2σ–1σ* Three-electron-bonded Radical Cations from Alkylthio(halogeno)alkanes

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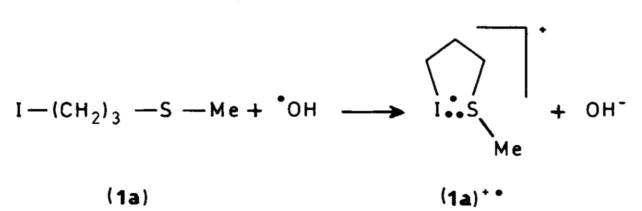
Intramolecular sulphur–iodine $(>S\therefore I-)^+$ and sulphur–bromine $(>S\therefore Br-)^+$ three-electron-bonded radical cations have been observed during the oxidation of various iodo- and bromo-alkylthioalkanes by •OH radicals. For the bromo compounds, in addition, intermolecular $(>S\therefore S<)^+$ radical cations are stabilized at high solute concentrations. Oxidation of alkylthio(chloro)alkanes leads only to the dimer sulphur–sulphur three-electron-bonded radical cations. All these radical cations exhibit optical absorptions in the visible and near u.v. with extinction coefficients in the order of 4 000—8 000 mol^{-1} dm^3 cm^{-1}. In general, increasing the chain length between the sulphur and the halogen atoms, and increasing the electron release by the sulphur substituent, results in a red shift of the $\lambda_{max.}$ value and a decrease in radical cation yields. In aqueous solutions most of the three-electron-bonded species decay by first-order kinetics with $t_{1/2}$ up to 110 μs.

It is well established that one-electron oxidation of organic sulphides leads to radical cations of the general structures $R_2S^{+\bullet}$ and $(R_2S\therefore SR_2)^+$.[1] The three-electron-bonded species are long-lived enough to be easily detectable by e.s.r. spectroscopy[2] or time-resolved pulse radiolysis experiments. Their formation is based on the interaction of the unpaired *p*-electron in $R_2S^{+\bullet}$ with a free *p*-electron pair of an unoxidized sulphur atom. The result is a sulphur–sulphur bond which contains two bonding σ-electrons and one antibonding σ*-electron.

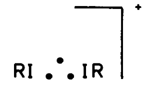
Establishment of a 2σ–1σ* bond is not restricted to an intermolecular sulphur–sulphur interaction involving two different molecules but is equally possible intramolecularly, *e.g.* in oxidized dithia compounds. In these cases sufficient *p*-orbital overlap is mainly controlled by conformational parameters.[1] Stabilization of an oxidized sulphur centre can also occur by interaction with a free electron pair provided by any other heteroatom such as nitrogen, oxygen, or halogen atoms.[3–5] Generally these three-electron bonds exhibit, however, a lower stability than their sulphur–sulphur analogues. This can be explained by the differences in electronegativities which cause destabilization owing to an asymmetric electron density distribution between the two interacting heteroatoms.

Recently we reported the first example of a radical cation, (**1a**)$^{+\bullet}$, with a 2σ–σ* three-electron bond between sulphur and a monovalent heteroatom, generated by pulse radiolysis of 1-iodo-3-methylthiopropane (**1a**) in aqueous solution.[6] It is formed intramolecularly *via*

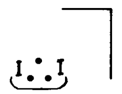


(**1a**) (**1a**)$^{+\bullet}$

and has been characterized by time-resolved optical and conductivity pulse radiolysis experiments. The present paper is concerned with a systematic investigation on the possible formation of radical cations from alkylthio(halogeno)alkanes [I derivatives: (**1a**—**k**); Br derivatives: (**2a**—**n**); Cl derivatives: (**3a**—**x**)]. The sulphur-halide three-electron-bonded radical cations are an interesting link between the purely sulphur- and purely halogen-centred species. Stabilization of the latter, namely (**4**)$^{+\bullet}$ and (**5**)$^{+\bullet}$, in solution has also been described recently.[7,8]



(**4**)$^{+\bullet}$



(**5**)$^{+\bullet}$

Experimental

Synthesis of Alkylthio(halogeno)alkanes.—Alkylthio(halogeno)alkanes were synthesized *via* reaction of 1,*n*-dihalogenoalkanes with thiolates according to the literature.[9–12] Only 1-iodo-3-methylthiopropane (**1a**) was prepared by the ring-opening reaction of thiirane with methyl iodide.[13]

Pulse Radiolysis.—All the pulse radiolysis investigations were carried out with aqueous solutions. The water was deionized and 'Millipore' filtered. The purity of the solutes was generally ⩾99%.

