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Formation of Intramolecular Three-Electron-Bonded 2σ/1σ* Radical Cations upon Reduction of Dialkylsulfinyl Sulfides by H-Atoms

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The reaction of H-atoms with sulfinyl sulfides $RS(CH_2)_nSOR'$ (R, R′ = alkyl) in strongly acidic aqueous medium leads, among other reactions, to the reduction of the sulfoxide moiety. This results in the formation of a $S^{\bullet+}$ radical cation entity which coordinates with the original sulfide moiety to yield the $(>S\therefore S<)^+$ three-electron-bonded 2σ/1σ* radical cation. The optical properties of this reductively generated species are identical to those for the transients obtained previously upon one-electron oxidation of dithiaalkanes. At sulfinyl sulfide concentrations in the $10^{-4}-10^{-2}$ M range the $H^\bullet$-atom-induced process occurs intramolecularly. The most stable three-electron-bonded radical cation is formed when the two interacting sulfurs are linked via a $-(CH_2)_3-$ chain and a five-membered ring structure can be established. The yields of the $(>S\therefore S<)^+$-type transients range from $G = 0.2-0.7$ (species per 10 J absorbed energy) with the high value pertaining to the reduction of $MeS(CH_3)_3SOMe$ (0.01 M) in aqueous, N_2-purged, 3 M $HClO_4$ solutions. These yields are significantly below the yield of $H^\bullet$-atoms, indicating competing processes such as H-atom abstraction and reaction of $H^\bullet$ with 2-methyl-2-propanol (which was added for removal of $^\bullet OH$ radicals). The rate constant estimate of $(1.8 \pm 0.2) \times 10^7$ M^{-1} s^{-1} for the reaction of $H^\bullet + MeS(CH_2)_3SOMe$ appears to be typical with respect to the order of magnitude for the $H^\bullet$-induced reduction of the sulfoxide moiety. Electrochemical cyclic voltammetry experiments on the oxidation of $RS(CH_2)_nSR'$, $RS(CH_2)_nSOR'$, $RSO(CH_2)_nSOR'$, and $RS(CH_2)_nSO_2R'$ showed relatively little influence of the sulfur-linking alkyl chain length and the nature of the terminal alkyl substituents except for the dithiaalkanes. This may indicate the lack of any significant electronic interaction between the S and SO moieties in the alkylsulfinyl sulfides, SO and SO, in the bis(alkylsulfinyl)alkanes, and S and SO_2 in the alkylsulfonyl sulfides. The electrochemical data further suggest that, concerning $RS(CH_2)_nSOR'$, the lower oxidation potential pertains to the oxidation of the sulfide moiety (yielding $RSO(CH_2)_nSOR'$). The SO → SO_2 oxidation, on the other hand, requires potentials which are more positive by about 0.2 V. It appears that the $RS(CH_2)_3SOR' \rightarrow RS(CH_2)_3SO_2R'$ oxidation prevails when R′ is electron density releasing, while an electron density releasing R favors the $RS(CH_2)_nSOR' \rightarrow RSO(CH_2)_3SOR'$ oxidation.

Introduction

There are many reports on the formation and properties of sulfur-centered three-electron-bonded 2σ/1σ* radical species. Essential aspects have been summarized in a number of review articles.[1−5] Their main characteristics include a relatively weak sulfur−sulfur bond, caused by the presence of the antibonding σ* electron, and strong optical absorptions in the UV/vis. While much information has been gathered from solution experiments using the time-resolving radiation chemical method of pulse radiolysis, essential contributions to the understanding of such species have also been made especially by complementary ESR, photochemical, gas phase, and mass spectrometry and theoretical studies.[6−19]

Radical cations of the type $[R_2S\therefore SR_2]^+$ may be generated, for example, upon oxidation of organic sulfides, while oxidation of thiols or reduction of disulfides typically leads to radical anions, $[RS\therefore SR]^-$. Whenever the parent sulfur organic compound contains only one sulfur atom, such three-electron bond can only be formed intermolecularly. However, if two (or more) sulfur atoms are located in the same molecule, intramolecular sulfur−sulfur coupling is also possible, provided this process is not hindered by steric constraints. All these radical species are of transient nature and exist in equilibria such as the one formulated in eq 1 for the sulfide-derived radical cation $[R_2S\therefore SR_2]^+$.

$$[R_2S\therefore SR_2]^+ \rightleftharpoons R_2S^{\bullet+} + R_2S \qquad (1)$$

The stability of the 3e species is mainly controlled by the equilibrium constant of eq 1, the rate of $S\therefore S$ cleavage, and the deprotonation rate of the molecular radical cation $R_2S^{\bullet+}$. Evaluation of these data was achieved through time-resolved pulse radiolysis measurements and analysis of formation and decay of the strong and characteristic $[R_2S\therefore SR_2]^+$ absorption. The actual data for the all-methylated species ($R = CH_3$) in aqueous solution, for example, are $K = 5 \times 10^{-6}$ M, $k^{\rightarrow} = 1.5 \times 10^4$ s^{-1}, $k_{deprot} = 1.3 \times 10^6$ s^{-1}, and $\lambda_{max} = 465$ nm.[20−22]

