On the Oxidation of Organic Sulphoxides by Potassium t-Butyl Peroxide

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The kinetics of the oxidation of some representative organic sulphoxides (to the corresponding sulphones) by potassium t-butyl peroxide in toluene have been studied in the presence of crown polyethers. A two-step reaction mechanism involving preliminary nucleophilic attack by the peroxide on the sulphoxide, followed by the breakdown of the reactive intermediate thus formed *via* heterolysis of the O–O bond is envisaged. Addition of the protic species Bu^tOH and Pr^iOH in large excess over the reactants depresses the rates. However, with initial concentrations of Ph_2SO and Bu^tOOK of *ca.* 5×10^{-2} and 0.5×10^{-2}M, respectively, addition of up to *ca.* 10^{-2}M-Bu^tOH is observed to enhance the rate. On changing the alcohol from Bu^tOH to Pr^iOH, and the substrate from Ph_2SO to $(p\text{-}MeOC_6H_4)_2SO$, to Me_2SO, the variation $k_{2,obs.}$ with alcohol concentration follows a trend which depends on the nature of the alcohol and on structure of the sulphoxide. This yields useful information on the reaction mechanism.

In the past 20 years much progress has been achieved in understanding the oxidation of organic substrates by peroxoanions ROO^- ($R = H$, alkyl, acyl, *etc.*).[1] Such species are known to be both effective oxidizing agents and powerful nucleophiles;[1-4] in reacting with organic substrates, the first step generally results in the displacement of an existing group or addition to a multiple bond with formation of a peroxide intermediate.[1] Due to the weakness of the O–O bond, such intermediates are often labile and, in a subsequent rapid step, they break down to yield the oxidized substrate and the oxyanion RO^-.[1]

In a series of papers,[5,6] we presented evidence that the oxidation of sulphoxides by peroxoacid anions in aqueous media also follows a mechanism of this general type (Scheme). At high pH nucleophilic oxidation of

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[1] R. Curci and J. O. Edwards, in ' Organic Peroxides,' ed. D. Swern, Wiley–Interscience, New York, 1970, vol. I, ch. 4 and references therein.

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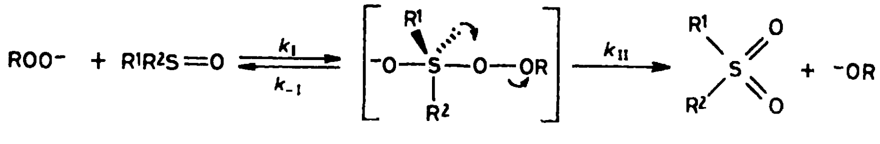
[5] R. Curci and G. Modena, *Tetrahedron Letters*, 1963, 1749; 1965, 863; *Gazzetta*, 1964, **94**, 1257; *Tetrahedron*, 1966, **22**, 1227.

[6] R. Curci, A. Giovine, and G. Modena, *Tetrahedron*, 1966, **22**, 1235.

sulphoxides to sulphones by peroxoacid anions occurs more readily than at low pH values, and it is much faster than peroxoacid decomposition.[5] On the other hand, we observed that sulphoxide oxidation by hydroperoxides in aqueous media, both at high and low pH, does not compete effectively with peroxide decomposition.[5,6]

Recently, Ogata *et al.* have also observed that hydroperoxides are unable to oxidize sulphoxides in aqueous media.[7a] By working with the sodium salt of 1-methyl-1-phenylethyl hydroperoxide in mixtures of benzene and alcohols, however, these authors found that oxidation of dialkyl sulphoxides to the parent sulphones could be carried out effectively.[7] Since increasing the amount of alcohol in benzene results in a decrease of the rate of oxidation, it was concluded that solvation by protic solvent molecules greatly reduces the reactivity of the peroxoanion ROO^- in the first (addition) step; Ogata *et al.* also suggested that step II (Scheme 1) is rate determining.[7b]



(1)

SCHEME

TABLE 1

Oxidation rates of diphenyl sulphoxide by potassium t-butyl peroxide in toluene[a]

