Three-electron bonded σ/σ* radical cations from mixedly substituted dialkyl sulfides in aqueous solution studied by pulse radiolysis

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The formation of several radical cations $([R^i,R^j]S \therefore S[R^i,R^j])^+$, $([R^i]_2S \therefore S[R^j]_2])^+$ and $([R^i,R^j]S \therefore S[R^j]_2)^+$ with mixed alkyl substitution in aqueous solution has been investigated by means of pulse radiolysis. The following substituents were involved: $R^{i,j}$ = H, methyl, ethyl, propyl, isopropyl, butyl, *sec*-butyl, *tert*-butyl, pentyl, hexyl, heptyl and octyl. Two methods of generation have been applied: (*i*) $^{\cdot}$OH-induced oxidation of a sulfide and (*ii*) one-electron reduction of the corresponding sulfoxide in very acidic solution. The 2σ/1σ* three-electron bonded $(>S \therefore S<)^+$-type species exhibit optical absorptions with maxima ranging from 420 nm for $(Me_2S \therefore SH_2)^+$ to 600 nm for $([Me,Bu^t]S \therefore S[Bu^t]_2)^+$. The actual transition energy can be related to the electron induction by the substituents as concluded from a linear free energy correlation between the respective λ_{max} and weighted Taft's inductive σ* parameters. For unbranched substituents λ_{max} (in eV) = $1.40\,(\sigma^*)_w + 2.65$. Evidence is also provided for the destabilization of the three-electron bond by steric demands of bulky substituents and by the effect of the substitution pattern on the 'σ-lone pair' interaction. The latter becomes apparent by comparing $([Me_2]S \therefore S[Bu^t]_2)^+$ (λ_{max} 545 nm) with $([Me,Bu^t]S \therefore S[Me,Bu^t])^+$ (λ_{max} 510 nm). Kinetically, a number of rate constants have been determined for the forward and back reactions of the equilibrium $>S^{\cdot+} + S< \rightleftharpoons (>S \therefore S<)^+$. They are typically of the order of 10^9 dm^3 mol^{-1} s^{-1} and 10^4–10^5 s^{-1}, respectively. Equilibrium constants derived from these kinetic data range from 2.0×10^5 dm^3 mol^{-1} for $(Me_2S \therefore SMe_2)^+$ (confirming an earlier measurement) to $\leqslant 5 \times 10^3$ dm^3 mol^{-1} for $([Me,Bu^t]S \therefore S[Bu^t]_2)^+$. Their decrease parallels the total electron-releasing power of the substituents and the steric constraints exerted by them. The decay of the three-electron bonded radical cations includes first-order release of protons, possibly in association with the dissociation of the three-electron bond and second-order processes, presumably disproportionation. By and large, the kinetic stabilities are reflected in the trend in λ_{max} with shorter lifetimes referring to more red-shifted absorptions.

Introduction

Hydroxyl radicals, owing to their electrophilic character, are well known to initiate oxidation of organic sulfides, R_2S, by addition to the free electron pair at sulfur. The resulting $R_2S^{\cdot}(OH)$ sulfuranyl radical has been experimentally identified, or invoked as a precursor of sulfur-centred radical cations.[1–7] Recently, detailed studies were concerned with its kinetic stability, particularly if the substituent R contained some functional groups allowing hydrogen bridging.[5–7] The species derived from simple aliphatic sulfides generally has, however, a rather short lifetime of generally less than 1 µs. Depending on the sulfide concentration, it either yields a carbon-centred radical *via* net loss of a water molecule (if the α-carbon in R carries an H atom) [reaction (1)] or reacts with a second sulfide

$$R_2S^{\cdot}(OH) \longrightarrow H_2O + >C^{\cdot}\text{–}S\text{–}R \qquad (1)$$

molecule to yield a dimer, three-electron bonded radical cation [reaction (2)]. The formation of such three-electron bonded radical cations (two bonding σ- and one antibonding σ*-electrons) may occur *inter*- as well as *intra*-molecularly for compounds containing both interacting sulfur atoms in the same molecule. Numerous examples have been reported and substantiated by experimental data and theoretical calculations.[1–36]

$$R_2S^{\cdot}(OH) + R_2S \longrightarrow (R_2S \therefore SR_2)^+ + OH^- \qquad (2)$$

The (thioalkyl)alkyl radicals, $>C^{\cdot}$–S–R, formed *via* reaction (1), absorb at *ca.* 280 nm and usually decay by second-order kinetics.[1,37,38] The radical cations, on the other hand, exhibit broad absorption bands at comparatively higher wavelengths with λ_{max} depending on the nature of R (*e.g.* 370 nm for R = H and 555 nm for R = Pr^i).[1,19,30] The three-electron bonded species is further known to establish an equilibrium with the molecular radical cation‡ as formulated in general form in equilibrium (3).[1,12,19,23,30]

$$>S^{\cdot+} + S< \rightleftharpoons (>S \therefore S<)^+ \qquad (3)$$

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‡ It is understood that all molecular radical cations $>S^{\cdot+}$ are likely to exist as water complexed $(R_2S \therefore OH_2)^+$ species.[24,29,30] Accordingly, the forward reaction of equilibrium (3) constitutes a displacement process in which the water molecule is exchanged by a sulfide. For convenience, we will, however, generally use the simple formula.

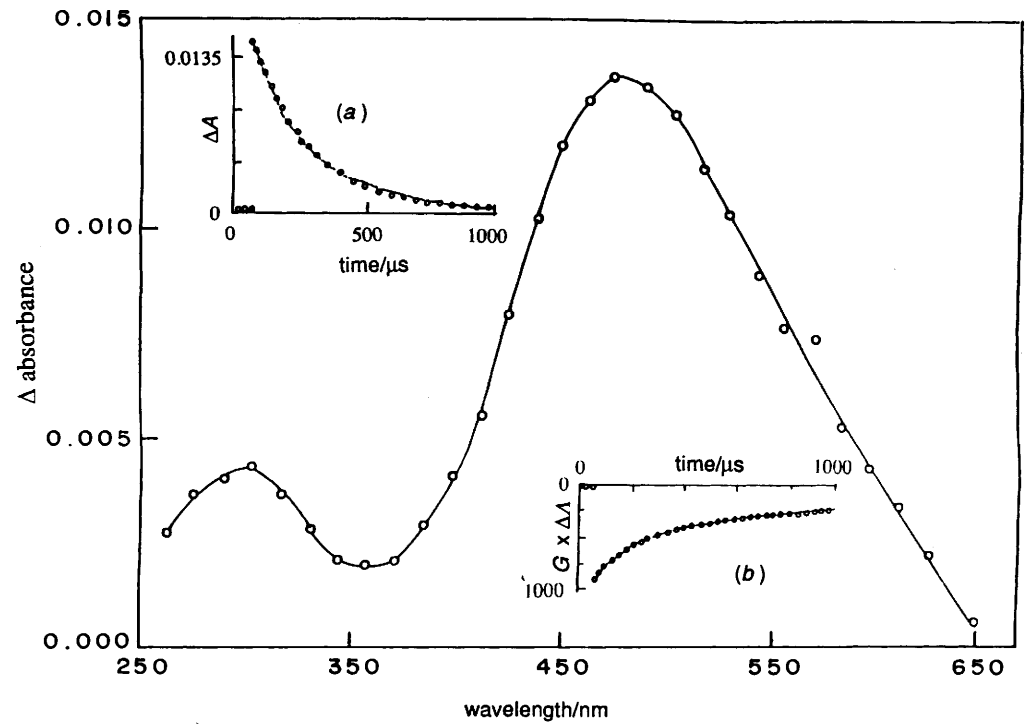


Fig. 1 Transient optical absorption spectrum obtained on pulse radiolysis of a pH 3.5, N_2O-saturated aqueous solution containing 5×10^{-4} mol dm^{-3} [MePr]S. Inset (*a*): trace of optical absorption at 480 nm as a function of time. Inset (*b*): Trace of conductivity signal as a function of time.

