The ^{19}F Nuclear Magnetic Resonance Spectra of Oxygen Fluorides[1]

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Abstract: The ^{19}F nuclear magnetic resonance (nmr) spectra of liquid F_2, OF_2, O_2F_2, and O_3F_2 are presented. The shifts of O_2F_2 and O_3F_2 are the furthest downfield of any simple fluorine compound yet reported. The structural implications of these shifts are discussed. A model for O_3F_2 is postulated in which this species is made up of O_2F_2 and "interstitial" O_2.

The nuclear magnetic resonance (nmr) spectra of the series F_2, OF_2, O_2F_2, and O_3F_2 have been observed. The shifts observed for O_2F_2 and O_3F_2 represent the least shielded of any fluorine compounds yet reported. The vast difference in chemical shift of O_2F_2 and O_3F_2 indicates that the fluorine nuclei (hence fluorine–oxygen bonding) are considerably different in O_2F_2 and O_3F_2 as compared to OF_2. A summary of chemical shifts is presented in Table I. The O_3F_2 is given in quotations, since there is some uncertainty about the reality of the compound. This uncertainty will be discussed in some detail later.

Table I. ^{19}F Nmr Shifts for Liquid F_2, OF_2, O_2F_2, and O_3F_2 ($CFCl_3$ reference)

Compound	Shift, ppm
F_2 (77°K)	−422 ± 1
OF_2 (77°K)	−249 ± 1
O_2F_2 (145°K)	−865 ± 1
"O_3F_2" (<145°K)	−877 ± 5

The nmr spectra of liquid F_2 and OF_2 have been reported by Nebgen, Rose, and Metz.[2a] Recently Lawrence, Ogden, and Turner[2b] have reported the ^{19}F nmr spectrum of O_2F_2 in CF_3Cl to be at −825 ± 10 ppm with respect to a Freon 11 ($CFCl_3$) reference. This signal is about 40 ppm higher than our observation in the neat liquid. No open literature reports of the ^{19}F nmr signal in O_3F_2 are available; however, Solomon and co-workers have observed the ^{17}O and ^{19}F nmr signals from O_3F_2.[3] Their observations on the ^{19}F nmr spectrum of O_3F_2 at temperatures near 145°K are identical with ours. Solomon, *et al.*, had better means of temperature control than we, and hence could study the chemical shift of O_3F_2 as a function of temperature. They found that the shift was very far downfield (−1900 ppm at 85°K) and moved upfield to −868 ppm at 145°K. The −868-ppm peak is that of O_2F_2. This upfield shift with temperature is the same as we observed in O_3F_2.

Experimental Section

Commercially available F_2 (The Matheson Co., Inc.) and OF_2 (General Chemical Division, Allied Chemical Corp.) were used in the studies. Prior to sampling, each of the compounds was passed through a hydrogen fluoride trap. The OF_2 contained additional impurities (primarily oxygen) not removed by the HF trap and was further purified by gas chromatography.

The O_2F_2 and O_3F_2 were prepared using the usual discharge techniques. The reaction vessel is similar to that used by Streng,[4] with the exception that the whole vessel is made of Pyrex. A standard taper male connection is placed at the bottom of the reactor to attach sample tubes. The sample tubes were 2-mm capillaries for use in a constant-temperature nmr dewar.[5]

The nmr spectra of the liquid F_2 and OF_2 samples were recorded at 77°K on a Varian Associates HA-100 nmr spectrometer operating at a frequency of 94.075 Mc. That of O_2F_2 was recorded at 145°K using liquid CF_4 as a cryogenic. The nmr signals were externally referenced to the ^{19}F signal from $CFCl_3$. Referencing was accomplished by carefully removing the sample from the magnet probe and replacing it with the reference material. This transfer occurred while the magnetic field was being swept at a constant rate. No significant variations in the field sweep rate were observed in the transfer operation. Each sample was scanned several times, and the transfer done at different intervals during the field sweep.

The spectrum of O_3F_2 required a different technique. After scanning several samples of O_3F_2, it became apparent that the recorded signal was due to O_2F_2 which is the major decomposition product. In other words, O_3F_2 is not sufficiently stable to permit scanning over the period of time required for a recorder trace. To circumvent this stability problem, the oscilloscope display of the nmr signals was used.

