Stabilization of Oxidized Sulphur Centres by Halide Ions. Formation and Properties of $R_2S\therefore X$ Radicals in Aqueous Solutions

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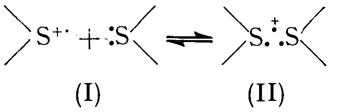
In the presence of halide ions, stabilization of oxidized sulphur centres in organic sulphides can occur *via* formation of three electron $S\therefore X$ bonds to yield $R_2S\therefore X$ radicals. An equilibrium is found to exist between these species, $X_2^{-\cdot}$ radical anions, and $(R_2S)_2^{+\cdot}$ radical cations. Equilibrium constants for the processes $X_2^{-\cdot} + R_2S \rightleftharpoons R_2S\therefore X + X^-$, $R_2S\therefore X + R_2S \rightleftharpoons (R_2S)_2^{+\cdot} + X^-$, $R_2S\therefore X \rightleftharpoons R_2S^{+\cdot} + X^-$, and $R_2S\therefore X \rightleftharpoons R_2S + X\cdot$ have been determined, together with the optical properties of $R_2S\therefore X$, where R = Me and Et, and X = Cl, Br, and I. The absolute stability of the $S\therefore X$ bond increases as the difference in electronegativity between S and X decreases and is thus highest for $R_2S\therefore I$. In addition, rate constants for formation and decay processes of $R_2S\therefore X$ are reported.

SULPHUR organic radical cations, $>S^{+\cdot}$, show a marked tendency to undergo stabilization by co-ordination of the unpaired *p*-electron with a free *p*-electron pair from a second sulphur atom.[1-6] This process gives rise to a radical cation (II) which is characterized by a new sulphur–sulphur bond containing three electrons, two of which have bonding σ character and the third antibonding σ^* character. The complex (II) and the molecular radical cation (I) establish an equilibrium which usually lies well to the right (K is of the order of 10^3).[3,7] MNDO/2 calculations on a number of these species yield values for the overall stability of the $\overset{+}{S}\therefore S$ bond between 40 and 130 kJ mol^{-1}.[8] These values lie considerably below those for normal σ bonds, which clearly reflects the bond weakening σ^* character of the third, unpaired electron. Species (II) generally shows a strong and broad optical absorption [3,5-7,9] peaking in the visible, attributable to a $\sigma \longrightarrow \sigma^*$ transition.[5-7]


(1)

(I) (II)

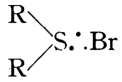
Species of basically similar type to (II) should also be obtainable from compounds containing oxidizable heteroatoms other than sulphur. Such species have in fact been shown to exist in a number of cases, *e.g.* organic selenium [10] and phosphorus [11,12] compounds.

Three-electron-bond species do not necessarily have to be cationic. Corresponding anionic complexes are, for example, formed in the oxidation of halide ions.[13-19] Here equilibrium (2) is established between the halide atom (III) and its complex $X_2^{-\cdot}$ (IV). This equilibrium normally lies to the right (K is of the order of 10^6),[16,19] and (IV) shows a distinct optical absorption in the visible and near-u.v., which can again be attributed to a $\sigma \longrightarrow \sigma^*$ transition. Another anionic example is the disulphide radical anion which is in equilibrium with the corresponding thiyl radical according to $RSSR^{-\cdot} \rightleftharpoons RS\cdot + RS^-$.[20]

$$\underset{\text{(III)}}{X\cdot} + X^- \rightleftharpoons \underset{\text{(IV)}}{X\overset{-}{\therefore}X} \qquad (2)$$

Since the three-electron bond results from combination of an unpaired *p*-electron with a non-bonding *p*-electron pair from a second atom, such a configuration should also be possible between two different heteroatoms. A number of mixed species have indeed been observed. Anionic examples are $Br\overset{-}{\therefore}SCN$ and $I\overset{-}{\therefore}SCN$ radical anions.[21] Further, addition of a bond-weakening σ^* electron into a carbon–halide bond, to yield intermediate $-\overset{-}{C}\therefore X$, has been invoked to explain the mechanism of electron capture by organic halides.[22,23] A positively charged species with a three-electron bond between sulphur and nitrogen has recently been described,[24] and an interaction of this type has been suggested to occur between the nitrogen of the amino-function and the sulphur atom in oxidized methionine.[25]