The most common ways to generate and study $[S\therefore S]$-bonded radical cations proceeds via oxidation of a sulfide function (e.g.,

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by $^{\bullet}$OH radicals or ^{3}(4-carboxybenzophenone) triplet states),[23−25] followed by coupling of the unpaired p-electron orbital with the doubly occupied p-orbital of a second, unoxidized sulfur. One of the disadvantages intrinsically associated with this mode of generation is that, because of the dominating presence of the three-electron-bonded species, it precludes direct investigation of almost all molecular radical cations, $R_2S^{\bullet+}$. To circumvent this problem, a method is required by which $R_2S^{\bullet+}$ is generated in the absence of free sulfide, i.e., the absence of the nonradical component which pushes equilibrium 1 to the left-hand side. An elegant way to achieve this was found in the reduction of sulfoxides by H-atoms in highly acidic solution (pH < 2).[22,26] The overall stoichiometry is given in eq 2.

$$R_2SO + H^{\bullet} + H_{aq}{}^{+} \rightarrow R_2S^{\bullet+} + H_2O \tag{2}$$

The $R_2S^{\bullet+}$ generated this way exhibited an optical absorption which is significantly blue-shifted relative to that of $(>S\therefore S<)^+$ and peaks in the 280−310 nm range (e.g., at 285 nm for $R = CH_3$). As to be expected, $R_2S^{\bullet+}$ immediately establishes equilibrium 1 upon deliberate addition of small amounts of sulfide. But more interestingly, by adding sulfides with different alkyl substituents than in the sulfoxide, this approach opened a path to mixedly substituted three-electron-bonded radical cations as depicted, for example, in eq 3.

$$R_2S^{\bullet+} + (R')_2S \rightleftharpoons [R_2S\therefore S(R')_2]^+ \tag{3}$$

Such kind of species have also been subject of extensive gas phase, mass spectrometry and theoretical studies which provided, in particular, thermodynamic data on the three-electron bond energies.[11−19]

In our previous reports we have described a representative, although limited, number of intermolecular systems based on the above-outlined sulfoxide reduction. In our present follow-up investigation we now extend our studies to intramolecular analogues. This will be achieved by H-atom-induced reduction of the sulfoxide moiety in molecules which also contain a sulfide function. The technique employed is pulse radiolysis with time-resolved detection of optical absorptions.

The data obtained for the generation of intramolecular $S\therefore S$-bonded species via oxidation of one of the sulfide functions suggested a possible preoxidation p-orbital "lone pair/lone pair" interaction, resulting in more or less separated, doubly occupied σ and σ^* energy levels. This and neighboring group participation, as a general important parameter, would express itself in significantly lower potentials for the electrochemical oxidation of dithia compounds as compared to a simple sulfide, with the actual numbers strongly depending on structural parameters.[27−31] It should be recognized, however, that direct correlations between spectroscopic and electrochemical results must be handled with care, particularly if the electrochemical results do not pertain to reversible processes. In this context it was, nevertheless, of interest if there was also a corresponding electronic ground state interaction or neighboring group participation between the sulfide and sulfoxide moieties in sulfinyl sulfides which could affect the redox behavior. Our optical pulse radiolysis experiments were, therefore, complemented by some electrochemical cyclic voltammetry investigations.

Experimental Section

The alkylsulfinyl sulfides and dithia compounds were synthesized and characterized as reported before.[32] All other chemicals were of reagent grade quality. Aqueous solutions were prepared with "Millipore"-filtered water (ca. 18 MΩ). Solute concentrations were typically of the order of 10^{-2} M or lower, depending on solubility. Acidification of the solution was achieved by appropriate addition of 3 N $HClO_4$.

Radiolysis of aqueous solutions leads to three highly reactive radical species, namely, hydrated electrons ($e_{aq}{}^{-}$), H-atoms ($H^{\bullet}$), and hydroxyl radicals ($^{\bullet}OH$). In neutral solutions they are generated at concentrations, available for reaction in dilute solutions, of approximately 0.29, 0.06, and 0.29 μmol/J of absorbed energy, respectively. Radiation chemical yields are frequently referred as *G* values denoting the number of species generated per 100 eV absorbed energy. In more timely SI terms $G = 1$ corresponds to 0.1034 μmol/J. In order to study selectively the reaction of H-atoms, as in this investigation, hydrated electrons are converted into H-atoms by reaction with protons ($e_{aq}{}^{-} + H_{aq}{}^{+} \rightarrow H^{\bullet}$). In acid solution the total yield of H-atoms amounts, correspondingly, to $\approx$0.35 μmol/J ($G \approx 3.6$). The other potentially disturbing primary radical $^{\bullet}OH$ is usually inactivated by reaction with 2-methyl-2-propanol. The C-centered radical, $^{\bullet}CH_2C(CH_3)_2OH$, resulting from this process via H-atom abstraction, does not engage in redox reactions with alkylsulfinyl sulfides. H-atoms react with 2-methyl-2-propanol in a similar fashion, however, by a more than 3 orders of magnitude lower rate (1.7×10^5 M^{-1} s^{-1}) than $^{\bullet}OH$ (6.0×10^8 M^{-1} s^{-1}).[33] Concentrations of 2-methyl-2-propanol were thus adjusted to about 1 M, ensuring quantitative removal of $^{\bullet}OH$ while allowing H-atoms to at least compete for reaction with the alkylsulfinyl sulfides. All solutions were deoxygenated by purging with N_2 (ca. 1 h/L). Experiments were carried out at room temperature.