The signal from pure O_2F_2 was centered on the scope of the HA-100. The O_2F_2 "reference" was removed and replaced with a sample of O_3F_2 at 77°K. The liquid nitrogen in the nmr dewar was then replaced with liquid CF_4 and the scope signal monitored with time. After 1 min, the sample began to melt and a weak signal appeared on the scope downfield from the O_2F_2 "reference." Within 2 min, this signal was fairly well defined. During the third minute the signal shifted, and at 3 min reappeared at the same spot where the O_2F_2 "reference" signal was located. The experiment was reproduced several times, and we feel confident that the signals observed in the first 2 min represent the nmr peak for O_3F_2 which then rapidly decomposes to O_2F_2 and O_2. The time sequence of spectra, taken from Polaroid photographs of the events, is shown in Figure 1.

Discussion

The nmr spectra of F_2, OF_2, O_2F_2, and O_3F_2 clearly indicate that the ^{19}F nuclei in the latter two are very different from those in the former two Thus some fundamental structural considerations are in order.

Linnett[6] has discussed a novel approach to electronic structure of molecules using the concept of two

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[1] Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 12–16, 1966.

[2] (a) J. W. Nebgen, W. B. Rose, and F. I. Metz, *J. Mol. Spectry.*, 20, 72 (1966); (b) N. J. Lawrence, J. S. Ogden, and J. J. Turner, *Chem. Commun.*, 102, (1966).

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[6] J. W. Linnett, "The Electronic Structure of Molecules," John Wiley and Sons, Inc., New York, N. Y., 1964.

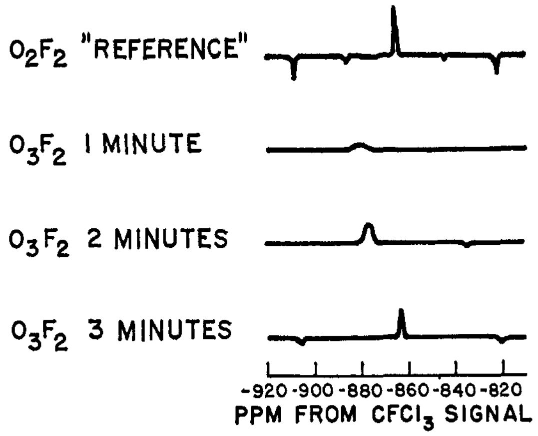

Figure 1. ^{19}F nuclear magnetic resonance spectra of "O_3F_2" as a function of time.

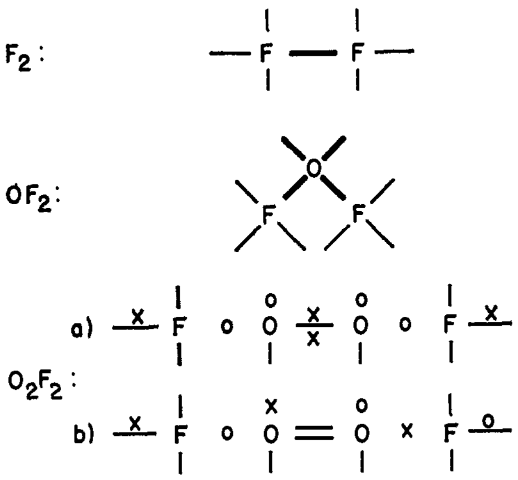

Figure 2. Linnett structures for F_2, OF_2, and O_2F_2.

sets of four electrons around a nucleus rather than the classical Lewis structures of four sets of two electrons. He has postulated structures for F_2, OF_2, and O_2F_2. These structures are presented in Figure 2. In these schematic structures, a heavy line indicates two electrons having opposite spins occupying the same spatial orbital; a light line indicates two electrons on the same atom (or between the same pair of atoms) having opposite spins but not occupying the same orbital; and the crosses and circles represent electrons of differing spins in a particular region. Recently Spratley and Pimentel[7] have proposed a molecular orbital treatment of oxygen–fluorine bonding which results in essentially the same structure for O_2F_2.

The structures of F_2, OF_2, and O_2F_2 can be well characterized, and hence their ^{19}F nmr signals can be interpreted in accordance with their structures. The "one-electron" bond model in O_2F_2 would result in a ^{19}F nucleus which has a very low shielding constant and is thus consistent with the ^{19}F nmr spectrum. The classical theory of ^{19}F nmr shifts as proposed by Saika and Slichter[8] is inadequate to explain the shift in O_2F_2. This inadequacy lies in the fact that the theory is concerned with "normal" fluorine bonds and does not consider the "one-electron" fluorine bonds as postulated by Linnett.

