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Registry No. 2, 78305-12-1; 3, 89046-70-8; 4, 100899-04-5; 5, 100899-05-6; 6, 100899-06-7; 7, 100899-07-8; 8, 100899-08-9; 9, 89046-69-5; 10, 100899-09-0; 11, 100899-10-3; 12, 100899-11-4; 14, 100899-12-5; 16, 98078-51-4; 17, 100899-14-7; 19, 98078-52-5; 20, 100899-13-6; 2,2,5,5-tetramethylcyclopenteneselone, 79958-61-5; 2,2,6,6-tetramethylcyclohexaneselone, 87842-37-3; diphenyldiazomethane, 883-40-9.

Three-Electron-Bonded Sulfur-Centered Radical Cations and Possible Ylide Formation during the Oxidation of Various 1,3-Dithiacyclopentanes

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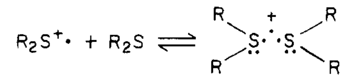
Transient radical cations with intramolecular S∴S three-electron bonds have been identified in the ·OH and Tl^{2+} induced oxidation of various 1,3-dithiacyclopentanes and 2,2-dimethyl-1,3-dithiacyclohexane. The stability of these three-electron-bonded species is greatly enhanced by dialkylation at C-2. This is attributed to the establishment of a conformation which favors sulfur–sulfur p-orbital interaction. The relative thermodynamic stability of the intramolecular S∴S bond is reflected in optical absorptions; λ_{max} increases with decreasing stability from 550 to 650 nm. Optical absorption spectra with λ_{max} ranging from 275 to 320 nm have been measured for neutral, predominantly carbon-centered radicals which are formed upon deprotonation of the radical cations. If C-2 centered, these radicals decay via second-order ionic disproportionation. The cationic products generated in this process and also via one-electron oxidation of the C-2 radicals are considered to stabilize by deprotonation to sulfur ylides and establishment of resonance structures.

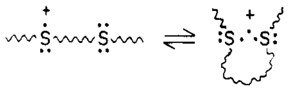
Introduction

In a number of studies we have demonstrated that the optical absorption of three-electron-bonded radical cations of the general nature (>S∴S<)$^+$ obtained in the one-electron oxidation of organic sulfides are a sensitive probe for structural parameters.[1–6] The underlying rationale is that the unpaired p electron of an oxidized sulfur atom has a high tendency to coordinate with a free p-electron pair of a second sulfur. this leads to the establishment of an equilibrium,[7] e.g., as formulated for monosulfides (eq 1). Oxidation of di- (and poly-) thia compounds (except disulfides) may at low solute concentrations also lead to intramolecular stabilization as has been observed for open chain[3,4] and cyclic dithia[1–4,8,9] compounds in the equilibria (eq 2 and 3).



(1)

I



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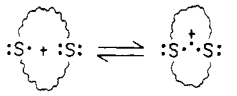
II



(3)

III

Three-electron bonds in I–III contain two bonding σ electrons and one antibonding, i.e., bond-weakening σ* electron.[4] The optical absorptions of these three-electron-bonded systems have experimentally been shown[1–6,10] and theoretically verified[11] to be attributable to a—in first approximation —σ→σ* transition[12] and thus to be a measure for the three-electron bond strength (at least for aliphatic R$_2$S∴SR$_2$$^+$). Generally, an increasing bond strength is associated with a blue shift in optical absorption and vice versa. Optimum conditions for the stabilization of an intramolecular radical cation of type III are given, for example, in 1,5-dithiacyclooctane, i.e., for a molecule which has three carbon atoms each located between the two interacting sulfur atoms. Such a configuration ensures an excellent p-orbital overlap, and λ_{max} = 400 nm has been observed.[3,4] Only a much weaker interaction of sulfur p orbitals (which are perpendicular to the carbon–sulfur–carbon plain) is possible in the corresponding species from 1,3-dithiacyclohexane, for example, for which a considerably red-shifted absorption maximum at 600 nm is observed.[2] No long-lived intramolecular S∴S bonded radical cation could finally be detected in the oxidation of the relatively planar 2-methyl-1,3-dithiacyclopentane.[3,4] In view of the flexibility which nevertheless appears to exist to a certain extent in five-membered rings[13–22] and which may assist some sulfur–sulfur interaction, we now con-

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(12) The σ-energy level contains a contribution from the nonbonding s electrons of the sulfur atoms.[11]

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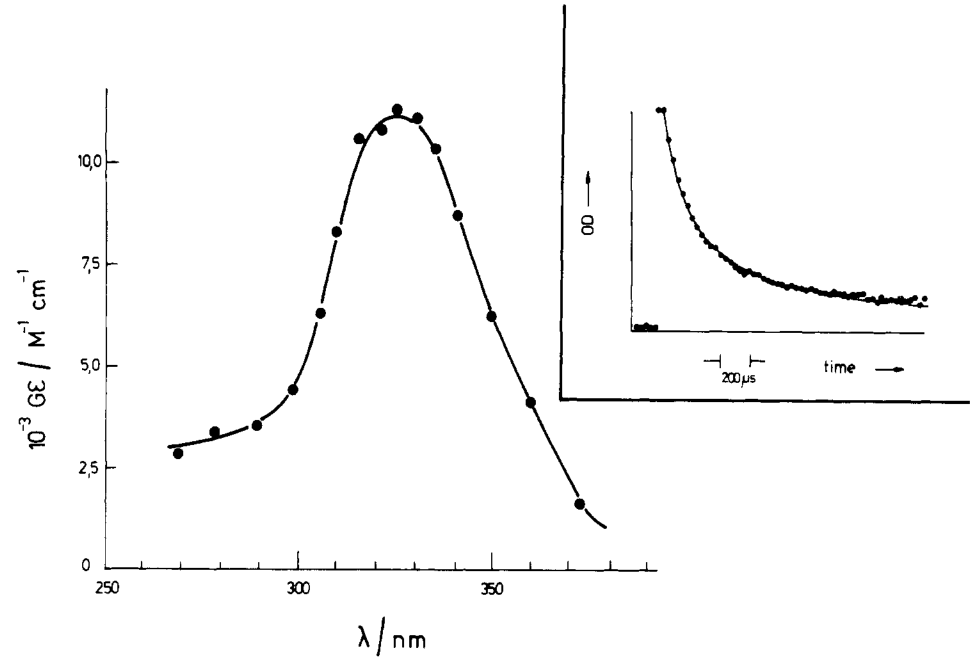
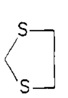
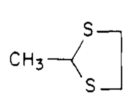


