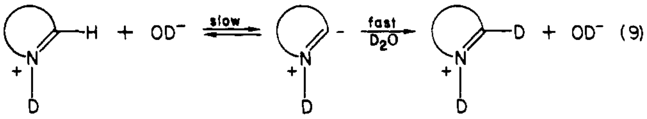
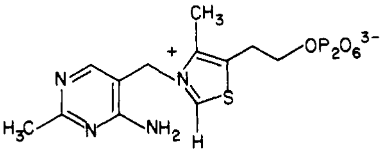
Moreover the process has ample literature precedent in base-catalyzed deuterium exchange of C–H bonds adjacent to a heterocyclic sp^2 N.[26] It is a general observation that pyridines,[27] imidazoles,[28] and benzimidazoles[29] exchange their 2-hydrogens via an OH^--mediated deprotonation of the C_2-H of the N-protonated base as in eq 9.



Zoltewicz[26c] has provided evidence that a (+) annular nitrogen atom in an aromatic ring activattes the adjacent sp^2 C–H for deprotonation via ylide formation by a factor of 10^{14}–10^{16}: in the case of imidazole, N-protonation reduces the pK_a of the 2-H to values approaching 17.[27c]

Nature too employs the activating effects of an adjacent (+)-N in facilitating ylide formation within a thiazolium ring in the many reactions catalyzed by the coenzyme thiamine pyrophosphate (**8**).[28]



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Registry No. 1, 35342-89-3; **2**, 13737-04-7; **4**, 91631-71-9; **5**, 91631-72-0; **6**, 91631-73-1; F^-, 16984-48-8; D_2, 7782-39-0; 1,2-dimethylimidazole, 1739-84-0; chlorotrimethylsilane, 75-77-4.

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[26] (a) Elvidge, J. A.; Jones, R. R.; O'Brien, C.; Evans, E. A.; Sheppard, H. C. *Adv. Heterocycl. Chem.* **1974**, *16*, 1–31. (b) Zoltewicz, J. A.; Kauffman, G. M.; Smith, C. L. *J. Am. Chem. Soc.* **1968**, *90*, 5939–5940. (c) Zoltewicz, J. A.; Helmick, L. S. *Ibid.* **1970**, *92*, 7547–7552. (d) Zoltewicz, J. A.; Smith, C. L. *Ibid.* **1967**, *89*, 3358–3359.

[27] (a) Vaughan, J. D.; Mughrabi, Z.; Wu, E. C. *J. Org. Chem.* **1970**, *35*, 1141–1145. (b) Harris, T. M.; Randall, J. C. *Chem. Ind.* (*London*) **1965**, 1728. (c) Haake, P.; Bauscher, L. P.; Miller, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 1113–1119.

[28] Elvidge, J. A.; Evans, E. A.; Jones, J. R.; O'Brien, C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 432–437.

[29] Dugas, H.; Penney, C. "Bioorganic Chemistry"; Springer-Verlag: New York, 1981; pp 447–458.

Substituent Effects on the Stability of Three-Electron-Bonded Radicals and Radical Ions from Organic Sulfur Compounds

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Abstract: Optical absorption spectra have been measured for a variety of $(R_2S\therefore SR_2)^+$, $(RS\therefore SR)^-$, $R_2S\therefore Br$ radicals and radical ions by using pulse radiolysis techniques. The results substantiate that the optical properties of such species are a sensitive measure for the strength of their three-electron (2σ, $1\sigma^*$) bonds. A considerable red shift in λ_{max} parallels the inductive power of the substituents R. This is explained by bond weakening due to electron induction into the antibonding σ^* orbital. Linear free energy correlations allow us to quantify the inductive effect and, in addition, to evaluate the influence of steric hindrance on the stability of the three-electron bonds.

The formation of three-electron-bonded radicals which are characterized by a relatively weak bond between two hetero atoms has been well established over recent years in several liquid- and solid-state studies. Typical examples are $(R_2S\therefore SR_2)^+$,[1-9] $(R_2Se\therefore SeR_2)^+$,[10] $(>N\therefore N<)^+$,[11-13] and $(>S\therefore N<)^+$ [14,15] radical cations (the latter two refer to intramolecularly stabilized species), $R_2S\therefore SR$[16-18] and $R_2S\therefore X$ (X = halide)[3,19-21] neutral radicals, $(RS\therefore SR)^-$[16,22] and $(RS\therefore X)^-$[23] radical anions, and others (although not always assigned to such structures). All these three-electron bonds contain two bonding σ electrons and one antibonding σ^* electron. The bond-weakening effect of the latter,

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[1] Gilbert, B. C.; Hodgeman, D. K. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1748.

[2] Bonifačić, M.; Möckel, H.; Bahnemann, D.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1975**, 675.

[3] Asmus, K.-D.; Bahnemann, D.; Bonifačić, M.; Gillis, H. A. *Discuss. Faraday Soc.* **1977**, *63*, 1748.

[4] Peterson, R. L.; Nelson, D. J.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1978**, 225.

