If this interpretation is correct, the variable transition-state theory seems to be valid also for dehalogenation reactions. With *meso*-1,2-dibromo-1,2-diphenylethane as the substrate, the transition-state structure is central when the nucleophile is a halide ion and shifts toward the E1cb-like side with Ph$_3$P. It is possible that with the latter base the incipient positive charge on the phosphorus atom in the transition state favors the buildup of negative charge at C$_\beta$, thus promoting a transition state with carbanion character.

The factors affecting base reactivity in dehalogenation reactions have been primarily investigated using the reactions of *erythro*-1-chloro-2-iodo-1,2-diphenylethane (eq 1, X = I, Y = Cl).[61] The base attacks the iodine atom in this case, and elimination of ICl takes place. The main conclusion of this study is that polarizability and desolvation energy are by far more important factors than basicity in determinating the reactivity of a base in a dehalogenation process. In particular, the role of polarizability is clearly shown by the reactivity order I$^-$ > Br$^-$ > Cl$^-$ observed in dipolar aprotic solvent in both the reactions of *erythro*-1-chloro-2-iodo-1,2-diphenylethane and *meso*-1,2-dibromo-1,2-diphenylethane.

Concluding Remarks

The above discussion has shown that, despite the fact that quantitative work in this area has started only

recently, some important conclusions regarding the influence of the base on the E2 transition state have been reached. This appears to be particularly true when the effects of basicity are considered. Little doubt now exists that, at least in anti eliminations, the stronger base generally produces a transition state with higher carbanion character. Confirmation of this conclusion in the case of syn eliminations is highly desirable.[62]

Additional work on the effects of base associations appears to be necessary in light of the somewhat contradictory results obtained so far. Moreover, the effects of the steric requirements of the base should be further investigated. Also of great interest would be studies aimed at determining (through α-carbon and leaving group isotope effects) the influence of the base nature on the extent to which the bond between α-carbon and leaving group is weakened in the transition state. Such information would complement that given by ρ and k_H/k_D values, thus allowing a complete picture of the transition-state structure to be obtained.

(61) E. Baciocchi and C. Lillocci, *J. Chem. Soc., Perkin Trans. 2*, 802 (1975).

(62) Unpublished results from this laboratory have however shown that in syn eliminations from 12 promoted by phenoxides in Me$_2$SO change in base strength does not significantly influence the carbanion character of the transition state.

Stabilization of Oxidized Sulfur Centers in Organic Sulfides. Radical Cations and Odd-Electron Sulfur–Sulfur Bonds
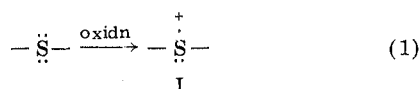
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Organic sulfur compounds, among them sulfides, are known to undergo chemical oxidation reactions fairly readily. This can be related to the relatively low ionization potentials of these molecules which in the gas phase are often found to be considerably below 10 eV. Similar and even lower ionization energies can be expected in the liquid phase. The likely site of oxidative attack is the sulfur atom, from which an electron can be removed with relative ease by suitable oxidants.

What is likely to be the primary result of one-electron oxidation of a sulfide function? Formally the molecular radical cation is expected to be formed (eq 1). Since

$$-\overset{..}{\underset{..}{S}}- \xrightarrow{\text{oxidn}} -\overset{+\;\cdot}{\underset{..}{S}}- \qquad (1)$$

$$\text{I}$$

sulfur bonds usually exhibit a high degree of p character, the two nonbonded electron pairs will not be equivalent; i.e., one of them will have more s, the other more p character. The electron removed in the ionization process (oxidation) is likely on energetic grounds to be one of the nonbonded p electrons. Accordingly the unpaired electron in the radical cation will remain largely in a p orbital.

Radical cations such as I have been shown kinetically and spectroscopically to be intermediates in many oxidation processes of sulfides, and in several cases of heteroaromatic species a positive identification has been possible.[1] Particularly in aprotic solvents, some of

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(1) See, for example: (a) K. Kim, S. R. Mani, and H. J. Shine, *J. Org. Chem.*, 40, 3857 (1975); (b) A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, 13, 155–278 (1976); (c) H. J. Shine, B. K. Bandlish, S. R. Mani, and A. G. Padilla, *J. Org. Chem.*, 44, 915 (1979); (d) S. Hünig, G. Kieslich, H. Quast, and D. Schentzow, *Justus Liebigs Ann. Chem.*, 310 (1973); (e) K. Deuchert and S. Hünig; *Angew. Chem., Int. Ed. Engl.*, 17, 875 (1978); (f) G. Vincow in "Radical Ions", E. T. Kaiser and L. Kevan, Eds., Interscience, New York, 1968, Chapter 4, pp 190–193.

these species were found to have lifetimes long enough to permit assignment through direct observation of physical or chemical parameters. Often, however, the radical character and short lifetimes of these species prevent unambiguous identification. Particularly in polar solvents such as water it has been difficult to stabilize any sulfur-containing radical cation sufficiently to allow direct observation with conventional detection techniques.

