

S–O stretches in  $\text{SOF}_2$  and  $\text{SOCl}_2$  occur at 1312 and 1229  $\text{cm}^{-1}$ , respectively.<sup>22</sup> Kagarise<sup>23</sup> was able to demonstrate a linear relationship between carbonyl stretching frequency and the sum of the electronegativity values (Gordy scale<sup>24</sup>) of atoms X and Y in molecules of the type XCOY. However, when this was applied to structurally similar sulfinyl compounds,<sup>25</sup> the points fell on a smooth curve and it was noted that changes in electronegativities of substituents in XSOY had smaller effects on S–O stretching frequency than on C–O analogs. This is in agreement with Moffitt<sup>26</sup> who showed that there is a relatively small variation in bond order in many XSOY compounds. When the electronegativities<sup>22,23</sup> of the trifluoromethylsulfinyl halides are superimposed on this curve, the absorption bands at 1268, 1238, and 1235  $\text{cm}^{-1}$  for  $\text{CF}_3\text{S(O)F}$ ,  $\text{CF}_3\text{S(O)Cl}$ , and  $\text{CF}_3\text{S(O)Br}$ , respectively, correspond to the S–O stretching frequency. By the same process, bands at 1260 and 1258  $\text{cm}^{-1}$  in the spectra of  $\text{C}_2\text{F}_5\text{S(O)F}$  and  $i\text{-C}_3\text{F}_7\text{S(O)F}$  are attributable to S–O stretch. Based

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on the above, CF asymmetric stretching frequencies are assigned to 1227, 1216, and 1205  $\text{cm}^{-1}$  and symmetric bands to 1147, 1123, and 1116  $\text{cm}^{-1}$  in  $\text{CF}_3\text{S(O)F}$ ,  $\text{CF}_3\text{S(O)Cl}$ , and  $\text{CF}_3\text{S(O)Br}$ , respectively. As the size and electronegativity of the substituent halide increase, there is a concomitant decrease in the S–O and asymmetric and symmetric C–F stretching frequencies. This decrease is observed for asymmetric and symmetric S–O stretch in  $\text{CF}_3\text{SO}_2\text{F}$  and  $\text{CF}_3\text{SO}_2\text{Cl}$ <sup>9</sup> at 1463 and 1239  $\text{cm}^{-1}$  and 1439 and 1239  $\text{cm}^{-1}$ , respectively, and, from this work, for  $\text{CF}_3\text{SO}_2\text{Br}$  at 1424 and 1236  $\text{cm}^{-1}$ . For  $\text{CF}_3\text{SBr}$ , by comparison with  $\text{CF}_3\text{SCl}$ ,<sup>8</sup> bands at 1180 and 1116 are asymmetric and symmetric C–F stretches and the band at 760 is a  $\text{CF}_3$  deformation. The characteristic broad band centered at approximately 748  $\text{cm}^{-1}$  in  $\text{CF}_3\text{S(O)F}$ ,  $\text{C}_2\text{F}_5\text{S(O)F}$  and  $i\text{-C}_3\text{F}_7\text{S(O)F}$  is probably due to S–F stretch; however,  $\text{CF}_3$  deformation occurs in this region.

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## Additional Studies Concerning the Existence of “ $\text{O}_3\text{F}_2$ ”

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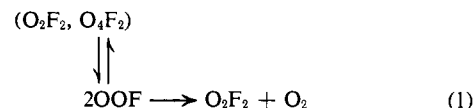
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**Abstract:** Additional  $\text{O}^{17}$  and  $\text{F}^{19}$  data on the oxygen fluorides have been obtained. The reactions of the oxygen fluorides with boron trifluoride are also described. All of the evidence obtained supports the conclusion that “ $\text{O}_3\text{F}_2$ ” is actually a mixture of  $\text{O}_2\text{F}_2$  and  $(\text{OOF})_n$ .

Several oxygen fluorides have been reported, namely  $\text{SOF}_2$ ,<sup>1</sup>  $\text{O}_2\text{F}_2$ ,<sup>2</sup>  $\text{O}_3\text{F}_2$ ,<sup>3</sup>  $\text{O}_4\text{F}_2$ ,<sup>4</sup> and recently  $\text{O}_5\text{F}_2$ <sup>5</sup> and  $\text{O}_6\text{F}_2$ .<sup>5</sup> The structures of  $\text{OF}_2$  and  $\text{O}_2\text{F}_2$  are well known, but very little is known about the higher oxygen fluorides. Recently, the structure and even the existence of “ $\text{O}_3\text{F}_2$ ” have been subjects of considerable concern.

