Primary Processes in the Reaction of OH·-Radicals with Sulphoxides

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The primary processes in the OH· radical-induced oxidation mechanism of sulphoxides have been investigated by pulse radiolysis and, in particular, by an improved conductivity detection method with a time resolution of *ca.* 50 ns in aqueous solution. Electrophilic addition of the OH· radical to the sulphoxide group leads to a transient adduct, $R_2SO(OH)\cdot$ which decays unimolecularly with $t_{1/2}$ up to 100 ns into a sulphinic acid, RSO_2H, and a radical R·. The various RSO_2H have been identified by their pK_a, and R· (including t-butyl and phenyl radicals) by direct optical measurement or chemical scavenging experiments. The probability of radical split-off from $R_2SO(OH)\cdot$ for mixed sulphoxides depends on the stability of the radical leaving. Depending on the nature of the sulphoxide substituents two other OH· radical reactions compete with, and may even predominate over, the addition at the sulphoxide group. Thus hydrogen-atom abstraction readily occurs from longer chain and branched aliphatic groups and in the presence of aromatic substituents OH· radicals add to the π-system to form a hydroxycyclohexadienyl radical. The respective yields, kinetics and some physico-chemical properties of the primary species are presented and discussed.

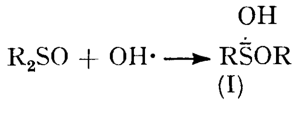
SULPHUR-CARBON bond rupture as a result of OH· radical attack on sulphoxides was first reported by Norman and his co-workers in 1964.[1] Using e.s.r./rapid mixing techniques they were able to demonstrate elimination of a methyl radical during the OH·-induced oxidation of dimethyl sulphoxide in aqueous solutions. The system used for OH· radical production was Ti^{III}–H_2O_2. Since then a number of similar reactions have been studied, and radicals from the general reaction (1) have been identified

$$R_2SO + OH\cdot \longrightarrow R\cdot + RSO_2H \qquad (1)$$

either directly or through spin-trapping experiments.[2-6] It is interesting to note that often it has not been possible to detect phenyl and t-butyl radicals from corresponding sulphoxides although reaction (1) should, in principle, also apply to all these compounds.

The rate of reaction of OH· radicals with sulphoxides is practically diffusion controlled; for example, a bimolecular rate constant of $k = 7 \times 10^9$ l mol^{-1} s^{-1} has been measured for OH· + Me_2SO.[7] A likely site of OH· attack is the sulphur atom in the sulphoxide molecule. The S-atom is known to be at the centre of a pyramidal structure with the free electron pair pointing towards one of the corners.[8] This provides easy access for the OH· radical which is known for its electrophilic character.

The formation of radicals R· and the corresponding sulphinic acid RSO_2H may not be a one-step process. It has been suggested that a transient OH· adduct (I) is



$$R_2SO + OH\cdot \longrightarrow \underset{\text{(I)}}{R\overset{\text{OH}}{\dot{S}}OR} \qquad (2)$$

formed as a short-lived intermediate although so far no direct experimental evidence has been presented for such a species.[1,4,5,9,10]

The object of the present study was to obtain kinetic and mechanistic information on the primary processes in the OH· radical-induced oxidation of sulphoxides. Particular attention was directed to the possible intermediate OH· adduct (I), to the C–S bond rupture probability as a function of the nature of substituent R in the sulphoxide, and to reactions which may compete with the OH· radical attack at the sulphur atom. A suitable technique for such investigations is the pulse radiolysis of aqueous solutions where relatively high concentrations of homogeneously distributed OH· radicals (*ca.* 10^{-5}M) can conveniently be produced within ns—μs time intervals. Pulse radiolysis also provides detection techniques with high time resolution. In the present study in particular a considerably improved conductivity technique with a time resolution of *ca.* 50 ns in the aqueous system was successfully applied.

EXPERIMENTAL

Solutions were prepared according to the usual radiation chemical standards. Commercially obtained aliphatic and aromatic sulphoxides were of anlytical grade. Diethyl, diisopropyl, and di-t-butyl sulphoxides were synthesized by oxidation of the corresponding sulphides with perfluoroacetic acid.[11] The purity of the sulphoxides were generally checked by gas chromatography. If necessary, purification to $\geqslant 99\%$ was achieved by vacuum distillation or recrystallization from n-heptane. The solvent H_2O was deionized and ' Millipore ' filtered.

The experimental technique and analytical treatment of pulse radiolysis data has already been described.[12] The improved conductivity detection technique is discussed in a recent publication.[13]

OH· Radicals were produced by exposing N_2O saturated aqueous solutions to short pulses (5 ns and 1 μs duration) of high-energy electrons from a 1.6 and 4.0 MeV Van de Graaff accelerator. The N_2O was added to convert hydrated electrons, formed with about equal yield as OH· radicals in the radiolysis of water, into hydroxyl radicals *via* $N_2O + e_{aq}^- \longrightarrow N_2 + OH^- + OH\cdot$. Typical doses per pulse were ≈ 1 krad (10 Gy). Under these conditions *ca.* 6×10^{-6}M OH· radicals are produced per pulse in the irradiated solution. (The radiation chemical yield of OH· in terms of G units is 6.0 OH· radicals per 100 eV absorbed energy.) Solute concentrations generally were $\geqslant 10^{-4}$M to ensure quantitative scavenging of the OH· radicals by the solute molecules.

Reactions of small yields of hydrogen atoms ($G = 0.6$) which are also present in the irradiated system at pH >3

and conversion of hydrated electrons into H· atoms in acid solutions ($e_{aq}^- + H_{ap}^+ \longrightarrow H\cdot$) have been taken into account wherever appropriate.

Optical pulse radiolysis experiments were possible at all pH values. Conductivity experiments, however, were only possible at pH greater than *ca.* 2 on account of rapid loss of sensitivity of the technique as a critical total ion concentration in the solution is exceeded. Appropriate sensitivity factors [12,13] in the range near pH = 2 have been applied for the evaluation of conductivity data from such solutions.

