

Pulse radiolysis of some aromatic sulphoxides in aqueous solutions

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Abstract. Reactions of e_{aq}^- and H-atoms with aromatic sulphoxides such as dibenzyl, diphenyl and di-4-chlorophenyl sulphoxides have been studied at various pH values and the spectral and kinetic properties of the transients determined. e_{aq}^- addition to dibenzyl sulphoxide was found to lead to the scission of the C-S bond giving benzyl radicals, but such bond breakage was not observed in other cases.

Keywords. Pulse radiolysis; aromatic sulphoxides; transients.

1. Introduction

Aromatic sulphoxides such as dibenzyl and diphenyl sulphoxides are good corrosion inhibitors (Trabanelli *et al* 1969). The study of the radiation chemistry of these compounds has not received much attention as compared to the aliphatic sulphoxides (Veltvisch *et al* 1980; Kishore and Asmus 1989). OH radical reaction with diphenyl and dibenzyl sulphoxides is known to lead to C-S bond breakage giving aryl radicals and sulphinic acid besides giving rise to hydroxycyclohexadienyl radicals (Veltvisch and Asmus 1982). The reactions of other primary species of water radiolysis such as e_{aq}^- and H-atoms with aryl sulphoxides have not been studied till now. We have studied these reactions in the case of dibenzyl, diphenyl and di-4-chlorophenyl sulphoxides as also the reactions of some one-electron reductants at various pH values by the pulse radiolysis technique. These results are presented in this paper.

2. Experimental

The sulphoxides used were obtained from Aldrich Chemicals and were used as such without further purification. All other chemicals employed were AnalaR reagents. Water from a Barnstead "Nanopure" unit (conductivity $< 0.1 \mu\text{s cm}^{-1}$) was used for making all the solutions. Gases used for saturating the solutions were Iolar/Instrument grade from Indian Oxygen Ltd. A 7-MeV linear electron accelerator giving 50 ns single pulses (dose ≈ 20 Gray) was used for irradiating the sample solutions. The pulse radiolysis set-up has been described earlier (Guha *et al* 1987) in detail. Aerated decimolar KSCN solutions were used for measuring the pulse dose taking $G_e = 21500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (Fielden 1984). The accuracies of the rate constant values reported in this paper are within $\pm 20\%$.

3. Results and discussion

3.1 Reactions of e_{aq}^- with dibenzyl sulphoxide

These reactions were studied in the pH range 4–7 and the transient spectra obtained at pH values 4 and 7 are shown in figure 1. For this purpose N_2 -saturated $2 \times 10^{-4} \text{ mol dm}^{-3}$ dibenzyl sulphoxide (BSO) solutions containing 0.1 mol dm^{-3} *t*-butanol were employed. The transient spectrum obtained at pH 7 resembles that of benzyl radicals with λ_{max} at 260 and 320 nm (Mittal and Hayon 1972). The extinction coefficient values at 260 and 320 nm determined by taking a *G*-value of 2.7 (assuming that all e_{aq}^- react with BSO to give benzyl radicals) are only about one-fourth the reported values (Mittal and Hayon 1972). However, the ratio of the extinction coefficients ($\epsilon_{260}/\epsilon_{320} \approx 3$) is almost the same as that for benzyl radicals. This indicates that the yield of benzyl radicals is only about 25%. Thus it can be assumed that the rest of the e_{aq}^- react with BSO giving a transient which has negligible absorbance in the wavelength region investigated.

The presence of benzyl radicals was further confirmed by studying their reaction with *p*-benzoquinone. It has been reported (Veltvisch and Asmus 1982) that alkyl and aryl radicals add on to *p*-benzoquinone and this adduct further reacts with a

