

PREPARATION AND PROPERTIES OF PENTA- AND HEXACOORDINATED PERSULFURANES

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N-alkylsulfurtrifluorideimide-cations and their derivatives ($\text{RNSF}_2\text{R}'^+$: $\text{R}=\text{CH}_3$, C_2H_5 , $\text{R}'=\text{F}, \text{N}(\text{CH}_3)_2$, R_f) add fluoride ions to form persulfuranes with pentacoordinated sulfur. Stable pentacoordinated cations R_2NSF_4^+ are obtained by F^- -abstraction from pentafluoroaminosulfuranes ($\text{R}\neq\text{H}$), monoalkylated derivatives will undergo disproportionation under formation of RNSF_3^+ and $\text{RNH}_2\text{SF}_5^+$. An alternative route to pentacoordinated cations is the F^- -addition to tetracoordinated S(VI)-dications ($[\text{R}_2\text{NSF}_n(\text{NR}'_2)_{3-n}]^{2+}$) which is investigated under various conditions. The reactivities of the $(\text{CH}_3)_2\text{NSF}_4^+$ -cation and the isoelectronic phosphorane $(\text{CH}_3)_2\text{NPF}_4$ are compared. The interactions of various pentafluorosulfanyl- and bis(pentafluorosulfanyl)-nitrogen-derivatives with fluoro-Lewis acids, superacids (HF/AsF_5) and the 'supermethyating' $\text{CH}_3\text{OSO}^+\text{AsF}_6^-$ will be reported.