An investigation by means of correlation analysis into the mechanisms of oxidation of aryl methyl sulfides and sulfoxides by dimethyldioxirane in various solvents†

Peter Hanson,* Ramon A. A. J. Hendrickx‡ and John R. Lindsay Smith*

Relative rate constants have been measured for the oxidation of aryl methyl sulfides and sulfoxides by dimethyldioxirane in acetone, in mixtures of acetone with aprotic co-solvents of both higher and lower relative permittivity, and in aqueous acetone mixtures. Correlation analyses of the effects of substituents in the different solvents show that, with one exception, reactions take place *via* a single step mechanism in which the formation of the new SO bond and the elimination of acetone occur concertedly. The exception was oxidation of the sulfides in aqueous acetone containing the highest proportion of water of those studied (20% v/v). Here, the behaviour of the reaction is consistent with a two-step mechanism in which the oxidant reversibly attacks the sulfide to form an open-chain sulfonium betaine that subsequently fragments to sulfoxide and acetone. There is no evidence for the participation of an intermediate dioxathietane as has been found in the case of sulfide oxidations by (trifluoromethyl)methyldioxirane in CH₂Cl₂ and similar aprotic solvents. It is not justified to generalise a mechanism involving a betaine, with or without a derived dioxathietane, to the reactions of dimethyldioxirane in acetone.

Introduction

Numerous oxidations of organosulfur compounds by hydroperoxidic reagents have been studied over the past five decades.[1–13] The early expectation was that the oxidation of sulfides would involve the formation of a sulfonium intermediate by S_N2 displacement of nucleophilic S upon the peroxo bond (Scheme 1a);[1] however, inconsistencies with this assumption became apparent. For example, reaction rates are strongly dependent neither on the relative permittivity of the solvent[2] nor on the ionic strength[3] as would be expected for a reaction involving a large separation of charge; on the other hand, reaction rates are strongly dependent on the protic nature of the solvent[4] and, if an aprotic solvent is used, the order of reaction in the hydroperoxide may increase

from one to two.[5] These observations were explained in terms of a cyclic transition state with the participation of a protic solvent molecule allowing proton transfer without the separation of full ionic charges (Scheme 1b); in the absence of a protic solvent, a second molecule of the hydroperoxide may fulfil this role.[3] Entries 1–8 of Table 1 illustrate typical activation parameters for oxidation of sulfides to sulfoxides, *i.e.* low $\Delta H^{\ddagger}$ and relatively large negative $\Delta S^{\ddagger}$ values. The oxidation of sulfoxides to sulfones is generally more difficult, and entries 9–11 of Table 1 indicate that changes in both activation parameters contribute to a higher free energy of activation for these substrates.

Table 2 gives Hammett reaction constants, ρ, for a selection of oxidations of sulfides and sulfoxides by hydroperoxidic oxidants. The small negative ρ values found for both types of substrate are consistent with a modest demand for electron density from sulfur in the rate-determining transition states. In general, the ρ values found for sulfoxides are smaller than those found for sulfides (note especially entries 5 and 6 where the oxidant and reaction medium are the same), which indicates that these oxidations fail to follow the reactivity–selectivity principle: oxidations of the more reactive sulfides are more selective than those of the less reactive sulfoxides. Thus although both oxidations result in the formation of a new S–O bond and their general mechanisms are believed to be comparable, there must be subtler differences between the two types of transition state than a simple application of the Hammond postulate would suggest.

Dimethyldioxirane, **1**, is a three-membered cyclic peroxide which has been used for the oxidation of various substrates including sulfides and sulfoxides.[14,15] The mechanistic evidence indicates that, in general, the oxidant is electrophilic. For example, in the epoxidation of alkenes, 1-(phenyl)propene[16] is 10³ times more reactive than ethyl *trans*-3-(phenyl)propenoate[17] and, for the

Scheme 1
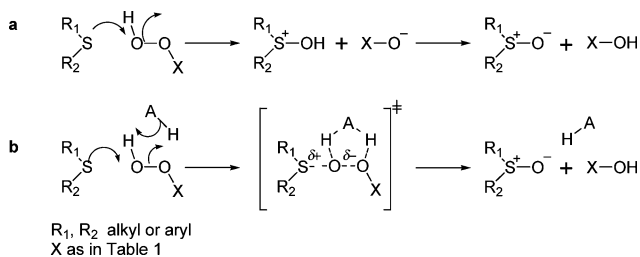
R₁, R₂ alkyl or aryl
X as in Table 1

Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK. E-mail: ph8@york.ac.uk, jrls1@york.ac.uk

Table 1 Activation parameters for the oxidation of selected sulfides, R_1SR_2, and sulfoxides, $R_1S(O)R_2$, by hydroperoxidic reagents, XOOH

Entry	R_1	R_2	X	Solvent	$\Delta H^{\ddagger}/kJ\ mol^{-1}$	$\Delta S^{\ddagger}/J\ mol^{-1}\ K^{-1}$	Ref.
Sulfides							
1	$(CH_2)_2-O-(CH_2)_2$		H	H_2O	54.6	−113.4	3
2	$(CH_2)_2-O-(CH_2)_2$		H	MeOH	60.9	−121.8	3
3	$(CH_2)_2-O-(CH_2)_2$		t-Bu	H_2O	56.7	−113.4	3
4	$(CH_2)_2-O-(CH_2)_2$		t-Bu	MeOH	57.5	−142.8	3
5	$4-O_2N-Ph$	$4-O_2N-Ph$	PhC(O)	$CHCl_3$	35.7	−121.8	2
6	Ph	HO_2CCH_2	MeC(O)	$MeCO_2H$	43.5	−96.2	6
7	Ph	Me	$P(O)(OH)_2$	MeCN, 40% v/v H_2O	47.3	−123.0	7
8	Ph	Me	$S(O)_2OH$	H_2O, 0.5% v/v MeCN	17.4	−124.0	8
Sulfoxides							
9	Ph	Me	PhC(O)	H_2O	58.2	−78.7	9
10	Ph	HO_2CCH_2	MeC(O)	$MeCO_2H$	59.0	−105.0	6
11	Ph	Me	$P(O)(OH)_2$	$MeCO_2H$, 50% v/v H_2O	56.3	−89.3	10

Table 2 Hammett reaction constants, ρ, for reactions of organosulfur compounds with hydroperoxidic oxidants

Entry	Substrate	Oxidant	Solvent	ρ	Ref.
1	ArSMe	$H_2O_2/HClO_4$	EtOH (6% v/v H_2O)	−1.13	11
2	ArSPh	$H_2O_2/HClO_4$	EtOH (6% v/v H_2O)	−0.98	11
3	ArSMe	$3\text{-Cl-}PhCO_3H$	MeOH	−0.90	12
4	ArSMe	H_3PO_5	MeCN (40% v/v H_2O)	−1.09	7
5	$ArSCH_2CO_2H$	$MeCO_3H$	$MeCO_2H$	−1.07	6
6	$ArS(O)CH_2CO_2H$	$MeCO_3H$	$MeCO_2H$	−0.49	6
7	ArS(O)Me	$PhCO_3H$	Dioxan (50% v/v H_2O)	−0.64	13
8	ArS(O)Ph	$PhCO_3H$	Dioxan (50% v/v H_2O)	−0.54	13

substituted series $ArCH=CH_2$[16] and *trans*-$ArCH=CHCO_2Et$[17] reacting in Me_2CO, negative reaction constants, ρ, of −0.90 and −1.53, respectively, were obtained. Although sulfides have been reported by Ballistreri and co-workers[18] to be *ca.* 30 times more reactive than sulfoxides, similar ρ values were reported for the oxidation of ArSMe and ArS(O)Me by Murray and co-workers[19] (−0.77 and −0.76, respectively, in Me_2CO); thus, unlike the alkenes and, as was the case with the hydroperoxidic oxidants, the organosulfur compounds do not follow the reactivity–selectivity principle on reaction with **1**. The relative reactivity of sulfides and sulfoxides in reaction with **1**, the size and sign of their reaction constants and the similarity of these with those of hydroperoxidic oxidants (Table 2) imply the oxidative sequence sulfide → sulfoxide → sulfone has mechanisms in which O-transfer is concerted with elimination of Me_2CO in *both* steps (Scheme 2a).