The thermodynamic stability of the $2\sigma/1\sigma^*$ bond appears to depend on the electronic and steric properties of the substituents.[23,30] Electron induction into the three-electron bond or steric demands exerted by the substituents seemingly weaken the S–S bond and cause a red-shift in the optical absorption. The optical transition takes place between the doubly occupied (σ–n) level, which results from 'σ–lone pair' interaction, and the singly occupied σ* energy level.[24] Because of this 'lone pair' influence there is no implicit linear relationship between bond strength and λ_{max}, as pointed out and corroborated by some experimental results on $(H_2S \therefore SH_2)^+$ and $(Me_2S \therefore SMe_2)^+$ in a recent gas phase and theoretical study.[36] On the other hand, looking at $(Me_2S \therefore SMe_2)^+$ and $(Pr^i{}_2S \therefore SPr^i{}_2)^+$, respectively, the observed red-shift in optical absorption (465 to 555 nm) is, indeed, accompanied by a decrease in S ∴ S bond strength (*ca.* 100 *vs. ca.* 85 kJ mol^{-1}).[23,30]

In the present study we wish to focus further on the effect of substituents in $(>S \therefore S<)^+$ bonded species on optical transition energies by extending our earlier investigations to a larger number of mixed substituted sulfides. In addition we will report on some kinetic parameters in these systems.

Experimental

All dialkyl sulfides were commercially available and distilled prior to use. Their purity was >99% as checked by gas chromatography. The solutions were prepared with deionized, 'Millipore'-filtered water. The pH of the solutions was generally adjusted by $HClO_4$.

Pulse radiolysis experiments were carried out with high energy electrons (1.55 and 4 MeV) from two Van de Graaff accelerators whose details have been described elsewhere.[39] The reaction of ˙OH radicals was studied in N_2O saturated solutions where hydrated electrons (formed initially in the irradiation of an aqueous solution in about equal yield to ˙OH radicals) are converted into hydroxyl radicals *via* the overall reaction $e_{aq}^- + N_2O + H_2O \rightarrow {}^{\bullet}OH + OH^- + N_2$. The total yield of hydroxyl radicals in such a system amounts to $G = 6.0$ (G denotes the number of species formed or converted per 100 eV, or the micromolar concentration per 10 J absorbed energy). Reactions of hydrogen atoms were studied in solutions containing high concentrations of perchloric acid (1–2 mol dm^{-3} $HClO_4$) in which all hydrated electrons are scavenged by protons *via* $e_{aq}^- + H^+ \rightarrow H^{\bullet}$. Under these conditions $G(H^{\bullet}) = 3.3$.

The dose delivered per pulse was determined from the formation of $(SCN)_2^{\bullet -}$ generated *via* ˙OH + SCN^- reaction in an N_2O saturated solution of 10^{-2} mol dm^{-3} KSCN. It was generally 1–2 Gy (1 Gy = 1 J kg^{-1}) and resulted in an ˙OH radical concentration of (0.6–1.2) + 10^{-6} mol dm^{-3}.

Conductivity changes in the pulse irradiated solution were monitored in a dual functional cell, one part being irradiated and the other one, containing an unirradiated sample, serving as reference. Details of this technique have also been described.[39,40]

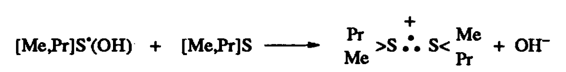
All data refer to room temperature. Error limits are ±10% unless specifically noted.

Results and discussion

Oxidation of sulfides

Fig. 1 shows the transient optical absorption spectrum obtained on pulse radiolysis of an N_2O saturated aqueous solution of methyl propyl sulfide, [Me,Pr]S (5×10^{-4} mol dm^{-3}; pH 3.5). It exhibits a broad absorption band with λ_{max} at 480 nm and a small shoulder in the 280–300 nm region. The transient 480 nm band was found to decay exponentially with a half-life of 150 µs [Fig. 1(*a*)]. The intensity of this band and its half-life increased with solute concentration. This suggested, in analogy also to the ˙OH-induced oxidation of sulfides with only one kind of substituent,[1,19,30,33] that the absorption is due to the mixed substituted, three-electron bonded dimer radical cation formed in reactions (4) and (5).

$$[Me,Pr]S + {}^{\bullet}OH \longrightarrow [Me,Pr]S^{\bullet}(OH) \quad (4)$$



$$[Me,Pr]S^{\bullet}(OH) + [Me,Pr]S \longrightarrow \left({}^{Pr}_{Me}\!>S \overset{+}{\therefore} S<^{Me}_{Pr}\right) + OH^- \quad (5)$$

The radical cation formation is also indicated by time-resolved conductivity measurements in the above solution

Table 1 Properties of $(>SS<)^+$ radical cations with mixed alkyl substitution

No.	Radical cation	λ_{max}/nm	$(\sigma^*)_w$[a]	G	ε/dm^3 mol^{-1} cm^{-1}	$t_{1/2}$/μs
1	$([Me,Et]S \therefore S[Me,Et])^+$	475	-0.050	3.8	4490	160[b]
2	$([Me,Pr]S \therefore S[Me,Pr])^+$	480	-0.058	3.7	5030	150[b]
3	$([Me,Pr^i]S \therefore S[Me,Pr^i])^+$[c]	500	-0.100	ng	ng	ng
4	$([Me,Bu]S \therefore S[Me,Bu])^+$	485	-0.065	2.6	5520	150[b]
5	$([Me,Pn]S \therefore S[Me,Pn])^+$	490	$\geqslant -0.065$[d]	2.1	5710	110[b]
6	$([Me,Hx]S \therefore S[Me,Hx])^+$	495	$\geqslant -0.065$[d]	1.7	5470	75[b]
7	$([Me,Hp]S \therefore S[Me,Hp])^+$	500	$\geqslant -0.065$[d]	1.5	5890	55[b]
8	$([Me,Oc]S \therefore S[Me,Oc])^+$	515	$\geqslant -0.065$[d]	0.4	5240	40[b]
9	$([Et,Pr]S \therefore S[Et,Pr])^+$	490	-0.108	3.2	5640	55[b]
10	$([Et,Bu^s]S \therefore S[Et,Bu^s])^+$	515	-0.155	1.6	5535	15[b]
11	$([Pr,Pr^i]S \therefore S[Et,Pr^i])^+$	520	-0.158	2.4	4300	20[b]
12	$([Me,Bu^t]S \therefore S[Me,Bu^t])^+$	510	-0.160	nd	nd	130[e]
13	$(Me_2S \therefore S[Me,Bu^t])^+$	495	-0.080	nd	nd	180[e]
14	$([Me,Bu^t]S \therefore SBu^t{}_2)^+$	600	-0.240	nd	nd	[f]
15	$(Me_2S \therefore SBu^t{}_2)^+$[g]	545	-0.160	nd	nd	25[e]
16	$(Me_2S \therefore SPr^i{}_2)^+$	530	-0.100	nd	nd	17[e]
17	$(Me_2S \therefore SEt_2)^+$	480	-0.050	nd	nd	100[e]
18	$(Me_2S \therefore SH_2)^+$	420	$+0.245$	5.5	4150	90[e]
19	$(Et_2S \therefore SH_2)^+$	425	$+0.145$	nd	nd	15[e]