The oxidation of the alkylthio(halogeno)alkanes was initiated by •OH radicals which were generated upon radiolysis of the aqueous systems. For maximum yield of hydroxyl radicals the solutions were deoxygenated by bubbling N_2 through for *ca.* 1 h dm^{-3} solution and subsequent saturation with N_2O for *ca.* 1 h dm^{-3} solution. Under these conditions hydrated electrons—which are generated at about equal yield as •OH radicals as primary species upon irradiation—are converted into hydroxyl radicals *via*:

$$N_2O + e_{aq}^- \longrightarrow N_2 + OH^- + {}^\bullet OH$$

Some oxidations were carried out with $CCl_3OO^\bullet$ radicals. The latter were generated in air-saturated solutions containing 30% (vol) propan-2-ol and 0.1% (vol) CCl_4 *via*:

$$CCl_4 + e_{aq}^- \longrightarrow \dot{C}Cl_3 + Cl^-$$

$$^\bullet OH/H^\bullet + Me_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + H_2O/H_2$$

$$(CH_3)_2\dot{C}OH + CCl_4 \longrightarrow \dot{C}Cl_3 + Cl^- + H^+ + Me_2CO$$

$$\dot{C}Cl_3 + O_2 \longrightarrow CCl_3OO^\bullet$$

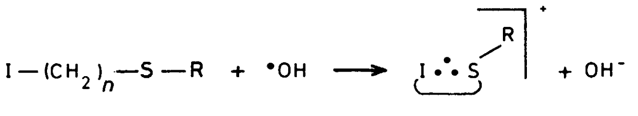
Irradiations were carried out by means of pulse radiolysis. The essential aspects of this technique and the analysis of data have been described elsewhere.[14] The radical species were generated by short pulses of high-energy (1.5 MeV) electrons from a Van de Graaff accelerator. Pulse lengths were typically in the order of 1 μs, and absorbed doses per pulse amounted to 1—2 Gy (J kg^{-1}). The yield of $^\bullet$OH radicals in irradiated N_2O-saturated aqueous solutions amounts to $G \approx 6$ which corresponds to *ca.* 6 × 10^{-7} mol dm^{-3} $^\bullet$OH radicals per 1 Gy pulse. Identification of the radicals was achieved by time-resolved optical and conductivity measurements. Dosimetry was based on the formation of $(SCN)_2^{-\bullet}$ radical anions in N_2O-saturated aqueous solutions of 10^{-3} mol dm^{-3} KSCN.

All experiments have been carried out at room temperature.

Results and Discussion

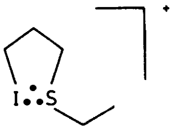
Optically absorbing transient species are generated upon pulse radiolysis of alkylthio(halogeno)alkanes in aqueous solutions. Their formation is based on a reaction of these compounds with hydroxyl radicals. The identity and the properties of the transients vary with the nature of the halogen and the molecular structure of the solutes.

Oxidation of Alkylthio(*iodo*)*alkanes* (**1a**—**k**).—The $^\bullet$OH-induced oxidation of (**1a**—**k**) leads to transient radical cations of the general type (**1**)$^{+\bullet}$.



(1) (1)$^{+\bullet}$

They exhibit broad optical absorptions in the 440—500 nm range. An example is displayed in Figure 1 which shows the optical absorption recorded immediately after a 1—2 μs pulse given to a N_2O-saturated aqueous solution of 10^{-4} mol dm^{-3} 1-ethylthio-3-iodopropane (**1b**) at pH 4. The main peak at $\lambda_{max.}$ 445 nm is attributed to the intramolecular radical cation (**1b**)$^{+\bullet}$



(**1b**)$^{+\bullet}$

The assignment is principally based on the same experimental facts and arguments as described already for the analogue radical cation (**1a**)$^{+\bullet}$.[6] The essential features are the following:

(a) The positive charge is deduced from simultaneous time-resolved conductivity measurements. In the acid solution a decrease in conductance is observed after the pulse owing to a net replacement of a highly conducting proton (Λ = 315 Ω^{-1} cm^2 at 18 °C) by a 'normal' cation (Λ = *ca.* 50 Ω^{-1} cm^2) in the overall reaction sequence:

$$(\mathbf{1b}) + {}^\bullet OH \longrightarrow (\mathbf{1b})^{+\bullet} + OH^-$$

$$OH^- + H^+_{aq} \longrightarrow H_2O$$

(b) The lifetimes of the optical (445 nm) and conductivity signal are the same (within experimental error limits). Both decay exponentially with $t_{1/2}$ = 90 μs.