[5] Asmus, K.-D.; Bahnemann, D.; Fischer, Ch.-H.; Veltwisch, D. *J. Am. Chem. Soc.* **1979**, *101*, 5322.

[6] Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436.

[7] Gara, W. B.; Giles, J. R. M.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1444.

[8] Chaudhri, S. A.; Asmus, K.-D. *Angew. Chem.* **1981**, *93*, 690; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 672.

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

[10] Nishikada, K.; Williams, Ff. *Chem. Phys. Lett.* **1975**, *34*, 302.

[11] Alder, R. W.; Sessions, R. B.; Mellor, R. B.; Rawlins, J. M. *J. Chem. Soc., Chem. Commun.* **1977**, 747.

[12] Alder, R. W.; Sessions, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 3651.

[13] Nelsen, S. F.; Alder, R. W.; Sessions, R. B.; Asmus, K.-D.; Hiller, K.-O.; Göbl, M. *J. Am. Chem. Soc.* **1980**, *102*, 1429.

[14] Musker, W. K.; Hirschon, A. S.; Doi, J. T. *J. Am. Chem. Soc.* **1978**, *100*, 7754.

[15] (a) Göbl, M. Ph.D. Thesis, Techn. Univ. Berlin, 1981, D83. (b) Mönig, J. Ph.D. Thesis, Techn. Univ. Berlin, 1983, D83. (c) Mönig, J.; Göbl, M.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2*, in press.

[16] Nelson, D. J.; Peterson, R. L.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 2005.

[17] Gilbert, B. C.; Marriott, P. R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1425.

[18] Giles, J. R. M.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1497.

[19] Symons, M. C. R.; Petersen, R. L. *J. Chem. Soc., Faraday Trans. 2* **1978**, 210.

[20] Bonifačić, M.; Asmus, K.-D.; *J. Chem. Soc., Perkin Trans. 2* **1980**, 758.

[21] Hiller, K.-O.; Asmus, K.-D. *Int. J. Radiat. Biol.* **1981**, *40*, 583.

[22] Adams, G. E.; McNaughton, G. S.; Michael, B. D. In "Excitation and Ionization", Scholes, G., Johnson, G. R. A., Eds.; Taylor and Francis: London, 1967; p 281.

[23] Packer, J. E. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1015.

0002-7863/84/1506-5984$01.50/0

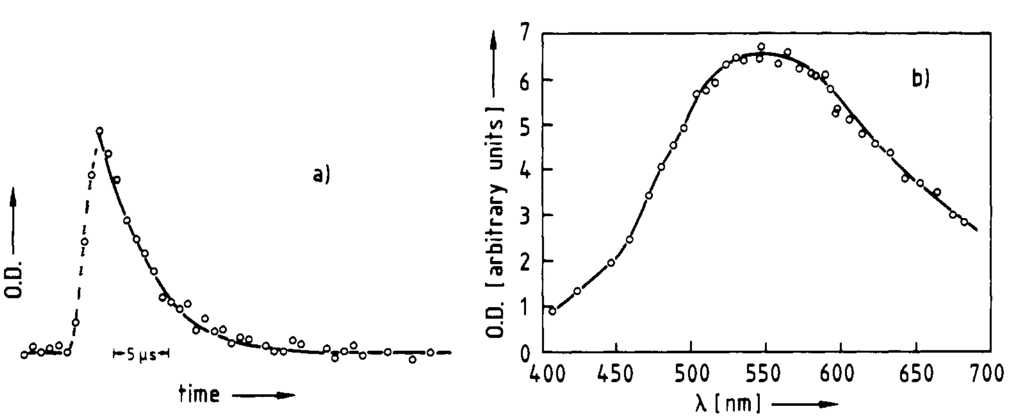


Figure 1. (a) Optical absorption as function of time in pulse-irradiated, N_2O-saturated solutions of 1×10^{-3} M diisopropyl sulfide (pH 4) recorded at 550 nm. Pulse length ca. 1 µs. Solid decay line: least mean square first order fit. (b) Optical absorption spectrum of $[(i\text{-}Pr)_2S\therefore S(i\text{-}Pr)_2]^+$ in the 400–700-nm range.

incidentally, is responsible for the easy dissociation of these bonds and the establishment of dissociation equilibria such as

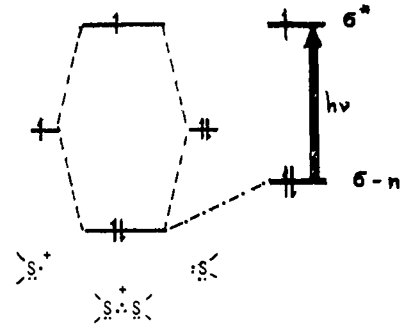
$$(R_2S\therefore SR_2)^+ \rightleftharpoons R_2S^{+\cdot} + R_2S \qquad (1)$$

