An Oxygen-17 and Fluorine-19 Nuclear Magnetic Resonance Study of the Oxygen Fluorides

Irvine J. Solomon, Jack K. Raney, Andrew J. Kacmarek, Richard G. Maguire, and Gordon A. Noble

Contribution from IIT Research Institute, Chicago, Illinois.

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Abstract: The O^{17} and F^{19} nmr spectra of O_2F_2 and what has been referred to as O_3F_2 have been studied. The results for O_2F_2 were as expected: one fluorine line and one oxygen line. For O_3F_2 three O^{17} lines were observed; one of the three was shown to be due to O_2F_2 and the other two, which were of equal intensity, were attributed to O_3F_2. The F^{19} spectra of O_3F_2 consisted of two closely spaced lines and as in the O^{17} case, one of these lines was attributed to O_2F_2. The nmr shows conclusively that what has been called O_3F_2 is truly a mixture of O_2F_2 and O_4F_2.

A number of oxygen fluorides have been reported, namely, OF_2,[1] O_2F_2,[2] O_3F_2,[3] O_4F_2,[4] and recently O_5F_2 and O_6F_2.[5] The structures of OF_2 and O_2F_2 are well known, but very little is known about the higher oxygen fluorides. There is considerable question concerning the nature of O_3F_2 and, in particular, the role played by the OOF radical. Kasai and Kirshenbaum[6] have shown that O_3F_2 and O_2F_2 showed identical epr spectra, which could be attributed to OOF. They suggest the reaction shown in eq 1, but rule out this

$$2(O_3F_2) \rightleftharpoons O_2F_2 + 2(OOF) \qquad (1)$$

equilibrium and state that for both O_2F_2 and O_3F_2 the radical is formed as the result of the respective decomposition processes.

We have obtained both O^{17} and F^{19} nmr spectra of what has been called O_3F_2 as a means of elucidating this system. Also, the O^{17} and F^{19} nmr spectra of O_2F_2 will be presented.

Experimental Section

The oxygen fluorides were prepared using previously reported procedures.[2-4] Since distillation into an nmr tube would cause partial decomposition, the nmr sample tubes were sealed directly to the bottom of the discharge apparatus. During the nmr analysis, the nmr tube was attached to a 500-ml gas-collection system in order to avoid excess pressure due to decomposition of the sample to oxygen and fluorine.

The nmr spectrometer used was the conventional Varian DP-60 equipped with a low-temperature, wide-line dewar coil. The cooling system was altered slightly in order to obtain better temperature control and to allow rapid insertion of the sample. Cooling was achieved with gaseous nitrogen that was previously cooled by passage through a copper coil immersed in liquid nitrogen. The temperature was controlled by varying the flow of the nitrogen.

Since it was not possible to use an internal standard for the calculation of chemical shifts, the magnetic field was calibrated before and after each experiment. A uniform drift was assumed for the interval of the experiment. Whenever possible, high-resolution data were taken, but, when excessive noise was a problem, wide-line techniques were employed. In the case of high resolution, intensity ratios were computed by integration of signal areas, and, where wide-line techniques were employed, the intensities were computed from the line widths and signal heights. The F^{19} and O^{17} spectra were observed at 56.4 and 8.13 Mc, respectively.

Results

O^{17} Nmr Spectroscopy. The reported melting point of O_3F_2 is 83°K.[3] Therefore our nmr measurements were initiated at this temperature. At 83°K, no reproducible O^{17} resonance signal could be obtained for a freshly prepared sample of O_3F_2. Subsequently, the sample temperature was gradually raised to 103°K, at which temperature a signal was barely detected. At 108°K, three well-defined resonance lines were observed (Figure 1): one at −647, one at −971, and one at −1512 ppm relative to H_2O^{17}. The two low-field signals were always of equal intensity. The high-field signal was approximately 60% of the sum of the other two signals. The signal at −647 ppm could be resolved and showed a spin–spin splitting of 424 cps. In a separate experiment this signal was shown to be identical with that of a freshly prepared sample of O_2F_2 (Figure 2). This triplet is thought to be due to the spin–spin coupling between the O^{17} and F^{19} nuclei. Thus it is concluded that the line at −647 ppm is due to O_2F_2 and that the other two lines are due to some other species.

As the sample temperature was raised, the intensity ratio of the two low-field lines remained constant. However, the two low-field lines decreased, and the high-field line increased. At 117°K, the intensity of the high-field line was approximately seven times the sum of the intensities of the low-field lines (Figure 3). The total intensity of the three lines was approximately constant during all of these experiments.

