

## LOWER SULFUR FLUORIDES

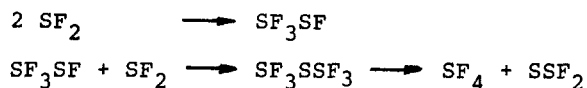
O. Lösling\* and H. Willner

Institut für Anorganische Chemie der Univ. Hannover, Callinstr. 9, D-3000 Hannover 1 (F.R.G.)

The reaction of sulfur with fluorine, discovered in 1900 by MOISSAN has remained an interesting and important one to date. The chemically inert, and therefore technically important compound SF<sub>6</sub>, is obtained - under drastic conditions - in high yield. A large number of partly very reactive sulfur fluorides, with unusual properties, are formed under milder conditions. The next best known sulfur fluoride after SF<sub>6</sub> is the fluorinating agent SF<sub>4</sub>. Between these compounds, the highly toxic, less reactive S<sub>2</sub>F<sub>10</sub> is classified. Sulfur is found in its lowest oxidation states in the isomers SSF<sub>2</sub> and FSSF, and the polysulfanes FS<sub>x</sub>F (x = 3, 4).

Our aim is to elucidate the structural, thermodynamic, kinetic and chemical properties of these lower sulfur fluorides [1]. The standard enthalpies of formation for both isomers were estimated from photoionization mass spectra. By fragmentation reactions, bond energies of the S-S bond in S=SF<sub>2</sub> and FS-SF were surprisingly found to be equal. The reaction enthalpy for gas phase isomerization FSSF ⇌ SSF<sub>2</sub> was determined by thermolysis. FSSF has a half-life value of up to 500 hours at room temperature, in conditioned i.r. cell. Lewis acids were found to catalyze isomerization. Rapid isomerization occurs in the liquid phase. The structure in the gas phase was determined accurately by electron diffraction measurements.

SF<sub>2</sub> prepared by gas phase fluorination of COS decays quantitatively as follows:



The intermediates  $\text{SF}_3\text{SF}$  and  $\text{SF}_3\text{SSF}_3$  are preparatively isolable. The new sulfur fluorides  $\text{SF}_3\text{SSF}_3$  and  $\text{SF}_3\text{SSF}$  are to be examined by means of low temperature X-ray structure analysis.  $\text{S}_2\text{F}_{10}$  is thus being examined at present.

- 1 O. Lösking, H. Willner, H. Baumgärtel, H. W. Jochims and E. Rühl, Z. Anorg. Allg. Chem. 530 (1985) 169.