Radical Cations from One-electron Oxidation of Aliphatic Sulphoxides in Aqueous Solution. A Radiation Chemical Study

Kamal Kishore and Klaus-Dieter Asmus *
Hahn-Meitner-Institut Berlin, Bereich Strahlenchemie, Postfach 39 01 28, D-1000 Berlin 39, FRG

Sulphoxide radical cations, $(R_2SO)^{+\bullet}$, have been observed upon one-electron oxidation of simple aliphatic sulphoxides by strongly oxidizing radicals with redox potentials $\geq +2$ V, *e.g.* $SO_4^{-\bullet}$, $(CH_3I)^{+\bullet}$, $(CH_3I\therefore ICH_3)^+$, or Ti^{2+} in pulse-irradiated aqueous solutions. They exhibit optical absorptions in the u.v. with λ_{max} depending on the substituent (*e.g.* 300, 320, and 330 nm for R = Me, Et, and Pr, respectively). Extinction coefficients are of the order of 10^3 mol^{-1} dm^{-3} cm^{-1}. The sulphoxide radical cations exist only at low pH and are probably best formulated in terms of an adduct with one water molecule, $(R_2SO\therefore OH_2)^+$. The p*K* values for the equilibrium $(R_2SO\therefore OH_2)^+ \rightleftharpoons R_2SO(OH)^\bullet + H^+$ have been estimated to be 5.6, 6.1, and 6.5, for R = Me, Et, and Pr, respectively, from yield measurements. The neutral $R_2SO(OH)^\bullet$ is identical with the hydroxyl radical adduct to sulphoxides formed at any pH in the reaction of $R_2SO + {}^\bullet OH$, and decays irreversibly into $R^\bullet + RSO_2^- + H^+$. The sulphoxide radical cations are very good oxidants. Absolute rate constants have been measured for their reactions with a variety of electron donors, namely, organic sulphides, dithia compounds, disulphides, Br^-, I^-, and SCN^-. The optical and kinetic results are discussed in the light of the electronic properties of the radical species.

Direct identification and characterization of transient intermediates generated during the one-electron oxidation of sulphoxides has been the subject of only relatively few investigations. Although formation of radical cations was indicated in some of these studies, their assignment from optical and e.s.r. measurements remained, nevertheless, mostly speculative. The formation of a transient absorption around 600 nm was reported in early pulse-radiolysis investigations with neat dimethyl sulphoxide (DMSO) solutions [1–3] and tentatively considered to be due to a radical cation, possibly a dimer $(DMSO)_2^{+\bullet}$. The existence of both this dimer as well as the molecular radical cation, $DMSO^{+\bullet}$, was deduced from e.s.r. spectra obtained during the γ-irradiation of low-temperature (77 K) glassy matrices.[4] Unambiguous assignment in this case was hampered, however, by the simultaneous presence of other, dominating radical species, particularly sulphinyl radicals, $MeS^\bullet(O)$. Formation of a transient $DMSO^{+\bullet}$ radical cation was also invoked in the $SO_4^{-\bullet}$ induced oxidation mechanism of sulphoxides in aqueous solution[5] although it completely escaped detection in these e.s.r. studies.

Practically no ambiguity remains for the neutral intermediates generated during the oxidation of sulphoxides by $^\bullet OH$ radicals as studied, for example, by pulse radiolysis[6] or e.s.r. flow photolysis.[5,7,8] This process proceeds by addition of the hydroxyl radical to the sulphoxide function followed by sulphur–carbon bond breakage to yield sulphinic acid and a carbon-centred radical, Scheme 1. Several other radicals identified by e.s.r., *e.g.* $RSO^\bullet$, $RSO_2^\bullet$, and carbon-centred radicals resulting from H-atom abstraction in the side chain are the result of secondary reactions. The corresponding investigations with $NH_3^{+\bullet}$ and $Bu^tO^\bullet$ as oxidants suggest similar reaction routes.[9,10]

$$R_2SO + {}^\bullet OH \longrightarrow R_2SO(OH)^\bullet \longrightarrow R^\bullet + RSO_2H$$

Scheme 1.

Since there still exists ambiguity about the possible radical cations it seemed an interesting challenge to look for conditions under which more direct experimental evidence could be provided for such species. In the present paper we communicate on such a system, namely, pulse radiolysis of aqueous solutions of sulphoxide, and oxidations initiated by a number of inorganic and organic one-electron oxidants. It allows one to characterize sulphoxide radical cations and to determine absolute rate constants for their chemical reactions.

Experimental

Sulphoxides and methyl iodide were purified by distillation. All other chemicals were of analytical grade purity and used as received. The solvent was deionized, Millipore-filtered water. The pH of acid solutions was adjusted by addition of $HClO_4$, in basic solutions by NaOH. For measurements within the pH 6–8 range phosphate buffers were used. Solutions were deoxygenated by bubbling with N_2 for *ca.* 1 h per dm^3 sample. For $^\bullet OH$ radical induced studies solutions were subsequently saturated with N_2O by a similar bubbling procedure.

Irradiation of aqueous solutions yields e_{aq}^-, $^\bullet OH$, and $H^\bullet$ as primary radical species available for chemical reactions. In neutral and slightly acidic solutions the yield of hydrated electrons and hydroxyl radicals is about equal (0.28 μmol^{-1} J or *G ca.* 2.7, with *G* denoting the number of species generated or transformed per 100 eV absorbed energy) and significantly exceeds that of hydrogen atoms (0.06 μmol J^{-1}, *G ca.* 0.6). At low pH or in the presence of N_2O hydrated electrons are converted by the reactions $e_{aq}^- + H^+ \longrightarrow H^\bullet$ or $e_{aq}^- + N_2O \longrightarrow N_2 + OH^- + {}^\bullet OH$, respectively. Selective investigations on reactions initiated by e_{eq}^- were performed in the presence of high concentrations of t-butyl alcohol (usually 0.5 mol dm^{-3}) which scavenges both $^\bullet OH$ and $H^\bullet$.