F^{19} Nmr Spectroscopy. The F^{19} resonance patterns were also obtained and were of great value in further interpretation of the system. A sample of O_3F_2 containing normal oxygen was prepared and maintained at 83°K in the spectrometer cavity. It was difficult to obtain a reproducible signal at this temperature. The signal consisted of a single unsymmetrical line, which was later resolved to give two closely spaced lines. An analysis of the line shapes showed that the resonance pattern consisted of a strong line on the high-field side with a weak line on the low-field side. As the temperature was increased, an increase in chemical shift was observed along with a reversal of the line symmetry; that is, the strong line was on the low-field side, and the weak line was on the high-field side.

The effect of temperature on the F^{19} chemical shift was studied in greater detail. The results of one of these experiments are shown in Figures 4 and 5. The

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[1] P. Lebeau and A. Damiens, *Compt. Rend.*, **185**, 652 (1927).

[2] O. Ruff and W. Menzel, *Z. Anorg. Allgem. Chem.*, **229**, 423 (1932).

[3] A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.*, **81**, 1277 (1959).

[4] A. V. Grosse, A. G. Streng, and A. D. Kirshenbaum, *ibid.*, **83**, 1004 (1961).

[5] A. G. Streng and A. V. Grosse, *ibid.*, **88**, 169 (1966).

[6] P. H. Kasai and A. D. Kirshenbaum, *ibid.*, **87**, 3069 (1965).

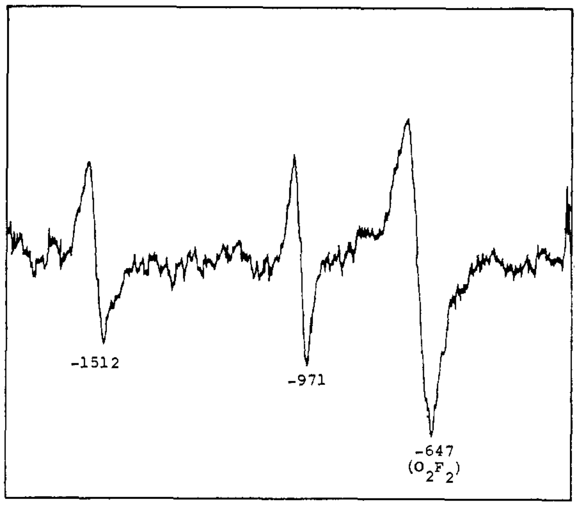

Figure 1. O^{17} nmr spectra of O_3F_2(?) at 108°K.

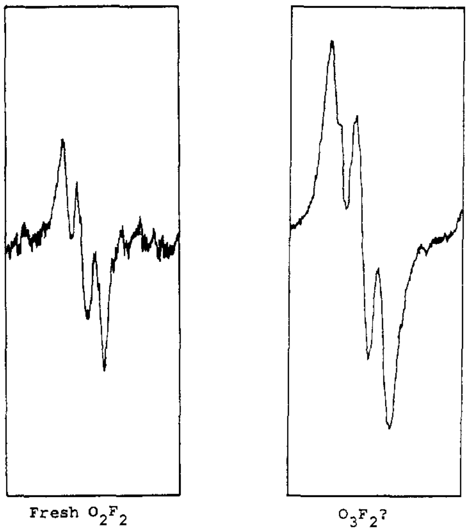
Fresh O_2F_2 O_3F_2?

Figure 2. O^{17} nmr spectrum of O_2F_2.

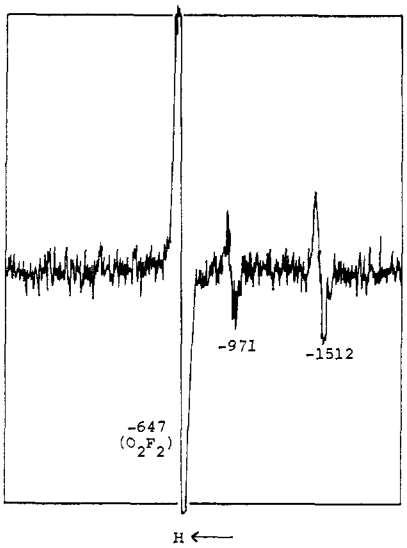

Figure 3. O^{17} nmr spectra of O_3F_2(?) after decomposition.