Pulse radiolysis was carried out with a 1.5 MeV Van de Graaff accelerator at the Hahn-Meitner-Institute Berlin (Germany). Generally pulses of $\approx$1 μs duration were applied providing an H-atom concentration of about 10^{-6} M. Actual concentrations were determined on the basis of the oxidation of SCN^- to $(SCN)_2{}^{\bullet-}$ by $^{\bullet}OH$ in N_2O-saturated solutions as dosimetry system. Details of the experimental setup and data analysis have been described earlier.[34]

The electrochemical cyclic voltammetry investigations have been conducted with a PAR Model 362 scanning potentiostat with Pt foil as working as well as counter electrode in Ag/AgCl (in saturated solution of LiCl in ethanol). The solvent was acetonitrile and the supporting electrolyte tetrabutylammonium hexafluorophosphate. The Pt electrode was cleaned after each run either by polishing with fine alumina powder or by exposure to an oxidizing flame. The sweep rate was 100 mV/s, and potentials were usually scanned from −0.5 V to +2.5 V.

Results and Discussion

Intramolecular $S\therefore S$ Bonded Radical Cations. Figure 1 shows the transient spectrum obtained upon pulse radiolysis of an N_2-purged solution of 10^{-2} M $MeS(CH_2)_3S(O)$-*t*-Bu, containing also 1 M 2-methyl-2-propanol and 3 N $HClO_4$. It is characterized by a strong and broad absorption band with maximum at 450 nm, and a comparatively much smaller peak at 300 nm. Analysis of the formation kinetics at 450 nm (see inset) revealed an exponential process with the first-order rate being a linear function of the alkylsulfinyl sulfide concentration. From this, a bimolecular rate constant of $(2.0 \pm 0.3) \times 10^7$ M^{-1} s^{-1} has been evaluated. The absorbing transient is relatively long-lived and, under our experimental conditions, decayed with a first half-life of 230 μs via a mixed order process (a more detailed analysis of the decay kinetics has not been attempted in this study).

TABLE 1: λ_{max} and Yields of Intramolecular Three-Electron-Bonded Radical Cations Obtained upon H$^•$-Induced Reduction of Sulfinyl Sulfides and $^•$OH-Induced Oxidation of Corresponding Dithiaalkanes

reduction by H-atoms[a]				oxidation by $^•$OH radicals[b]			
compound	λ_{max}, nm	G	G(rel)[c]	compound	λ_{max}, nm	G	G(rel)[d]
MeS(CH$_2$)$_3$SOMe	440	0.4	0.11	MeS(CH$_2$)$_3$SMe	440	3.4	0.57
MeS(CH$_2$)$_3$SOEt	445	0.5	0.14	MeS(CH$_2$)$_3$SEt	445	3.4	0.57
MeS(CH$_2$)$_3$SO-*i*-Pr	445	0.7	0.19	MeS(CH$_2$)$_3$S-*i*-Pr	450	2.9	0.48
MeS(CH$_2$)$_3$SO-*t*-Bu	450	0.6	0.17	MeS(CH$_2$)$_3$S-*t*-Bu	450	2.7	0.45
EtS(CH$_2$)$_3$SOEt	445	0.5	0.14	EtS(CH$_2$)$_3$SEt	445	2.7	0.45
i-PrS(CH$_2$)$_3$SO-*i*-Pr	450	0.6	0.17	*i*-PrS(CH$_2$)$_3$S-*i*-Pr	455	1.9	0.32
MeS(CH$_2$)$_4$SOMe	465	0.7	0.19	MeS(CH$_2$)$_4$SMe	460	2.9	0.48
MeS(CH$_2$)$_4$SO-*t*-Bu	470	0.6	0.17	MeS(CH$_2$)$_4$S-*t*-Bu	470	2.0	0.33
t-BuS(CH$_2$)$_4$SO-*t*-Bu	480	0.2	0.06	*t*-BuS(CH$_2$)$_4$S-*t*-Bu	485	1.0	0.17
MeS(CH$_2$)$_5$SOMe	470	0.7	0.19	MeS(CH$_2$)$_5$SMe	475	3.1	0.52
i-PrS(CH$_2$)$_5$SO-*i*-Pr	510	0.2	0.06	*i*-PrS(CH$_2$)$_5$S-*i*-Pr	510	1.4	0.23
MeS(CH$_2$)$_6$SOMe	490	0.6	0.17	MeS(CH$_2$)$_6$SMe	490	2.0	0.33

[a] Experiments perfomed with N$_2$-purged solutions containing 0.01 M sulfinyl sulfide, 1 M 2-methyl-2-propanol, and 3 M HClO$_4$. [b] Data from ref 36. [c] G (μmoles per 10 J absorbed energy) calculated on the basis of reported extinction coefficients (ref 36), and an estimated G(H$^•$) = 3.4. [d] G based on G($^•$OH) = 6.0.