The formation of a neutral three-electron-bond radical (V) has been shown [7] for reactions (3) and (4)


(V)

$$Br_2^{-\cdot} + R_2S \longrightarrow R_2S\therefore Br + Br^- \qquad (3)$$

$$R_2S(OH)\cdot + Br^- \longrightarrow R_2S\therefore Br + OH^- \qquad (4)$$

[$R_2S(OH)\cdot$ is the primary intermediate radical in the oxidation of R_2S by $OH\cdot$ radicals]. The optical absorption of (V; R = Et) shows a maximum at 400 nm which lies between that of $Br_2^{-\cdot}$ (360 nm) and $(R_2S)_2^{+\cdot}$ (480 nm). Unambiguous identification of a type (V; R = Me) species has been possible by e.s.r. experiments in methanolic and acidic aqueous glasses.[26]

The present investigation was undertaken to obtain more information on the formation and stability of such species, in particular of $R_2S\therefore X$ with X = Cl, Br, and I.

EXPERIMENTAL

Commercially available dimethyl and diethyl sulphide were purified by fractional distillation to $\geqslant 99\%$. The purity was checked gas-chromatographically. All other chemicals (analytical grade) were used without further processing.

Solutions were prepared from deionized, Millipore filtered water and deoxygenated by bubbling with N_2. The solutions were subsequently saturated with N_2O to effect quantitatively conversion of hydrated electrons, e_{aq}^-, into $OH\cdot$ radicals *via* $N_2O + e_{aq}^- \longrightarrow N_2 + OH^- + OH\cdot$ (e_{aq}^- is formed in about the same yield as $OH\cdot$ in irradiated aqueous systems). The total yield of oxidizing $OH\cdot$ radicals formed in such solutions is characterized by G values of *ca.* 6 (G = number of species formed per 100 eV absorbed energy), *i.e. ca.* 6×10^{-6} mol dm^{-3} for an absorbed dose of 1 000 rad.

Pulse-radiolysis experiments were performed by application of short pulses (0.2—2 μs duration) of high energy electrons (1.5 MeV) from a Van de Graaff accelerator. The absorbed dose per 1-μs pulse was *ca.* 500 rad. Dosimetry was based on the reduction of $C(NO_2)_4$ in deoxygenated solutions of 10^{-1} mol dm^{-3} propan-2-ol and 10^{-3} mol dm^{-3} $C(NO_2)_4$. The experimental arrangement and the analysis of pulse-radiolytic data have been described elsewhere.[27]

The accuracy of the experimental data is estimated at ±10%, unless otherwise indicated. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Reaction of $X_2^{-\cdot}$ *with Sulphides.*—In N_2O-saturated solutions of 10^{-1} mol dm^{-3} Cl^- (pH < 3), Br^-, and I^- (any pH), reaction of these halide ions with $OH\cdot$ radicals leads to the formation of the radical anion complexes $Cl_2^{-\cdot}$, $Br_2^{-\cdot}$, and $I_2^{-\cdot}$, respectively. The latter species show strong optical absorptions in the near-u.v. ($\lambda_{max.}$ at 345, 365, and 380 nm, respectively)[15–19] and in the absence of suitable reaction partners decay by second-order disproportionation processes.

Addition of relatively low concentrations (10^{-5}—10^{-2} mol dm^{-3}) of R_2S (Me_2S or Et_2S) to chloride or bromide solutions results in an exponential decay of the $Cl_2^{-\cdot}$ and $Br_2^{-\cdot}$ absorption which is of pseudo-first-order with respect to the sulphide concentration. This is explained in terms of reactions (5) and (3). The corresponding rate

$$Cl_2^{-\cdot} + R_2S \longrightarrow R_2S\therefore Cl + Cl^- \quad (5)$$

$$Br_2^{-\cdot} + R_2S \longrightarrow R_2S\therefore Br + Br^- \quad (3)$$

constants ranging from 2.0×10^9 to 4.7×10^9 dm^3 mol^{-1} s^{-1} are listed in Table 1.

