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Report No. IITRI-C227-20
(Technical Summary Report)

ADVANCED OXIDIZER CHEMISTRY

Air Force Office of Scientific Research
Washington D.C.

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(Technical Summary Report)

ADVANCED OXIDIZER CHEMISTRY

April 1 through June 30, 1967

Contract No. AF 49(638)-1175
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Prepared by

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of

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FORWORD

This is report No. IITRI-C227-20 (Technical Summary Report) of IITRI Project C227, Contract No. Af 49(638)-1175, entitled "Advanced Oxidizer Chemistry." The report covers the period from April 1 through June 30, 1967.

In addition to the author, personnel who contributed to the program during this report period are: R. Maguire, Research Chemist; J. N. Keith, Research Chemist; A. Kacmarek, Associate Chemist; J. Raney, Associate Chemist; and J. McDonough, Assistant Chemist.

Respectfully submitted,

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ABSTRACT

Work on the structure of dioxygenyl fluoroborate is now nearing completion. Raman spectral data, and F^{18} tracer studies, are consistent with the O_2^+ structure. Decomposition kinetics point to an OOF intermediate in the decompostion of O_2BF_4. It has also been found that dioxygenyl fluoborate can be prepared by two new and interesting photochemical reactions: the reaction of oxygen, fluorine and boron trifluoride and the reaction of oxygen difluoride and boron trifluoride.

Tracer techniques have shown that the reaction of O_2F_2 with SO_2 proceeds via an OOF intermediate. This work is now complete and all the O^{17} NMR data is presented.

The OOF group has also been transferred to carbon in that at least two OOF compounds are prepared by the reaction of either O_2F_2 or O_4F_2 with perfluoropropylene.

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ADVANCED OXIDIZER CHEMISTRY

I. INTRODUCTION

The major objectives of this program are: (1) elucidation of the chemistry of oxygen fluoride (O_4F_2) and dioxygen defluoride (O_2F_2) with inorganic compounds, (2) study of the structure and the reactions of dioxygenyl fluoroborate (O_2BF_4) and (3) study of the properties of O_4F_2 by using NMR and EPR spectroscopy to reveal the structure and the presence or absence of ionic species and radicals.

II. RESULTS AND DISCUSSION

A. Reactions of Dioxygenyl Compounds

We have done considerable amount of work on the dioxygenyl compounds, and most of the work has been completed. A paper entitled "The Chemistry and Structure of Dioxygenyl Fluoroborate - F^{18} Tracer Studies and Decomposition Kinetics" was included in the last Technical Summary Report. This paper, which was a joint publication with Argonne National Laboratory, has been accepted for publication in Inorganic Chemistry.

O_2BF_4 is prepared from the reaction of boron trifluoride (BF_3) with O_2F_2 or with O_4F_2 at low temperatures. Isotopic tracer studies of the reaction indicated that the product is $O_2^+BF_4^-$ rather than a coordination compound, $O_2F \longrightarrow BF_3$. O_2F may be the intermediate in both the preparation and the decomposition of O_2BF_4. The kinetic data for the thermal decomposition were consistent with the rate law: $dP/dt = k_1 K_{eq}^2/P_{BF_3}^2$. The data are explained in terms of the equilibrium $O_2BF_4(s) \rightleftharpoons O_2F(g) + BF_3(g)$ and a bimolecular process for the decomposition of O_2F. Values for the product $k_1K_{eq}^2$ are presented for the temperature range of 0 to 32°C, from which the sum $2\Delta H_s + E_a$ was 40 kcal/mole.

1. Raman Spectra of O_2BF_4

In cooperation with E. L. Gasner at Argonne, we initiated a study of the Raman spectra of solid O_2BF_4 by using the helium-neon laser at Argonne. In the spectra recorded to date, two of the expected four lines for BF_4^- have been observed. The other two lines were quite broad and probably could not be observed for the sample used because it was a solid. Another line, at approximately 1800 cm^{-1}, which is in the region expected for O_2^+, was also observed.

A sample of O_2BF_4 with enriched oxygen (O_2) was prepared, and the Raman spectrum was observed. By observing the isotopic shifts for the enriched sample, it is possible to determine whether the line at 1800 cm^{-1} observed in the sample of O_2BF_4 containing ordinary oxygen actually was the line due to O_2^+. The composition of the enriched O_2 used was approximately 60% O^{18}, 30% O^{16}, and 10% O^{17}. Six lines are possible for the various combinations of these isotopes to make O_2^+, and with the use of simple statistics the abundance for each line was calculated:

O_2^+	Abundance %
$O^{18}-O^{18}$	36
$O^{18}-O^{16}$	36
$O^{18}-O^{17}$	12
$O^{16}-O^{16}$	9
$O^{17}-O^{16}$	6
$O^{17}-O^{17}$	1

Ideally, the observed spectrum should contain six lines and the ratio of the intensity of each line should be consistent with the above percentages. Actually, four lines were observed, it is likely that the two weakest lines were not observed. All these data are being correlated, and a paper based on them will be included in the next report.

2. New Methods of Preparation of O_2BF_4

Since the structure of O_2BF_4 is now known and the mechanism of formation and the kinetics and the mechanism of decomposition are better understood, the study of other reactions is interesting.

The dioxygenyl salts dioxygenyl hexafluoroarsenate (O_2AsF_6) and dioxygenyl hexafluoroantimonate (O_2SbF_6) were successfully prepared by an autoclave reaction; the thermal reaction failed, however, in the case of O_2BF_4. Because of the instability of O_2BF_4, failure of a simple autoclave synthesis is surprising.

There seems to be no reason to suppose that the mechanism of the thermal reaction is different in the case of O_2BF_4: if the product can be quenched in a suitable manner, the thermal reaction should succeed. The obvious solution was the hot-cold tube.

A 250-ml hot-cold tube having a 10-mm annular space was filled with a gas mixture having the following approximate composition: 2 O_2:fluorine (F_2):3 BF_3. The reaction conditions were: initial temperature, 245°C; final temperature, -80°C; pressure, 440 mm. After 5 hr, no change in pressure was observed and no solid product was found. A much longer reaction time, however, may be necessary.

In another experiment O_2BF_4 was successfully prepared from a similar gas mixture by ultraviolet (UV) irradiation. A 1-liter Pyrex flask, fitted with a small internal ultraviolet lamp, was filled with a gas mixture having the following approximate composition: 2 O_2:F_2:4 BF_3. The flask was immersed in a dry-ice bath, and the lamp was turned on. The pressure decreased during the reaction as shown in Table 1.