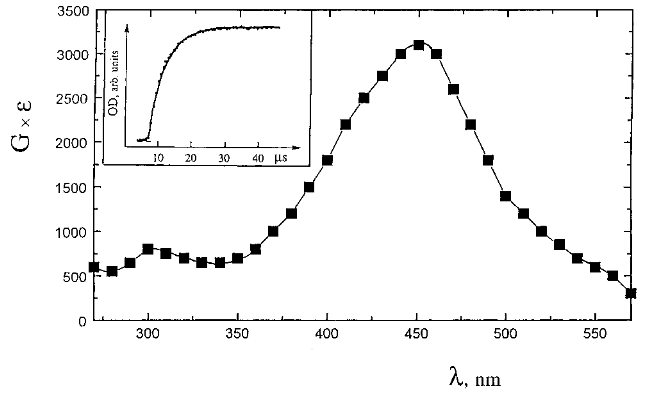
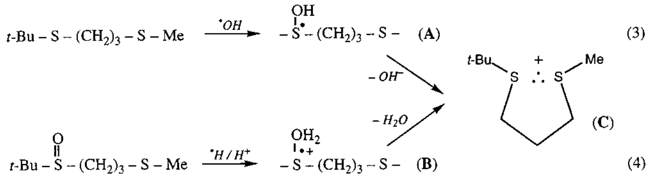


Figure 1. Transient absorption spectrum observed in pulse irradiated aqueous solution containing 0.01 M MeS(CH$_2$)$_3$SO-*t*-Bu, 3 M HClO$_4$ and 1 M 2-methyl-2-propanol. The spectrum was recorded ca. 10 μs after a 1 μs pulse. Inset: Absorption−time trace at 450 nm.

Corresponding experiments have been carried with a large number of other alkylsulfinyl sulfides, RS(CH$_2$)$_n$S(O)R′, with, in principle, similar results. The various λ_{max} of the long-lived absorption are listed in Table 1. For comparison, absorption maxima are also listed for the intramolecular S∴S-bonded radical cations generated upon oxidation of RS(CH$_2$)$_n$SR′.[1,35,36] The excellent agreement of the optical transition energies is taken as proof for the identical structure of the transients. This conclusion is further corroborated by a lack of concentration dependence on the transient's yield, contrasting the situation typically prevailing for the formation of intermolecular 3-e species.

The underlying overall processes for the $^•$OH-induced oxidation of the dithia compounds and the reduction of the alkylsulfinyl sulfide both involve a transitory sulfuranyl state (>S$^•$−OH, **A**, and/or >S$^•$−$^+$OH$_2$, **B**) which then, upon elimination of OH$^-$ or H$_2$O, leads to a sulfur−sulfur three-electron bond coupling in radical cation **C**. This is formulated in eqs 3 and 4 for the methyl/*tert*-butyl-substituted compounds in which the two sulfur functions are separated by three methylene groups.



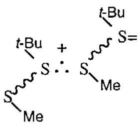
The high stability of this, and corresponding species with other R and R′, arises from the five-membered ring structure the radical cation assumes upon interaction of the two sulfurs. Comparison of the optical (Table 1) and kinetic decay data shows relatively little influence of the terminal alkyl groups. A stronger dependence is observed upon increasing the length of the alkyl linkage between the two sulfurs which, in our present sample systems, affords formation of six-, seven-, and eight-membered rings. The less favorable sulfur−p-orbital overlap in these larger rings results in marked red shifts of the absorptions. All this has been elaborated and discussed already in detail in earlier publications.[1,2,4] In the present study, it is only recorded and presented in support of the identity of the absorbing transient formed in the reduction of the alkylsulfinyl sulfides.

The yields of the **C**-type intramolecular radical cations generated from the alkylsulfinyl sulfides via the reductive route range from $G = (0.2-0.7) \times 10^{-7}$ mol J^{-1}, based on the extinction coefficients determined in our earlier combined optical and conductivity pulse radiolysis experiments on the $^•$OH-induced oxidation of the dithiaalkanes.[23] These G values are considerably smaller than that of the reducing H$^•$-atoms, which is not exactly known for 3 N HClO$_4$ solutions but most likely exceeds $G = 3.4$.[37] Two reasons can be forwarded for the less than unity efficiency for the sulfinyl sulfide reduction. One of them is a competing H-atom reaction with the 2-methyl-2-propanol. Based on the published bimolecular rate constant of $k = 1.7 \times 10^5$ M^{-1} s^{-1} for this process[33] and a 2-methyl-2-propanol concentration of 1 M, a first-order rate constant of 1.7×10^5 s^{-1} is evaluated. The observed first-order rate constant for the formation of the radical cation via reaction 4, as derived from $t_{1/2} \approx 3.8\ (\pm\ 0.2)$ μs, amounts to 1.8×10^5 s^{-1}. This means that only one out of two H-atoms will reduce a sulfoxide function in this competitive scheme, to begin with. Mutual H-atom combination (2H$^•$ → H$_2$) has probably little effect (<10%) as can be estimated from the known combination rate constant[33] and the low H-atom concentration under the prevailing pulse radiolysis conditions. The fact that the radical cation formation occurs exponentially with hardly any noticeable dose dependence also supports this conclusion. However, there are other competing processes which need to be considered, namely, H-atom-induced H-atom abstractions from any of the C−H bonds in the alkylsulfinyl sulfides. These are, indeed, the most likely reactions to account for the remaining deficit. Corroborating evidence can be derived from the yield data, listed in Table 1, on the $^•$OH-induced oxidation of the dithiaalkanes. Even in these latter systems the yields of intramolecular radical cations hardly exceeds the 50% mark despite the fact that the initiating reaction (eq 3 and analogous processes) occurs with practically diffusion controlled rate constants. The relative trends within the series of radical cation yields with increasing number of bridging methylene units may be taken as additional support for this competing H-atom abstraction hypothesis.