(c) The positions of $\lambda_{max.}$ and the yield of (**1b**)$^{+\bullet}$ do not change within a solute concentration range of 5 × 10^{-5} – 2 × 10^{-3} mol dm^{-3} (higher concentrations are not possible due to limited solubility). This observation is in contrast to that made on the formation of intermolecular, purely iodine- or sulphur-centred radical cations, (RI.∴. IR)$^+$ and (R_2S.∴. SR_2)$^+$, which are formed in the general equilibria:

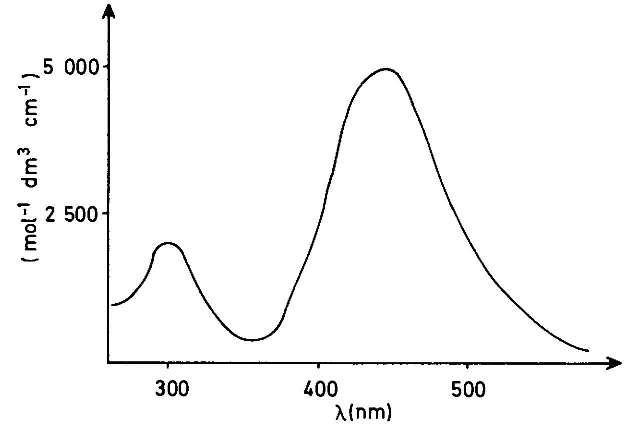


Figure 1. Optical transient absorption spectrum obtained by pulse radiolysis of an N_2O-saturated 10^{-4} mol dm^{-3} aqueous solution of (**1b**) at pH 4 recorded 5 μs after a 1.5 μs pulse

$$RI^{+\bullet} + RI \rightleftharpoons (RI \therefore IR)^+$$

$$R_2S^{+\bullet} + R_2S \rightleftharpoons (R_2S \therefore SR_2)^+$$

The measurable yields of both these three-electron-bonded dimer radical cations show a pronounced dependence on the solute concentration.[1,7]

(d) A further argument against a purely iodine-centred species is that this is stabilized only at low pH (<5),[7] while (**1b**)$^{+\bullet}$ is formed over the entire pH 3—10 range covered in our experiments (at higher pH the lifetime of the radical cation becomes, however, increasingly shorter which is presumably due to its reaction with OH^- ions).

(e) Analogous with known systems a purely sulphur-centred dimeric species would be expected to absorb at red-shifted wavelengths around 500 nm.[1]

(f) Finally, the monomer radical cations $RI^{+\bullet}$ and $R_2S^{+\bullet}$ have been found to absorb around 300 nm.[1,7] We can therefore exclude the 445 nm absorption to be due to one of these species. Furthermore they are generally much shorter lived ($t_{1/2} \leqslant 20$ μs) than (**1b**)$^{+\bullet}$.

The yield of (**1b**)$^{+\bullet}$ can be calculated on the basis of the conductivity results and [assuming Λ (**1b**)$^{+\bullet}$ = 50 Ω^{-1} cm^2] amounts to G = 4.0 or *ca.* 70% of the $^\bullet$OH radicals. The remaining 30% probably react *via* hydrogen atom abstraction to yield a neutral carbon-centred radical. Among these, α-thioalkyl radicals, for example, are well known and typically exhibit an absorption around 270—320 nm.[15] The small, relatively long-lived absorption band (mainly second-order decay, with a first half-life around 100 μs under our pulse radiolytic conditions) can thus be attributed to such a species.

Knowing the yield of (**1b**)$^{+\bullet}$ it is possible to calculate its extinction coefficient to ε = 5 100 mol^{-1} dm^3 cm^{-1}.

The oxidation of (**1b**) to (**1b**)$^{+\bullet}$ can be achieved not only by $^\bullet$OH radicals but also by other oxidants. The reaction of (**1b**) with $CCl_3OO^\bullet$ radicals, for example, occurs with a rate constant of 1.4 × 10^8 mol^{-1} dm^3 s^{-1}. This is comparable with $CCl_3OO^\bullet$ radical-induced oxidations of various organic sulphides.[16] Simple alkyl iodides, on the other hand, cannot be oxidized by $CCl_3OO^\bullet$ radicals.[7] We therefore conclude that the sulphur