or

$$(RS\therefore SR)^- \rightleftharpoons RS\cdot + RS^- \qquad (2)$$

When time-resolved pulse radiolysis techniques are used, it has been shown that particularly the sulfur-containing species exhibit strong optical absorptions in the visible and near UV.[2,3,5,6,8,9,13,15,20-23] On the basis of the results obtained for various sulfur-containing three-electron-bonded radical cations these optical absorptions were attributed, in first approximation, to a $\sigma \rightarrow \sigma^*$ transition.[5,6,24] A more detailed theoretical treatment on $(H_2S\therefore SH_2)^+$ (ab initio MP2/4-31G)[25] and several $(R_2S\therefore SR_2)^+$ (MNDO/2)[26] essentially confirms this picture but also reveals a considerable influence of the nonbonding s-electrons at sulfur on the σ-energy level. An excellent agreement between the thus calculated $a_g(\sigma\text{–}n^-)$ and $b_u(\sigma^*)$ energy difference of 3.25 eV (380 nm) for $(H_2S\therefore SH_2)^+$ and the experimentally found λ_{max} 370 nm (3.35 eV), for example, clearly supports the assignment of this optical absorption.[8,25]

As an immediate consequence of this consideration, the position of the respective λ_{max} is expected to be a direct measure for the strength of the three-electron bond. This is illustrated in the following diagram:



Accordingly, any change in bond strength will affect the position of the energy levels in the sense that a decrease in bond strength will result in a red shift of the optical absorption and vice versa.

In the organic sulfur containing species the three-electron bond results from the overlap of a singly occupied p-orbital with a doubly occupied p-orbital, both standing practically perpendicular to the C–S–C plane. Consequently, the geometry of the three-electron-bonded species which controls the possible extent of p-orbital overlap should be one of the important parameters for bond strength and associated λ_{max}. This is indeed the case, as has been demonstrated in our previous studies on the intramolecular three-electron bond formation in the oxidation of various open-chain and cyclic dithia compounds.[3,5,6]

In the present investigation we now report on the effect of electron-inducing substituents R on the stability of $(R_2S\therefore SR_2)^+$, $(RS\therefore SR)^-$, and $R_2S\therefore Br$. On the basis of the above considerations electron induction is expected to increase the electron density in the three-electron hetero atom center, possibly even in the antibonding σ* orbital. This would in any case affect the position of the σ and σ* energy levels which would result in a decrease in bond strength and correspondingly to a red shift in the optical absorption.

Experimental Section

The experiments were carried out with aqueous solutions of the various solutes. Concentrations of the sulfides and disulfides where 10^{-3}–10^{-2} M, solubility permitting, or at saturation level. The sulfur compounds were distilled prior to use and a purity >99% was confirmed by gas chromatography. The solvent was deionized, Millipore-filtered water. Prior to introduction of the solutes into the solution, the water was deoxygenated by bubbling with N_2 or N_2O for ca. 1 h/dm³ solution.

Irradiation of an aqueous solution leads to the formation of ·OH radicals, hydrated electrons, e_{aq}^-, and hydrogen atoms, H·, as reactive primary species. The yield of the former two is about 3×10^{-7} mol per J absorbed energy (or $G = 3$ species per 100 eV) whereas hydrogen atoms are formed at a comparatively lower yield of ca. 0.6×10^{-7} mol H· per J. The function of the N_2O in the solution is to convert hydrated electrons into ·OH radicals via $N_2O + e_{aq}^- \rightarrow N_2 + OH^- + \cdot OH$. As a result ca. 90% of the radiation chemically produced primary reactive species are oxidizing ·OH radicals.

The irradiation energy was introduced into the solutions by applying short pulses of high-energy electrons from either a 1.5- or a 3.8-MeV Van de Graaff accelerator; typical pulse widths were 1 µs and 50 ns for these two machines, respectively. Typical doses were in the order of 3–10 J/kg^{-1} (3–10 Gy or 300–1000 rd), yielding an ·OH radical concentration of ca. (2–6) $\times 10^{-6}$ M generated per pulse in N_2O bubbled solutions. In N_2 saturated solutions ·OH and e_{aq}^- are each formed with half these concentrations.

The formation of transient species was directly observed by recording the optical density of the pulsed solution as a function of time. Details and principles of the pulse radiolysis technique and the evaluation of data have already been reported.[27]

All experiments were carried out at room temperature.

Results

$(R_2S\therefore SR_2)^+$ Radical Cations. Pulse radiolysis of N_2O saturated aqueous solutions of various aliphatic organic sulfides leads to the formation of transient absorbing species which exhibit strong optical absorptions in the visible and near UV.[2,3,5,6,8,28] A typical

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[24] Symons, M. C. R. *Discuss. Faraday Soc.* **1977**, *63*, 280 (discussion remark).

[25] Clark, T. *J. Comput. Chem.* **1981**, *2*, 261.

[26] Clark, T., private communication.

[27] See, for example: (a) Matheson, M. S.; Dorfman, L. M.; In "Pulse Radiolysis"; M.I.T. Press: Cambridge, MA, 1969. (b) "The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis" (NATO Advanced Study Institute Series); Baxendale, J. H., Busi, F., Eds.; Reidel: Dordrecht, 1982. (c) Asmus, K.-D. "Methods in Enzymology"; Packer, L., Ed.; Academic Press: New York, 1984; p 167.