$10^2[Ph_2SO]_0$/M	$10^2[Bu^tOOK]_0$/M	10^2[crown][b]/M	t/°C	10^4k_1/s^{-1}	10^3k_2[c]/l mol^{-1} s^{-1}	Other
5.08	0.59	None	25.0	<0.002[d]		
5.03	0.53	0.92[e]	25.0	0.98	1.95	
5.08	0.55	0.93	25.0	0.96	1.90	
3.80	2.50	None	40.0	<0.005[d]		
3.80	2.42	3.64	40.0		7.10[g]	
3.80	1.15	1.82	40.0		7.37[g]	
3.80	0.55	0.90	40.0	3.14	8.25[h]	
5.03	0.53	0.93	40.0	3.81	7.57	10^{-3}M-RT[i]
7.60	0.53	0.95	40.0	6.00	7.85	
5.00	0.55	1.3	40.0	3.80	7.60[l]	
5.00	0.62	1.5	40.0	10.85	2.71	0.65×10^{-2}M-Bu^tOK
4.00	0.58	1.2	40.0	1.6	4.00	0.65×10^{-2}M-TsOK[m]

[a] Reactions carried out under dry nitrogen. [b] 18-Crown-6, unless otherwise noted. [c] Estimated as $k_1/[Ph_2SO]_0$, unless otherwise noted. [d] No change in peroxide titre after 20 h. [e] Dicyclohexyl-18-crown-6. [f] Initial rate v_0, 0.53×10^{-6} mol l^{-1} s^{-1}, to be compared with peroxide decomposition, in the absence of sulphoxide, v_0 (decomp.) *ca.* 0.01×10^{-6} mol l^{-1} s^{-1}. [g] From integrated second-order kinetics law plots. [h] v_0 1.7×10^{-6}, v_0 (decomp.) 0.04×10^{-6} mol l^{-1} s^{-1} (*cf.* note *f*). [i] RT = radical trap, di-t-butyl nitroxide. [l] v_0 4.15×10^{-6}, v_0 (decomp.) *ca.* 0.3×10^{-6} mol l^{-1} s^{-1}. [m] Ts = tosyl.

In order to gain further insight into this two-step oxidation process, we undertook an investigation of the kinetics of the reaction of a number of sulphoxides with potassium t-butyl peroxide in toluene (an aprotic, low dielectric constant solvent) both in the absence and presence of protic species. In conjunction with the dry peroxosalt, we used the polyethers 18-crown-6 or dicyclohexyl-18-crown-6 (see Experimental section), as it is known that these macrocyclic complexes are able not only to solubilize potassium salts in organic solvents, but also to promote separation of tight ion-pairs, thus providing highly reactive, weakly solvated anions.[8-11]

RESULTS

Reactants and Stoicheiometry.—Stable, alcohol free peroxide solutions in toluene could be obtained by using dry potassium t-butyl peroxide.[9] This salt was synthesized by slow addition of 99% Bu^tOOH to a suspension of potassium hydride in dry ethyl ether at −30°; the peroxosalt can be stored dry at 0° for long periods without appreciable decomposition. Potassium t-butyl peroxide is poorly soluble in aprotic, low polarity solvents; however, solutions containing up to 0.04M-Bu^tOOK as the crown polyether complex were obtained by stirring equimolar amounts of the peroxosalt and polyether in dry toluene at 25°. As these solutions tend to absorb atmospheric CO_2, they were handled under dry nitrogen using degassed solvents.[9] Reaction of polyether-complexed Bu^tOOK with equimolar amounts of diphenyl sulphoxide gives Bu^tOH and the related sulphone; the 1 : 1 stoicheiometry is demonstrated by the nearly quantitative (yield >90%) production of diphenyl sulphone.

Kinetics.—The decay of peroxide concentration with time was followed employing a titrimetric technique (see Experimental section). A first crop of data, obtained in a variety of conditions, is collected in Table 1. In most cases kinetic runs were performed under pseudo-first-order conditions,

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[7] Y. Ogata and S. Suyama, (*a*) *Chem. and Ind.*, 1971, 707; (*b*) *J.C.S. Perkin II*, 1973, 755.

[8] C. J. Pedersen and H. K. Frendsdorff, *Angew. Chem. Internat. Edn.*, 1972, **11**, 16 and references therein.

[9] (*a*) R. Curci and F. Di Furia, *Int. J. Chem. Kinet.*, 1975, **7**, 341; (*b*) unpublished results.

[10] C. L. Liotta and H. P. Harris, *J. Amer. Chem. Soc.*, 1974, **96**, 2250.

[11] J. Smid, *Angew. Chem. Internat. Edn.*, 1972, **11**, 112.

with the sulphoxide being in large excess over $\mathrm{Bu^tOOK}$. In the absence of crown polyethers, both sulphoxide oxidation and peroxide decomposition are too slow to be conveniently measured. Addition of the crown polyethers greatly enhances the rates, but an increase of the crown polyether : $\mathrm{Bu^tOOK}$ ratio from 1.2 to *ca.* 5 produces practically no further enhancement.

