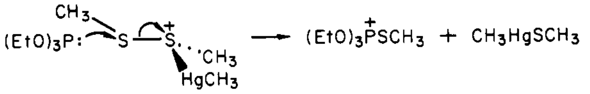
Ab initio calculations[31] have provided convincing evidence that the role of the proton in acid-catalyzed concomitant -SS- scission (eq 2) is to affect an increase in the electron affinity of the disulfide, as evidenced by a marked decrease in the energy of LUMO, and to transform RSE (eq 2) into a neutral leaving group. We attribute the catalytic efficiency of CH_3Hg^{II} to its Lewis acidity which causes a similar lowering of the -SS- σ^* orbital energy upon formation of sulfonium ion **1**. This reduction in energy difference between the frontier molecular orbitals involved in displacement will facilitate the approach of $P(OEt)_3$ and increase the rate of displacement on the low-lying σ^* orbital of **1** (eq 18).



(18)

1

HOMO (n) LUMO (σ^*)

In conclusion, we have delineated some of the essential features required for -SS- bond cleavage by CH_3Hg^{II} in a simple disulfide and developed a model system for the study of the interaction of this important functional group with CH_3Hg^{II}. Our kinetic study provides the first mechanistic evidence for a concomitant metal-assisted disulfide cleavage, and we have developed a highly sensitive method for measuring the equilibrium constants for the interaction of the mercury nucleus with a variety of ligands. Most importantly, this study provides a convincing argument that the *disulfide linkage in proteins is not a primary target for methylmercury* since an ionic form of methylmercury is required and essentially all CH_3Hg^{II} in living systems is present as its highly covalent methylmercury mercaptide.

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Xenon-Nitrogen Bonds. The Synthesis and Characterization of [Imidobis(sulfuryl fluoride)]xenon(II) Derivatives $Xe[N(SO_2F)_2]_2$, $FXeN(SO_2F)_2$, and $[(FSO_2)_2NXe]_2F^+AsF_6^-$ and the Radical $\cdot N(SO_2F)_2$

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Abstract: The synthesis and characterization of three compounds containing xenon-nitrogen bonds are described. The novel compounds $Xe[N(SO_2F)_2]_2$ and $FXeN(SO_2F)_2$ are obtained by low-temperature reactions of XeF_2 with the nitrogen acid, $HN(SO_2F)_2$. The complex salt $[(FSO_2)_2NXe]_2F^+AsF_6^-$ is prepared by the reaction of $FXeN(SO_2F)_2$ with AsF_5. The compounds have been characterized by Raman and NMR (^{19}F, ^{129}Xe) spectroscopy. The $\cdot N(SO_2F)_2$ free radical is formed on decomposition of $Xe[N(SO_2F)_2]_2$ and $FXeN(SO_2F)_2$, and its EPR spectrum is reported.

The ability of very electronegative elements to form bonds to xenon in ground-state molecules is now established for fluorine, chlorine, and oxygen.[1] These bonds to xenon may be divided into several types which can be classified informally in the following way: normal xenon-fluorine bonds as found in the binary fluorides such as XeF_2, XeF_4, and XeF_6;[2] bridging xenon-fluorine bonds as found in many complex xenon fluorides like $Xe_2F_3^+AsF_6^-$[3] and $Xe_2F_{11}^+AuF_6^-$;[4] weaker xenon-oxygen bonds as observed in compounds containing xenon bonded to electronegative radicals such as $FXeOC(O)CF_3$[5] and $Xe(OSeF_5)_2$;[6] stronger xenon-oxygen bonds as observed in xenon oxides and oxyfluorides like $OXeF_4$[7] and XeO_3;[8] and weak xenon-chlorine bonds as in $Cs_9(XeO_3Cl_2)_4Cl$.[9] In addition to the above well-established examples, there is good evidence to support the existence of a xenon-xenon bond in Xe_2^+ in solution.[10] Also, preliminary reports have been made on two compounds containing a xenon-nitrogen bond,[11,12] a xenon-boron bond,[13] and a xenon-carbon bond.[14] Thus the total number of elements which form bonds to xenon in compounds isolable under ordinary laboratory conditions is seven or less.

In 1974, the synthesis of $FXeN(SO_2F)_2$ was reported and this provided the first potential example of a xenon-nitrogen bond.[11]

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Somewhat later, a second example was proposed in $[(FSO_2)_2NXe]_2F^+AsF_6^-$.[12] This paper describes in detail the synthesis and characterization of these materials as well as the new compound $Xe[N(SO_2F)_2]_2$ and some unsuccessful attempts to prepare other Xe(II) compounds with nitrogen ligands. The compounds are characterized by ^{19}F and ^{129}Xe NMR and by Raman spectroscopy. In addition, the free radical $\cdot N(SO_2F)_2$, formed on decomposition of $Xe[N(SO_2F)_2]_2$ or $FXeN(SO_2F)_2$, has been identified by EPR. In the absence of a structural analysis by single-crystal X-ray diffraction, which has not yet been possible with any of these materials, the evidence is otherwise convincing for the existence of xenon–nitrogen bonds.

Experimental Section

General Data. The manipulation of volatile compounds was carried out in stainless-steel or glass vacuum systems. The metal system employed Teflon-packed stainless-steel valves and connections to the system were by means of compression fittings. The glass system utilized Teflon-glass valves throughout, and connections to this system were by means of standard-taper joints lubricated with Halocarbon grease or by stainless-steel or Teflon compression fittings. Pressures were measured with a Wallace and Tiernan differential pressure gauge (series 1500). Temperatures were measured with a digital indicating iron–constantan thermocouple. Amounts of reactants and products were measured by direct weighing or by PVT measurements assuming ideal-gas behavior.