The pressure drop was nearly linear for the first 6 hr; then it began to level off. The reaction was stopped after 8 hr, and the flask was evacuated. The white solid that clung to the walls of the flask decomposed at room temperature, and the resulting gas mixture was subjected to the same analytical procedure previously used for the characterization of O_2BF_4. For two samples taken from this mixture, the results for O_2:F_2:BF_3 are:

(1) 10.5:4.0:10.0 and (2) 73.5:31.6:79.2. The empircal compositions calculated from these data, respectively, are: (1) $O_{2.1}F_{0.8}BF_3$ and (2) $O_{1.88}F_{0.8}BF_3$. An orange-colored impurity, which probably resulted from an attack of BF_3 and F_2 on the Vinton "O" rings used in the apparatus, was present in the BF_3 fraction.

Table 1

PRESSURES DURING REACTION OF O_2, F_2, and BF_3 UNDER ULTRAVIOLET IRRADIATION

Time hr	Pressure, mm
0	350
1	320
3	250
4	230
5	200
6	170
7	150
8	140

It has been reported[1] that the UV-induced decomposition of peroxysulfuryl difluoride (FSO_2OOF) produced OOF radicals. It

[1] Neumayr, F. and Vanderkooi, N., Jr., Inorg. Chem., Vol. 3, p. 321, 1965.

was deduced that if these radicals were scavenged with BF_3, O_2BF_4 should result. This deduction was based on the fact that O_4F_2 reacts with BF_3 as follows:

$$(OOF)_2 + 2\ BF_3 \longrightarrow 2\ O_2BF_4 \qquad (1)$$

FSO_2OOF was allowed to react with a large excess of BF_3 in the presence of 350-mμ ultraviolet light. No O_2BF_4 was formed. The conditions were then changed somewhat by incorporating a -30°C cold finger in the apparatus. It was thought that if O_2BF_4 was formed, this modification would prevent its subsequent decomposition; however, no O_2BF_4 was observed.

The photolysis of oxygen difluoride (OF_2) has been reported[2] to result in the OF radical. We decided to study the reaction of OF_2 with BF_3 in the presence of UV light to determine whether O_2BF_4 would result. A 2:1 mixture of OF_2:BF_3 was irradiated with 350-mμ UV light in a reactor that contained a -78°C cold finger. A white solid was deposited on the cold surface. The white solid was allowed to decompose, and analysis of the decomposition products showed that it was O_2BF_4. The mechanism of this reaction is not presently understood, but it may involve the OF radical.

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[2] Arkell, A., Reinhard, R. R., and Larson, L. P., J. Am. Chem. Soc., Vol. 87, P. 1016, 1965.

B. Reactions of O_2F_2 and O_4F_2.

1. Perfluoropropene

Work continued on the reactions of oxygen fluorides with perfluoropropene (C_3F_6). It was found that the reaction of O_4F_2 with C_3F_6 in liquid Freon 13 at -183°C proceeded smoothly with a gradual rise in pressure; the final pressure after 2 or 3 days never exceeded 100mm. Some orange color remained after 3 days when O_4F_2 was used in excess.

After the solvent was stripped off by distillation through a trap at -138°C, the products were subjected to F^{19} NMR analysis, and found to contain, in every experiment performed with excess O_4F_2, evidence of an OOF compound, in a small NMR line at approximately -290 ppm tricflorofluoromethane, (CCl_3F, reference). Since the desired product appears as a very minor component of the mixture, a series of samples was prepared and OOF-containing fractions were combined and more carefully redistilled. Several redistillations, with traps at -45, -80, -95, -112, and -126°C, resulted in isolation of a small fraction, which passed through the -95°C trap and was held by the -112°C trap, which contained essentially all of the OOF compound. The line at -290 ppm was much stronger for this sample than for any of the individual samples and could be identified as a doublet. The positive region of the spectrum still contained several significant lines and a few very small ones, a result that indicates the presence of residual impurities, one of which was tentatively assumed to be octafluoropropane (C_3F_8). Further attempts to purify this sample resulted in progressive small losses of the sample without any real improvement. The OOF compound passed through a -107° trap very slowly, but the spectrum of the distillate was not significantly different from that of the condensate. It will probably be necessary to resort to gas chromatography or Cady codistillation to resolve this mixture.

2. Sulfur Oxides

For some time the mechanism of the reaction of O_2F_2 with sulfur dioxide (SO_2) has been studied by using O^{17}-labeled compounds. Some difficulty had been encountered in observing the O^{17} NMR spectra of the oxygen atom in the $O^{17}F$ position of FSO_2OOF, but this problem was solved. Since the work is now complete, a summary that includes all the spectra is presented in this report. All the spectra presented are derivative lines and the actual spectra are the integrals of these. A list of the chemical shifts of all the O^{17}-labeled compounds is given in Table 2.

The reaction of O_2F_2 with SO_2 produces sulfuryl fluoride (F_2SO_2) as the main product:

$$O_2F_2 + SO_2 \longrightarrow F-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-F + O_2 \qquad (2)$$

The minor products, which are of more interest, were FSO_2OOF and pyrosulfuryl fluoride (FSO_2OSO_2F).

Table 2

O^{17} NMR DATA FOR VARIOUS COMPOUNDS

Compound	O^{17} Position	Chemical Shift, ppm Relative H_2O^{17}	
FSO_2OF	$F\overset{O^{17}}{\underset{O^{17}}{S}} - OF$	-142	(doublet)
F_2SO_2	$F\overset{O^{17}}{\underset{O^{17}}{S}}F$	-148	(triplet)
FSO_2OOF	$F\overset{O^{17}}{\underset{O^{17}}{S}} - OOF$	-152	(doublet)
FSO_2OSO_2F	$FSO_2O^{17}SO_2F$	-238	(triplet)
FSO_2OOF	$FSO_2O^{17}OF$	-365	
FSO_2OF	$FSO_2O^{17}F$	-419	(doublet)
SO_2	SO_2^{17}	-492	
O_2F_2	$O_2^{17}F_2$	-647	(triplet)
FSO_2OOF	$FSO_2OO^{17}F$	-669	(doublet)
OF_2	$O^{17}F_2$	-830	(triplet)
$(O_2F)n$	?	-971	
O_3		-1032	
$(O_2F)n$	?	-1512	
O_3		-1598	