Figure 1. Absorption spectrum of IV-1/IV-2 recorded immediately after application of a 1-μs pulse (6.7 Gy) to an N_2O saturated, pH ~ 4 solution of 10^{-4} M 1,3-dithiacyclopentane (IV). Insert: Absorption vs. time trace recorded at 325 nm in the same solution.

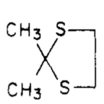
ducted a more detailed study on the radical-induced oxidation of various 1,3-dithiacyclopentanes (IV–IX) and 2,2-dimethyl-1,3-dithiacyclohexane (X).



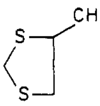
IV



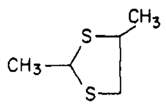
V



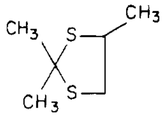
VI



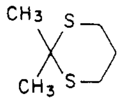
VII



VIII



IX



X

The investigation has been focussed in particular on the effect of methyl substitution on the orientation of the sulfur p orbitals, i.e., possible S∴S three-electron-bond formation, and also on the identification and the fate of other transients.

Experimental Section

The dithia compounds (IV–X) were synthesized according to a method described in principle by Ch.-H. Fischer.[3,23] It is essentially based on a condensation of a dithiol (1,2-ethanedithiol and 1,2- and 1,3-propanedithiol) with a carbonyl function (1,3,5-trioxane, acetaldehyde, or acetone). Identification of the compounds was achieved by mass spectrometry and NMR. Purification to ≥99% was done by fractional distillation or recrystallization.

The solvent used in all experiments was deionized, "Millipore" filtered water, the quality of which corresponded to triply quartz distilled water. Adjustments of pH were achieved by addition of $HClO_4$. Solutions were always deoxygenated by bubbling with purified N_2 and N_2O (ca. 1 h per dm^3 solution). The latter gas was used to convert hydrated electrons into hydroxyl radicals via $N_2O + e^-_{aq} \rightarrow N_2 + OH^- + \cdot OH$. In such solutions the ·OH radical is formed with a total radiation chemical yield of $G \approx 6$ (species per 100 eV absorbed energy) and is practically the only primary radical species available for reaction with other solutes.[24]

Irradiations were carried out by exposing the solutions to short pulses of high-energy electrons from 1.55- or 3.8-MeV Van de Graaff accelerators at typical pulse durations of 1 μs and 50 ns for the two machines, respectively. Absorbed doses per pulse were generally in the range of 3–10 Gy (1 Gy = 1 J kg^{-1} = 100 rad) corresponding to a concentration of ca. (2–6) × 10^{-6} M ·OH radicals.

Experimental details on the pulse radiolysis technique, dosimetry, and analysis of time-resolved optical and conductivity measurements have been described already.[24] All experiments were carried out at room temperature.

Results

(1) Oxidation of 1,3-Dithiacyclopentane. The most prominent transient species which results from ·OH reaction with the unsubstituted 1,3-dithiacyclopentane IV (10^{-4} M) exhibits a UV absorption and a lifetime of several hundred μs under our pulse radiolysis conditions. Its optical absorption spectrum recorded immediately after a 1-μs pulse is shown in Figure 1 and seen to have a maximum at 320 nm. An absorption-time trace monitored at this wavelength and shown in the insert reveals that the absorbing species is generated practically instantaneously. It then decays to products which incidentally exhibit no optical absorption in the experimentally scanned 260–700 nm range.

Simultaneous time-resolved conductivity measurements did not show any change in conductance in the irradiated solution associable with this transient. This unambiguously identifies it as an overall neutral species.

The same transient, i.e., a species with identical characteristics is generated if the oxidation of IV is induced

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(16) Wilson, G. E., Jr.; Huang, Muy Guey; Bovey, F. A. *J. Am. Chem. Soc.* **1970**, *92*, 5907.

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(23) Fischer, Ch.-H. *Justus Liebigs Ann. Chem.* **1981**, 1899.

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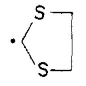
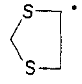
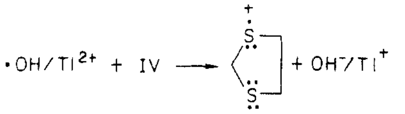
by Tl^{2+} ions instead of ·OH radicals. These investigations were carried out with N_2O saturated, pH 3–4 solutions containing 2×10^{-3} M Tl^+ besides 10^{-4} M IV. Under these conditions the ·OH radicals react almost quantitatively with Tl^+ to yield Tl^{2+} prior to direct reaction with IV.

Considering all these observations and their analogy to the oxidation of simple aliphatic sulfides,[1,25–27] this long-lived transient optical absorption can be assigned to the α-thioalkyl radicals IV-1 and/or IV-2.