Infrared spectra were recorded on a Perkin-Elmer Model 337 or 180 spectrometer using a stainless-steel or glass cell fitted with silver chloride windows. Raman spectra were taken with a Spex 14018 double monochromator utilizing photon-counting detection and Spectra Physics Model 164-03 argon ion laser for excitation. Samples were contained in a low-temperature glass cell similar to that of Brown et al.[15] but modified to permit the direct introduction of solid samples under inert atmosphere conditions. Spectra were normally recorded by using a liquid-nitrogen coolant which maintained the sample near 77 K.

EPR spectra were taken on a Bruker B-ER 418 spectrometer equipped with a Bruker NMR gaussmeter for field calibration and Eip 35/D frequency counter for measuring the resonance frequency. ^{19}F NMR spectra were recorded on a Varian XL-100-15 spectrometer equipped with an external proton lock. Chemical shifts were measured relative to internal or external $CFCl_3$, depending on the solvent employed. ^{129}Xe NMR spectra were recorded on a Bruker 270 MHz multinuclear spectrometer operating at 55.6 MHz.[16] Chemical shifts were obtained relative to external neat $OXeF_4$ at 25 °C.

Reagents. Fluorine, Cl_2, xenon, CF_2Cl_2, $CFCl_3$, BrF_5, $(CF_2CO_2H)_2$, $(CF_3)_2CO$, H_2NSO_3H, $ClSO_3H$, AsF_3, PCl_5, As_2O_5, N_2F_4, CF_3NO, C_2F_4 and HF were obtained from commercial sources and were appropriately purified before use. The compounds $CsN(SO_2F)_2$,[17] $HN(SO_2F)_2$,[18] XeF_2,[19] HNF_2,[20] $(CF_3)_2NH$,[21] perfluorosuccinimide,[22] and $(CF_3)_2C{=}N\text{-}H$[23] were prepared by literature methods.

Chlorine monofluoride was obtained by heating equimolar amounts of F_2 and Cl_2 for 18 h at 250 °C in Monel bomb. Arsenic pentafluoride was prepared by heating As_2O_5 with excess F_2 at 200 °C in a Monel bomb. A sample of $ClN(SO_2F)_2$[24] for Raman spectroscopy was obtained by reaction of $HN(SO_2F)_2$ with ClF at −111 to −10 °C for 24 h. Removing the volatile materials by pumping at −55 °C yielded pure $ClN(SO_2F)_2$ in the Kel-F reactor.

Reactions with XeF_2. All reactions were carried out in Teflon FEP or Kel-F reactors fitted with stainless-steel valves. The size of the reactors varied from ~4 to 50 mL. All reactions were carried out at least twice, and those involving $HN(SO_2F)_2$ were repeated many times. The following descriptions are for a representative case.

Reaction of $HN(SO_2F)_2$ with XeF_2 (1:1). Into a 50-mL Kel-F reactor was added 20.1 mmol of XeF_2 in a drybox. The reactor was then closed and evacuated, and ~8 mL of CF_2Cl_2 was added to the reactor at −195 °C by vacuum transfer. The reactor was warmed to liquify the CF_2Cl_2 and to cover the XeF_2 with solvent. It was then recooled to ~−170 °C, filled with dry N_2, and opened. Liquid $HN(SO_2F)_2$ (15.0 mmol) was then quickly added on top of the frozen CF_2Cl_2, and the reactor was closed and evacuated at −195 °C. It was then held at 0 °C with stirring for 3 days. The reactor was then pumped on at 0 °C to remove the solvent, HF, unreacted XeF_2, decomposition products, and any byproducts. After the reactor was pumped for 3 h at 0 °C, a nearly white solid remained, which was shown to be pure $FXeN(SO_2F)_2$ (3.96 g) corresponding to an 80% yield based on the starting $HN(SO_2F)_2$.

Analysis for Xe was carried out by reaction with H_2O and by thermal decomposition at 55 °C followed by reaction with H_2O. The moles of Xe per mole of compound were 1.02 for both cases. The infrared spectrum of the gas thought to be xenon always showed the presence of small amounts of SO_2F_2, increasing the Xe value slightly above the expected 1.00. Xenon gas was measured by first removing any noncondensables at −195 °C followed by collection of Xe at −195 °C by pumping on the hydrolysate at −140 °C. Equation 1 summarizes these results.

$$\begin{tikzcd} 2FXeN(SO_2F)_2 + 2H_2O \arrow[r] \arrow[d, "55\ °C"] & 2Xe + (O_2, SO_2F_2, [N(SO_2F)_2]_2, HF, other) \\ Xe + XeF_2 + [N(SO_2F)_2]_2 + <SO_2F_2 + <other \arrow[ur, "H_2O"'] & \end{tikzcd} \tag{1}$$

Reaction of $HN(SO_2F)_2$ wtih XeF_2 (2:1). Into a 15-mL Kel-F reactor at −195 °C was added 3.4 mmol of XeF_2 by vacuum transfer followed by ~2 mL of CF_2Cl_2. The $HN(SO_2F)_2$ (7.0 mmol) was then condensed into the reactor followed by ~2 mL of CF_2Cl_2. The reactor was then placed in an ice–salt bath and maintained between −22 to −12 °C for 2 weeks. The volatile materilas were then removed at −4 °C by pumping and found to be Xe, CF_2Cl_2, SO_2F_2, $[N(SO_2F)_2]_2$, HF, and $HN(SO_2F)_2$. The remaining white solid (0.3369 g) was shown to be $Xe[N(SO_2F)_2]_2$ contaminated with a very small amount of $FXeN(SO_2F)_2$. The yield was 20%, based on the starting XeF_2.