Table I. Optical Absorption Maxima of $(R_2S{\therefore}SR_2)^+$, $(RS{\therefore}SR)^-$, and $R_2S{\therefore}Br$ for Various Substituents R[29]

		λ_{max}, nm		
no.	R	$(R_2S{\therefore}SR_2)^+$	$(RS{\therefore}SR)^-$	$R_2S{\therefore}Br$
1	H	370[a]	380[b]	(370)[c]
2	CH_3	465	407	400
3	C_2H_5	485	415	407
4	n-C_3H_7	495		
5	n-C_4H_9	495		
6	i-C_4H_9	545		
7	i-C_3H_7	555	420	415
8	*sec*-C_4H_9	580		
9	t-C_4H_9	not stable	430	433

[a] Taken from ref 8. [b] Experimentally confirmed value from ref 32. [c] Extrapolated value.

absorption/time curve is shown in Figure 1a obtained from an N_2O-saturated solution of 1×10^{-3} M diisopropyl sulfide (pH 4) recorded at 550 nm, for example. The absorption is assigned to the $[(i\text{-Pr})_2S{\therefore}S(i\text{-Pr})_2]^+$ radical cation which is formed in the overall general reaction

$$\cdot OH + 2R_2S \rightarrow (R_2S{\therefore}SR_2)^+ + OH^- \qquad (3)$$

via an ·OH adduct (at sulfur), ionic dissociation of the latter, and stabilization of the molecular radical cation in the reaction with an unattacked diisopropyl sulfide molecule according to the back reaction of the equilibrium in eq 1. All these processes are completed within the 1-μs pulse. The assignment of the absorption to the three-electron-bonded cationic species is based on the same criteria as for other sulfides in previous studies including conductivity measurements and the yield dependence on the sulfide concentration[2,3,5,6,8,28] and therefore needs no further evaluation in this paper.

The decay of the absorption in Figure 1a occurs exponentially with a half-life of 3.1 μs. As in the case of other sulfides, the lifetime of the three-electron-bonded species increases with increasing sulfide concentration (equilibrium 1)[2] and reaches 9.5 μs in saturated solutions (ca. 5×10^{-3} M) for the isopropyl species.

The optical absorption spectrum evaluated from the maximum absorption immediately after the pulse at different wavelengths is shown in Figure 1b. It shows a strong and broad band with a maximum at 555 nm (±10 nm) which, in analogy to our previous findings with other sulfides, is assigned to a $\sigma \rightarrow \sigma^*$ transition in the three-electron bond. A second smaller band around 300 nm (not shown in the figure) is also observable and likely to be due to a hydrogen abstraction product, $(CH_3)_2\dot{C}SCH(CH_3)_2$, and possibly a contribution of the molecular radical cation $\{(CH_3)_2CH\}_2S^{+\cdot}$ which is in equilibrium with the three-electron-bonded species. Similar UV absorptions are also found in the oxidation of other sulfides.[2]

Corresponding experiments with various sulfides reveal that the $(R_2S{\therefore}SR_2)^+$ absorption band in the visible strongly depends on the nature of R. The respective λ_{max} are listed in Table I. Error limits range from ±5 nm for the low-wavelength to ±20 nm for the high-wavelength maxima. The relatively larger uncertainty at the red end results mainly from two facts, namely, solubility limitations which prevent quantitative formation of $(R_2S{\therefore}SR_2)^+$ in equilibrium 1 and also the decreasing lifetime of the radical cations. The λ_{max} for $(H_2S{\therefore}SH_2)^+$ has been taken from a previous publication of ours.[8]

In case of di-*tert*-butyl sulfide oxidation leads only to the molecular radical cation $(t\text{-Bu})_2S^{+\cdot}$ with $\lambda_{max} \approx 310$ nm.[3] The latter seems to react with a second di-*tert*-butyl sulfide molecule since its absorption decays increasingly faster with increasing solute concentration, but no $\{(t\text{-Bu})_2S{\therefore}S(t\text{-Bu})_2\}^+$ can be stabilized, as indicated by a complete lack of a corresponding absorption even at the highest possible concentration.

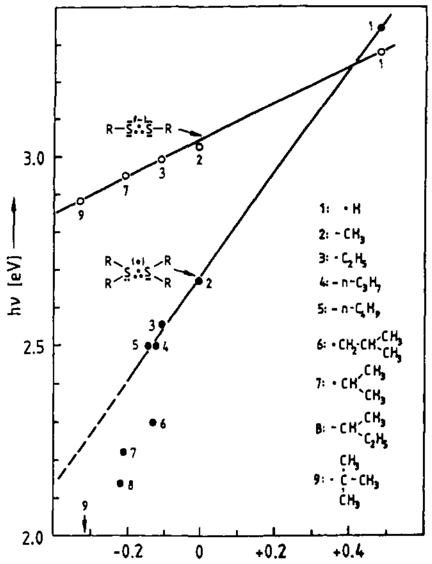

Figure 2. Plot of energy of optical transition (*hν* in eV) vs. Taft's inductive σ^* parameter for various $(R_2S{\therefore}SR_2)^+$ radical cations (●) and $(RS{\therefore}SR)^-$ radical anions (○). (Numbers refer to the various R listed in this Figure and Table I.)