Irradiations were carried out by means of pulse radiolysis. This technique provides short pulses, *e.g.* of 1 μs duration, of high-energy electrons (*e.g.* 1.5 MeV) delivered by a Van de Graaff accelerator. The concentration of radicals generated was of the order of 6×10^{-7} mol dm^{-3} per 1 Gy absorbed energy (1 Gy = 1 J kg^{-1}) for a radiation chemical yield *G ca.* 6 (0.62 μmol^{-1} J), *i.e.* the yield of $^\bullet OH$ radicals in N_2O saturated solution. Further details including dosimetry (based on the oxidation of SCN^- to $(SCN)_2^{-\bullet}$), detection of time-resolved optical and conductivity signals, and the evaluation and

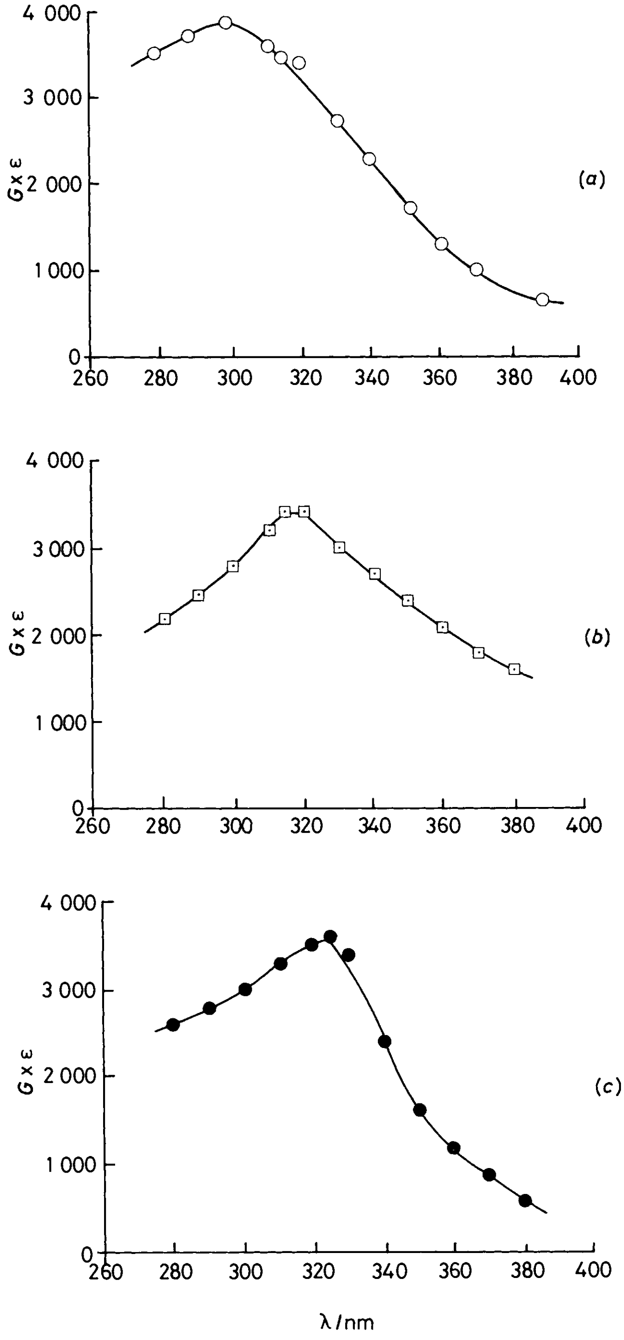


Figure 1. Absorption spectra of (*a*) DMSO$^{+\bullet}$, (*b*) DESO$^{+\bullet}$, and (*c*) DPSO$^{+\bullet}$. [The sulphoxide radical cations are likely to be associates with one water molecule, *i.e.* $(R_2SO\therefore OH_2)^+$ (see text)].

interpretation of pulse radiolysis data have been documented elsewhere.[11]

Error limits are generally estimated to ±10%, unless specifically noted. All experiments were carried out at room temperature.

Results and Discussion

Formation of $R_2SO^{+\bullet}$ *Radical Cations*.—One-electron oxidation of sulphoxides could be achieved by a number of strongly oxidizing radical species. A most powerful one is the $SO_4^{-\bullet}$ radical anion.[12] It can conveniently be generated by reduction of peroxy disulphate. Pulse irradiation of N_2 saturated, pH *ca.* 4 solutions containing 5×10^{-3} mol dm^{-3} $S_2O_8^{2-}$ (and 0.5 mol dm^{-3} t-butyl alcohol to scavenge $^\bullet OH$ radicals) yielded $SO_4^{-\bullet}$ radicals corresponding to the yield of hydrated electrons (0.28 μmol^{-1} J, $G = 2.7$).

$$S_2O_8^{2-} + e_{aq}^- \longrightarrow SO_4^{2-} + SO_4^{-\bullet}$$

Scheme 2.

They are easily detectable using their optical absorption at 450 nm.[13] Upon addition of increasing amounts of DMSO this absorption decays increasingly faster with $t_{1/2}$ inversely proportional to [DMSO], and it is replaced by another transient absorption with λ_{max} 300 nm [Figure 1(*a*)]. The underlying reaction is assumed to be the one-electron redox reaction, Scheme 3.

$$SO_4^{-\bullet} + DMSO \longrightarrow SO_4^{2-} + DMSO^{+\bullet}$$

Scheme 3.