Malone and McGee<sup>6</sup> applied cryogenic mass spectrometry to the problem and concluded that “ $\text{O}_3\text{F}_2$ ” consists of loosely bonded  $\text{O}_2\text{F}$  and  $\text{OF}$  radicals. Nebgen, *et al.*,<sup>7</sup> studied the  $\text{F}^{19}$  nmr spectrum of “ $\text{O}_3\text{F}_2$ ” and postulated an “ $\text{O}_3\text{F}_2$ ” model consisting of  $\text{O}_2\text{F}_2$  and interstitial oxygen. Previous work in our laboratories<sup>8</sup> on both  $\text{F}^{19}$  and  $\text{O}^{17}$  nmr spectroscopy of

“ $\text{O}_3\text{F}_2$ ” led us to conclude that the system is best explained as



We wish to report recent results that we believe further substantiate this conclusion.

### Experimental Section

$\text{OF}_2$  was obtained from the Allied Chemical Corp. The other oxygen fluorides were prepared by using previously reported procedures.<sup>2-4</sup> The  $\text{O}^{17}$ -enriched  $\text{OF}_2$  was obtained from the Texaco Research Center.

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 to obtain better temperature control and to allow rapid insertion of the sample. Cooling was achieved with gaseous nitrogen previously cooled by passage through a copper coil immersed in liquid nitrogen. The temperature was controlled by varying the flow of the nitrogen.

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Figure 1.  $F^{19}$  nmr spectrum of 50 vol % solution of " $O_3F_2$ " in  $OF_2$ .

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

Dioxygenyl fluoroborate ( $O_2BF_4$ ) was prepared by using previously described methods.<sup>9,10</sup> The gas mixtures formed as by-products in the preparation of  $O_2BF_4$  were analyzed by passing them through (1) a series of  $-196^\circ$  traps to remove any condensable gases, (2) a heated sodium chloride chamber to convert the fluorine ( $F_2$ ) to chlorine ( $Cl_2$ ), (3)  $-196^\circ$  traps to remove the  $Cl_2$ , and (4) an automatic Toepler pump to collect the  $O_2$ . The components were measured as gases in calibrated volumes; the  $Cl_2$  was equated to the  $F_2$  in the original mixture.

## Results and Discussion

**$F^{19}$  Nmr Spectroscopy.** We previously reported<sup>8</sup> that the  $F^{19}$  nmr spectrum of " $O_3F_2$ " consists of an unsymmetrical line that was resolved with much difficulty into two overlapping lines. Nebgen, *et al.*,<sup>7</sup> also determined the  $F^{19}$  nmr spectrum of " $O_3F_2$ " but observed only one line. These workers postulated an " $O_3F_2$ " model made up of  $O_2F_2$  and interstitial oxygen. If this model were correct, the  $F^{19}$  nmr spectrum would consist of only one line. Therefore, we felt that an unequivocal answer to the question, "Does the  $F^{19}$  nmr spectrum of ' $O_3F_2$ ' consist of one or two lines?" was extremely important.

The measurements on neat " $O_3F_2$ " were repeated several times, but, as before, two overlapping lines were

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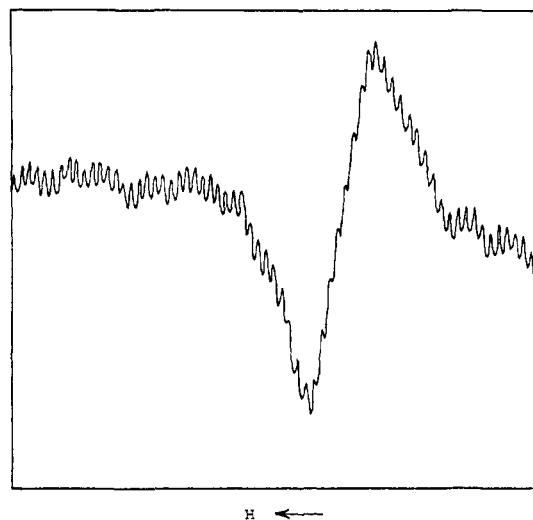
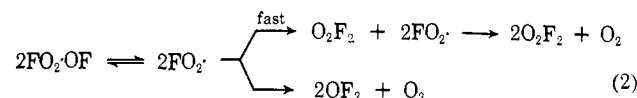