Analysis for Xe was carried out by warming a sample to 22 °C where it liquifies and rapidly decomposes. The moles of Xe per mole of compound averaged 0.97. The decomposition was essentially quantitative according to eq 2.

$$Xe[N(SO_2F)_2]_2 \rightarrow Xe + [N(SO_2F)_2]_2 \tag{2}$$

Reaction of $FXeN(SO_2F)_2$ with AsF_5. Into a 50-mL Kel-F reactor containing 11.0 mmol of $FXeN(SO_2F)_2$ at −195 °C was condensed 20 mmol of AsF_5. The mixture was warmed from −78 to −5 °C over 36 h. The bright yellow product was then pumped on for 8 h at 20 °C yielding 3.8 g of a light yellow solid shown to be pure $[(FSO_2)_2NXe]_2F^+AsF_6^-$. The yield was 83% based on the starting $FXeN(SO_2F)_2$. The compound was analyzed for Xe by hydrolysis. The average moles of xenon per mole of compound was 1.97.

Reaction of HNF_2 with XeF_2. Into a 6-mL Kel-F reactor at −195 °C were condensed 1.5 mmol of XeF_2 and 1.3 mmol of HNF_2. (*Caution*: HNF_2 is highly explosive under certain conditions and extreme care must be exercised in handling this material.) Approximately 2 mL of CF_2Cl_2 were then added, and the mixture was allowed to stand for 10 h at 0 °C. The CF_2Cl_2 was then removed and found to contain Xe, HF, and N_2F_4. The solid residue was shown to be pure XeF_2 by Raman spectroscopy. Attempts to isolate an intermediate xenon compound at lower temperatures were unsuccessful. The stoichiometry of the reaction appeared to be

$$\begin{tikzcd} 2XeF_2 + 2HNF_2 \arrow[r] & 2HF + 2[FXeNF_2] \arrow[d, rounded corners, to path={-- ([yshift=-4ex]\tikztostart.south) -| (\tikztotarget)}] \\ & XeF_2 + N_2F_4 + Xe \end{tikzcd}$$

Reaction of $(CF_3)_2NH$ with XeF_2. Into a 6-mL Kel-F reactor at −195 °C were condensed 1.2 mmol of XeF_2 and 1.1 mmol of $(CF_3)_2NH$. The mixture was held at −78 °C for 1 day with no evidence of reaction. The mixture was then warmed slowly to 0 °C and held at 0 °C for 1 day. The volatile materials at −78 °C were found to be unreacted $(CF_3)_2NH$ and very small amounts of Xe and HF. The solid residue was pure XeF_2 as shown by Raman spectroscopy.

Reaction of XeF_2 wtih Perfluorosuccinimide. Into a 4-mL Kel-F reactor containing 1.2 mmol of perfluorosuccinimide at −195 °C was condensed 1.8 mmol of XeF_2. The mixture was allowed to stand at 0 °C for 18 h. The reactor was then cooled to −195 °C, and considerable material volatile at this temperature was pumped out (N_2 and/or CO). The remaining materials volatile at 0 °C were mainly C_2F_6 and HF with

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Table I. NMR of [Imidobis(sulfuryl fluoride)]xenon(II) Compounds[a]

	$FXeN(SO_2F)_2$[b]	$Xe[N(SO_2F)_2]_2$	$[(FSO_2)_2NXe]_2F^+AsF_6^-$[b]	$FXeN(SO_2F)_2$/ $[(FSO_2)_2NXe]_2F^+AsF_6^-$[b]
δ(SF)	57.7 (m)[d]	57.9 (s)[c]	61.2 (s)[d]	59.6 (br s)[d,f]
δ(XeF)	−127 (m)[d]		no	no
δ(^{129}Xe)	−2053 (d)[e]	−2101 (s)[b,e]	−1933 (br s)[e]	
$^1J_{^{129}Xe-F}$	5600 (^{19}F) 5624 (^{129}Xe)		no	no
$^3J_{^{129}Xe-F}$	18 (^{19}F)	no	no	no
δ(AsF_6)			−61.0 (br s)	−61.5 (br s)

[a] ^{19}F chemical shifts relative to $CFCl_3$. ^{129}Xe chemical shifts relative to $OXeF_4$. Shifts to high fields of the reference are negative. no = not observable. [b] BrF_5 solvent. [c] $CFCl_3$ solvent, 0 °C. [d] −45 °C. [e] −5 °C. [f] Two additional sharp resonances of much lower intensity were observed at 58.4 and 60.2 ppm and were assumed to be impurities.

smaller amouts of COF_2 and an unknown isocyanide. The solid residue in the reactor was shown to be pure XeF_2 by Raman spectroscopy.

Reaction of XeF_2 with $(CF_3)_2C{=}NH$. Onto 1.4 mmol of XeF_2 in 4-mL Kel-F reactor at −195 °C was condensed 1.3 mmol of $(CF_3)_2C{=}NH$. There was no evidence of reaction at 0 °C, even after several hours.