All experiments were carried out at room temperature.

RESULTS

Formation of Sulphinic Acids.—(a) *Yields.* The reaction of sulphoxides with hydroxyl radicals according to equation (1) leads to the formation of sulphinic acids which at pH > 3.5 are completely dissociated. The ion pair formed, for example, in reaction (3) is responsible for a change in the conductivity of the irradiated solution. This is typically demonstrated in Figure 1 which shows oscilloscope traces of conductivity *vs.* time in pulsed, N_2O-saturated solutions of 10^{-3}M dimethyl sulphoxide at pH = 4.4 (Figure 1a) and pH = 9.0 (Figure 1b), respectively. At this solute concentration reaction (3) is complete within the duration of the 1 μs pulse.

$$Me_2SO + OH\cdot \rightsquigarrow Me\cdot + MeSO_2^- + H_{aq}^+ \qquad (3)$$

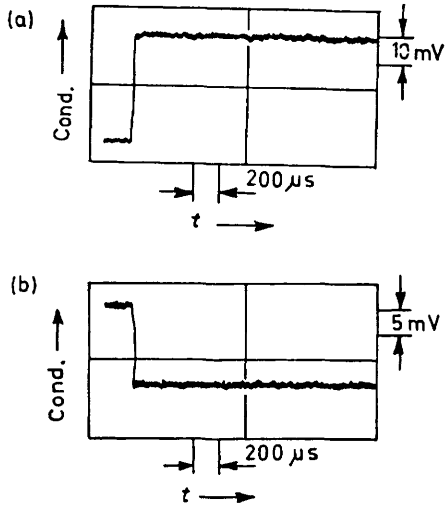


FIGURE 1 Conductivity *vs.* time curves in pulse-irradiated, N_2O-saturated solutions of 10^{-3}M-dimethyl sulphoxide at pH = 4.4 (a) and pH = 9.0 (b). Pulse width: 1 μs; absorbed dose: *ca.* 500 rad

In the acid solution an increase in conductivity is observed. The signal resembles a step function since the $MeSO_2^-/H_{aq}^+$ ion pair is stable over the detection period. In the basic solution the signal is seen to decrease owing to the fact that now the proton will immediately be neutralized.[14]

$$H_{aq}^+ + OH^- \longrightarrow H_2O \qquad (4)$$

The net effect in this case is thus the replacement of an OH^- ion which has a relatively high specific conductivity ($l = 178\ \Omega^{-1}\ cm^2$) by a less conducting $MeSO_2^-$ anion. The latter is a ' normal ' anion with l expected to be in the 30—60 Ω^{-1} cm² range.[15]

The exact values of $l(MeSO_2^-)$ and the yield of reaction (3) can be determined [12] from the signals in Figure 1 which yield the following:

$$G \times [l_{(MeSO_2^-)} + l_{(H_{aq}^+)}] = 1\,950$$

and

$$G \times [l_{(MeSO_2^-)} - l_{(OH^-)}] = -743$$

for the acid and basic solution, respectively. Since $l(H_{aq}^+)$ and $l(OH^-)$ are known to be 315 and 178 Ω^{-1} cm², respectively,[15] the yield and the specific conductivity of the $MeSO_2^-$ anion can be calculated as $G = 5.46$ and $l(MeSO_2^-) = 42\ \Omega^{-1}$ cm². Both values are entirely plausible. The yield is to be compared with $G(OH\cdot) = 6.0$, *i.e.* the total yield of OH· radicals available for reaction with the solute. The experimental result means that reaction (3) accounts almost quantitatively for the OH· attack on dimethyl sulphoxide. The remaining 10% (approx.) of the OH· radicals probably undergo hydrogen-atom abstraction from a methyl group; direct proof of the latter was not, however, possible.

Results of the same kind were found in pulse radiolysis conductivity experiments with other aliphatic and aromatic sulphoxides. The yields of sulphinic acids calculated from the respective changes in conductivity are listed in the second column of Table 1. It is interesting to note that these yields vary significantly with the nature of the substituent in the sulphoxide. The percentages of OH· radical reaction leading to sulphinic acid [based on $G(OH\cdot) = 6.0$] are given in the third column of Table 1. A yield of the same order as that for dimethyl sulphoxide is only found for the cyclic tetramethylene sulphoxide. The lower yields for the other aliphatic compounds are explained on the basis of hydrogen-atom abstraction from the substituent competing with the OH· radical attack on the sulphur atom.

TABLE 1

R_2SO	$G(RSO_2^-/H^+_{aq})$	% OH·	pK_a Exp.	pK_a Lit.
R = Me	5.5	92	2.35	2.28 [16]
Et	4.8	80	2.3	
Pr^i	4.75	79	2.3	
Pr^n	3.3	55	2.35	
Bu^n	2.9	48	2.1	2.1 [17]
Bu^t	4.75	79	2.75	
$HO(CH_2)_2$	3.9	65	2.1	
Ph	1.85	31	1.3	1.29 [17]
$PhCH_2$	0.9	15	1.8	1.45 [17]
$O{:}S\cdot[CH_2]_3\cdot CH_2$	5.4	90	2.4	

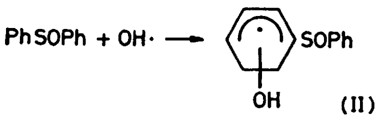
Yield of sulphinic acid formation relative to $G(OH\cdot) = 6.0$, *i.e.* to the total yield of OH· radicals available, and pK_a values of the sulphinic acids determined from conductivity experiments. Limits of error: G-values: ±10%, pK_a values: ±0.1 pH unit.