Recently, Asensio and co-workers[20] found that (trifluoromethyl)methyldioxirane, **2**, a more electrophilic oxidant than **1** on account of the fluorination, oxidises a range of sulfides directly to sulfones even in the presence of an excess of sulfide. A mechanism was proposed (Scheme 2b) in which the sulfide reacts with **2** to form a sulfonium betaine, **3**, that rapidly cyclises to a dioxathietane (cyclic sulfurane) **4**, faster than it eliminates MeCOCF$_3$ (*i.e.* $k_2 > k_3$); **4** then reacts with **2** faster than does the initial sulfide (*i.e.* $k_4 > k_1$) to produce sulfone plus two molecules of $MeCOCF_3$. The conclusions regarding the nature and behaviour of **4** were based on an investigation of the effects of variation in substitution, solvent composition and temperature on the sulfone/sulfoxide ratio, supported by convincing isotopic (^2H and ^{18}O) tracer studies. It was concluded that, although sulfoxide-to-sulfone oxidation is a known reaction of **2** (reaction 5, k_5 in Scheme 2b), for which Ballistreri *et al.*[18] had obtained $\rho = -0.34$
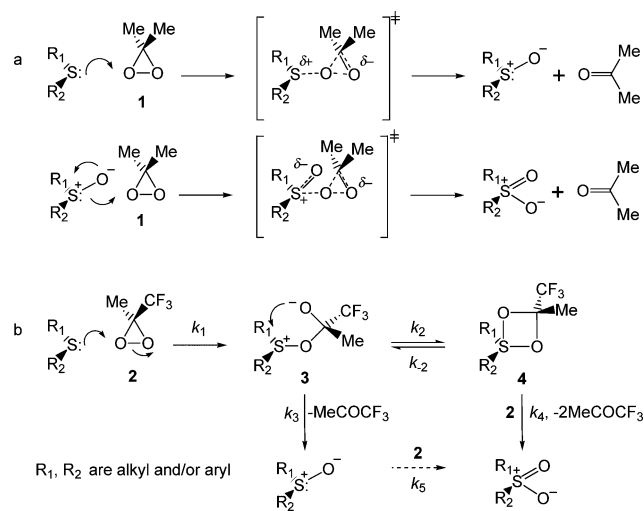
Scheme 2

in $CHCl_3$, it is unimportant in comparison to the oxidation of **4** in the conversion of sulfides into sulfones, though no detail of the latter was given.

It was further suggested that oxidation of sulfides by **1** also follows a path analogous to Scheme 2b but with reactions 3 and 5 now superseding reactions 2 and 4. This suggestion implies a change in the nature of the rate-determining step (reaction 1, k_1 in Scheme 2b) from that illustrated in Scheme 2a: it implies that the oxidation of sulfides by **1** involves the formation of an entity with a full sulfonium charge (the betaine) despite the low reaction constant found by Murray[19] and the similarity with oxidation by

hydroperoxides where low ρ values are taken to indicate transition states in which only partial charge separation occurs.

The purpose of this paper is to report a fuller investigation than hitherto into the effects of substituents on the oxidation of aryl methyl sulfides and sulfoxides by **1**, and into the dependence of such effects on the nature of the reaction medium, with a view to clarifying the reaction mechanism and to understanding the differences between the behaviour of sulfides and sulfoxides.

Results and discussion

(i) Oxidations in acetone solution

The previous investigation by Murray and co-workers,[19] into the effects of ring-substituents on the oxidations of aryl methyl sulfides and sulfoxides by **1** in acetone, had involved only a few 4-substituted substrates. We therefore decided first to extend these series and to include 3-substituted members. Oxidations were carried out at 293 K in which (with two exceptions) the substituted aryl methyl sulfides and sulfoxides, in turn, were in competition with the corresponding unsubstituted parent compound for a limited amount of **1**. (The exceptions were, in each series, the slowly reacting 4-nitrophenyl compound, which was made to compete against the corresponding 4-cyano analogue). On the assumption that the kinetics have a first-order dependence on each reactant, in each experiment a 15–20-fold excess of both competing substrates over the oxidant was used, hence ensuring pseudo-first-order conditions for the oxidant with respect to each. For each series the yields of reaction products at completion of reaction were quantified by GC (See Experimental). Here our method differed from that of Murray and co-workers,[19] who had measured substrate depletions of up to 25%. Given the much smaller depletion of substrates in our case (5–7%), we felt safe in the assumption that the molar ratio of the products at the end of reaction approximates the ratio of the rates at which they were produced and hence, when the initial molar ratio of the competing substrates, r_0, was taken into account, the relative rate constant, k_X/k_H [eqn (1)]:

$$\frac{[\text{Product(X)}]}{[\text{Product(H)}]} = \frac{-d[\text{Substrate(X)}]}{dt} \bigg/ \frac{-d[\text{Substrate(H)}]}{dt}$$

$$= \frac{k_X[\text{Substrate(X)}]_0[\mathbf{1}]}{k_H[\text{Substrate(H)}]_0[\mathbf{1}]}$$

$$= r_0 \frac{k_X}{k_H} \qquad (1)$$

The combined yields of products corresponded closely (95–98%) to the amount of oxidant consumed, showing that side-reactions such as self-degradation of the oxidant[21] were not significant. Product analysis also showed that, in the case of sulfide oxidation, no sulfone was produced. Table 3 presents the relative rate constants determined and Table 4 a correlation analysis of the dependence of the logarithms of these constants upon various substituent constants. Simple correlations of $\log(k_X/k_H)$ by single substituent constants (σ_m, σ_p, σ_p^+)[22] (σ_m^0)[23] are given together with dual parameter correlations which use the constants σ_I and σ_R of Taft and co-workers.[24] There are 4 scales of σ_R falling in the order $\sigma_R^- \rightarrow \sigma_R^0 \rightarrow \sigma_R^{BA} \rightarrow \sigma_R^+$ for decreasing $-M$ character and increasing $+M$ character (see ESI, Section S1†). We report results only for

Table 3 Relative rate constants for the oxidation of aryl methyl sulfides and sulfoxides by dimethyldioxirane in acetone at 293 K

Aryl substituent, X	$(k_X/k_H)_{\text{sulfide}}$ [a]	$(k_X/k_H)_{\text{sulfoxide}}$ [a]
4-OMe	1.581 ± 0.091	1.475 ± 0.144
4-Me	1.262 ± 0.069	1.317 ± 0.067
4-Cl	0.659 ± 0.068	0.701 ± 0.072
4-C(O)Me	0.385 ± 0.036	0.384 ± 0.036
4-CN	0.322 ± 0.018	0.297 ± 0.034
4-NO$_2$	0.243 ± 0.026^b	0.215 ± 0.019^b
H	1.000 ± 0.000	1.000 ± 0.000
3-OMe	0.811 ± 0.087	0.679 ± 0.082
3-Cl	0.574 ± 0.071	0.502 ± 0.058
3-CF$_3$	0.496 ± 0.035	0.383 ± 0.050
3-CN	0.371 ± 0.018	0.333 ± 0.022
3-NO$_2$	0.282 ± 0.032	0.300 ± 0.038

[a] Uncertainties are the 95% confidence intervals. [b] Measured as $(k_{4\text{-NO}_2}/k_{4\text{-CN}}) \times (k_{4\text{-CN}}/k_H)$.

the σ_R scale, giving the best fit of the data as judged by the various statistics tabulated.

