I_{60}

LOWER SULFUR FLUORIDES

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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_6, 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_6 is the fluorinating agent SF_4. Between these compounds, the highly toxic, less reactive S_2F_{10} is classified. Sulfur is found in its lowest oxidation states in the isomers SSF_2 and FSSF, and the polysulfanes FS_xF (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 $S{=}SF_2$ and FS-SF were surprisingly found to be equal. The reaction enthalpy for gas phase isomerization $FSSF \rightleftharpoons SSF_2$ 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_2 prepared by gas phase fluorination of COS decays quantitatively as follows:

$$2\ SF_2 \longrightarrow SF_3SF$$

$$SF_3SF + SF_2 \longrightarrow SF_3SSF_3 \longrightarrow SF_4 + SSF_2$$

The intermediates SF_3SF and SF_3SSF_3 are preparatively isolable. The new sulfur fluorides SF_3SSF_3 and SF_3SSF are to be examined by means of low temperature X-ray structure analysis. S_2F_{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.