Reactions (5) and (6) account only for 31 and 15% of the OH· radicals, respectively.

$$Ph_2SO + OH\cdot \longrightarrow Ph\cdot + PhSO_2^-/H_{aq}^+ \qquad (5)$$

$$PhCH_2{\cdot}SO{\cdot}CH_2Ph + OH\cdot \longrightarrow PhCH_2\cdot + PhCH_2SO_2^-/H_{aq}^+ \qquad (6)$$

The relatively low yields of sulphinic acid formation from these compounds cannot, however, be directly correlated with those from the purely aliphatic sulphoxides, since H-atom abstraction does not usually take place from aromatic systems. Owing to its electrophilic character, however, the OH· radical adds readily to the π-system to yield hydroxycyclohexadienyl-type radicals [see *e.g.* reaction (7)]. These species are indeed formed with appreciable yields and can easily be detected through their characteristic optical absorption. The relevant results will be presented in a later section.



(II) (7)

(*b*) *p*K$_a$-*Values of the sulphinic acids.* Detection of sulphinic acids by means of conductivity methods is, of course, only possible at pH values above or close to the pK_a of the equilibrium (8). Experimentally the pK_a values were

$$RSO_2H \rightleftharpoons RSO_2^- + H_{aq}^+ \qquad (8)$$

determined from the pH dependence of the conductivity signals. Figure 2 shows the relative yields of RSO_2^-/H_{aq}^+ ion-pair formation, normalized with respect to the yields at complete dissociation of the sulphinic acid, α, as a function of pH for pulse-irradiated N_2O-saturated solutions of 10^{-3}M di-t-butyl, dimethyl and diphenyl sulphoxide respectively. A complete pK curve is obtained for the t-butyl compound and a pK_a value of 2.75 is derived for Bu^tSO_2H. For the other two compounds the conductivity signals decrease at relatively lower pH values and the respective pK curves could only be determined partially since the experimental technique is limited to a total ion concentration corresponding to pH ≈ 2.0. For $MeSO_2H$ the experimental points still allow the determination of pK_a = 2.35 which is in good agreement with the known literature value of 2.28.[16] In the case of diphenyl sulphoxide the experimental points are seen to follow the theoretical curve (solid line) calculated on the basis of the known pK_a = 1.29 of the benzenesulphinic acid [17] within the accessible pH range. All these results clearly support reaction (1), *i.e.* the formation of sulphinic acids in the reaction of OH· radicals with sulphoxides.

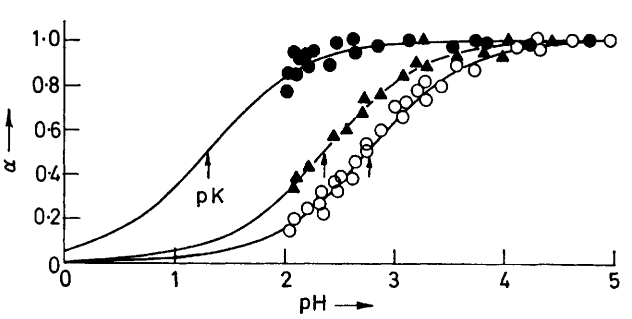


FIGURE 2 Yield of RSO_2^-/H_{aq}^+ ions relative to total yield of sulphinic acids as function of pH. N_2O saturated solutions of 10^{-3}M-di-t-butyl sulphoxide (○), dimethyl sulphoxide (▲), and diphenyl sulphoxide (●),

All pK_a values determined in the present study and some values available from the literature [16,17] are listed in columns 4 and 5 of Table 1, and found to be in the range of 1—3. The variations in pK_a are explained by inductive and electron-withdrawing effects of the substituents. Accordingly, the pK_a for the alkanesulphinic acids is expected to increase in the series Me < Et < Pr^n < Pr^i < Bu^t, and the net electron-withdrawing effect of an aromatic system should lead to a pK_a value for toluene- and benzene-sulphinic acids still lower than that of methanesulphinic acid. A more quantitative description is provided by the Taft equation which correlates the pK_a values with the inductive substituent parameter σ*.[18] Figure 3 shows such a plot of our experimental data and the known literature values. The data are reasonably described by a straight line given by pK = 2.12 − 1.34σ*. A significant difference between our experimental value (pK_a = 1.80) and the literature value (1.45) [17] is found for only one compound, namely toluene-sulphinic acid. It will be noted that the higher value determined in the present investigation is in much better agreement with the Taft correlation.

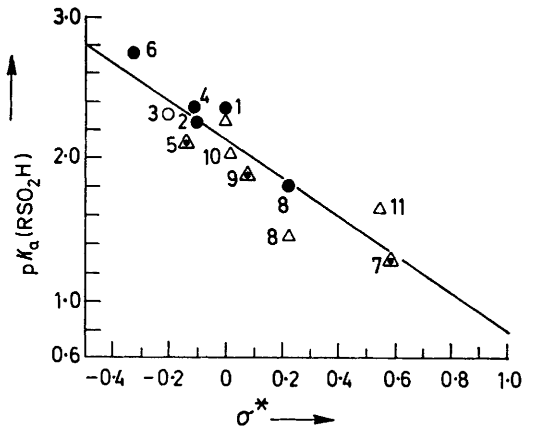


FIGURE 3 pK_a Values of the sulphinic acids as a function of the Taft parameter σ*. (●), exp. values, (△), lit. values [16,17] (1, Me; 2, Et; 3, Pr^i; 4, Pr^n; 5, Bu^n; 6, Bu^t; 7, Ph; 8, $PhCH_2$; 9, $Ph[CH_2]_2$; 10, $Ph[CH_2]_3$; 11, $OHCH_2$)

(*c*) *Formation kinetics.* Figure 4 shows conductivity traces with much better time resolution than those of Figure 1. The traces were obtained for N_2O-saturated