[a] Weighted Taft's inductive σ^* parameter. [b] First half-life under comparable dose conditions and at 5×10^{-4} mol dm^{-3} solute concentration. [c] Taken from ref. 45. [d] Exact values not available. [e] Referring to individual experimental conditions, not directly comparable with lifetimes of other radical cations. [f] Not determinable. [g] Taken from ref. 21. ng: not given; nd: not determinable because acidic solution prevents yield measurements *via* conductivity.

which show an immediate decrease in signal after the pulse irradiation [Fig. 1(*b*)]. This is rationalized by the formation of the ion pair in reaction (5), followed by immediate neutralization of the hydroxide ion by H^+ in the acid solution. The net effect is, therefore, a replacement of a highly conducting proton (Λ 315 S cm^2 mol^{-1} at 18 °C) by the less conducting 'normal' cation ($\Lambda \approx 45 \pm 15$ S cm^2 mol^{-1}).[41]

From the conductivity signal it is also evident that both reactions (4) and (5) are fast and practically completed within the 1 μs pulse duration. At the sulfide concentration of 5×10^{-4} mol dm^{-3} this translates into a bimolecular rate constant for reaction (5) of $\geqslant 10^9$ dm^3 mol^{-1} s^{-1}. The subsequent recovery of the conductivity signal is explained by a liberation of a free proton. The kinetics of the decay of the optical signal almost match the kinetics of the conductivity recovery during the first two half-lives suggesting that the underlying process is a deprotonation of either the dimer radical cation directly or of the monomer in equilibrium [reaction (6)]. The fact that there is

$$>S^{\bullet+}/(>S \therefore S<)^+ \longrightarrow H^+ + >C^\bullet\text{–}S\text{–} + (>S) \quad (6)$$

more than one process involved in the conductivity changes emerges also from the behaviour of the signal at longer times. As can be recognized from Fig. 1(*b*) there is no complete recovery of the original pre-pulse conductivity and also the kinetics of the recovery seem to be slowed down at longer times compared with the decay process of the optical signal in Fig. 1(*a*). A detailed kinetic analysis of the overall rather complex decay of $(>S \therefore S<)^+$ and of all processes involved has already been published.[1,23]

The initial conductivity change allows us to quantify the radical cation formation. Considering that $\Delta\Lambda \approx -270$ S cm^2 mol^{-1} if an equivalent of protons is replaced by radical cations, the total measured $G \times (\Delta\Lambda) = -990$ S cm^2 mol^{-1} represents a yield of $G \approx 3.7$ (± 0.5). It is reasonable to assume that this yield is mainly due to the dimer three-electron bonded radical cation $([MePr]S \therefore S[MePr])^+$ and not to the molecular radical cation $[MePr]S^{\bullet+}$. Formation of the latter requires equilibration according to equilibrium (3) in a process which is probably too slow to be operative at the short timescale of $\leqslant 1$ μs. With the above yield and the measured $G\varepsilon = 18\,600$ it is then possible to calculate the extinction coefficient of $([MePr]S \therefore S[MePr])^+$ to be $\varepsilon = 5030$ dm^3 mol^{-1} cm^{-1} (at 480 nm). The latter is in line with published values of similar species.[1,42–44]

The radical cation yield amounts to *ca.* 62% of the initial $^\bullet$OH radical yield at the solute concentration used. The remainder is mainly attributed to a fast water elimination process from the

$$[MePr]S^\bullet(OH) \longrightarrow H_2O + >C^\bullet\text{–}S\text{–} \quad (7)$$

sulfuranyl radical which competes with the radical cation formation according to reaction (5). Evidence for this latter reaction has been provided in many corresponding cases.[1,37,38] This is substantiated by a corresponding increase in radical cation yield with increasing sulfide concentration (quantification is hampered by solubility limits). The presence of the carbon-centred radical, which typically absorbs at *ca.* 280 nm,[1,37,38] is indicated by the observed UV band in Fig. 1. The preferred site of deprotonation in the methyl, propyl substituted sulfide radical cation is considered to be the propyl group, as concluded by extrapolation from the data obtained with radical cations with CH_3–, –CH_2– and >CH– groups adjacent to sulfur.[1,23]

The method of radical cation generation *via* sulfide oxidation by hydroxyl radicals has been applied to investigate also several other mixed substituted compounds, $[R^i,R^j]S$. The various λ_{max}, extinction coefficients, yields and first half-lives for the respective $([R^iR^j]S \therefore S[R^iR^j])^+$ radical cations have been summarized in Table 1 under Nos. **1–12**. The λ_{max} range from 475–520 nm and it appears that an increase in alkyl chain length, branching and inductive power of the substituents result in a red-shift of the optical absorption, just as in the case of the analogue species which contain only one kind of substituent.[19,30] The extinction coefficients are more or less of the same order of magnitude for all species.

In order to allow comparison of yields and lifetimes all data given refer to the same sulfide concentration of 5×10^{-4} mol dm^{-3} except for **12** where the concentration was 10 times higher (see following section). By and large, the yields and lifetimes, listed as first half-lives for species **1**, **2** and **4–11**, follow the trends in λ_{max}. In all cases the decay of $([R^iR^j]S \therefore S[R^iR^j])^+$ species can be fitted reasonably well by an exponential rate law. However, second-order contributions are indicated in most cases by some acceleration with increasing dose, *i.e.* initial radical concentration.

Reduction of sulfoxides

An alternative method to generate $(>S \therefore S<)^+$-type radical cations with mixed substitution is by the one-electron reduction of the corresponding sulfoxides. This method was first successfully applied to the formation of $Me_2S^{\cdot+}$ radical cations by reduction of dimethyl sulfoxide. Owing to the lack of Me_2S in this system it prevents immediate complexation of $Me_2S^{\cdot+}$ to $(Me_2S \therefore SMe_2)^+$. The stoichiometry of the overall sulfoxide reduction process requires high proton concentrations ($\geqslant 10^{-2}$ mol dm^{-3}) and therefore is likely to proceed *via* hydrogen atoms *e.g.* reaction (8).[21] The proton is needed to prevent stabilization

$$R_2SO + H^\cdot + H^+ \longrightarrow R_2S^{\cdot+} + H_2O \qquad (8)$$

of $R_2S^{\cdot+}$ as $R_2S^\cdot(OH)$. In the present study we have carried out some further experiments with Me_2SO and Bu^t_2SO. Transient absorptions with maxima at 285 (± 10) and 310 (± 10) nm for the respective $R_2S^{\cdot+}$ radical cations confirm our earlier results.[21]

In the case of $Bu^t_2S^{\cdot+}$ there is, of course, the possibility of generating this radical cation oxidatively from the sulfide *via* reaction (9), undisturbed by any stabilization of the

$$Bu^t_2S + {}^\cdot OH \longrightarrow Bu^t_2S^\cdot(OH) \longrightarrow Bu^t_2S^{\cdot+} + OH^- \quad (9)$$