Entry 1 of Table 4 presents details of the Hammett correlation for the oxidation of the full data set of 3-and 4-substituted sulfides. The squared correlation coefficient, R^2, indicates that 99.4% of the variation in $\log(k_X/k_H)_{\text{sulfide}}$ is explained by the simple linear model; the correlation is highly significant as indicated by the high value of F and the low value of F_{signif}, and precise as indicated by the low standard error of the estimate, s; the fit of the model to the data as expressed by Exner's statistic,[25] ψ, is 'good'. Most importantly, the reaction constant, ρ, is very close to that of Murray and co-workers,[19,26] confirming their result. Entries 2 and 3 are the Hammett correlations of the separate *para* (4-substituted) and *meta* (3-substituted) subsets of experimental data. As with the full set, the intercepts are insignificant. Comparison of the respective values of s and ψ for the subsets shows that the data of the *para* subset are less scattered than those of the *meta* subset although their reaction constants, ρ, do not differ significantly.

Entries 4 and 5 present dual parameter correlations of $\log(k_X/k_H)_{\text{sulfide}}$ for the separate subsets. The use of two explanatory variables does not lead to a statistically improved account of the data in either case but, interestingly, neither shows its best correlation to involve σ_I with σ_R^{BA}, which is expected since these constants, in principle, represent the separate inductive and mesomeric 'components' of the Hammett substituent constants.[24] For the *para* subset (entry 4), the best dual parameter correlation is given by σ_I with σ_R^0 with both variables statistically significant at the 0.01 level. If this observation has chemical significance, it suggests that, in the observed reactivity, the sulfur centre is insulated from the direct mesomeric effects of substituents.[27] However, the observation could be due to experimental error, as OMe is the only substituent of those in the subset for which the value differs between the σ_R^{BA} and σ_R^0 scales.[24] If $k_{4\text{-OMe}}/k_H$ were to be 1.65 rather than 1.58, *i.e.* still within the 95% confidence interval (see Table 3), the best correlation *would* involve σ_I with σ_R^{BA}. For the *meta* subset (entry 5), the best correlation is given by σ_I with σ_R^-, with significance levels of 0.01 and 0.03, respectively. The deterioration in statistical quality between entries 3 and 5, as judged by the values of and s and ψ, is not very marked and, of the five substituents in the subset, only Cl has the same value in both the σ_R^- and σ_R^{BA} scales; it therefore seems unlikely that this

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Table 4 Correlation analysis of the logarithms of the relative rate constants for oxidations of aryl methyl sulfides and sulfoxides by dimethyldioxirane in acetone

Entry	Substituted position	Explanatory variables	n^a	$R^{2\,b}$	F^c	$F_{\text{signif}}{}^d$	s^e	ψ^f	Intercept^g c	ρ	$\rho_{\text{I}}, \beta_{\text{I}}{}^h$	$\rho_{\text{R}}, \beta_{\text{I}}{}^h$	$\lambda, \lambda_{\text{st}}{}^i$
Sulfides													
1	3 or 4	σ_{m} or σ_{p}	12	0.994	1608.35	2.22×10^{-12}	0.022	0.086	-0.004 ± 0.020	-0.756 ± 0.042	—	—	—
2	4	σ_{p}	7	0.997	1937.60	1.14×10^{-7}	0.017	0.060	-0.012 ± 0.020	-0.761 ± 0.044	—	—	—
3	3	σ_{m}	6	0.991	455.97	2.84×10^{-5}	0.021	0.114	0.011 ± 0.044	-0.768 ± 0.100	—	—	—
4	4	σ_{I} and σ_{R}^0	7	0.989	180.37	1.20×10^{-4}	0.040	0.139	-0.025 ± 0.073	—	-0.707 ± 0.179 -0.596 ± 0.151	-0.889 ± 0.208 -0.648 ± 0.151	$1.26 \pm 0.16,$ 1.09 ± 0.14
5	3	σ_{I} and σ_{R}^-	6	0.992	195.72	6.63×10^{-4}	0.023	0.123	0.003 ± 0.071	—	-0.659 ± 0.170 -0.747 ± 0.192	-0.218 ± 0.115 -0.365 ± 0.192	$0.33 \pm 0.06,$ 0.49 ± 0.09
Sulfoxides													
6	3 or 4	σ_{m} or σ_{p}	12	0.983	567.89	3.85×10^{-10}	0.038	0.144	-0.026 ± 0.034	-0.778 ± 0.073	—	—	—
7	4	σ_{p}	7	0.993	754.21	1.20×10^{-6}	0.029	0.096	-0.014 ± 0.034	-0.796 ± 0.075	—	—	—
8	3	σ_{m}	6	0.955	85.02	7.69×10^{-4}	0.048	0.260	-0.046 ± 0.097	-0.736 ± 0.221	—	—	—
9	3	σ_{m}^0	6	0.981	102.65	5.34×10^{-4}	0.043	0.237	-0.051 ± 0.087	-0.699 ± 0.192	—	—	—
10	4	σ_{I} and σ_{R}^-	7	0.995	363.40	3.00×10^{-5}	0.030	0.098	0.026 ± 0.052	—	-0.629 ± 0.141 -0.506 ± 0.114	-0.613 ± 0.104 -0.669 ± 0.114	$0.97 \pm 0.10,$ 1.32 ± 0.13
11	3	σ_{I}	6	0.947	71.86	1.06×10^{-3}	0.051	0.281	0.030 ± 0.124	—	-0.838 ± 0.275	—	—

^{a} No. of data points (includes the unsubstituted compounds). ^{b} R is the correlation coefficient. ^{c} $F = R^2(n - m)/[(1 - R^2)(m - 1)]$ where $(m - 1)$ is the no. of explanatory variables. ^{d} F_{signif} the greater the value of F_{signif} the greater is the significance level of the regression. ^{e} Standard error of the estimate. ^{f} $\psi = [n(1 - R^2)/(n - m)]^{1/2}$; $\psi < 0.02$, very good; $0.02 < \psi < 0.1$, good; $0.1 < \psi < 0.2$, fair; $0.2 < \psi < 0.5$, poor (cf. ref. 25). ^{g} The uncertainties on the intercepts and regression coefficients are the 95% confidence intervals (see text). ^{h} β_{I} and β_{R} are regression coefficients from standardised regressions. ^{i} $\lambda = \rho_{\text{R}}/\rho_{\text{I}}$; $\lambda_{\text{st}} = \beta_{\text{R}}/\beta_{\text{I}}$. The uncertainties on the λ ratios are standard errors.

observation is accidental. As the 3-substituents cannot conjugate directly with the sulfur centre, the observation implies their $-M$ effects augment the polarisation of the aromatic π-system induced by their inductive effects (see **5a–d**), giving an accumulation of positive charge adjacent to the S-bearing ring C-atom, which will inhibit the development of similar charge on sulfur in the transition state for oxidation.
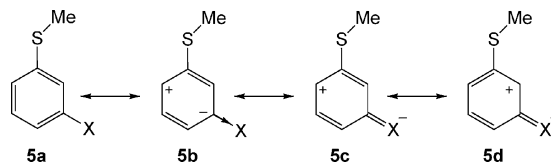
The relative importance of the different electronic effects in the overall substituent effect may be assessed from the ratio, λ, of the individual regression coefficients: $\lambda = \rho_{\text{R}}/\rho_{\text{I}}$ (see Table 4). For the *para* subset the mesomeric effect apparently predominates, whereas for the *meta* subset the inductive effect is the more important, as expected. However, since the σ_{I} and various σ_{R} scales have different ranges, the value of λ may be somewhat misleading as a measure of relative electronic effects. This difficulty can be reduced by the standardisation of all variables by unit normal scaling, which eliminates the intercept c and gives the scale of each variable a mean value of zero and a standard deviation and variance of 1.[28] Thus $E_{\text{st}} = \zeta_{\text{I}}\beta_{\text{I}} + \zeta_{\text{R}}\beta_{\text{R}}$ where E_{st} is the standardised experimental observable, $\log(k_{\text{X}}/k_{\text{H}})$, ζ_{I} is the standardised σ_{I} scale, ζ_{R} is the appropriate standardised σ_{R} scale and β_{I} and β_{R} are the corresponding regression coefficients. In Table 4 we compare the standardised inductive and mesomeric contributions as λ_{st} (*i.e.* $\beta_{\text{R}}/\beta_{\text{I}}$). It is seen that by this assessment, for the *para* subset, the *I* and *M* effects contribute about equally to the combined substituent effect whereas for the *meta* subset, the *I* effect is twice as important as the *M* effect.