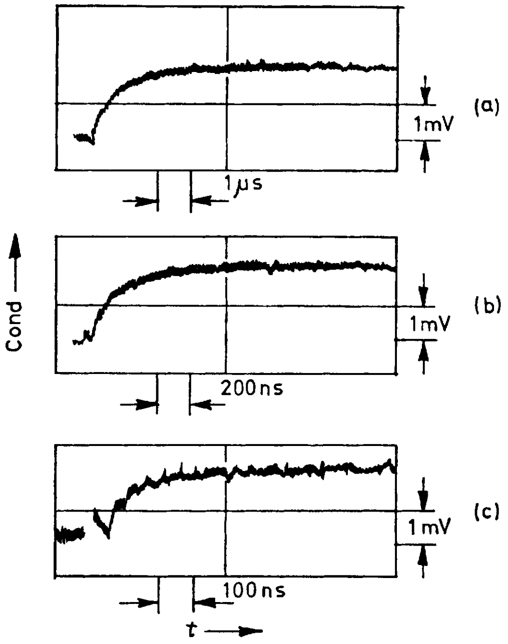


FIGURE 4 Conductivity *vs.* time traces from pulse-irradiated N_2O-saturated solutions of 2 × 10^{-4} (a) 8.5 × 10^{-4}; (b) and 8 × 10^{-3}M; (c) $(HOCH_2CH_2)_2SO$ at pH = 3.0. Pulse width: 5 ns; absorbed dose: *ca.* 800 rad. (Electronical signal distortion during initial 50 ns period)

solutions of 2×10^{-4}M (Figure 4a), 8.5×10^{-4}M (Figure 4b), and 8×10^{-3}M (Figure 4c) 2,2′-Sulphinyldiethanol $(HOCH_2CH_2)_2SO$, respectively, irradiated with pulses of 5 ns duration (pH = 3.0). The build-up of the signals occurs exponentially at all concentrations. At low sulphoxide concentrations the half-lives are inversely proportional to the concentrations as can be deduced from the half-lives, $t_{1/2}$ = 650 and 153 ns for the 2×10^{-4} and 8.5×10^{-4}M-solutions, respectively. Under these conditions the rate law is of pseudo-first order since $[OH\cdot] \ll$ [sulphoxide]. The bimolecular rate constant $k_2 = 5.3 \times 10^9$ l mol^{-1} s^{-1} derived from the data is attributed to the initial reaction of the OH· radical with the sulphoxide. At higher solute concentrations the latter process no longer appears to be the rate-determining step for the formation of the RSO_2^-/H_{aq}^+ ion pair since the half-lives level off to a constant value of 73 ± 8 ns. This becomes apparent on comparison of the results at 8.5×10^{-4} and 8×10^{-3}M, respectively, *i.e.* an increase in solute concentration by a factor of 9.5 is accompanied by a decrease in $t_{1/2}$ by a factor of only 2.3. This result indicates that a pure first-order process comes into play which at high enough solute concentrations completely predominates over the bimolecular (pseudo-first-order) process.

Qualitatively similar results were also obtained for other sulphoxides. Owing to the limited time-resolution of the conductivity technique it was not always possible to make measurements in the range where $t_{1/2}$ became completely independent of the solute concentrations. Estimates for the pure first-order rate constants can be obtained, however, by extrapolation.

The respective second- and first-order rate constants derived from the conductivity build-up for a number of sulphoxides are listed in Table 2. The values of k_1, which are assigned to the reaction of OH· radicals with the sulphoxides, afford strong evidence that the rate of these reactions is essentially diffusion-controlled. The pure first-order process at high solute concentrations indicates the existence of an intermediate whose unimolecular decay becomes the rate-determining step for the RSO_2^-/H_{aq}^+ ion pair formation at such concentrations. This species is suggested to be the OH· radical adduct to the sulphoxide and the data can be satisfactorily accounted for by the reaction sequence (9).

TABLE 2

R_2SO	k_2/l mol^{-1} s^{-1}	k_1/s^{-1}	$t_{1/2}$/ns
R = Me	7.0×10^9	1.5×10^7	45
Et	6.5×10^9	$\approx 2.3 \times 10^7$	≈30
Pr^i	6.8×10^9	1.0×10^7	70
Pr^n	6.3×10^9	7.7×10^6	90
Bu^n	8.0×10^9	1.4×10^7	50
Bu^t	5.3×10^9	1.1×10^7	63
$HO(CH_2)_2$	5.3×10^9	9.5×10^6	73
Ph	1.0×10^{10}	$\geqslant 1.5 \times 10^7$	≤50
$O{:}S{\cdot}[CH_2]_3{\cdot}CH_2$	7.0×10^9	7.3×10^6	95

Bimolecular rate constants for the reaction of OH· radicals with the sulphoxides (k_2), and first-order rate constants (k_1) and half-lives ($t_{1/2}$) for the decay of the transient OH· adduct, $R_2SO(OH)\cdot$. Limits of error: ±10%.

$$R_2SO + OH\cdot \xrightarrow{k_2} R_2SO(OH)\cdot \xrightarrow{k_1} R\cdot + RSO_2^-/H_{aq}^+ \qquad (9)$$

The $t_{1/2}$ values listed in Table 2 would then refer to the lifetime of the transient OH· adduct. It is noted that no such species is indicated in the OH·-induced oxidation of diphenyl sulphoxide where, up to the solubility limit of $\approx 6 \times 10^{-3}$M, the initial OH· radical reaction was invariably found to be rate-determining for the $PhSO_2^-/H_{aq}^+$ formation. No information can be given either on an intermediate OH· adduct for dibenzyl sulphoxide. In this case the solubility is too low to allow appropriate experiments.

Although the assignment of the transient OH· radical adduct $R_2SO(OH)\cdot$ seems to be quite reasonable, it is still not unambiguous at this stage. Some additional results presented in the forthcoming sections will, however, shed further light on this problem. A detailed discussion is given later in the appropriate section.