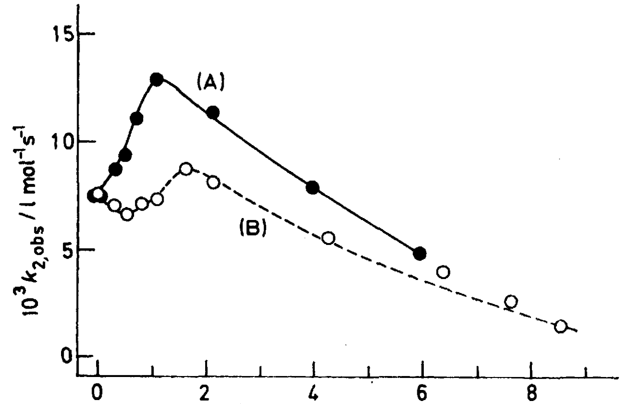


FIGURE 1 Dependence of second-order rate constant on alcohol concentration for the oxidation of diphenyl sulphoxide by polyether-complexed potassium t-butyl peroxide, at 40.0°, in toluene containing t-butyl alcohol (A) or propan-2-ol (B)

In $\log[a/(a - x)]$ *versus* time plots good linearity was observed over the first 30—40% reaction. Thereafter, a positive deviation of kinetic data points from linearity, which becomes more pronounced as the reaction progresses, is observed, signalling the onset of a reaction path seemingly similar to autocatalysis. This can probably be ascribed to $\mathrm{Bu^tO^-}$ ions produced during the reaction (see below). Therefore, rate constant values were estimated on the basis of data points yielding straight lines obeying the pseudo-first-order (or second-order) rate law for the first 30—40% reaction. Under these conditions, rate constants are reproducible and the presence of radical traps does not influence the rate.

Addition of crown-complexed $\mathrm{Bu^tOK}$ markedly increase the rate of sulphoxide oxidation (Table 1); initial rates indicate that, in the absence of sulphoxide, decomposition of the peroxosalt is also significantly enhanced by added $\mathrm{Bu^tOK}$. It is unlikely that this is due to simple ionic strength effects, as data in Table 1 show that addition of potassium tosylate actually depresses the rate. Furthermore, we find that addition of complexed potassium fluoride causes a remarkable depression of the oxidation rate.

The results in Table 1 suggest that, limited to the initial 30—40% reaction, the rate law (1) holds; $\mathrm{Bu^tOO^-,K^+}$ stands for loose ion pairs and/or crown-separated pairs.

$$v = k_{2,\mathrm{obs}}[\mathrm{R_2SO}][\mathrm{Bu^tOO^-,K^+}] \qquad (1)$$

Substituent Effects.—Inspection of the data in Table 2 reveals that electron-withdrawing substituents increase the rate; *e.g.* $\mathrm{Ph_2SO}$ is oxidized *ca.* 3.5 times faster than dimethyl sulphoxide. It is noteworthy that the presence of two effective electron-donating substituents such as *p*-methoxy, one for each phenyl group, brings about only a mild decrease in rate with respect to $\mathrm{Ph_2SO}$. By way of contrast, introducing two mild, overall electron-withdrawing *p*-chloro-substituents increases the oxidation rate by a factor >12. Finally, an effective electron-withdrawing group such as trifluoromethyl directly linked to sulphur renders the reaction too fast to follow by titrimetric techniques.

TABLE 2

Substituent effects on the oxidation of sulphoxides by polyether complexed potassium t-butyl peroxide in toluene [a]

Substrate	t/°C	10^3k_2 [b]/ l mol^{-1} s^{-1}
$(p\text{-}\mathrm{ClC_6H_4})_2\mathrm{SO}$	40.0	95.0
	25.0	23.4
$(\mathrm{C_6H_5})_2\mathrm{SO}$	40.0	7.6
	25.0	1.9
$(p\text{-}\mathrm{CH_3OC_6H_4})_2\mathrm{SO}$	40.0	4.02
	25.0	0.72
$(\mathrm{CH_3})_2\mathrm{SO}$	40.0	2.2
$\mathrm{C_6H_5SOCF_3}$	40.0	>1 000 [c]

[a] Reactions carried out under dry nitrogen. [b] Estimated as $k_1/[\text{sulphoxide}]_0$, with k_1 being obtained from runs performed under pseudo-first-order conditions. [c] Too fast to follow with the titrimetric technique chosen.