The same 300 nm species is obtained with two other strong oxidants, namely, Tl^{2+} [14–16] and MeI$^{+\bullet}$/(MeI$\therefore$IMe)$^+$ [17] instead of $SO_4^{-\bullet}$. In these cases solutions of pH *ca.* 3.2 were N_2O saturated and contained 5×10^{-3} mol dm^{-3} mol dm^{-3} Tl$^+$ or methyl iodide (MeI), and no t-butyl alcohol. The oxidizing species were generated by the reactions illustrated in Schemes 4 and 5, and identified by their well characterized optical absorptions (Tl^{2+} [15,18,19] and MeI$^{+\bullet}$/(MeI$\therefore$IMe)$^+$ [20]).

$$Tl^+ + {}^\bullet OH + H_{aq}^+ \longrightarrow Tl^{2+} + H_2O$$

Scheme 4.

$$MeI + {}^\bullet OH + H_{aq}^+ \longrightarrow MeI^{+\bullet} + H_2O \qquad (a)$$

$$MeI^{+\bullet} + MeI \rightleftharpoons (MeI\therefore IMe)^+ \qquad (b)$$

Scheme 5.

The absolute rate constants for the radical-induced oxidation of DMSO (Schemes 3, 6, and 7) were generally evaluated from the decay of the Tl^{2+}, $SO_4^{-\bullet}$, and MeI$^{+\bullet}$/(MeI$\therefore$IMe)$^+$ absorptions.

$$Tl^{2+} + DMSO \longrightarrow DMSO^{+\bullet} + Tl^+$$

Scheme 6.

$$MeI^{+\bullet} + DMSO \longrightarrow DMSO^{+\bullet} + MeI \qquad (a)$$

$$(MeI\therefore IMe)^+ + DMSO \longrightarrow DMSO^{+\bullet} + 2\,MeI \qquad (b)$$

Scheme 7.

The kinetics were pseudo-first order with the half-lives of the exponential processes depending only on the DMSO concentration, *i.e.* $k = \ln 2/t_{1/2}$ [DMSO]. The results are listed in Table 1. The most rapid oxidation is seen to occur with the oxidant of highest redox potential, namely, $SO_4^{-\bullet}$ ($E^0 \approx +2.5$ V *vs.* NHE[12]) with $k_3 = 2.7 \times 10^9$ mol^{-1} dm^3 s^{-1} indicating a practically diffusion-controlled reaction. The three-electron bonded (MeI$\therefore$IMe)$^+$ and/or the molecular MeI$^{+\bullet}$ (a distinction is not possible since both species exist in equilibrium, Scheme 5(*a*) and exhibit equally good oxidative power)[17] oxidize DMSO with a considerably lower rate constant of $k_{7a,b} = 7.8 \times 10^7$ mol^{-1} dm^3 s^{-1}. The redox potentials of the species derived from methyl iodide are not known exactly and could only be estimated to $> +2.0$ V (possibly $> +2.3$ V) *vs.* NHE.[17] A still lower rate constant applies to the oxidation by Tl^{2+} with $k_6 = 1.1 \times 10^7$ mol^{-1} dm^3 s^{-1} ($E^0 = +2.22$ V[14]). No oxidation of DMSO has been observed by oxidants with $E^0 \leqslant +2$ V such as Ag^{2+}, $Br_2^{-\bullet}$, $R_2S^{+\bullet}$, and RSSR$^{+\bullet}$, for example.

Table 1. Rate constants for the oxidation of dimethyl sulphoxide (DMSO), diethyl sulphoxide (DESO), and dipropyl sulphoxide (DPSO). Error limits: ± 10%.

Oxidizing radical	pH	$k/10^8$ dm^3 mol^{-1} s^{-1}		
		DMSO	DESO	DPSO
$SO_4^{-\cdot}$	4.0	27	39	50
	6.5	27		
$MeI^{+\cdot}/(MeI\therefore IMe)^+$	3.1	0.78	1.1	1.4
$MeI(OH)^\cdot$	6.0	0.95	1.2	1.7
Tl^{2+}	3.2	0.11	0.14	0.22

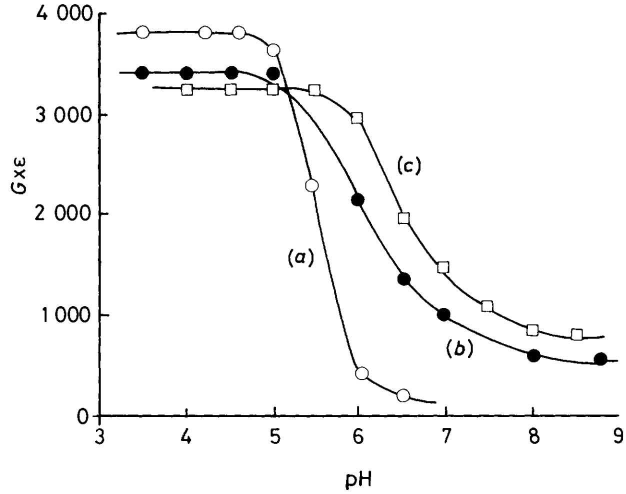


Figure 2. pH Dependence of the sulphoxide radical cation yields: (*a*) $DMSO^{+\cdot}$ [○], (*b*) $DESO^{+\cdot}$ [●], (*c*) $DPSO^{+\cdot}$ [□]. Solutions: N_2 saturated, 5 × 10^{-3} mol dm^{-3} $S_2O_8^{2-}$, 5 × 10^{-3} mol dm^{-3} R_2SO, 0.5 mol dm^{-3} t-butyl alcohol.

Table 2. Equilibrium constants and p*K* values for Scheme 19. Experimental error limits: ±0.2 for p*K* values; factor 1.6 for equilibrium constant.