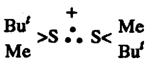
corresponding $(>S \therefore S<)^+$ species in aqueous solution.[19,30] In fact, this is the much better system to apply since this oxidative route results in higher yields of $Bu^t_2S^{\cdot+}$ than the reductive route. This emerges from the much higher $G\varepsilon$ (measured at 310 nm) in acid, pH > 2, for deaerated solutions of Bu^t_2S compared with those containing Bu^t_2SO. Considering that the yields of ${}^\cdot OH$ and $H^\cdot$, *i.e.* the $>S^{\cdot+}$-generating radicals in the respective systems, are $G({}^\cdot OH) = 2.8$ and $G(H^\cdot) = 3.3$ this calls for an additional pathway by which hydrogen atoms must react with Bu^t_2SO besides reaction (8). We suggest this to be a hydrogen atom induced alkyl elimination process as shown in reaction (10).

$$Bu^t_2SO + H^\cdot \longrightarrow (CH_3)_3C^\cdot + Bu^tS(O)H \qquad (10)$$

This resembles the well documented alkyl radical elimination upon ${}^\cdot OH$ attack on sulfoxides[46–49] and presumably proceeds *via* an intermediate hydrogen adduct. There is, in fact, spectroscopic evidence for *tert*-butyl radicals in the irradiated acidic (1 mol dm^{-3} $HClO_4$) Bu^t_2SO solutions. A transient absorption below 300 nm, which steadily increases towards the UV region, shows the same characteristics as that observed for $(CH_3)_3C^\cdot$ in the ${}^\cdot OH$-induced process.[48,49] In our present experiment the measured absorption at 250 nm amounts to $G\varepsilon = 5000$. Based on an extinction coefficient of *ca.* 1250 dm^3 mol^{-1} cm^{-1} for the $(CH_3)_3C^\cdot$ radical at this wavelength[48,49] this corresponds to a radiation chemical yield of $G \approx 4$. This is clearly higher than the yield of $(CH_3)_3C^\cdot$ generated by ${}^\cdot OH$ radical reaction with Bu^t_2SO in acidic solutions ($G \approx 2.8$) and, therefore, is compatible with an additional formation of *tert*-butyl radicals by hydrogen atoms.

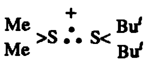
A reaction analogous to reaction (10) for the reduction of Me_2SO with generation of methyl radicals does not seem to be of any significance. This is deduced from the comparatively high $G\varepsilon$ values attributable to $Me_2S^{\cdot+}$ (8000 at 285 nm[21]) *vs.* that for $Bu^t_2S^{\cdot+}$ (*ca.* 1200 at 310 nm) and the assumption that $Me_2S^{\cdot+}$ and $Bu^t_2S^{\cdot+}$ have similar extinction coefficients. It also makes sense considering the much higher probability of resonance stabilization of $(CH_3)_3C^\cdot$ compared with ${}^\cdot CH_3$.

The sulfoxide route is, therefore, particularly suited for the investigation of reactions of the $Me_2S^{\cdot+}$ radical cation. In the present study $(Me_2S \therefore SPr^i_2)^+$ and $(Me_2S \therefore SEt_2)^+$ were generated by pulse radiolysis of 2 mol dm^{-3} $HClO_4$ solutions, 0.5 mol dm^{-3} Me_2SO and 10^{-3} mol dm^{-3} of either Pr^i_2S or Et_2S. The results are listed under species No. 16 and 17 in Table 1. The absorption maxima of the two three-electron bonded radical cations are located at 480 and 530 nm, respectively.



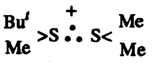
$$^{\mathrm{Bu}^t}_{\mathrm{Me}}\!>\overset{+}{\mathrm{S}\therefore\mathrm{S}}<^{\mathrm{Me}}_{\mathrm{Bu}^t}$$

12



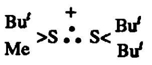
$$^{\mathrm{Me}}_{\mathrm{Me}}\!>\overset{+}{\mathrm{S}\therefore\mathrm{S}}<^{\mathrm{Bu}^t}_{\mathrm{Bu}^t}$$

15



$$^{\mathrm{Bu}^t}_{\mathrm{Me}}\!>\overset{+}{\mathrm{S}\therefore\mathrm{S}}<^{\mathrm{Me}}_{\mathrm{Me}}$$

13



$$^{\mathrm{Bu}^t}_{\mathrm{Me}}\!>\overset{+}{\mathrm{S}\therefore\mathrm{S}}<^{\mathrm{Bu}^t}_{\mathrm{Bu}^t}$$

14

Their lifetimes differ significantly with first half-lives of *ca.* 17 µs for $(Me_2S \therefore SPr^i_2)^+$ and 100 µs for $(Me_2S \therefore SEt_2)^+$ under the experimental conditions. The respective decays can be reasonably well adjusted to an exponential rate law with some acceleration with increasing dose similar to the situation of the $([R^1R^2]S \therefore S[R^1R^2])^+$ species. Nevertheless, the lifetimes of the latter should not directly be compared with those of the $([R^1]_2S \therefore S[R^2]_2)^+$ radical cations which are generated *via* the sulfoxide route. The reason is that the sulfide concentrations, which affect the various equilibria the three-electron bonded species are involved in, were different in the respective systems.

Mixed methyl–*tert*-butyl radical cations

The complementarity of the two methods, oxidation of sulfides *vs.* reduction of sulfoxides, is nicely demonstrated by the following examples on mixed [methyl, *tert*-butyl]-substituted species (Nos. 12–15 in Table 1). Oxidation of [methyl, *tert*-butyl]sulfide (N_2O, 1 mol dm^{-3} $HClO_4$, 4×10^{-3} mol dm^{-3} $[MeBu^t]S$) yields exclusively the three-electron bonded radical cation **12**. As shown in Table 1 this absorbs at λ_{max} 510 nm. By comparison, the symmetric $(Me_2S \therefore SMe_2)^+$ shows a maximum absorption at 465 nm while the corresponding λ_{max} for a hypothetical $(Bu^t_2S \therefore SBu^t_2)^+$ would presumably be considerably red-shifted to > 650 nm.[19,30]

The less symmetric bisMe, bisBu^t substituted radical cation **15** is best generated *via* reductive formation of $Me_2S^{\cdot+}$ from Me_2SO and subsequent reaction of this radical cation with Bu^t_2S (N_2, 2 mol dm^{-3} $HClO_4$, 0.5 mol dm^{-3} Me_2SO, 10^{-3} mol dm^{-3} Bu^t_2S). As described already in an earlier publication its optical absorption peaks at 545 nm.[21] Alternatively, it is possible to generate **15** *via* oxidative formation of $Bu^t_2S^{\cdot+}$ from Bu^t_2S and subsequent complexation of the radical cation by Me_2S, *e.g.* in N_2O-saturated, pH 3 solutions of 5×10^{-3} mol dm^{-3} Bu^t_2S and 10^{-4} mol dm^{-3} Me_2S. Reductive formation of $Bu^t_2S^{\cdot+}$ from Bu^t_2SO is less suitable because of the low yield, as discussed above.

Irrespective of its formation, **15** preferably equilibrates according to equilibrium (11) rather than equilibrium (12).[21]

$$\mathbf{15} \rightleftharpoons Me_2S + [Bu^t]_2S^{\cdot+} \qquad (11)$$

$$\mathbf{15} \rightleftharpoons Me_2S^{\cdot+} + [Bu^t]_2S \qquad (12)$$

This can be rationalized by the lower redox potential of the $Bu^t_2S^{\cdot+}/Bu^t_2S$ couple and a higher resonance stabilization of $Bu^t_2S^{\cdot+}$ compared with the respective methyl substituted species. Further details on the formation of **15** *via* $Me_2S^{\cdot+}$ and its properties have already been published.[21] They have now been confirmed by the results obtained *via* the $Bu^t_2S^{\cdot+}$ routes.

