Radical Cations with a Sulphur–Iodine 2σ–1σ* Three-electron Bond

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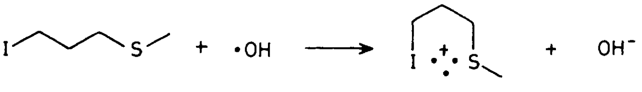
A transient radical cation with an intramolecular sulphur–iodine 2σ–1σ* three-electron bond is generated during the oxidation of 1-iodo-3-methylthiopropane (**1**).

2σ–1σ* Three-electron bonded radical cations of the general type $(> S \therefore S <)^+$ have been investigated as prominent species in the oxidation of organic sulphides.[1—7] They are formed inter- as well as intra-molecularly *via* association of an oxidized with an unoxidized sulphur atom. Stabilization of the oxidized sulphur centre with other heteroatoms is also possible.[8—15] This includes sulphur–halogen interaction for which so far intermolecularly formed neutral $R_2 \therefore X$ or negatively charged $(RS \therefore X)^-$ species were observed. Theoretical calculations[16] suggest that cationic species of the general type $(> S \therefore X^+)$ should also exhibit a considerable degree of stability. We now report on the first example of such a three-electron bonded radical cation generated intramolecularly as an intermediate in the oxidation of 1-iodo-3-methylthiopropane (**1**), which was synthesized as described in the literature.[17]

A characteristic feature by which all these three-electron bonded species can be identified is a broad optical absorption band in the visible spectral region conveniently detectable by time-resolved techniques such as laser photolysis or pulse radiolysis.[1] Figure 1 shows such an optical fingerprint of the transient species obtained by pulse radiolysis of an N_2O saturated, 10^{-3} M aqueous solution of (**1**) at pH 3. The main absorption band with $\lambda_{max.}$ 440 nm is assigned to the radical cation formed *via* Scheme 1, *i.e.*, to a species which contains an intramolecular 2σ–1σ* bond between the sulphur and the iodine atom. The transient absorption band is not observed in the presence of an ·OH radical scavenger, *e.g.* propan-2-ol.



(1) (2)

Scheme 1

The yield and the lifetime of (**2**) (first order decay with $t_{1/2}$ 110 μs) are not affected by the solute concentration (5×10^{-5} to 2×10^{-3} M); both properties usually exhibit a pronounced dependence for intermolecularly generated species.[4] Therefore any assignment to purely sulphur or iodine centred

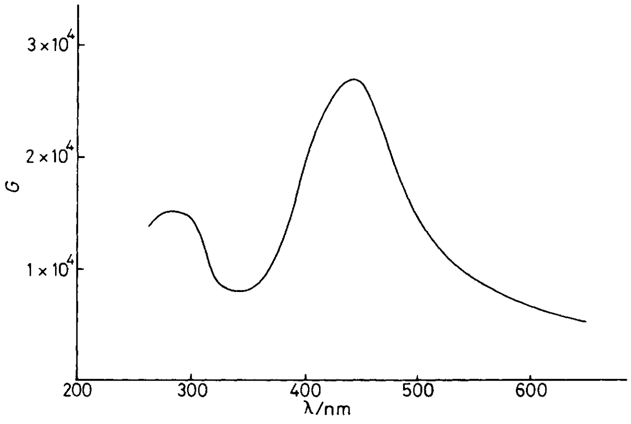


Figure 1. Absorption spectrum recorded in a pulse-irradiated N_2O saturated 10^{-3} M aqueous solution of (**1**) at pH 3.0.

radicals is precluded. The positive charge is deduced from time resolved conductivity measurements with (**2**). Assuming the specific conductivity of (**2**) to be 50 Ω^{-1} cm^2 (*i.e.* to be of the typical magnitude for normal monovalent cations) the yield of three-electron bonded radical cations is calculated as $G = 4.8$. This corresponds to *ca.* 80% of the •OH radicals which are available for the reaction with (**1**). [The remaining 20% probably abstracts a hydrogen atom from (**1**) yielding mainly a carbon-centred α-thio radical. The latter typically absorbs around 280—300 nm[4] and thus accounts for the small u.v. band in Figure 1]. Knowing the yield, the extinction coefficient of (**2**) is evaluated as 5100 dm^3 mol^{-1} cm^{-1}.

The $S \therefore I$ three-electron bond can be formed irrespective of whether the initial oxidation occurs at the sulphur or the iodine atom. The following facts identify the sulphur as the primary reaction site. (a) The yield of (**2**) does not change within the experimentally scanned pH 3—10 range, while radical cation formation from unsubstituted alkyl iodides is only observed at pH <5.5. (b) The oxidation of (**1**) to (**2**) can also be initiated by $CCl_3OO\cdot$ radicals instead of •OH radicals. Our previous studies have shown that $CCl_3OO\cdot$ radicals oxidize sulphides but not alkyl iodides.[13,18]

Corresponding intramolecular sulphur–iodine and sulphur–bromine three-electron bonded radical cations have also been observed for various other compounds which provide a geometrically favourable arrangement for the intramolecular interaction. Increasing chain length between sulphur and iodine results in lower radical cation yields and a red shifted absorption, which is an indication for a decreased stability.[1] The $(> S\therefore I-)^+$ radical cation from 1-iodo-6-ethylthiohexane,[19] for example, is formed with $G = 0.8$ and exhibits $\lambda_{max.}$ at 485 nm. The bromo analogue of (**1**) even allows observation of both the intramolecular $(>S\therefore Br-)^+$ and the intermolecular $(>S\therefore S<)^+$ radical cations. The former absorbs at 370 nm and is exclusively formed at low solute concentrations ($\leq 10^{-4}$ M), while at higher concentrations the bimolecular species ($\lambda_{max.}$ 470 nm) prevails.

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