It was postualted that Reaction 2 is a simple fluorination. Therefore, no oxygen should transfer from O_2F_2 to F_2SO_2. This point was proved by carrying out the following reactions with O^{17}-labeled compounds:

$$SO_2^{17} + O_2F_2 \longrightarrow F_2SO_2^{17} + O_2 \qquad (3)$$

$$SO_2 + O_2^{17}F_2 \longrightarrow F_2SO_2 + O_2^{17} \qquad (4)$$

The O^{17} NMR spectrum of $F_2SO_2^{17}$ is shown in Figure 1. A triplet was obtained for the line due to $S{=}O^{17}$. The triplet results because of coupling of the sulfur with the two fluorine atoms. The chemical shift of triplet (-148 ppm) is important because it helps to define the region expected for the $S{=}O^{17}$ line in similar compounds.

The O_2 formed in Reaction 3 did not contain O^{17}, and the F_2SO_2 formed in Reaction 4 did not contain O^{17}. Therefore, since scrambling was not observed, F_2SO_2 is formed by a simple fluorination reaction.

A more interesting product resulting from the reaction of O_2F_2 with SO_2 is FSO_2OOF. It has been suggested in past reports that this compound is formed via an OOF intermediate. We proved this point by indentifying the O^{17} in the FSO_2OOF formed in Reactions 5 through 7:

$$O_2^{17}F_2 + SO_2^{17} \longrightarrow FSO_2^{17}O^{17}O^{17}F \qquad (5)$$

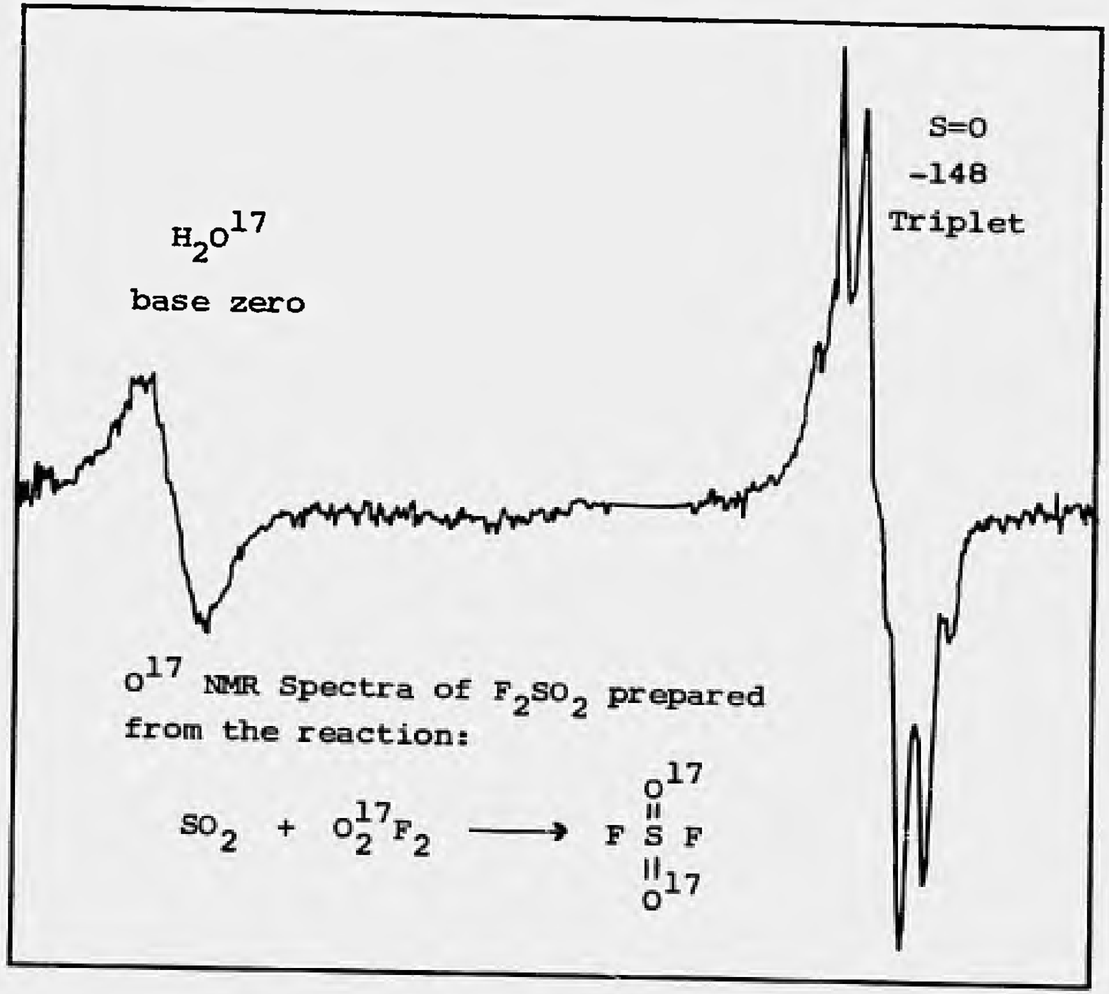


Figure 1

O^{17} NMR SPECTRUM OF F_2SO_2 PREPARED FROM THE REACTION OF SO_2 WITH $O_2^{17}F$

$$O_2{}^{17}F_2 \quad + \quad SO_2 \quad \longrightarrow \quad FSO_2O^{17}O^{17}F \qquad (6)$$

$$O_2F_2 \quad + \quad SO_2{}^{17} \quad \longrightarrow \quad FSO_2{}^{17}OOF \qquad (7)$$

If FSO_2OOF is formed via an OOF intermediate, the O^{17} should be in the positions indicated in Reactions 6 and 7. Reaction 5 was run for indentification purposes to assign the O^{17} lines. As seen in Figure 2, three lines were observed. The line at -152 ppm is in the $S=O^{17}$ region and is assigned to this oxygen atom in the molecule. The line at -669 ppm is a doublet, as expected for the oxygen atom in $FSO_2OO^{17}F$ (because of coupling with F^{19}), this assignment is further verified in Section IIC. The remaining line, at -365 ppm, is due to the oxygen in $FSO_2O^{17}OF$.