R_2SO	p*K*	*K*/mol dm^{-3}
DMSO	5.6	2.5 × 10^{-6}
DESO	6.1	7.9 × 10^{-7}
DPSO	6.5	3.2 × 10^{-7}

The same observations as for DMSO were made, in principle, for the oxidations of diethyl (DESO) and dipropyl sulphoxide (DPSO). The rate constants are also listed in Table 1 and, by comparison, are seen to increase from DMSO, through DESO to DPSO oxidation. The observed trend is satisfactorily accounted for by the increasing electron densities at the sulphur lone pairs (where the oxidation is presumed to take place) due to increasing electron release by the substituents Me, Et, and Pr.

The optical absorption spectra of $DESO^{+\cdot}$ and $DPSO^{+\cdot}$ are displayed in Figure 1(*b*) and (*c*) and exhibit maxima at 320 and 330 nm, respectively.

pH Dependence of R_2SO *Oxidation.*—The formation of sulphoxide radical cations is a pH dependent process. This can be seen from Figure 2 which displays the $R_2SO^{+\cdot}$ yields from the $SO_4^{-\cdot}$ induced oxidations. The experimental curves are sigmoidal with points of inflection at pH 5.6, 6.1, and 6.5 for the DMSO, DESO, and DPSO systems, respectively. The observed decrease in the yields at higher pH cannot be explained by a lower reactivity of $SO_4^{-\cdot}$ towards the sulphoxides. The rate constants for Scheme 3, for example, stays the same if the pH is changed from 4.0 to 6.5.

Radical cations are accordingly only formed in acid solutions and it is reasonable to assume that at higher pH they are neutralized within an equilibrium (Scheme 8), which yields the

$$R_2SO^{+\cdot} + OH^-(H_2O) \rightleftharpoons R_2SO(OH)^\cdot\,(+H^+)$$

Scheme 8.

same product as in the direct reaction of $^\cdot OH$ radicals with sulphoxides.[6] The inflection points of the curves in Figure 2 would accordingly represent, or at least correlate with, the p*K* values for the equilibrium in Scheme 8. The observed trend is reasonable in view of an increased electron density at the positive sulphur centre in changing the substituent from Me through Et to Pr. The p*K* values and equilibrium constants listed in Table 2 are based on the assumption that the observable yields are not affected by side reactions on the time scale of observation.

The $R_2SO(OH)^\cdot$ adduct radical is known to be very unstable and to decay unimolecularly with $t_{1/2} < 100$ ns (depending on the nature of R) by the reaction in Scheme 9, into an alkyl

$$R_2SO(OH)^\cdot \longrightarrow R^\cdot + RSO_2^-/H_{aq}^+$$

Scheme 9.

radical and the corresponding sulphinic acid.[6] The very short lifetime of $R_2SO(OH)^\cdot$ with respect to this irreversible decay explains why $R_2SO^{+\cdot}$ radical cations escaped detection in the early $^\cdot OH + R_2SO$ studies. In the hydroxyl radical induced oxidation the radical cations can only be generated *via* the back reaction of Scheme 8. Even if this process was diffusion controlled it would take a relatively high H_{aq}^+ concentration to compete with Scheme 9 (k_9 *ca.* 10^7 s^{-1}). We have now conducted a pulse experiment at an appropriately high time resolution in order to, possibly, identify $R_2SO^{+\cdot}$ radical cations as an intermediate also in the $^\cdot OH$ induced oxidation. Irradiation of an N_2O saturated, pH *ca.* 3 solution of 5 × 10^{-3} mol dm^{-3} DMSO with short pulses of only *ca.* 5 ns duration lead indeed to a transient species with an absorption around 300 nm although only at a very small yield. The latter increased with proton concentration as would be expected if the back reaction of Schemes 8 and 9 were competitive, but even at pH 2 it is still relatively low. Furthermore, at this low pH ($\leqslant 2$) an increasing amount of $H^\cdot$ atoms are generated (reaction of $e_{eq}^- + H_{aq}^+$). These are known to react with DMSO to yield $Me_2S^{+\cdot}$ radical cations which exhibit an absorbtion (λ_{max} 285 nm)[21] similar to that of $Me_2SO^{+\cdot}$. Therefore, our low pH results are, at most supportive, but not conclusive evidence for the suggested mechanism.

*Oxidation of Sulphoxides at Higher pH (>p*K *of* $^\cdot OH$ *Adduct).*—Sulphoxides can also be oxidized at pHs higher than the p*K* of Scheme 8. The rate constant for the reaction of $SO_4^{-\cdot}$ with DMSO, for example, as measured from the decay kinetics of the $SO_4^{-\cdot}$ absorption at pH 6.5, is 2.7 × 10^9 mol^{-1} dm^3 s^{-1}, *i.e.* identical with that at pH 4. Generally, the reactivity of $SO_4^{-\cdot}$ towards sulphoxides is invariant with pH within the limits of experimental error. Only the lifetime of the resulting $R_2SO^{+\cdot}$ radical cation becomes increasingly shorter with increasing pH, as discussed above. Evidence for the reaction sequence Schemes 3, 8, and 9 is provided, for example, by the formation of semiquinone radicals, $BQ^\cdot$, in pulse irradiated, N_2 saturated, pH 7 solutions containing 5 × 10^{-3} mol dm^{-3} $S_2O_8^{2-}$, 5 × 10^{-3} mol dm^{-3} DMSO, 0.5 mol dm^{-3} t-butyl alcohol and 2 × 10^{-4}