Results and Discussion

The ligand requirements for forming a xenon–element bond cannot be precisely defined. All well-characterized compounds containing polyatomic ligands bound to xenon prior to 1974 had the ligand bound to xenon through oxygen. A variety of xenon esters of the type FXeA and $Xe(A)_2$ (A = $OTeF_5$,[25] $OSeF_5$,[6] OSO_2F,[26] OSO_2CF_3,[26] $OClO_3$,[26] $OPOF_2$,[27] ONO_2,[5] and $OC(O)CF_3$[5]) were obtained via reactions of strong oxyacids with XeF_2 in most cases.[28] These materials provided a qualitative picture of the ligand properties necessary to form a bond to xenon. The ligand had to have a high group electronegativity, it had to exist as a stable anion, and in nearly every case, the corresponding Cl(I) derivative is known.[29]

In order to extend the number of xenon–element bond types, we postulated that nitrogen was the most likely candidate. A suitable nitrogen ligand appeared to be the imidobis(sulfuryl fluoride) group, $-N(SO_2F)_2$. The available data suggested that this group was very electronegative, the anion $N(SO_2F)_2^-$ was stable,[30] the corresponding Cl(I) derivative $ClN(SO_2F)_2$[24] was known, and the anhydrous acid $HN(SO_2F)_2$[17] was available to provide a route for substituting a fluorine on xenon by the $-N(SO_2F)_2$ group. The subsequent reaction of the acid with XeF_2 provided evidence for a new compound containing a xenon–nitrogen bond.[11]

Synthesis of $FXeN(SO_2F)_2$. The reaction of XeF_2 with $HN(SO_2F)_2$ proceeds readily at temperatures near 0 °C forming HF and $FXeN(SO_2F)_2$. The choice of solvent is critical, since low yields were obtained in the absence of a solvent or in HF. In these cases, extensive degradation of the $-N(SO_2F)_2$ groups was observed forming N_2, SO_2F_2, Xe, and other products. The most effective solvent proved to be CF_2Cl_2. While neither XeF_2 or $HN(SO_2F)_2$ are appreciably soluble in CF_2Cl_2 at 0 °C, the Freon provides an effective heat sink and minimizes the degradative fluorination of the $-N(SO_2F)_2$ group.

Fluoro[imidobis(sulfuryl fluoride)]xenon is a white crystalline solid which is thermally unstable at 22 °C. The rate of decomposition at 22 °C depends on a variety of factors, but it is normally quite slow. In one instance, a 1-mmol sample stored in a Kel-F vessel at 22–25 °C had not decomposed completely after 2 weeks. The products formed were Xe, XeF_2, and $[N(SO_2F)_2]_2$. At 70–75 °C, the decomposition of $FXeN(SO_2F)_2$ is rapid and quantitative according to eq 3. The volatility of $FXeN(SO_2F)_2$ at 22 °C, was

$$2FXeN(SO_2F)_2 \rightarrow XeF_2 + Xe + [N(SO_2F)_2]_2 \qquad (3)$$

demonstrated by pumping on the compound at 22 °C through a −195 °C trap for several hours. The material collected was then pumped on for a few minutes at 22 °C to remove decomposition products Xe, XeF_2, and $[N(SO_2F)_2]_2$. The remaining white solid was then examined by Raman spectroscopy and shown to have the same spectra as the initial $FXeN(SO_2F)_2$.

The solubility of $FXeN(SO_2F)_2$ in low polarity solvents is very low. Thus detection of the ^{19}F NMR of saturated solutions in CF_2Cl_2, $CFCl_3$, or CH_2Cl_2 was not possible. Attempts to dissolve the material in HF or CH_3CN resulted in decomposition. The only suitable solvent found was BrF_5. This gave colorless stable solutions of the compound at −40 °C, and brief warming to 22 °C did not result in appreciable decomposition.

Synthesis of $Xe[N(SO_2F)_2]_2$. Initial attempts to prepare the disubstituted xenon compound were unsuccessful. Under the same conditions used to prepare $FXeN(SO_2F)_2$, no real evidence for $Xe[N(SO_2F)_2]_2$ was found when a 2:1 ratio of acid to XeF_2 was employed. These attempts resulted in large amounts of Xe, $[N(SO_2F)_2]_2$, unreacted $HN(SO_2F)$, and some $FXeN(SO_2F)_2$. It was apparent that if $Xe[N(SO_2F)_2]_2$ was being formed, it was decomposing at about the same rate as its formation. Subsequent reaction at lower temperatures for a longer time led to low yields of the disubstituted compound. The latter is a white solid at −4 °C which melts near room temperature with rapid decomposition. This decomposition was quantitative according to eq 4. By Raman

$$Xe[N(SO_2F)_2]_2 \rightarrow Xe + [N(SO_2F)_2]_2 \qquad (4)$$

spectroscopy, small amounts of $FXeN(SO_2F)_2$ were present in all preparations of this compound. Thus it is clear that the reaction of $HN(SO_2F)_2$ with XeF_2 is stepwise and the first step is much faster than the second one.

The solubility of $Xe[N(SO_2F)_2]_2$ in low polarity solvents such as $CFCl_3$ is much higher than that of $FXeN(SO_2F)_2$. The solubility in $CFCl_3$ was sufficient at 0 °C to obtain good ^{19}F NMR spectra of the compound. Warming the NMR sample tube to 20 °C for 30 min and rerunning the spectrum at 0 °C showed only traces of $Xe[N(SO_2F)_2]_2$ remaining and large amounts of $[N(SO_2F)_2]_2$.

Synthesis of $[(FSO_2)_2NXe]_2F^+AsF_6^-$. The reaction of $FXeN(SO_2F)_2$ with AsF_5 was carried out in an attempt to prepare $(FSO_2)_2NXe^+AsF_6^-$. This idea was based on the premise that the xenon–fluorine bond in $FXeN(SO_2F)_2$ was very similar to that in XeF_2 and that the canonical form $F^-XeN(SO_2F)_2^+$ was important in the bonding. By low-temperature reaction of $FXeN(SO_2F)_2$ with excess AsF_5, an unstable 1:1 adduct could indeed be isolated. However, all attempts to characterize this species met with uncertain results. It fluoresced strongly in attempts to obtain Raman spectra, and the decomposition of the material in a static system gave a plethora of products, whose relative amounts could not be readily determined. During attempts to study the decomposition it was decided to remove all volatile decomposition products as they formed by pumping under dynamic vacuum at 22 °C. Surprisingly, the main product removed was AsF_5 and

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the amount was very close to half the amount of AsF_5 required for the 1:1 adduct.[12] It was then clear that a stable 2:1 adduct of $2FXeN(SO_2F)_2{\cdot}AsF_5$ was being formed. The absence of any terminal Xe–F stretches as indicated by the Raman spectrum, dictated that it must be a fluorine-bridged species $[(FSO_2)_2NXe]_2F^+AsF_6^-$.