Entry 6 of Table 4 presents details of the Hammett correlation for the oxidation of the full data set of 3-and 4-substituted sulfoxides; as for the sulfides, the value of ρ obtained fully confirms that reported by Murray and co-workers.[19] Entries 7 and 8 (Hammett correlations of the separate *para* and *meta* subsets) show that, as with the sulfides, the *meta* subset of sulfoxides gives results which are more scattered than those of the *para* subset. The Hammett correlation for the *meta* subset (entry 8) is 'poor' by the criterion of Exner's statistic, ψ;[25] it is marginally improved by use of σ_{m}^0 (entry 9) in place of σ_{m} but, nevertheless, remains 'poor'. The reaction constants for the separate subsets show greater variation than those of the sulfides, probably as a result of the greater scatter in the *meta* subset. The greater scatter in both *meta* subsets in comparison to their respective *para* counterparts is most likely to be due to experimental error. The range of $(k_{\text{X}}/k_{\text{H}})_{\text{sulfide}}$ in the *meta* subset is half that in the *para* subset, and the range of $(k_{\text{X}}/k_{\text{H}})_{\text{sulfoxide}}$ in the *meta* subset is less than one third of that in the *para* subset but the uncertainty intervals on all the values average *ca.* ± 0.05 (Table 3). The uncertainty, being a greater proportion of the range for the *meta* subsets, produces their greater scatter.

The best dual parameter correlation of $\log(k_{\text{X}}/k_{\text{H}})_{\text{sulfoxide}}$ for the *para* subset is given by σ_{I} with σ_{R}^-, with both variables significant at the 0.01 level (entry 10); in terms of s and ψ, this correlation is only marginally poorer than that with σ_{p} (entry 7). The mesomeric effects of the 4-substituents play a greater role relative to their inductive effects for the sulfoxides ($\lambda_{\text{st}} = 1.32$) than for the sulfides

($\lambda_{st} = 1.09$). The reason for this probably arises from the partial positive charge on the S-atom in the sulfoxides. Such charge will counter the π-polarisation of the aromatic sextet induced by the substituents (I_π effect) thus relatively enhancing their mesomeric effects. The application of a dual parameter correlation to the *meta* subset of sulfoxides fails: no σ_R scale is significant at a level ≤ 0.1 and correlation by σ_I alone is poor.

Although subdivision of the data sets for both series of oxidations and of the explanatory variables used to express them allows possible differences between the subsets to be articulated, the fact remains that the best overall account of the reactivity of both series is given by the Hammett equation applied to the whole data set in each case. Hence, if the data for one series are plotted against those of the other there is a linear correlation (Fig. 1). The line in Fig. 1 is given by eqn (2):

$$\log(k_X/k_H)_{\text{sulfoxide}} = (1.067 \pm 0.084) \log(k_X/k_H)_{\text{sulfide}} \qquad (2)$$

with $n = 12$, $R^2 = 0.970$, $F = 361.6$, $F_{\text{signif}} = 3.51 \times 10^{-9}$, $s = 0.047$ and $\psi = 0.188$. The standard error of the estimate, s, is of very similar magnitude to the uncertainty in the plotted ordinates ($+0.042$ to -0.046) calculated from the average of the 95% confidence intervals given in Table 3. Since the $\log(k_X/k_H)$ terms are proportional to the differences in free energy of activation between the substituted and unsubstituted substrate in both series, the 1 : 1 correspondence shown by eqn (2) indicates that, in acetone, the factors whe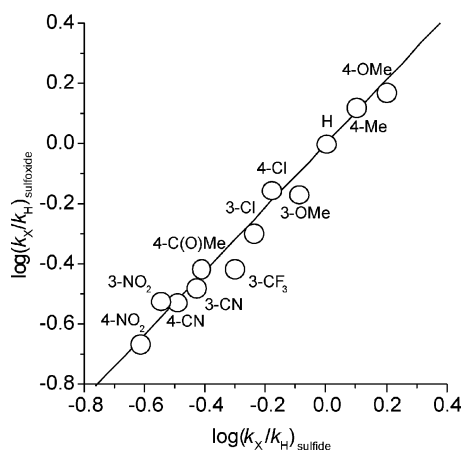reby the substituents affect the oxidation of sulfoxides by **1** are identical to those affecting the oxidation of sulfides, implying the mechanisms are essentially the same.

(ii) Oxidations in acetone with aprotic co-solvents

Table 5 presents relative rate constants measured at 293 K for oxidations performed in mixtures of acetone with aprotic co-solvents, namely 60% v/v hexane and 80% v/v DMF. Acetone was necessarily present as **1** was synthesised and isolated in acetone solution. The constraint on the extent of dilution by hexane was the need for a sufficient solubility of more polar substrates such as methyl 4-nitrophenyl sulfoxide; DMF itself reacts slowly with **1**, which limited the use of this co-solvent to oxidations of sulfides only.

Table 6 details the correlation analysis of the logarithms of the relative rate constants of the reactions studied. The substrates were restricted to 4-substituted compounds which had given data with less scatter than 3-substituted analogues when oxidised in acetone; however, for the reactions in 60% v/v hexane in acetone, these included 4-methoxy-3-methylphenyl methyl sulfide and sulfoxide. In correlation analyses including these compounds, additivity of substituent constants was assumed for the disubstituted phenyl group. For the sulfides, a better Hammett correlation, as judged by the values of s and ψ, was obtained by inclusion of the point so parameterised than by exclusion of data for this substrate. Entry 1 reports the inclusive Hammett correlation for which the goodness of fit, as indicated by ψ, is 'good'. The chemically important result is that the reaction constant, ρ, obtained in this solvent is twice as large as that obtained in acetone alone (see later for discussion of solvent effects on reaction constants). Entry 2 reports the corresponding best dual parameter correlation; this gives no statistical improvement but the best σ_R scale is σ_R^{BA} (with both variables significant at the 0.01 level) whereas for reaction in acetone alone the best scale was σ_R^0 (*cf.* Table 4 entry 4). This is not the consequence of inclusion of the disubstituted substrate, as the same σ_R scale remains the best if it is excluded. The balance of the inductive and mesomeric effects in the mixed solvent ($\lambda_{st} = 1.17$) is somewhat greater than that in acetone alone ($\lambda_{st} = 1.09$), consistent with the change of σ_R scale to one giving greater weight to the $+M$ effects of substituents.

$\log(k_X/k_H)_{\text{sulfoxide}}$ in 60% v/v hexane in acetone (entry 3) is poorly correlated by Hammett's σ_p. The use of σ_p^+ in place of σ_p improves the linear model somewhat (entry 4) and also allows recognition of the point for the 4-Me substituent as a statistical outlier,[29] deletion of which gives a much improved correlation

Fig. 1 Plot of the logarithms of relative rate constants for the oxidation of aryl methyl sulfoxides by **1** in acetone *versus* those for the oxidation of the corresponding sulfides.