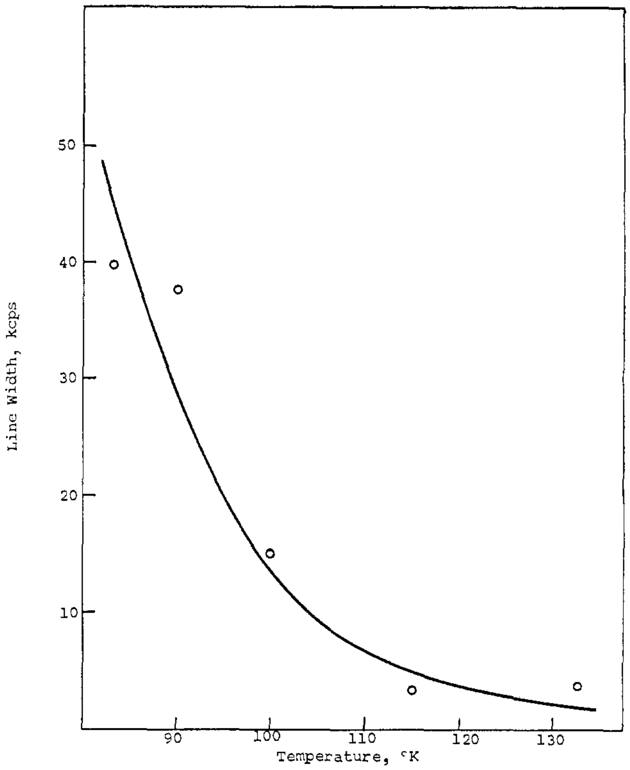

Figure 4. F^{19} line width *vs.* temperature for O_3F_2(?).

line width was approximately 40 kcps wide at the beginning of the decomposition and decreased to 3.5 kcps at the end of the experiment (Figure 4). During this period, the chemical shift changed from −1900 to −868 ppm relative to CCl_3F (Figure 5). A freshly prepared sample of O_2F_2 exhibited one line (which could not be resolved) with a chemical shift of approximately −868 ppm and a line width of 3.5 kcps.

Discussion

It is not possible to establish a single structure for the O_3F_2 molecule from nmr data. Instead, it is concluded that the sample is a mixture and that one component of the mixture is O_2F_2. It is further suggested that the other component of the mixture is $(O_2F)_n$ and that the $(O_2F)_n$ probably exists as O_2F and O_4F_2.

For the simplest case, that is, a chain molecule FOOOF, the fluorine atoms are equivalent or nonequivalent, depending on the geometry, and two of the three oxygen atoms are equivalent. Thus, one or two F^{19} signals and two O^{17} signals should be observed. Also, one of the O^{17} lines should be twice the intensity of the other. For the case of all nonequivalent oxygens in O_3F_2, the O^{17} nmr spectrum would consist of three lines of equal intensity. On the other hand, for all equivalent oxygens one nmr signal would be expected. Two O^{17} lines of equal intensity cannot, under ordinary circumstances, be accounted for by the molecular species, O_3F_2. By using epr measurements Kasai and Kirshenbaum[6] reported that the concentration of OOF in O_3F_2 is approximately 6 molar %. These epr measurements were verified in our laboratories. If the F^{19} and O^{17} nmr spectra of $(O_2F)_n$ or O_4F_2 were obtained, it would be expected that one fluorine line or two oxygen lines would be observed. If the oxygen atoms are equivalent, one line would be observed and for the nonequivalent case two equal lines would be observed. Fessenden and Schuler[7] have studied the epr spectrum obtained during the electron irradiation of liquid CF_4 containing trace amounts of oxygen. The simplest radical that explains these results is OOF. The addition of small amounts of oxygen enriched in

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(7) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **44**, 434 (1966).

O^{17} showed that the radical observed in this system probably contains two nonequivalent oxygen atoms.

The OOF radical was also reported by Arkell,[8] who produced this radical during photolysis of OF_2–O_2 or F_2–O_2 mixtures in oxygen, nitrogen, and argon matrices at 40°K. Spratley, Turner, and Pimentel[9] also observed the OOF radical.

If the F^{19} nmr data are considered independently, there is a possibility that the two incompletely resolved lines observed are due to two slightly different fluorine atoms in O_3F_2. If however, it is assumed that the two F^{19} signals are due to $(OOF)_n$ and O_2F_2 (which substantiates the O^{17} nmr results), it can be concluded that the $(OOF)_n$ species observed probably does not contain a free electron. The presence of a free electron in the molecule should substantially shift the F^{19} signal, and it would not be in approximately the same position as the F^{19} signal of O_2F_2. The fact that the chemical shift and the line width of the F^{19} signal change with temperature also helps to explain the system.

The paramagnetic species in solution could produce a distribution of local magnetic fields. Changing the lifetime of the spin states in turn changes both the chemical shift and the line width. From the fact that the chemical shift increases and the line width decreases as the temperature increases, it can be concluded that the concentration of free radicals decreases with increasing temperature; that is, the OOF radicals are decomposing as the temperature is increased.