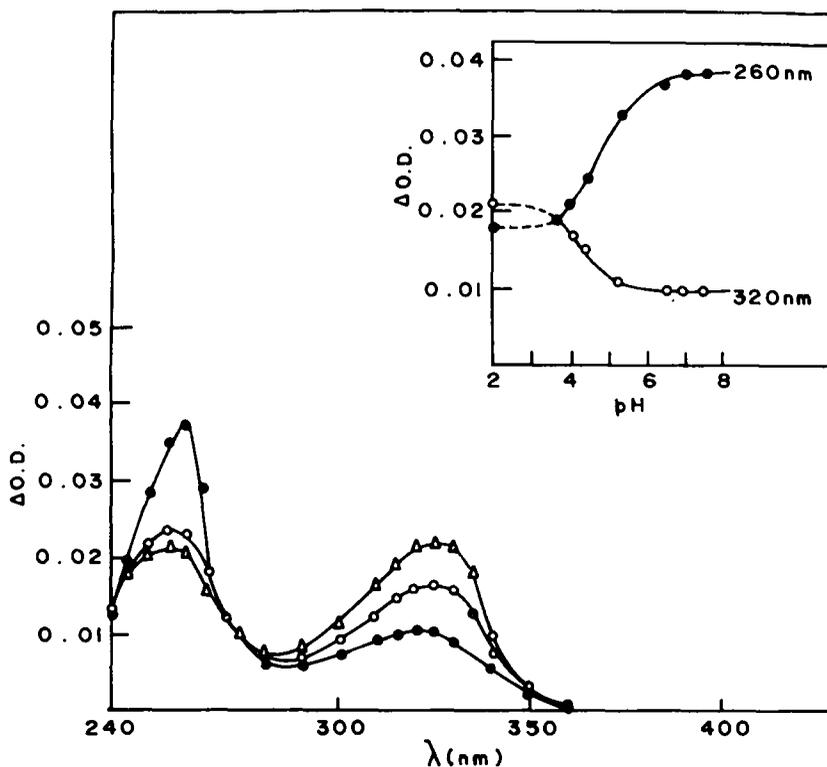


Figure 1. Transient spectra obtained by the reaction of e_{aq}^- with BSO at pH 7 – ●; at pH 4 – ○; and by H-atom reaction with BSO at pH 2 – △, immediately after the electron pulse. Inset: Plot of Δ O.D. vs pH. Points at pH 2 correspond to absorbance obtained by H-atom reaction with BSO.

p-benzoquinone molecule to give semiquinone radicals. For this purpose, N₂-saturated 10⁻³ mol dm⁻³ BSO solutions containing 0.1 mol dm⁻³ *t*-butanol and 10⁻⁴ mol dm⁻³ *p*-benzoquinone (pH 7), were pulse-irradiated. The transient spectrum obtained after about 20 μs was similar to that of the semiquinone radical with λ_{max} at 320 and 430 nm. The rate constant for the reaction of this transient species with *p*-benzoquinone was evaluated to be 1.4 × 10⁹ dm³ mol⁻¹ s⁻¹. Thus it is clear that e_{aq}⁻ addition to BSO leads to the scission of the C-S bond giving benzyl radicals.



where R is benzyl and Q is *p*-benzoquinone. Although any reducing radical may react with *p*-benzoquinone to produce semiquinone radicals, the transient species formed by e_{aq}⁻ reaction with BSO was found to be non-reducing in nature. It did not react even with O₂. This was inferred from the observation that in air-saturated 10⁻³ mol dm⁻³ BSO solutions, containing 0.5 mol dm⁻³ *t*-butanol i.e. even in presence of 2 × 10⁻⁴ mol dm⁻³ O₂, the decay of the transient species was unaffected. Hence, semiquinone radicals must have been formed by reactions such as (2)–(3).

At pH 4, a part of the hydrated electrons react with H⁺ to give H-atoms which may also react with BSO. Thus a mixture of species may be generated at this pH. The transient spectrum obtained at pH 4 showed a decrease in absorbance at 260 nm and an increase in absorbance at 320 nm. The effect of pH on the absorbance at the two maxima is shown in figure 1 (inset). It can be seen that there is a systematic change in the absorbance at the two maxima. The transient spectrum obtained by H-atom reaction with BSO at pH 2 (2 × 10⁻⁴ mol dm⁻³ BSO in N₂-saturated 0.1 mol dm⁻³ *t*-butanol) is also shown in figure 1. It shows two absorption bands, with λ_{max} at 260 and 320 nm, and resembles the spectrum obtained at pH 4 which is due to the reaction of both e_{aq}⁻ and H-atoms with BSO. It is possible that the electron adduct of BSO gets protonated at lower pH values to give a species which is similar to that obtained by H-atom reaction with BSO. However, H-atoms can also react with BSO at the benzene ring giving cyclohexadienyl radicals (Sauer and Ward 1967) which have absorption maximum in the 315 nm region. Thus it is difficult to say whether the transient spectrum obtained by H-atom reaction with BSO is a single species or a mixture of species. The decay of the H-adduct followed second order kinetics at 320 nm.

3.2 Reaction of e_{aq}⁻ with diphenyl sulphoxide

The rate constant for the reaction of e_{aq}⁻ with diphenyl sulphoxide (PSO) was determined by following the formation of transient absorption at 340 nm and was equal to 1.8 × 10¹⁰ dm³ mol⁻¹ s⁻¹. The spectrum of the resulting transient species is shown in figure 2. It shows two bands with λ_{max} at 340 and 750 nm. The absorption in the visible region indicated the formation of a 3-electron bonded species as simple S-centred radicals usually absorb only in the uv region. The transient species decayed by second-order kinetics at both the maxima with 2k = 2.7 × 10⁹ dm³ mol⁻¹ s⁻¹.

