

The Preparation and Oxygen-17 Nuclear Magnetic Resonance Spectrum of XeO¹⁷F₄

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The preparation and O¹⁷ n.m.r. spectrum of XeO¹⁷F₄ is described. The O¹⁷ chemical shift is -313 ± 2 p.p.m. (relative to H₂O¹⁷) and the Xe¹²⁹-O¹⁷ spin-spin coupling constant is 692 ± 10 c.p.s.

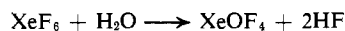
Introduction

The n.m.r. parameters of xenon compounds are of interest for the elucidation of their structure. They are also of value as criteria for the validity of various theoretical models.² Since oxygen compounds are formed on hydrolyzing xenon tetra- and hexafluorides, it is therefore possible to prepare such compounds labeled with O¹⁷ and to examine the O¹⁷ n.m.r. spectrum. The O¹⁷ n.m.r. spectrum of xenic acid, Xe(O¹⁷H)₆, has already been described.³ It consists of a single line with a line width of 420 c.p.s. and a chemical shift of -278 ± 2 p.p.m., using O¹⁷-enriched water as an internal reference.

Only two xenon isotopes have nonzero spin (Xe¹²⁹, spin $\frac{1}{2}$; and Xe¹³¹, spin $\frac{3}{2}$), and spin-spin coupling between these two isotopes and other nuclei with nonzero spin is to be expected. In xenon oxide tetrafluoride, XeOF₄, the coupling between xenon and fluorine has already been observed.⁴ In this paper the synthesis of O¹⁷-labeled xenon oxide tetrafluoride is described and the O¹⁷ n.m.r. parameters of its spectrum are reported.

Experimental

Preparation of XeO¹⁷F₄. The general methods of preparation of XeOF₄ reported in the literature^{5,6} are not suitable for isotopic synthesis of an O¹⁷-labeled compound. The method described by Chernick, *et al.*,⁵ in which XeF₆ is allowed to react with the silica of a quartz vessel is obviously not practical for isotopic labeling. Other methods⁵ are based on the hydrolysis reaction



Preparation by controlled hydrolysis requires either large nickel vessels⁵ or a special circulating loop,⁶ neither of which are readily available. In addition these methods of preparation require relatively large quantities of water. Using the limited amounts of highly O¹⁷-

enriched water available, XeO¹⁷F₄ has now been prepared by the slow distillation of such water directly into XeF₆. The same method can, of course, be used for the synthesis of O¹⁸-labeled XeOF₄, using O¹⁸-enriched water.

Xenon hexafluoride was synthesized according to Malm, *et al.*⁷ This synthesis and the subsequent partial hydrolysis of XeF₆ were performed on an all-metal vacuum line constructed of nickel and monel. XeF₆ was then distilled into a nickel weighing can and the amount required for partial hydrolysis distilled from this can into a reaction vessel. The amount of XeF₆ in the reaction vessel was determined from the differences in weight of the weighing can. It is important to determine this amount accurately to ensure that a slightly less than equivalent amount of O¹⁷-enriched water is used in the hydrolysis in order to maintain an excess of XeF₆ throughout the experiment to avoid formation of the explosive XeO₃. The calculated quantity of O¹⁷-enriched water (containing 11.5 atom % O¹⁷) was introduced into a second vessel connected in such a way that it could be opened either directly to the reaction vessel or to the vacuum line. The water was first degassed by repeating a freezing, pumping, and melting cycle three times. The reaction vessel containing the XeF₆ was then cooled by an ice bath and the vessel containing the O¹⁷-enriched water kept at room temperature. The two nickel vessels were then opened to each other. As the vapor pressure of water at room temperature was fairly low and since the temperature difference was small, the water distilled into the XeF₆ slowly. The reaction was left to go to completion overnight, and the volatile products (XeO¹⁷F₄ and HF) were then distilled into a 0.25-in. Kel-F vessel and closed off with an all-Kel-F valve. After the n.m.r. measurements were completed, the XeO¹⁷F₄ was separated from the HF by keeping the material at Dry Ice temperature (-78°) and pumping off the HF. The infrared spectrum of the residue was then recorded on a Perkin-Elmer Model 21 infrared instrument, equipped with KBr optics, using a 10-cm. gas cell made of nickel and fitted with silver chloride windows. The infrared spectrum was similar to that reported by Smith⁶ for XeOF₄.