The observed changes in λ_{max} for the other $(R_2S{\therefore}SR_2)^+$ radical cations parallel the electron-inductive properties of the substituents R with the lowest wavelength being observed for R = H (λ_{max} 370 nm) and the highest for R = *sec*-butyl (λ_{max} 580 ± 20). The results are in agreement with our expectation that electron induction leads to bond weakening. The latter could be envisaged in terms of an increasing electron density in the antibonding orbital.[30]

The direct correlation between the strength of the sulfur–sulfur three-electron bond and its λ_{max} justifies a linear free energy consideration. This is done in Figure 2 where the energy *hν* of the optical transition (in eV) is plotted vs. Taft's induction parameter σ^*[31] (not to be mistaken with the antibonding orbital) for the various substituents R. A good straight line can be obtained for those compounds with R = H and unbranched alkyl groups. Quantitatively this linear relationship is given by

$$h\nu[\text{eV}]\{(R_2S{\therefore}SR_2)^+\} = 2.66 + 1.40\sigma^*$$

The points obtained from sulfides with branched alkyl groups all fall below the straight line, indicating an additional bond weakening effect (showing up as an additional red shift in λ_{max}). The deviation furthermore seems to increase with the degree of branching and the proximity of the branching center to the sulfur atoms in the three-electron bond. We therefore attribute this additional effect to steric hindrance. In the case of di-*tert*-butyl sulfide, it seems to be steric hindrance, in fact, which actually prevents stabilization of a $(R_2S{\therefore}SR_2)^+$ type radical cation. Bond widening as a result of the bulkiness of substituents has also been concluded from ESR experiments on various $(R_2S{\therefore}SR_2)^+$.[7]

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(28) Meissner, G.; Henglein, A.; Beck, G. *Z. Naturforsch. B* **1967**, *B22*, 13.

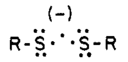
(29) The numerical data listed in this table have been obtained from a set of experiments using pulse sampling and averaging techniques. The accuracy in determination of λ_{max} of the generally very broad absorptions is therefore considerably higher than in our previous investigations on the methyl- and ethyl-substituted $(R_2S{\therefore}SR_2)^{+}$[2] and $R_2S{\therefore}Br$.[20] Although the old data on these species agree with the present data within their ±15–20-nm experimental error limit (±5 nm for new data), we did not include them into the present comparative study.

(30) It has been suggested by one of the referees of this paper that a similar effect into the same direction would also be expected by applying a three-electron, three-center concept with colinear C–S–S bonds (our concept is based on a three-electron, two-center system). Such a structure has been discussed in an ESR study on a number of sulfuranyl radicals by Perkins et al. (Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753). In this case the stabilizing interaction of the C–S σ^* orbital would be expected to decrease with increasing electron induction by the substituents. The result would then also be S∴S bond weakening and a red shift in optical absorption.

(31) Taft, R. *J. Am. Chem. Soc.* **1953**, *75*, 4231; *Ibid.* **1958**, *80*, 2436; *J. Chem. Phys.* **1957**, *26*, 93.

As the observed red shifts in optical absorption, in going from R = H to *sec*-butyl, are interpreted in terms of $S\therefore S$ bond weakening, it may be expected that this is also reflected in the lifetime of the corresponding transients, as has been observed, for example, also for several sterically stabilized $S\therefore S$-bonded radical cations.[5,6] This is indeed the case also in the present system. Thus the first half-life decreases from about 60 μs for $(H_2S\therefore SH_2)^{+}$ [8] to $\lesssim 1\,\mu s$ for $[(sec\text{-}Bu)_2S\therefore S(sec\text{-}Bu)_2]^+$ under comparable conditions. A quantitative evaluation shall, however, not be attempted at this point owing to the rather complex decay mechanisms (the short-lived species decay more or less exponentially, for the longer lived increasingly second-order contributions come into play[2,3,8]) and in view of the consideration that the lifetimes of our transients are not only controlled by the thermodynamic stability of the three-electron bond itself but also by the kinetics of the associated chemistry, e.g., deprotonation, etc.