Recently, Baker, Anderson, and Ramsey[9] have discussed nuclear magnetic antishielding of ^{19}F nuclei. Their calculation of antishielding is based on the combination of molecular beam data on spin-rotational interactions in molecules with chemical shift data. This combination is used to calculate the paramagnetic part of the nuclear shielding constant in the Ramsey equation.[10]

Our observations of the ^{19}F nmr signal from O_2F_2 would indicate that considerable antishielding exists in that molecule. Furthermore, we suggest that the antishielding is associated with the long O–F bond in O_2F_2[11] (1.58 A for O_2F_2 compared to 1.41 A for OF_2). This suggestion then leads to the possibility that antishielding may be related in some way to the overlap of the fluorine atom p orbital with the antibonding orbitals in the oxygen molecule as postulated by Spratley and Pimental.[7]

Structural considerations for O_3F_2 are not as straightforward, since supporting data from infrared and microwave are not available as they are for O_2F_2.[12] In order to interpret the nmr shifts observed, three assumptions about the O_3F_2 molecule must be made. The first assumption is that O_3F_2 is structurally similar to O_2F_2; that is to say that the fluorine–oxygen bond is essentially a "one-electron" bond. Secondly, the fluorine nuclei in O_3F_2 are equivalent. This assumption is based on the observation that the intensity which is observed in the O_3F_2 signal is about the same as that observed in the O_2F_2 decomposition product indicating that the same number of fluorine nuclei are giving rise to both signals. The third assumption is that O_3F_2 should have a ready route back to an O_2F_2 decomposition product. This assumption explains the ready decomposition of O_3F_2 to O_2F_2 and the lack of OF_2 and F_2 as decomposition products.

Using these assumptions and following Linnett's rules, several structures for O_3F_2 can be postulated. The classical model of three catenated oxygens terminated by two fluorines (Figure 3a) is not satisfactory since a formal charge of $+1$ exists on the middle oxygen. If other structures are drawn using this same nuclear distribution, they can be rejected because of excessive charge on the oxygen nuclei and because the fluorine nuclei are nonequivalent. However, the principal reason for rejecting this model (and others involving catenated oxygen atoms) is that there is no simple way to get only O_2F_2 and O_2 as decomposition products.

Another possible structure involves a cyclic configuration of three oxygen atoms with fluorine attached to two of them (Figure 3b). This model can readily release oxygen forming O_2F_2 as a decomposition product; however, the two "O_2F_2" oxygens each have a formal charge of $+1$, and the "out-of-line" oxygen has a charge of -1. On the basis of charge distribution, this model is rejected.

A third structure in which O_3F_2 is described as a dimer (Figure 3c) can be postulated. This structure suffers the same shortcomings as the monomer (Figure

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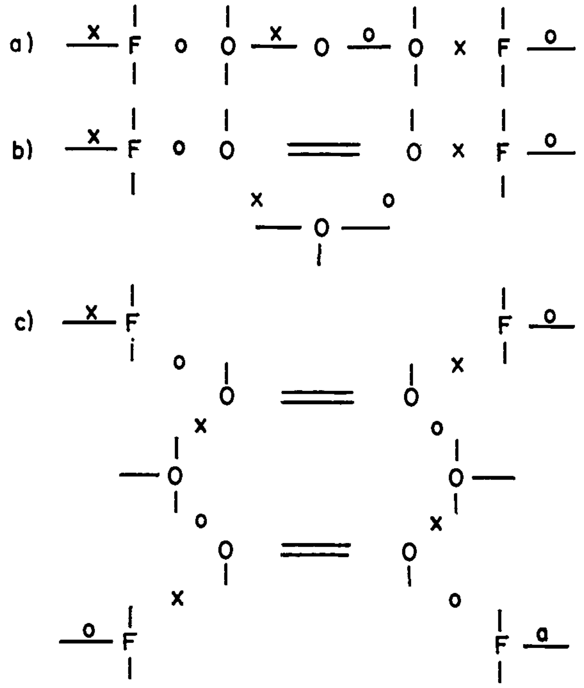

Figure 3. Linnett structures for "O_3F_2" assuming its existence as a molecular entity.