The formation of $R_2S\therefore Cl$ and $R_2S\therefore Br$ radicals is indicated by the appearance of absorptions peaking at 390 and 400 nm, respectively (Table 2); the formation kinetics of these absorptions is identical to the decay kinetics of the respective $Cl_2^{-\cdot}$ and $Br_2^{-\cdot}$ species.

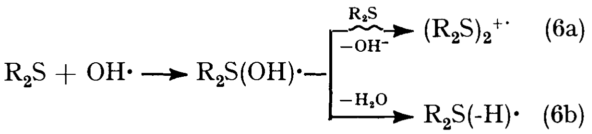
Decay of the $I_2^{-\cdot}$ absorption in 10^{-1} mol dm^{-3} I^- solutions cannot be effected by addition of R_2S (up to 10^{-2} mol dm^{-3}), which implies that a possible reaction between $I_2^{-\cdot}$ and R_2S is probably too slow to be observed on this time scale. (These investigations were done at ⩽380 nm where $I_2^{-\cdot}$ absorbs significantly stronger than $R_2S\therefore I$.)

TABLE 1

Reaction	k/dm^3 mol^{-1} s^{-1}
$Cl_2^{-\cdot} + Me_2S$	3.0×10^9
$Cl_2^{-\cdot} + Et_2S$	4.7×10^9
$Br_2^{-\cdot} + Me_2S$	3.2×10^9
$Br_2^{-\cdot} + Et_2S$	2.0×10^9
$(Me_2S)_2^{+\cdot} + I^-$	1.1×10^{10}
$(Et_2S)_2^{+\cdot} + I^-$	1.0×10^{10}

Rate constants for the formation reactions of $R_2S\therefore X$. Estimated limit of error ±10%.

Reaction of $(R_2S_2)_2^{+\cdot}$ *and* $R_2S(OH)\cdot$ *with Halide Ions.*—In solutions containing an excess of sulphide over the halide ion concentration, the oxidizing $OH\cdot$ radicals react with the sulphide yielding an adduct $R_2S(OH)\cdot$ as the primary intermediate.[3] The latter can subsequently be complexed by a second sulphide molecule, eventually forming an $(R_2S)_2^{+\cdot}$ radical cation.[3] On account of a competitive unimolecular H_2O elimination from $R_2S(OH)\cdot$, however, the yield of $(R_2S)_2^{+\cdot}$ is found to be strongly dependent on the sulphide concentration[3] [reaction (6)]. Under the experimental conditions, at



$$R_2S + OH\cdot \longrightarrow R_2S(OH)\cdot \begin{cases} \xrightarrow[-OH^-]{R_2S} (R_2S)_2^{+\cdot} & (6a) \\ \xrightarrow{-H_2O} R_2S(\text{-}H)\cdot & (6b) \end{cases}$$

$>10^{-4}$ mol dm^{-3} R_2S the formation of $(R_2S)_2^{+\cdot}$ occurs within 1 μs, *i.e.* within the usual duration of the applied electron pulse, and the strong, long lived $(R_2S)_2^{+\cdot}$ absorption ($\lambda_{max.}$ at 480 nm) is immediately observable. Addition of only small amounts of I^- ions leads to a faster decay of this absorption which is exponential and of pseudo-first-order with respect to I^- ion concentration. Simultaneously to the $(R_2S)_2^{+\cdot}$ decay the formation of a new absorption peaking at 410 nm is observed. The latter is assigned to the $R_2S\therefore I$ radical formed in reaction (7) with a rate constant of *ca.* 10^{10} dm^3 mol^{-1} s^{-1} (see Table 1).

$$(R_2S)_2^{+\cdot} + I^- \longrightarrow R_2S\therefore I + R_2S \quad (7)$$

In contrast to a number of $(R_2S)_2^{+\cdot}$ reactions, which have been found to occur through the molecular radical cation $R_2S^{+\cdot}$ subsequent to equilibration [equation (1)][3,28] it appears that reaction (7) proceeds directly. This is indicated by the independence of k_7 on the R_2S concentration. The formation of $R_2S\therefore I$ thus constitutes a substitution of an R_2S molecule in the $(R_2S)_2^{+\cdot}$ complex by an I^- ion.