Figure 3 shows the O^{17} NMR spectrum of the FSO_2OOF prepared as illustrated in Reaction 6. If FSO_2OOF results via an OOF transfer, it should contain two O^{17} lines -- the $FSO_2O^{17}OF$ line and the $FSO_2OO^{17}F$ line, and as can be seen from Figure 3 this was the case. The alternative spectrum (Figure 4) is expected for the FSO_2OOF prepared according to Reaction 7. This spectrum should contain the $FSO_2{}^{17}OOF$ line only, and it does. Therefore O_2F_2 reacts with SO_2 to form FSO_2OOF via an OOF intermediate.

As stated earlier, FSO_2OSO_2F is also a product of the reaction of O_2F_2 with SO_2. To identify the O^{17} lines in this compound, FSO_2OSO_2F containing a random distribution of O^{17} was prepared as shown in Reaction 8:

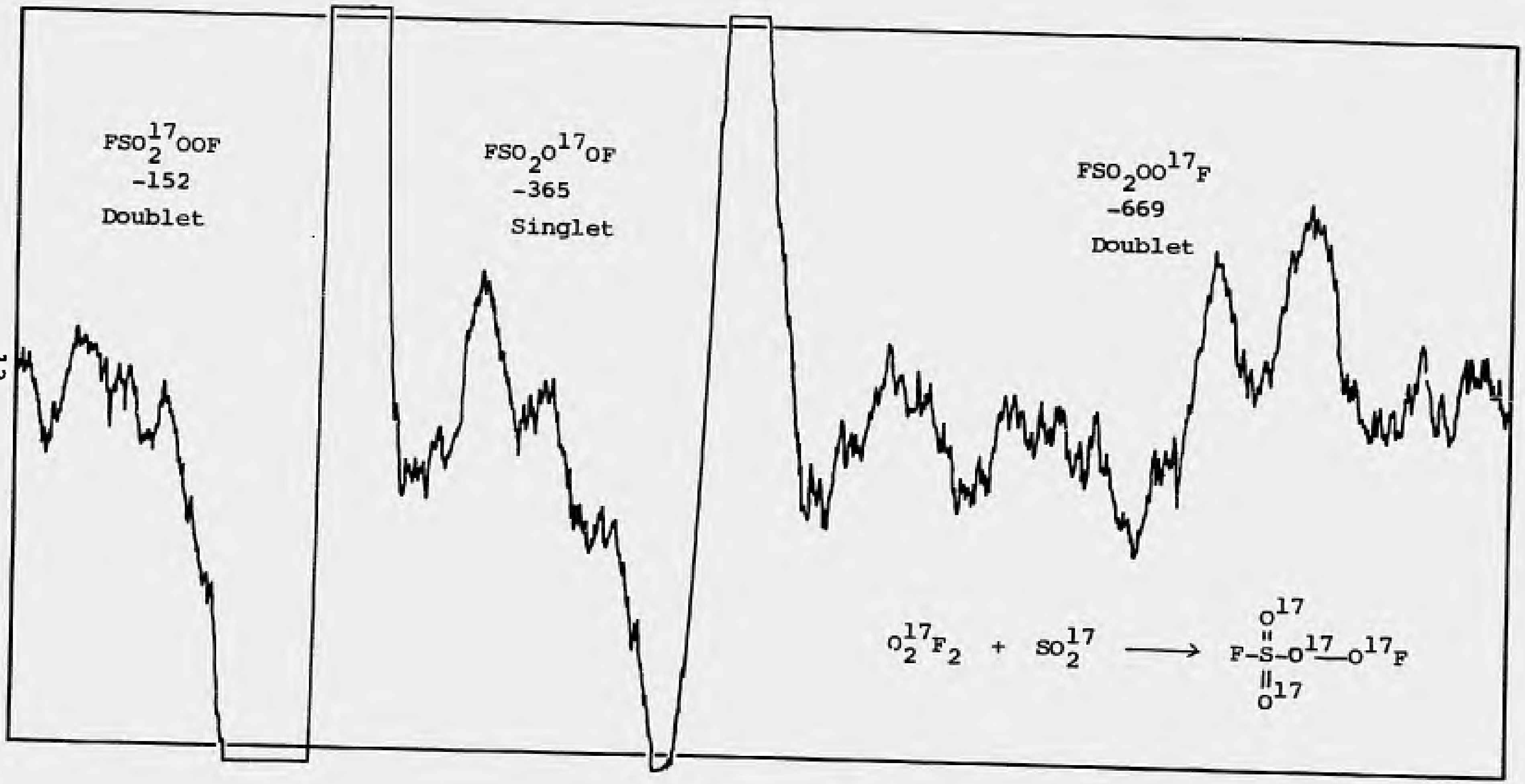


Figure 2

O^{17} NMR SPECTRUM OF FSO_2OOF PREPARED FROM THE REACTION OF SO_2^{17} WITH $O_2^{17}F_2$

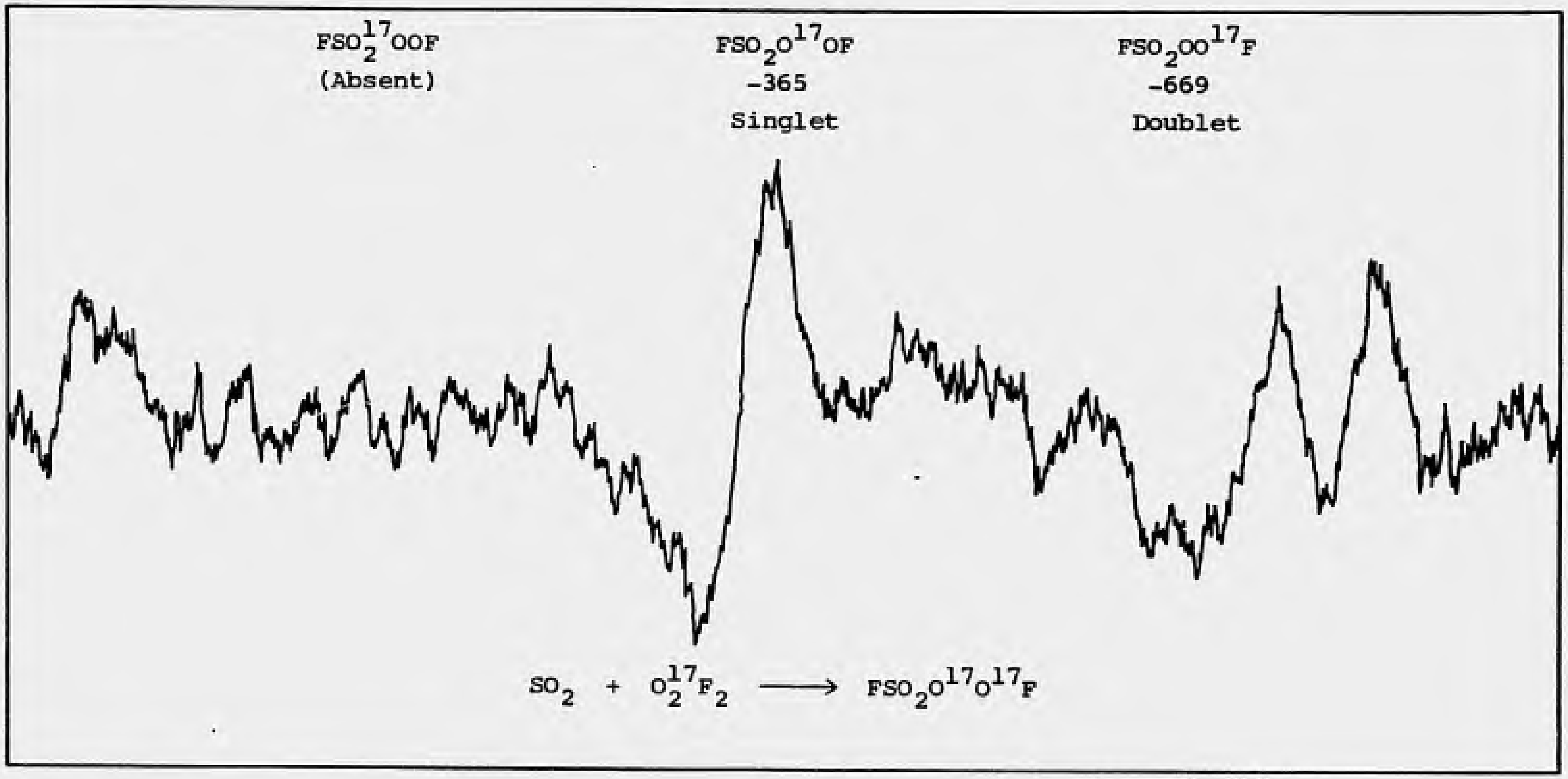


Figure 3

O^{17} NMR SPECTRUM OF $FSO_2O^{17}O^{17}F$ PREPARED FROM THE REACTION OF SO_2 WITH $O_2^{17}F$

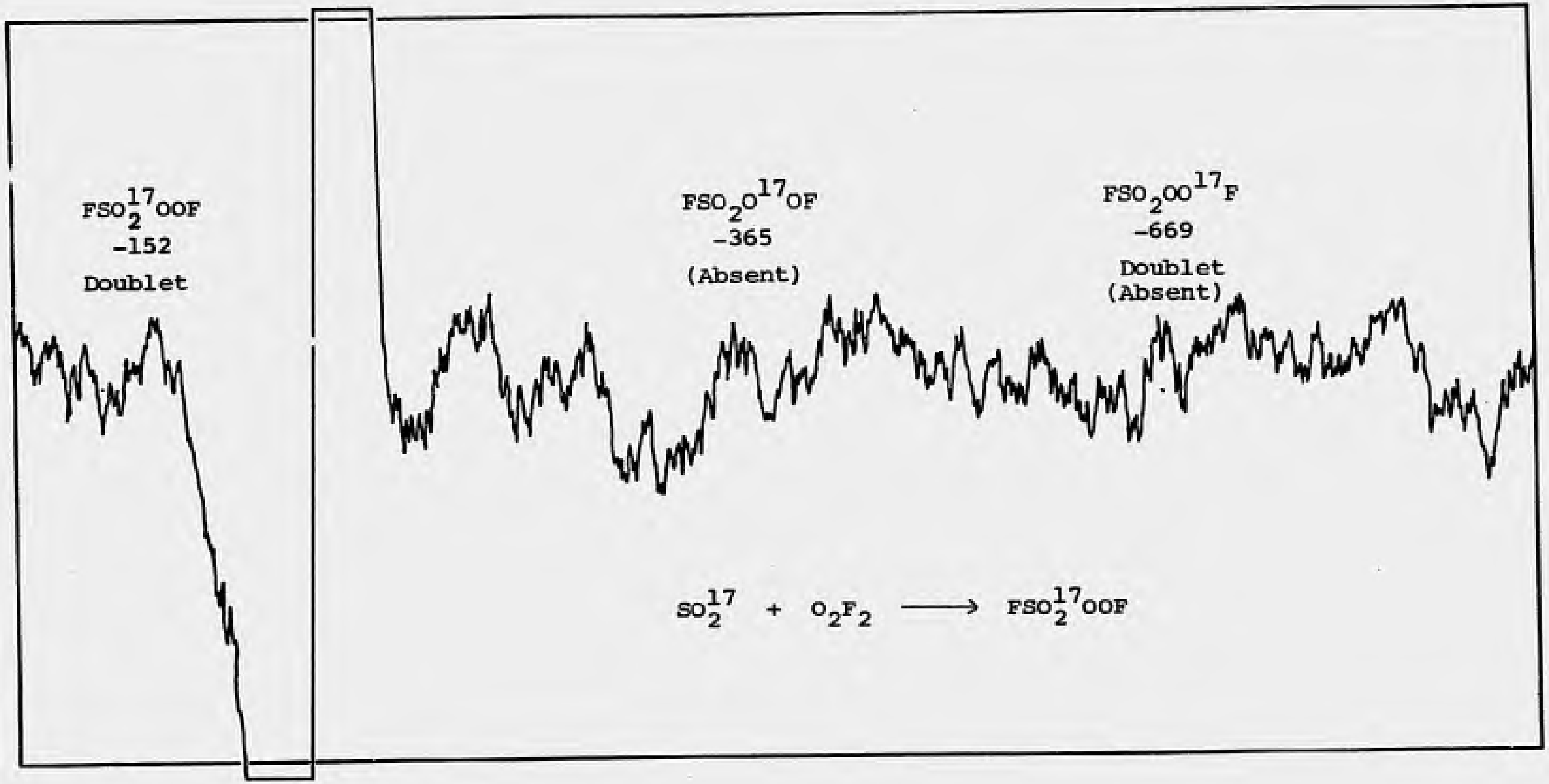


Figure 4