Formation of Alkyl, Aryl and Hydroxycyclohexadienyl Radicals.—According to the reaction scheme [equations (1) and (9)] the formation of sulphinic acid is associated with the elimination of alkyl or aryl radicals. Direct observation of these radicals in pulse radiolysis experiments is often difficult. Optically, these species do not in most cases show any significant or characteristic absorption in the accessible wavelength range (down to 230 nm) and owing to their neutral character their presence cannot be inferred from the conductivity signals.

One of the few exceptions is found for the t-butyl sulphoxide where the formation of a transient optical absorption is observed. The absorption increases steadily towards the u.v. and at 240 nm an extinction coefficient of ε = 1 500 l mol^{-1} cm^{-1} is calculated. The latter value is based on the assignment of the optical absorption to the $Me_3C\cdot$ radical, which is assumed to be formed with the same yield as the corresponding 1,1-dimethylethanesulphinic acid. There might, of course, be some contribution to the absorption by the hydrogen-atom abstraction product $\cdot CH_2(Me)_2CSOCMe_3$ but the total absorption is too high to be accounted for by this latter radical alone. This optical evidence for the formation of t-butyl radicals from the symmetrical sulphoxide is of interest since e.s.r. detection has not been possible on account of the short lifetime of the $Me_3C\cdot$ radical, which under these experimental conditions decays by a mainly second-order process with $2k = 2.8 \times 10^9$ l mol^{-1} s^{-1}.

The other alkyl and phenyl radicals could not be identified directly but were detected by their reactions with appropriate scavengers. Thus radicals readily added to *aci*-nitromethane anions [19] [see for example reaction (10)].

$$R\cdot + CH_2 = NO_2^- \longrightarrow RCH_2 - NO_2^{-\cdot} \qquad (10)$$

These reactions were examined with basic N_2O saturated solutions containing high concentrations (10^{-1}M) sulphoxide and variable, lower concentrations (10^{-4}—10^{-3}M) of nitromethane. Under these conditions the elimination of R· occurs within the duration of a 1-µs pulse and reaction (10) can easily be followed through the build-up of the characteristic absorption of the nitroalkane radical-anion.[19a,b] The latter absorbs in the u.v. region with $\lambda_{max.} \approx 280$ nm and quite appreciable extinction coefficients of around 3 000 l mol^{-1} cm^{-1}.

Scavenging of R· was also possible with *p*-benzoquinone [9,20] where stoicheiometrically two quinone molecules are involved [21] [see equation (11)]. The semiquinone radical (pK = 4.0) [22] has been identified by its characteristic absorption [23] and by means of conductivity experiments. The substituted quinone was quantitatively analysed by using a newly developed liquid chromatography method.[24] Reaction (11) was particularly shown to occur for phenyl radicals [21] which is interesting since attempts to detect these radicals directly have failed so far.

More detailed information on the radical trapping by *aci*-nitromethane anions and *p*-benzoquinone will be presented in a separate publication.[21]

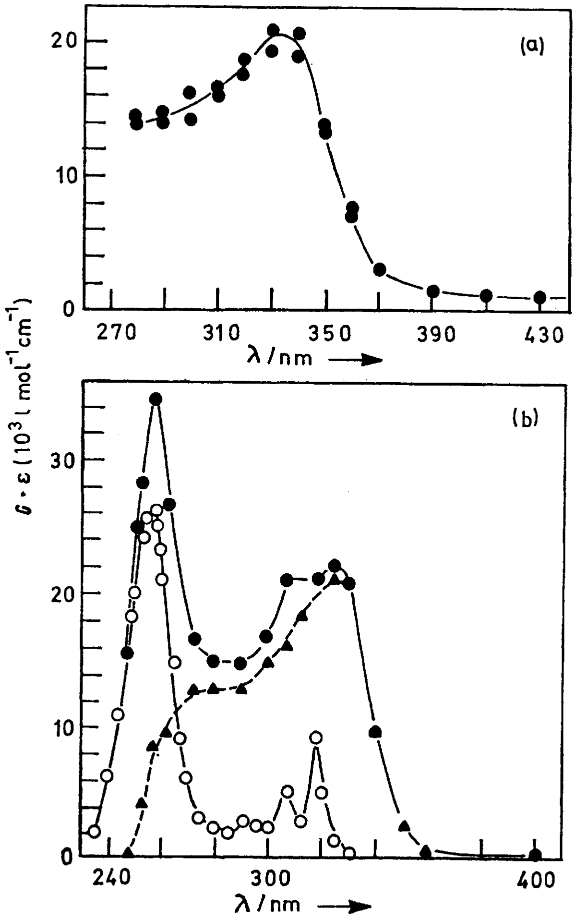
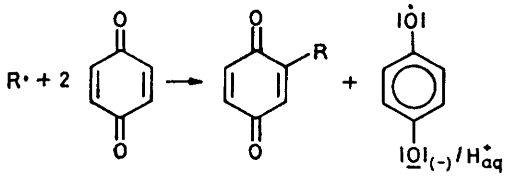


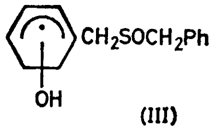
FIGURE 5 (a) Absorption spectra of the hydroxycyclohexadienyl radical from diphenyl sulphoxide. (b) Total absorption (●) measured 5 μs after a 1-μs pulse in N_2O-saturated solutions of $\approx 10^{-4}$M-dibenzyl sulphoxide, spectrum of the benzyl radical (○) calculated for $G = 0.9$, and evaluated spectrum of the hydroxycyclohexadienyl radical from dibenzyl sulphoxide (▲)

In the presence of aromatic systems OH• radical addition to the π-system competes with the attack at the sulphoxide group, resulting in a transient hydroxycyclohexadienyl radical [equation (7)]. The absorption spectrum of the species (II) formed from diphenyl sulphoxide is shown in Figure 5a. The shape of the spectrum is typical for hydroxycyclohexadienyl radicals.[25] The absorption has a maximum at 330 nm.



