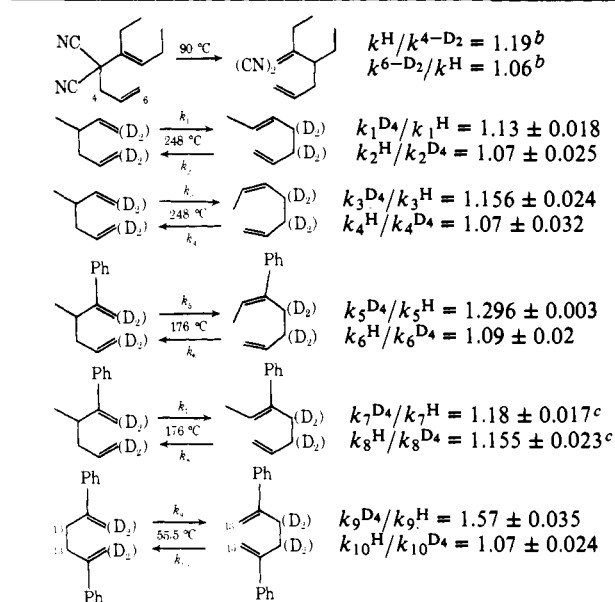


Table I. Secondary Deuterium KIE's in Various 3,3 Shifts^a

^a The standard deviations were determined as indicated in footnote 12. ^b Reference 9. ^c Despite the favorable error analysis, we have no confidence in these since k_7 and k_8 are only $1/10$ – $1/30$ th of k_5 and k_6 . Large variations in k_7 or k_8 will affect the calculated concentrations much less than similar variations in k_5 and k_6 .

state structures, as deduced by changes in the relative KIE's, vary as predicted above.¹⁰

The KIE's are shown in Table I; the rate constants for the three-component reversible reactions were determined by a SIMPLEX^{11a,b} fit to the data using the integrated rate expressions of Frey and Solly.^{11c} Each reaction was sampled roughly 12 times and each sample was analyzed at least 4 times using GC and an electronic integrator giving reproducibility of $\pm 1\%$. The diphenyl-1,5-hexadiene reaction was monitored by HR-220 ¹H NMR spectroscopy which gave reproducibility in integrations of $\pm 1\%$.

Since no functional relationship between secondary KIE's and bond-order changes is available, the absolute location of the various transition states on the diagram are unknown. However, if the relationship is nearly linear,¹³ then the behavior of most degenerate 3,3 shifts can be reasonably rationalized,¹⁴ recognizing that the transition states should resemble the nonconcerted alternative, i.e., two allyl radicals or cyclohexane-1,4-diyl, that is more stable.

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$$-\ln(A - A_e)/(A_0 - A_e) = (k_f + k_b)t$$

- While we realize that a complete force-field analysis is useful in more carefully assigning the origin and magnitudes of these KIE's and that KIE's are not necessarily simply related to the bond orders in question, most literature suggests that our assumption is a reasonable starting point for more detailed analysis.
- For instance, the entropy of activation of acyclic boat 3,3 shifts is much less negative than chair 3,3 shifts,¹⁵ indicating that the transition state is looser and more two-allyl radical-like; this is because the boat-like diyl should be 5–10 kcal/mol less stable than the chair-like diyl, while the relative stabilities of the two allyl radicals in boat and chair geometries should be much less affected. The full paper will consider the myriad of other observations which are rationalizable in this framework.
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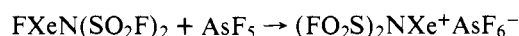
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An Unusual Xenon Cation Containing Xenon–Nitrogen Bonds

Sir:

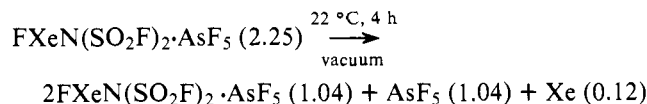
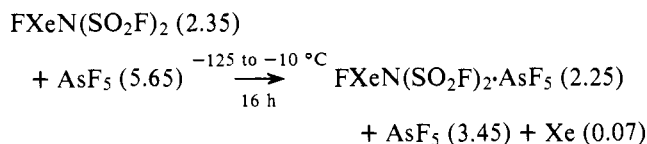
The earlier synthesis of $\text{FXeN}(\text{SO}_2\text{F})_2^1$ from XeF_2 and $\text{HN}(\text{SO}_2\text{F})_2$ demonstrated that xenon was capable of forming bonds to elements other than oxygen and fluorine under ordinary laboratory conditions. Since this report there have been no further examples of new compounds of this type. We have been working to provide additional examples of xenon–nitrogen bonds and to prepare the first xenon–carbon bond. Recently, we have been successful in the preparation of several new xenon–nitrogen species, thus eliminating the possibility that $\text{FXeN}(\text{SO}_2\text{F})_2$ is unique. This work describes one of these new compounds, an unusual complex salt containing a dinuclear xenon cation with xenon–nitrogen bonds.

After the synthesis of $\text{FXeN}(\text{SO}_2\text{F})_2$, we looked for ways to further identify the xenon–nitrogen bond. Because the xenon–fluorine bond in $\text{FXeN}(\text{SO}_2\text{F})_2$ appears to be very similar to that in XeF_2 , the canonical form $\text{FXe}^+\text{N}(\text{SO}_2\text{F})_2^-$ does not appear to dominate the bonding. It therefore seemed reasonable that $\text{FXeN}(\text{SO}_2\text{F})_2$ might react with a strong Lewis acid, such as AsF_5 , in the following way:



A 1:1 adduct is indeed formed, but it is unstable and we have been unable to determine its structure. We have found that the

1:1 adduct decomposes under dynamic vacuum at 22 °C very cleanly to a stable compound of the composition 2FXeN(SO₂F)₂·AsF₅. The following equations (millimoles) indicate a typical reaction sequence:



Small amounts of other products, consisting mainly of SO₂F₂, [N(SO₂F)₂]₂, and Xe₂F₃⁺AsF₆⁻, are observed in the material pumped out at 22 °C, but only Xe and AsF₅ could be effectively measured. These results are very close to the expected values allowing for minor side reactions and some volatility of the 1:1 and 2:1 adducts. No reasonable alternative stoichiometry could be found.