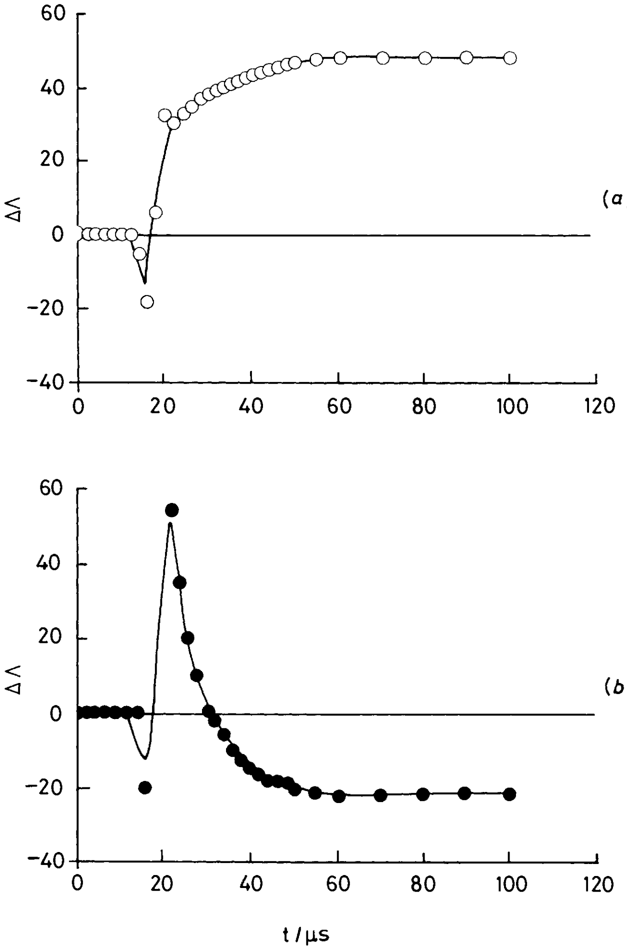


Figure 3. Conductivity–time traces obtained in pulse irradiated, N_2O saturated solutions containing 5×10^{-3} mol dm^{-3} MeI and 2×10^{-3} mol dm^{-3} DMSO at pH (*a*) 5.8 and (*b*) 8.2. The ΔΛ values are calculated for the maximum possible yield of 0.57 J μmol^{-1} or $G(^{\bullet}OH)$ 5.5.

mol dm^{-3} *p*-benzoquinone (BQ). In such solutions the $SO_4^{-\bullet}$ radical anions should quantitatively react with the DMSO. The methyl radicals which are subsequently generated *via* Schemes 8

$$^{\bullet}CH_3 + BQ \longrightarrow BQ(CH_3)^{\bullet} \qquad (a)$$

$$BQ(CH_3)^{\bullet} + BQ \longrightarrow BQ^{\bullet} + \text{Me-BQ} \qquad (b)$$

Scheme 10.

and 9, are then expected to be scavenged by the *p*-benzoquinone by the known reaction sequence[22] (Scheme 10) to yield the optically absorbing semiquinone radical (λ_{max} 310 and 430 nm). It is noted though that the measured semiquinone yield amounts to only *ca.* one third of the theoretically possible yield. This may be explained by an inefficiency of the semiquinone formation at the low BQ concentrations owing to a relatively low rate constant (4.5×10^7 dm^3 mol^{-1} s^{-1}) of Scheme 10.[22] We, therefore, consider the semiquinone experiment only as supporting but not as conclusive evidence for the $SO_4^{-\bullet}$ induced mechanism at higher pH.

Another interesting oxidation of sulphoxides at higher pH is achieved in methyl iodide containing solutions. $MeI^{+\bullet}$ radical cations (and their three-electron bonded dimers $MeI \therefore IMe^+$) are sufficiently stabilized only in acid solution and exist in an equilibrium with a p*K* *ca.* 3.5.[20] The neutral $MeI(OH)^{\bullet}$ radical is almost as good an oxidant as the corresponding radical cations.[17] Reactions of $MeI(OH)^{\bullet}$ can conveniently be followed since this species exhibits a characteristic optical absorption spectrum, quite different to that of the methyl iodide radical cations, with λ_{max} at 310 and 350 nm.[23] The rate constants for the general reaction, Scheme 12, derived from kinetic analysis of the $MeI(OH)^{\bullet}$ decay in the presence of various concentrations of sulphoxides are included in Table 1. It is interesting to note that they are, in fact, marginally higher than those for the sulphoxide oxidations by the methyl iodide radical cations. This is in contrast to all other oxidation processes investigated so far for which rate constants for the $MeI(OH)^{\bullet}$ induced processes were found to be comparatively slower by a factor of up to three.[17] A reasonable suggestion for the present finding might be that the reaction (Scheme 12) proceeds *via* an outer-sphere hydroxyl radical transfer, and does not involve electron transfer combined with subsequent neutralization.

$$MeI^{+\bullet} + H_2O \rightleftharpoons MeI(OH)^{\bullet} + H_{aq}^{+}$$

Scheme 11.

$$MeI(OH)^{\bullet} + R_2SO \longrightarrow R_2SO(OH)^{\bullet} + MeI$$

Scheme 12.

The occurrence of the reaction Scheme 12 provides an independent possibility to prove the generation of sulphinic acid (Scheme 8) in a process where the sulphoxide is not directly oxidized by free hydroxyl radicals. Figures 3(*a*) and 3(*b*) show the time-resolved conductivity traces recorded upon pulse radiolysis of N_2O saturated solutions containing 5×10^{-3} mol dm^{-3} MeI and 2×10^{-3} mol dm^{-3} DMSO at pH 5.8 and 8.2, respectively. The stable positive signal obtained at longer times at pH 5.8 indicates the formation of an anion/H_{aq}^{+} pair (specific conductivity change $\Delta\Lambda \approx 40 + 315 = 355$ Ω^{-1} cm^2 at 18 °C).[11,24] In basic solution the H_{aq}^{+} will, of course, be neutralized by excess OH^- ions. From the conductivity point of view this means that the more conducting hydroxide anion is replaced by a comparatively less conducting 'normal' anion ($\Delta\Lambda \approx -170 + 40 = -130$ cm^2 Ω^{-1}).[11,24] This is represented by the stable negative signal at longer times of the pH 8.2 experiment (the initial transient positive signal is due to $H_{aq}^{+} + OH^-$ neutralization). In the absence of DMSO the permanent change in conductivity is zero at both pH's.