This situation changed dramatically when highly time-resolved detection techniques such as rapid mixing, pulse radiolysis, and (laser) flash photolysis became available and investigations of species with lifetimes well below the millisecond and even microsecond time range became possible. Early experiments with these fast techniques have already brought many new and interesting facts to light.[2,3] It was convincingly demonstrated, for example, that a large number of radical cations from cyclic and acyclic organosulfur compounds, particularly thioethers, with lifetimes of milliseconds and more exist in aqueous solutions. Even more striking, however, was the discovery that not the molecular radical cation I but a complex radical cation containing two molecules seems to be the more stable configuration in the majority of cases. The existence of $(R_2S)_2^{+\cdot}$ complexes from thioethers has in the meantime been proven unambiguously by ESR experiments in the liquid[3] and solid phase,[4] by optical and kinetic pulse radiolysis investigations in the liquid phase,[5] and most recently by chemical ionization mass spectrometry in the gas phase.[6]

The most interesting aspect of these findings is that a new sulfur–sulfur bond containing three electrons is apparently established in the complex radical cation II.

II
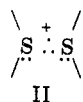
Evidence for this structure has been provided by ESR investigations in liquid- and solid-state studies of oxidized sulfur compounds.[3,4] Valuable information has also been derived from the analogous selenium system where [77]Se hyperfine couplings and g tensors lead to the unambiguous conclusion that two of the electrons in a three-electron selenium–selenium bond form a $\sigma(p,p)$ bond while the third electron is promoted into the associated antibonding σ^* orbital.[7] The same electronic configuration has been invoked for the sulfur–sulfur three-electron bond.

Radicals with three-electron bonds are also known to exist between atoms other than sulfur or selenium and have attracted increasing attention in recent years. The best described example is the $Cl_2^-\cdot$ radical anion,[8]

$$Cl \stackrel{-}{\therefore} Cl$$

but other $X_2^-\cdot$ (X = halogen, pseudohalogen) and

three-electron bonds between P, N, O, As, Br, and I atoms in organic and inorganic systems have also been described[9] (although these have not always been specifically assigned to three-electron species).

Almost the reverse of the formation of a new sulfur–sulfur bond as in the oxidation of a sulfide function is the addition of an electron to (reduction of) an already existing σ bond. Thus, electron attachment to a disulfide bridge[10] or carbon–halogen bond[11] has been shown to yield transient σ^* radicals with considerably stretched, i.e., weakened, S–S or C–X bonds.

The possibility of direct observation and investigation of three-electron bond species initiated considerable research activity and increased interest in the general field of odd-electron bonds. Most interesting, for example, is a one-electron bond radical anion $[(MeO)_3B\cdot B(OMe)_3]^-$ formed during the reduction of $B(OMe)_3$.[12] In its electronic structure it resembles the H_2^+ ion, which may be considered the prototype of one-electron bond species.

Theoretical considerations on the subject have been concerned mainly with the electronic nature and the stability of odd-electron bonds.[13] The overall picture, however, is still far from complete. Too few experimental results were available, particularly for the sulfur species since ESR measurements, one of the principal radical detection methods, are often hampered by the lack of nuclear spin on the principal isotope [32]S. Over the past few years, however, a number of systematic and successful investigations on the oxidation of organic thia compounds have provided an abundance of interesting information on the subject of S radical cations. Musker et al., for example, were able to stabilize radical cations and dications formed *intra*molecularly during conventional oxidation of mesocyclic dithia compounds in aprotic solvents and evaluate some of their chemical properties.[14] They were also able to offer clear evidence for the formation of a new sulfur–sulfur bond as the result of the oxidation process by appropriate mass spectrometry experiments.[15]

Our present discussion is based on the results of pulse radiolysis studies of transient radical cations from organic thia compounds, in particular via optical absorption measurements.[5,16-19] Early experiments carried out in the liquid phase, together with supporting

(2) G. Meissner, A. Henglein, and G. Beck, *Z. Naturforsch. B*, **22**, 13 (1967).

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

(4) M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1618 (1974).

(5) M. Bonifačić, H. Möckel, D. Bahnemann, and K.-D. Asmus, *J. Chem. Soc., Perkin Trans. 2*, 657 (1975).

(6) H. Möckel, *Fresenius Z. Anal. Chem.*, **295**, 241 (1979).

(7) K. Nishikada and Ff. Williams, *Chem. Phys. Lett.*, **34**, 302 (1975).

(8) W. Kanzig and M. H. Cohen, *Phys. Rev. Lett.*, **3**, 509 (1959).