IV-1


IV-2

Formation of such carbon-centered radicals is known to proceed mainly via deprotonation of sulfur-centered radical cations,[7,28] i.e., in this case via the reaction sequence as in eq 4 and 5. (In the ·OH induced process formation of IV-3

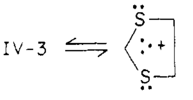


(IV-3) (4)

$$\text{IV-3} \longrightarrow H^+_{aq} + \text{IV-1/IV-2} \qquad (5)$$

is likely to be preceded by a very short-lived ($t_{1/2} \ll 1$ μs)·OH adduct at sulfur[7,29]).

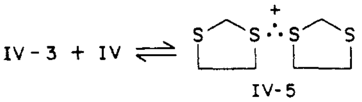
A competing process with reaction 5 is in principle a stabilization of the oxidized sulfur center in a sulfur–sulfur three-electron bond. At low solute concentration this is envisaged as an intramolecular process in the equilibrium as in eq 6.



IV-4 (6)

Owing to the high degree of planarity of the five-membered ring which is not very suitable for the necessary sulfur p-orbital overlap only a low if any detectable yield is expected. Time-resolved optical and conductivity pulse radiolysis experiments in the submicrosecond time range with 50 ns pulses do indeed indicate such a radical cation with an optical absorption >600 nm. Its very low yield which is estimated to $G < 0.3$ from conductivity measurements (for evaluation of conductivity data see next section) and its very short lifetime ($t_{1/2} \lesssim 0.3$ μs) do not allow any further quantification though.

Additional evidence for a radical cation as the intermediate stage is provided, however, by formation of an intermolecular three-electron-bonded radical cation (see eq 7) (analogous to species I[2–4,7]) at higher solute concentrations and an absorption around 520 nm. The measurable yield of IV-5 is also only small owing to the fast and irreversible deprotonation of IV-3 and the low solubility of IV. The unstabilized radical cation IV-3 itself can incidentally be excluded as cause for the VIS/IR absorption since such electronic configurations have been found to absorb in the 300-nm range.[2,29]



IV-5 (7)

Considering the yields and particularly the lifetimes of the various transient species, it can be expected that the chemistry of the oxidized 1,3-dithiacyclopentane system will markedly reflect the properties of the neutral radicals IV-1/IV-2. α-Thioalkyl radicals in general are known to be reductants and readily react, for example, with tetranitromethane.[27] This reaction does indeed occur with IV-1/IV-2, namely

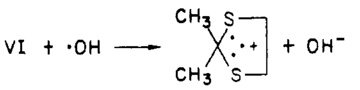
$$\text{IV-1/IV-2} + C(NO_2)_4 \rightarrow C(NO_2)_3^- + NO_2 + \text{products} \qquad (8)$$

It can be monitored through the decay of the IV-1/IV-2 absorption (lower wavelength side) or better through formation of the stable $C(NO_2)_3^-$ absorption (λ_{max} = 350nm, ϵ = 15 000 $M^{-1}\,cm^{-1}$). The bimolecular rate constant derived from experiments with varying $C(NO_2)_4$ concentrations amounts to $k_8 = (4.3 \pm 0.5) \times 10^9\ M^{-1}\,s^{-1}$.[30] The yield of $C(NO_2)_3^-$ was measured to $G = 5.5$ which accounts practically for all ·OH radicals initially available for reaction with IV.

In the absence of suitable partners the IV-1/IV-2 radicals decay via a process which is mostly of second-order. The first half-life at an applied dose of 6.7 Gy (corresponding to 3.8×10^{-6} M radical concentration) in the Figure 1 experiment was measured to $t_{1/2}$ = 190 μs.

(2) Oxidation of 2,2-Dimethyl-1,3-dithiacyclopentane. A qualitatively significantly different picture with respect to transient formation is obtained for the oxidation of 2,2-dimethyl-1,3-dithiacyclopantane (VI). The transient absorption spectrum recorded immediately after a 1-μs pulse to an N_2O saturated pH ≈4 solution of 10^{-4} M VI is now dominated by a long-lived (first half-life of 100 μs at a dose of 7 Gy) and broad band in the vis/IR range with a maximum around 610 nm. In addition, the spectrum (shown in Figure 2) also includes a UV band with a maximum around 275 nm which decays with a first half-life of 130 μs at 7 Gy. The differences in lifetime of the two bands clearly indicate the presence of more than one species.

Time-resolved traces of the optical absorption at 610 nm and of the conductivity are exhibited in the insert of Figure 2. The latter is seen to become negative immediately after the pulse and then decays (increases) with the same kinetics ($t_{1/2} \approx$ 100 μs) as the optical signal decays. The direction of the conductivity signal reveals the formation of a positively charged transient.[31] On the basis of the combined data and corresponding findings in the oxidation of various open-chain and some larger cyclic dithia compounds[1–4] we assign the 610-nm band to the intramolecular three-electron-bonded radical cation VI-4 formed in the overall reaction[32] (eq 9).



(VI-4) (9)

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[25] Hiller, K.-O.; Masloch, B.; Göbl, M.; Asmus, K.-D. *J. Am. Chem. Soc.* **1981**, *103*, 2734.

[26] Hiller, K.-O.; Asmus, K.-D. *Int. J. Radiat. Biol.* **1981**, *40*, 597.

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[29] Mönig, J.; Göbl, M.; Asmus, K.-D. *J. Chem. Soc. Perkin Trans 2* **1985**, 647.