The absolute conductivity yields, *i.e.* the measurable RSO_2^-/H_{aq}^{+} concentrations are relatively low, presumably due to competing reaction pathways. The signal ratio for the pH 5.8 *vs.* 8.2 experiments of *ca.* 2.5 corresponds, however, very reasonably to the expected ratio of *ca.* 2.7 calculated from the specific conductivities.

$R_2SO^{+\bullet}$ *Radical Cations as Oxidants*.—The sulphoxide radical cations are relatively good oxidants themselves. Rate constants have been measured for several reactions of the general type, Scheme 13, by following either the decay of the $R_2SO^{+\bullet}$ absorption in the presence of an oxidizable substrate D or from the formation kinetics of its oxidized form $D^{+\bullet}$ (this notation does not necessarily indicate a positively charged species but represents, in general terms, the one-electron oxidation product of D). Generally, experiments have been carried out with N_2-saturated solutions containing 5×10^{-3} mol dm^{-3} $S_2O_8^{2-}$, 0.5 mol dm^{-3} t-butyl alcohol, 5×10^{-3} mol dm^{-3} R_2SO and various concentrations of the donor substrate D. The latter were kept low enough to avoid direct oxidation of

$$R_2SO^{+\bullet} + D \longrightarrow D^{+\bullet} + R_2SO$$

Scheme 13.

Table 3. Rate constants for oxidation reactions by sulphoxide radical cations.

Electron donor D	$k(R_2SO^{+\cdot} + D)/10^8$ dm^3 mol^{-1} s^{-1} DMSO$^{+\cdot}$	DESO$^{+\cdot}$	DPSO$^{+\cdot}$
Me_2S	7.3	6.2	5.0
Et_2S	7.8	6.6	6.0
Pr_2S	7.8	6.2	5.3
Me-S-$(CH_2)_3$-S-Me	13.5	11	10
Me-SS-Me	21	18	15.5
Et-SS-Et	14	9.4	8.0
Pr^i-SSPr^i	7.0	5.8	5.0
Br^-	100	75	73
SCN^-	100	75	75
I^-	100	78	78

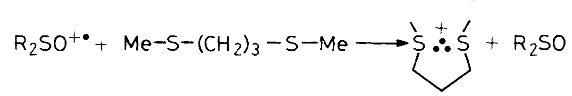
[a] Solutions: N_2 saturated, pH 4, 5×10^{-3} mol dm^{-3} $S_2O_8^{2-}$, 5×10^{-3} mol dm^{-3} R_2SO, 0.5 mol dm^{-3} t-butyl alcohol. Error limits: ±10%. [The sulphoxide radical cations are likely to be associated with one water molecule, *i.e.* $(R_2SO\therefore OH_2)^+$ (see the text)].

D by $SO_4^{-\cdot}$ and to ensure that $D^{+\cdot}$ was only formed *via* Scheme 13. Table 3 summarizes the results.

Sulphoxide radical cations readily oxidize organic sulphides, dithia compounds, disulphides, Br^-, I^-, and SCN^-, *i.e.* essentially all substrates with redox potentials of $E^0(D^{+\cdot}/D) \leqslant +1.8$ V. Considering that the sulphoxides themselves can be oxidized by species with $E^0 \geqslant +2.0$ V it can be assumed that $E^0(R_2SO^{+\cdot}/R_2SO)$ is of the order of $+(1.8 - 2.0)$ V.

The rate constant data reveal a number of trends. Thus DMSO$^{+\cdot}$ is generally a better oxidant than DESO$^{+\cdot}$ while DPSO$^{+\cdot}$ is the weakest in this series. This corroborates the results on the oxidation of the sulphoxides discussed in the first part of the Results and Discussion section; electron donation into the centre of the redox process by the substituents R facilitates oxidation but in turn reduces the oxidizing, *i.e.* electron-accepting capability of the oxidized form.

A similar consideration applies, in principle, for the oxidation of organic sulphides. The most difficult to oxidize should accordingly be the dimethyl sulphide. The observed differences between the rate constants for the oxidations of dimethyl, diethyl, and dipropyl sulphide, respectively, are too small though for any conclusion to be made; they probably just reflect the normal limits of error. The comparatively higher rate constants for the oxidation of the dithia compound 1,3-bis(methylthio)propane, Scheme 14, are, however, of significance. They are reasonably explained by sulphur–sulphur lone-pair interaction, probably taking place already in the unoxidized compound, and stabilization of the resulting three-electron bonded radical cation in a sterically very favourable 5-membered ring after the removal of one antibonding electron.[25,26]



Scheme 14.