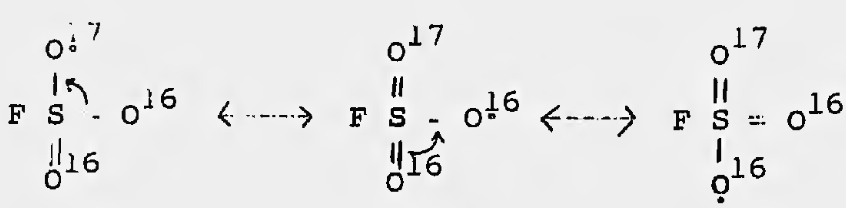
O17 NMR SPECTRUM OF $FSO_2{}^{17}OOF$ PREPARED FROM THE REACTION OF $SO_2{}^{17}$ WITH O_2F_2

$$SO_2^{17} + O_2^{17}F_2 \longrightarrow FSO_2^{17}O^{17}SO_2^{17}F \qquad (8)$$

The tracer experiment shown in Reaction 9 was also carried out:

$$SO_2 + O_2^{17}F_2 \longrightarrow \qquad (9)$$

For FSO_2OSO_2F containing a random distribution of O^{17}, the O^{17}NMR spectrum should contain two lines. The two $S{=}O^{17}$ lines for this compound are equivalent, and the chemical shift should appear in the $S{=}O^{17}$ region and the line should be a doublet due to O^{17}-F^{19} coupling, this was verified by experiment, and the line at -167 ppm (Figure 5) was assigned to the $S{=}O^{17}$. The other line, at -238 ppm is due to the oxygen atom in $FSO_2O^{17}SO_2F$. Figure 6 is identical to Figure 5 and it can be stated that scrambling occurs in Reaction 9. Actually, this result might be expected, since FSO_2OSO_2F probably results via an $FSO_3\cdot$ intermediate. If this intermediate contained O^{17} in a preferred position, it would scramble in the following manner:



(10)