(9) See, for example: (a) A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1589 (1972); (b) T. Gillbro, C. M. L. Kerr, and Ff. Williams, *Mol. Phys.*, **28**, 1225 (1974); (c) S. F. Nelsen and J. M. Buschek, *J. Am. Chem. Soc.*, **96**, 6424 (1974); (d) R. W. Alder, R. Gill, and N. C. Goode *J. Chem. Soc., Chem. Commun.*, 973 (1976); (e) K. Toriyama and M. Iwasaki, *J. Chem. Phys.*, **55**, 2181 (1971).

(10) (a) H. C. Box, H. G. Freund, K. T. Lilga, and E. E. Budzinski, *J. Phys. Chem.*, **74**, 40 (1970); (b) J. H. Hadley and W. Gordy, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 3106 (1974); **72**, 3486 (1975).

(11) (a) Several papers by M. C. R. Symons et al. since 1972; (b) A. Hasegawa and Ff. Williams, *Chem. Phys. Lett.*, **45**, 275 (1977).

(12) R. L. Hudson and Ff. Williams, *J. Am. Chem. Soc.*, **99**, 7714 (1977).

(13) N. C. Baird, *J. Chem. Educ.*, **54**, 291 (1977).

(14) (a) W. K. Musker and T. L. Wolford, *J. Am. Chem. Soc.*, **98**, 3055 (1976); (b) W. K. Musker, T. L. Wolford, and P. B. Roush, *ibid.*, **100**, 6416 (1978).

(15) W. K. Musker, B. V. Gorewit, P. B. Roush, and T. L. Wolford, *J. Org. Chem.*, **43**, 3235 (1978).

(16) D. Bahnemann and K.-D. Asmus, *J. Chem. Soc., Chem. Commun.*, 238 (1975).

(17) K.-D. Asmus, D. Bahnemann, M. Bonifačić, and H. A. Gillis, *Faraday Discuss. Chem. Soc.*, **No. 63**, 213 (1977).

(18) K.-D. Asmus, H. A. Gillis, and G. G. Teather, *J. Phys. Chem.*, **82**, 2677 (1978).

(19) K.-D. Asmus, D. Bahnemann, Ch.-H. Fischer, and D. Veltwisch, *J. Am. Chem. Soc.*, **101**, 5322 (1979).
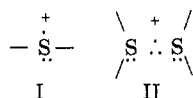
information from solid-phase studies, revealed strong optical absorptions attributable to three-electron bonded sulfur radical cations. More important, a possible dependence of the optical parameters on the structure of the radical cation species was indicated.

Experimental Technique

Since many readers may not be fully familiar with the pulse radiolysis technique, a brief description of how oxidation reactions can be initiated and observed with this technique seems appropriate. The principal idea is to produce the oxidant directly at the site of reaction with the solute in a time short compared to the lifetime of the species to be formed by their reaction. Moreover, it is necessary to produce measurable concentrations and to use highly time-resolved analyzing techniques to detect the transient species. Most suited are optical and conductivity measurements with time resolutions in the nanosecond range, which are sensitive enough to detect concentrations as low as 10^{-7} M. These requirements are met, and direct observation of oxidation reactions is possible, when N_2O-saturated[20] solutions of the solute to be investigated are irradiated with short pulses (e.g., 5 ns) of high-energy electrons (e.g., 4 MeV) from an accelerator. The energy thus distributed and absorbed by the solvent typically yields around 10^{-5} M of oxidizing species. These are, for example, $OH\cdot$ radicals in aqueous systems and $RH^{+}\cdot$ radical cations in a hydrocarbon, RH. The primary species can, when required, be converted readily into other oxidizing species by addition of suitable scavengers to the solution (e.g., $Tl^{+} + OH\cdot \rightarrow Tl^{2+} + OH^{-}$).

Radical Cations from Thioethers

In aqueous solutions the most convenient oxidant is the $OH\cdot$ radical. Its reaction mechanism with organic sulfides is unfortunately rather complex, starting with an addition of $OH\cdot$ to the sulfur atom; this, however, will not be discussed here in further detail. The interested reader is referred to ref 5. In all cases positively charged transient species are generally formed within the duration of 1 μs, whether the oxidation of the thia compound is initiated by $OH\cdot$ radicals or more directly by another suitable oxidant such as Tl^{2+}, Ag^{2+}, etc. The lifetime of these species is usually much longer than this period and allows their identification as either I or II,

$$-\overset{+}{\underset{\cdot\cdot}{S}}- \qquad \overset{\backslash}{\underset{/}{S}}\overset{+}{\therefore}\overset{/}{\underset{\backslash}{S}}$$
$$\quad\ \text{I} \qquad\qquad \text{II}$$

i.e., a molecular or complex radical cation. The charged nature of the species is demonstrated unambiguously by conductivity measurements.[5]

Clear distinction between the two cations I and II is possible on the basis of kinetic arguments and their optical absorptions which are particularly characteristic for the complex II.[5] The latter, which contains the newly established sulfur–sulfur three-electron bond, typically exhibits extremely broad and structureless absorption bands in the visible with maxima in the 460–530-nm range, extinction coefficients of around 6000 M^{-1} cm^{-1}, and halfwidths of around 1 eV.[5,17]

(20) N_2O scavenges electrons which are produced simultaneously with the oxidizing species. In aqueous solutions N_2O even converts e_{aq}^{-} into $OH\cdot$ radicals.
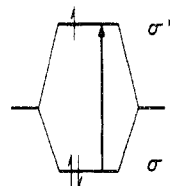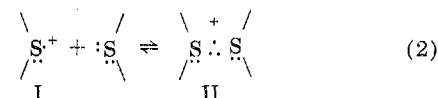

Figure 1.

