# KINETICS AND MECHANISM OF SULPHOXIDE OXIDATIONS

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Oxidation of diphenyl sulphoxide, $p,p'$-dimethyl-, $p,p'$-dimethoxy-, $p,p'$-dichloro-, and $p,p'$-dintro-diphenyl sulphoxides with peroxybenzoic acid in toluene, acetone and methanol at 25°, 35° and 45°C ($\pm 0.5°$) has been studied. Activation energies, frequency factors and entropies of activation for these oxidations were calculated. The differences in rate constants have been found to be approximately 55% dependent on differences in energy of activation and 45% on differences in entropy of activation. The rate constants have been observed to be inversely proportional to the dielectric constants of the solvents employed.

In an earlier study it was shown that the oxidation of sulphoxides to their corresponding sulphones follow second order kinetics. It was further pointed out there that electron donating groups in the $p$-position of the peroxybenzoic acid decreased the rate of oxidation while electron withdrawing groups increased it; reverse effects were shown to be exerted by these groups when present in the $p$-positions of the $p,p'$-disubstituted diphenyl sulphoxides.[1] It was, therefore, concluded that in these oxidations there is a nucleophilic attack by the sulphur atom of the sulphoxide on the oxygen of the peroxy acid. This conclusion was contrary to the observation by Szmant, Harnsberger and Krahe[2] who reported that the oxidation of diphenyl sulphoxide by peroxybenzoic acid involved a nucleophilic attack of the latter on the sulphur atom of the former, athough there was no evidence on this point.

In continuation of our previous work,[1] therefore, the kinetics of the oxidation of diphenyl sulphoxide, $p,p'$-dichloro-, $p,p'$-dinitro-, $p,p'$-dimethyl-, and $p,p'$-dimethoxy-diphenyl sulphoxides by peroxybenzoic acid have now been studied in various solvents and at different temperatures. These studies have been carried out with a view to obtaining a clearer insight into the mechanism of sulphoxide oxidations.

## Experimental

Absolute methanol, toluene and acetone used as solvents in these oxidations were purified according to the standard procedures.

Peroxybenzoic acid, diphenyl sulphoxide and $p,p'$-disubstituted diphenyl sulphoxides were prepared as described previously.[1] The peroxybenzoic acid was prepared just before use in the kinetic runs, dissolved in the desired solvent and stored in a refrigerator (0°). The acid was iodometrically standardised and the solutions of different concentrations were then prepared by dilution. All the five sulphoxides were purified by crystallisation to constant melting points.

Kinetic measurements were carried out with solutions (50 ml) of each sulphoxide and peroxybenzoic acid in the desired solvent at 25°, 35° and 45°C ($\pm 0.5°$). The temperature was thermostatically controlled and for each run a blank (containing only peroxybenzoic acid solution and no sulphoxide) experiment was also carried out to account for the loss of peroxybenzoic acid. The progress of oxidation was followed iodometrically at regular time intervals as described before.[1]

## Discussion

The rate data for the oxidation of diphenyl sulphoxide, $p,p'$-dimethyl-, $p,p'$-dimethoxy-, $p,p'$-dichloro-, and $p,p'$-dinitrodiphenyl sulphoxides with peroxybenzoic acid in toluene, acetone and methanol were obtained at three temperatures i.e., 25°, 35°, and 45°C ($\pm 0.5°$). In all the cases, second order law was observed to be obeyed accurately. The activation energies and frequency factors were calculated from the variations of $\log k$ with $1/T$. The entropy of activation, $\Delta S^{\neq}$, was calculated from the frequency factor A by means of the equation:[3]

$$A = e\,(k'T/h)\,(\exp \Delta S^{\neq} R)$$

The rate constant data alongwith $E$, $\ln A$ and $\Delta S^{\neq}$ as obtained in these studies are given in Table 1. The experimental data employed in the determination of the order of these oxidations are recorded in Table 2. This data relate to all the five sulphoxides that have been studied in the three solvents at the three temperatures. Second order rate plots were excellent straight lines and some typical representatives are shown in Fig. 1; several representative Arrhenius plots are shown in Fig. 2. A plot of $E$ versus $T\Delta S^{\neq}$ for these oxidations in toluene, acetone and methanol at 25°