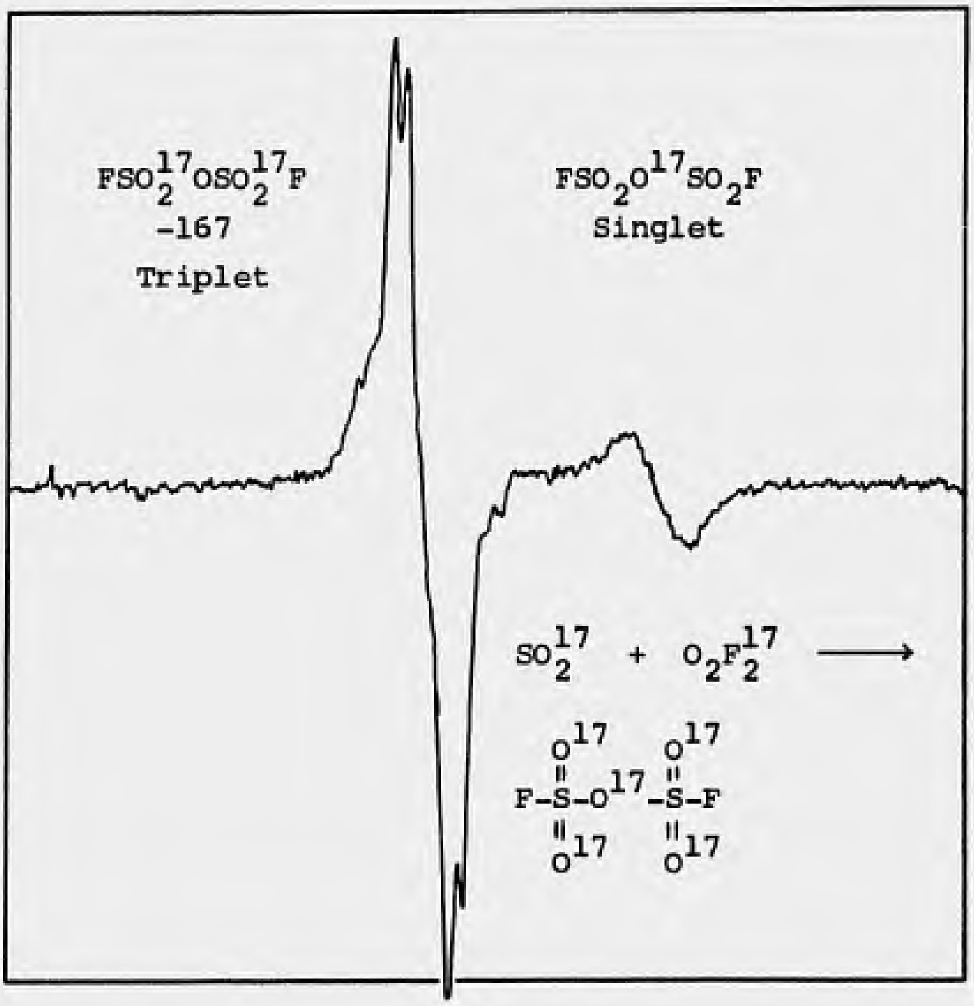


Figure 5

O^{17} NMR SPECTRUM OF FSO_2OSO_2F PREPARED FROM THE REACTION OF SO_2^{17} WITH $O_2^{17}F_2$

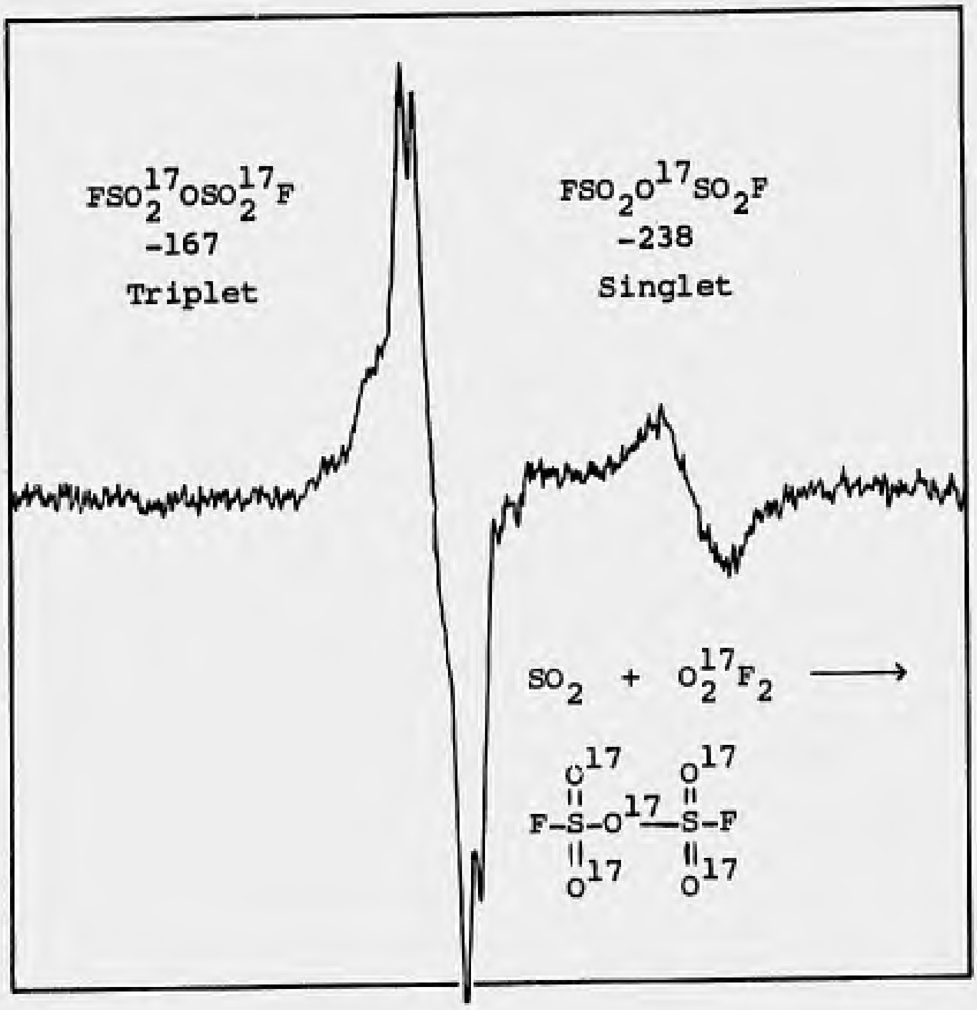


Figure 6

O^{17} NMR SPECTRUM OF FSO_2OSO_2F PREPARED FROM THE REACTION OF SO_2 WITH $O_2^{17}F_2$

C. Reactions of OF_2

The type of experiments discussed in Section II B have also been useful in further understanding the chemistry of OF_2. Gatti and coworkers[3] investigated the photolytic reaction shown in Reaction 11 and, from kinetic data, deduced the presence of the OF radical:

$$OF_2 + SO_3 \xrightarrow[365\ m\mu]{h\nu} FSO_2OOF \qquad (11)$$

We carries out Reactions 12 and 13 and substantiated Schumacher's conclusion:

$$O^{17}F_2 + SO_3 \xrightarrow[350\ m\mu]{h\nu} FSO_2OO^{17}F \qquad (12)$$

$$OF_2 + SO_3^{17} \xrightarrow[350\ m\mu]{h\nu} FSO_2{}^{17}O^{17}OF \qquad (13)$$

If the FSO_2OOF prepared in Reaction 12 results via on OF intermediate, only one O^{17} line at -669 ppm should be observed in the O^{17} spectrum of the product. In addition, this line should be a doublet, as previously discussed. As can be seen in Figure 7, only one O^{17} NMR line, a doublet centered at -669 ppm, was obtained. Alternatively, if the proposed mechanism is correct, the FSO_2OOF obtained in Reaction 13 should contain two O^{17} lines, at -152 and -365 ppm, which are attributed to the

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[3] Gatti, R., Starico, E. H., Sicre, J.E., and Schumacher H. J., Angew. Chem. Intern. Ed. Engl. 21149 (1963)