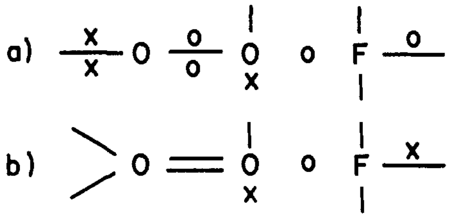

Figure 4. Linnett structures for OOF radical.

3b) in that excessive formal charge is placed upon the oxygen nuclei.

Thus one is drawn to the conclusion based upon structural considerations and upon electronic distribution considerations that O_3F_2 does not exist as discreet molecular units. This conclusion supports that drawn by Solomon and co-workers[3] on their nmr studies and is consistent with the observation of Malone and McGee[13] that the mass spectral cracking pattern of O_3F_2 does not arise from a single molecular species.

What then is the nature of material with composition O_3F_2? Two possibilities exist. The first possibility is that O_3F_2 is a 1:1 mixture of O_2F_2 and O_4F_2. The structure of O_4F_2 has recently been postulated as $(OOF)_n$,[14] indicating that this compound is a polymer of the radical OOF. Linnett structures for the OOF radical can readily be drawn and are presented in Figure 4. In this case, "one-electron" bonds are favored over the normal fluorine–oxygen covalent bonds. The appearance of only one signal for "O_3F_2" suggests that the model of discreet O_2F_2 and OOF species from O_4F_2 is not correct. If it were, then two ^{19}F signals should be observed, one for each fluorine in the two species.

The second possibility, and the one which is preferred by the authors, is a model of O_2F_2 containing "interstitial" oxygen molecules. This "interstitial" oxygen is held in the O_2F_2 by forces too strong for it to be considered dissolved, but too weak for it to be considered bonded, even with "one-electron" bonds. However, the oxygen is bound strongly enough to alter significantly the ^{19}F nmr shift for O_2F_2.

This model is consistent with several observations on the system. First, although repeated analyses yielded an average stoichiometry of $O_{3.0}F_2$, individual analyses ranged from $O_{2.9}F_2$ to $O_{3.1}F_2$. Although small amounts of O_2F_2 and O_4F_2 can be formed during the preparation of O_3F_2, procedures were developed to remove both impurities prior to sampling. In addition, a much wider stoichiometric range ($O_{3.5}F_2$ to $O_{2.5}F_2$) is found in the analyses if O_4F_2 and O_2F_2 are intentionally prepared with O_3F_2. Secondly, the recorded behavior of O_3F_2 with temperature is indicative of unusual bonding. At 77°K, O_3F_2 is a dark brownish red solid; at 83–84°K, the material melts to a dark red liquid; in the temperature interval 85 to 105°K (where O_3F_2 is said to decompose[4]), the color becomes orange-red and nucleation of O_2F_2 (yellow crystals) can be seen on the sides of sample tubes. The decomposition of the red liquid proceeds rapidly at 109°K and above. The color changes are accompanied by changes in the chemical shift of O_3F_2. However, temperature was found to have little effect on the chemical shift of pure O_2F_2. The shift of pure O_2F_2 varied only about 2 ppm in the range of 110–145°K. Third, the only decomposition products of O_3F_2 are O_2F_2 and O_2. There is no evidence of other decomposition products such as F_2 or OF_2. Finally, epr spectra of samples of O_3F_2 at 77°K showed the same anisotropic pattern present in spectra of O_2F_2 samples at temperatures below 116°K. O_3F_2 is said to melt at 84°K and to decompose quantitatively at 115°K.[15] Epr spectra of O_3F_2 at temperatures between 88 and 115°K do not show the isotropic doublet expected from $\cdot O_2F$ in *liquid* O_3F_2, but rather the same anisotropic pattern observed in the spectrum of $\cdot O_2F$ in *solid* O_2F_2; a doublet is observed at temperatures above 110°K, the melting point of O_2F_2. From the behavior of the color changes described above and from the epr observations, it is concluded that samples of O_3F_2 contain significant amounts of O_2F_2, and it is the epr spectrum of $\cdot O_2F$ in the latter compound which is observed from 88 to 115°K.[16]

The conclusions which we have reached are somewhat different from those reported by Solomon, *et al.*[3] These authors reported two incompletely resolved signals, whereas we observed only one broad signal which became more narrow with increasing temperature. Because of their observation of two ^{19}F nmr signals, Solomon, *et al.*, concluded that the two signals were due to O_2F_2 and $(OOF)_n$. However, we observed no significant shift of the ^{19}F nmr signal from pure O_2F_2 in the range of 110 to 145°K. Solomon, *et al.*, report a considerable shift (−1900 ppm at 85°K) in both signals which they report. It is the opinion of the authors of this paper that if the Solomon model of O_3F_2 as a mixture of O_2F_2 and $(OOF)_n$ is correct, the

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[16] F. E. Welsh, private communication.