Table 5 Relative rate constants for the oxidation of aryl methyl sulfides and sulfoxides by dimethyldioxirane in acetone with aprotic co-solvents at 293 K

	Co-solvent: 60% v/v hexane		Co-solvent: 80% v/v DMF
	---	---	---
Aryl substituent, X	$(k_X/k_H)_{\text{sulfide}}$ [a]	$(k_X/k_H)_{\text{sulfoxide}}$ [a]	$(k_X/k_H)_{\text{sulfide}}$ [a]
4-OMe-3-Me	3.149 ± 0.391	2.373 ± 0.088	
4-OMe	2.477 ± 0.289	2.068 ± 0.109	1.444 ± 0.085
4-Me	1.312 ± 0.165	1.765 ± 0.133	1.063 ± 0.072
H	1.000 ± 0.000	1.000 ± 0.000	1.000 ± 0.000
4-Cl	0.494 ± 0.048	0.721 ± 0.072	0.668 ± 0.027
4-CN	0.094 ± 0.011	0.445 ± 0.023	0.352 ± 0.016
4-NO$_2$	0.059 ± 0.012 [b]	0.404 ± 0.024 [b]	

[a] Uncertainties are the 95% confidence intervals. [b] Measured as $(k_{4\text{-NO}_2}/k_{4\text{-CN}}) \times (k_{4\text{-CN}}/k_H)$.

Table 6 Correlation analysis of the logarithms of the relative rate constants for oxidations of aryl methyl sulfides and sulfoxides by dimethyldioxirane in acetone with aprotic co-solvents

Entry	Explanatory variables[a]	n[b]	R^2[c]	F[d]	F_{signif}[e]	s[f]	ψ[g]	Intercept[h] c	Regression coefficients[h] ρ, ρ_I, β_I[i]	ρ_R, β_R[i]	λ, λ_{st}[j]
Hexane 60% v/v, Sulfides											
1	σ_p	7	0.993	724.34	1.32×10^{-6}	0.061	0.098	-0.031 ± 0.072	-1.503 ± 0.143	—	—
2	σ_I and σ_R^{BA}	7	0.992	250.23	6.29×10^{-5}	0.074	0.118	-0.041 ± 0.145	-1.444 ± 0.326, -0.571 ± 0.129	-1.300 ± 0.252, -0.667 ± 0.129	0.90 ± 0.10, 1.17 ± 0.13
Hexane 60% v/v, Sulfoxides											
3	σ_p	7	0.963	130.47	9.01×10^{-5}	0.067	0.227	0.095 ± 0.068	-0.693 ± 0.156	—	—
4	σ_p^+	7	0.965	137.82	7.89×10^{-5}	0.065	0.221	-0.019 ± 0.063	-0.483 ± 0.106	—	—
5	σ_p^+	6	0.991	439.88	3.05×10^{-5}	0.035	0.116	-0.038 ± 0.039	-0.469 ± 0.062	—	—
6	σ_I and σ_R^+	6	0.994	229.76	5.22×10^{-4}	0.034	0.099	-0.001 ± 0.108	-0.537 ± 0.219, -0.395 ± 0.122	-0.437 ± 0.092, -0.771 ± 0.122	0.81 ± 0.12, 1.95 ± 0.24
DMF 80% v/v, Sulfides											
7	σ_p	5	0.983	169.82	9.76×10^{-4}	0.036	0.170	-0.032 ± 0.053	-0.632 ± 0.154	—	—
8	σ_I and σ_R^{BA}	5	0.991	114.16	8.68×10^{-3}	0.031	0.147	-0.031 ± 0.096	-0.610 ± 0.250, -0.691 ± 0.284	-0.577 ± 0.237, -0.690 ± 0.284	0.95 ± 0.13, 1.00 ± 0.14

[a] Additivity of substituent constants is assumed for 4-methoxy-3-methyl derivatives. [b] No. of data points (includes the unsubstituted compounds). [c] R is the correlation coefficient. [d] $F = R^2(n-m)/[(1-R^2)(m-1)]$ where $(m-1)$ is the no. of explanatory variables. [e] The smaller the value of F_{signif} the greater is the significance level of the regression. [f] Standard error of the estimate. [g] $\psi = [n(1-R^2)/(n-m)]^{\frac{1}{2}}$; $\psi < 0.02$, very good; $0.02 < \psi < 0.1$, good; $0.1 < \psi < 0.2$, fair; $0.2 < \psi < 0.5$, poor ($cf.$ ref. 25). [h] The uncertainties on the intercepts and regression coefficients are the 95% confidence intervals. [i] β_I and β_R are regression coefficients from standardised regressions (see text). [j] $\lambda = \rho_R/\rho_I$; $\lambda_{st} = \beta_R/\beta_I$. The uncertainties on the λ ratios are standard errors.

(entry 5). Entry 6 reports the corresponding dual parameter correlation. The data are best expressed by σ_I and σ_R^+ at significance levels of 0.02 and 0.01, respectively. There is thus a striking contrast between the effect of substituents on the oxidation of sulfoxides by **1** in the two solvent systems so far considered (*cf.* Table 4 entry 10). Although in both solvent systems the mesomeric effects predominate, $\lambda_{st} = 1.32$ in acetone alone and 1.94 in the 60% v/v hexane in acetone, it is the $-M$ effects that are the more important in acetone whereas in the mixed solvent it is the $+M$ effects (see later for discussion).

Entries 7 and 8 relate to the oxidation of sulfides by **1** in 80% v/v DMF in acetone. As with the oxidations of sulfides in other solvents, the data are correlated by σ_p (entry 7) but the smaller values of s and ψ shown by the dual parameter correlation (σ_I and σ_R^{BA}) (entry 8), indicate that the latter gives a more precise account of the data. Fig. 2 shows plots of the logarithms of the relative rate constants for oxidation of sulfides in 60% v/v hexane in acetone and 80% v/v DMF in acetone *versus* those for oxidation in acetone alone. Both are linear but with different gradients. The lines are given by eqn (3) and eqn (4).

$$\log(k_X/k_H)^{hexane-acetone}_{sulfide} = (2.002 \pm 0.151) \log(k_X/k_H)^{acetone}_{sulfide} \quad (3)$$

with $n = 6$, $R^2 = 0.994$, $F = 878.28$, $F_{signif} = 7.72 \times 10^{-6}$, $s = 0.049$, and $\psi = 0.092$ and

$$\log(k_X/k_H)^{DMF-acetone}_{sulfide} = (0.891 \pm 0.168) \log(k_X/k_H)^{acetone}_{sulfide} \quad (4)$$

with $n = 5$, $R^2 = 0.979$, $F = 183.59$, $F_{signif} = 8.69 \times 10^{-4}$, $s = 0.035$, and $\psi = 0.189$.
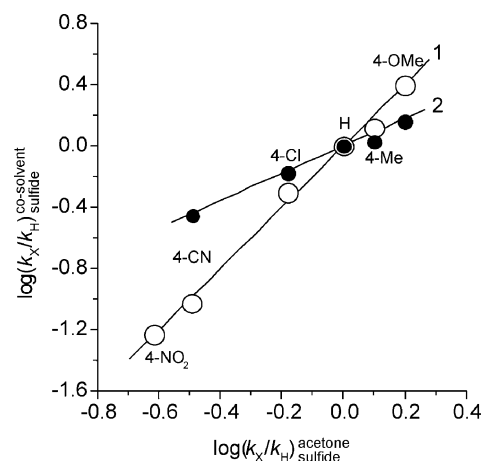

Fig. 2 Plots of the logarithms of relative rate constants for the oxidation of aryl methyl sulfides by **1** in acetone with aprotic co-solvents *versus* those for their oxidation in neat acetone: 1, 60% v/v hexane in acetone; 2, 80% v/v DMF in acetone.

It is seen from eqn (3) that the effect of dilution of acetone (relative permittivity, $\varepsilon_r = 21.01$[30a]) with the less polar hexane ($\varepsilon_r = 1.89$[30b]), giving a mixture with $\varepsilon_r = 7.92$[31a] (see ESI, Section S2†), is to double the overall substituent effect on the oxidation of sulfides by **1** relative to that in neat acetone, whereas eqn (4) shows that dilution by the more polar DMF ($\varepsilon_r = 38.25$[30a]), giving a mixture with $\varepsilon_r = 33.60$[31b] (see ESI, Section S2†), has little effect (a t-test shows the difference in the reaction constants of entry 2 in Table 4 and entry 7 in Table 6 is not significant at the 0.05 level of probability). It thus seems that, in the less polar solvent

mixture, solvation cannot stabilise the development of charge on S as much as in acetone alone, which results in a greater demand for electron density upon the substituents and consequently in an enhanced reaction constant. In the more polar solvent mixture, the fact that the reaction constant remains essentially unchanged suggests that, for each substituent, the extent of charge separation has reached an upper limit in acetone and increasing the solvent's relative permittivity produces no further increase.

