $XeF^{\bullet}$ radical as the other initial product of decomposition. If this radical occurs, it must be stable towards either dissociation into atoms or mutual anhilation,

$$\text{i.e.,} \quad 2XeF^{\bullet} \not\rightarrow 2Xe + F_2 \quad , \qquad (2)$$

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

$$2XeF^{\bullet} \rightarrow Xe + XeF_2 \quad , \qquad (3)$$

since the entropy change is slightly unfavorable for XeF_2 formation in this reaction.[27] Therefore, if the $XeF^{\bullet}$ radical is an intermediate in the $FXeOSO_2F$ decomposition, the bond energy must be < 32 kcal mole^{-1} to be

compatible[1] with process (3) and > 18 kcal mole^{-1} to account for the absence of fluorine[28] [Equation (2)]. It is pertinent that the $XeF^{\cdot}$ radical has also been postulated[11] as an intermediate, which disproportionates, in the redox reaction:

$$3XeF^{+}OsF_6^{-} \rightarrow Xe_2F_3^{+}OsF_6^{-} + 2OsF_6 + Xe.$$

Bonding.- In the valence-bond description of XeF_2, Coulson[56] 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 $^{-\frac{1}{2}}F\ Xe^{+1}F^{-\frac{1}{2}}$, indicated by nmr,[29] Mossbauer,[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 $^{\frac{1}{2}}F\ Xe^{+1}\ F^{-\frac{1}{2}}$, is 13.3 kcal mole^{-1}, whereas the experimental value reported[33] in 1968 is 13.2 kcal mole^{-1}. It should be recognised 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 $\Delta H(\text{electron-pair})(G^{+} + L \rightarrow GL^{+})$; $\Delta H(\text{electrostatic})(G\text{-}L^{+} + L^{-} \rightarrow (L\text{-}G^{+}L^{-})g)$ and R(resonance), to ensure a bound species GL_2. If L is sufficiently electronegative $(G\text{-}L)^{+}$ 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 ΔH(electrostatic) be, 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[37,28] (thus the bond energies for ICl and I-F are 58 and 67 kcal $mole^{-1}$, 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 $mole^{-1}$, respectively. Although the electron affinity of chlorine is 3 kcal $mole^{-1}$ greater than for fluorine[28], this is the only term in the cycle which is more favorable for the chlorine case and the summation indicates that the enthalpy of formation of $XeCl_{2(g)}$ from the gaseous atoms would be less favorable than for XeF_2, by 34 kcal $mole^{-1}$, with $\Delta H_{at}(XeF_2) = 65$ and $\Delta H_{at}(XeCl_2) \sim 31$ kcal $mole^{-1}$. These values are in harmony with the stretching force constants given by Nelson and Pimentel, which are $k_r = 1.32$ mdyne/Å for $XeCl_2$ and $k_r = 2.6$ mdyne/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. However, these multiatom ligands, while conferring advantages from their high

electron affinities, are nevertheless sizeable 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 $mole^{-1}$ less than for $F\text{-}Xe^+F^-$, since the lattice energies of Rb and Cs perchlorates are ~ 40 kcal $mole^{-1}$ 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[10], 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/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 $F^-(Xe\text{-}F)^+RuF_5$[40]. The ability of the hexafluororuthenate(V) to form a $Xe_2F_3^+$ salt[11]:

$$FXe^+RuF_6^- + XeF_2 \rightarrow (Xe_2F_3)^+(RuF_6)^- \quad ,$$

and the failure of $FXeOSO_2$ to do likewise, gives 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 mole^{-1}.[11b] Electron or F^- transfer will occur if the cation has sufficiently high affinity and the lattice energy is sufficiently low. Previous work[11] has shown that the compound $(FXe)^+(AsF_6)^-$ is thermally unstable with respect to F^- abstraction from the anion:

$$2FXe^+AsF_6^- \rightarrow Xe_2F_3^+AsF_6^- + AsF_5 \quad .$$

It may be that the fate of the xenon fluorosulphate cation in the hexafluoroarsenate is similar:

$$3FXeOSO_2F + AsF_5 \rightarrow ((FXe)_2O_2SOF)^+(AsF_6)^- + Xe(OSO_2F)_2 \quad .$$

The close similarity of the vibrational spectra of $((FXe)_2O_2S(O)F)^+(AsF_6)^-$ 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 $(F\text{-}Xe)^+(SO_3F)^-(Xe\text{-}F)^+$ canonical form therefore being the anticipated dominant one.