Table 1. Data of the intramolecular radical cations generated by pulse radiolysis of N_2O-saturated aqueous 10^{-5}—10^{-3} mol dm^{-3} solutions of (1) at pH 3.5, recorded 5 μs after a 1.5 μs pulse ($\lambda_{max.}$ ± 5 nm, $t_{1/2}$ ± 10%, G ± 10%, ε ± 20%)

(1)			$(1)^{+\bullet}$			
Compound	n	R	$\lambda_{max.}$(nm)	$t_{1/2}$(μs)	G	ε(mol^{-1} dm^3 cm^{-1})
a	3	Me	440	110	4.8	5 100
b	3	Et	445	90	4.0	4 850
c	3	Pr	450	40	2.3	5 000
d	3	Pr^i	450	30	2.2	6 050
e	3	Bu^t	455	30	1.8	7 500
f	3	c-Hex	440	60	1.4	6 400
g	5	Pr^i	500	5	1.0	3 300
h	5	Bu^t	500	5	0.8	3 400
i	5	c-Hex	455	20	0.5	6 200
j	6	Me	470	20	0.8	6 050
k	6	Et	480	15	0.5	5 800

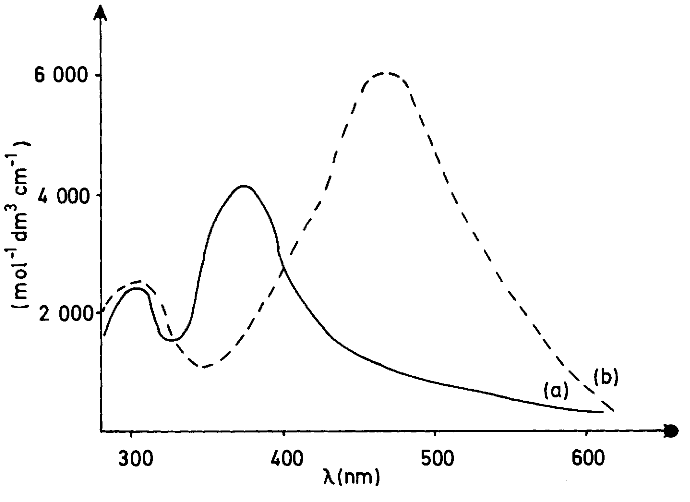
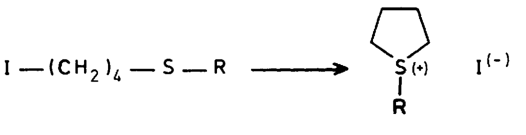


Figure 2. Optical transient absorption spectrum obtained by pulse radiolysis of an N_2O-saturated aqueous solution of (**2b**) at pH 3.5; 10^{-5} mol dm^{-3}; 10^{-3} mol dm^{-3}

atom is directly involved and probably the primary target in any oxidation of (**1**).

The assignment of corresponding transient optical absorptions to intramolecular radical cations of type $(\mathbf{1})^{+\bullet}$ from various alkylthio(iodo)alkanes (**1a**—**k**) is principally based on the same arguments as outlined above. The respective $\lambda_{max.}$, $t_{1/2}$, yields (in terms of G), and ε-values are summarized in Table 1. The yields and lifetimes are found to decrease with increasing chain length between the sulphur and iodine atoms (for $n \geqslant 3$). The transient absorption bands show a red shift with a longer chain. This suggests a decrease in stability of the 2σ–1σ* three-electron bonds which can be rationalized by the fact that seven- and eight-membered rings, as in $(\mathbf{1g}$—$\mathbf{k})^{+\bullet}$, are structurally less favourable than their five- and six-membered analogues. The latter radical cations, *i.e.* species with n = 4, unfortunately could not be investigated because of the instability of the 1-alkylthio-4-iodobutane solutes in aqueous solution. These compounds cyclize immediately after preparation to the stable five-membered sulphonium salts.[9,17]



Investigation of 1-alkylthio-2-iodoethanes (n = 2) is also prevented due to their instability in aqueous solutions.[18] Compounds (**1g**—**i**) also show a tendency to cyclize but in water they are stable for up to one hour.

A second parameter which contributes to the position of $\lambda_{max.}$ is the electron release by the substituent *R*.[19] In our present system this effect is, however, only minor as compared with the structural component.