An interesting and, at first glance, seemingly opposing trend is observed in the respective series of disulphide oxidation, *i.e.* for the general electron-transfer reaction, Scheme 15. The highest rate constants are always found for the oxidation of MeSSMe and the lowest for the oxidation of Pr^iSSPr^i although the first (gas-phase) ionization potentials decrease from 8.97 to 8.54 eV, respectively.[27] This parameter seems to be overruled, however, by steric considerations. Particularly important is the structure of the disulphide radical cations formed in the reaction of Scheme 15. After one-electron oxidation the disulphide bridge is known to assume partial π-character owing to an overall 5-electron bond (2σ, 2π, and 1π*)[28] with a practically negligible torsional CS–SC angle.[29] In the unoxidized aliphatic disulphides this torsional angle is not only relatively high (84.7° for MeSSMe) but also increases slightly with increasing length and bulkiness of the alkyl substituent.[29] The least conformational change is, therefore, required during the oxidation of dimethyl disulphide and this provides the most probable explanation for the observed trend in rate constants. Corresponding trends, although less pronounced, have been observed for a series of aliphatic disulphide oxidations by methyl iodide radical cations.[17] The fact that structure exerts a deciding influence on the ease of oxidation and on the redox properties of the resulting disulphide radical cations has particularly been demonstrated for a number of cyclic disulphides (1,2-dithiolanes,[29] lipoic acid[30]). For these compounds the torsional angle is already relatively low in the unoxidized form and consequently they are easier to oxidize and their radical cations are worse oxidants than the respective aliphatic analogues.

$$R_2SO^{+\cdot} + RSSR \longrightarrow RSSR^{+\cdot} + R_2SO$$

Scheme 15.

The yields of $RSSR^{+\cdot}$ formed by Scheme 15 and evaluated from the known extinction coefficients of the disulphide radical cations[31] do not vary significantly for the series of sulphoxides and disulphides investigated in this study, and amount to a yield of *ca.* 0.21 μmol^{-1} (±0.03) or *G ca.* 2(±0.3). This accounts for about 75% of the maximum possible $R_2SO^{+\cdot}$ yield (0.28 J μmol^{-1}, *G* 2.7) generated under the experimental conditions ($S_2O_8^{2-}$/ t-butyl alcohol containing solutions). Assuming that the reaction in Scheme 15 is quantitative and the yield of $RSSR^{+\cdot}$ reflects the true yield of $R_2SO^{+\cdot}$ radical cations generated initially, the extinction coefficients of $R_2SO^{+\cdot}$ can be estimated to $\varepsilon \approx (1.8 \pm 0.4) \times 10^3$ dm^3 mol^{-1} cm^{-1}.

Comparatively very high rate constants are measured for the oxidations of Br^-, I^-, and SCN^- corroborating results on the oxidation of these (pseudo)halides, X, by methyl iodide radical cations.[17] In all these reactions dimer radical anions are formed *via* the overall mechanism, Scheme 16. Considering the probable association of the 'molecular' radical cation $R_2SO^{+\cdot}$ with one solvent molecule to $(R_2SO\therefore OH_2)^+$, in analogy to $(R_2S\therefore OH_2)^+$ in the oxidation of sulphides,[21,32,33] it is suggested that Scheme 16 does not proceed by simple electron transfer. A ligand-exchange sequence, schemes 17 and 18, seems more likely to occur. The intermediate $(R_2SO\therefore X)$ could not be detected for X = Br, I, and SCN, since its transformation into $X_2^{-\cdot}$ *via* Scheme 18 is too fast and practically irreversible. The neutral adduct could, however, positively be identified in the case of X = Cl through the optical absorption of $R_2SO\therefore Cl$ (λ_{max} *ca.* 400 nm) for which Scheme 18 becomes reversible. Further details on the formation and properties of this species will be dealt with in a separate communication.[34]

$$R_2SO^{+\cdot} + 2X^- \longrightarrow X_2^{-\cdot} + R_2SO$$

Scheme 16.

$$(R_2SO\therefore OH_2)^+ + X^- \rightleftharpoons (R_2SO\therefore X) + H_2O$$

Scheme 17.

$$(R_2SO\therefore X) + X^- \longrightarrow X_2^{-\cdot} + R_2SO$$

Scheme 18.

Considering the redox reactions described in this and earlier sections the question may arise as to what extent the reactions proceed by an outer-sphere electron transfer and to what extent by a transient bond formation, *i.e.* an inner-sphere mechanism. The rate constants for the oxidation of the sulphoxides by the various oxidizing radicals and metal ions ($SO_4^{-\bullet}$, Tl^{2+}, $MeI^{+\bullet}$ *etc.*) seem to correlate with the redox potentials of the latter, and the same applies apparently to the oxidation of sulphides and disulphides by the $R_2SO^{+\bullet}$ radical cations. This would suggest an outer-sphere electron transfer for these redox processes. The formation of transient hydroxyl and chlorine adducts, on the other hand, indicates that alternative (inner sphere) reaction routes are also possible. Such addition–elimination mechanisms may be envisaged, in particular, for the $R_2SO^{+\bullet}$ induced oxidation of the halides and pseudo-halides. Similarly, it cannot be excluded that the oxidation of R_2SO itself may partially proceed by an inner-sphere (bond formation) mechanism. The fact that the observable yields of most of the redox processes described in this paper (*e.g.* semiquinone formation, conductivity in MeI–DMSO solutions, RSSR oxidation *etc.*) are lower than the maximum possible yields would also point towards this conclusion. It has to be mentioned though that our experiments on the $SO_4^{-\bullet}$, Tl^{2+}, and $MeI^{+\bullet}$ induced oxidations of the sulphoxides did not provide any directly observable evidence for transient adducts. A quantitative account for the entire oxidation mechanism would probably require a detailed product analysis.