[30] Reduction of tetranitromethane (TNM) by α-thioalkyl radicals has in several cases been found to proceed via a short-lived adduct.[27] This may also be true for the present system but would be difficult to detect since the absorption of IV-1/IV-2 and $C(NO_2)_3^-$ are close together. At the TNM concentrations used ($\leq 10^{-4}$ M) the measured half-lives for IV-1/IV-2 decay and $C(NO_2)_3)^-$ buildup were identical and inversely proportional to TNM concentration within the experimental limit of error, i.e, an adduct was not indicated.

[31] Asmus, K.-D.; Janata, E. In "The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis"; Baxendale, J. H.; Busi, F., Eds.; D. Reidel: Amsterdam, 1982; pp 91–113.

[32] As in all other cases the mechanism is considered to proceed via a short-lived ·OH adduct at sulfur with subsequent ionic dissociation.

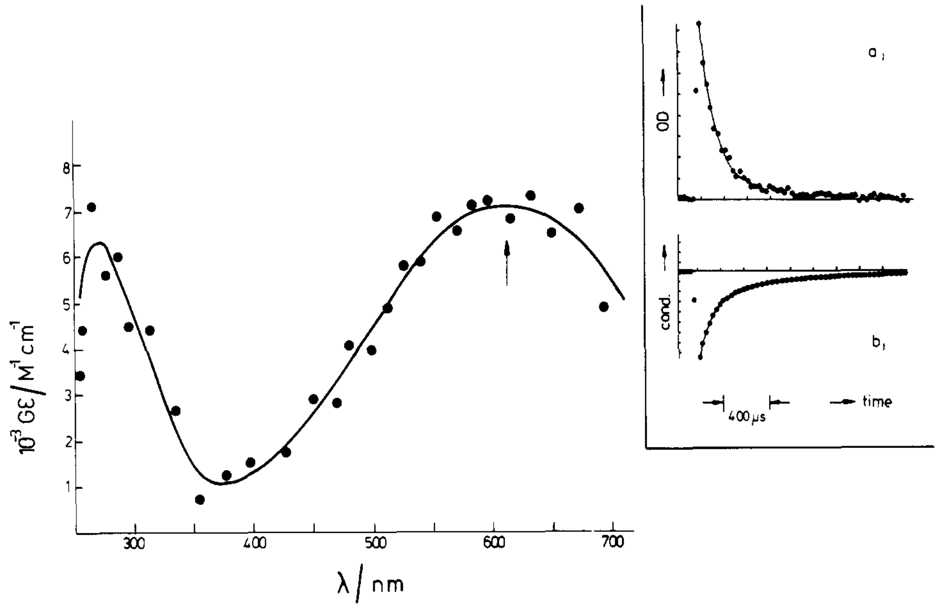


Figure 2. Absorption spectrum recorded immediately after application of a 1-µs pulse to an N_2O saturated, pH ~ 4 solution of 10^{-4} M 2,2-dimethyl-1,3-dithiacyclopentane (VI). Insert a: Absorption vs. time trace recorded at 600 nm in the same solution. Insert b: Conducitivity vs. time trace in same solution.

In the slightly acid solution the OH^- ions will immediately be neutralized, i.e., the negative conductivity signal is accounted for by the net replacement of a highly conducting proton (Λ = 315 Ω^{-1} cm^2 at 18 °C) by a less conducting "normal" cation (Λ taken as 65 Ω^{-1} cm^2). Conductivity therefore also provides a quantitative measure for the yield of the radical cations of $G = 4.5 \pm 0.5$, which corresponds to about 75% of the ·OH radicals. With the assumption that VI-4 is the only radical cation formed in the pulsed solution, the extinction coefficient of VI-4 at 610 nm is estimated to 1300 ± 150 M^{-1} cm^{-1}.

Sulfur-centered radical cations are known to exhibit oxidizing properties.[7,33,34] This could be demonstrated in the present case in the reaction

$$\text{VI-4} + I^- \rightarrow I\cdot + \text{VI} \tag{10}$$

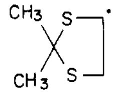
The generation of an iodine atom can easily be monitored through the known $I_2^-\cdot$ absorption at 380 nm formed upon equilibration in the I^- containing solution. Reaction 10

$$I\cdot + I^- \rightleftharpoons I_2^-\cdot \tag{11}$$

incidentally occurs quantitatively, and with a bimolecular rate constant of (8.9 ± 0.9) × 10^9 M^{-1} s^{-1}.

With increasing solute (VI) concentration the 610-nm absorption is more and more replaced by an absorption around 500 nm while the conductivity yield remains the same. This is attributed to the formation of the intermolecular radical cation VI-5 analogous to IV-5 and I.

The UV absorption finally is attributed to the neutral radical formed via deprotonation of the radical cation (VI–4) or direct hydrogen-atom abstraction by the remaining ·OH radicals.



VI-2

(3) Oxidation of 2-Methyl-1,3-dithiacyclopentane. Qualitatively similar results as for VI, plus an additional long-lived absorption of a nonradical cation are the characteristic features in the oxidation of the C-2 monomethylated compound V.