One of the problems which has been encountered in the oxidation of alkyl iodides is their hydrolysis to yield free I^- ions.[7] Hydrolysis was therefore assessed for the alkylthio(iodo)alkanes in aqueous solutions by measurement of I^- produced on storage of the prepared N_2O-saturated solutions. For compounds (**1a**—**f**) no I^- was generated within two hours, *i.e.* within the period in which the pulse radiolysis experiments were carried out. After longer storage, transient absorption bands with $\lambda_{max.}$ 385 nm and >700 nm were observed upon pulse radiolysis. These are characteristic for $I_2^{-\bullet}$ radical anions [7,20] and result from an ˙OH radical-induced oxidation of I^-. The extent of hydrolysis increases with time. Consequently, if pulse radiolysis studies were carried out a day or more after preparing the solutions none of the $(\mathbf{1})^{+\bullet}$ radical cations were observable.

Oxidation of Alkylthio(bromo)alkanes (**2a**—**n**).—The ˙OH-induced oxidation of alkylthiobromoalkanes also yields radical cations. Their nature depends, however, not only on the chain length between the bromine and sulphur atoms but also on the solute concentration. Compounds (**2a**—**d**) and (**2l**) thus gave two distinctively different absorption bands in the visible, one around 370 nm at low solute concentrations (10^{-5}—10^{-4} mol dm^{-3}), and a second around 480 nm at higher concentrations (up to 10^{-3} mol dm^{-3}).

An example for the low-concentration conditions is displayed in Figure 2(a) which shows the transient absorption spectrum obtained upon pulse radiolysis of an N_2O-saturated aqueous solution (10^{-5} mol dm^{-3}) of 1-bromo-3-ethylthiopropane (**2b**) at pH 3.5. The band at 375 nm is found to decay exponentially with $t_{1/2}$ = 15 μs. The small absorption band at 290 nm is ascribed to a carbon-centred radical. The yield and the lifetime of the transient absorption band at 375 nm is found to decrease with increasing solute concentration and, at its expense, a new, broad absorption band appears at 495 nm [Figure 2(b)]. The concentration dependences of the two species at 375 nm and 495 nm are exhibited in Figure 3. Time-resolved conductivity measurements reveal both species to be positively charged.

Analogous to the discussion for the iodo analogues the species formed at low concentration (375 nm) is assigned to the intramolecular sulphur–bromine three-electron-bonded radical

Table 2. Data of transient radical cations generated by pulse radiolysis of N_2O-saturated aqueous solutions of (**2**) at pH 3.5, recorded 5 μs after a 1.5 μs pulse ($\lambda_{max.}$ ± 5 nm, $t_{1/2}$ ± 10%, G ± 10%, ε ± 20%). Solute concentrations: 10^{-5} and 10^{-3} mol dm^{-3} for the investigation of $(\mathbf{2})^{+\bullet}$ and $(\mathbf{2})_2^{+\bullet}$, respectively

(**2**)			$(\mathbf{2})^{+\bullet}$				$(\mathbf{2})_2^{+\bullet}$			
Compd.	*n*	R	$\lambda_{max.}$(nm)	$t_{1/2}$(μs)	G	ε(mol^{-1} dm^3 cm^{-1})	$\lambda_{max.}$(nm)	$t_{1/2}$(μs)	G	ε(mol^{-1} dm^3 cm^{-1})
a	3	Me	370	20	1.7	5 300	470	60	3.1	6 700
b	3	Et	370	20	1.5	4 200	480	40	3.0	6 200
c	3	Pr	375	15	1.3	5 400	495	20	2.8	5 700
d	3	Pr^i	380	10	1.2	7 000	495	15	1.8	7 200
e	3	Bu^t	390	10	1.0	6 400				
f	3	c-Hex	375	10	0.8	5 800				
g	5	Me	405	25	2.0	7 000	490	30	2.0	6 900
h	5	Et	410	20	1.8	7 000				
i	5	Pr^i	415	20	1.2	7 300				
j	5	Bu^t	420	15	0.8	6 100				
k	5	c-Hex	415	15	0.5	6 300				
l	6	Me	420	15	1.1	5 600				
m	6	Et	425	10	0.8	5 400				
n	6	Pr^i	430	10	0.4	4 000				