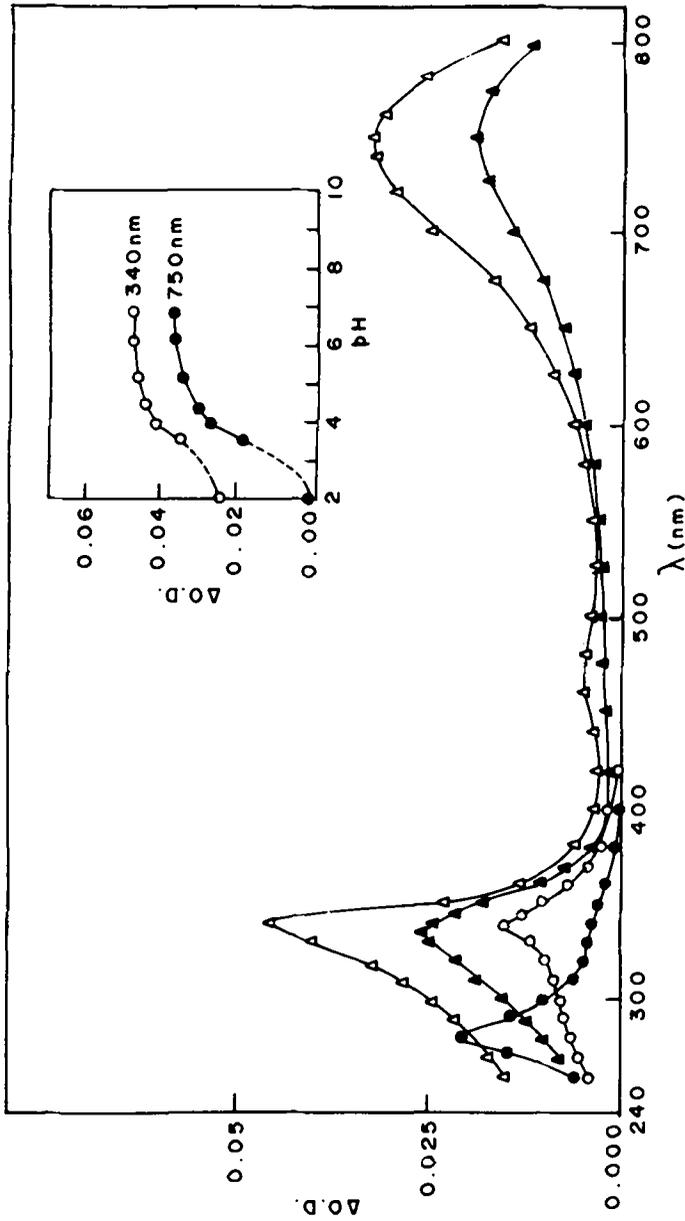
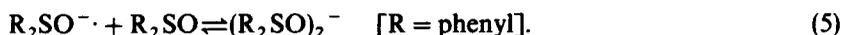


Figure 2. Transient spectra obtained by the reaction of ϵ_{sp} with PSO at pH 7 in N_2 -saturated - Δ ; and air-saturated solutions - \bullet ; and with CPSO at pH 7 in N_2 -saturated solutions - \blacktriangle ; by H-atom reaction with PSO at pH 2 - \circ . Inset: Plot of $\Delta O.D.$ vs pH. Points at pH 2 correspond to the absorbance obtained by H-atom reaction with PSO.

Thus both the bands are due to a single species. The kinetic salt effect on the decay of the transient indicated that it is a charged species.

The effect of the concentration of PSO on the yield of the transient was also studied. The absorbance at both 340 and 750 nm was found to increase with increasing PSO concentration indicating that the transient species initially formed reacts with the parent molecule. It is proposed that the electron adduct of PSO forms a dimer anion radical with the parent molecule as shown below.



For the equilibrium reaction (5), a plot of the reciprocal of the transient absorbance vs the reciprocal concentration of PSO is expected to be linear. In figure 3 are shown such plots for the transient absorbance at both 340 and 750 nm. These are linear and support the supposition of equilibrium in reaction (5). The ratio of intercept-to-slope of the plots shown in figure 3 give a value of $2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ for the equilibrium constant for this reaction. Thus the absorption in the visible region may be due to the dimer anion radical containing an intermolecular 3-electron bond between two sulphur atoms.

