

FLUORINE FLUOROSULFATE REVISITED

F. Mistry^{a)}, H. Willner^{b)} and F. Aubke^{a)}

a) Department of Chemistry, The University of British Columbia, Vancouver,
B.C., Canada V6T 1Z1

b) Institut für Anorganische Chemie der Universität Hannover,
Callinstrasse 9 W-3000, Hannover FRG

Fluorine fluorosulfate, FOSO_2F , appears to be ideally suited to introduce both fluorine and fluorosulfate into a molecule and a number of such oxidative addition reactions have been reported early on¹⁾. Once the highly explosive nature of FOSO_2F was recognized²⁾, almost all synthetic work stopped.

A number of these addition reactions with the fluorides S_2F_2 , SF_4 , SeF_4 , AsF_3 , SbF_3 and MoF_5 and the halogen Br_2 and I_2 have been re-investigated or studied for the first time. The following conclusions are reached: (i) All reactions of FOSO_2F are vigorous and often explosive with FOSO_2F acting primarily as fluorinating agent. (ii) Byproducts observed include always bis(fluorosulfonyl) peroxide, $\text{S}_2\text{O}_6\text{F}_2$, and sometimes SO_2F_2 and O_2 .

(iii) Except for additions to SF_4 and SeF_4 where $\text{SF}_5\text{SO}_3\text{F}$ and $\text{SeF}_5\text{SO}_3\text{F}$ form in low yield, and are studied by heteronuclear NMR and vibrational spectroscopy, the reaction products are frequently non-stoichiometric eg. $\text{IF}_n(\text{SO}_3\text{F})_{5-n}$, or $\text{BrF}(\text{SO}_3\text{F})_{3-n}$ with n noninteger numbers. (iv) In most instances safe alternative routes are explored to avoid the use of FOSO_2F .

1) F. Aubke and D.D. Des Marteau, Fluor. Chem. Rev., Vol. 8, 73 (1977).

2) G.H. Cady, Inorg. Syn. 11, 155 (1968); Chem. Eng. News 44(8), 40 (1966).