Figure 2.  $F^{19}$  nmr spectrum of 0.7 vol %  $OF_2$  in  $O_2F_2$ .

always obtained. It was thought that the overlapping lines could be better resolved by obtaining the  $F^{19}$  nmr spectrum of " $O_3F_2$ " dissolved in a solvent. The  $F^{19}$  nmr spectrum of a 50 vol % solution of " $O_3F_2$ " in  $OF_2$  (Figure 1) definitely shows that " $O_3F_2$ " consists of two separate  $F^{19}$  lines. The  $F^{19}$  line due to the  $OF_2$  (not shown in Figure 1) appeared in the region expected for  $OF_2$  (approximately  $-250$  ppm, relative to  $CFCl_3$ ).

Malone and McGee<sup>6</sup> applied cryogenic mass-spectrometric techniques to study oxygen fluorides. They were unable to obtain currents attributable to  $O_2F_2$ ,  $O_3F_2$ , or  $O_4F_2$ , but they did obtain peaks attributable to  $OF^+$ ,  $OF_2^+$ ,  $O_2^+$ ,  $O_2F^+$ ,  $O_2^+$ , and  $F_2^+$ . They concluded that " $O_3F_2$ " is basically an  $O_2F$  and an  $OF$  radical loosely bonded together and that it undergoes thermal decomposition to  $O_2F$  and  $OF$  *via* the reaction shown in eq 2.



These conclusions were based mainly on the fact that  $OF^+$  and  $OF_2^+$  were observed in their mass-spectrometric studies. Malone and McGee<sup>6</sup> stated, "That the appearance potential of the  $OF^+$  and the ratio of  $OF^+/OF_2^+$  confirm the parent substance to be  $OF_2$ ." They believe that  $OF_2$  can be accounted for in at least two ways. It could be formed as a by-product in the electrical discharge tube when " $O_3F_2$ " is formed, and it could result from the decomposition of " $O_3F_2$ " as shown in reaction scheme 2. Smaller amounts of  $OF^+$  and  $OF_2^+$  than the other species were observed, but Malone and McGee<sup>6</sup> did not measure their absolute amounts.

We added 0.7 vol %  $OF_2$  to  $O_2F_2$  and observed the  $F^{19}$  nmr line (Figure 2) due to this small amount of  $OF_2$ . " $O_3F_2$ " was then allowed to decompose to  $O_2F_2$  and other possible products while the sample was maintained at  $115^\circ K$  in the nmr cavity. No  $F^{19}$  signal due to  $OF_2$  was observed, so it can be stated that if  $OF_2$  is formed as a decomposition product of " $O_3F_2$ " less than 0.7 vol %  $OF_2$  is present. These observations are not surprising, since  $OF_2$  has never been observed as a

decomposition product of "O<sub>3</sub>F<sub>2</sub>" in our laboratory or in other studies.<sup>11</sup>

**O<sup>17</sup> Nmr Spectroscopy.** Previous work in our laboratory<sup>8</sup> produced a three-line O<sup>17</sup> nmr spectrum for "O<sub>3</sub>F<sub>2</sub>." The largest line was definitely due to the O<sub>2</sub>F<sub>2</sub>, and the other two lines, which were equally intense, were attributed to (OOF)<sub>n</sub>. There are three possible O<sup>17</sup> nmr spectra for the molecular species "O<sub>3</sub>F<sub>2</sub>." If all the oxygen atoms were similar, a one-line spectrum would result. If all the oxygen atoms were different, a three-line spectrum would result. And if two oxygen atoms were equivalent and one was different, a two-line spectrum in which one of the lines is twice as intense as the other would result. It was concluded that two equally intense O<sup>17</sup> lines cannot account for the molecular species "O<sub>3</sub>F<sub>2</sub>."