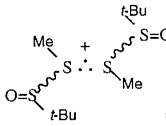
Intermolecular $S\therefore S$ Bonded Radical Cations. With reference to the spectrum shown in Figure 1, it has been noticed that, upon increasing the $MeS(CH_2)_3S(O)$-*t*-Bu concentration to above 10^{-2} M, an additional band begins to emerge in the 500−550 nm region. Solubility limitations prevented, however, experiments at concentrations high enough for this band to become significant. Time-resolved traces recorded in this wavelength region, nevertheless, revealed formation of a transient that had a much shorter lifetime (e.g., $\approx 4\ \mu$s in 2×10^{-2} M solutions) than the intramolecular radical cation. Because of its exclusive appearance at higher solute concentrations and corresponding observations in the $^{\bullet}$OH-induced oxidation of dithiaalkanes we assign this red-shifted band to intermolecularly bonded $S\therefore S$ species.

Two structural possibilities need to be considered. One, namely radical cation **D**, results when the sulfur radical site of the protonated sulfoxide H-atom adduct (**B**) coordinates, under elimination of H_2O, with the sulfide function of a second alkylsulfinyl sulfide molecule. The second possibility arises from an increasing probability of an $^{\bullet}$OH-induced oxidation of the sulfide moiety (in competition to the $^{\bullet}$OH scavenging by 2-methyl-2propanol), followed by an intermolecular reaction of the thus formed **A**-type sulfuranyl radical with the sulfide function of a second alkylsulfinyl sulfide molecule to yield species **E**. The difference between **D** and **E** is the number of remaining sulfoxide functionalities and the alkyl substitution pattern.

Our earlier studies on three-electron-bonded radical cations have shown electron density releasing substituents at the central sulfur atoms, as well as steric constraints exerted by them on the sulfur−sulfur p-orbital overlap, cause a red shift in absorptions. They also revealed that these red shifts are more pronounced in intermolecular species than in the more rigid intramolecular entities. Remotely located functionalities, on the other hand, generally have little effect. On this basis, species **D** should probably absorb slightly further in the red than **E**. However, by comparison with the *inter*molecular radical cation $[(Me,t\text{-}Bu)S\therefore S(Me,t\text{-}Bu)]^{+}$, which absorbs at 510 nm, and $[(Me,t\text{-}Bu)S\therefore SMe_2]^{+}$, which has not been measured but by extrapolation should absorb between 510 and 465 nm (the latter λ_{max} referring to $[Me_2S\therefore SMe_2]^{+}$),[20] the difference will not be very big. Given also the probably somewhat greater steric constraints expected to apply for **D** and **E**, the 500−550 nm range observed for our presumed *inter*molecular species appears to be of the right order for either species.



(**D**)



(**E**)

The formation of **E** would just be controlled by the competition of $^{\bullet}$OH with 2-methyl-2-propanol and the alkylsulfinyl sulfide. Since the rate constant for the $^{\bullet}$OH + 2-methyl-2-propanol is about 1 order of magnitude below that for the $^{\bullet}$OH + alkylsulfinyl sulfide reaction, which by analogy with similar reaction partners should be a diffusion-controlled event, the onset at $\geq 10^{-2}$ M alkylsulfinyl sulfide concentration would be right on target. (Variation of the alkylsulfinyl sulfide/2-methyl-2-propanol concentration ratio is, in principle, a possibility to verify this scheme. However, solubility problems, which include the role of 2-methyl-2-propanol as a cosolvent, did not allow unambiguous experiments along this line).