ACKNOWLEDGMENTS

The work carried out at Princeton University was supported by The National Science Foundation (Grant No. GP-7153X) and that done at Berkeley was supported by The United States Atomic Energy Commission under Grant number W-7405-eng-48.

We are indebted to Dr. J. Scherrer of The Western Regional Laboratories of The United States Department of Agriculture, Albany, California, for help in obtaining the Raman spectra.

The following Tables are not to be reproduced in the regular edition:

Tables I

IV

V

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37. L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, 3rd Edition, 1960.

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., 46A 143 (1957)); for KSO_3F, a = 8.62, b = 5.84, c = 7.35 (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 (G. Brunton, Acta Cryst., B25 2161 (1969)). A Thermochemical radius of 2.1 Å has been advocated (A. H. Sharpe, "Halogen Chemistry" Vol. 1, V. Gutmann, ed., Academic Press, London and New York, 1971, p.1). for BF_4^- in lattice energy calculations, using the second Kapustinskii equation, from which $U(RbBH_4)$ = 149 and $U(CsBH_4)$ = 144 kcal $mole^{-1}$. It is probable, in view of the slightly greater size of ClO_4^- and SO_3F^- relative to Br_4^-,

that the lattice energies for the Rb and Cs salts of these anions will be a little less than the values quoted for Br_4^-. The lattice energies, quoted by Sharpe, for RbF and CsF are 186 and 179 kcal $mole^{-1}$ respectively.

39. The electron affinity of ClO_4 ahs been estimated from a Born-Haber cycle, employing a lattice energy calculation, to be 134 kcal $mole^{-1}$ (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, 1966), whereas the electron affinity of F atom has been determined spectroscopically to be 79.5 ± 0.1 kcal $mole^{-1}$ (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 published.

Table I. X-Ray Powder Data for $FXeOSO_2F$ (orthorhombic: a=9.88; b=10.00; c=10.13Å; S. G. Pbca)

dÅ	$10^4 1/d^2_{obs}$	$10^4 1/d^2_{calc}$	h k l	I/I_0
5.03	395	390	002	60
4.56	481	497	021	80
4.09	596	600	121	50
3.588	777	790	022	100
3.554	792	799	202	60
3.375	878	891	123	60
3.042	1081	1080	113	30
3.018	1098	1100	131	20
2.777	1297	1277	023	40
		1287	203	
2.712	1360	1377	123	80
2.705	1366	1387	213	
2.512	1585	1558	004	30
		1600	040	
2.474	1633	1638	400	40

Table II. Vibrational Spectra and Assignments for $FXeOSO_2F$[a] and $FXeOSO_2CF_3$[d]

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

References for Table II.

(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 $(SO_3F)_2$ as illustrated in Table III, but the assignment of the Xe-O and Xe-F stretching was 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, Xe-O stretching bands in the Raman would be intense, as in the $Xe_2F_3^+$ salt spectra[c].

(b) N. Bartlett, D. Gibler, M. Gennis, and H. Zalkin, to be published.

(c) F. O. Sladky, P. A. Bulliner, and N. Bartlett , J. Chem. Soc., (A), 1969, 2179.

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

w = weak, m = medium, s = strong, v = very

ν = stretching, δ = deformation, ρ_w = wagging (ρ_w(S-F) can also be written as $\rho_r(SO_3)$).

References for Table III.

(a) For bands occuring at frequencies > 700 cm^{-1} the assignments were straightforward, as the Table itself indicates, but the $\underline{\nu}$(Xe-O) + $\underline{\nu}$(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 $\underline{\nu}$(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", John Wiley and Sons, Inc., New York (1963).

(c) F.O. Sladky, Angew. Chem. Int. Edn., 8, 523 (1969).

(d) F. Aubke, H. A. Carter, and S. P. L. Jones, Inorg. Chem., 9, 11, 2485 (1970).

