Journal of Fluorine Chemistry
Elsevier Sequoia S.A., Lausanne — Printed in Switzerland

Preliminary Note

The reaction of O_4F_2 and sulfur dioxide

I. J. SOLOMON AND A. J. KACMAREK
IIT Research Institute, 10 West 35th Street, Chicago, Ill., 60616 (U.S.A.)
(Received September 3rd, 1971)

It has recently been reported[1] that the reaction of O_4F_2 with boron trifluoride (BF_3) to form dioxygenyl fluoroborate (O_2BF_4) probably occurs *via* OOF. There have been no other reports concerning the chemistry of O_4F_2. The purpose of this work was to increase the knowledge of the chemistry of O_4F_2.

The reaction of dioxygen difluoride (O_2F_2) with sulfur dioxide (SO_2) at $-160°$ or lower produces mainly sulfuryl fluoride (F_2SO_2); smaller amounts of fluorosulfuryl oxyfluoride (FSO_2OOF) and pyrosulfuryl fluoride ($F_2S_2O_5$) are also produced. The mechanism of this reaction was studied[2] by using ^{17}O-tracer and ^{17}O NMR measurements. It was concluded that F_2SO_2 is formed by a simple fluorination reaction. The $F_2S_2O_5$ is formed *via* an $FSO_3\bullet$ intermediate, and FSO_2OOF results *via* an OOF intermediate.

The OOF radical was first characterized by Arkell[3] by the use of the matrix-isolation technique. Arkell suggested that the OOF radical is in equilibrium with O_4F_2. Thus, O_4F_2 may be a better source of the OOF radical than O_2F_2. Therefore, we decided to study the reaction of O_4F_2 with SO_2. O_4F_2 was prepared by using a previously discussed method[4], and the products were separated and characterized as previously described[1]. A comparison of the products formed in the reaction of SO_2 with O_2F_2 and O_4F_2 is presented in Table 1. The major product in both cases was F_2SO_2, but the yield was lower in the O_4F_2 reaction. The yield of $F_2S_2O_5$ in the O_4F_2 reaction was also considerably lower than in the O_2F_2 reaction. Perhaps the most interesting observation is the comparison of the yields of FSO_2OOF (5 % from O_2F_2 and 32 % from O_4F_2).

It can be concluded that the primary reactions of both O_2F_2 and O_4F_2 are similar; that is, simple fluorination predominates. However, O_4F_2 appears to be a better source of OOF than O_2F_2.

Financial support was provided by the Director of Engineering Sciences, SREP, Air Force Office of Scientific Research, under Contract No. AF44620-70-C0027.

TABLE 1

PRODUCTS OF REACTION OF O_2F_2 OR O_4F_2 WITH SO_2[a]

Reactants (mmole)			Products		
				Yield	
SO_2	O_2F_2[b]	O_4F_2[b]	Formula	mole	%[c]
15.4	18.0		F_2SO_2	11.2	72
			FSO_2OOF	0.8	5
			$F_2S_2O_5$	1.8	23[d]
			O_2	14.3	
			F_2	0.1	
7.6		6.7	F_2SO_2	4.1	54
			FSO_2OOF	2.4	32
			$F_2S_2O_5$	0.3	8[d]
			O_2	10.2	
			F_2	0.1	

[a] Solvent, trifluorochloromethane (CF_3Cl); reaction temperature, –183°.
[b] These numbers are approximate, since the liquid volumes were measured.
[c] Based on the SO_2 charged.
[d] Based on 2 moles of SO_2 needed per mole of $F_2S_2O_5$.

REFERENCES

1 J. N. KEITH, I. J. SOLOMON, I. SHEFT AND H. H. HYMAN, *Inorg. Chem., 7* (1968) 230.
2 I. J. SOLOMON, A. J. KACMAREK AND J. K. RANEY, *Inorg. Chem., 7* (1968) 1221.
3 A. ARKELL, *J. Amer. Chem. Soc., 87* (1965) 4057.
4 A. V. GROSSE, A. G. STRENG AND A. D. KIRSHENBAUM, *J. Amer. Chem. Soc., 83* (1961) 1004.