The 1:1 adduct, which we believe is most probably (FO₂S)₂NXe⁺AsF₆⁻, is a bright yellow solid, whereas the 2:1 compound is a pale yellow solid. The Raman spectrum of a small sample (~0.1 mmol) of the 2:1 adduct contained in a glass apparatus for low temperature Raman had not changed after 4 days under dynamic vacuum at 22 °C. This indicates a low vapor pressure and thermal stability at 22 °C. Analysis of the compound for xenon by reaction with H₂O gave an average of 1.967 mol of Xe/mol of compound, very close to the expected 2:1 ratio.

The formulation of the 2:1 adduct as [(FO₂S)₂NXe]₂F⁺AsF₆⁻ is supported by Raman and ¹⁹F NMR spectroscopy. The Raman spectrum taken at ca. -100 °C shows strong bands at 1494, 1236, 906, 832, 647, 333, 289, 261, and 226 cm⁻¹, which can readily be assigned to covalently bound -N(SO₂F)₂ groups.² The relatively high frequency for the ν(SO) symmetric and ν(SO) antisymmetric frequencies at 1236 and 1494, compared with those of FXeN(SO₂F)₂, are in harmony with the -N(SO₂F)₂ groups being more covalent in the cation than in the neutral compound. The most striking difference between FXeN(SO₂F)₂ and the 2:1 spectrum is the complete absence of ν(XeF) at 504 cm⁻¹ and the absence of any other intense Raman bands in the 500–620-cm⁻¹ region. This clearly indicates the absence of terminal xenon–fluorine bonds.³ With regard to ν(XeN) and ν(XeFXe) a moderately strong band at 486 cm⁻¹ and a very weak band at 408 cm⁻¹ may be tentatively assigned to these modes.⁴ Finally, ν₁ of AsF₆⁻ is clearly evident as a moderately intense band at 683 cm⁻¹.

The ¹⁹F NMR of [(FO₂S)₂NXe]₂F⁺AsF₆⁻ was obtained in BrF₅ at ca. -45 °C. The compound is quite soluble forming a clear yellow solution, which undergoes little or no change after several hours at -45 °C. The initial interpretation of the NMR spectrum was difficult. Only two resonances are observed (external CFCl₃) at -61.2 [N(SO₂F)₂] and 61.0 (AsF₆⁻) along with the expected AX₄ spectrum of BrF₅. The relative areas are 4.0:6.0 as expected for [(FO₂S)₂NXe]₂F⁺AsF₆⁻, but no signal could be found for the bridging¹fluorine.⁵ Either there is no bridging fluorine or that the resonance is unobservable because of some exchange process.

We summarize that [(FO₂S)₂NXe]₂F⁺ ionizes in the following way:



Such a process could broaden the Xe–F resonance to a point where it could not be observed. This is supported by our finding that a ¹⁹F NMR spectrum of a BrF₅ solution of a mixture

(~1:1) of FXeN(SO₂F)₂ and [(FO₂S)₂NXe]₂F⁺AsF₆⁻ shows no F on Xe resonance, whereas resonance for FXeN(SO₂F)₂ is easily observed under identical conditions for the pure compound. The S–F resonance of FXeN(SO₂F)₂ and [(FO₂S)₂NXe]₂F⁺AsF₆⁻, which are different in the pure compounds by ~400 Hz, coalesce into a single peak, essentially at the midpoint of the two original signals. The relative area of this signal to that of the AsF₆⁻ is ~1:1.

The above data clearly establishes the existence of [(FO₂S)₂NXe]₂F⁺AsF₆⁻ and further amplifies the similarity between XeF₂ and FXeN(SO₂F)₂. Whereas XeF₂ forms both 1:1 and 2:1 adducts with AsF₅, the 1:1 adduct FXe⁺AsF₆⁻ is unstable at 22 °C to form the 2:1 adduct Xe₂F₃⁺AsF₆⁻.^{3,6} Interestingly, none of the xenon esters of the type FXeOR exhibit the same chemical behavior. While FXeOSO₂F forms an unstable 1:1 adduct with AsF₅, decomposition results in the formation of Xe(OSO₂F)₂ and (FXe)₂SO₃F⁺AsF₆⁻.⁷ The latter compound has been prepared in various ways using HF solvent.^{8,9} On the other hand, FXeOTeF₅ is reported to form a stable 1:1 adduct with AsF₅ which is said to be XeOTeF₅⁺AsF₆⁻.¹⁰

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this research.

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Stereochemistry of Free-Radical Substitution at Trivalent Phosphorus. Permutational Processes Available for Stereochemically Nonrigid Phosphoranyl-Radical Intermediates

Sir:

The rapid pairwise exchange of substituents attached to pentacoordinate phosphorus (**1** ⇌ **2**) has been well established.¹ In trigonal–bipyramidal SF₄² and related sulfuranes,³ where the lone pair can be considered a fifth ligand, DNMR studies suggest that an analogous process with the electron pair as pivot is operative. Such pairwise ligand permutations have been classified as mode 1⁴ for which Berry⁵ and turnstile⁶ processes have been postulated as mechanistic alternatives. Phosphoranyl radicals, X₄P•, bear at least superficial similarity to the above intermediates in that they are near-trigonal–bipyramidal in