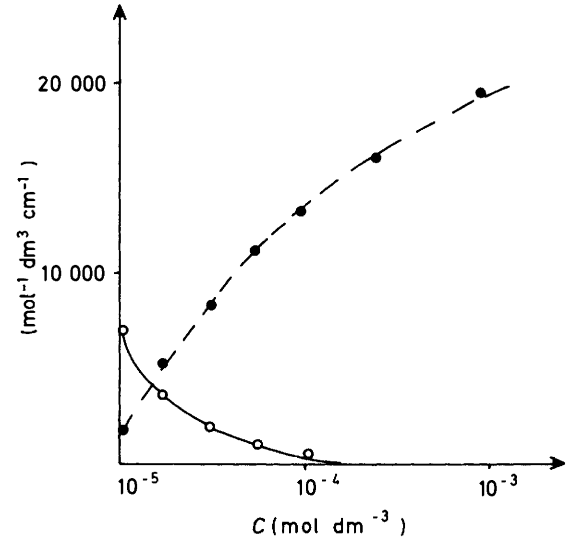
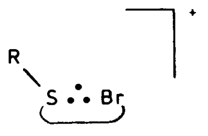
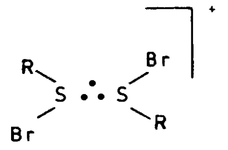


Figure 3. Dependence of the initial yield of $(\mathbf{2b})^{+\bullet}$ (○) and $(\mathbf{2b})_2^{+\bullet}$ (●) on the solute concentration upon pulse radiolysis of N_2O-saturated solutions of (**2b**) (pH 3.5). (Gε to be converted into SI units, cm^{-1} Gy^{-1}, by multiplication by 10^{-7})

cation of the general type $(\mathbf{2})^{+\bullet}$. It results from an interaction between sulphur and bromine *p*-orbitals in the oxidized state of the molecule. The yield and extinction coefficient of the particular species $(\mathbf{2b})^{+\bullet}$ amount to $G = 1.5$ and ε (375 nm) = 4 000 mol^{-1} dm^3 cm^{-1}, respectively.