The kinetic stabilities of **12** and **15** are *ca.* 130 and 25 µs, respectively, under the experimental conditions. There may well be some inherently different properties which could be reflected in the lifetimes. But, as mentioned above, the different conditions under which these radical cations have been generated preclude any warranted conclusions from the lifetimes.

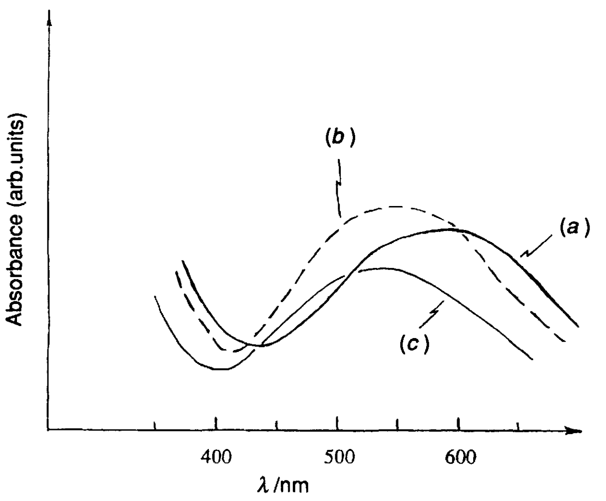


Fig. 2 Transient absorption spectra recorded upon pulse irradiation of a pH 3.3, N_2O-saturated aqueous solution containing 5×10^{-3} mol dm^{-3} Bu^t_2S and 1×10^{-4} mol dm^{-3} [MePr]S; (*a*) immediately after the pulse; (*b*) *ca.* 3 μs and (*c*) *ca.* 50 μs after the pulse

The tri-methylated species **13** may, in principle, also be formed *via* an oxidative route, namely, in systems containing Me_2S besides [Me,Bu^t]S. To ensure the desired cross combination both sulfides should be present at similar concentration which, however, means that not only **13**, but also the symmetric radicals **12** and $(Me_2S \therefore SMe_2)^+$, can be anticipated. Undisturbed formation of **13** is again much better achieved *via* reduction of Me_2SO and subsequent reaction of $Me_2S^{\cdot+}$ with the mixed sulfide [equilibrium (13)]. The λ_{max} (495 nm) of the tri-methylated species **13** is in between that of $(Me_2S \therefore SMe_2)^+$(465 nm)[19,30] and those of the di-methylated species (**12** and **15**) substantiating the generally additive influence of electronic and steric parameters of the substituents.[12,18,24,30]

$$Me_2S^{\cdot+} + [MeBu^t]S \rightleftharpoons \mathbf{13} \qquad (13)$$

The tri-*tert*-butylated radical cation **14** may be formed *via* the analogue mechanism (reduction of Bu^t_2SO), but for the reasons discussed above its yield from this route is relatively small. Nevertheless, some new transient absorption is apparent at >500 nm. Much higher yields of **14** are obtained if the molecular $Bu^t_2S^{\cdot+}$ is generated oxidatively and then reacted with the mixed sulfide [forward reaction of equilibrium (14)].

$$Bu^t_2S^{\cdot+} + [MeBu^t]S \rightleftharpoons \mathbf{14} \qquad (14)$$

At a 50 : 1 molar ratio (5×10^{-3} mol dm^{-3} Bu^t_2S and 10^{-4} mol dm^{-3} [$MeBu^t$]S), for example, two absorption bands are observed immediately after the pulse as shown in curve (*a*) of Fig. 2. The UV band, peaking at 310 nm, is attributable to $Bu^t_2S^{\cdot+}$. The visible band with a maximum at *ca.* 600 nm we like to assign to **14**. Both **14** and $Bu^t_2S^{\cdot+}$ are detectable at a *Gε* ratio of *ca.* 2 : 1. Since the extinction coefficient of $Bu^t_2S^{\cdot+}$ is at most the same as that of **14** (probably somewhat smaller) this would yield an equilibrium constant $K_{14} \leqslant 5 \times 10^3$ dm^3 mol^{-1}, well in line with values for other $(>S \therefore S<)^+ \rightleftharpoons\ >S^{\cdot+} + S<$ equilibria[23,30] and some measured for the mixed substituted species in this paper (see below).

The possibility that radical cation **14** with its three *tert*-butyl substituents can still be stabilized in aqueous solution is quite interesting since this is not the case anymore for the tetra-*tert*-butylated species for which the corresponding equilibrium lies fully on the left-hand side.[19,30]

$$Bu^t_2S^{\cdot+} + Bu^t_2S \rightleftharpoons (Bu^t_2S \therefore SBu^t_2)^+ \qquad (15)$$

The conclusion that the 310 and 600 nm absorption bands of spectrum (*a*) in Fig. 2 have to be attributed to two different species is supported by the associated kinetics. The UV absorption ($Bu^t_2S^{\cdot+}$) immediately begins to decay after the end of the (*ca.* 1 μs) pulse by a mixed order process with a significant second-order component. The visible band, on the other hand, first suffers a blue-shift as indicated by curve (*b*) in Fig. 2 which refers to a time *ca.* 3 μs after the pulse. At this time the maximum lies at 550 nm. The kinetics of the blue-shift can actually be followed at, for example, 510 nm, where, within the first 3 μs after the pulse, an exponential increase in absorption is observed. Eventually this absorption decays by a more or less first-order process ($t_{1/2} \approx 25$ μs, corresponding to an overall decay rate constant of 2.8×10^4 s^{-1}) and, as this process proceeds, the maximum of the remaining absorption is further shifted towards 530–510 nm [curve (*c*) in Fig. 2]. The yield of the transient and the extent of the blue-shift is much less pronounced at lower [$MeBu^t$]S concentration. In solutions containing exclusively [$MeBu^t$]S, or higher concentrations thereof, only the absorption of the symmetric radical cation **12** is present (λ_{max} 510 nm). Accordingly, we interpret the blue-shift by a conversion of the initially formed tri-*tert*-butylated species **14** to the thermodynamically more stable radical cation **12** in the forward reaction of equilibrium (16). No attempt has been made to quantitatively unravel the kinetics associated with the various reactions and equilibria involved. A rough estimate derived for the **14**→**12** conversion from the build-up at 510 nm and the [$MeBu^t$]S concentration yields a rate constant k_{16} for the forward reaction of equilibrium (16) in the order of 10^9 dm^3 mol^{-1} s^{-1}.