TABLE 1.—SPECIFIC RATE CONSTANTS, ACTIVATION ENERGIES, FREQUENCY FACTORS, AND ACTIVATION ENTROPIES FOR THE OXIDATION OF DIPHYENYL SULPHOXIDE AND $p,p'$-DISUBSTITUTED DIPHENYL SULPHOXIDES IN TOLUENE, METHANOL AND ACETONE BY PEROXYBENZOIC ACID.

| Sulphoxides | Temp. °C | $k$, l mole$^{-1}$ sec$^{-1}$ | $E$, kcal mole$^{-1}$ | lnA | $\Delta S^{\ddagger}$ cal mole$^{-1}$ deg$^{-1}$ |
|---|---|---|---|---|---|
| | | Toluene | | | |
| Di-($p$-methoxyphenyl) sulphoxide .. | 25° | 0.66 ±0.04 | | | |
| | 35° | 1.58 ±0.3 | | | |
| | 45° | 3.00 ±0.3 | 15.1 | 24.7 | −9.5 |
| Di-($p$-methylphenyl) sulphoxide .. | 25° | 0.29 ±0.03 | | | |
| | 35° | 0.44 ±0.08 | | | |
| | 45° | 0.90 ±0.1 | 15.02 | 23.90 | −11.2 |
| Diphenyl sulphoxide .. | 25° | 0.28 ±0.06 | | | |
| | 35° | 0.42 ±0.04 | | | |
| | 45° | 0.84 ±0.1 | 10.9 | 16.7 | −25.6 |
| Di-($p$-chlorophenyl) sulphoxide .. | 25° | 0.14 ±0.01 | | | |
| | 35° | 0.22 ±0.03 | | | |
| | 45° | 0.34 ±0.01 | 8.8 | 12.9 | −32.9 |
| Di-($p$-nitrophenyl) sulphoxide .. | 25° | 0.012 ±0.001 | | | |
| | 35° | 0.033 ±0.004 | | | |
| | 45° | 0.071 ±0.02 | 17.7 | 25.4 | −8.9 |
| | | Acetone | | | |
| Di-($p$-methoxyphenyl) sulphoxide .. | 25° | 0.31 ±0.02 | | | |
| | 35° | 0.46 ±0.03 | | | |
| | 45° | 0.63 ±0.03 | 6.9 | 10.3 | −38.1 |
| Di-($p$-methylphenyl) sulphoxide .. | 25° | 0.13 ±0.01 | | | |
| | 35° | 0.23 ±0.04 | | | |
| | 45° | 0.45 ±0.04 | 14.2 | 21.9 | −15.0 |
| Diphenyl sulphoxide .. | 25° | 0.11 ±0.01 | | | |
| | 35° | 0.15 ±0.06 | | | |
| | 45° | 0.21 ±0.06 | 6.5 | 8.7 | −41.3 |
| Di-($p$-chlorophenyl) sulphoxide .. | 25° | 0.02 ±0.01 | | | |
| | 35° | 0.038 ±0.01 | | | |
| | 45° | 0.08 ±0.03 | 13.8 | 19.5 | −19.8 |
| Di-($p$-Nitrophenyl) sulphoxide .. | 25° | 0.02 ±0.002 | | | |
| | 35° | 0.036 ±0.002 | | | |
| | 45° | 0.063 ±0.007 | 11.0 | 14.7 | −29.4 |
| | | Methanol | | | |
| Di-($p$-methoxyphenyl) sulphoxide .. | 25° | 0.052 ±0.004 | | | |
| | 35° | 0.116 ±0.003 | | | |
| | 45° | 0.23 ±0.05 | 14.8 | 22.0 | −14.9 |
| Di-($p$-methylphenyl) sulphoxide .. | 25° | 0.045 ±0.02 | | | |
| | 35° | 0.089 ±0.003 | | | |
| | 45° | 0.158 ±0.02 | 12.6 | 18.1 | −22.6 |
| Diphenyl sulphoxide .. | 25° | 0.037 ±0.003 | | | |
| | 35° | 0.051 ±0.004 | | | |
| | 45° | 0.103 ±0.003 | 10.1 | 13.7 | −31.4 |
| Di-($p$-chlorophenyl) sulphoxide .. | 25° | 0.027 ±0.003 | | | |
| | 35° | 0.047 ±0.004 | | | |
| | 45° | 0.073 ±0.005 | 9.5 | 12.3 | −34.1 |
| Di-($p$-nitrophenyl) sulphoxide .. | 25° | 0.012 ±0.001 | | | |
| | 35° | 0.026 ±0.003 | | | |
| | 45° | 0.043 ±0.003 | 12.7 | 17.00 | −24.7 |