O_2F_2 signal should remain in its usual region while the $(OOF)_n$ signal would migrate with temperature until it coalesces with that of O_2F_2. Our results would indicate, and we believe that the temperature studies of Solomon, *et al.*, indicate also, that "O_3F_2" cannot be as simply described as a mixture of O_2F_2 and $(OOF)_n$.

The ease with which O_3F_2 reverts to O_2F_2, together with the fact that no really adequate structure can be drawn for O_3F_2, suggests a model of "O_3F_2" in which "interstitial" oxygen is being held by O_2F_2 molecules. Such a model fits the observations most fully. This model is further substantiated by mass spectral studies[13] which show that "O_3F_2" can be described as O_2F_2 plus O_2.

If one extends the model one step further and considers a 1:1 ratio of O_2F_2 and O_2, it becomes apparent that the most reasonable structure in this instance is $(OOF)_n$, or the model for O_4F_2 as suggested by infrared studies.[14]

An unequivocal interpretation of the ^{19}F nmr signal from O_3F_2 cannot be made at this time. It would appear that the key lies in the determination of ^{19}F nmr shifts in the O_4F_2 or in the OOF species. Our attempts to determine chemical shifts for O_4F_2 were not successful, since the instability of this species is very much greater than that associated with O_2F_2 or even "O_3F_2." With the development of more refined low-temperature nmr techniques, however, such information should be made available.

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On the Crystal Structure of Trimethylaluminum

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Abstract: The crystal structure of trimethylaluminum has been redetermined by three-dimensional, single-crystal X-ray diffraction techniques from photographic data obtained at $-50°$. Hydrogen as well as aluminum and carbon atoms were located. The structure consists of $Al_2(CH_3)_6$ molecules with symmetrical Al–C–Al bridges. An Al–C–Al bridge angle of $74.7 \pm 0.4°$ and an Al–C bridge distance of 2.14 ± 0.01 A were found. The nonbridged Al–C distance is 1.97 ± 0.01 A. An Al–Al distance of 2.600 ± 0.004 A was found, ~ 0.1 A longer than previous results indicated. A significant molecular distortion involving the terminal carbon atoms makes the nuclear framework (excluding hydrogen) belong to point group C_{2h} instead of the idealized D_{2h}. There exists no experimental evidence to indicate that the bridge is not correctly described with a carbon sp_3 orbital participating in a four-center, four-electron, electron-deficient bridge bond.

The original example of electron-deficient methyl bridge bonding was tetramethylplatinum,[3] which is now generally recognized as nonexistent.[4] Trimethylgallium has been shown to be monomeric down to very low temperatures[5] in benzene solution and in the pure liquid at room temperature.[6] Trimethylindium[7,8] is, at best, only very weakly bonded into a higher polymer. Hence, there exist at this time only three examples of "five-coordinate carbon" or electron-deficient methyl bridge bonds: dimethylberyllium,[9] dimethylmagnesium[10] (powder data only), and trimethylaluminum.[11] Previously, Amma[12] had attempted a refinement of the three-dimensional data of trimethylaluminum collected in the original two-dimensional structure determination,[11] but the refinement failed to converge properly. Similar results have been obtained for the refinement of the photographic data of dimethylberyllium.[13] The failure of these refinements is probably due to the quality of the original diffraction data. With the availability of better vacuum-line[14] and low-temperature[15] techniques, we decided to reinvestigate this crystal structure because this compound is the prototype of methyl bridge electron-deficient bridging bonding and is important not only to the understanding of metal–alkyl bonds but also to the nature of intermediates in many organic reactions.

Experimental Section

Trimethylaluminum was purchased from the Ethyl Corp. in a small cylinder, and a sample from this was removed into a storage tube in a vacuum line. The sample was sublimed several times and then sublimed directly into very thin-walled Pyrex capillaries.[13] The capillaries were then cut off under liquid nitrogen, and the melting point of the sample in each capillary was checked. Crystals were grown in a cold room at 0° and annealed with a small electric

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