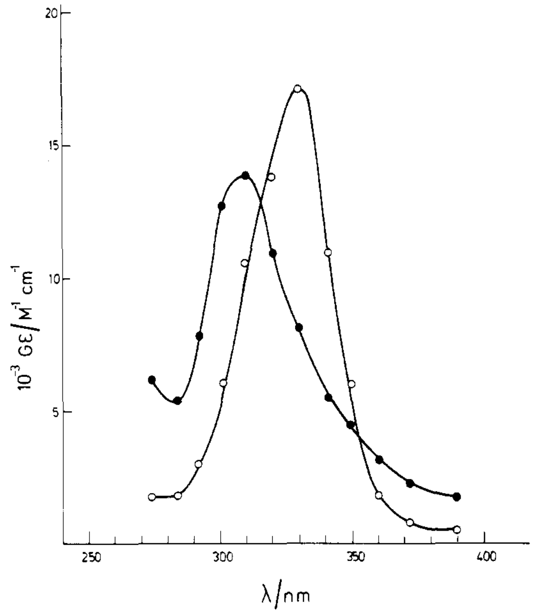
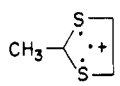


Figure 3. Absorption spectrum of V-1 (●) and V-6 (○) recorded immediately and 1.5 ms after a 1-µs pulse, respectively, in an N_2O saturated pH ~ 4 solution of 10^{-4} M 2-methyl-1,3-dithiacyclopentane (V).

The intramolecular three-electron bonded radical cation (V-4) identified again through conductivity measurements absorbs with a maximum around 650 nm, i.e., slightly



V-4

red-shifted as compared with VI-4. Its lifetime is however much shorter than that of VI-4 by about two orders of magnitude, namely $t_{1/2} \approx 1$ µs.

With increasing solute concentration formation of the intermolecular radical cation V-5 (analogous to VI-5, IV-5, I) with λ_{max} in the 500-nm range is also indicated. It has,

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(33) Chaudhri, S. A.; Göbl, M.; Freyholdt, T.; Asmus, K.-D. *J. Am. Chem. Soc.* **1984**, *106*, 5988.

(34) Asmus, K.-D. In "Radioprotectors and Anticarcinogens"; Nygaard, D. F.; Simic, M. G., Eds.; Academic Press: New York, 1983; pp 23–42.

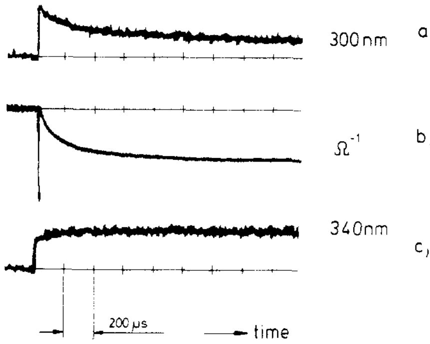
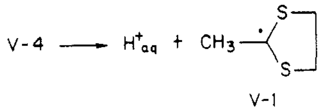


Figure 4. (a) Optical absorption vs. time trace at 300 nm in pulse-irradiated N_2O saturated pH ~ 4 solution of 10^{-4} M 2-methyl-1,3-dithiacyclopentane (V). (b) Conductivity vs. time trace in the same solution. (c) Optical absorption vs. time trace at 340 nm in the same solution.

however, a similarly short lifetime as V-4.

A strong transient UV band with λ_{max} at 310 nm (full circles in Figure 3) is attributed to the α-thioalkyl radical V-1 formed in the deprotonation reaction (eq 12).



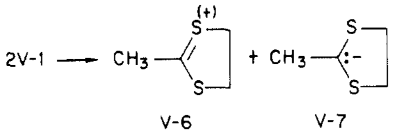
(12)

Accordingly the formation of V-1 parallels the decay of V-4 and is already fully completed a few μs after the pulse. Time-resolved optical (at 300 nm) and conductivity traces shown in Figures 4a and 4b on a compressed time scale clearly reveal the neutral nature of V-1, i.e., the initial negative spike of the conductivity which is due to formation of V-4 has completely recovered as V-1 is still fully present.

The radical generated in reaction 12 has been formulated as C-2 centered. In principle, a C-4 centered radical may, of course, also be envisaged. Owing to the tertiary nature of the C-2 hydrogen and possible additional labilization by two α-sulfur functions hydrogen cleavage from C-2 should be well favored over cleavage from C-4.

The extinction coefficient of V-1 is estimated to 2350 ± 300 M^{-1} cm^{-1} at 310 nm based on the assumption that the yield of V-1 equals the yield of ·OH radicals, i.e., $G \approx 6$.

The additional interesting feature in the oxidation of this compound is revealed in the decay process of V-1. This purely second-order reaction occurs with $2k = (4.0 \pm 0.4) \times 10^9$ M^{-1} s^{-1} and is accompanied by a negative change in conductivity, i.e., formation of another positively charged species, and an increase in optical absorption in the 320–350 nm range, as shown in Figures 4a–c. The spectrum of the new and long-lived optical absorption is included in Figure 3 (open circles) and is seen to have a maximum at 330 nm. The magnitude of this second slow conductivity decrease amounts of $G \times \Delta\Lambda = -775$ Ω^{-1} cm^2. With $\Delta\Lambda = -250$ Ω^{-1} cm^2 (substitution of a proton by a normal cationic species[31]) the total conductivity decrease after a few ms corresponds to $G = 3.1$, i.e., to just half the yield of the radical V-1. All these data are compatible with an ionic disproportionation followed by immediate protonation of V-7 to yield the original compound V.[35,37] The long-lived optical absorption with an extinction coefficient of 5500 ± 600 M^{-1} cm^{-1} at 330 nm would then be attributable to species V–6.