The molecular radical cation I, whenever observable, shows optical absorptions in the UV around 300 nm. Only few such species have been found, however, among the nonheteroaromatics which, in a reaction environment like water, are stabilized for a time considerably longer than a microsecond. This is the case for the radical cation from thioanisole[21] or di-*tert*-butyl sulfide,[17] where the relative stability can be accounted for by resonance of the unpaired p electron with the adjacent π system, or by steric considerations.

Usually, the molecular radical cation I is converted into the complex II in a fast, practically diffusion-controlled reaction, i.e., in the forward process of equilibrium 2. The degree of stabilization of II relative to I

$$\overset{\backslash}{\underset{/}{S}}{}^{+} + \ :\overset{\backslash}{\underset{/}{S}} \ \rightleftharpoons \ \overset{\backslash}{\underset{/}{S}}\overset{+}{\therefore}\overset{/}{\underset{\backslash}{S}} \qquad\qquad (2)$$
$$\text{I} \qquad\qquad\qquad \text{II}$$

and the involvement of both in an equilibrium are clearly shown by the dependence of the overall lifetime of the complex II on the solute concentration. As the latter is increased and the equilibrium consequently shifted toward the right in eq 2 the lifetime of II increases considerably. For example, $t_{1/2}$ increases from ~30 μs to almost 1 ms in solutions containing 10^{-4} to 10^{-2} M $(C_2H_5)_2S$. Kinetic investigations further indicate that chemical reactions of the radical cations occur preferably through the molecular species I; that is, they initially require equilibration in the reverse direction. Quantitatively this equilibrium is characterized by constants of the order 10^3–10^4 in favor of complex II (for simple aliphatic thioethers).

Assignment of Optical Absorptions

It is thus seen that the oxidized sulfur atom has a high tendency to coordinate with a second sulfur atom and that the resulting complex II gives rise to a new strong optical absorption band. The question now arises as to the assignment of this optical transition. So far all experimental work and theoretical considerations, including evidence discussed in more detail later in this Account, indicate σ/σ* character of the new three-electron sulfur–sulfur bond. Looking now at the likely structure of I with the unpaired electron in a p orbital more or less perpendicular to the C–S–C plane as shown in structure III, one can see that coordination with the free p-electron pair of a second sulfur atom should yield structure IV. The corresponding energy level diagram

III   IV
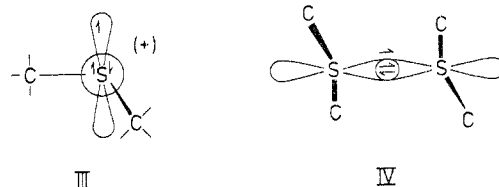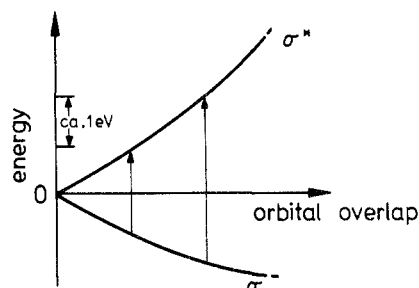
(21) M. Göbl and K.-D. Asmus, to be published.

Figure 2.

for the three-electron bond containing two σ and one σ^* electrons is represented in Figure 1. The broadness of the absorption and the high extinction coefficient (estimated oscillator strength ~ 0.5) suggest that the transition is allowed, and it therefore seems most reasonable to attribute the optical absorption of II/IV to a $\sigma \rightarrow \sigma^*$ transition.

If this assignment is correct, certain conclusions can be drawn, open to verification by appropriate experiments. Thus the optical absorption energy should depend on the relative positions of the σ and σ^* levels. An obvious parameter affecting the latter would be the extent of mutual p-orbital overlap. As shown in Figure 2, an increasing degree of overlap will be associated with a lowering of the σ level, a corresponding rise in σ^*, and consequently an increasing σ/σ^* separation. In other words, an increasing overlap should result in a blue shift, a decreasing overlap in a red shift of the absorption. In summary, the σ/σ^* separation varies with the extent of p-orbital overlap, which, in turn, is expected to be a function of the internuclear distance, $r(S \therefore S)$, and is strongly dependent on the angular orientation of the interacting orbitals relative to one another.