TABLE 2

Radical	K_{12}	K_{13}	K_{15}	K_{17}	$\lambda_{max.}$/nm	$10^{-3}\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}
$Me_2S\therefore Cl$	$\geqslant 10^4$	2.44×10^3	$\leqslant 10^{-10}$	4.4	390	8
$Et_2S\therefore Cl$	$\geqslant 10^4$	9.09×10^2	$\leqslant 10^{-10}$	1.6×10^{-1}	390	8
$Me_2S\therefore Br$	1.1×10^4	1.64	4.2×10^{-10}	3.0×10^{-3}	400	6.7
$Et_2S\therefore Br$	8.3×10^3	1.43	5.5×10^{-10}	4.1×10^{-4}	400	7.0
$Me_2S\therefore I$	2.0×10^{-1}	$\leqslant 1$	4.4×10^{-5}	$\leqslant 10^{-4}$	410	5.7
$Et_2S\therefore I$	4.5×10^{-1}	$\leqslant 1$	2.0×10^{-5}	$\leqslant 10^{-4}$	410	5.0

Equilibrium constants (see text) and optical parameters for the three-electron-bonded radicals $R_2S\therefore X$. Estimated limits of error for the K values is a factor of 2, for $\varepsilon_{max.}$ of $R_2S\therefore Cl$ ±20%, and for the other data ±10%.

Direct reactions between $(R_2S)_2^{+\cdot}$ and Br^- or Cl^- could not be resolved. It seems not unlikely that $R_2S\therefore Br$ and $R_2S\therefore Cl$ radicals are formed by a fast reaction (8) of the halide ions with a precursor of $(R_2S)_2^{+\cdot}$, namely the primary OH• radical adduct, in these

$$R_2S(OH)\cdot + X^- \longrightarrow R_2S\therefore X + OH^- \quad (8)$$

systems.[7] The $R_2S\therefore X$ then equilibrates with $(R_2S)_2^{+\cdot}$ [see equation (13)]. The relative yield of these two radicals depends only on the $[R_2S] : [X^-]$ concentration ratio and the observable absorption spectra vary accordingly.

The occurrence of this reaction is substantiated by conductivity experiments. The conversion of a normally conducting halide ion (*ca.* 50 Ω^{-1} cm^2) into OH^- ions (*ca.* 180 Ω^{-1} cm^2) leads to an increase in conductivity in basic solutions. In acidic solutions neutralization of OH^- by H_{aq}^+ effectively means the disappearance of a halide ion and a proton, and thus a net decrease in conductivity is expected and indeed observed. Quantitative analysis of the conductivity data further shows that reaction (8) not only accounts for all $R_2S(OH)\cdot$, which in the absence of halide would lead to the formation of $(R_2S)_2^{+\cdot}$, but can also successfully compete with the H_2O elimination process (6b).

Competition between reactions (8) and (9) is described

$$R_2S(OH)\cdot + R_2S \rightsquigarrow (R_2S)_2^{+\cdot} + OH^- \quad (9)$$

by relation (10) where the left-hand side of the equation

$$[(R_2S)_2^{+\cdot}]/[(R_2S)_2^{+\cdot}]_0 = k_9[R_2S]/(k_9[R_2S] + k_8[X^-]) \quad (10)$$

represents the ratio of the $(R_2S)_2^{+\cdot}$ yields in the presence and absence of halide ions. Rearrangement leads to (11).

$$[(R_2S)_2^{+\cdot}]_0/[(R_2S)_2^{+\cdot}] = 1 + k_8[X^-]/k_9[R_2S] \quad (11)$$

A corresponding plot of $[(R_2S)_2^{+\cdot}]_0/[R_2S)_2^{+\cdot}]$ *versus* $1/[R_2S]$ is shown in Figure 1 for solutions containing iodide ions at a concentration of 1.3×10^{-5} mol dm^{-3}, and various concentrations of Me_2S. From the slope of the straight line obtained the ratio $k_8 : k_9 = 5.2$ is calculated, *i.e.* k_8 is greater than k_9. With estimates of k_9 in the 10^9—10^{10} dm^3 mol^{-1} s^{-1} range,[3] reaction (8) is thus seen to be essentially diffusion-controlled.