(13)

The yield of V-6 is doubled as expected if V-1 does not disproportionate but is quantitatively oxidized, e.g., by tetranitromethane in the reaction

$$V\text{-}1 + C(NO_2)_4 \rightarrow V\text{-}6 + C(NO_2)_3^- + NO_2 \quad (14)$$

(4) Oxidation of Other 1,3-Dithia Compounds. Methylation at the C-4 position had no such dramatic effect as methylation at C-2, i.e., the oxidations of VII–IX essentially gave comparable results with the oxidations of IV–VI, respectively. Particularly noteworthy are a relatively long-lived intramolecular S∴S bonded radical cation (IX-4) from 2,2,4-trimethyl-1,3-dithiacyclopentane with $\lambda_{max} \approx 600$ nm, and a stable (ms range) 300-nm absorption of a nonradical species VIII-6 (analogous to V-6) which results from ionic disproportionation of the carbon-centered radical VIII-1 (analogous to V-1) in the oxidation of 2,4-dimethyl-1,3-dithiacyclopentane. A relatively stable intramolecularly S∴S bonded radical cation X-4 ($t_{1/2} = 225$ μs at 3 Gy and 10^{-4} M X) in high yield ($G \approx 4$) is also formed in the oxidation of 2,2-dimethyl-1,3-dithiacyclohexane. As compared to the corresponding five-membered ring system VI-4, its absorption maximum is, however, slightly blue-shifted to 550 nm.

All numerical data from optical and kinetic measurements which could be determined within reasonable limits of error (±50%) are summarized in Table I.

Discussion

(1) Intramolecular Three-Electron-Bonded Radical Cations. Our results have shown that formation of intramolecular three-electron-bonded radical cations in the oxidation of 1,3-dithiacyclopentanes is possible in principle. It has been demonstrated that interaction of the sulfur p orbitals in 1,3-dithiolanes gives rise to bonding and antibonding combinations in the ground state.[38-40] Oxidation simply removes an electron from the antibonding orbital to yield the σ^2/σ^* three-electron-bonded radical cation. Particular stabilization of this system apears to occur, however, only upon dimethylation (dialkylation) at the C-2 carbon atom between the two sulfur atoms.

Two parameters have been found to generally influence the stability of three-electron bonds, namely electron induction and the geometrical structure of the radical species.[3,4,6] Electron induction can clearly be ruled out, however, since increasing methylation should weaken the three-electron bond and thus would be associated with a red-shift in optical absorption.[6] As described, just the opposite is observed for our species.

This leaves geometry as the stability-controlling parameter for the radical cations. Conformational studies

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(35) Ionic disproportionation of the C-centered V-1 would formally yield a corresponding carbo cation as a positively charged product, but its mesomeric sulfonium form can be expected to be more stable in the aqueous solution. The radical V-1 itself should, in fact, also not be considered to be purely carbon centered. In analogy to other α-thioalkyl radicals some spin delocalization towards sulfur is expected.[36]

(36) Gilbert, B. C.; Larkin, J. P.; Norman, R. O. C. *J. Chem. Soc. Perkin Trans 2* **1973**, 272.

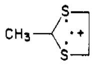
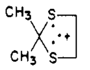
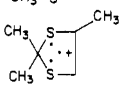
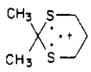
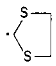
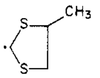
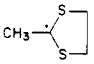
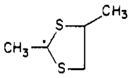
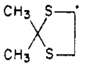
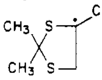
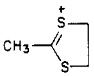
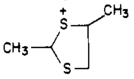
(37) Conventional UV analysis made several minutes after irradiation could not provide any conclusive information on a possible stability of V-6 at longer times. A 2 × 10^{-3}M solution which was irradiated with several hundred pulses turned slightly opake and showed an uncharacteristic absorption which increased more or less steadily from about 600 nm towards UV.

(38) Jaffe, H.; Orchin, M. "Theory and Applications of Ultraviolet Spectroscopy"; Wiley: New York, 1962; pp 475–476.

(39) Sweigart, D. A.; Turner, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 5599.

(40) Bock, H.; Wagner, G. *Angew. Chem.* **1972**, *84*, 119.

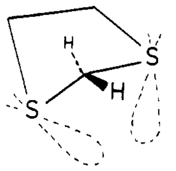
Table I. Optical and Kinetic Data of Radical Cations and Neutral Radicals Formed in the Radical-Induced Oxidation of N_2O Saturated, pH 4 Solutions of Various 1,3-Dithia Compounds at ≤10^{-4} M (Always Only One Mesomer Form Shown)

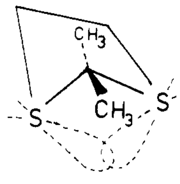
radical	λ_{max}, nm (±10 nm)	ϵ, M^{-1} cm^{-1}	remarks and kinetic data
	(>600)		very short-lived, $t_{1/2} \leq 0.2$ μs
	650		short-lived, $t_{1/2} \approx 1$ μs
	610	1300	$t_{1/2}$ = 100 μs (at dose of 7 Gy), oxidizes I^- with $k = (8.9 \pm 0.9) \times 10^9$ M^{-1} s^{-1}
	≈600		
	550	1500	$t_{1/2}$ = 140 μs (7 Gy)
	320	2500	mostly second-order decay, $t_{1/2}$ = 190 μs (6.7 Gy), reduces $C(NO_2)_4$ with $k = (4.3 \pm 0.5) \times 10^9$ M^{-1} s^{-1}
	320	2500	
	310	2350	$2k = (4.0 \pm 1.0) \times 10^9$ M^{-1} s^{-1}
	315	2000	$2k = (4.0 \pm 2.0) \times 10^9$ M^{-1} s^{-1}
	275		
	275		
	330	5500	stable over >10 ms
	330	5500	stable over >10 ms