As pointed out, the O^{17} nmr spectrum of O_3F_2 consists of a large line (due to O_2F_2) and two equivalent smaller signals. It is concluded that the two equivalent lines are due to $(O_2F)_n$. It is most likely that the $(O_2F)_n$ species is O_4F_2, although there is a remote possibility that the observed spectrum is due to OOF bonded in some way to O_2F_2. If, as reported by Kasai and Kirshenbaum,[6] the OOF species is present in the range of 5% compared to the O_3F_2 species, it probably would not be observed in the O^{17} nmr spectrum. Under the best of circumstances it is difficult to observe an nmr signal of such a small amount of material. Also, the free electron in the same molecule as the observed nucleus would be expected to broaden and shift the signals.

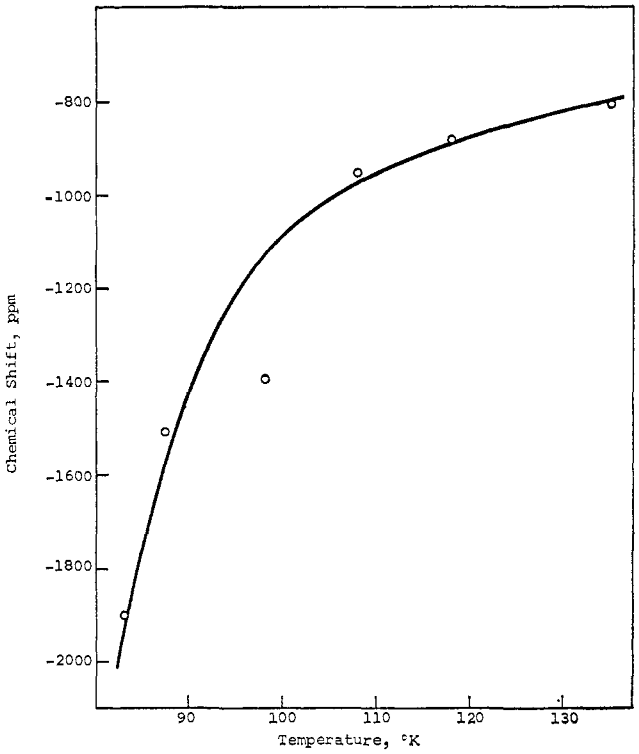

Figure 5. F^{19} chemical shift *vs.* temperature for O_3F_2(?).

The F^{19} nmr data, although not independently conclusive, substantiates the conclusions drawn from the O^{17} nmr results; that is, one F^{19} signal is due to O_2F_2 and the other to $(O_2F)_n$.

Thus considering all of the data, the system is best explained as

$$\begin{tikzcd} {[O_2F_2, O_4F_2]} \arrow[d, shift left] \\ 2OOF \arrow[u, shift left] \arrow[r] & O_2F_2 + O_2 \end{tikzcd}$$

that is, what has been called O_3F_2 does not exist as a molecular species and is actually a mixture of O_2F_2 and probably O_4F_2 in equilibrium with O_2F, which decomposes irreversibly as the temperature is increased.

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[8] A. Arkell, *J. Am. Chem. Soc.*, **87**, 4057 (1965).

[9] R. D. Spratley, J. J. Turner, and G. C. Pimentel *J. Chem. Phys.*, **44**, 2063 (1966).

Synthesis and Characterization of HPF_4 and H_2PF_3[1]

P. M. Treichel, Ruth A. Goodrich, and S. B. Pierce

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Abstract: The gas-phase reaction of $(CH_3)_3SnH$ and PF_5 results in formation of the gaseous fluorophosphoranes HPF_4 and H_2PF_3. The deuterium derivatives DPF_4 and D_2PF_3 were prepared in an analogous reaction with $(CH_3)_3SnD$. These compounds were characterized by vapor pressure data, mass spectrographic studies, infrared spectra, and ^{19}F, ^1H, and ^{31}P nmr spectra. A decomposition product of HPF_4, $HPOF_2$, was isolated and characterized also.

While the field of alkylfluorophosphorane chemistry has been extensively studied in recent years,[2a,b] only brief and indirect mention has been made of the simple related molecules H_xPF_{5-x}.[3] In

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[1] Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract O-83.

[2] (a) R. Schmutzler, *Angew. Chem., Intern. Ed. Engl.*, 4 496 (1965); (b) R. Schmutzler, "Fluorophosphoranes," International Review on Halogen Chemistry, Academic Press Inc., New York, N. Y., in press. We are indebted to R. Schmutzler for a prepublication copy of this review.