Notes.—(a) Mean values of all the constants are reported.   (b) Temperature variation ±0.5°

TABLE 2.–DETERMINATION OF THE OVER-ALL ORDER OF THE OXIDATION OF DI-(p-NITROPHENYL)SULPHOXIDE (at 25°) AND DI-(p-CHLOROPHENYL) SULPHOXIDE (at 45°) BY PEROXYBENZOIC ACID IN TOLUENE BY THE INTEGRATION METHOD.

| Time sec | $(a-x)$ | $(b-x)$ | $\log (a-x)$ | $\log (b-x)$ | $10^2 \times \log \frac{(a-x)}{(b-x)}$ |
|---|---|---|---|---|---|
| | | Di-(p-nitrophenyl) sulphoxide | | | |
| 0 | 0.00602 | 0.0024 | −2.2204 | −2.6198 | 39.94 |
| 1200 | 0.005815 | 0.002195 | −2.2354 | −2.6586 | 42.32 |
| 1800 | 0.00575 | 0.00215 | −2.2403 | −2.6676 | 42.73 |
| 2400 | 0.005645 | 0.002025 | −2.2483 | −2.6935 | 44.52 |
| 3000 | 0.00553 | 0.00189 | −2.2573 | −2.7273 | 46.62 |
| | | Di-(p-chlorophenyl) sulphoxide | | | |
| 0 | 0.00622 | 0.0024 | −2.2062 | −2.6198 | 41.36 |
| 600 | 0.00467 | 0.00085 | −2.3307 | −3.0706 | 73.99 |
| 1200 | 0.00417 | 0.00032 | −2.3799 | −3.4949 | 111.50 |
| 1800 | 0.00399 | 0.00015 | −2.399 | −3.8239 | 142.49 |
| | | Di-(p-nitrophenyl) sulphoxide (at 45°) in acetone | | | |
| 0 | 0.0064 | 0.0024 | −2.1938 | −2.6198 | 42.6 |
| 1200 | 0.00546 | 0.00156 | −2.2628 | −2.8069 | 54.41 |
| 2700 | 0.00485 | 0.00099 | −2.3143 | −3.0044 | 68.01 |
| 3300 | 0.00472 | 0.00084 | −2.3261 | −3.0757 | 74.96 |
| 3900 | 0.00462 | 0.0008 | −2.3354 | −3.0969 | 76.15 |
| | | Di-(p-methoxyphenyl)-sulphoxide (at 35°) in methanol | | | |
| 0 | 0.00641 | 0.0024 | −2.1931 | −2.6198 | 42.67 |
| 1200 | 0.00561 | 0.0016 | −2.2510 | −2.7959 | 54.49 |
| 1800 | 0.00473 | 0.00083 | −2.3251 | −3.0909 | 76.58 |
| 2400 | 0.0044 | 0.00058 | −2.3565 | −3.2366 | 88.01 |
| 3000 | 0.0042 | 0.00041 | −2.3768 | −3.3872 | 101.04 |
| | | Di-(p-methylphenyl) sulphoxide (at 35°) in methanol | | | |
| 0 | 0.00651 | 0.0024 | −2.1864 | −2.6198 | 43.34 |
| 1200 | 0.00529 | 0.00129 | −2.2765 | −2.8894 | 61.29 |
| 1800 | 0.00498 | 0.001 | −2.3028 | −3.0 | 69.74 |
| 2400 | 0.0048 | 0.00082 | −2.3188 | −3.0862 | 76.74 |
| 3000 | 0.00452 | 0.00054 | −2.3449 | −3.2676 | 92.27 |
| | | Diphenyl sulphoxide (at 35°) in methanol | | | |
| 0 | 0.005745 | 0.0024 | −2.2407 | −2.6198 | 37.91 |
| 1200 | 0.0054 | 0.00177 | −2.2676 | −2.752 | 48.44 |
| 1800 | 0.00484 | 0.00143 | −2.3152 | −2.8447 | 52.95 |
| 3000 | 0.00445 | 0.00119 | −2.3516 | −2.9245 | 57.29 |
| 3600 | 0.00423 | 0.000965 | −2.3737 | −3.0155 | 64.18 |
| 4200 | 0.004015 | 0.000805 | −2.0942 | −3.3964 | 69.79 |