(iii) Oxidations in aqueous acetone

Relative rate constants for the oxidation of aryl methyl sulfides and sulfoxides by **1** in various aqueous acetone mixtures at 293 K are given in Table 7 and the corresponding correlation analyses of their logarithms in Table 8a and b. Entry 1 of Table 8a reports the Hammett correlation for the oxidation of sulfides in acetone containing 1% by volume of water and entry 2 the best dual parameter correlation (σ_I and σ_R^{BA}) of the same data. Comparison of the values of s and ψ between these two entries shows that the latter entry gives the better account of the data. Analogous results for oxidations of the same sulfides in 5% v/v aqueous acetone are given in entries 3 and 4 and, again, a dual parameter correlation (now σ_I and σ_R^0) gives the more precise account of the data. Comparison of the regression coefficients of entries 1 and 3 with that of entry 2 in Table 4 shows that the Hammett reaction constant increases considerably with the proportion of water in the solvent (by 57% for 1% water and by 75% for 5% water). Similar scrutiny of the regression coefficients of entries 2 and 4 together with those of entry 4 in Table 4 shows that the changes in the Hammett reaction constant are matched by changes in both ρ_I and ρ_R. The finding that σ_R^0 is preferred to σ_R^{BA} in two of the three cases might arise as experimental error as suggested above [see (i)].

The Hammett correlations for the oxidation of sulfoxides in 1% and 20% aqueous acetone are reported in Table 8a, entries 5 and 7, respectively. Comparison of their reaction constants with that for oxidation in acetone alone (Table 4 entry 7) shows that the values are very similar ($\rho_{mean} = -0.751 \pm 0.044$), though a small decrease with increasing proportion of water may be discerned (by 6% for 1% water and by 11% for 20% water). The dual parameter correlations of the same data sets (entries 6 and 8 in Table 8a) do not give improved precision, but comparison with entry 10 in Table 4 shows a consistent preference for the σ_R^- scale for reactions in neat acetone and aqueous acetone solvents.

Fig. 3 shows the contrasting Hammett plots obtained for the oxidation of sulfides and sulfoxides in 20% aqueous acetone. The plot for sulfoxides is normal (*cf.* entry 7 in Table 8a) but that for sulfides is curved; indeed, it is well represented by a quadratic equation in σ_p (Table 8b). The coefficients found for this equation are somewhat sensitive to the small differences between values of $\log(k_X/k_H)_{sulfide}$ close to zero. Entry 9 of Table 8b gives the statistical analysis for the full set of sulfides. If the sole di-substituted substrate is excluded on grounds of its structural difference, the decrease in s and ψ in entry 10 indicates improved precision in the fit of the residual data; however, the 95% confidence intervals for the regression coefficients are larger than those in entry 9. If the datum for the di-substituted substrate is restored and that for the 4-OMe substrate excluded on the grounds that $\log(k_X/k_H)_{sulfide}$ is out of sequence with those adjacent in the σ_p scale, a significant improvement is seen: F_{signif}, s and ψ are all decreased relative to entry 2, and the 95% confidence intervals on the regression coefficients are decreased relative to entry 1. Curve 2 in Fig. 3 is given by eqn 5 (*cf.* entry 11 of Table 8b).

$$\log(k_X/k_H)_{sulfide} = -(0.566 \pm 0.123)\sigma_p - (1.279 \pm 0.193)\sigma_p^2 \quad (5)$$
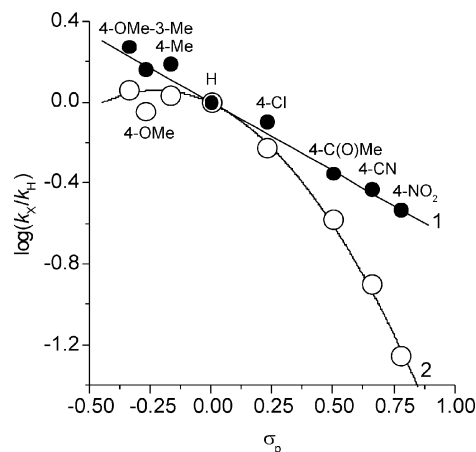

Fig. 3 Hammett plots for the oxidation of aryl methyl sulfides and sulfoxides in acetone containing 20% v/v water: 1, sulfoxides; 2, sulfides.

Curvature in a Hammett plot, where the gradient changes from zero through increasingly negative values as σ_p increases, is diagnostic of the occurrence of a change of rate-determining step within the range of substituents considered. It is apparent from Fig. 3 that only substrates having $\sigma_p > 0$ show a significant

Table 7 Relative rate constants for the oxidation of aryl methyl sulfides and sulfoxides by dimethyldioxirane in aqueous acetone at 293 K

	1% v/v Water		5% v/v Water	20% v/v Water	
Aryl substituent, X	$(k_X/k_H)_{sulfide}$ [a]	$(k_X/k_H)_{sulfoxide}$ [a]	$(k_X/k_H)_{sulfide}$ [a]	$(k_X/k_H)_{sulfide}$ [a]	$(k_X/k_H)_{sulfoxide}$ [a]
4-OMe-3-Me	—	—	—	1.152 ± 0.116	1.900 ± 0.062
4-OMe	1.712 ± 0.133	1.441 ± 0.091	1.844 ± 0.146	0.905 ± 0.106	1.462 ± 0.135
4-Me	1.213 ± 0.126	1.309 ± 0.052	1.322 ± 0.171	1.089 ± 0.125	1.559 ± 0.087
H	1.000 ± 0.000	1.000 ± 0.000	1.000 ± 0.000	1.000 ± 0.000	1.000 ± 0.000
4-Cl	0.456 ± 0.041	0.702 ± 0.063	0.476 ± 0.041	0.599 ± 0.075	0.803 ± 0.067
4-C(O)Me	0.265 ± 0.025	0.402 ± 0.028	0.210 ± 0.022	0.264 ± 0.034	0.448 ± 0.026
4-CN	0.114 ± 0.016	0.331 ± 0.022	0.112 ± 0.015	0.126 ± 0.020	0.372 ± 0.014
4-NO$_2$	0.099 ± 0.009 [b]	0.230 ± 0.014 [b]	0.071 ± 0.005 [b]	0.056 ± 0.009 [b]	0.295 ± 0.017 [b]

[a] Uncertainties are the 95% confidence intervals. [b] Measured as $(k_{4-NO_2}/k_{4-CN}) \times (k_{4-CN}/k_H)$.

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Table 8 Correlation analysis of the logarithms of the relative rate constants for oxidations of aryl methyl sulfides and sulfoxides by dimethyldioxirane in aqueous acetone