$(RS\therefore SR)^-$ Radical Anions. Steric effects should be minimized if each sulfur atom of an $S\therefore S$-three-electron bond would carry only one instead of two substituents. This is the case for disulfide radical anions



$$\overset{(-)}{R\text{-}\ddot{\underset{..}{S}}\cdot\dot{}\cdot\ddot{\underset{..}{S}}\text{-}R}$$

which can conveniently be generated either via electron addition to the corresponding disulfide or association of thiyl radicals RS· to a thiolate anion RS^-. In the present study the disulfide radical anions were generated via

$$RSSR + e_{aq}^- \rightarrow (RS\therefore SR)^- \qquad (4)$$

in the presence of the corresponding thiolate RS^- to stabilize $(RS\therefore SR)^-$ according to equilibrium 2. The pulse-irradiated solutions were generally of 10^{-3} M RSSR or at saturation concentration, ca. 10^{-3} M RS^-, 5×10^{-1} M *tert*-butyl alcohol (to scavenge unwanted ·OH radicals), N_2 saturated, and at a pH > p*K* of the thiol. In case of $(HS\therefore SH)^-$ literature data[32] were confirmed by generating HS· radicals from the oxidation of H_2S/HS^- near the p*K* of this compound.

The maxima of the $(RS\therefore SR)^-$ absorptions are also listed in Table I and are seen to depend on the substituent R similar to those of $(R_2S\therefore SR_2)^+$, but to a much lesser extent. Moreover, a three-electron-bonded radical anion can be stabilized even for R = *tert*-butyl. But most important, the corresponding linear free energy correlation now yields a perfect straight line for all species from R = H to R = *tert*-butyl. This is taken as evidence that, as expected, steric hindrance plays no longer any significant role, and only electron induction determines the strength of the three-electron bond and thus the position of λ_{max}. Quantitatively the straight line is given by

$$h\nu[\mathrm{eV}]\{(RS\therefore SR)^-\} = 3.05 + 0.49\sigma^*$$

$R_2S\therefore Br$ Radicals. Pulse irradiation of N_2O saturated solutions containing R_2S and Br^- leads to the formation of transient $R_2S\therefore Br$ radicals either via the forward reactions of the equilibria

$$(R_2S\therefore SR_2)^+ + Br^- \rightleftharpoons R_2S\therefore Br + R_2S \qquad (5)$$

and

$$R_2S^{+}\cdot + Br^- \rightleftharpoons R_2S\therefore Br \qquad (6)$$

at high $[R_2S]/[Br^-]$ ratios or via

$$Br_2^{-}\cdot + R_2S \rightleftharpoons R_2S\therefore Br + Br^- \qquad (7)$$

at low $[R_2S]/[Br^-]$ ratios.[3,20] The $Br_2^-\cdot$ is then formed in the overall reaction

$$\cdot OH + 2Br^- \rightarrow Br_2^-\cdot + OH^- \qquad (8)$$

In any case the $R_2S\therefore Br$ radicals can be stabilized for observation at sulfide/bromide concentration ratios between 10^{-2} and 10^2.

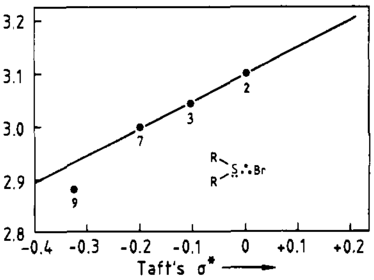


Figure 3. Plot of energy of optical transition (*hν* in eV) vs. Taft's inductive σ* parameter for various $R_2S\therefore Br$. (Numbers refer to same R as in Figure 2 and Table I.)

The λ_{max} listed in Table I are again seen to be red-shifted in going from R = CH_3 to R = *tert*-butyl. Figure 3 shows that a linear free energy correlation is obtained for all species except for $(t\text{-}Bu)_2S\therefore Br$. The latter falls below the straight line which is taken as a measure for a slight (compared with the $(R_2S\therefore SR_2)^+$ radical cations) steric hindrance. Analysis of the straight line gives

$$h\nu[\mathrm{eV}]\{R_2S\therefore Br\} = 3.1 + 0.51\sigma^*$$

The lack of experimental data for a possible $H_2S\therefore Br$[33] leaves a relatively larger uncertainty for the slope of the curve than in the case of the corresponding $(R_2S\therefore SR_2)^+$ and $(RS\therefore SR)^-$ species. Extrapolation of the straight line to $\sigma^* = +0.49$ (i.e., for R = H) would yield, however, an adsorption maximum of 370 nm for the $H_2S\therefore Br$ radical. This is most reasonable considering that the similarly structured $(H_2S\therefore SH_2)^+$ and $(Br\therefore Br)^-$[34] absorb at 370[8] and 360 nm,[35] respectively.

Discussion

The results confirm our previous rationale that the optical properties of three-electron-bonded radicals and radical ions derived from organic sulfides and H_2S are a sensitive measure for the strength of three-electron bonds. The data demonstrate in particular that electron induction occurs into the antibonding σ* orbital. This concept also agrees well with the observed differences in the slopes of the linear free energy correlations for $(R_2S\therefore SR_2)^+$ and $(RS\therefore SR)^-$ (Figure 2 and *hν* vs. σ* equations). Thus it is plausible to assume that electron induction into a positively charged center, as in $(R_2S\therefore SR_2)^+$, results in a relatively large change in electron density and consequently in λ_{max}. In the case of the $(RS\therefore SR)^-$ radical anions, on the other hand, electron induction has to occur into an already negatively charged center, i.e., necessarily should be much less efficient. For quantitative considerations one has, of course, also to take into account that the radical cation carries twice as many substituents as the radical anion.