Intramolecular Radical Cation Complexes

The stabilization of an oxidized S atom by interaction with an intact S atom should not only occur *inter*molecularly, as discussed, but also *intra*molecularly, for example in molecules containing two S atoms separated by a carbon chain, either open or cyclic. Such intramolecular complexes, with relatively inflexible structures compared to the intermolecular complexes, are best suited for study of the influence of nuclear separation and p-orbital orientation on the $\sigma \rightarrow \sigma^*$ transition. The formation of an intramolecular complex is shown schematically in eq 3. Both species V and VI

$$\tag{3}$$
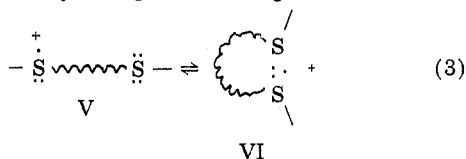
are also assumed to establish an equilibrium.

Such intramolecular complexation occurs quite readily at low solute concentrations. At 10^{-4} M, for example, intermolecular complexation can usually no longer compete with the intramolecular process. In the following, a number of examples are discussed in the light of these considerations.[16-19]

In accordance with expectation, large variations in λ_{max}, i.e. in the σ/σ^* energy separation, are observed for intramolecular radical cation complexes. The values listed in Table I are seen to range from $\lambda_{max} = 400$ nm to 650 nm, where these particular values refer to the species from 1,5-dithiacyclooctane and 1,4-dithiacyclo-

Table I
Optical Data of Intramolecularly S-S Bonded Radical Cations

compound[a]	radical	λ_{max} nm	λ_{max} eV	ϵ_{max}, M^{-1} cm^{-1}
2 / S S \ 2	VII	650	1.91	1070
2 / S S \ 3	VIII	470	2.64	3500
3 / S S \ 3	IX	400	3.10	5800
1–1 S / S \ 2	X			
1 / S S \ 3	XI	600	2.07	1650
4 / S S \ 4	XII	425	2.92	4900
— S — 2 — S —	XIII	525	2.36	3400
— S — 3 — S —	XIV	440	2.80	5800
— S — 4 — S —	XV	450	2.76	5300
S — 2 / 1 — 1 \	XVI	570	2.18	2500
S — 2 / S — 1 \ 1 S 1 \ / S — 1	XVII	610	2.03	720
S / 2 — S — 1 — 1 2 \ / S	XVIII	520	2.38	3000

[a] The numbers denote carbon atoms (CH_3, CH_2, or CH).

hexane, respectively (structures IX and VII), and are specifically indicated in Figure 2.

A significant trend is also observed for the corresponding extinction coefficients. For those species absorbing in the 400–450 nm range, ϵ values around 5×10^3 M^{-1} cm^{-1} (similar to those of the intermolecular complexes) are usually found. For the intramolecular radicals absorbing at the lower energies, a marked decrease in ϵ with increasing λ_{max} is noted; e.g., $\epsilon = 1070$ M^{-1} cm^{-1} for VII, which absorbs at 650 nm. From MNDO/2 calculations it would appear that this may be related to the probability of electron localization between the two interacting sulfur atoms.[22]

Parameters Influencing λ_{max}

To illustrate the significance of the geometrical parameters pictorial representations of the most likely

(22) T. R. Clark, private communication and to be published.

VII   VIII   IX

X   XVI
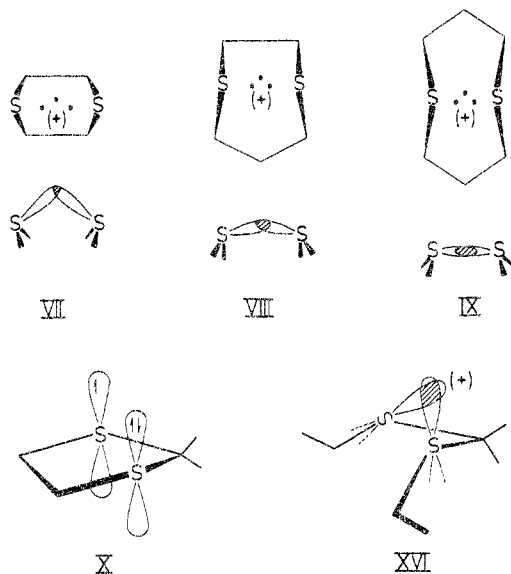
structures of the intramolecular complexes are shown in structures VII–XVI, in some cases including overlap regions of the interacting p orbitals and views from two different angles.

