THE KINETICS AND THERMODYNAMICS OF SOME HALOGEN FACILITATED OXIDATION REACTIONS OF AsF_5; and THE PREPARATION AND ENERGETICS OF FORMATION AND X-RAY CRYSTAL STRUCTURE OF $S_3N_2(AsF_6)_2$ CONTAINING THE LATTICE STABALIZED $S_3N_2^{2+}$

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An excess of AsF_5 oxidises sulphur only as far as $S_8(AsF_6)_2$ even under forcing conditions, whereas in the presence of a trace of halogen X_2(X=BrCℓI) crystalline $S_4(AsF_6)_2$ is quantitatively formed according to eq. (1) in SO_2 within minutes.

$$1/2\ S_8 + 3AsF_5 \xrightarrow[\text{trace } X_2]{SO_2} S_4(AsF_6)_2 + AsF_3 \qquad (1)$$

The thermodyamics and kinetics of this reaction and related reactions leading to $SNSAsF_6$ and $SNAsF_6$ will be presented.

$(S_3N_2)_2(AsF_6)_2$ is quantitatively oxidised by AsF_5 in the presence of traces of bromine to give $SNAsF_6$ and $SNSAsF_6$ in SO_2. Single crystals of $S_3N_2(AsF_6)_2$ are obtained at 0°C effecting the concerted symmetry allowed cycloaddition of SN^+ and SNS^+. The crystal structure of $S_3N_2(AsF_6)_2$ is isomorphous with all $Se_xS_{3-x}N_2(AsF_6)_2$ (x = 1,2,3) salts, and contains planar $\overline{SNSNS}^{2+}$ rings with a geometry very similar to that calculated. Although it is a 6π system and often cited in sulphur-nitrogen chemistry, it very readily abstracts F^-, accepts an electron to form the stable radical cation $S_3N_2^{+\bullet}$ and also dissociates completely in SO_2 at r.t. This latter result is reflected in the results of 6-31G* calculations, which predict that $S_3N_2^{2+}$ is unstable with respect to SN^+ and SNS^+ by 400 kJ/mol in the gas phase with a small activation energy barrier. However, we estimate that $S_3N_2(AsF_6)_2(s)$ is about 80 kJ/mol more stable than $SNAsF_6(s)$ and $SNSAsF_6(s)$, and owes its existence to the high lattice energy of the 2:1 salt. The identity of $S_3N_2(AsF_6)_2$ is also supported by vibrational spectroscopy and a normal coordinates analysis.