A numerical comparison of the $(R_2S\therefore SR_2)^+$ and $(RS\therefore SR)^-$ (λ_{max}, slope of *hν* vs. σ*, etc.) on the one hand with those of $R_2S\therefore Br$ on the other hand is not feasible, since the different nature of the bromine hetero atom and the influence of its nonbonding electron pairs will undoubtedly affect the energy levels of the radical.

The inductive effect may also explain or at least contribute significantly to some effects reported in the literature. Thus it is very difficult to stabilize $R_2S\therefore SR$ neutral radicals (e.g., from $R_2S^{+}\cdot + RS^-$, or $RS\cdot + R_2S$, or $R\cdot + RSSR$ reactions). In fact, all experiments in the liquid for species with identical R have failed.[3,36] A reasonable explanation is provided by the structural

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[32] Karmann, W.; Meissner, G.; Henglein, A. *Z. Naturforsch. B* **1967**, *B22*, 273.

[33] $H_2S\therefore Br$ like the other $R_2S\therefore Br$ is likely to exist in the equilibria given by eq 5–7. Since the absorption of $H_2S\therefore Br$ is not expected to be significantly different from that of $(H_2S\therefore SH_2)^+$ and $Br_2^-\cdot$, it is practically not possible to assign the observed absorption in the oxidation of H_2S/Br^- solutions unambiguously to either of the three-electron-bonded species.

[34] $(Br\therefore Br)^-$ is identical with $Br_2^-\cdot$. Like $Cl_2^-\cdot$, $I_2^-\cdot$, $(SCN)_2^-\cdot$ etc. This species is characterized by a bond which contains two bonding σ electrons and one antibonding σ* electron.

[35] (a) Sutton, H. A.; Adams, G. E.; Boag, J. W.; Michael, B. D. In "Pulse Radiolysis"; Ebert, M., Keene, J. P., Swallow, A. J., Baxendale, J. H., Eds.; Academic Press: London, 1965; p 61. (b) Cercek, B.; Ebert, M.; Gilbert, C. W.; Swallow, A. J. in ref 35a, p 83.

asymmetry of the radical which is likely to yield different energy levels of the overlapping SOMO and HOMO of the R_2S and RS constituents.

A better match of the energy levels and therefore higher stability of the three-electron bond can be achieved by introducing unequal substituents. Thus $R_2S\therefore SCF_3$ and $R_2S\therefore SCOR'$ could be stabilized in solution and their structure evaluated from ESR experiments.[18] It would now appear that the stability of these $R_2S\therefore SR$ type radicals is enhanced by the CF_3 or COR′ substituents, both of which are good electron-withdrawing substituents,[31] i.e., would reduce the electron density in the antibonding orbital.

Another interesting result reported in the literature is a λ_{max} of 430 nm for $(R'R''S\therefore SR'R'')^+$ with $R' = C_2H_5$ and $R'' = CH(CH_3)SC_2H_5$.[5] This λ_{max} is considerably blue-shifted compared to those radical cations obtained from the simple aliphatic sulfides (see Table I). Since steric effects would rather lead to a red shift, this experimental result would strongly indicate a net electron withdrawal from the antibonding orbital of the three-electron bond. Going into the $(R_2S\therefore SR_2)^+$ curve in Figure 2, the combined substituent effect would correspond to +0.15 of Taft's σ^* scale. At least qualitatively, this is quite plausible owing to the electronegativity of the sulfur atom and the fact that mesomery between the $S\therefore S$ bond and the β-sulfur atom in R″ is not possible across the $CH(CH_3)$ group in between.

The present investigation also allows us to separate electron induction from steric effects. The latter may act through widening of the C–S–C bond angle in the sulfide constituents of $(R_2S\therefore SR_2)^+$ and $R_2S\therefore Br$. This, in turn, would affect the direction and at least in $(R_2S\therefore SR_2)^+$ the possible extent of the p-orbital overlap. In addition, steric hindrance could also occur through space across the three-electron-bonded sulfur bridge in $(R_2S\therefore SR_2)^+$ with the result of a sulfur–sulfur bond lenghtening. Similar observations of steric hindrance across an odd-electron-bonded bridge have also been made for oxidized hydrazines ($R_2N\overset{\cdot}{-}NR_2^+$ with 2σ, 2π, and $1\pi^*$ electrons between the two nitrogen atoms).[37]