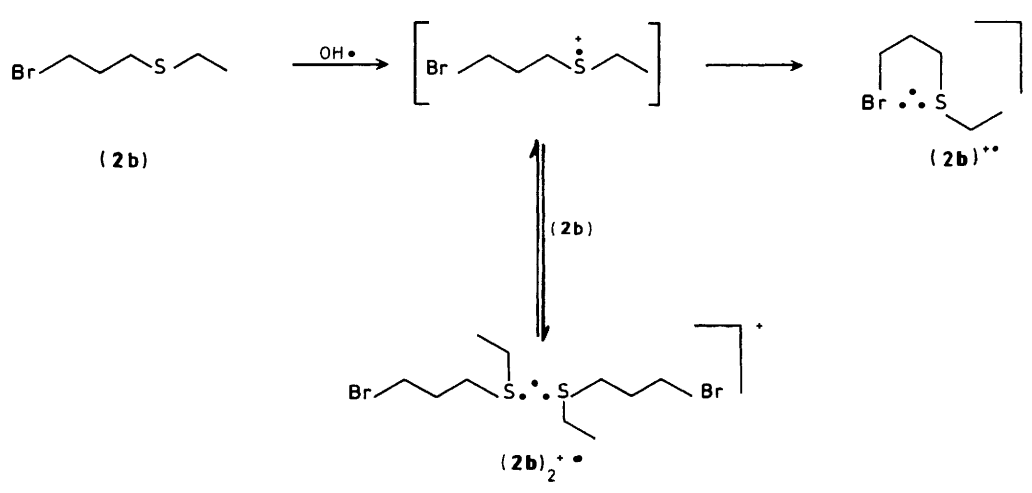
$(2)^{+\bullet}$



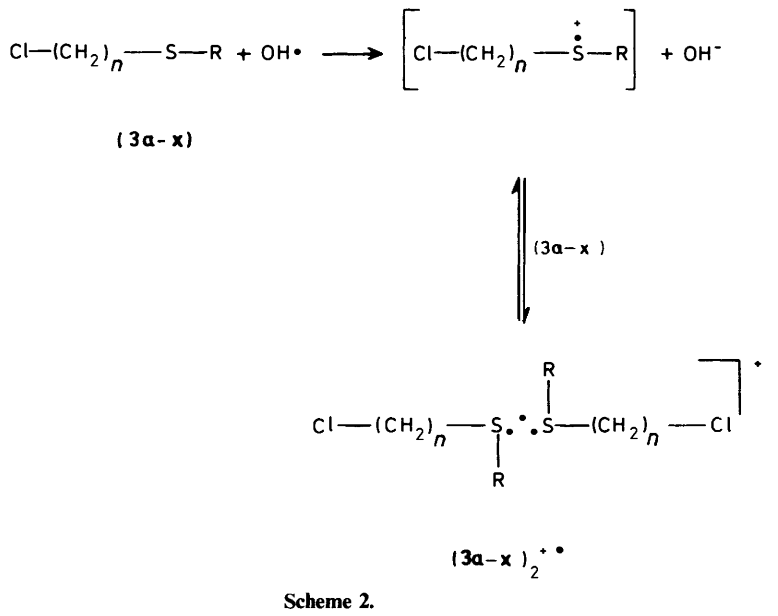
$(2)_2^{+\bullet}$

The absorptions of all $(\mathbf{2})^{+\bullet}$ radical cations are clearly distinguishable from those of the purely sulphur-centred molecular radical cations $R_2S^{+\bullet}$ which generally absorb at much lower wavelengths around 300 nm. Nevertheless, it is assumed that the initial oxidation takes place at the sulphur atom since oxidation does not take place at bromine itself, *e.g.* as in simple bromoalkanes.

The absorption at 495 nm, observable at high concentrations, is attributed to the dimer sulphur-centred radical cation $(\mathbf{2b})_2^{+\bullet}$. This and corresponding assignments of other $(\mathbf{2})_2^{+\bullet}$ species are



Scheme 1.



Scheme 2.

in accord with findings for $(R_2S \therefore SR_2)^+$ radical cations in general. The underlying reactions are summarized in Scheme 1.

Pulse radiolytic investigations of (**2e**, **f**, **h**—**n**) afford only the intramolecular transient species. This is due to the limited solubility of these compounds in water. Table 2 shows various physical properties of the radical cations generated by pulse radiolysis of (**2a**—**n**) $[Br(CH_2)_nSR]$ in low and high solute concentrations (10^{-5} and 10^{-3} mol dm^{-3}). As described for the iodo compounds the 1-alkylthio-4-bromobutanes and 1-alkylthio-2-bromoethanes could not be investigated due to their instability.

The fact that the purely sulphur-centred species $(\mathbf{2})_2{}^{+\bullet}$ can be stabilized in contrast to the analogous alkylthio(iodo)alkane systems is explained by the larger difference in electronegativity between sulphur and bromine relative to that between sulphur and iodine. This would render a $S \therefore Br$ bond to be weaker than a $S \therefore I$ bond and thus an easier subject for conversion into a $S \therefore S$-bonded system. In earlier work on the neutral species $R_2S \therefore X$ (X = halide) it has been found that $S \therefore I$ bonds are of comparable stability to $S \therefore S$ bonds.[4] In order to form the latter from the iodine compounds much higher solute concentrations beyond the solubility limit would be required.

The decrease in yield and the red shift of the transient absorption bands with increasing chain length indicates the

Table 3. Data of the transient radical cations generated by pulse radiolysis of N_2O-saturated aqueous 5×10^{-4} mol dm^{-3} solutions of (**3**) at pH 3.5, recorded 5 μs after a 1.5 pulse ($\lambda_{max.} \pm 5$ nm, $t_{1/2} \pm 10\%$, $G \pm 10\%$, $\varepsilon \pm 20\%$)

(3)			$(3)_2{}^{+\bullet}$			
Compd.	n	R	$\lambda_{max.}$(nm)	$t_{1/2}$(μs)	G	ε(mol^{-1} dm^3 cm^{-1})
a	3	Me	485	60	3.7	7 700
b	3	Et	490	50	1.7	7 650
c	3	Pr	495	40	1.3	9 000
d	3	Pr^i	500	25	1.1	8 600
e	3	Bu^t	500	20	0.9	8 100
f	3	c-Hex	490	25	0.8	7 900
g	4	Me	485	65	1.1	8 000
h	4	Et	490	40	0.8	8 250
i	4	Pr	495	25	0.6	6 500
j	4	Pr^i	500	20	0.5	8 000
k	4	Bu^t	520	5	0.4	6 900
l	4	c-Hex	510	—	—	—
m	5	Me	490	70	1.1	8 700
n	5	Et	490	80	0.9	8 800
o	5	Pr	500	40	0.8	4 500
p	5	Pr^i	520	15	0.7	6 300
q	5	Bu^t	530	5	0.2	9 000
r	5	c-Hex	510	—	—	—
s	6	Me	495	50	0.8	8 900
t	6	Et	500	40	0.6	8 300
u	6	Pr	505	40	0.4	7 800
v	6	Pr^i	520	20	0.2	6 300
w	6	Bu^t	530	—	—	—
x	6	c-Hex	520	—	—	—