We have obtained additional O<sup>17</sup> nmr results that we believe substantiate our previous conclusion. Malone and McGee report<sup>6</sup> that "O<sub>3</sub>F<sub>2</sub>" may contain foreign species such as ozone (O<sub>3</sub>) and/or OF<sub>2</sub>. The O<sup>17</sup> nmr spectra of both O<sub>3</sub> and OF<sub>2</sub> were obtained. These results and a comparison of the O<sup>17</sup> nmr spectra of O<sub>2</sub>F<sub>2</sub> and (OOF)<sub>n</sub> are present in Table I. The spec-

**Table I.** O<sup>17</sup> Nmr Data for Various Compounds

Compound	O <sup>17</sup> position	Chemical shift relative to H <sub>2</sub> O <sup>17</sup> , ppm
O <sub>2</sub> F <sub>2</sub>	O <sub>2</sub> <sup>17</sup> F <sub>2</sub>	-647 <sup>a</sup>
(O <sub>2</sub> F) <sub>n</sub>	?	-971
		-1512
O <sub>3</sub>	O-O <sup>17</sup> -O	-1032
	O <sup>17</sup> -O-O <sup>17</sup>	-1598
OF <sub>2</sub>	O <sup>17</sup> F <sub>2</sub>	-830 <sup>a</sup>

<sup>a</sup> Triplet.

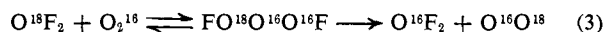
trum of OF<sub>2</sub> consisted of a single line, and, as expected, this line was a triplet due to O<sup>17</sup>-F<sup>19</sup> spin coupling with the two fluorine atoms. From these results it can be concluded that none of the O<sup>17</sup> lines previously reported for "O<sub>3</sub>F<sub>2</sub>" were OF<sub>2</sub> or O<sub>3</sub> lines.

We also determined that under ordinary conditions the oxygen atom of OF<sub>2</sub> does not exchange with those of either O<sub>2</sub>F<sub>2</sub> or "O<sub>3</sub>F<sub>2</sub>." A solution containing 50 vol % O<sup>17</sup>-labeled "O<sub>3</sub>F<sub>2</sub>" and ordinary OF<sub>2</sub> was placed in the nmr cavity and maintained at 93°K for 30 min. No signal was observed for O<sup>17</sup>F<sub>2</sub>. The "O<sub>3</sub><sup>17</sup>F<sub>2</sub>" in the solution was then allowed to decompose to O<sub>2</sub><sup>17</sup>F<sub>2</sub>; again, no signal was observed for O<sup>17</sup>F<sub>2</sub>. The O<sub>2</sub><sup>17</sup>F<sub>2</sub> solution was warmed to room temperature to allow the O<sub>2</sub><sup>17</sup>F<sub>2</sub> to decompose to O<sub>2</sub> and F<sub>2</sub>. The OF<sub>2</sub> was separated from the O<sub>2</sub> and the F<sub>2</sub> and replaced in the nmr cavity; no O<sup>17</sup>F<sub>2</sub> signal was observed.

Malone and McGee<sup>6</sup> stated that they believe there is a rapid exchange of fluorine atoms in O<sub>2</sub>F<sub>2</sub>-O<sub>3</sub>F<sub>2</sub> mixtures. They argued that this is reasonable in the light of their model of "O<sub>3</sub>F<sub>2</sub>" consisting of loosely bonded O<sub>2</sub>F and OF radicals. They compared this exchange to one proposed by Arkell.<sup>12</sup> When photolyzed in an O<sub>2</sub><sup>16</sup> matrix at 4°K, O<sup>18</sup>F<sub>2</sub> yields O<sup>16</sup>F<sub>2</sub> and the amount of O<sup>18</sup>F<sub>2</sub> decreases. In this system, Arkell suggested an exchange mechanism involving "O<sub>3</sub>F<sub>2</sub>."

(11) A. G. Streng, *Chem. Rev.*, **63**, 607 (1963).

(12) A. Arkell, *J. Amer. Chem. Soc.*, **87**, 4057 (1965).

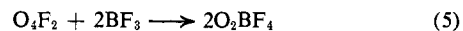


Arkell used photolytic conditions, and his experiments are probably not comparable to either our work or that of Malone and McGee.<sup>6</sup>

**Reactions of Oxygen Fluorides with Boron Trifluoride.** The existence of the dioxygenyl ion (O<sub>2</sub><sup>+</sup>) in dioxygenyl hexafluoroplatinate<sup>13</sup> and in the salts of the group V fluorides<sup>14</sup> is well established. It has also been shown<sup>9</sup> that the product of the reaction of O<sub>2</sub>F<sub>2</sub> with boron trifluoride (BF<sub>3</sub>) is O<sub>2</sub>BF<sub>4</sub>.



O<sub>2</sub>BF<sub>4</sub> can also be formed<sup>10</sup> by allowing O<sub>4</sub>F<sub>2</sub> to react with BF<sub>3</sub>.