$$\mathbf{14} + [MeBu^t]S \rightleftharpoons \mathbf{12} + Bu^t_2S \qquad (16)$$

Generation and properties of $(Me_2S \therefore SH_2)^+$

Another interesting example concerning the formation of a three-electron bonded radical cation with mixed substitution is the $(Me_2S \therefore SH_2)^+$ radical cation (No. **18** in Table 1). Direct evidence for this species is provided in a pulsed, N_2-saturated, highly acidic (2 mol dm^{-3} $HClO_4$) aqueous solution containing 0.5 mol dm^{-3} Me_2SO and varying concentrations (3×10^{-5}–10^{-2} mol dm^{-3}) of H_2S (added as Na_2S) by a transient optical absorption which peaks at 420 nm. It emerges from the initial $Me_2S^{\cdot+}$ and is, therefore, attributed to reaction (17). The precursor $Me_2S^{\cdot+}$ radical cation, which absorbs at 280 nm, is only traceable at lower H_2S concentration. Upon decay the 420 nm absorption suffers a blue-shift, similar to the situation described in connection with Fig. 2, which becomes increasingly pronounced with increasing H_2S concentration. At high concentrations of H_2S the only observable transient is, in fact, the species which absorbs at 370 nm and shows all the characteristics of the symmetric $(H_2S \therefore SH_2)^{\cdot+}$ radical cation.[16] This is indicative for a conversion of the mixed three-electron bonded radical cation *via* the forward reaction of equilibrium (18). The fact that $(H_2S \therefore SH_2)^{\cdot+}$ appears to be generated *via* the mixed intermediate shows that its formation is not based on a one-electron oxidation of H_2S by $Me_2S^{\cdot+}$ to a possible $H_2S^{\cdot+}$ intermediate but proceeds *via* a displacement mechanism.

$$Me_2S^{\cdot+} + H_2S \rightleftharpoons (Me_2S \therefore SH_2)^{\cdot+} \qquad (17)$$

$$(Me_2S \therefore SH_2)^{\cdot+} + H_2S \rightleftharpoons Me_2S + (H_2S \therefore SH_2)^{\cdot+} \qquad (18)$$

The presence of different species is also indicated by the decay kinetics of the transient absorption at different wavelengths. At 5×10^{-3} mol dm^{-3} H_2S, for example, the 420 nm band decays exponentially with $t_{1/2} = 25$ μs, associable with the overall

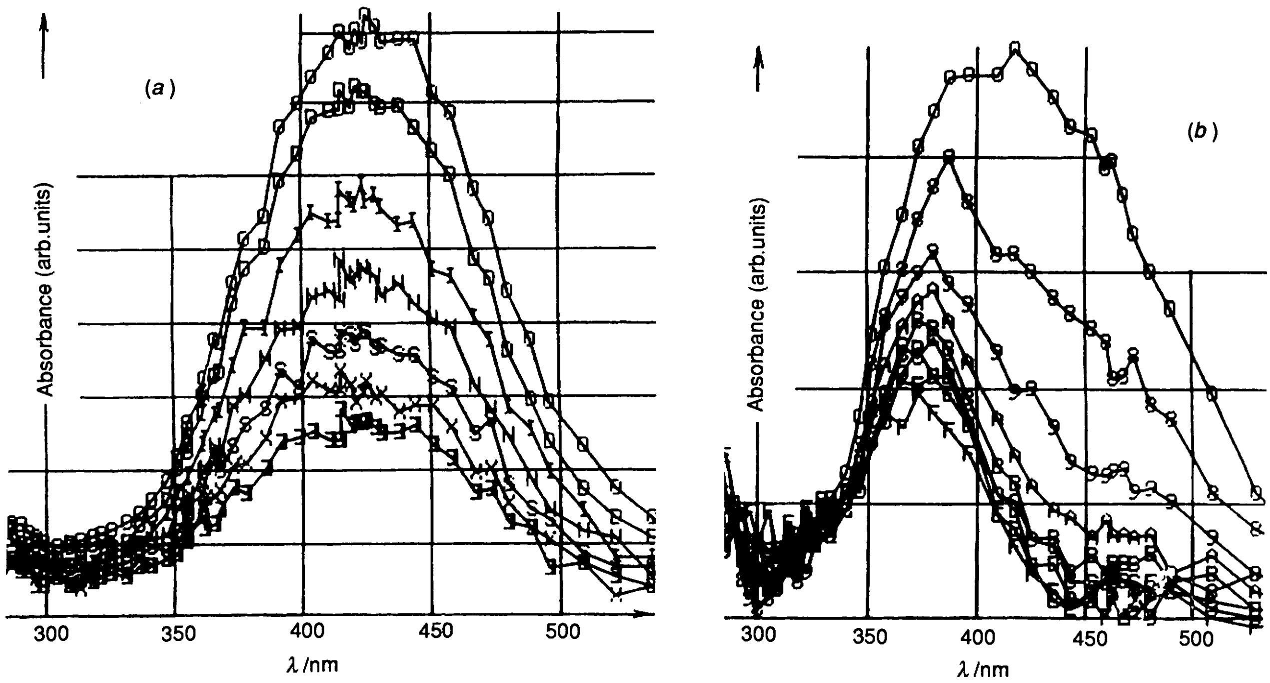


Fig. 3 Transient absorption spectra recorded over a period of 200 μs after pulse irradiation of an aqueous N_2O-saturated, 1 molar $HClO_4$ solution containing (*a*) 1 × 10^{-3} mol dm^{-3} Na_2S and 5 × 10^{-3} mol dm^{-3} Me_2S, or (*b*) 1 × 10^{-2} mol dm^{-3} Na_2S and 1 × 10^{-2} mol dm^{-3} Me_2S

equilibration kinetics and possibly some unimolecular deprotonation. The eventual decay at 370 nm at later times, on the other hand, proceeds by second-order kinetics with the first half-lives decreasing from 115 to 38 μs if the dose is increased by a factor of 3.4.

Upon addition of Me_2S the 420 nm band becomes increasingly red-shifted with increasing $[Me_2S]/[H_2S]$ ratio and eventually assumes a maximum at 465 nm where the symmetric $(Me_2S \therefore SMe_2)^{\bullet +}$ absorbs. This indicates the second equilibrium (19).

$$(Me_2S \therefore SH_2)^{\bullet +} + Me_2S \rightleftharpoons H_2S + (Me_2S \therefore SMe_2)^{\bullet +} \quad (19)$$

Both equilibria (18) and (19) can also be established with solutions containing H_2S and Me_2S in an oxidizing environment (N_2O-saturated solutions; 1 mol dm^{-3} $HClO_4$). Since all radical cations are also involved in equilibria with their molecular counterparts according to equilibrium (3) and, furthermore, the absorptions of the respective species overlap to some extent it is very difficult to extract any equilibrium constant within reasonable error limits. Qualitatively it seems that the thermodynamic stability increases in the order $(Me_2S \therefore SMe_2)^{\bullet +} < (Me_2S \therefore SH_2)^{\bullet +} < (H_2S \therefore SH_2)^{\bullet +}$. This order is derived from the observation that stabilization of $(Me_2S \therefore SMe_2)^{\bullet +}$ requires significant excess of Me_2S over H_2S, and that in the above discussed reductive sulfoxide route $(Me_2S \therefore SH_2)^{\bullet +}$ is converted to $(H_2S \therefore SH_2)^{\bullet +}$ at already low H_2S concentrations.