The complex salt is a pale yellow solid which shows little or no decomposition at 22 °C. It is nonvolatile at 22 °C, and the sample remained essentially unchanged after pumping for 4 days under dynamic vacuum. The material is insoluble in $CFCl_3$ and reacts vigorously with CH_3CN. It is rather soluble in BrF_5 forming a yellow solution which is stable for several hours at −45 °C.

NMR of Xenon–Nitrogen Compounds. The ^{19}F and ^{129}Xe NMR results for $Xe[N(SO_2F)_2]_2$, $FXeN(SO_2F)_2$, and $[(FSO_2)_2NXe]_2F^+AsF_6^-$ are summaried in Table I. The chemical shifts for the sulfur fluorines are close to values reported for other covalent $-N(SO_2F)_2$ derivatives and dissimilar to values for the $N(SO_2F)_2^-$ anion. The latter is found at 52–53 ppm relative to $CFCl_3$, and covalent compounds show lower field shifts at 57–60 ppm.[24,30] The S–F resonance for $[(FSO_2)_2NXe]_2F^+AsF_6^-$ is at the lowest field as expected for a cationic species, where the covalent bonding between xenon–nitrogen should be enhanced. The true value of this chemical shift is undoubtedly at even lower fields due to the apparent dissociation of the species in BrF_5 (see below).

The only observable long-range spin-spin coupling is observed as $^3J_{^{129}Xe-F}$ in $FXeN(SO_2F)_2$. The value of 18 Hz is small, as expected, since xenon–fluorine coupling over more than two bonds is often absent. In $FXeOEF_5$ and $Xe(OEF_5)_2$ (E = Te, Se), the $^3J_{^{129}Xe-F}$ couplings are 30–37 Hz to the equatorial fluorines of OEF_5 and are not observable to the axial fluorines of OEF_5.

The chemical shift of the fluorine on xenon in $FXeN(SO_2F)_2$ is unusual. All other related Xe(II) compounds that have been measured have the shift to higher fields ($OTeF_5$,[33] −143 ppm; $OSeF_5$,[6] −156 ppm; OSO_2F,[31] −194 ppm to external $CFCl_3$). Although these chemical shifts have been shown to be solvent and temperature dependent, the values indicated were all measured in solution and the unusual shift for $FXeN(SO_2F)_2$ is probably significant in terms of xenon being bonded to nitrogen. The value of $^1J_{^{129}Xe-F}$ in $FXeN(SO_2F)_2$ is ~5600 Hz, which is comparable to other Xe(II) compounds. It is the smallest coupling constant for any compound of this type and is quite similar to XeF_2 in BrF_5 (J = 5583 Hz).[31] Again, this is consistent with a xenon–nitrogen bond. It is clear from NMR data that $^1J_{^{129}Xe-F}$ is sensitive to the charge on xenon, with the largest values observed in XeF^+ and $Xe_2F_3^+$ (terminal Xe–F).[31] It can be assumed that as the contribution of the resonance structure FXe^+A^- in the bonding decreases in importance relative to F^-XeA^+ (A = OSO_2F, $OSeF_5$, $N(SO_2F)_2$, etc.), $^1J_{^{129}Xe-F}$ will decrease in value. In comparing FXeA compounds, where A is bonded to xenon through oxygen or nitrogen, the value for nitrogen would be expected to be lower on the basis of the relative electronegativities.

In $[(FSO_2)_2NXe]_2F^+AsF_6^-$, the unique bridging fluorine could not be observed in BrF_5 and no other suitable solvent for the compound could be found. At first this raises serious questions regarding the existence of an Xe–F–Xe bridge bond, but this delimma was resolved to our satisfaction in the following way. If the bridging fluorine could not be observed, a reasonable cause for this could be an exchange process involving this fluorine as shown in eq 5. If this proposal is valid, then addition of $FXeN(SO_2F)_2$

$$[(FSO_2)_2NXe]_2F^+ = FXeN(SO_2F)_2 + XeN(SO_2F)_2^+ \quad (5)$$

to a solution of $[(FSO_2)_2NXe]_2F^+AsF_6^-$ in BrF_5 should have a pronounced effect on this exchange. This was indeed the case. The FXe resonance of $FXeN(SO_2F)_2$, which is easily observed in the pure compound, could not be found in a 1:1 mixture in BrF_5. In addition, all sulfur-fluorine resonances became equivalent in the mixture with a new chemical shift in between that of pure $FXeN(SO_2F)_2$ and $[(FSO_2)_2NXe]_2F^+AsF_6^-$.[12] While this does not prove the postulated exchange mechanism, it certainly lends strong support to it. This proposal is also supported by ^{129}Xe nmr (see below).