It was concluded<sup>10</sup> that in both cases BF<sub>3</sub> reacts with O<sub>2</sub>F to form O<sub>2</sub>BF<sub>4</sub>. The reaction of O<sub>4</sub>F<sub>2</sub> with BF<sub>3</sub> does not release F<sub>2</sub> but the reaction of O<sub>2</sub>F<sub>2</sub> with BF<sub>3</sub> must be accompanied by the rupture of an O-F bond and the release of F<sub>2</sub>. Reactions of this type are very useful in further elucidating the "O<sub>3</sub>F<sub>2</sub>" system.

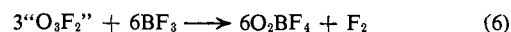
O<sub>4</sub>F<sub>2</sub>, "O<sub>3</sub>F<sub>2</sub>," and O<sub>2</sub>F<sub>2</sub> were allowed to react with BF<sub>3</sub> to form O<sub>2</sub>BF<sub>4</sub>; the composition and the amount of the by-product gases were monitored (Table II).

**Table II.** By-Products Formed in the Preparation of O<sub>2</sub>BF<sub>4</sub>

Ratio O <sub>2</sub> :F <sub>2</sub> charged	BF <sub>3</sub> consumed, cc	F <sub>2</sub> formed, cc	O <sub>2</sub> formed, cc	Ratio O <sub>2</sub> :F <sub>2</sub> formed	Theoret ratio <sup>a</sup> BF <sub>3</sub> consumed: F <sub>2</sub> formed
0.94	61.0	29.0	0.9	2.10	2
1.49	16.5	16.5	0.4	5.40	6
1.96	...	1.4	2.3	46.4	∞

<sup>a</sup> Theoretical ratios assume eq 4 for O<sub>2</sub>F<sub>2</sub>, eq 5 for O<sub>4</sub>F<sub>2</sub>, and eq 6 for "O<sub>3</sub>F<sub>2</sub>."

The results obtained with O<sub>2</sub>F<sub>2</sub> and O<sub>4</sub>F<sub>2</sub> were entirely consistent with eq 4 and 5. The small amount of O<sub>2</sub> were entirely consistent with eq 4 and 5. The small amount of O<sub>2</sub> formed was the result of the unavoidable decomposition of a small amount of O<sub>2</sub>F<sub>2</sub> and O<sub>4</sub>F<sub>2</sub> during handling; it is interesting that approximately the same small percentage of O<sub>2</sub> was observed in the reaction of "O<sub>3</sub>F<sub>2</sub>" with BF<sub>3</sub>, and the results are consistent with the following equation.



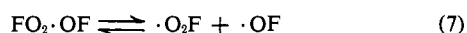
If the assumption that "O<sub>3</sub>F<sub>2</sub>" is a 1:1 mixture of O<sub>4</sub>F<sub>2</sub> and O<sub>2</sub>F<sub>2</sub> were made, the stoichiometry obtained by adding eq 4 and 5 would be expected. Even of more importance is the fact that no O<sub>2</sub> was observed in the formation of O<sub>2</sub>BF<sub>4</sub> from "O<sub>3</sub>F<sub>2</sub>" and BF<sub>3</sub>. The fact that "O<sub>3</sub>F<sub>2</sub>" reacts with BF<sub>3</sub> to form O<sub>2</sub>BF<sub>4</sub> and F<sub>2</sub> as depicted in reaction eq 6 is therefore completely consistent with a model of "O<sub>3</sub>F<sub>2</sub>" consisting of a 1:1 mixture of O<sub>4</sub>F<sub>2</sub> and O<sub>2</sub>F<sub>2</sub>.

This information will now be considered in terms of Malone's<sup>6</sup> and Nebgen's proposed models for "O<sub>3</sub>F<sub>2</sub>."

(13) N. Bartlett and D. H. Lohmann, *J. Chem. Soc.*, 5233 (1962).

(14) A. R. Young, II, T. Hirata, and S. I. Morrow, *ibid.*, **86**, 20 (1964).

Malone and McGee<sup>6</sup> proposed an "O<sub>3</sub>F<sub>2</sub>" model consisting of loosely bonded O<sub>2</sub>F and OF radicals. They proposed that O<sub>2</sub>F and OF are in equilibrium with "O<sub>3</sub>F<sub>2</sub>."