The generation of **D**, on the other hand, implies that its bimolecular formation process effectively must compete with the intramolecular cyclization according to eq 4. From the observed onset of the **D** formation, a lower limit first-order rate of about 10^8–10^9 s^{-1} can be extracted for the cyclysation part of reaction 4. Clearly, this is too fast for the latter to become the rate determining and thus a directly observable step in our system. However, if this scheme applies in principle, it raises an interesting question. In the oxidation of dithiaalkanes, to yield the intramolecular radicals **C** (via eq 3), a ground state electronic interaction between the two sulfur centers prior to the oxidation, and leading to doubly occupied σ and σ^* energy levels, has been discussed. The oxidation would then just require removal of an antibonding electron accompanied by a further collapse of the sulfur−sulfur interaction into the three-electron bond.[27,31] Electrochemical CV experiments are, at least with respect to the observed trend, fully in line with this consideration. Under this type of scenario the above-estimated first-order rate constant might still be much too small to account for the further collapse of the S−S bond. In general terms, such a consideration requires existence of a corresponding sulfoxide−sulfide interaction already in the alkylsulfinyl sulfide ground state. This aspect will be further pursued in the final electrochemical section of this paper.

Another interesting observation is the relatively short lifetime of the suggested **D** and/or **E** transients. Usually the decay of such three-electron-bonded species occurs on the upper microsecond to millisecond time scale,[23] but half-lives of just a few microseconds have also been observed, e.g., for the bimolecular $S\therefore S$ bonded species obtained upon oxidation of methionine in acid solution.[38] The decay usually reflects either equilibration with the monomer radical cation (see eq 1) followed by deprotonation of the latter, or deprotonation of the three-electron-bonded species itself.[21] The former scenario, given a diffusion-controlled rate for the forward reaction of eq 1 and an extrapolated (from the concentration onset) equilibrium constant of about 10 M^{-1} for the current system of interest, would yield an $S\therefore S$ dissociation rate constant of 10^8−10^9 s^{-1}. This high value would render the deprotonation of the monomer radical cation, $>S^{\bullet+}$, the rate-determining step for the decay in our present system. The measured rate constants of about 2×10^5 s^{-1} ($t_{1/2} \approx 4\ \mu s$) would then apply to this particular process. However, considering the high (both thermodynamic and kinetic) stability of the intramolecular radical cation **C** one should expect that on the nanosecond time scale the $S^{\bullet+}$ species, besides being involved in the equilibrium with **D**, also cyclizes to the long-lived **C** (see above). The observed first-order decay could then not apply to either the monomer, $>S^{\bullet+}$, or **C** but would have to be assigned to the deprotonation of the three-electron-bonded radical cation. Deprotonation, irrespective from which species, requires favorable alignment of an orbital carrying the unpaired electron and the C−H σ-bond which loses the proton.[2] Although the half-filled σ^* orbital in $S\therefore S$ fulfills this requirement probably to a lesser extent than the half-filled p-orbital in $S^{\bullet+}$, the molecular geometry in **D** (and/or **E**) may still be satisfactory.

Electrochemical Oxidation of Alkylsulfinyl Sulfides. As mentioned already, electrochemical cyclic voltammetry (CV)

TABLE 2: Oxidation Peak Potentials for Dimethyl Sulfide, Dimethyl Sulfoxide, MeS(CH$_2$)$_n$SMe, and MeS(CH$_2$)$_n$SOMe (with n = 1, 3, and 5) in Acetonitrile Solutions[a]

compound	(1) $E_{p(ox)}$ (V)	(2) $E_{p(ox)}$ (V)	(3) $E_{p(ox)}$ (V)	compound	(1) $E_{p(ox)}$ (V)	(2) $E_{p(ox)}$ (V)
MeSMe	1.93			MeSOMe	2.18	
MeSCH$_2$SMe	1.70			MeSCH$_2$SOMe	1.80 (sh)	2.2 (sh)
MeS(CH$_2$)$_3$SMe	1.32	1.90 (sh)	2.15	MeS(CH$_2$)$_3$SOMe	1.74	2.2 (sh)
MeS(CH$_2$)$_5$SMe	1.50	1.90	2.08	MeS(CH$_2$)$_5$SOMe	1.85	2.1

[a] Supporting electrolyte: tetrabutylammonium hexafluorophosphate. Electrode: Pt. Counter electrode: Ag/AgCl in LiCl-saturated ethanol solution. Sweep rate: 100 mV/s. Scanning range: −0.5 to 2.5 V.

experiments on the oxidation of dithiaalkanes have indicated that the second sulfur, particularly if aligned favorably for possible p-orbital overlap, significantly enhances the oxidizability of these compounds as compared to simple sulfides. For example, the first oxidation peak potential for MeS(CH$_2$)$_3$SMe was observed at 0.742 V while for MeSMe the corresponding value was 1.450 V (both measured against 0.1 M Ag/AgNO$_3$ in acetonitrile).[27,31] In order to see whether a similar effect (neighboring group participation) exists between the sulfoxide and sulfide moieties, corresponding CV experiments were now conducted with a series of alkylsulfinyl sulfides.