(11)

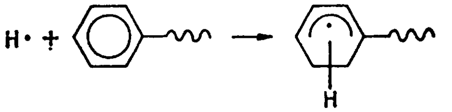
The optical absorption for the primary species in the OH• radical-induced oxidation of dibenzyl sulphoxide is shown in Figure 5b. The overall absorption (full circles) partially results from the benzyl radical which is formed *via* reaction (6) with a yield of $G = 0.9$ and whose spectral parameters are well known.[26] Subtraction of the thus calculable benzyl radical absorption (open circles) leads to the spectrum (triangles) of (III) which has an absorption maximum at 325 nm.



(III)

The yields of (II) and (III) are given by the difference in the total yield of OH• radicals available and the measured yields of sulphinic acids, *i.e.* $G(\mathrm{II}) = 6.0 - 1.85 = 4.15$ and $G(\mathrm{III}) = 6.0 - 0.9 = 5.1$, respectively. For calculation of extinction coefficients a small contribution of a hydrogen atom adduct formed with $G = 0.6$ *via* reaction (12) has to be taken into account. These types of species generally exhibit absorptions very similar to those of hydroxycyclohexadienyl radicals.[27] Taking this into account $\varepsilon_{330} = 4\,210$ l mol^{-1} cm^{-1} and $\varepsilon_{325} = 3\,685$ l mol^{-1} cm^{-1} are calculated for species (II) and (III), respectively.

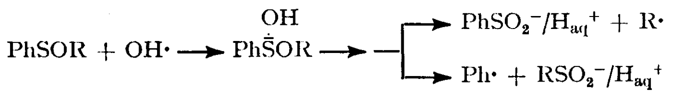
These extinction coefficients are very similar to those of the hydroxycyclohexadienyl radicals from phenol [28] ($\varepsilon_{350\,\mathrm{nm}} = 4.4 \times 10^3$ l mol^{-1} cm^{-1}) and benzene [25] ($\varepsilon_{313\,\mathrm{nm}} = 3.5 \times 10^3$ l mol^{-1} cm^{-1}). The slight variations in $\lambda_{\max.}$ and ε are probably explained by differences in the degree of electron delocalisation in the respective species.



(12)

The rate-determining step for the formation of the hydroxycyclohexadienyl radicals at all solute concentrations was the reaction of the OH• radical with the sulphoxides. The decay of the radicals occurred *via* second-order disproportionation/combination with $2k_2 \approx 1.5 \times 10^9$ l mol^{-1} s^{-1}.

Reaction of OH• *Radicals with Mixed Sulphoxides.*—Experiments were also carried out with mixed alkyl phenyl sulphoxides. For these compounds OH• radical attack at the sulphoxide leads to the elimination of either alkyl (R•) (13a) or phenyl radicals (Ph•) (13b):



$$\mathrm{PhSOR} + \mathrm{OH}\cdot \longrightarrow \mathrm{Ph}\overset{\mathrm{OH}}{\dot{\mathrm{S}}}\mathrm{OR} \longrightarrow \left\{\begin{array}{ll} \longrightarrow \mathrm{PhSO_2^-/H_{aq}^+} + \mathrm{R}\cdot & (13a)\\ \longrightarrow \mathrm{Ph}\cdot + \mathrm{RSO_2^-/H_{aq}^+} & (13b)\end{array}\right.$$

As will be shown later these reactions also proceed *via* a transient OH• adduct. The sulphinic acids can, in principle, be identified from their different p*K* values. Since, however, the pK_a values differ only by about one pH unit (see Table 1), the experimental ' p*K* ' curve (conductivity signal *vs.* pH) for these compounds will be a composition of two individual p*K* curves. Figure 6 shows, for example, the normalized conductivity values as a function of pH obtained from irradiated solutions (N_2O saturated) of 10^{-3}M methyl phenyl sulphoxide. The ' best-fit ' p*K* curve from these results yields a ' p*K* ' = 1.50 which differs

TABLE 3

R–S(=O)–Ph	G (sulphinic acid)	% OH·	' pK '	pK_a RSO$_2$H	pK_a PhSO$_2$H	x_A	x_B	$G(C_6H_5\cdot) = G(RSO_2H)$	$G(R\cdot) = G(PhSO_2H)$
R = Ph	1.85	31			1.29			1.85	
Me	2.8	47	1.50	2.28	1.29	0.25	0.75	0.7	2.1
Et	2.6	43	1.32	2.27	1.29	≈0.04	≈0.96	≈0.1	≈2.5
C_2H_4Cl	2.6	43	1.29	1.6	1.29	0	1.0	0	2.6
Pr^i	2.6	43	1.29	2.32	1.29	0	1.0	0	2.6

Absolute and relative yields of radicals and sulphinic acids formed in the reaction of OH· radicals with mixed alkyl–phenyl sulphoxides and diphenyl sulphoxide. Limits of error: ±10%.

significantly from the actual values, pK_a(PhSO$_2$H) = 1.29 [17] and pK_a(MeSO$_2$H) = 2.28.[16] The exact pK curves of the latter two sulphinic acids can be calculated by the general equation (14) where α ($0 \leqslant \alpha \leqslant 1$) is the relative degree of dissociation of the acid. The respective curves are included in the Figure (dotted lines). The composite ' pK ' curve is

$$\alpha = \frac{1}{1 + 10^{pK-pH}} \qquad (14)$$

$$\alpha = \frac{x_A}{1 + 10^{pK_A-pH}} + \frac{1 - x_A}{1 + 10^{pK_B-pH}} \qquad (15)$$

generally described by equation (15). In this equation the index A refers to one of the sulphinic acids, here MeSO$_2$H, and the index B to the other, here PhSO$_2$H; x_A is the relative contribution of MeSO$_2$H to the total yield of sulphinic acids and $1 - x_A = x_B$ is the relative contribution of PhSO$_2$H. The total amount of dissociated sulphinic acid which yields