The  $\cdot \text{O}_2\text{F}$  would be expected to react with BF<sub>3</sub> and release OF radicals. Subsequent decomposition of the OF radicals would then be expected to result in F<sub>2</sub>, O<sub>2</sub>, and perhaps OF<sub>2</sub>. However, neither O<sub>2</sub> nor OF<sub>2</sub> was observed.

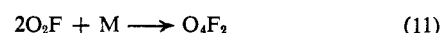
If Nebgen's<sup>7</sup> model consisting of O<sub>2</sub>F<sub>2</sub> and interstitial oxygen is assumed correct, the reaction of "O<sub>3</sub>F<sub>2</sub>" with BF<sub>3</sub> to form O<sub>2</sub>BF<sub>4</sub> should result in the release of the loosely bound interstitial oxygen. However, the reaction of "O<sub>3</sub>F<sub>2</sub>" with BF<sub>3</sub> to form O<sub>2</sub>BF<sub>4</sub> releases only F<sub>2</sub>, not O<sub>2</sub>.

### Conclusion

In view of all the evidence obtained to date, it is concluded that "O<sub>3</sub>F<sub>2</sub>" and its decomposition to O<sub>2</sub>F<sub>2</sub> can best be explained by eq 1. It has been shown<sup>8</sup> that "O<sub>3</sub>F<sub>2</sub>" has a three-line O<sup>17</sup> nmr spectrum. The largest line is definitely O<sub>2</sub>F<sub>2</sub>, and the other two lines, which have equal intensities, are attributed to (OOF)<sub>n</sub>. The present work shows that these two lines are not due to either O<sub>3</sub> or OF<sub>2</sub>. Explaining two equally intense O<sup>17</sup> lines in terms of the molecular species "O<sub>3</sub>F<sub>2</sub>" is not possible. Therefore, we believe that the model prepared by Malone and McGee<sup>6</sup> cannot be correct. The model proposed by Nebgen and coworkers<sup>7</sup> can be correct only if there are two nonequivalent interstitial oxygen atoms and the O<sup>17</sup> nmr line due to the O<sub>2</sub>F<sub>2</sub> part of Nebgen's<sup>7</sup> model is the same as the O<sup>17</sup> lines of independently prepared O<sub>2</sub>F<sub>2</sub>. Also, the F<sup>19</sup> nmr spectrum expected from the Nebgen<sup>7</sup> model should contain only one line, but the present work shows that

"O<sub>3</sub>F<sub>2</sub>" exhibits two F<sup>19</sup> lines. The results of the reaction of "O<sub>3</sub>F<sub>2</sub>" with BF<sub>3</sub> are also inconsistent with the models proposed by either Malone and McGee<sup>6</sup> and Nebgen, *et al.*<sup>7</sup> For these reasons all the evidence supports the conclusion that "O<sub>3</sub>F<sub>2</sub>" is actually a mixture of O<sub>2</sub>F<sub>2</sub> and (OOF)<sub>n</sub>.

A question that could be asked is "Why is it possible to prepare O<sub>2</sub>F<sub>2</sub> and (OOF)<sub>n</sub> (or O<sub>4</sub>F<sub>2</sub>) but not "O<sub>3</sub>F<sub>2</sub>?" In considering the facts, the answer is evident. The heats of dissociation of O<sub>2</sub> into 2O and F<sub>2</sub> into 2F are 119.1 and 37.7 kcal/mole, respectively.<sup>15</sup> The formation of "O<sub>3</sub>F<sub>2</sub>" requires the dissociation of O<sub>2</sub> or the formation of the oxygen atoms by some other process. It has been shown that relatively little or no O<sub>3</sub> is formed under the conditions used for the preparation of "O<sub>3</sub>F<sub>2</sub>." Of course, the formation of O<sub>3</sub> also requires the formation of oxygen atoms. The formation of oxygen atoms, however, is not a necessary event for forming either O<sub>2</sub>F<sub>2</sub> or O<sub>4</sub>F<sub>2</sub>.



"O<sub>3</sub>F<sub>2</sub>" is probably not formed under the present conditions, but it should not be implied from this work that it is not capable of existence. If conditions for producing O atoms or OF radicals were used, preparation of molecular O<sub>3</sub>F<sub>2</sub> may be possible. Experiments of this type are being carried out.

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(15) "JANAF Thermochemical Tables with Revisions," Dow Chemical Co., Midland, Mich.,