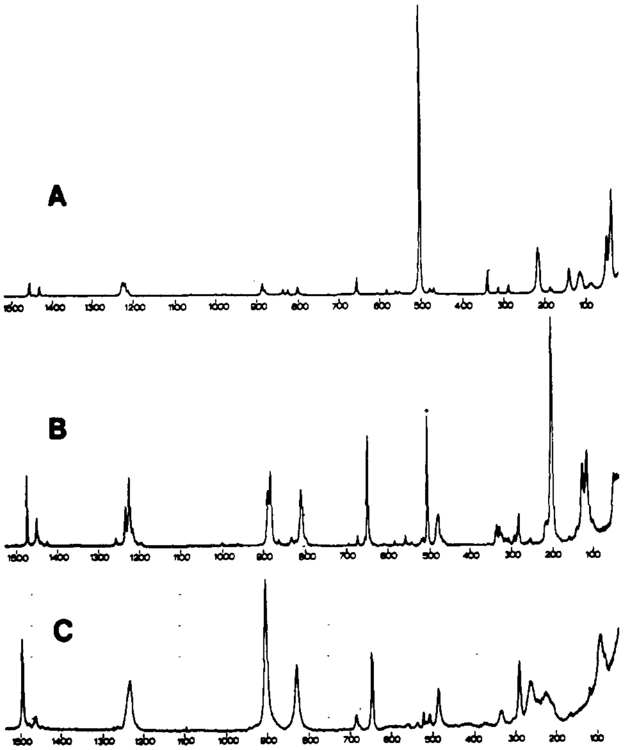

Figure 1. Low-temperature Raman spectra of solid $FXeN(SO_2F)_2$ (A), $Xe[N(SO_2F)_2]_2$ (B), and $[(FSO_2)_2NXe]_2F^+AsF_6^-$ (C). Band marked with + in B is due to A impurity.

^{129}Xe NMR has been shown to be an effective structural and analytical probe in xenon chemistry.[32,34] Therefore, the ^{129}Xe NMR of $FXeN(SO_2F)_2$, $Xe[N(SO_2F)_2]_2$, and $[(FSO_2)_2NXe]_2F^+AsF_6^-$ were measured in BrF_5 as solvent.[35] The values given in Table I are quite informative. The chemical shifts of the mono- and disubstituted compounds are very reasonable for a xenon compound of the type proposed. ^{129}Xe chemical shifts are quite dependent on conditions and solvent, but the trends in the values for the Xe–N compounds are probably meaningful. While any simple correlation between chemical shift and structure based on theory is not possible, the higher field shifts for the xenon–nitrogen compounds compared to xenon–oxygen compounds of the type FXeA and XeA_2 is very reasonable, as is the higher field shift of $Xe[N(SO_2F)_2]_2$ vs. that of $FXeN(SO_2F)_2$.

The ^{129}Xe NMR of $[(FSO_2)_2NXe]_2F^+AsF_6^-$ shows only a broad, temperature-dependent signal, consistent with the postulated equilibrium based on the ^{19}F NMR. The chemical shift value is also in accord with this proposal, as the observed value must represent some average of the species involved, but the average should be to lower field of $FXeN(SO_2F)_2$.

Raman Spectra of Xenon–Nitrogen Compounds. The utility of Raman spectroscopy in the characterization of unstable xenon compounds cannot be overemphasized. Most of the compounds are very agressive solids having low vapor pressures, and spectra must be recorded at low temperature. Experimentally, this is easily and cheaply accomplished in Raman spectroscopy. Without routine capabilities in this regard, these new xenon compounds might well have remained uncharacterized.

The Raman spectra of $FXeN(SO_2F)_2$, $Xe[N(SO_2F)_2]_2$, and $[(FSO_2)_2NXe]_2F^+AsF_6^-$ are shown in Figure 1 and Table II. For comparison, the Raman spectra of other related compounds are also given in Table II. Because there has been no detailed vibrational analysis of any compound containing the $-N(SO_2F)_2$

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(35) The ^{129}Xe chemical shift of $FXeN(SO_2F)_2$ has been determined independently,[34] and our value is in good agreement with this work.

Table II. Raman Spectra (cm^{-1}) of $-N(SO_2F)_2$ Derivatives[a]

$Xe[N(SO_2F)_2]_2$[b]	$FXeN(SO_2F)_2$[b]	$[(FSO_2)_2NXe]_2$-$F^+AsF_6^-$[b]	$CsN(SO_2F)_2$[c,g]	$HN(SO_2F)_2$[d,g]	$ClN(SO_2F)_2$[d]	$[N(SO_2F)_2]_2$[c,h]
1477 (18)	1454 (4.0)	1496 (59)	1361 (18)	1492 (7)	1490 (13)	1506 (14)
1456 (13)	1442 (0.5)	1479 (2)		1480 (8)	1470 (10)	1485 (12)
1430 (2)	1425 (3.0)	1462 (9)		1350 (2)		
	1412 (0.2)					
1261 (4)[e]						1261 (100)
1237 (18)	1227 (4.2)	1263 (3)	1215 (100)	1247 (100)	1310 (3)	1240 (?)
1228 (31)	1220 (4.3)	1234 (34)	1173 (7.5)	1218 (?)	1250 (?)	1225 (31)
1221 (8)	1210 (2.0)		1103 (3)		1245 (100)	
1200 (1)					1200 (?)	
1004 (2)	1001 (0.3)					
916 (1)	979 (0.3)					
892 (29)	888 (4.1)	908 (100)	909 (4)	900 br (2)	922 (4)	925 (1)
887 (33)	880 (1.5)		845 (12)	838 (?)	836 (20)	864 (50)
865 (2)[e]			825 br (2)	808 (52)	805 (5)	850 (?)
834 (4)	837 (1.9)	820 (43)	747 (32)			
810 (26)	827 (1.8)		730 (75)			
	801 (2.7)					
674 (3)[e]		685 (10)				675 (78)
652 (49)	656 (5.4)	677 (52)	650 (3)	638 (8)	652 (46)	
585 (2)	584 (1.1)	647 (3)	568 (17)	563 (3)	567 (6)	560 br (2)
559 (4)	562 (0.9)	600 (2)	527 (35)	558 (4)	552 (5)	520 (6)
545 (1)	553 (0.9)	561 (3)	490 (13)	518 (8)	539 (6)	506 (7)
518 (3)	518 (?)	537 (4)	466 (17)	505 (2)	514 (4)	
507 (56)[f]	506 (100)	510 (9)	428 br (3)	482 (5)	504 (14)	
481 (14)	482 (2.1)	487 (26)		468 (7)	479 (4)	475 (11)
	473 (1.9)				438 (2)	460 (?)
	425	411 (2)			378 (45)	
338 (9)	337 (6.4)	373 (2)	362 (40)	333 (40)	315 (3)	327 (25)
331 (8)	313 (1.6)	332 (10)	333 (13)		310 (42)	316 (11)
325 (5)		303 (?)	294 (30)			
318 (2)						
308 (2)						
295 (4)	289 (2.3)	289 (42)		285 (16)	283 (21)	294 (31)
285 (14)		262 (29)				
255 (3)	221 (15)	250 (?)				260 (30)
216 (11)	188 (1.8)	223 (19)	179 (10)	170 (3)	220 (6)	
204 (100)	183 (1.0)	205 (?)				
159 (2)		165 (2)				
144 (7)	142 (7.7)	118 (?)			128 (1)	
128 (3)	118 (5.8)	93 (33)				
119 (39)	92 (3.0)	81 (?)				
	53 (15)					
	44 (31)					