Fig. 1.—Second-order rate plots for peroxybenzoic acid oxidations of diphenyl sulphoxide and p, p′-disubstituted diphenyl sulphoxides. (O, points obtained in methanol; ●, points obtained in acetone; ×, points obtained in toluene in the peroxybenzoic acid oxidation of: 1, di-(p-methoxyphenyl) sulphoxide in methanol at 35°′. 2, di-(p-methylphenyl) sulphoxide in methanol at 35°, 3, diphenyl sulphoxide in methanol at 35°. 4, di-(p-nitrophenyl) sulphoxide in acetone at 45°. 5, di-(p-nitrophenyl) sulphoxide in toluene at 25°. 6, di-(p-chlorophenyl) sulphoxide in toluene at 45°. (Temperature variation ±0.5°).

is given in Fig. 3. This plot shows that there is approximately linear increase of $\Delta S^{\ddagger}$ with the increasing activation energy. The oxidation of sulphide with peroxy acids[4] hydrolysis of esters, amides and many other reactions show a similar behaviour.[5]

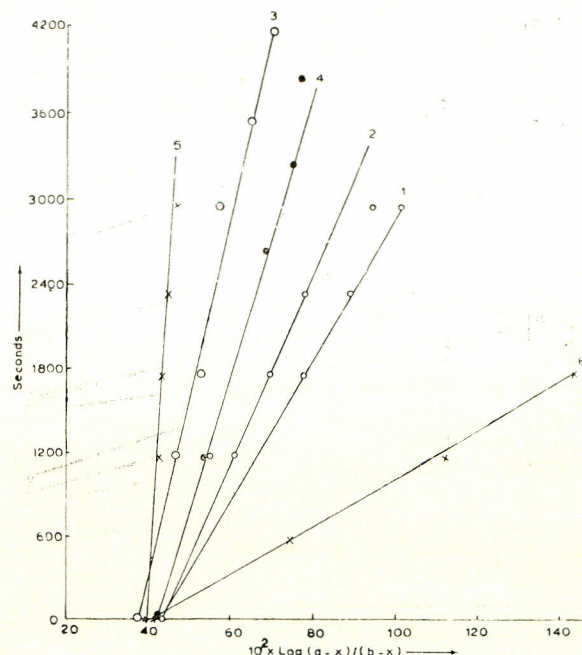The rates of the reactions are usually affected by the nature of the solvents in which the reactions are carried out. In order, therefore, to study such solvent effects, it was considered appropriate to carry out these oxidations in different solvents. The choice of these solvents was based on a large difference in their dielectric constants and polarity. It is seen from Table 1 that the oxidation rates are considerably affected when the solvent is changed from toluene to acetone and then to methanol. The dielectric constants of toluene[6] (2.379), acetone[6] (20.7), and methanol[6] (32.63) are in ascending order whereas the rate constants are larger in toluene than either in acetone or methanol respectively. It can, therefore, be observed that in these oxidations the rate constants are inversely proportional to the dielectric constants of the solvents employed. However, to confirm this generalization, more work needs to be done and in fact is under study at the moment.