Effect of Adding Protic Species.—Starting with the dry, alcohol-free peroxosalt $\mathrm{Bu^tOOK}$ we were able to determine the effect of adding protic species $\mathrm{Bu^tOH}$ and $\mathrm{Pr^iOH}$ on the reaction rates, beginning with alcohol concentrations comparable with those of the reactants. For the oxidation of diphenyl sulphoxide, with $[\mathrm{Ph_2SO}]_0$ *ca.* 5×10^{-2} and $[\mathrm{Bu^tOOK}]_0$ *ca.* 0.5×10^{-2}M, a maximum is found at *ca.* 10^{-2}M-$\mathrm{Bu^tOH}$ in the $k_{2.\mathrm{obs}}$ *versus* protic species (ZOH) concentration plot; the same plot, when $\mathrm{Pr^iOH}$ is the protic species added, shows a more complex profile in the range 0—2.5×10^{-2}M-alcohol, presenting just a shallow maximum at *ca.* 1.8×10^{-2}M-$\mathrm{Pr^iOH}$ (see Figure 1). In Figure 2 it is shown how the $k_{2,\mathrm{obs}}$–$\mathrm{Bu^tOH}$ concentration plot varies on changing sulphoxide from $\mathrm{Ph_2SO}$ to $(p\text{-}\mathrm{MeOC_6H_4})_2\mathrm{SO}$ to $\mathrm{Me_2SO}$.

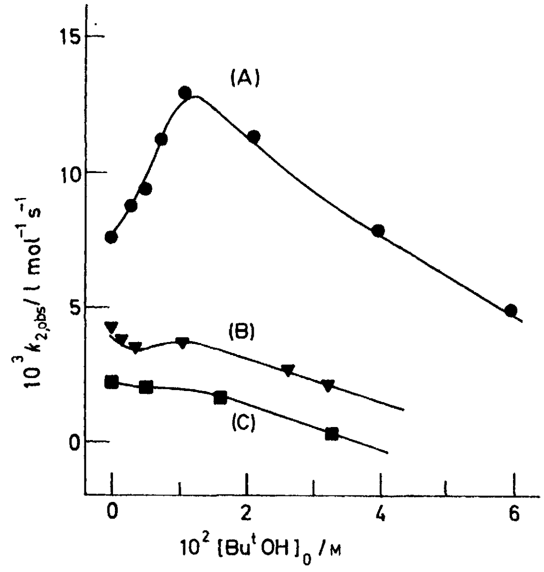


FIGURE 2 Dependence of second-order rate constants on t-butyl alcohol concentration for the oxidation of diphenyl sulphoxide (A), *p,p'*-dimethoxydiphenyl sulphoxide (B), and dimethyl sulphoxide (C) by polyether-complexed potassium t-butyl peroxide in toluene at 40 °C

DISCUSSION

The straightforward stoicheiometry, the reproducibility of kinetic data, and the failure of radical traps to influence the rate, suggest it is unlikely that the oxidation occurs by a radical pathway under the conditions adopted. Therefore, for reactions in toluene, the same general mechanism outlined in the Scheme is believed to hold.

As no build-up of reaction intermediate (1) is observed, the steady-state approximation shows the observed rate constant to be a composite [equation (2)]. The observed

$$k_{2,\mathrm{obs.}} = k_{\mathrm{I}}k_{\mathrm{II}}/(k_{-\mathrm{I}} + k_{\mathrm{II}}) \qquad (2)$$

substituent effect on rates does not contrast with the composite nature of $k_{2,\mathrm{obs}}$; by varying the substituents, in fact, major changes in k_{I}, and in k_{II} with respect to $k_{-\mathrm{I}}$ might occur on passing from electron-donating to electron-withdrawing substituents, leading to substituent effects of the kind observed.[12]

Turning to the effect of added alcohols on rates (Figures 1 and 2), there is the possibility that protic species can yield specific solvation of both reactants by hydrogen bonding [equations (3) and (4)], as there is ample evidence that nucleophilic anions,[13] and also sulphoxides[14,15] give this kind of interaction.

$$\mathrm{Bu^tOO^-} + x\,\mathrm{ZOH} \rightleftharpoons \mathrm{Bu^tOO^-(ZOH)}_x \quad , \quad K_{\mathrm{s}} \qquad (3)$$

$$\mathrm{R_2S{=}O} + y\,\mathrm{ZOH} \rightleftharpoons \mathrm{R_2S{=}O(ZOH)}_y \quad , \quad K'_{\mathrm{s}} \qquad (4)$$