XI   XII   XIII

XIV   XV   XVIII

XX   XIX
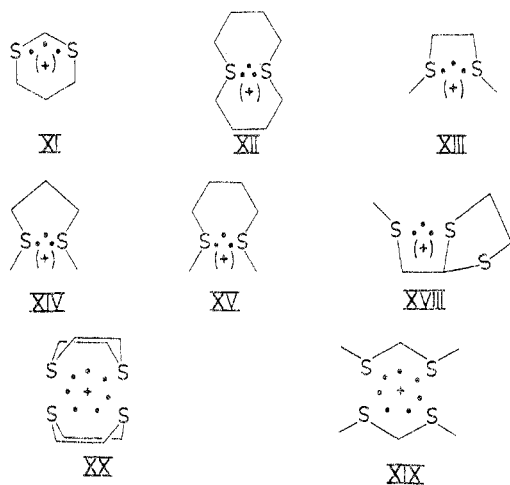
The influence of $r(S \therefore S)$ becomes apparent, at least qualitatively, by comparison of the intramolecular radical cations from 1,3-dithiacyclohexane (XI), 1,4-dithiacycloheptane (VIII), 2,6-dithiaheptane (XIV), and 1,5-dithiacyclooctane (IX) which show absorption maxima at 600, 470, 440, and 400 nm, respectively. The increasing number of carbon atoms between the two sulfur atoms and the increasing flexibility of the molecules permit an increasingly closer approach of the two interacting sulfur atoms. This qualitative line of reasoning has been substantiated by some recent MNDO/2 calculations by Clark[22] who derives $r(S \therefore S)$ values of 2.315, 2.234, 2.178, and 2.136 Å for the respective intramolecular three-electron sulfur–sulfur bonds.

In general, however, it is difficult to account for changes in λ_{max} solely on the basis of internuclear distances. Equally important for the total orbital overlap and closely linked with the distance parameter is the angular orientation of the p orbitals. This becomes evident on comparison of the structures of XI, VIII, IX, and in particular VII. The latter is considered to have established a through-space three-electron bond with the 1,4-dithiacyclohexane in the boat configuration. In both XI and VII, the free p orbitals perpendicular to
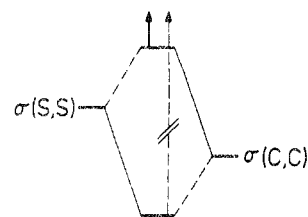
the C–S–C plane cannot point directly toward each other, whereas this should easily be possible for VIII and particularly for IX. Again, MNDO/2 calculations[22] support this conclusion with optimized C–S$\therefore$S angles of 66.9°, 96.6°, and 98.4° in the intramolecular radical cations VII, VIII, and IX, respectively (in the case of VIII the angle refers to the newly formed five-membered ring). Thus the angular parameter certainly contributes to the σ/σ^* separation for VII, VIII, and XI.

The best demonstration of the effect of angular p-orbital orientation is afforded by the oxidized 2-methyl-1,3-dithiacyclopentane. The almost planar structure of this molecule (structure X) does not allow mutual p-orbital overlap between the two sulfur atoms, and it is now not surprising that no optical absorption associable with an intramolecular radical cation complex is observable. This is probably the best experimental evidence for the σ/σ^* character of the three-electron sulfur–sulfur bond and the assignment of the optical absorption to a $\sigma \rightarrow \sigma^*$ transition. Interestingly but not surprisingly, opening of the rigid five-membered ring as in XVI allows the two sulfur atoms to twist toward each other and to establish an intramolecular three-electron bond which absorbs at 570 nm ($\epsilon = 2500$ M^{-1} cm^{-1}).

Looking at some of the λ_{max} values and considering possible extents of p-orbital overlap it is noted that species VII exhibits a rather low σ/σ^* transition energy. This becomes particularly apparent in comparison with species VIII and XIII where the two S-atoms are separated by the same number of C atoms as in VII. A reasonable and theoretically founded possibility to account for this would be interactions between the new S$\therefore$S bond with other bond orbitals of similar symmetry, e.g., σ(C,C) bonds located preferably parallel and close to the S$\therefore$S bond. As shown in Figure 3 such an interaction should lead to a rise of the probably more energetic σ(S,S) level and thus to a smaller σ/σ^* energy separation. The effect will be even larger if the σ^*(S,S) level is also affected, although for our species the latter seems less likely.[22] In any case, it can be expected that σ(C,C) bonds parallel to and in close proximity with the S$\therefore$S bond account for a net red shift in the radical cations VIII, XIII, and XVI, and particularly in VII. At greater distance between the C–C and S$\therefore$S bonds the effect will rapidly diminish but may still be responsible for the slight red shift in λ_{max} of XII and XV relative to IX and XIV, respectively. (A transition from the lower σ level in Figure C is probably forbidden and concealed in the UV absorptions.)