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Registry No. $H_2SSH_2^{+}\cdot$, 77386-59-5; $Me_2SSMe_2^{+}\cdot$, 63228-83-1; $Et_2SSEt_2^{+}\cdot$, 51137-16-7; $Pr_2SSPr^{+}\cdot$, 91523-20-5; $Bu_2SSBu_2^{+}\cdot$, 91523-21-6; i-Bu_2SS-i-$Bu_2^{+}\cdot$, 91523-22-7; i-Pr_2SS-i-$Pr_2^{+}\cdot$, 72517-96-5; *sec*-Bu_2SS-*sec*-$Bu_2^{+}\cdot$, 91523-23-8; $HSSH^{-}\cdot$, 91523-24-9; $MeSSMe^{-}\cdot$, 34527-95-2; $EtSSEt^{-}\cdot$, 91603-20-2; i-PrSS-i-$Pr^{-}\cdot$, 34525-29-6; t-BuSS-t-$Bu^{-}\cdot$, 34525-33-2; $BrH_2S\cdot$, 91523-25-0; $Me_2BrS\cdot$, 71149-19-4; $Et_2BrS\cdot$, 66851-58-9; i-$Pr_2BrS\cdot$, 91523-26-1; t-$Bu_2BrS\cdot$, 91523-27-2.

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(36) Giles, J. R. M.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1978**, 623.

(37) Nelsen, S. F. *Acc. Chem. Res.* **1981**, *14*, 131.

A Method To Generate and Study $(CH_3)_2S^{+}\cdot$ Radical Cations. Reduction of Me_2SO by H· Atoms in Aqueous $HClO_4$ Solutions

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Abstract: Radical cations $(CH_3)_2S^{+}\cdot$ were found to be formed as intermediates in the reaction of dimethyl sulfoxide with hydrogen atoms in aqueous solutions containing high concentrations of $HClO_4$. This method allows one to study the properties of this cation, e.g., by pulse radiolysis, under conditions which are not disturbed by the usually rapid complexation with excess sulfide. Absolute rate constants were measured for the reactions of $(CH_3)_2S^{+}\cdot$ with $(CH_3)_2S$ ($k = (3.0 \pm 0.3) \times 10^9$ M^{-1} s^{-1}), CH_3SSCH_3 ($k = (4.0 \pm 0.4) \times 10^9$ M^{-1} s^{-1}), and $(t\text{-Bu})_2S$ ($k = 2.1 \times 10^9$ M^{-1} s^{-1}). The latter reaction leads to the formation of $\{(CH_3)_2S\therefore S(t\text{-Bu})_2\}^+$ three-electron-bonded radical cations which exhibit an optical absorption at 545 nm and equilibrate with the molecular radical cation $(t\text{-Bu})_2S^{+}\cdot$ (λ_{max} 310 nm). In the presence of chloride ions $(CH_3)_2S\therefore Cl$ (or its protonated form) with λ_{max} 380 nm is formed. The $(CH_3)_2S^{+}\cdot$ itself absorbs at 285 nm and is, in fact, assumed to exist as $\{(CH_3)_2S\therefore O(H)ClO_3\}^+$, possibly in equilibrium with $\{(CH_3)_2S\therefore OH_2\}^+$, i.e., in stoichiometrically defined three-electron-bonded complexes with $HClO_4$ or H_2O. In pure $H_2O/HClO_4$ matrix an optically absorbing transient with λ_{max} 335 nm is observed which is attributed to $(HClO_4)_2^{+}\cdot$.

Molecular radical cations $R_2S^{+}\cdot$ from one-electron oxidation of aliphatic sulfides are generally difficult to observe directly. This is mainly due to the usually rapid reaction of these species with excess sulfide in the forward reaction of the equilibrium

$$R_2S^{+}\cdot + R_2S \rightleftharpoons (R_2S\therefore SR_2)^+ \qquad (1)$$

and stabilization in a three-electron-bonded radical cation.[1-10] An exception in the aliphatic series is only the $(t\text{-Bu})_2S^{+}\cdot$ radical cation which, mainly for steric reasons, is not able to associate with an unattacked *tert*-butyl sulfide molecule.[3,10] In aqueous solutions the $(t\text{-Bu})_2S^{+}\cdot$ has been found to exhibit an optical absorption

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(1) Gilbert, B. C.; Hodgeman, D. K. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1748.

(2) Bonifačić, M.; Möckel, H.; Bahnemann, D.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1975**, 675.

(3) Asmus, K.-D.; Bahnemann, D.; Bonifačić, M.; Gillis, H. A. *Discuss. Faraday Soc.* **1977**, *63*, 1748.

(4) Peterson, R. L.; Nelson, D. J.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1978**, 225.

(5) Asmus, K.-D.; Bahnemann, D.; Fischer, Ch.-H.; Veltwisch, D. *J. Am. Chem. Soc.* **1979**, *101*, 5322.

(6) Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436.

(7) Gara, W. B.; Giles, J. R. M.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1444.

(8) Chaudhri, S. A.; Asmus, K.-D. *Angew. Chem.* **1981**, *93*, 690; *Ibid. Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 672.

(9) Hiller, K.-O.; Masloch, B.; Göbl, M.; Asmus, K.-D. *J. Am. Chem. Soc.* **1981**, *103*, 2734.

(10) Göbl, M.; Bonifačić, M.; Asmus, K.-D. *J. Am. Chem. Soc.*, preceding paper in this issue.