The mixed $(Me_2S \therefore SH_2)^{\bullet +}$ radical cation as sole species appears to exist in solutions with a 1:5 molar ratio of H_2S/Me_2S (1 × 10^{-3} *vs.* 5 × 10^{-3} mol dm^{-3}). At this condition only one transient absorption with λ_{max} 420 nm can be monitored which upon decay does not suffer any spectral shift as demonstrated in Fig. 3(*a*). In N_2O-saturated solution the yield amounts to $G\varepsilon = 22\,825$. Taking a radical cation yield of $G = 5.5$, as determined for such a sulfide concentration at pH ≈ 4 by time resolved conductivity measurements,[1] an extinction coefficient of $\varepsilon = 4150$ dm^3 mol^{-1} cm^{-1} is derived. It lies in between that of $(Me_2S \therefore SMe_2)^{\bullet +}$ (6200 dm^3 mol^{-1} cm^{-1})[1] and $(H_2S \therefore SH_2)^{\bullet +}$ (1600 dm^3 mol^{-1} cm^{-1}).[16]

The diethyl sulfide derived mixed species $(Et_2S \therefore SH_2)^{\bullet +}$ (No. **19** in Table 1) has a lifetime of *ca.* 15 μs as deduced from the transient spectra obtained from acidic (1 molar $HClO_4$) solutions containing a 1:10 molar ratio of H_2S and Et_2S (10^{-3} *vs.* 10^{-2} mol dm^{-3}). Under these conditions $(Et_2S \therefore SH_2)^{\bullet +}$ appears to be the only absorbing transient. At a 1:1 molar ratio and (10^{-2} mol dm^{-3} H_2S *vs.* 10^{-2} mol dm^{-3} Et_2S) the $(Et_2S \therefore SH_2)^{\bullet +}$ band is not stable but, upon decay, converts into the 370 nm band of $(H_2S \therefore SH_2)^{\bullet +}$. This is shown in Fig. 3(*b*). The maximum of the $(Et_2S \therefore SH_2)^{\bullet +}$ absorption is found at 420–425 nm and thus not very different from that of $(Me_2S \therefore SH_2)^{\bullet +}$. This is reasonable considering that the respective maxima of $(Et_2S \therefore SEt_2)^{\bullet +}$ and $(Me_2S \therefore SMe_2)^{\bullet +}$ radical cations also differ only slightly (485 *vs.* 465 nm).

Rate constants for formation of three-electron bonded radical cations

The sulfoxide method provides a convenient method to determine the rate constants for the forward reaction of the general equilibrium (20) (R^i = or ≠ R^j). A number of

$$Me_2S^{\bullet +} + [R^i,R^j]S \rightleftharpoons (Me_2S \therefore S[R^i,R^j])^{+} \quad (20)$$

individual rate constants k_{20} have now been determined from the decay of the $Me_2S^{\bullet +}$ absorption and/or the formation of the resulting $>S \therefore S<$ bonded radical cations in deaerated solutions containing 0.5 mol dm^{-3} Me_2SO and various low concentrations [(1–5) × 10^{-4} mol dm^{-3}] of sulfides. Numerically they were evaluated from the slopes of a k_{obs} s^{-1} *vs.* [sulfide] plot and listed in Table 2. All processes are seen to occur with rate constants in the order of 10^9 dm^3 mol^{-1} s^{-1} and do not show any significant dependence on the substituents.

All k_{obs}/s^{-1} *vs.* [sulfide] plots exhibit intercepts which are also listed in Table 2. It seems reasonable to associate them with the respective back reactions of equilibrium (20), *i.e.* k_{-20} for the re-dissociation of the three-electron bonded species and thus, together with k_{20}, with their overall thermodynamic stability in terms of $K_{20} = k_{20}/k_{-20}$. In the case of $(Me_2S \therefore SMe_2)^{+}$ the present data are in excellent agreement with those (K_{20} = 2.0 × 10^5 dm^3 mol^{-1} and k_{-20} = 1.5 × 10^4 s^{-1}) obtained earlier *via* a completely different k_{-20} determination.[23] For the other species, both the values assigned to K_{20} and k_{20} clearly follow the trend expected on the basis of an $S \therefore S$ bond weakening by increasing electron induction and steric

Table 2 Rate constants for the reaction of $\mathrm{Me_2S^{\bullet +}}$ and $\mathrm{Bu^t{}_2S^{\bullet +}}$ radical cations with various sulfides

Radical cation	Sulfide ($\mathrm{R_2S}$)	$k(\mathrm{Me_2S^{\bullet +}} + \mathrm{R_2S}) = k_{20}$/ 10^9 dm^3 mol^{-1} s^{-1}	$k_{-20}{}^a/10^4$ s^{-1}	$K_{20}{}^a = (k_{20}/k_{-20})$/ 10^3 dm^3 mol^{-1}
$\mathrm{Me_2S^{\bullet +}}$	$\mathrm{Me_2S}$	3.05^b	1.5	200
$\mathrm{Me_2S^{\bullet +}}$	$\mathrm{Et_2S}$	2.1	6.3	33
$\mathrm{Me_2S^{\bullet +}}$	$\mathrm{Pr^i{}_2S}$	1.5	19	7.9
$\mathrm{Me_2S^{\bullet +}}$	$\mathrm{Bu^t{}_2S}$	2.15^b	44	4.8
$\mathrm{Me_2S^{\bullet +}}$	$\mathrm{[MeBu^t]S}$	1.5	3.5	43
$\mathrm{Bu^t{}_2S^{\bullet +}}$	$\mathrm{[MeBu^t]S}$	2.5^c	$\geqslant 50^d$	$\leqslant 5^d$

[a] Under the assumption that intercept of k_{obs} *vs.* $[\mathrm{R_2S}]$ plot represents only re-dissociation of the three-electron bonded radical cation formed in the respective reaction. [b] Taken from ref. 21. [c] Single concentration experiment. [d] Calculated from single concentration experiment.

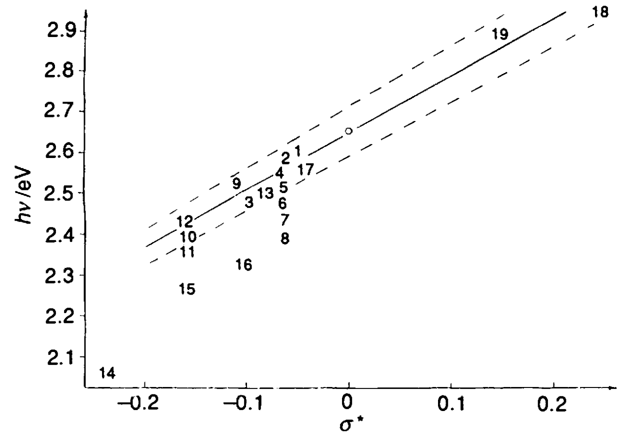


Fig. 4 Linear free energy correlation plot between optical transition energy (in eV) for UV–VIS band of three-electron bonded $>\mathrm{S} \therefore \mathrm{S}<$-type radical cation against weighted Taft's inductive σ^* parameter. Numbers refer to respective species in Table 1; (○) $(\mathrm{Me_2S} \therefore \mathrm{SMe_2})^+$

constraints from the substituents. For comparison, it is further reassuring that the respective values for $(\mathrm{Me_2S} \therefore \mathrm{S^iPr^i{}_2})^+$ are almost in the middle of those for $(\mathrm{Me_2S} \therefore \mathrm{SMe_2})^+$ and $(\mathrm{Pr^i{}_2S} \therefore \mathrm{SPr^i{}_2})^+$, for which $K_{20} = 5.4 \times 10^2$ dm^3 mol^{-1} and $k_{-20} = 5.6 \times 10^6$ s^{-1} have been measured.[23]

Linear free energy correlations

In earlier studies on symmetrically substituted $(\mathrm{R_2S} \therefore \mathrm{SR_2})^+$ radical cations[19,30] a good linear free energy correlation with $\lambda_{\max}$ (in eV) $= 1.40\ \sigma^* + 2.66$ was established between the energy of the optical transition and Taft's inductive σ^*-parameter[50] for the various substituents, provided that the latter were unbranched alkyl ($\leqslant \mathrm{C_4}$) groups. Deviation from this linear relationship was found for all branched and bulkier substituents, such as isopropyl and *tert*-butyl suggesting a strong steric effect in addition to the inductive one. The same picture is now observed for the mixed substituted radical cations by applying weighted Taft $(\sigma^*)_{\mathrm{w}}$ values. In the calculation of $(\sigma^*)_{\mathrm{w}}$ each of the four substituents in the $>\mathrm{S} \therefore \mathrm{S}<$ bonded species contributes a quarter of its listed[50] Taft value. As shown in Fig. 4, most of the mixed substituted radical cations (given by numbers as in Table 1) can be accommodated on the same linear relationship as the corresponding species with only one kind of substituent (solid line) within the experimental error limit of ± 10 nm (dashed lines). Deviations from this linearity, all towards lower optical transition energies, are obtained only for those species which carry long chain alkyl groups (**6**–**8**) or two branched and, therefore, particularly bulky substituents at one of the sulfur atoms (**14**–**16**).