$$\alpha = x_A \,.\, \alpha_A + (1 - x_A)\alpha_B = x_A\alpha_A + x_B\alpha_B \qquad (16)$$

a conductivity signal is given by equation (16). Knowing pK_A and pK_B, and $\alpha = 0.5$ at pH = 1.5 from the experimental ' pK ' curve x_A and x_B can be calculated as 0.25 and 0.75, respectively. This means that the proportion of MeSO$_2$H and phenyl radicals yielded by attack of OH· radicals at the sulphoxide group is 25%, whereas 75% of the reaction leads to methyl radical cleavage and PhSO$_2$H formation. For the other mixed sulphoxides investigated (R = Et, C_2H_4Cl, MeCH) the ' pK ' values determined were almost identical with the pK_a of PhSO$_2$H, as can be seen from Table 3, and analysis of the data shows that phenyl radical elimination from these compounds is almost negligible.

The total yield of sulphinic acid from these mixed sulphoxides is generally higher than that from diphenyl sulphoxide but lower than that from the corresponding dialkyl sulphoxides (see Table 3) and accounts for about 45% of the total OH· radical yield. The remaining 55% of the OH· radicals will mainly undergo addition to the aromatic π-system. The corresponding hydroxycyclohexadienyl radicals have been identified through their optical absorption, and their respective $\lambda_{max.}$, ε values and second-order decay rate constants are listed in Table 4.

The rate of formation of the hydroxycyclohexadienyl radicals was found to be of pseudo-first-order over the entire solute concentration range, and bimolecular rate constants of the order of 10^{10} l mol^{-1} s^{-1} (Table 4) were derived for the OH· reaction with the sulphoxides. Identical rate constants, within the experimental limits, were obtained for the build-up kinetics of the conductivity signal at low solute concentrations. At higher concentrations the results were similar to those obtained for the symmetrical sulphoxides. The rate of increase of the conductivity signal became increasingly independent of the solute concentration, and eventually pure first-order kinetics were observed for the PhSO$_2^-$/H$_{aq}^+$ or RSO$_2^-$/H$_{aq}^+$ ion-pair formation. This again indicates a transient OH· adduct (IV). The first-order rate constants and $t_{1/2}$ values listed in the last two columns of Table 4 are assigned to the unimolecular decay of this species into the radicals (R· or Ph·) and the sulphinic acids (PhSO$_2^-$/H$_{aq}^+$ or RSO$_2^-$/H$_{aq}^+$).

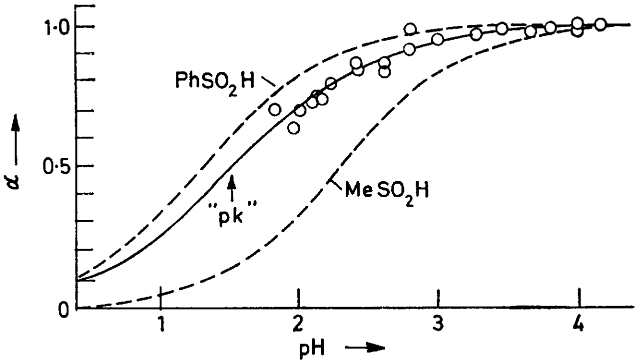
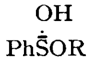


FIGURE 6 Experimental ' pK ' curve for the formation of RSO$_2^-$/H$_{aq}^+$ from methyl phenyl sulphoxide (—○—) measured by conductivity, and theoretical pK-curves for the dissociation of MeSO$_2$H and PhSO$_2$H (— — —). Solution: N$_2$O-saturated, 10^{-3}M-MeSOPh



$$\overset{OH}{Ph\dot{S}OR}$$

(IV)

TABLE 4

R–S(=O)–Ph	Hydroxycyclohexadienyl radical λ_{max}/nm	ε_{max}/l mol^{-1} cm^{-1}	$2k_2$/l mol^{-1} s^{-1}	$\frac{k_2(OH\cdot + S)}{l\ mol^{-1}\ s^{-1}}$	k_1/s^{-1}	$t_{1/2}$/ns
R = Ph	330	4 210	1.5×10^9	1.0×10^{10}	$\geqslant 1.5 \times 10^7$	$\leqslant 50$
Me	320	3 160	1.85×10^9	9.7×10^9	6.5×10^6	107
Et	320	2 750	1.8×10^9	8.4×10^9	8.0×10^6	87
Br^i	320	2 750		1.0×10^{10}	8.45×10^6	82

λ_{max}, ε_{max} and second-order decay rate constants for the decay ($2k_2$) and formation (k_2) of the OH· radical adduct to the aromatic π-system in mixed alkyl phenyl sulphoxides; and first-order rate constants (k_1) and half-lives ($t_{1/2}$) for the decay of the transient OH· adduct to the sulphoxide bridge, R–$\dot{S}$O(OH)–C$_6$H$_5$. Limits of error: ±10%.

DISCUSSION

On the Existence of a Transient OH· *Adduct to Sulphoxides.*—The suggestion that the transient precursor of the sulphinic acid is the OH· radical adduct to the sulphoxide (I) is based on the following considerations.

$$\overset{\text{OH}}{\mathrm{R}\dot{\bar{\mathrm{S}}}\mathrm{OR}}$$

(I)

At high solute concentration the formation of (I) is so fast that its decay [equation (17)] will be the rate-determining step for the formation of the sulphinic acid.

$$\begin{tikzcd}
\text{(I)} \arrow[r, "k_1"] & \mathrm{R\cdot} + \mathrm{RSO_2H} \arrow[d, shift right, "k_d"'] \\
& \mathrm{RSO_2^-} + \mathrm{H_{aq}^+} \arrow[u, shift right, "k_n"']
\end{tikzcd} \qquad (17)$$

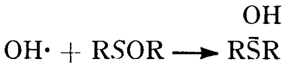
This is in perfect agreement with the experimental kinetic data. At this point, however, an alternative possibility must also be considered. In principle, the kinetic observations could be explained equally well by assigning the first-order rate constant k_1 not to the decay of (I), but to the dissociation of the undissociated $\mathrm{RSO_2H}$ into its ions ($k_1 = k_d$). This implies in turn that the formation of (I) would not even be necessary and the sulphinic acid could be formed directly by dissociative attachment of the OH· radical to the sulphoxide.