Entry	Explanatory variables[a]	n[b]	R^2[c]	F[d]	F_{signif}[e]	s[f]	ψ[g]	Intercept[h] c	Regression coefficients[h] ρ	ρ_I, β_I[i]	ρ_R, β_R[i]	λ, λ_{st}[j]
a)												
1% Aqueous acetone, Sulfides												
1	σ_p	7	0.984	316.18	1.03×10^{-5}	0.068	0.148	-0.069 ± 0.078	-1.195 ± 0.173	—	—	—
2	σ_I and σ_R^{BA}	7	0.994	322.93	3.89×10^{-5}	0.047	0.104	-0.047 ± 0.086	—	-1.264 ± 0.210, -0.674 ± 0.112	-1.050 ± 0.200, -0.588 ± 0.112	0.83 ± 0.08, 0.87 ± 0.08
5% Aqueous acetone, Sulfides												
3	σ_p	7	0.993	662.42	1.65×10^{-6}	0.052	0.102	-0.059 ± 0.059	-1.330 ± 0.133	—	—	—
4	σ_I and σ_R^0	7	0.997	576.98	1.19×10^{-5}	0.040	0.078	-0.051 ± 0.072	—	-1.318 ± 0.177, -0.634 ± 0.085	-1.477 ± 0.204, -0.614 ± 0.085	1.12 ± 0.08, 0.97 ± 0.07
1% Aqueous acetone, Sulfoxides												
5	σ_p	7	0.992	625.48	1.90×10^{-6}	0.030	0.105	-0.013 ± 0.035	-0.751 ± 0.077	—	—	—
6	σ_I and σ_R^-	7	0.993	287.04	4.79×10^{-5}	0.032	0.110	0.026 ± 0.055	—	-0.598 ± 0.150, -0.510 ± 0.128	-0.574 ± 0.111, -0.665 ± 0.128	0.96 ± 0.11, 1.30 ± 0.15
20% Aqueous acetone, Sulfoxides												
7	σ_p	8	0.988	492.93	5.46×10^{-7}	0.037	0.139	0.027 ± 0.034	-0.705 ± 0.077	—	—	—
8	σ_I and σ_R^-	8	0.987	191.43	1.89×10^{-5}	0.041	0.144	0.061 ± 0.066	—	-0.540 ± 0.180, -0.433 ± 0.144	-0.562 ± 0.111, -0.730 ± 0.144	1.04 ± 0.16, 1.69 ± 0.25
b)										ρ_1[h]	ρ_2[h]	
20% Aqueous acetone, Sulfides												
9	σ_p quadratic	8	0.993	444.48	2.34×10^{-6}	0.044	0.104	None	—	-0.489 ± 0.154	-1.391 ± 0.240	—
10	σ_p quadratic	7[k]	0.997	753.39	7.01×10^{-6}	0.032	0.076	None	—	-0.371 ± 0.176	-1.565 ± 0.253	—
11	σ_p quadratic	7[l]	0.998	1002.7	3.96×10^{-6}	0.028	0.066	None	—	-0.566 ± 0.123	-1.279 ± 0.193	—

[a] Additivity of substituent constants is assumed for 4-methoxy-3-methyl derivatives. [b] No. of data points (includes the unsubstituted compounds). [c] R is the correlation coefficient. [d] $F = R^2(n − m)/[(1 − R^2)(m − 1)]$ where $(m − 1)$ is the no. of explanatory variables. [e] The smaller the value of F_{signif} the greater is the significance level of the regression. [f] Standard error of the estimate. [g] $\psi = [n(1 − R^2)/(n − m)]^{1/2}$; $\psi < 0.02$, very good; $0.02 < \psi < 0.1$, good; $0.1 < \psi < 0.2$, fair; $0.2 < \psi < 0.5$, poor (cf. ref. 25). [h] The uncertainties on the intercepts and regression coefficients are the 95% confidence intervals. [i] β_I and β_R are regression coefficients from standardised regressions (see text). [j] $\lambda = \rho_R/\rho_I$; $\lambda_{st} = \beta_R/\beta_I$. Uncertainties on λ ratios are standard errors. [k] Excludes the 4-OMe point. [l] Excludes the 4-OMe-3-Me point.

substituent effect: a step which is initially not rate-determining becomes so for substrates having electron-withdrawing substituents, consistent with the step concerned being an electrophilic attack on the substrate.

This finding can be understood in terms of Scheme 3. Here, in reaction 1, an aryl methyl sulfide, S, undergoes an electrophilic attack by 1 in which the O–O bond stretches and breaks heterolytically to give a betaine, B; the separation of charges can be assisted by the high polarity of the medium and by solvation of the ionic centres by water. The betaine reacts in three ways determined by the internal site at which the anionic oxygen attacks. If the site is the S-bonded oxygen, the result is reversal of reaction 1 (*i.e.* reaction −1). The principle of microscopic reversibility relates this reaction to the scissoring of the OCO angle, which shortens the O-to-O distance in the betaine. If the site is the adjacent carbon atom, B fragments to give the sulfoxide product, P, and acetone (reaction 2). This reaction can originate from the same ground-state conformation as reaction −1 but corresponds to the 'asymmetric stretching' of the two C–O bonds in B, *i.e.* shortening of C–O$^-$ concurrent with stretching of C–OS. The third possibility is that the anionic oxygen attacks the sulfonium centre to produce a dioxathietane, D, as found by Asensio and co-workers[20] for 2 as oxidant (reaction 3, *cf.* Scheme 2b). This reaction would originate from a rotamer of B different from that assumed for reactions 2 and −1. However, in the present case, the fact that no sulfone results (providing that S is in excess over 1) shows that D, if formed, does not undergo further oxidation. Since the yield of P is equivalent to the amount of 1 used, any formation of D must be reversible; D is thus a cul-de-sac which merely stores B until it reacts either by reaction −1 or by reaction 2.
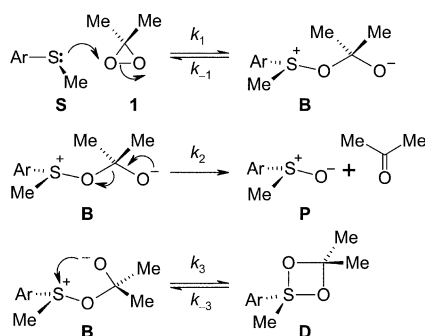
Scheme 3

A kinetic analysis with application of the steady state approximation to B and D shows that, in general,

$$\frac{d[P]}{dt} = -\frac{d[S]}{dt} = \frac{k_1 k_2 [S][1]}{k_{-1} + k_2} \tag{6}$$

The usual assumption for simplifying eqn (6) is that either $k_{-1} \ll k_2$ or *vice versa*, which allows expression of a curved Hammett plot in terms of two intersecting linear arms. However, the degree of curvature implicit in the parabolic character of the present plot suggests that such an assumption is not justified and that, within the substituent range, k_{-1} and k_2 are presumably of comparable magnitudes.

Suppose $f = k_2/k_{-1}$. Then

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [S][1]}{k_{-1}(1+f)} = \frac{K_e k_2 [S][1]}{1+f} \tag{7}$$

where K_e is the equilibrium constant for the reversible reaction 1 (pre-equilibrium).

Applying this notation to both substituted and unsubstituted substrates (initially equimolar and in large excess over 1), it follows that the experimental relative rate constant, $(k_X/k_H)_{sulfide}$, is given by eqn (8).

$$\left(\frac{k_X}{k_H}\right)_{sulfide} = \frac{K_e^X k_2^X (1+f_H)}{K_e^H k_2^H (1+f_X)} \tag{8}$$

and taking logarithms,

$$\log\left(\frac{k_X}{k_H}\right)_{sulfide} = \log\left(\frac{K_e^X}{K_e^H}\right) + \log\left(\frac{k_2^X}{k_2^H}\right) - \log\left(\frac{1+f_X}{1+f_H}\right)$$

Application of the Hammett equation to the first two terms on the right hand side gives eqn (9),

$$\log\left(\frac{k_X}{k_H}\right)_{sulfide} = \sigma_p(\rho_e + \rho_2) - \log\left(\frac{1+f_X}{1+f_H}\right) \tag{9}$$

As reaction 1 is an electrophilic attack on S, the pre-equilibrium will lie further to the right the more strongly electron-donating is the substituent X. The reaction constant ρ_e will therefore be negative. In reaction 2, the full ionic charge on S in B is reduced to the dipolar charge of the sulfoxide, P (S$^+$–O$^-$ ↔ S=O), a process disfavoured by electron-donating X; ρ_2 is therefore expected to be positive. If ρ_e and ρ_2 are of similar absolute magnitudes it follows that the first term on the right hand side of eqn (9) will be small. If, as suggested above, the excitation to the transition state for reaction −1 originates in an OCO in-plane bending (scissoring) vibration in B whereas that for reaction 2 originates in an OCO bond-stretching vibration of higher energy, in the absence of any substituent effect and other factors such as desolvation being equal, it is expected that $k_2^H < k_{-1}^H$, *i.e.* $0 < f_H < 1$.