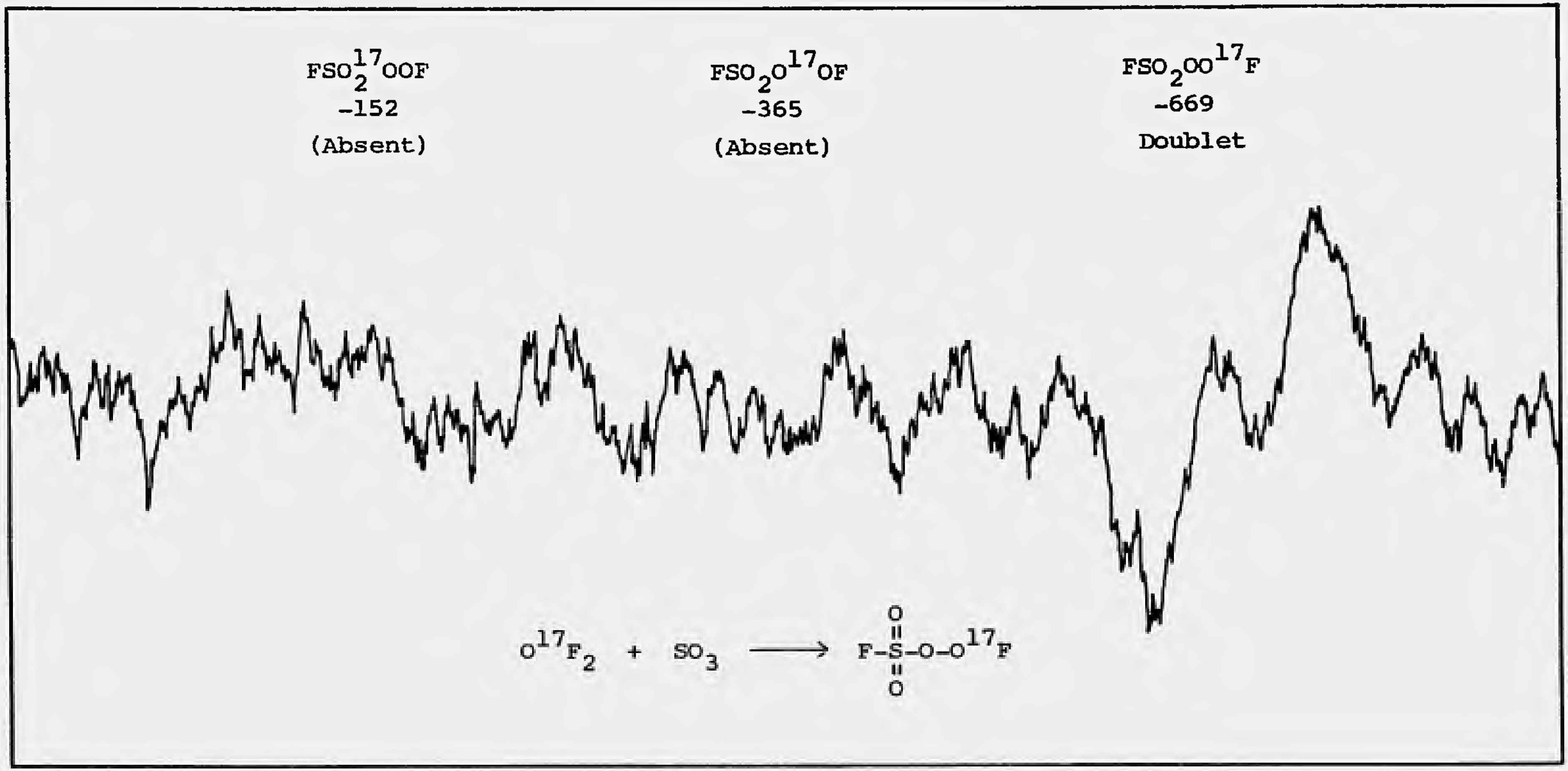

Figure 7

O^{17} NMR SPECTRUM OF FSO_2OOF PREPARED FROM THE REACTION OF SO_3 WITH O^{17}F$_2$

oxygen atoms in $FSO_2{}^{17}O^{17}OF$. These two lines were observed (Figure 8). Therefore, the reaction appears to result via an OF intermediate.

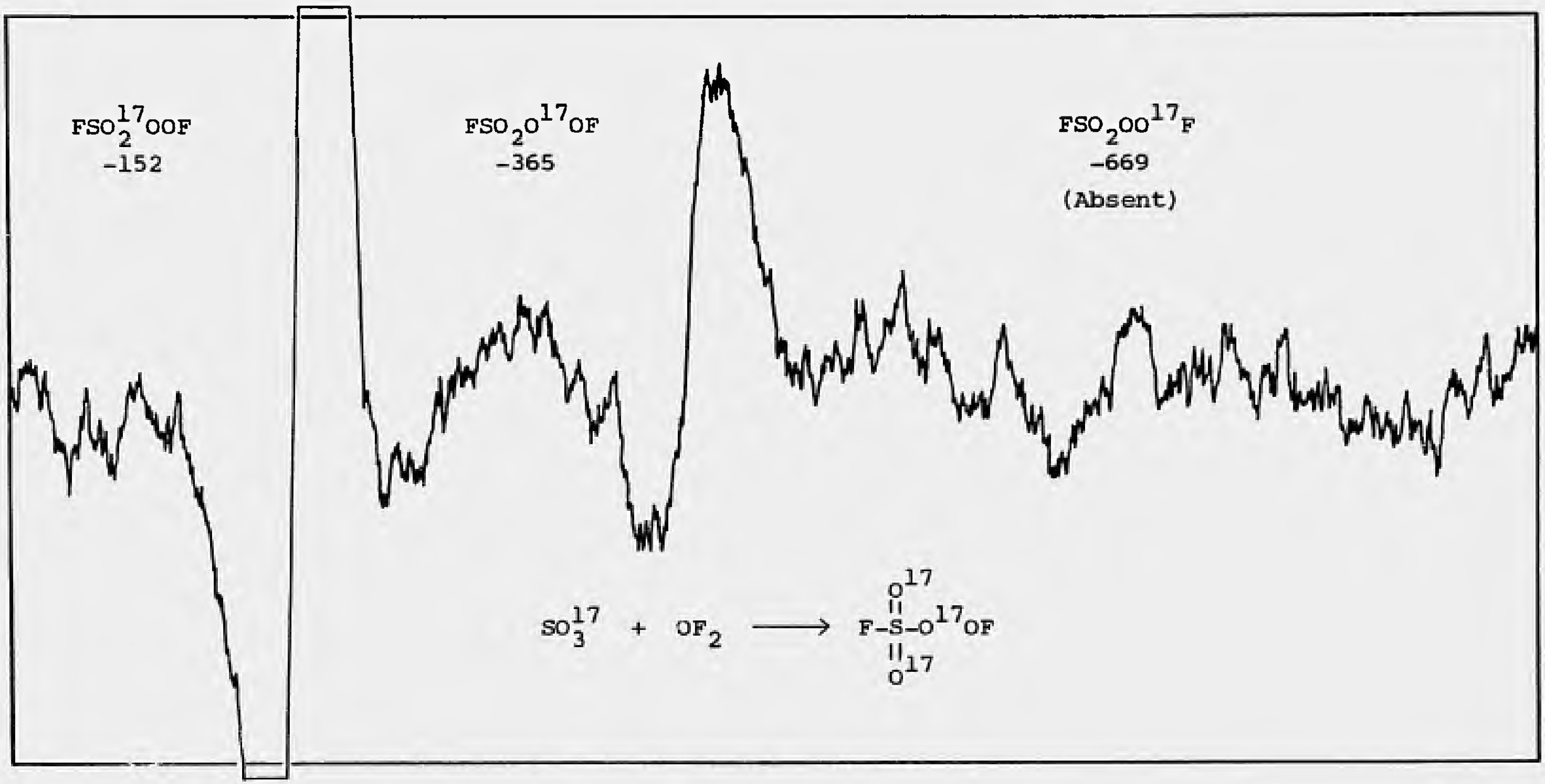

Figure 8

O^{17} NMR SPECTRUM OF FSO2OOF PREPARED FROM THE REACTION OF $SO_3{}^{17}$ WITH OF_2

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13. ABSTRACT

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	ROLE	WT	ROLE	WT	ROLE	WT
$O_2 + BF_4$ - Structure						
O_2BF_4 - Raman spectrum						
O_2BF_4 - F^{18} tracer studies						
O^{17} NMR studies						
O^{17} tracer studies						
O_2F_2						
O_4F_2						
OF_2						
FSO_2OF						
FSO_2OOF						
$F_2S_2O_5$						