It thus seems appropriate initially to compare k_1 with likely values of k_d, since k_d must be greater than k_1 if species (I) is to exist at all. An estimate of k_d can be derived from the pK_a (= — log K) of the sulphinic acid and the bimolecular rate constant k_n for the neutralization reaction of the $\mathrm{RSO_2^-}$ anion. The lowest value of $k_d = K \cdot k_n$ is expected for the sulphinic acid with the highest pK_a, which is the 1,1-dimethylethanesulphinic acid (pK_a = 2.75 and $K = 1.78 \times 10^{-3}$). The neutralization rate constant k_n is not known but should be in the range of 5×10^{10}—1×10^{11} l mol^{-1} s^{-1}.[29] Those values are typical for the neutralization reaction of 'oxygen' anions (*e.g.* $\mathrm{MeCO_2^-}$, $\mathrm{SO_4^{2-}}$) and for acids with similar pK_a.[30] Taking the lower value of k_n a minimum value of $k_d = 1.78 \times 10^{-3} \times 5 \times 10^{10} = 8.9 \times 10^{7}$ s^{-1} is obtained. This corresponds to a maximum half-life of 7.8 ns for the dissociation of $\mathrm{RSO_2H}$ into its ions, and means that this reaction is at least an order of magnitude faster than the observed formation of the $\mathrm{RSO_2^-/H_{aq}^+}$ ion pair.

Further evidence for the formation of species (I) is obtained from the results on the mixed sulphoxides. For ethyl phenyl and isopropyl phenyl sulphoxide, from which benzenesulphinic acid is formed almost exclusively, a transient intermediate is clearly indicated which decays with $t_{1/2} \approx 80$ ns into the $\mathrm{PhSO_2^-/H_{aq}^+}$ ions. On the other hand, the same $\mathrm{PhSO_2^-/H_{aq}^+}$ ion pair is formed much faster in the diphenyl sulphoxide system where, in fact, no indication for such an intermediate was found. It is also noted that the lifetime of the transient from methyl phenyl sulphoxide is considerably longer than those of the symmetric dimethyl and diphenyl sulphoxides. These results, together with the kinetic considerations on k_d, thus seem to rule out the possibility that the conductivity data at high sulphoxide concentrations be explainable in terms of the $\mathrm{RSO_2H}$ dissociation, and clearly suggest the existence of the transient OH· radical adduct (I).

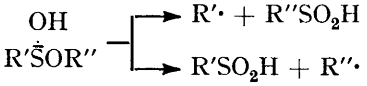
The formation of such a species is, in fact, not so surprising in view of the nature of quite a number of OH· radical reactions. Owing to its electrophilic character the OH· radical readily adds not only to π-systems, but also to free electron pairs, *e.g.* of sulphur atoms in sulphides [13b,31] or nitrogen atoms in nitrosobenzene,[32] to form more or less stable adducts. It has further been shown recently that the OH·-induced oxidation of metal ions often proceeds *via* OH· radical adducts as intermediates.[33]

Reaction Mechanism.—The overall mechanism of the primary events in the OH· radical-induced oxidation of sulphoxides is given by the following summarizing scheme. Addition of the OH· radical to the sulphoxide groups leads to an intermediate



$$\mathrm{OH\cdot} + \mathrm{RSOR} \longrightarrow \overset{\text{OH}}{\mathrm{R}\bar{\mathrm{S}}\mathrm{R}} \qquad (2)$$

which decays unimolecularly with $t_{1/2}$ up to *ca.* 100 ns into a sulphinic acid and the corresponding radical. In case of mixed sulphoxides two pathways have to be considered:

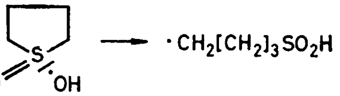


$$\overset{\text{OH}}{\mathrm{R'}\dot{\bar{\mathrm{S}}}\mathrm{OR''}} \begin{cases} \longrightarrow \mathrm{R'\cdot} + \mathrm{R''SO_2H} \\ \longrightarrow \mathrm{R'SO_2H} + \mathrm{R''\cdot} \end{cases} \qquad (18)$$

The probability of the respective C–S bond rupture increases with the stability of the leaving radical. Thus elimination of the π-type alkyl radicals is generally favoured over elimination of the generally less stable and more reactive σ-type phenyl radicals.

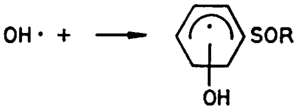
Cyclic sulphoxides undergo the same initial steps. C–S Bond rupture in this case, however, leads to a sulphinic acid radical [see *e.g.* reaction (19)].

Depending on the nature of the sulphoxide substituents, two other OH· radical reactions can compete with and even predominate over the addition at the sulphoxide group.



(19)

$$\mathrm{OH\cdot} + \mathrm{RSOR} \longrightarrow \mathrm{RSOR(\text{-}H)\cdot} + \mathrm{H_2O} \qquad (20)$$



(21)

Thus hydrogen atom abstraction readily takes place from longer chain or substituted aliphatic groups [reaction (20)]. In the case of aromatic substituents, OH· addition [see *e.g.* reaction (21)] yields a hydroxycyclohexadienyl radical. The radical species formed in reactions (19)—(21) then undergo the usual radical reactions, *i.e.* disproportionation, combination, and hydrogen-atom abstraction.

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