A comparison of energies and entropies of activation for these oxidations in toluene, acetone and methanol reveals some differences. It is evident that the energies and entropies of activation are comparatively higher in toluene than in either acetone or methanol. This may be attributed
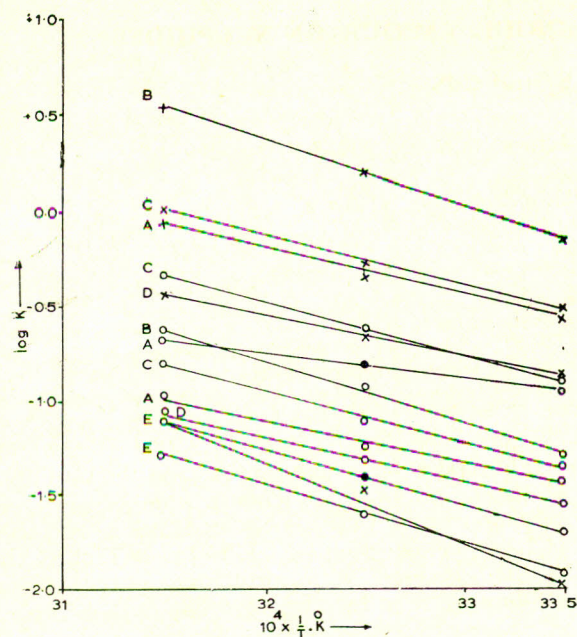
Fig. 2.—Arrhenius plots for peroxybenzoic acid oxidations of diphenyl sulphoxide and $p, p'$-disubstituted diphenyl sulphoxides in methanol, acetone and toluene, (O, points obtained in methanol; ●, points obtained in acetone; ×, points obtained in toluene in the peroxybenzoic acid oxidations of: A, diphenyl sulphoxide. B, di-($p$-methodyphenyl sulphoxide. C, di-($p$-methylphenyl) sulphoxide. D, di-($p$-chlorophenyl) sulphoxide. E, di-($p$-nitrophenyl) sulphoxides.
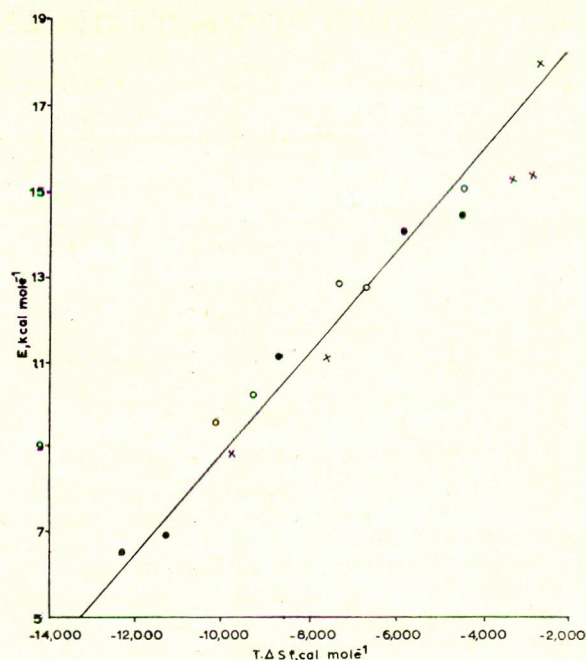


Fig. 3.—Plot of E vs, T $\triangle$S $^{\neq}$ for peroxybenzoic acid oxidations of diphenyl sulphoxide and $p.p'$-disubstituted diphenyl sulphoxides in toluene. acetone and methanol at $25° \pm 0.5°$ (×, points obtained in toluene; ●, points obtained in acetone. O, points obtained in methanol.)

to less solvation of peroxybenzoic acid in toluene. The differences in specific rate constants were estimated[7] to be about 55% dependent on differences in energies of activation and 45% on differences in entropies of activation. The corresponding dependency in the oxidations of sulphides to sulphoxides have been shown to be 60% and 40% respectively.[4]

The present studies, therefore, suggest that a similar mechanism is operative in the oxidation of sulphoxides to sulphones with peroxybenzoic acid as in the oxidation of sulphides to sulphoxides and this is in line with the previous mechanism proposed by us for these oxidations.[1]

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