[a] Relative intensities in parentheses. The question mark indicates shoulder. [b] Solid near 77 K. [c] Solid at 22 °C. [d] Liquid at 22 °C. [e] Impurity band due to $[N(SO_2F)_2]_2$. [f] Impurity band due to $FXeN(SO_2F)_2$. [g] Samples fluoresced causing difficulty in observing bands below 250 cm^{-1}. [h] Relatively weak Raman emission, some weaker bonds are undoubtedly absent.

group, it seems pointless to us to attempt any detailed assignments of the observed bands. It is more appropriate to compare the Raman spectra of the xenon-nitrogen compounds with other $-N(SO_2F)_2$ derivatives to establish similarities and differences and thereby build support for the proposed structures.

The first point that can be made is that the Raman spectra of the Xe-N compounds show a great similarity to those of other covalent $-N(SO_2F)_2$ derivatives. This similarity is most readily apparent in the 1100–1500-cm^{-1} region, where the S═O stretching frequencies are expected. The spectrum of $CsN(SO_2F)_2$, which represents a very ionic compound, is clearly very different in this region.[36] The trends between the three xenon compounds in this region are also as expected. The highest frequencies are for $[(FSO_2)_2NXe]_2F^+AsF_6^-$ which should contain the least ionic $-N(SO_2F)_2$ groups.

The presence of more than one band for both the antisymmetric and symmetric S═O stretches in the 1400- and 1200-cm^{-1} region, respectively, is expected. Each compound contains two or more $-SO_2F$ groups which could have in phase and out of phase vibrations. In addition, site symmetry splittings of these modes in the low-temperature, solid-state spectra are probably present. It is clear, however, that the S═O frequencies offer no support for an oxygen-bonded species. The latter would result in a unique S═O bond for an $FO_2S—N═S(═O)F—O—$ group, which should occur at higher frequency than the symmetric ν(S═O). An analogy can be made with fluorosulfates which are bidentate through oxygen. Here the resulting unique S═O frequency is approximately midway between the symmetric and antisymmetric ν(S═O) frequencies of a monodentate fluorosulfate.[37]

The second important point to note about the xenon nitrogen compounds is the very strong ν(XeF) at 506 cm^{-1} in $FXeN(SO_2F)_2$ which is very characteristic of terminal XeF bonds in Xe(II) compounds.[38] The position of this band is strong proof of the covalent nature of this compound and indicative of the fact that the valence bond structures $FXe^+N(SO_2F)_2^- \rightleftarrows F^-XeN(SO_2F)_2^+$ are equalliy important in the bonding.[39] The weak band at the same position in $Xe[N(SO_2F)_2]_2$ is due to a small amount of $FXeN(SO_2F)_2$ impurity. The intensity of this band was clearly variable in different preparations of $Xe[N(SO_2F)_2]_2$ and was almost totally absent in some spectra. The absence of any strong band in the 500–620-cm^{-1} region in $[(FSO_2)_2NXe]_2F^+AsF_6^-$ is proof of the absence of any terminal Xe–F bond in this compound.

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(36) Similar differences between covalent and ionic $N(SO_2F)_2$ derivatives have been observed in the IR (see ref 30).

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(39) ν(XeF) in some FXeA compounds are (A, cm^{-1}) OSO_2F, 521;[38] $OClO_3$, 507;[26] $OTeF_5$, 520;[33] $OSeF_5$, 501.[6]

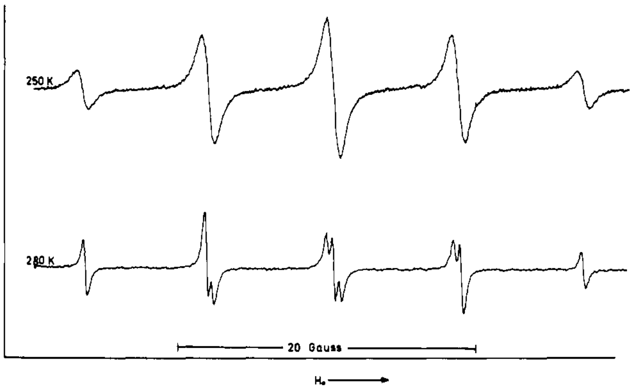

Figure 2. EPR spectra of the $\cdot N(SO_2F)_2$ free radical formed on decomposition of $Xe[N(SO_2F)_2]_2$ in $CFCl_3$.