Radical cations from sulphoxides exist in equilibrium with the neutral $^{\bullet}OH$ adduct as formulated in Scheme 8. On consideration of the water associate it might be better formulated as Scheme 19, with $R_2SO\therefore OH$ and $R_2SO(OH)^{\bullet}$ representing two

$$(R_2SO\therefore OH_2)^+ \rightleftharpoons R_2SO\therefore OH + H_{aq}^+$$

Scheme 19.

different notations for the same species. (The validity of viewing the interaction between an oxidized sulphur and an oxygen-centred function in terms of a three-electron bond, and the problems associated therewith, has been discussed in detail in a previous publication of ours[35]). Corresponding equilibria between 'molecular radical cations and neutral $^{\bullet}OH$-adduct radicals exist for alkyl iodides[20] and dialkyl sulphides.[36] It is noted that the respective p*K* values can be correlated with the redox properties of the 'radical cation–unoxidized substrate' pair. The lowest p*K* (*ca.* 3.5) is obtained for the methyl iodide, the highest for the aliphatic sulphide couples (not quantitatively determined but clearly >8) while those for the present sulphoxide system (5.6–6.5) fall in between. The lower the p*K* the more difficult it becomes apparently to oxidize the parent compound (in case of the MeI this can only be achieved through the $^{\bullet}OH$ radical *via* an adduct). At the same time the respective radical cations become increasingly better oxidants with estimates for $E^\circ \geq 2$ V, $+(1.8–2.0)$ V, and $+(1.5–1.7)$ V for the MeI, R_2SO, and R_2S systems, respectively. Although accurate determination of the redox potentials has not been possible so far it seems evident that a direct correlation exists between the redox properties and the basicity of the hydroxyl radical adducts. Measurement of p*K* values for the protonation of hydroxyl radical adducts may thus provide a possibility for estimation of the redox properties of radical cation–substrate redox pairs and *vice versa.*

Acknowledgements

This work has been supported by the International Bureau of the KfA Jülich within the terms of an agreement on scientific co-operation between the Federal Republic of Germany and the Republic of India. Dr. Kamal Kishore has been on deputation from Bhabha Atomic Research Centre, Bombay.

References

1 A. M. Koulkes-Pujo, L. Gilles, B. Lesigne, and J. Sutton, *Chem. Commun.*, 1971, 749.
2 D. C. Walker, N. V. Klassen, and H. A. Gillis, *Chem. Phys. Lett.*, 1971, **10**, 636.
3 R. Bensasson and E. J. Land, *Chem. Phys. Lett.*, 1972, **15**, 195.
4 M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1976, 908.
5 M. J. Davies, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1984, 503.
6 D. Veltwisch, E. Janata, and K.-D. Asmus, *J. Chem. Soc., Perkin Trans. 2*, 1980, 146.
7 B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J. Chem. Soc., Perkin Trans. 2*, 1975, 303, 308.
8 B. C. Gilbert and P. R. Marriott, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1425.
9 J. S. Chapman, J. W. Cooper, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1976, 407.
10 W. B. Gara and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1708.
11 K.-D. Asmus, in 'Oxygen Radicals in Biological Systems,' vol. 105, 'Methods in Enzymology,' ed. L. Packer, Academic Press, New York, 1984, 167.
12 L. Eberson, *Adv. Phys. Org. Chem.*, 1982, **18**, 79.
13 E. Hayon, A. Treinin, and J. Wilf, *J. Am. Chem. Soc.*, 1972, **94**, 47.
14 H. A. Schwarz, D. Comstock, J. K. Yandell, and R. W. Dodson, *J. Phys. Chem.*, 1974, **78**, 488.
15 P. O'Neill, S. Steenken, and D. Schulte-Frohlinde, *Angew. Chem.*, 1975, **87**, 417, *Angew. Chem. (Int. Ed. Engl.)*, 1975, **14**, 430.
16 K.-D. Asmus, M. Bonifačić, P. Toffel, P. O'Neill, D. Schulte-Frohlinde, and S. Steenken, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 1820.
17 H. Mohan and K.-D. Asmus, *J. Phys. Chem.*, 1988, **92**, 118.
18 B. Cercek, M. Ebert, and A. J. Swallow, *J. Chem. Soc. A*, 1966, 612.
19 M. Bonifačić and K.-D. Asmus, *J. Chem. Soc., Dalton Trans.*, 1976, 2074.
20 H. Mohan and K.-D. Asmus, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1795.
21 S. A. Chaudhri, M. Göbl, T. Freyholdt, and K.-D. Asmus, *J. Am. Chem. Soc.*, 1984, **106**, 5988.
22 D. Veltwisch and K.-D. Asmus, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1147.
23 U. Brühlmann, H. Büchler, F. Marchetti, and R. E. Bühler, *Chem. Phys. Lett.*, 1973, **21**, 412.
24 K.-D. Asmus and E. Janata, in 'The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis,' eds. J. H. Baxendale and F. Busi, D. Reidel Publ. Co., Dordrecht, 1982, 91.
25 K.-D. Asmus, *Acc. Chem. Res.*, 1979, **12**, 436.
26 E. Anklam, K.-D. Asmus, and H. Mohan, *J. Phys. Org. Chem.*, in press.
27 H. Bock and G. Wagner, *Angew. Chem.*, 1972, **84**, 119.
28 K.-D. Asmus, in 'Radioprotectors and Anticarcinogens,' eds. O. F. Nygaard and M. G. Simic, Academic Press, New York, 1983, 23.
29 H. Bock, U. Stein, and A. Semkow, *Chem. Ber.*, 1980, **113**, 3208.
30 M. Bonifačić and K.-D. Asmus, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1805.
31 M. Bonifačić, K. Schäfer, H. Möckel, and K.-D. Asmus, *J. Phys. Chem.*, 1975, **79**, 1496.
32 T. Clark, personal communication.
33 J. Mönig, R. Goslich, and K.-D. Asmus, *Ber. Bunsenges. Phys. Chem.*, 1986, **90**, 115.
34 K. Kishore and K.-D. Asmus, to be published.
35 S. Mahling, K.-D. Asmus, R. S. Glass, M. Hojjatie, and G. S. Wilson, *J. Org. Chem.*, 1987, **52**, 3717.
36 M. Bonifačić, H. Möckel, D. Bahnemann, and K.-D. Asmus, *J. Chem. Soc., Perkin Trans. 2*, 1975, 675.

Received 19*th July* 1989; *Paper* 9/02129I