For comparison of the above-mentioned dithiaalkane data with those obtained now on alkylsulfinyl sulfides it must be realized that both sets of experiments have been conducted in different solvents and against different reference electrodes. This means that the absolute numbers are not directly comparable without adjustment. Meaningful conclusions can, nevertheless, be drawn from the trends observed within a given series of compounds which are subjected to the same experimental conditions. The present data, obtained in acetonitrile solutions against a Ag/AgCl electrode (in LiCl-saturated ethanol) and with tetrabutylammonium hexafluorophosphate as electrolyte, are about 0.5−0.6 V higher than in the above cited acetonitrile system when taking the MeS(CH$_2$)$_3$SMe and MeSMe results as reference points. It should also be pointed out that practically all experiments, including those on the oxidation of alkylsulfinyl sulfides and sulfoxides, revealed irreversible waves. Furthermore, the investigations were restricted to oxidations since on the reductive side the only assignable process appeared to be the reduction of protons.

Table 2 lists oxidation peak potentials obtained for a series of MeS(CH$_2$)$_n$SMe and MeS(CH$_2$)$_n$SOMe with $n = 1$, 3, and 5 under the above-mentioned conditions. The control experiments with the dithia compounds essentially confirmed previous findings, especially that the first peak potential for the $n = 3$ compound is significantly lowered. Earlier studies, incidentally, have revealed that all the electrochemical oxidations are overall two-electron events, i.e., the first oxidation wave leads directly to the dication, $-S^{2+}-$, or corresponding sulfoxide, −SO−, even at the highest possible scan rates.[27,39] Mechanistically, these 2-e oxidations are, nevertheless, likely to be the result of two one-electron processes. In most cases, the sequence of the two 1-e steps cannot be resolved because the initial oxidation of the sulfide to the radical cation is energetically more demanding, i.e., occurs at more positive potentials, than the subsequent oxidation of the radical cation to the dication. Two steps could, however, be resolved in the reduction of some mesocyclic and acyclic sulfoxides by iodide at excess reductant, as has been described by Musker et al.[40] Their results clearly indicate the intermediacy of sulfur−sulfur three-electron-bonded radical cations. Another interesting example providing also direct evidence for such a transient is the electrochemical oxidation of 1,5-dithiacyclooctane. As evaluated in detail by Wilson et al.,[28,41] it shows that formal potentials for both the first and second oxidation step can be extracted from current−voltage curves even if the second step is more facile (here by 20 mV) than the first step. This was, however, only possible because of the reversibility of the involved redox events. Since this is not given in our present systems it can, therefore, in all likelihood be assumed that the first electrochemical oxidation step of the dithia compounds yields directly the corresponding alkylsulfinyl sulfides, i.e., the 2-e oxidation product.

The second peak potentials in the MeS(CH$_2$)$_n$SMe series are observed at about 1.9 V. They are, however, only detectable for the $n = 3$ and $n = 5$ systems, and also only as more or less pronounced shoulders. Since they match those for the oxidation of an isolated sulfide function, the second peak is attributed to the oxidation of the second, originally unoxidized sulfur. The fact that, upon variation of n, there is no lowering of the potential anymore can be taken as an indication for the absence of any significant neighboring group effect in the alkylsulfinyl sulfides.

A third peak potential in the oxidation of dithia compounds is observed in the 2.1−2.2 V range. By comparison with the oxidation of simple sulfoxides, this appears to be characteristic of the −SO− oxidation to the corresponding sulfone, $-SO_2-$, functionality.

The same experiments conducted with alkylsulfinyl sulfides practically confirm these assignments. The first oxidation peak potentials, in this case, are correspondingly attributable within reason only to the oxidation of the sulfide function. The measured values are only marginally lower than for the oxidation of dimethyl sulfide (1.93 V). Even for MeS(CH$_2$)$_3$SOMe the peak potential drops only by about 0.2 V, to 1.74 V. Second oxidation peak potentials are found at 2.1−2.2 V and they match, as expected, the oxidation of an isolated sulfoxide group.

The main conclusion that can be drawn from these results with dithiaalkanes and alkylsulfinyl sulfides is that there is only very little, if any, apparent neighboring group effect in alkylsulfinyl sulfides. Three reasons may be forwarded for this which may even be operative all together to some extent: (i) Because of the large difference of the HOMO energy levels of the sulfide and sulfoxide groups, the σ and σ^* energy levels resulting from an electronic interaction between these two functionalities may not differ very much from the original HOMOs; consequently the oxidative removal of a σ^*-electron would require only little less energy than for the removal of a nonbonding, noninteracting sulfide HOMO electron. (ii) Sulfur−sulfur orbital interaction is probably not as extensive in alkylsulfinyl sulfides as in dithiaalkanes because the sulfoxide moiety does not provide a sulfur p-orbital anymore but only an s-orbital. (iii) Possible steric constraints which prevent optimal interaction may be more pronounced in the alkylsulfinyl sulfides. The overall result and conclusions are further corroborated by some specific examples on three-electron-bonded species involving sulfoxides and, in more general terms, experimental and theoretical data on $X \therefore Y$ species obtained upon interaction of two different heteroatoms, i.e., centers of significantly different electronegativities.[2,31,42]

Further supporting data have been gathered in the present investigation by measuring the oxidation peak potentials ($E_{p,ox}$) of a large variety of alkylsulfinyl sulfides with varying terminal alkyl groups (Me, Et, *i*-Pr, *t*-Bu; for R = R′ and R ≠ R′) and chain length between the sulfide and sulfoxide moieties. The first $E_{p,ox}$ show only a small effect upon variation of the linking chain (e.g., 1.75 ± 0.05 V for $RS(CH_2)_3SOR'$ and 1.87 ± 0.01 V for $RS(CH_2)_6SOR'$) while the terminal alkyl groups exhibit no apparent influence at all.