The electron adduct of PSO at pH 7 did not react with *p*-benzoquinone to give semiquinone radicals. Thus it is neither a reducing species nor does it break up to give phenyl radicals as in the case of dibenzyl sulphoxide. The formation of the dimer anion radical may be responsible for the stability of this electron adduct species. In presence of oxygen, this adduct was not stable unlike in the case of BSO and reacted with oxygen with a rate constant of $1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ to give a peroxy radical having absorption maximum at 280 nm as shown in figure 2. The pH effect on the absorbance at 340 and 750 nm is shown in figure 3 (inset). It is seen that with decreasing pH, the absorbances at 340 and 750 nm decrease. The transient spectrum obtained by H-atom reaction with PSO at pH 2 is shown in figure 3. This shows only one band with λ_{max} at 335 nm. Thus, it would appear that the absorption spectrum of the electron adduct at lower pH values may approach that of the H-atom adduct as the electron adduct may get protonated at lower pH values. However, the H-atom can react with PSO at two sites, viz. the -SO site as well as at the benzene ring, giving a mixture of species as in the case of BSO. Thus, the spectra obtained by H-atom reaction with BSO and PSO should be similar. The rate constants for the

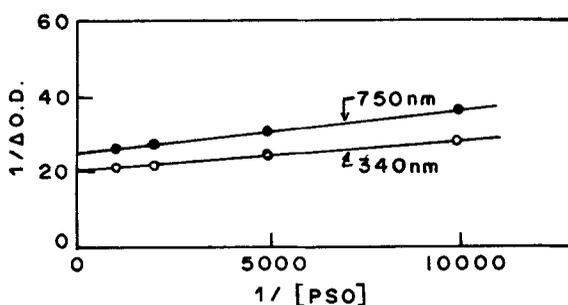


Figure 3. Plot of $1/\Delta$ O.D. vs $1/[\text{PSO}]$.

Table 1. Spectral and kinetic parameters of the transients formed by the reaction of e_{aq}^- and H-atoms with aromatic sulphoxides.

Sulphoxide	pH	λ_{max} (nm)	$G \times \epsilon$ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	$k_{\text{formation}}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	$2k/elt$ (s^{-1})
e_{aq}^- reaction					
BSO	7	260	18460	3.5×10^9	3.0×10^5
		320	5400	"	—
BSO	4	260	11600	"	—
		325	8100	"	—
PSO	7	340	25100	1.8×10^{10}	2.8×10^5
		750	19670	—	4.0×10^5
CPSO	7	340	—	1.0×10^{10}	—
		750	—	—	—
H-atom reaction					
BSO	2	325	12800	2.0×10^9	8×10^5
PSO	2	335	14400	1.5×10^9	4×10^5

G-value for the e_{aq}^- reaction was taken as 2.7 and for the H-atom reaction as 3.6.

reaction of the H-atom with these two compounds as well as the absorption maxima and extinction coefficient values of the resulting species are close to each other.

The reaction of e_{aq}^- with di-4-chlorophenyl sulphoxide (CPSO) ($10^{-4} \text{mol dm}^{-3}$ CPSO in N_2 -saturated 0.1mol dm^{-3} *t*-butanol solutions at pH 7) produced a transient spectrum with the same λ_{max} viz. 340 and 750 nm as in the case of PSO although with a lower yield (see figure 3). The lower yield could be attributed to the reaction of e_{aq}^- at the $-\text{Cl}$ site in addition to that at the $-\text{SO}$ site. The former reaction would lead to the release of chloride ions in solution. The formation of Cl^- ions was confirmed by the silver nitrate test on gamma-irradiated CPSO solutions. The rate constant for reaction of e_{aq}^- with CPSO was of the order of $1 \times 10^{10} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$. One-electron reductants such as isopropylketyl and CO_2^- radicals did not reduce PSO or CPSO.

The differences in the behaviour of benzyl and phenyl sulphoxides in their reaction with e_{aq}^- can be understood in terms of the inductive effect of benzyl and phenyl groups. The benzyl group is more electron-donating in character as compared to the phenyl group due to the presence of a $-\text{CH}_2-$ group. That is why the rate constant for the reaction of BSO with e_{aq}^- is lower as compared to that for PSO or CPSO. Actually, the chlorophenyl group is the least electron-donating and the rate constant for the electron reaction should be highest for CPSO. The rate constant values in the case of PSO and CPSO are of the order of $10^{10} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$. Addition of an electron to the $-\text{SO}$ group appears to be stabilized by the presence of phenyl groups (due to delocalisation over benzene rings) giving an electron adduct which further reacts with the parent molecule to form a dimer anion radical. In the case of BSO, however, the electron adduct is not stable due to the presence of a $-\text{CH}_2-$ group which may hinder delocalisation, leading to C-S bond breakage and consequent formation of benzyl radicals.

4. Conclusions

Addition of e_{aq}^- to dibenzyl sulphoxide leads to the formation of benzyl radicals with a G -value of about 0.7 i.e. 25% of the e_{aq}^- yield at neutral pH. Similar reaction with diphenyl and di-4-chlorophenyl sulphoxides does not lead to the formation of aryl radicals; instead a dimer anion radical is formed with a G -value dependent on the concentration of the parent compound. The electron adduct in all the three compounds gets protonated at lower values of pH to give a transient spectrum which is similar to that obtained by H-atom reaction with aromatic sulphoxides.

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