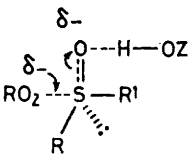
As for the rate of oxidation, the production of strongly solvated peroxoanion species is, of course, unfavourable, and we might assume that the rate of reaction between $\mathrm{Bu^tOO^-(ZOH)}_x$ and $\mathrm{R_2SO(ZOH)}_y$ is much smaller than the rate of reaction between ' naked ' reactants on the basis of existing evidence. We have seen, in fact, that t-butyl hydroperoxide anions are unable to oxidize sulphoxides in aqueous media.[5-7] At relatively high alcohol concentrations, provided both $K_{\mathrm{s}}[\mathrm{ZOH}]^x$ and $K_{\mathrm{s}}'[\mathrm{ZOH}]^y$ are $\gg 1$, the rate is given by equation (5) and $k_{2,\mathrm{cbs}}$ by equation (6). Indeed, for alcohol concentrations

$$v = k_{2,\mathrm{obs}}[\mathrm{sulphoxide}][\mathrm{peroxide}] \simeq k_2[\mathrm{R_2SO}][\mathrm{Bu^tOO^-}] \qquad (5)$$

$$k_{2,\mathrm{obs}} = (k/K_{\mathrm{s}}K'_{\mathrm{s}})[\mathrm{ZOH}]^{-(x+y)} \qquad (6)$$

higher than 0.02M, a negative order in protic species is observed (Figures 1 and 2). By plotting log $k_{2,\mathrm{obs.}}$ against log ZOH one might estimate the overall (negative) order in alcohol, but to relate this with alcohol acidity[7b] has no meaning, since kinetic order should not be confused with reactivity.

The fact that $k_{2,\mathrm{obs}}$ values for oxidation of $\mathrm{Ph_2SO}$ are found to increase in the range 0—*ca.* 0.01M-$\mathrm{Bu^tOH}$ (see Figures) indicates a *positive* order in the alcohol. This, in turn, points out that, at low alcohol concentration, the intervention of extra protic species molecules in the transition state(s) with respect to ground states lowers somewhat the energy barriers along the reaction co-ordinate of this two-step process, thus enhancing the rate. Such an effect can indeed be conceived for the transition state of both steps, as in (2) and (3). In drawing (2) and (3) the intervention of just one molecule of protic species is envisaged for the sake of clarity.



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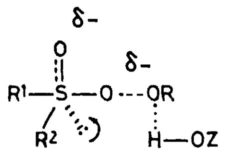

(3)

In (2), hydrogen bonding to the sulphinyl oxygen would augment polarization of the S=O group, thus assisting nucleophilic attack; in (3), solvation of the incipient anion $\mathrm{RO^-}$ (a poor leaving group) should effectively accelerate the stage leading from the intermediate to products. It is likely the latter phenomenon brings a greater contribution to the overall rate enhancement; in fact $\mathrm{ROO^-}$ species are powerful nucleophiles and, similarly to $\mathrm{Ad_N}$ type reactions on carbonyl substrates, addition of strong nucleophiles to the S=O centre (as in step I) should not be subject to marked general acid catalysis. Of course, unfavourable specific solvation of ground state peroxoanion and sulphoxide reactants by the alcohol may well submerge the catalytic effect determined by the intervention of protic species in the transition states. These two phenomena work in opposition and it is likely their overlapping determines the trend of $k_{2,\mathrm{obs}}$–[ZOH] plots. Given the composite nature of the measured rate constant [equation (2)], it is hardly surprising that the $k_{2,\mathrm{obs}}$–[ZOH] profile depends not only upon the nature of the alcohol (Figure 1), but also upon sulphoxide structure (Figure 2).

These findings underline the subtleties of the two-step mechanism advanced; in fact, varying protic species or substituents may result in significant changes in the relative values of k_{I}, $k_{-\mathrm{I}}$, and k_{II}, which yields different trends in the variation of $k_{2,\mathrm{obs}}$ with alcohol concentration. Therefore, generalizations should be avoided in defining the rate-determining step in these processes;[7b] as a matter of fact, this is implicit whenever the steady-state approximation is made for any reactive intermediate.