Oxidation of $RS(CH_2)_nSO_2R'$, with the unoxidized sulfide function being the only possible oxidation site, requires 1.98 (±0.04) V. This is an only slightly more positive potential than the 1.92 (±0.02) V necessary, on average, for the oxidation of simple sulfides RSR′. It is, therefore, probably safe to assume that the first $E_{p,ox}$ for $RS(CH_2)_nSOR'$ and the second $E_{p,ox}$ for $RS(CH_2)_nSR'$ (from which $RS(CH_2)_nSOR'$ are generated in the first oxidation step) refer to the same process, namely, the oxidation of the remaining sulfide moiety (−S− → −SO−). The second oxidation peaks in the $RS(CH_2)_nSOR'$ series (2.15 ± 0.05) and third ones in the $RS(CH_2)_nSR'$ series (2.1 ± 0.1 V), accordingly, are attributed to the seemingly more difficult oxidation of the sulfoxide to the respective sulfone moieties, i.e., $-SO- \rightarrow -SO_2-$). This is fitting considering the potentials required for the oxidation of the simple sulfoxides, R_2SO (2.12 ± 0.06 V).

Generally, the efficiency of the oxidation of $RS(CH_2)_nSOR'$ to yield $RSO(CH_2)_nSOR'$ is found to be lower than that for the formation of $RS(CH_2)_nSO_2R'$. In fact, no evidence for significant amounts of bis(alkylsulfinyl)alkanes generated by electrochemical means has been reported. This is corroborated by our results in that most of the peak potentials in the 1.8−1.9 V range, which would refer to a presumed $RS(CH_2)_nSOR' \rightarrow RSO(CH_2)_nSOR'$ oxidation, showed only up as shoulders in the CVs. However, some of the longer chain $RS(CH_2)_nSR'$ compounds (≥4) and those carrying strongly electron density releasing alkyl groups R at the sulfide function (in $RS(CH_2)_nSR'$ and $RS(CH_2)_nSOR'$) exhibited comparatively more pronounced waves in this potential range, while at the same time the corresponding 2.1−2.2 V ($-SO- \rightarrow -SO_2-$) waves diminished to shoulders. This would indicate that the formation of bis(alkylsulfinyl)alkanes is not impossible in the oxidation of alkysulfinyl sulfides but that the efficiency of this process is low and depends on the nature of the terminal alkyl substituents and the central chain length. No attempt has, however, been made to follow this up in more quantitative detail within the scope of this study.

One interesting question which has often been raised in the early days of intramolecular three-electron bond formation in dithia compounds concerned the possibility to see, by time-resolved optical spectroscopy, the intramolecular folding dynamics which brought the two interacting heteroatoms together after one of them had been oxidized. The existence of a preoxidation interaction explains why no such dynamics could be experimentally observed. The radical-induced oxidation process was simply too slow to allow resolution of what is the only subsequent process, namely, the collapse from the $2\sigma/2\sigma^*$ to the $2\sigma/1\sigma^*$ structure. The same original question may, however, be posed for the alkylsulfinyl sulfides for which our present data suggest only a small, if any, preexisting S ↔ SO interaction or neighboring group participation. Consequently, the coupling of the reduced sulfoxide moiety with the unoxidized sulfur to yield the intramolecular $S\therefore S$ bonded radical cation may require much more substantial structural changes, i.e., longer times to be achieved. However, under the conditions prevailing in our present experiments the initial reduction of the sulfoxide moiety still is too slow for any identification of such molecular dynamics, e.g., via a change in the transient spectral characteristics. A photochemically mediated reductive quenching of a sufficiently reducing excited state by the sulfoxide moiety in alkylsulfinyl sulfides may perhaps be a promising approach in future studies.

Conclusion

It has been demonstrated that one-electron oxidation of dithiaalkanes and reduction of alkylsulfinyl sulfides lead to the same transient, namely, a three-electron-bonded radical cation with an intramolecular $S\therefore S$ coupling. The latter can thus be viewed as a key intermediate between the sulfide and sulfoxide oxidation state. Complete reversibility is affected, however, by a deprotonation process which involves both the $S^{\bullet+}$ moiety and its conjugate $(>S\therefore S<)^+$. The reduction of the sulfoxide moiety by $H^\bullet$-atoms (in acid solution) is relatively slow, with rate constants in the 10^5 M^{-1} s^{-1} range. Consequently, the overall efficiency of the reaction leading to the three-electron-bonded species is relatively small. Cyclic voltammetry experiments with alkylsulfinyl sulfides show little effect of the sulfur-linking alkyl chain and terminal alkyl groups. One possible interpretation is the lack of any ground state interaction between the sulfide and sulfoxide moieties with the consequence that any structural dynamics leading to the three-electron-bonded species pertain to the time after the sulfoxide moiety has been reduced.

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