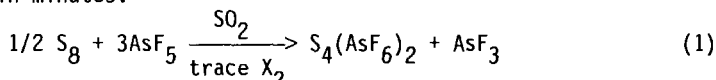


THE KINETICS AND THERMODYNAMICS OF SOME HALOGEN FACILITATED OXIDATION REACTIONS OF AsF_5 ; and THE PREPARATION AND ENERGETICS OF FORMATION AND X-RAY CRYSTAL STRUCTURE OF $\text{S}_3\text{N}_2(\text{AsF}_6)_2$ CONTAINING THE LATTICE STABILIZED $\text{S}_3\text{N}_2^{2+}$

E. Awere, W.V.F. Brooks, T.S. Cameron, F. Grein, S. Parsons and J. Passmore
Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada.

An excess of AsF_5 oxidises sulphur only as far as $\text{S}_8(\text{AsF}_6)_2$ even under forcing conditions, whereas in the presence of a trace of halogen X_2 ($\text{X}=\text{BrClI}$) crystalline $\text{S}_4(\text{AsF}_6)_2$ is quantitatively formed according to eq. (1) in SO_2 within minutes.



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

$(\text{S}_3\text{N}_2)_2(\text{AsF}_6)_2$ 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 $\text{S}_3\text{N}_2(\text{AsF}_6)_2$ are obtained at 0°C effecting the concerted symmetry allowed cycloaddition of SN^+ and SNS^+ . The crystal structure of $\text{S}_3\text{N}_2(\text{AsF}_6)_2$ is isomorphous with all $\text{Se}_x\text{S}_{3-x}\text{N}_2(\text{AsF}_6)_2$ ($x = 1,2,3$) salts, and contains planar 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^{+} 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 $\text{S}_3\text{N}_2^{2+}$ 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 $\text{S}_3\text{N}_2(\text{AsF}_6)_2(\text{s})$ is about 80 kJ/mol more stable than $\text{SNAsF}_6(\text{s})$ and $\text{SNSAsF}_6(\text{s})$, and owes its existence to the high lattice energy of the 2:1 salt. The identity of $\text{S}_3\text{N}_2(\text{AsF}_6)_2$ is also supported by vibrational spectroscopy and a normal coordinates analysis.