A few words are in order concerning the relative efficiency of the various systems employed to carry out ' alkaline ' oxidation of sulphoxides. Sodium cumyl peroxide in benzene–alcohol mixtures[7] seem more efficient than polyether complexed potassium t-butyl peroxide in toluene, used in this study. This can hardly be ascribed to a higher reactivity of $\mathrm{Ph(CH_3)_2COO^-}$ with respect to $\mathrm{Bu^tOO^-}$ in the first (addition) step, as the two peroxoanions should have fairly similar nucleophilic reactivity; instead, a better rationale is found considering the greater leaving group ability of solvated $\mathrm{Ph(CH_3)_2CO^-}$ with respect to $\mathrm{Bu^tO^-}$ in the second (elimination) step. An alternative explanation relies on the possibility that Ogata's system actually contains

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[13] A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

[14] R. Biscarini and S. Ghersetti, *Gazzetta*, 1962, **92**, 61.

[15] H. H. Szmant, in ' Sulfur in Organic and Inorganic Chemistry,' ed. A. Senning, Dekker, New York, 1971, vol. 1, ch. 5, see also references therein.

significant amounts of alkoxide ions, *e.g.* $Ph(CH_3)_2CO^-$, Bu^tO^-, *etc.*, which, as we have seen, markedly enhance the rates.

EXPERIMENTAL

Materials.—Potassium t-butyl peroxide was prepared on treating 99% t-butyl hydroperoxide (obtained by careful vacuum distillation of the commercial sample, b.p. 40° at 21 mmHg) with potassium hydride (50% suspension in oil; Ventron) in dry ether at $-20°$; the procedure and the product (98% pure, iodometric analysis) have already been described.[9] Diphenyl sulphoxide, m.p. 70—71° and 4,4′-dimethoxydiphenyl sulphoxide, m.p. 92—93° (lit.,[16] 93—94°) were prepared by oxidation of the corresponding sulphides [17] with H_2O_2 in methanol, using catalytic amounts of $HClO_4$,[18] and purified by column chromatography [silica gel; Et_2O–light petroleum (20 : 80)]. 4,4′-Dichlorodiphenyl sulphoxide, m.p. 142—143°,[17] was obtained by reaction of chlorobenzene with $SOCl_2$–$AlCl_3$ as described.[16] Phenyl trifluoromethyl sulphoxide was prepared upon oxidation of phenyl trifluoromethyl sulphide (P.C.R. Inc.) with *m*-chloroperbenzoic acid (Aldrich) in methylene chloride, b.p. 95° at 17 mmHg; $\nu_{max.}$ (CCl_4) 1 195 cm^{-1} (S=O), ^{19}F n.m.r. δ 40.56 p.p.m., Φ^* 122.3. Commercial dimethyl sulphoxide was purified by distillation, b.p. 72—73° at 11 mmHg, over calcium hydride. 1,4,7,10,13,16-Hexaoxacyclo-octadecane (18-crown-6) was prepared and purified as described;[19] commercial (Aldrich) 2,5,8,15,18,-21-hexaoxatricyclo[20,4,0,$0^{9,14}$]hexacosane (dicyclohexyl-18-crown-6) was purified by crystallization from n-pentane, m.p. 50—51°. The radical trap di-t-butyl nitroxide was prepared following a given procedure.[20] Toluene, t-butyl alcohol, and propan-2-ol were purified and dried by using standard methods.

Stoicheiometry.—The following procedure is representative. Potassium t-butyl peroxide (1.45 mmol) was dissolved, with prolonged stirring, in toluene (150 ml) containing 18-crown-6 (1.50 mmol) and diphenyl sulphoxide (1.31 mmol) was then added to this solution. When reaction was near completion (iodometric titre), the reaction mixture was washed with several portions of water in a separatory funnel. The combined aqueous layers were extracted with methylene chloride. The combined toluene and methylene chloride extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification of the solid residue by column chromatography [silica gel; Et_2O–light petroleum (50 : 50)] gave diphenyl sulphone (1.18 mmol, 90%), m.p. 127—128°, i.r. spectrum (CCl_4) identical with an authentic sample. For smaller scale experiments the stoicheiometry can be determined by g.l.c. (2.5 m column of 5% FFPA on 80—100 Chromosorb G AW–DMCS; He carrier gas, T_c 210°) using tetracosane as an internal standard.

Kinetics.—Runs were performed under dry nitrogen; standard solutions of sulphoxide and potassium t-butyl peroxide in toluene (or toluene–alcohol) containing the crown ether were mixed at zero time in an apparatus (designed as to allow the withdrawal of portions of the reaction solution under nitrogen) immersed in a thermostatted bath. The disappearance of the peroxide with time was monitored using a iodometric titration technique.[9]

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