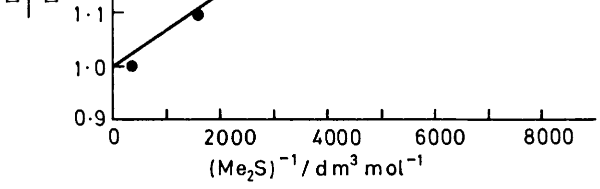


FIGURE 1 Plot of $[(R_2S)_2^{+\cdot}]_0/[(R_2S)_2^{+\cdot}]$ *versus* $1/[R_2S]$ for N_2O-saturated solutions containing 1.3×10^{-5} mol dm^{-3} I^- ions and various concentrations of Me_2S

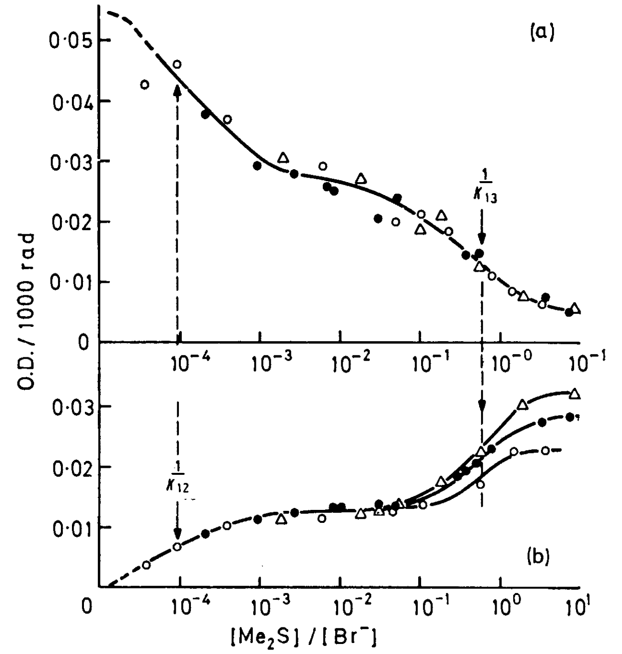


FIGURE 2 Optical densities at 360 (a) and 500 nm (b), normalized with respect to dose, as a function of the $[Me_2S] : [Br^-]$ concentration ratio. Solutions: N_2O-saturated, pH 4—5, Me_2S 1×10^{-2} mol dm^{-3} (△); 5×10^{-4} mol dm^{-3} (●), and 2×10^{-4} mol dm^{-3} (○), varying concentrations of Br^- ions

No significant differences or trends are found for the formation kinetics of the respective $R_2S\therefore X$ species between the methyl and ethyl sulphides.

Equilibrium Constants.—The production of $R_2S\therefore X$ radicals, either by oxidation of R_2S with $X_2^{-\cdot}$, or by reaction of $(R_2S)_2^{+\cdot}$ and X^-, suggests, together with other evidence presented below, that $R_2S\therefore X$ exists in equilibria (12) and (13). This is clearly demonstrated in

$$X_2^{-\cdot} + R_2S \rightleftharpoons R_2S\therefore X + X^- \quad (12)$$

$$R_2S\therefore X + R_2S \rightleftharpoons (R_2S)_2^{+\cdot} + X^- \quad (13)$$

the following example. Figure 2 shows the optical densities at 360 (Figure 2a) and 500 nm (Figure 2b) in pulse-irradiated, N_2O-saturated solutions containing Me_2S and Br^- at various concentration ratios. The optical densities were measured at 10 μs after the application of the 1-μs electron pulse, *i.e.* at a time when possible reactions of $Br_2^{-\cdot}$ with Me_2S or $Me_2S(OH)\cdot$, and $(Me_2S)_2^{+\cdot}$ with Br^- should have gone to completion and equilibrium conditions been established.

Particularly, Figure 2b shows a curve with two distinct breaks, the positions of which do not depend on the absolute concentrations but, in accord with the equilibrium scheme, only on the $[Mr_2S] : [Br^-]$ concentration ratio. At low ratios the $Br_2^{-\cdot}$ radical anion, which shows the strongest absorption of the three radical species at 360 nm is present. At high ratios the $(MeS)_2^{+\cdot}$ radical cation with $\lambda_{max.}$ at 480 nm dominates and in the intermediate range $Me_2S\therefore Br$ exists. From the points of inflection the equilibrium constants K_{12} 1.1 × 10^4 and K_{13} 1.64 are derived.

