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Reactivity of Chalcogen Cluster Polycations

A. M. Rosan

Corporate Research & Development, Allied Corporation, Morristown, NJ 07960, U.S.A.

The chalcogen polycations $S_8(AsF_6)_2$, $S_{19}(HS_2O_7)_2$, and $Se_4(HS_2O_7)_2$ are powerful oxidants entering into electron transfer reactions with hydrocarbons, aromatic compounds, and halides.

The polynuclear polycations of Group 6A constitute a fascinating class of compounds whose synthetic and structural chemistry has only recently been elucidated.[1,2] It has long been known that highly coloured ionic species are produced upon dissolution and subsequent oxidation of sulphur, selenium, or tellurium in oleum or fluorosulphonic acid.[3] Solution cryoscopic, spectroscopic,[4] crystallographic,[5,6] and theoretical[7] investigations have facilitated the study of cluster geometry and bonding in the derived dications S_{19}^{2+}, S_8^{2+}, Se_4^{2+}, Te_4^{2+}, and related species.[8] For example, S_{19}^{2+} (red, earlier postulated to be S_{16}^{2+}) and S_8^{2+} (blue) are produced upon oxidation of S_8 in SO_3–H_2SO_4, while a more convenient synthesis utilizing AsF_5–SO_2 permits isolation of the salt $S_8(AsF_6)_2$, equation (1).[9] This species has been shown to adopt a cyclic *exo–endo* conformation and to exhibit a weak 1,5 transannular sulphur–sulphur interaction. To date, studies of the reactivity of this class of electrophiles have been confined to reports of formation of perfluorinated sulphides,[10,11] selenides,[11,12] and tellurides[12—14] from oxidation of inert C_2F_4. We report herein on their reaction with hydrocarbons and other donors.

Deep blue $S_8(AsF_6)_2$[9] reacts with simple hydrocarbons in SO_2 solution. The salt is slowly reduced by methane providing methanethiol (~5%). Higher hydrocarbons are more reactive, equation (2).† For example, warming a frozen mixture of $S_8(AsF_6)_2$ and propane in SO_2 provides iso- and n-propyl sulphides, di-isopropyl disulphide, and isopropyl n-propyl sulphide (30%; relative proportions 50 : 5 : 1). From n-butane the homologous di-n-butyl disulphide and di-n-butyl trisulphide in addition to n-butyl n-butenyl sulphide are obtained (~45%; relative proportions 1 : 1 : 1). These reactions employed an excess of hydrocarbon and were accompanied by a series of colour changes below room temperature (blue → violet → red → orange → yellow → tan) with the ultimate precipitation of S_8 (Raman).

$$S_8 + 3AsF_5 \xrightarrow{SO_2} S_8(AsF_6)_2 + AsF_3 \qquad (1)$$

$$S_8(AsF_6)_2 + 2RH \xrightarrow{SO_2} R_2S_n\ (n = 1\text{—}3) \qquad (2)$$

Neither elemental sulphur nor S_8–SO_2 are reactive toward the cited substrates. In general, the oxidizing character of S_8 is not manifested at low temperatures[15] and, unlike S_8^{2+}, usually involves reduction to H_2S. The transformations reported herein result from electron transfer between hydrocarbon (donor–reductant) and polycation (acceptor–oxidant). A further manifestation of this reactivity is shown in the selective conversion of toluene by $S_8(AsF_6)_2$ into a series of isomeric dimethylbiphenyls (45%; relative proportions of 2–3′, 3–3′, and 4–4′ isomers 1 : 3 : 3), wherein electrophilic substitution predominates over benzylic activation. Aromatic cation radicals would be expected to be important intermediates.[16] A third reaction path reflecting the oxidizing power of S_8^{2+} is demonstrated by oxidation of cycloheptatriene to tropylium hexafluoroarsenate (20%).‡ As with similar oxidations induced by amine radical cations,[17] the sequence of hydride abstraction *vs.* electron transfer steps is unresolved.

We have not examined the reactions of simple hydrocarbons with the less accessible Se_4^{2+} cation,[18] but note that red selenium is produced immediately on contacting $Se_4(HS_2O_7)_2$–HSO_3F with cyclohexane or Nujol oil, although dilution with SO_2 does not lead to disproportionation. In contrast, $Te_4(AsF_6)_2$[9,19] is not reduced by hexane.

A number of other reactions reflect the high redox reactivity of the chalcogen polycations. Thus, CO is selectively converted into COS (20%) by $S_8(AsF_6)_2$–SO_2, but is oxidized to CO_2 by orange $Se_4(HS_2O_7)_2$, which in turn affords green Se_8^{2+} (Raman). This latter species is inert to O_2–HSO_3F at 300 K. It is noteworthy that AsF_5 is itself a sufficiently strong oxidant that exposure to CO–SO_2 slowly liberates CO_2 and deposits the characteristically blue $S_8(AsF_6)_2$, equation (3).

$$3AsF_5 + CO \xrightarrow{SO_2} S_8(AsF_6)_2 + CO_2 + AsF_3 \qquad (3)$$

Potassium fluoride in SO_2 slowly reacts with $S_8(AsF_6)_2$ producing SOF_2 (15%). Solvent participation may be involved

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† All products were identified by gas chromatography and gas chromatography–mass spectroscopy.

‡ Identified by ^1H n.m.r. spectroscopy in $(CD_3)_2CO$: δ 9.50 (s). AsF_5–SO_2 can also produce tropylium in low yield (<5%).

in this process as no simple sulphur fluorides are produced. In 30—33% oleum, addition of KF to S_{19}^{2+} produces SO_2 consistent with polycation disproportionation induced by the lower acidity of the KF–SO_3 mixture.

In summary, the remarkably electrophilic chalcogen cluster polycations, in which the elements are present in fractional oxidation states, are exceptionally strong oxidants toward C–H bonds and other weak donors. The ensuing reactions proceed *via* electron-transfer processes, which may lead to substrate sulphurization, dimerization, or oxidation.

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