N.m.r. Spectra. The n.m.r. spectrum of the sample (0.3 ml.) was recorded in a Varian DP-60 n.m.r. spectrometer, operating at 8.13 Mc./sec. The derivative of the absorption mode of the O¹⁷ resonance was recorded under conditions of slow passage. A capillary containing H₂O¹⁷ was used as an external standard for chemical shift measurements. Spectra were calibrated by the audio-modulation side-band technique.

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Results and Discussion

The O^{17} n.m.r. spectrum of $XeO^{17}F_4$ appeared as a triplet with a strong central peak and two symmetrically disposed satellites. A similar picture was found by Brown, *et al.*,⁴ for the F^{19} n.m.r. spectrum of $XeOF_4$.

The O^{17} chemical shift using water as an external reference was -313 ± 2 p.p.m. The spacing between the two satellites was 692 ± 10 c.p.s., which apparently is the coupling constant between Xe^{129} and O^{17} . Indeed the ratio of the intensities of the main peak to each of the two satellites as determined from the ratio of the recorded area on the chart was found to be 5.6, as would be expected if the satellites are due to Xe^{129} (spin $1/2$, natural abundance 26.2%) species and the main peak is due to all the other xenon isotopes. The failure to observe splitting due to coupling with Xe^{131} (spin $3/2$, abundance 21.2%) may be caused by fast relaxation due to the quadrupole moment of this nucleus in the asymmetric environment in the molecule. The large $Xe^{129}-O^{17}$ spin-spin coupling observed in $XeO^{17}F_4$ is of interest for the elucidation of the bonding in xenon compounds. This has recently

been discussed in connection with the calculation of chemical shifts where the magnitude of the coupling was found to lend support to the model involving d-orbital participation.⁸ It is of interest that the line width of the central peak is about 130 c.p.s. and that of the satellites about 110 c.p.s. It is apparent that the central peak which includes the Xe^{131} species is somewhat broader owing to incomplete averaging of the splitting.

The position of the O^{17} resonance line in $XeOF_4$ is to lower field than that of xenic acid³ which indicates greater double bond character of the xenon-oxygen bond in the former. However, it is still at a higher field than that of double-bonded oxygen (-500 to -600 p.p.m.) in most compounds⁹ which may in part be due to hydrogen bonding with the HF present.¹⁰

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Exchange of Parts between Molecules at Equilibrium. VII. Scrambling of Sulfur with Halogens on Dimethylgermanium

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Exchange on the dimethylgermanium moiety of the monofunctional thiomethyl group or of bridging sulfur with either chlorine, bromine, or iodine atoms has been studied by proton nuclear magnetic resonance. The resulting equilibria were found to deviate considerably from the statistically random case. Equilibrium constants are presented for the systems $(CH_3)_2GeX_2$ vs. $(CH_3)_2Ge(SCH_3)_2$, where $X = Cl, Br, \text{ or } I$. For the systems involving bridging sulfur, $(CH_3)_2GeX_2$ vs. $[(CH_3)_2GeS]$, it is shown that the resulting equilibrium compositions are mixtures of chain and ring molecules, with the trimeric ring compound $[(CH_3)_2GeS]_3$ being present in large amounts. Equilibrium constants are given for the distribution of structure-building units between the various sized chains and the trimeric ring.

In earlier studies from this laboratory, we have demonstrated that the equilibria resulting from exchange on the dimethylsilicon moiety of bridging sulfur with halogen atoms is shifted strongly toward the ring compounds,¹ with the trimer predominating over the dimer. The exchange of the same substituents on the dimethyltin moiety,² however, proceeded so fast that fine structure due to different types of build-

ing units could not be resolved by nuclear magnetic resonance (n.m.r.). It was therefore of interest to study the rate of equilibration and the resulting equilibria for exchange of bridging sulfur with halogen atoms on the dimethylgermanium moiety and to relate these data to the results reported earlier for the analogous silicon and tin compounds. In addition, the exchange on the dimethylgermanium moiety of halogen atoms with thiomethyl groups was investigated in order to compare the equilibrium constants for the *neso* compounds³ with those obtained for the related families of compounds based on Ge-S-Ge molecular backbones.

Experimental

Materials. Dimethyldichlorogermane and dimethyldibromogermane were prepared according to a modified version⁴ of Rochow's direct synthesis⁵ from metallic germanium (purchased from A. D. Mackay, Inc.) and methyl chloride and methyl bromide, respectively. Dimethyldiiodogermane was made by following the procedure worked out by Anderson⁶ for the corresponding *n*-propyl compound, b.p. 190° (760 mm.), as well as by the direct synthesis.⁴ Di-

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