on 1,3-dithiolanes,[13,14] 1,3-oxathiolanes,[15-18]) and 1,3-dioxolanes[19,20] have suggested a relatively high degree of flexibility of the five-membered rings within their overall rigid structure. A large number of minimum energy conformations seems to exist with relatively small stabilization energies of usually less than 10 kJ mol^{-1}. It was further noted that steric requirements of the substituents particularly at C-2 may significantly affect the position of a conformational energy minimum, but that methyl substitution at C-4 had only little steric demands.[18] The highest ring torsional angle in the sulfur- and oxygen-containing five-ring compounds was assigned to the 1,3-dithiolanes.[13] Our results would now suggest that increasing alkyl substitution at C-2 leads to an increasing twist of the ring system in favor of sulfur–sulfur p-orbital overlap which is necessary for the establishment of the three-electron bond. As mentioned already, the S∴S bond strength is reflected in the position of its λ_{max} which is red-shifted upon bond weakening and vice versa.[3,4,6] The λ_{max} of V-4 (650 nm), VI-4 (610 nm), IX-4 (610 nm), and X-4 (550 nm) may thus be compared with some examples described previously, namely the intramolecular three-electron-bonded radical cations from 1,4-dithia-cyclohexane (650 nm),[1] 1,3-dithiacyclohexane (600 nm),[2] and the open chain 4-methyl-3,5-dithiaheptane (570 nm).[3,4]

On a semiquantitative MNDO/2 basis Clark has estimated a bond energy of about 20 kJ mol^{-1} for the interaction of the unpaired sulfur p electron with the solvent water molecule, i.e., in $(>S\therefore OH_2)^+$.[41] Since S∴S is positively established in our species, this means that its formation must be accompanied by an energy gain of a least 20 kJ mol^{-1} (and most likely even more). Therefore any conformational energy barriers in the unoxidized parent compounds of <10 kJ mol^{-1} are easily overcome.

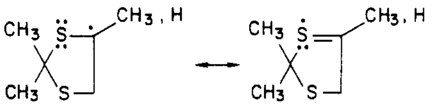
In our examples it is noted that dimethylation at C-2 leads to a dramatic increase in kinetic stability of the intramolecular three-electron bonded radical cation and also causes a significant blue shift of the λ_{max}. All this is clearly in agreement with a suggestion by C. K. Ingold[42] that substituents decrease the bond angle of the remaining valences. Accordingly we like to interpret our observations in terms of a geminal dialkyl effect in general, i.e, an effect which has been described already, for example, in connection with ring closure kinetics[43] and thermodynamic parameters of alkyl substitution.[44] Our data, of course, do not allow us to distinguish between an envelope with one of the sulfurs as flap atom or a half-chair structure. A pictorial for the half-chair conformation seems particularly suited, however, to demonstrate the gem-dialkyl effect on the S–C-2–S bond angle and sulfur p-orbital orientation.





Although the thermodynamic stability of the three-electron bond is not necessarily reflected in the overall decay kinetics of the radical cations,[28] we suggest that the very short lifetimes of IV-4 and V-4 as compared to VI-4 are related to their low thermodynamic stabilities with respect to the S∴S bonds. This is concluded from the observation that the intramolecular S∴S bonded species from 1,3-dithiacyclohexane and its C-2 dimethylated derivative X-4 are both long-lived and decay mostly by second-order processes although the former has two relatively labile and acidic H atoms at C-2.

(2) α-Thioalkyl Radicals. Alkyl substitution at C-2 appears also to be significant for the spectral properties of the α-thioalkyl radicals. Such species as generated from VI and IX, namely VI-2 and IX-2, are described by the mesomeric forms



They absorb at practically the same wavelength as the corresponding species from dimethyl sulfide,

$$CH_2—S—CH_3 \leftrightarrow CH_2=S—CH_3$$

i.e., at 275–280 nm.[7]

Whenever C-2 centered radicals can be formed (e.g., from compounds which carry at least one hydrogen atom at C-2), they are able to extend their mesomerism over both sulfur atoms (see **2a–c**) and accordingly absorb at lower energies in the 310–320-nm range. The underlying resonance forms may be written as simple carbon- or

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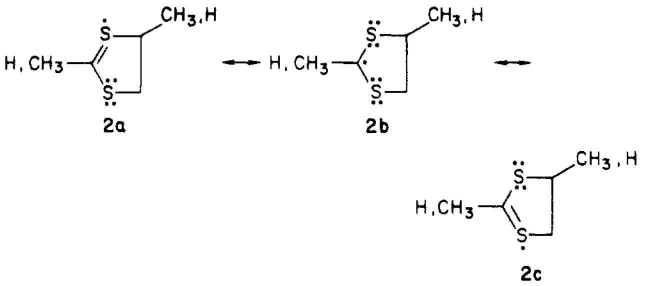
(41) Clark, T.; private communication.

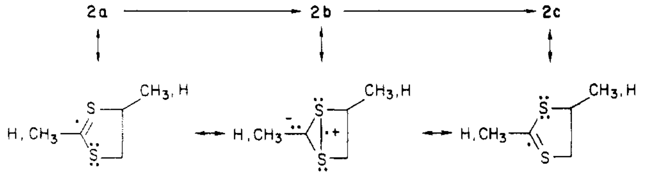
(42) Ingold, C. K. *J. Chem. Soc.* **1921**, 308.

(43) Bruice, T. C.; Pandit, U. K. *J. Am. Chem. Soc.* **1960**, *82*, 5858.

(44) Allinger, N. L.; Zalkow, V. *J. Org. Chem.* **1960**, *25*, 701.

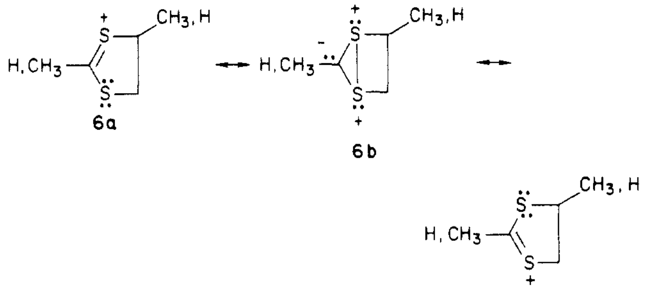


sulfur-centered radicals, or with π-type interactions between either sulfur and carbon or the two sulfur atoms. The charge-separated form **2e** constitutes a Lewis structure.