It is certainly more difficult to derive equilibrium constants from the measurements at 360 nm shown in Figure 2a. This curve is not as cleanly structured as the 500-nm curve in Figure 2b. But taking the known, *i.e.* calculable optical densities of the individual $(Me_2S)_2^{+\cdot}$, $Me_2S\therefore Br$, and $Br_2^{-\cdot}$ species, the respective 50% values between the $(Me_2S)_2^{+\cdot} : Me_2S\therefore Br$ and $Me_2S\therefore Br : Br_2^{-\cdot}$ absorptions are found at about the same $[Me_2S] : [Br^-]$ concentration ratios as in Figure 2b. The accuracy of the equilibrium constants derived from these measurements has to be viewed, of course, in the light of these considerations, and one should probably allow at least a factor of two for the limits of error.

It is noted in Figure 2b that at high concentration ratios the absolute yield of the $(R_2S)_2^{+\cdot}$ absorption increases with R_2S concentration. This is in agreement with the competitive scheme given in equation (6) according to which the primary OH· adduct $R_2S(OH)\cdot$ either undergoes unimolecular decay to $R_2S(-H)\cdot$ or is complexed by a second R_2S molecule to yield eventually $(R_2S)_2^{+\cdot}$. No such R_2S concentration dependence is observed in the $[Me_2S] : [Br^-]$ concentration range studied, where $R_2S\therefore Br$ is the most stable radical species. The latter supports the previous conclusion that $R_2S\therefore Br$ is not only formed *via* the radical cation but also directly through reaction of the $R_2S(OH)\cdot$ with Br^- [equation (8)].

Similar experiments have been carried out using Et_2S and Cl^- and I^- as well as Me_2S and Br^-. The corresponding equilibrium constants are listed in Table 2. Under the experimentally possible conditions K_{12} for X = Cl, and K_{13} for X = I could not be determined. Only lower and upper limits, respectively, can be given in these cases. No significant differences are observed between the methyl and ethyl compounds, whereas several orders of magnitude are apparent between the equilibrium constants for the $R_2S\therefore X$ radicals from different halides.

From K_{12} and K_{13}, determined here, and the relations $K_1 = [(R_2S)_2^{+\cdot}]/[R_2S^{+\cdot}][R_2S]$ and $K_2 = [X_2^{-\cdot}]/[X\cdot][X^-]$ derived from previous investigations [3,16,19] it is possible to calculate two additional equilibrium constants. Thus equation (14) describes equilibrium (15) and (16)

$$K_{15} = \frac{1}{K_{12}K_2} = \frac{[R_2S][X\cdot]}{[R_2S\therefore X]} \qquad (14)$$

$$R_2S\therefore X \rightleftharpoons R_2S + X\cdot \qquad (15)$$

$$K_{17} = \frac{K_{13}}{K_1} = \frac{[R_2S^{+\cdot}][X^-]}{[R_2S\therefore X]} \qquad (16)$$

$$R_2S\therefore X \rightleftharpoons R_2S^{+\cdot} + X^- \qquad (17)$$

describes (17). These equilibrium constants are also listed in Table 2.

Fully in accordance with expectation, it is noted that the degree of ionic dissociation of $R_2S\therefore X$, expressed in terms of K_{17}, is highest for the chlorine species where K_{17} has a value around unity. The degree of 'atomic' or 'neutral' dissociation, on the other hand, described by K_{15}, is highest for the iodine species and the value obtained by extrapolation (K_{17} for $R_2S\therefore I$ can only be estimated), in this case, would even dominate over the ionic dissociation. Considering the absolute values of K_{15} and K_{17}, the strongest $R_2S\therefore X$ radical complex is formed with X = I, *i.e.* where the difference in electronegativity between S and X is smallest.