The most interesting result is probably the significant difference in $\lambda_{\max}$ between $([\mathrm{Me,R^i}]\mathrm{S} \therefore \mathrm{S}[\mathrm{Me,R^i}])^+$ and $(\mathrm{Me_2S} \therefore \mathrm{S[R^i]_2})^+$ with $\mathrm{R^i} = \mathrm{Bu^t}$ and $\mathrm{Pr^i}$ (see **12** *vs.* **15**, and **3**[45] *vs.* **16**) although the number of substituents and weighted Taft values are the same for the respective $\mathrm{Bu^t}$ and $\mathrm{Pr^i}$ species. One of the possibilities to account for such a red-shift in optical absorption could be a weakening of the $>\mathrm{S} \therefore \mathrm{S}<$ bond strength. A correlation between these two parameters is indeed indicated in the literature, for example, for $(\mathrm{Me_2S} \therefore \mathrm{SMe_2})^+$ ($\lambda_{\max}$ 465 nm, bond strength *ca.* 110 kJ mol^{-1}) and $(\mathrm{Pr^i{}_2S} \therefore \mathrm{SPr^i{}_2})^+$ ($\lambda_{\max}$ 555 nm, bond strength *ca.* 80 kJ mol^{-1}).[23,30] In support of these experimental data, Clark[24] states in his theoretical calculations that the bond is, in fact, expected to be weakened when the ionization potentials of the components in the three-electron-bond system become different. Physically, such bond weakening can be envisaged by electron induction (increase in electron density in the anti-bonding σ* orbital) and steric forces causing S–S separation. However, the $\lambda_{\max}$/'bond strength' relationship is not implicitly given since it involves two independent steps. A lower bond strength clearly indicates a smaller σ/σ* energy level difference. The optical absorption of interest results, on the other hand, from a transition between a distorted σ-level, namely (σ–n), and σ* as shown by theoretical calculations.[18] This distortion is caused by the effect of the 'lone pair' electrons on σ. Caution is, therefore, advised to extrapolate linearly from $\lambda_{\max}$ to the $>\mathrm{S} \therefore \mathrm{S}<$ bond strength particularly if the latter is further related to the S–S distance. As emerging, for example, from recent gas phase and theoretical studies[26,36] the S–S distance in $(\mathrm{H_2S} \therefore \mathrm{SH_2})^+$ appears to be even slightly larger than in $(\mathrm{Me_2S} \therefore \mathrm{SMe_2})^+$ (2.853 *vs.* 2.838 Å in C_{2h} symmetry) although $(\mathrm{H_2S} \therefore \mathrm{SH_2})^+$ shows the much more blue-shifted absorption of the two species (370 *vs.* 465 nm).[16] Reduced electrostatic repulsion in $(\mathrm{Me_2S} \therefore \mathrm{SMe_2})^+$, because of better delocalization of the positive charge, has been forwarded as an explanation for this.[36]

The importance of 'σ-lone pair' interaction and the effect of alkyl substituents on this has been emphasized particularly in theoretical studies.[18,31,36] It can be appreciated that, in addition to the two above mentioned parameters which may drive the two sulfurs apart (electron induction and steric constraints), the overall three-dimensional structure of the three-electron bonded species becomes significant since this is the parameter which determines the degree of 'σ-lone pair' interaction. Referring to our present case of the bis-methyl, bis-*tert*-butyl (**12**/**15**) and bis-methyl, bis-isopropyl substituted radical cations (**3**/**16**) we can, indeed, envisage a greater distortion of the molecular symmetry if the two bulkyl *tert*-butyl or isopropyl substituents are attached to just one of the sulfurs than being equally distributed between both sulfur atoms. It appears that this, in turn, results in a stronger 'σ-lone pair' interaction and corresponding rise in the (σ–n) energy level. The same consideration may apply to the interpretation of the slight red-shift observed in the case of long chain alkyl substituents (species **6**–**8**) which cannot be explained on the basis of inductive effects since the latter should not vary anymore to any significant extent beyond butyl, and simple steric interactions may also not be so important since each sulfur carries only one of these large substituents. Generally, the discussed effect and the energetically higher lying (σ–n) level resulting therefrom can perhaps be understood in terms of a partial rotation around the S $\therefore$ S bond towards, *e.g.* a *gauche* conformation and/or a change in angle between 'lone pair' and σ orbitals.

With respect to the $(\mathrm{Me_2S} \therefore \mathrm{SR^i_2})^+$ type species yet another aspect may be worth considering, namely, that the asymmetry in the substitution pattern at the two sulfurs in **15** and **16** causes a certain degree of charge-spin separation with one of the sulfurs assuming more of a sulfuranyl, the other more of a sulfonium character, *viz* $(\mathrm{Me_2S^\bullet\text{-}S^+R^i_2})$. Whether this contributes to the anomalous $\lambda_{\max}$ for the species with $\mathrm{R^i} = \mathrm{Pr^i}$ and $\mathrm{Bu^t}$ remains, however, questionable since the corresponding radical cation with $\mathrm{R^i} = \mathrm{H}$ shows no deviation from the linear Taft relationship.

Conclusion

Three-electron bonded $>\mathrm{S} \therefore \mathrm{S}<$ type radical cations with mixed alkyl substitution pattern can conveniently be generated *via* two different reaction routes. One of them involves reductive formation of $\mathrm{R_2S^{\bullet +}}$ from the corresponding sulfoxide and subsequent reaction of this radical cation with any added sulfide. This route has the advantage that it avoids any disturbance by the reaction of the $\mathrm{R_2S^{\bullet +}}$ with the sulfide of its own kind. A disadvantage is the low yield if long-chain and branched alkyl substituents are involved, and possibly the fact that this route operates only under very acidic conditions. The alternative possibility, namely, oxidation of mixed sulfides or a mixture of two different sulfides generally affords high yields of the three-electron bonded radical cations. The generation of mixed substituted species may in this case suffer, however, from the simultaneous formation of all statistically possible sulfide combinations.

The optical properties of mixedly substituted three-electron bonded radical cations $(\mathrm{R^i,R^jS} \therefore \mathrm{SR^i,R^j})^+$ basically follow the same trend as has been observed for symmetrically substituted species $(\mathrm{R_2S} \therefore \mathrm{SR_2})^+$. In fact, they can even quantitatively be accommodated in the same linear free energy relationship between $\lambda_{\max}$ and Taft's inductive σ^* parameter. Deviations can probably best be rationalized by the influence of bulky substituents on 'σ-lone pair' interactions as a result of structural distortions.

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