In conclusion the magnitudes of the σ/σ^* energy level separations and thus the optical absorption parameters seem to depend markedly on the geometry of the radical cations and are contributed to by various parameters. There can be no doubt that the dynamic equilibrium
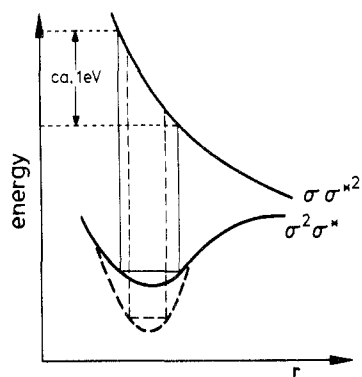
Figure 4.

between $>S^+\cdot$ and $>S\therefore^+S<$, the bulkiness of functional groups, and the flexibility of the molecules will also play a role. The latter parameter, for example, is assumed to account for the differences in λ_{max} for the intramolecular radical cations from open chain and cyclic dithia compounds, respectively.

Stability of Three-Electron Bonds

All the foregoing considerations are concerned with the stability of the new three-electron sulfur–sulfur bond, and a general comment on this aspect seems appropriate at this point. Theory predicts that the overall stability of a three-electron bond is not a linear function of the orbital overlap.[13] This is due to the fact that the destabilizing effect of the antibonding σ^* electron becomes increasingly large relative to the stabilizing effect of the two bonding σ electrons for positive overlap integral values. (Eventually, when the latter value is equal to or greater than $1/3$, no net bonding remains.) This means that the σ and σ^* curves in Figure 2 will not be linear. For all our radical cation complexes, however, an overall residual stabilization of the $S\therefore S$ bond is indicated. MNDO/2 calculated $S\therefore S$ bond energies range from ~ 40 to 130 kJ mol^{-1} and correlate more or less linearly with the respective λ_{max} values.[22] The magnitude of these bond energies also substantiates the antibonding, i.e., bond-weakening, character of the third electron. Without going into detailed discussion, it seems worthwhile to mention a further observation which is in accord with the σ/σ^* picture, namely that the relative ease of dissociation of the $S\therefore S$ bond also holds for other known three-electron bonded species (e.g., $Cl_2^-\cdot \rightleftharpoons Cl\cdot + Cl^-$; $RSSR^-\cdot \rightleftharpoons RS\cdot + RS^-$).

The optical data also permit some inferences to be made as to the shapes of the potential curves for the three-electron bonds. As schematically shown in Figure 4, the broadness of the absorption bands can be explained in terms of a broad, shallow $\sigma^2\sigma^*$ potential well in combination with a relatively steep repulsive $\sigma\sigma^{*2}$ curve in the Franck–Condon region. Further, an increase in bond strength, i.e., in p-orbital overlap, should effect a deepening and narrowing of the well in the region of the lower vibrational levels (dashed curve). Experiments clearly support this picture with measured halfwidths for the absorption bands of 1.15 eV, 0.86 eV, and 0.73 eV for VII, VIII and IX, respectively. Further line broadening may result from the fact that, owing to the dynamic equilibrium of eq 2, the p-orbital overlap cannot be regarded as a time-independent constant parameter.

Radical Cations from Trithia Compounds

After consideration of the oxidation of mono- and dithia compounds, the discussion can now be extended to include molecules containing more than two sulfur atoms. The first example is the intramolecular radical cation from 1,3,5-trithiacyclohexane, the absorption of which peaks at 610 nm, i.e., almost at the same place as that of XI. This suggests that the oxidized sulfur atom is mainly stabilized by interaction with just one of the other sulfur atoms. A contribution by the third sulfur atom may, however, be indicated by the more pronounced infrared tailing of the band and a greater halfwidth (1.45 eV) than for XI. It is interesting to note that photoelectron spectroscopy (PES) of the trithia compound shows a strong interaction between two sulfur atoms and a much weaker interaction with the third.[23]

Similar considerations prevail for 2-(ethylthiomethyl)-1,3-dithiacyclopentane, a derivative of 2-methyl-1,3-dithiacyclopentane with another sulfur atom in the side chain. While no intramolecular radical cation complex could be formed from the dithia compound (see X), the compound with three S atoms readily forms such a species with λ_{max} 520 nm ($\epsilon = 3.10^3$ M^{-1} cm^{-1}). Its formation is only possible if interaction of a sulfur atom in the ring with the sulfur atom in the chain is assumed. The resulting structure XVIII would be similar to that of XIII which in fact absorbs at practically the same wavelength (525 nm). These and other examples not mentioned here suggest that oxidized multithia compounds are preferably stabilized by coordination of two of the sulfur atoms. Participation of a third or more sulfur atoms cannot be completely excluded but generally seems to be slight. More quantitative information can probably be inferred from PES data.