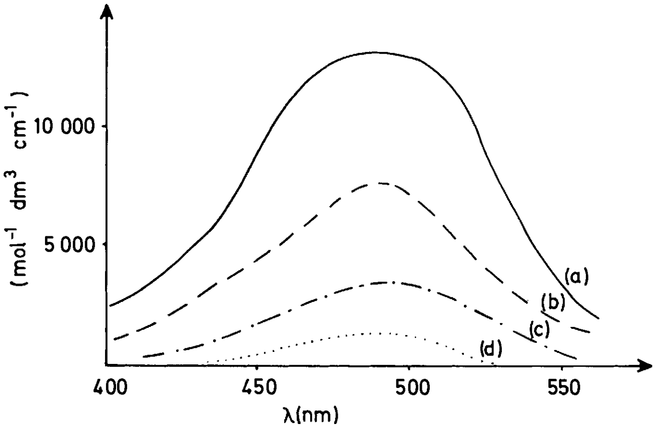


Figure 4. Optical transient absorption generated by pulse radiolysis of an N_2O-saturated aqueous solution of (**3b**) at pH 4 at various solute concentrations recorded 5 μs after a 1.5 μs pulse: (a): 10^{-3} mol dm^{-3}; (b) 5×10^{-4} mol dm^{-3}; (c) 10^{-4} mol dm^{-3}; (d) 5×10^{-5} mol dm^{-3}

decreased stability of the radical cations, as discussed already for the iodo analogues. The difference between the measurable yields of $(\mathbf{2})^{+\bullet}$ and $(\mathbf{2})_2^{+\bullet}$ can be explained by the higher lifetime of the dimer radical cation and the greater efficiency in $^{\bullet}$OH radical scavenging at the higher solute concentration.

Oxidation of the Alkylthio(chloro)alkanes (**3a**—**x**).—On the basis of the above considerations any possible $\mathrm{S}\therefore\mathrm{Cl}$ bond should be the weakest of all three-electron bonded systems. This is, in fact, fully supported by the findings on the oxidation of the alkylthio(chloro)alkanes (**3**). The $^{\bullet}$OH-induced oxidations of all these compounds yield only one absorption band at around 500 nm. This is due to a dimer radical cation $(\mathbf{3})_2^{+\bullet}$ which results from the stabilization of the oxidized sulphur centre by intermolecular interaction with an unattacked sulphur atom as exemplified in Scheme 2.

Figure 4 shows the absorption spectra obtained by pulse radiolysis of 1-chloro-3-ethylthiopropane (**3b**) in N_2O-saturated aqueous solutions at various solute concentrations (10^{-5}—10^{-3} mol dm^{-3}). In accord with expectation the yields are seen to increase with increasing concentrations of (**3b**). It is also noted that the lifetime of the dimeric species of *e.g.* $(\mathbf{3b})_2^{+\bullet}$ increases in the same direction, reflecting the relative stabilization of the $\mathrm{S}\therefore\mathrm{S}$-bonded radical cation in equilibrium as shown in Scheme 2. In addition to the visible band some long-lived absorption is detectable around 300 nm (not shown in Figure 4). This is due to a neutral species, presumably the α-thio carbon-centred radical. The intermediate sulphur-centred molecular radical cation, $[-\dot{\mathrm{S}}-]^{+}$, could not be observed which is most likely due to its very short lifetime.

All spectrophysical data of the various species $(\mathbf{3})_2^{+\bullet}$ are summarized in Table 3. The observed red shift of the absorption band with increasing chain length or alkyl group R is similar to that observed by pulse radiolysis of other organic sulphides.[19] Structural and electronic arguments can be advanced for this effect, as discussed in detail above. In particular, it is noted that bulky alkyl groups R exert a stronger effect with respect to a red shift of $\lambda_{\max.}$ for the dimer three-electron-bonded species $(\mathbf{2})_2^{+\bullet}$ and $(\mathbf{3})_2^{+\bullet}$ than for the intramolecularly stabilized species $(\mathbf{1})^{+\bullet}$ and $(\mathbf{2})^{+\bullet}$.

Conclusions

The results are in good agreement with the 2σ–$1\sigma^*$ concept developed originally for radical cations obtained upon oxidation of organic sulphides and later extended to corresponding electronic interactions between other hetero atoms.

Acknowledgements

This work has been supported by the International Bureau of the KFA Jülich within the terms of an agreement on scientific co-operation between the Federal Republic of Germany and the Republic of India. H. M. has been on deputation from the Bhabha Atomic Research Centre, Bombay. We thank Dr. F. Höfler for recording the mass spectra and Mrs. E. Darnstädt for help in synthesis.

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Received 26*th October* 1987; *Paper* 7/1905