The stability of the $S\therefore X$ bond relative to the $\overset{+}{S\therefore S}$ bond is reflected in K_{13}. For the iodine compound, where the atomic dissociation dominates over the ionic dissociation, the equilibrium constant for equation (18)

$$R_2S\therefore X + R_2S^{+\cdot} \rightleftharpoons (R_2S)_2^{+\cdot} + X\cdot \qquad (18)$$

can also be derived, $K_{18} = 1/K_1.K_{15} \approx 10^{-1}$. This value, together with K_{13}, indicates that the $S\therefore I$ bond is slightly more stable even than the $\overset{+}{S\therefore S}$ bond, which has been calculated by MNDO/2 to have a bond strength of 130 kJ mol^{-1}.[8] A plausible explanation is that the orbital interaction necessary for establishment of the three-electron bonds is favoured on steric grounds if one of the partners is an atom rather than a complete molecule.

The stability of $S\therefore X$ relative to that of $\overset{-}{X\therefore X}$ is reflected by K_{12} and found to be highest for the chlorine species $R_2S\therefore Cl$. In connection with the latter it is recalled that $Cl_2^{-\cdot}$ in aqueous solution is observed only in acidic solutions on account of the overall equilibrium (19) which in neutral or basic solutions lies well to the left.[19]

$$Cl^- + Cl(OH)^{-\cdot} + H^+ \rightleftharpoons Cl_2^{-\cdot} + H_2O \qquad (19)$$

Finally, the *K* values in Table 2 also allow a comment on the possibility of forming the analogous fluorine radical, $R_2S\therefore F$. According to the trend in K_{13} such a species would be expected to be very unstable relative to the corresponding $(R_2S)_2^{+\cdot}$. Even if $R_2S\therefore F$ could be stabilized under suitable experimental conditions, however, it should undergo complete ionic dissociation into $R_2S^{+\cdot}$ and F^- since K_{17} should be several orders of magnitude greater than unity. In fact, all experimental efforts to identify an $R_2S\therefore F$ radical had the expected negative result. (The extrapolated relative stability of $R_2S\therefore F$ over $F_2^{-\cdot}$ is meaningless, since the latter cannot be stabilized in aqueous solutions either.)

Some Physico-chemical Properties of $R_2S\therefore X$.—The optical absorption spectra of $R_2S\therefore X$ show structureless broad bands (halfwidths of *ca.* 1 eV), very similar to those of $X_2^{-\cdot}$ [15-19] and $(R_2S)_2^{+\cdot}$.[3,5-7,9] Maxima are observed at 390, 400, and 410 nm for $R_2S\therefore Cl$, $R_2S\therefore Br$, and $R_2S\therefore I$, respectively. *i.e.* lying between $\lambda_{max.}$ of $X_2^{-\cdot}$ and $(R_2S)_2^{+\cdot}$. Extinction coefficients calculated from the measured optical absorptions and, for $R_2S\therefore Cl$ taking into account the relatively high degree of ionic dissociation [equation (17)], are listed in Table 2. The values are similar to those for $X_2^{-\cdot}$ [15-19] and $(R_2S)_2^{+\cdot}$.[3,7] The optical absorptions are assigned to $\sigma \longrightarrow \sigma^*$ transitions in the $S\therefore X$ three-electron bond.

The $Me_2S\therefore X$ absorptions decay by pure second-order processes with bimolecular rate constants of (7 ± 2) × 10^9 dm^3 mol^{-1} s^{-1}. This decay process, incidently, is not affected by the total ion concentration, *i.e.* the lack of any kinetic salt effect demonstrates the neutral character of the $R_2S\therefore X$ radicals.

The decay kinetics of the corresponding $Et_2S\therefore X$ species are of mixed order and probably include a first-order contribution. This is similar to the decay of the corresponding $(Et_2S)_2^{+\cdot}$ radical cation, where a considerable first-order contribution from proton elimination was observed.[3] No indication is found that the mixed-order decay could be associated with more than one radical species since the decay kinetics did not change with wavelength. No attempt is to be made, however, to assign a detailed mechanism to the decay processes.

Conclusions.—The experiments here discussed show that the stabilization of an oxidized sulphur centre in a three-electron $S\therefore X$ bond, *i.e.* through a heteroatom other than sulphur, is characterized by various equilibria. Accordingly $R_2S\therefore X$ radicals can only be detected within certain limits of the concentration ratios $[R_2S]:[X^-]$. Generally the absolute stability of the $S\therefore X$ bond seems to increase with decreasing difference in electronegativity between S and X. The latter rule is probably also valid for heteroatoms other than halogen atoms.