Multicenter Odd-Electron Bonds

An interesting exception to the above general rule is observed when 1,3-dithia and, to some extent, 1,4-dithia compounds are oxidized in solvents of very low polarity, e.g., hydrocarbons.[18] At high solute concentrations, i.e., conditions where intermolecular complexation dominates over the intramolecular process, two absorption bands are observed in the visible and near-infrared. One is the expected strong band around 500 nm attributable to a species of type II/IV. The second, a new band not observable in polar solvents, peaks at lower energy around 750 nm and, for 1,3-dithia compounds, is even stronger than the 500-nm band. This is quite surprising since low-energy bands are generally associated with considerably lower extinction coefficients for three-electron species. In other words, this infrared band must be attributed to a radical cation complex containing more than one molecule, which cannot be explained on the basis of the arguments put forward so far for a three-electron bond between two sulfur atoms. A plausible explanation is provided by the assumption of a multicenter complex which involves all four sulfur atoms of two molecules and constitutes a radical cation with a total of seven electrons. Such structures (XIX and XX) are probably suppressed in polar solutions by dipole–dipole interactions and hydrogen bridging with

(23) (a) H. Bock and G. Wagner, *Angew. Chem.*, 84, 119 (1972); (b) P. Potzinger private communication.
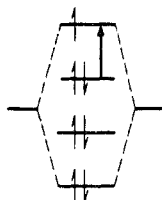
Figure 5.

the solvent. Naturally, the energy diagram must be adjusted to four levels, as shown schematically in Figure 5. The respective separations of these levels should be smaller than in the σ/σ^* two-center systems, and transitions between the upper two levels are allowed, giving rise to the observed strong infrared band. For more detailed discussion it must be borne in mind that such four-center complexes could also be viewed as a resonance-stabilized dimer between a three-electron and a four-electron system. This would lead to symmetrical and antisymmetrical hybrids, a lifting of the degeneracy of the levels, and an accompanying red shift of one of the absorptions, as observed, for example, in dimer dye complexes or negative ions of some aromatic systems.[24]

Several such examples have been observed in the meantime, and it is in accordance with expectation that a certain rigidity with respect to sulfur–sulfur configuration as in the 1,3-dithia compounds facilitates the formation of these multicenter radical cation complexes. Structural considerations can also be invoked to account for the comparatively much lower yield of XX than of XIX.
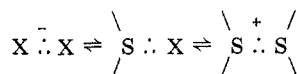
S∴X Bonds

Finally, the discussion of stabilization of an oxidized sulfur atom can be taken one step further. It has been shown that the most important stabilizing factor is the coordination of the unpaired p electron of the oxidized sulfur atom with free p-electron pairs of other sulfur atoms. In principle, however, any heteroatom providing a free p-electron pair should have the same effect. Investigations along these lines have in fact revealed the existence of three-electron bonded species of the type

$$>S∴X$$

with X = Cl, Br, and I, characterized either by their distinct optical absorptions (390–410 nm)[17,25] or by ESR experiments.[26] An interesting example of intramolecular sulfur–nitrogen three-electron bonding has also recently been described by Musker et al.[27]

Generally, species with three-electron bonds between two different heteroatoms are more difficult to stabilize since they are often in equilibrium with the corresponding symmetrical systems, as for example (X = halide):[25]

$$X∴X \rightleftharpoons \overset{\backslash}{\underset{/}{S}}∴X \rightleftharpoons \overset{\backslash}{\underset{/}{S}}\overset{+}{∴}\overset{/}{\underset{\backslash}{S}}$$

The neutral radicals with the sulfur–halogen three-electron bond are therefore only observable at appropriate solute concentrations. Consideration of the energy level diagrams also indicates that symmetrical systems should be favored over unsymmetrical ones in the establishment of a stabilized three-electron bond.

Finally, although fewer examples are known of stabilization of an oxidized S atom by a different heteroatom, the process may nevertheless be of importance, particularly in preorientated rigid systems.

Conclusion

The experimental data discussed in this Account show how oxidized sulfur centers in organic thia compounds possess a marked tendency to become stabilized by coordination with free electron pairs from other sulfur or heteroatoms. This process results in the formation of a new bond between the interacting atoms and is characterized by an odd number of electrons, usually three. In particular, evidence has been put forward which establishes a direct correlation between the optical properties and the geometrical parameters of the odd-electron species investigated.

The significance of these investigations is believed to extend far beyond the legitimate fundamental interest in odd-electron bonds and their physicochemical properties. The possibility of forming a new sulfur–sulfur bond may be particularly relevant to oxidation processes in biological systems, especially since these sulfur radical cations and odd-electron species are markedly unreactive toward molecular oxygen.[28] Further, the stabilization of positive charges in radical cation complexes via ready equilibration with a single oxidized S atom may play an important role in charge-transfer processes. Finally, the relevance of coordination of oriented p orbitals in enzymatic processes should be mentioned since, as has been recently suggested, this may represent an important extension of the well-established lock-and-key mechanism.[29]

In anticipation of future developments, an extension of these studies to investigations of specifically "tailored" molecules will, it is hoped, provide the necessary basis for a more quantitative approach and encourage both theoretical work on sulfur-containing radical cation complexes and general research activity in the field of odd-electron bonds. Problems still outstanding but entirely relevant include the question of apparently different stabilities of S-radical cations and complexes in various solvent systems, and experimental verification of the role suggested for multicentered radical cation complexes in solvents of low polarity.

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