Bridging Xe–F–Xe stretches are typically quite weak in the Raman effect and occur below 500 cm^{-1}.[38]

EPR of the $\cdot N(SO_2F)_2$ Radical. The thermal decomposition of nearly all xenon(II) compounds of the type FXeA and XeA_2 gives rise to products which are best rationalized on the basis of the formation of the intermediate free radicals A·. These radicals then dimerize or undergo further reactions depending on the nature of A and the conditions. In the decomposition of $FXeN(SO_2F)_2$ and $Xe[N(SO_2F)_2]_2$, $[N(SO_2F)_2]_2$ is formed in high yield. It is reasonable to suppose that this product arises via dimerization of $\cdot N(SO_2F)_2$. To gain support for this supposition, it was planned to photolyze a solution of $Xe[N(SO_2F)_2]_2$ at lower temperature. This turned out to be unnecesary, since surprisingly high concentrations of a radical species were observed in a solution of $Xe[N(SO_2F)_2]_2$ in $CFCl_3$ near 0 °C without photolysis. The EPR spectrum of the radical species is shown in Figure 2 at 250 and 280 K. The spectra are clearly explicable in terms of the $N(SO_2F)_2$ radical.

The five-line spectrum at 250 K with $a_{iso} = 8.3$ G and $g = 2.0063$ has peak heights of 1:3:4:3:1. This intensity ratio is expected for a species in which one unpaired electron interacts with one nucleus of spin $I = 1$ and two nuclei of spin $I = {}^1/_2$ and identical coupling constants for all nuclei. At higher temperatures, these lines show additional splitting. At 280 K, the nine-line spectrum can be exactly simulated by assuming that the unpaired electron interacts with one nitrogen and two equivalent fluorine nuclei. The isotropic hyperfine coupling constants are $A_N = 8.4$ and $A_F = 8.0$ G. Both the nitrogen and fluorine splittings are very small compared to related radicals such as NF_2,[40] $N(SO_3)_2^{2-}$,[41] and $ON(SO_3)_2^{2-}$.[42] This suggests that the unpaired electron is strongly delocalized and that the radical is probably planar.[43]

The properties of the $\cdot N(SO_2F)_2$ radical are probably related to the thermal stability of $FXeN(SO_2F)_2$ and $Xe[N(SO_2F)_2]_2$. The latter has much lower stability, and this is similar to the behavior of $FXeOSO_2F$ and $Xe(OSO_2F)_2$.[26] However, the thermal stabilities of $Xe(OSeF_5)_2$ and $Xe(OTeF_5)_2$ are both quite high. The $\cdot N(SO_2F)_2$ and $FSO_3\cdot$[44] free radicals are rather stable and easily observed at higher temperatures, whereas $\cdot OSeF_5$ and $\cdot OTeF_5$ have very short lifetimes in solution above −150 °C.[45] It can be argued that in $\cdot OTeF_5$ and $\cdot OSeF_5$, the unpaired electron is more localized on oxygen, favoring dimerization. On the other hand, $\cdot N(SO_2F)_2$ and $FSO_3\cdot$ appear to have the unpaired electron more delocalized. These differences can then have a marked effect on the activation energy for decomposition. The more ionic nature of $FXeN(SO_2F)_2$ and $FXeOSO_2F$ clearly raises the barrier to decomposition.

Conclusion

The ability of xenon to bond to a nitrogen atom of an electronegative ligand has been established in the compounds $FXeN(SO_2F)_2$, $Xe[N(SO_2F)_2]_2$, and $[(FSO_2)_2NXe]_2F^+AsF_6^-$. It was hoped that the discovery of $FXeN(SO_2F)_2$ in 1974 would lead to new advances in the chemistry of xenon with additional examples of new xenon–element bonds and a variety of xenon–nitrogen compounds. These hopes have not yet been realized to any great extent. It is obvious that the number of ligands possessing the necessary but still ill-defined properties needed to stabilize a xenon–element bond is very small. We hope to report on additional new examples of xenon–element bonds in the future and perhaps an example of a xenon–nitrogen multiple bond.

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Rate Constants and Arrhenius Parameters for the Reactions of Primary, Secondary, and Tertiary Alkyl Radicals with Tri-*n*-butyltin Hydride[1]

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Abstract: Rate constants for the title reactions have been measured over a range of temperatures by using laser flash photolytic techniques. At 300 K the rate constants are $10._8$, 2.0_1, 2.3_4, 1.3_5, 2.4_7, and $1.8_4 \times 10^6$ M^{-1} s^{-1} for methyl, ethyl, *n*-butyl, isopropyl, cyclohexyl, and *tert*-butyl, respectively. The Arrhenius preexponential factors range from $10^{9.39}$ M^{-1} s^{-1} for methyl to $10^{8.43}$ M^{-1} s^{-1} for *tert*-butyl and activation energies from 3.97 kcal/mol for cyclohexyl to 2.95 kcal/mol for *tert*-butyl. The rate constant (k_{10}) for the 1,5-cyclization of 5-hexenyl radical to cyclopentylmethyl radical can be represented by $\log k_{10}/\mathrm{s}^{-1} = (10.37 \pm 0.32) - (6.85 \pm 0.42)/\theta$, where $\theta = 2.3RT$ kcal/mol.

The reactions of carbon-centered radicals with triorganotin hydrides are of considerable importance in organic chemistry. Probably the best known and most useful reaction is the reduction of alkyl halides, RX, to the hydrocarbon, RH, with tri-*n*-butyltin

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