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REFERENCES

[1] B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 1748.

[2] M. C. R. Symons, *J.C.S. Perkin II*, 1974, 1618.

[3] M. Bonifačić, H. Möckel, D. Bahnemann, and K.-D. Asmus, *J.C.S. Perkin II*, 1975, 657.

[4] W. K. Musker and T. L. Wolford, *J. Amer. Chem. Soc.*, 1976, **98**, 3055.

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

[6] K.-D. Asmus, *Accounts Chem. Research*, 1979, **12**, 436.

[7] K.-D. Asmus, D. Bahnemann, M. Bonifačić, and H. A. Gillis, *Faraday Discuss.* 1978, **63**, 213.

[8] T. R. Clark, personal communication and to be published.

[9] G. Meissner, A. Henglein, and G. Beck, *Z. Naturforsch.*, 1967, **22b**, 13.

[10] K. Nishikada and Ff. Williams, *Chem. Phys. Letters*, 1975, **34**, 302.

[11] A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **68**, 1589.

[12] (*a*) T. Gillbro, C. M. L. Kerr, and Ff. Williams, *Mol. Phys.*, 1974, **28**, 1225; (*b*) C. M. L. Kerr, K. Webster, and Ff. Williams, *J. Phys. Chem.*, 1975, **79**, 2650.

[13] W. Kanzig and M. H. Cohen, *Phys. Rev. Letters*, 1959, **3**, 509.

[14] (*a*) P. W. Atkins and M. C. R. Symons, ' The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967, p. 114; (*b*) I. Marov and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 201.

[15] M. Anbar and J. K. Thomas, *J. Phys. Chem.*, 1964, **68**, 3829.

[16] M. S. Matheson, W. A. Mulac, J. L. Weeks, and J. Rabani, *J. Phys. Chem.*, 1966, **70**, 2092.

[17] B. Cercek, M. Ebert, L. W. Gilbert, and A. J. Swallow in ' Pulse Radiolysis,' eds. M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Academic Press, London, 1965, p. 83.

[18] J. K. Thomas, *Trans. Faraday Soc.*, 1965, **61**, 702.

[19] J. H. Baxendale, P. L. T. Bevan, and D. A. Stott, *Trans. Faraday Soc.*, 1968, **64**, 2389.

[20] (*a*) G. E. Adams, G. S. McNaughton, and B. D. Michael, in ' Excitation and Ionization,' eds. G. Scholes and G. R. A. Johnson, Taylor, and Francis, London 1967; (*b*) M. Z. Hoffman and E. Hayon, *J. Amer. Chem. Soc.*, 1972, **94**, 7950.

[21] (*a*) M. Schöneshöfer and A. Henglein, *Ber. Bunsengesellschaft. Phys. Chem.*, 1969, **73**, 289; 1970, **74**, 393; (*b*) M. Schöneshöfer, *Internat. J. Radiation Phys. Chem.*, 1969, **1**, 505.

[22] A. Hasegawa, M. Shiotani, and Ff. Williams, *Faraday Discuss.*, 1978, **63**, 157.

[23] M. C. R. Symons, *Faraday Discuss.*, 1978, **63**, 209.

[24] W. K. Musker, A. S. Hirschon, and J. T. Doi, *J. Amer. Chem. Soc.*, 1978, **100**, 7754.

[25] G. E. Adams, J. E. Aldrich, R. H. Bisby, R. B. Cundall, J. L. Redpath, and R. L. Willson, *Radiat. Res.*, 1972, **49**, 278.

[26] (*a*) M. C. R. Symons and R. L. Petersen, *J.C.S. Faraday II*, 1978, 210; (*b*) E. A. Lucken and C. Mazeline, *J. Chem. Phys.*, 1969, **48**, 1942.

[27] (*a*) A. Henglein, *Allg. prakt. Chem.*, 1966, **17**, 296; (*b*) G. Beck, *Internat. J. Radiation Phys. Chem.*, 1969, **1**, 361; (*c*) K.-D. Asmus, *ibid.*, 1972, **4**, 417.

[28] M. Bonifačić and K.-D. Asmus, *J. Phys. Chem.*, 1976, **80**, 2426.