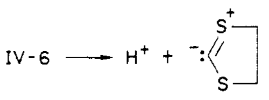


In the light of these considerations it seems that the radicals formed from IV are mostly C-2 centered since the corresponding spectrum in Figure 1 shows little absorption below 300 nm. This conclusion allows us in turn to assign an extinction coefficient to IV-1, namely $\epsilon = 2500 = \pm 300$ M^{-1} cm^{-1} at 320 nm.

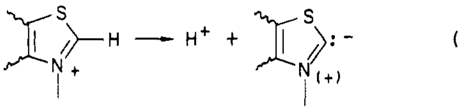
(3) Ylide Formation. The chemical fate of the α-thioalkyl radical from 2-methyl-1,3-dithiacyclopentane, V-1, has been rationalized in terms of a second-order ionic disproportionation. The structures of the oxidized forms V-6 and its analogues can be given in various resonance forms including a sulfur–sulfur bridged ylide structure. All these structures can directly be visualized simply by removal of the unpaired electron from the radical structures 2d–2f.



While the C-2 methyl substituted species is relatively stable (long-living absorption at 330 nm) the corresponding hydrogen-substituted species seems to be very short-lived (no detectable absorption). This finds, however, a reasonable explanation by the presumably strongly acidic proton at C-2. The cationic form IV-6 (formulated in terms of the resonance structure a) can therefore be expected to deprotonate in a fast reaction to yield an ylide. The lack of change in conductivity in the overall decay process of IV-1 is fully in accord with this mechanism if—as to be expected—the rate determining step for the ylide formation is reaction 13.[45] Ylide formation analogous to reaction 15 is, in fact, well-known.[46] An example with relevance to a biological system is the stabilization of the thiazolium part of thiamine (including mesomer forms with the positive center at sulfur).[47]



(15)



(16)

Corresponding ylide stabilization with mesomer structures involving both sulfur atoms is of course not possible for sulfonium ions which may be formed upon second-order decay of the C-4 centered radicals. Furthermore, the C-4 hydrogen atoms are not expected to be as acidic as the C-2 hydrogen atoms leaving ylide formation from these sulfonium ions a much less likely process. In analogy to the fate of simple α-thioalkyl radicals we anticipate that formation of sulfoxides and possibly some combination products are the major pathways of the C-4 radical decay processes.[7,48-50]

Acknowledgment. This study has in part been supported by the International Bureau of the KFA Jülich within the terms of an agreement on scientific cooperation between the Federal Republic of Germany and the Socialist Federal Republic of Yugoslavia. It is also a pleasure to acknowledge helpful discussions with Profs. R. S. Glass and S. F. Nelsen, and the assistance in the synthesis of various compounds by Dr. Ch.-H. Fischer and E. Darnstädt.

Registry No. IV, 4829-04-3; V, 5616-51-3; VI, 6008-78-2; VII, 50363-43-4; VIII, 54339-85-4; IX, 5862-53-3; X, 6007-22-3; Tl^{2+}, 14877-28-2; HO·, 3352-57-6; 1,2-ethanediol, 540-63-6; 1,2-propanedithiol, 814-67-5; 1,3-propanedithiol, 109-80-8; 1,3,5-trioxane, 110-88-3; acetaldehyde, 75-07-0; acetone, 67-64-1; 1,3-dithiolane radical cation, 90827-85-3; 2-methyl-1,3-dithiolane radical cation, 100334-32-5; 2,2-dimethyl-1,3-dithiolane radical cation, 100334-33-6; 2,2,4-trimethyl-1,3-dithiolane radical cation, 100334-34-7; 2,2-dimethyl-1,3-dithiane radical cation, 100334-35-8; 1,3-dithiolan-2-yl, 60144-61-8; 4-methyl-1,3-dithiolan-2-yl, 72256-97-4; 2-methyl-1,3-dithiolan-2-yl, 70086-32-7; 2,4-dimethyl-1,3-dithiolan-2-yl, 72256-98-5; 2,2-dimethyl-1,3-dithiolan-4-yl, 100334-36-9; 2,2,4-trimethyl-1,3-dithiolan-4-yl, 100334-37-0; 4,5-dihydro-2-methyl-1,3-dithiol-1-ium, 73857-67-7; 4,5-dihydro-2,4-dimethyl-1,3-dithiol-1-ium, 100334-38-1.

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(45) It should be noted that generation of the sulfonium ion IV-6 can in principle also be formulated if the disproportionation of IV-1 would proceed via H atom rather than e^- transfer. The products resulting from the radical–radical reaction would then be a directly regenerated molecule of IV and a carbene. Formation of IV-6 would then, however, require protonation of the carbene which seems less likely to occur in competition to other possibly faster and typical carbene reactions.

(46) Stirling, C. J. M. In "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977; pp 473–525 and references therein.

(47) White, F. G.; Ingraham, L. L. *J. Am. Chem. Soc.* **1962**, *84*, 3109.

(48) Weiss, J. Ph.D. Thesis, Technical University, Berlin, 1982, D83.

(49) Freyholdt, Ph.D. Thesis, Technical University, Berlin, 1982, D83.

(50) Goslich, R.; Weiss, J.; Möckel, H. J.; Mönig, J.; Asmus, K.-D. *Angew. Chem.* **1985**, *97*, 52; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 73.