Table IV. Partial X-Ray Powder Data for $Xe(OSO_2F)_2$

(Primitive monoclinic: a = 7.94, b = 13.7, c = 6.84Å, β = 96°)

dÅ	$10^4 1/d^2_{obs.}$	$10^4 1/d^2_{calc.}$	hkl	I/I_o*
6.13	266	265	011	50
5.17	375	372	120	30
5.08	388	385	111	30
4.65	462	465	$11\bar{1}$	50
4.27	550	544	121	50
3.993	627	624	$12\bar{1}$	40
3.951	641	640	200	80
3.792	695	693	210	70
3.478	827	809 825	$13\bar{1}$ $21\bar{1}$	90
3.415	857	848	040,002	5
3.345	894	889	131	10
3.168		981 985	$11\bar{2}$ 211	10

*Estimated visually

Table V. X-Ray Powder Data for $FXeOClO_3$

dÅ	I/I_0	dÅ	I/I_0
5.75	10	3.374	20
5.64	15	3.325	50
4.83	40	2.903	40
4.75	60	2.846	40
4.49	10	2.693	50
4.35	50	2.656	50
4.065	30	2.573	40
3.657	60	2.490	20
3.554	40	2.423	40
3.510	100	2.388	40
3.467	40	2.345	50

Table VI. Vibrational Spectra and Assignments for $FXeOClO_3$

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

References for Table VI.

(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 3 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 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-F. It is better to describe the modes as "symmetric" and "antisymmetric" F-Xe-O stretching, with the higher frequency attributable to 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)	409ρ(S-F)
	551(sh)	566
588(94)ν(XeF)sym	563(88)	
575(sh)$\nu_2(AsF_6^-)$	573(sh)	
600(100)ν(XeF)asym	581(100)	
	588(23)	592
	633(12.5)	
683(19)$\nu_1(AsF_6^-)$	685(13.5)	
	875(2)	786ν(S-F)
	1035(9)	1082ν(S-O)sym
	1090(3)	
	1350(5)	1287ν(S-O)asym

(a) F. O. Sladky, P. A. Bulliner, and N. Bartlett, J. Chem. Soc. (1969), 2179.

(b) K. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds", Wiley Interscience, 2nd Ed., New York, London, 1970, p. 114.

0 0 0 0 3 6 0 7 2 7 8

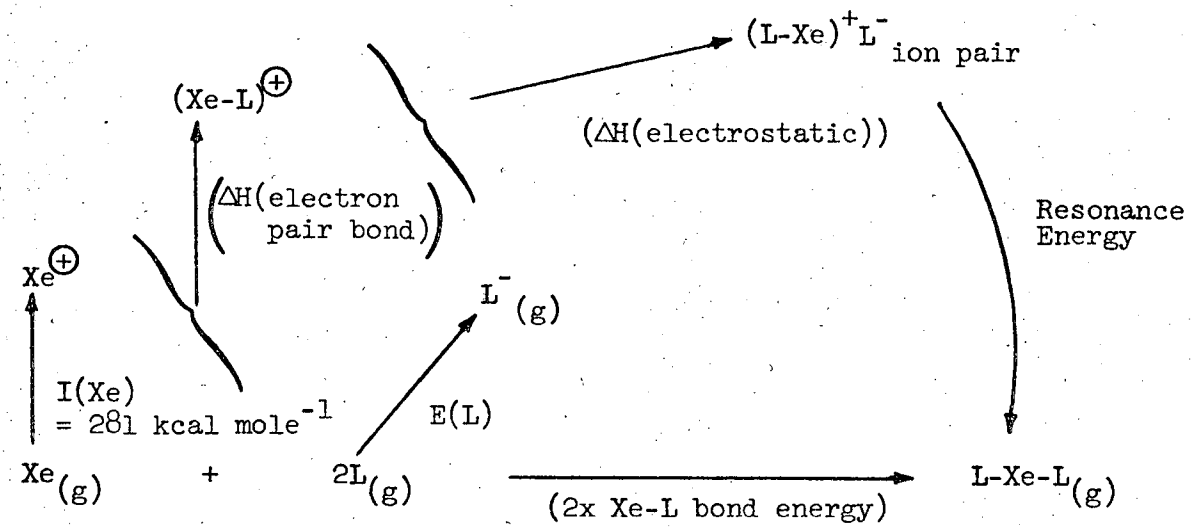

Figure 1 A Thermochemical Cycle for XeL_2

In the case of XeF_2, E(F) is -80[a], ΔH(Electron pair bond) is -48[b] and the total bond energy[c] is -65 kcal $mole^{-1}$. Thus $\sum$(ΔH(electrostatic) + Resonance Energy) = -218 kcal $mole^{-1}$.

(a) Reference 39

(b) J. Berkowitz and W. A. Chupka, Chem. Phys. Letters, 7, 447 (1970).

(c) Reference 1.

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720