The behaviour of f_X can be inferred from a comparison of hypothetical Hammett plots for reactions 2 and −1 (Fig. 4). As both reactions are disfavoured by electron-donating substitution, these are drawn with positive gradients intersecting the ordinate at $\sigma_p = 0$ such that $\log k_2^H < \log k_{-1}^H$ as required by the above argument. To agree with the observation of a change in rate-determining step for electron-withdrawing substituents, the intersection of the plots must occur at a positive value of σ_p. This requires that $\rho_2 > \rho_{-1}$.
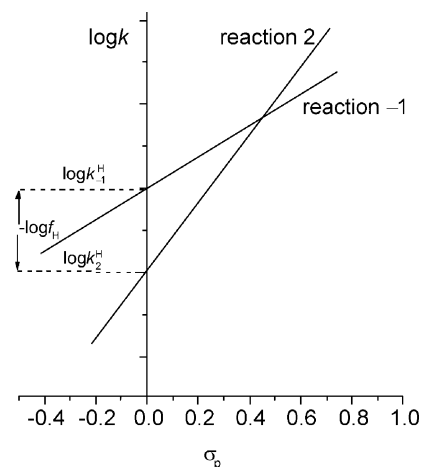

Fig. 4 Hypothetical Hammett plots for reactions −1 and 2 in Scheme 3 (see text).

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As f_X is defined as k_2^X/k_{-1}^X,

$$\log f_X = \log k_2^X - \log k_{-1}^X$$

Applying the Hammett equation,

$$\log f_X = (\log k_2^H + \sigma_p \rho_2) - (\log k_{-1}^H + \sigma_p \rho_{-1})$$

$$= \log f_H + \sigma_p \Delta\rho,$$

where $\Delta\rho = (\rho_2 - \rho_{-1}) > 0$. Hence,

$$f_H = f_X/\text{antilog}(\sigma_p \Delta\rho) \qquad (10)$$

Substituting for f_H in eqn (9) gives eqn (11),

$$\log\left(\frac{k_X}{k_H}\right)_{\text{sulfide}} = \sigma_p(\rho_e + \rho_2) - \log\left(\frac{1+f_X}{1+f_X/\text{antilog}(\sigma_p \Delta\rho)}\right) \qquad (11)$$

Comparison of eqn (11) with eqn (5) indicates $(\rho_e + \rho_2) = -(0.566 \pm 0.123)$, i.e. a small figure as required for ρ_e and ρ_2 being of opposite sign and similar magnitude and that,

$$\log\left(\frac{1+f_X}{1+f_X/\text{antilog}(\sigma_p \Delta\rho)}\right) = (1.279 \pm 0.193)\,\sigma_p^2$$

whence,

$$f_X = \frac{\text{antilog}(1.279\,\sigma_p^2) - 1}{1 - \text{antilog}(1.279\,\sigma_p^2 - \sigma_p \Delta\rho)} \qquad (12)$$

For assumed values of $\Delta\rho$, values of f_X can hence be found for a substituent from its Hammett constant. Values of f_X were obtained via eqn (12) for $0 < \Delta\rho < 4$, which is a reasonable range in the context of Hammett correlation of side-chain reactivity. All values of $\Delta\rho$ in this range gave negative f_X for substituents having $\sigma_p < 0$, which is physically meaningless. {Evidently for these substituents, the second term on the right of eqn (9) reduces to $-\log[1/(1+f_H)]$, i.e. $\log(1+f_H)$, which is constant}. Negative values of f_X were also found for $0 < \Delta\rho < 1$ and $\sigma_p > 0$, which eliminates $\Delta\rho$ in this range from further consideration. Positive values of f_X were obtained for $\Delta\rho \geq 1$ and $\sigma_p > 0$. In order further to narrow the range of $\Delta\rho$, values of f_H were found via eqn (10) from the calculated f_X values, the requirement being that f_H should be constant irrespective of the value of f_X and should lie in the range 0–1. This requirement is well met for $\Delta\rho = 2.45$, and the value of f_H found is 0.07. It is also found that, as anticipated, for electron-withdrawing X, k_2^X and k_{-1}^X are of similar magnitudes as all $f_X = k_2^X/k_{-1}^X < 6$ (Table 9 and ESI, Section S3†).

The finding that f_H is 0.07 and that f_X is without meaning for substituents with $\sigma_p < 0$ transforms eqn (9) into eqn (13) for such

Table 9 Evaluation of f_X and f_H for $\Delta\rho = 2.45$

Substituent, X	σ_p [a]	f_X [b]	f_H [c]
4-OMe-3-Me[d]	−0.34	−0.05	−0.32
4-OMe	−0.27	−0.05	−0.23
4-Me	−0.17	−0.05	−0.13
H	0.00	Indeterminate	Indeterminate
4-Cl	0.23	0.25	0.07
4-C(O)Me	0.50	1.24	0.07
4-CN	0.66	2.86	0.07
4-NO₂	0.78	5.40	0.07

[a] Ref. 22. [b] See eqn (12). [c] See eqn (10). [d] Additivity of substituent constants assumed: 'σ_p' $= \sigma_p^{\text{OMe}} + \sigma_m^{\text{Me}}$.

substituents, which accounts for the observed very small variation in $\log(k_X/k_H)_{\text{sulfide}}$.

$$\left(\frac{k_X}{k_H}\right)_{\text{sulfide}} = -0.566\,\sigma_p + \log(1 + 0.07) \qquad (13)$$

$$= -0.566\,\sigma_p + 0.029$$

We have $(\rho_e + \rho_2)$ i.e. $(\rho_1 - \rho_{-1} + \rho_2) = -0.566$; now we also have $\Delta\rho$ i.e. $(\rho_2 - \rho_{-1}) = 2.45$. Subtraction of the latter equation from the former gives $\rho_1 = -3.02$. A reaction constant of this magnitude is typical of a simple reaction step that creates a full positive ionic charge on the first atom attached to the substituted aromatic ring (cf. quaternisation of ArNMe₂),[32] as envisaged in the formation of **B** (Scheme 3).

A reaction constant is usually obtained as the gradient of a linear Hammett plot, but this is not possible when the plot is curved. However, the gradient of the tangent to the curve at any value of σ_p represents a 'local reaction constant' at that value. Differentiation of eqn (5) with respect to σ_p allows the determination of the gradient at particular points:

$$\frac{d[\log(k_X/k_H)_{\text{sulfide}}]}{d\sigma_p} = -0.566 - (2 \times 1.279\,\sigma_p) \qquad (14)$$

Thus, at $\sigma_p = 0.78$ (for X = 4-NO₂) the 'local reaction constant' is −2.56, which is smaller in absolute magnitude than the value of −3.02 obtained above. As shown in Table 9 for X = 4-NO₂, k_2^X is just over five times larger than k_{-1}^X and therefore is not sufficiently large for k_{-1}^X to be neglected in comparison with it. In the expression $k_X = k_1^X k_2^X/(k_{-1}^X + k_2^X)$ [cf. eqn (6)] the denominator is therefore significantly larger than k_2^X in the numerator, and k_1^X is underestimated, and hence so is the reaction constant, if the two are assumed to cancel. Also, it should be noted that the slowest step in the reaction sequence changes between H and NO₂, and therefore $(k_X/k_H)_{\text{sulfide}}$ does not strictly compare like with like. Nevertheless, it is clear that as substituents become more electron-withdrawing, the 'local reaction constant' approaches a value that is typical for the formation of a full positive ionic charge on the atom attached to the substituted ring.

The observed behaviour of the oxidation of aryl methyl sulfides by **1** in aqueous acetone containing 20% v/v water is thus consistent with the betaine-involving mechanism proposed in Scheme 3. This is different from the behaviour of the same oxidation in acetone alone. It is thereby demonstrated that sulfide oxidation by **1** in acetone alone does not proceed via a betaine intermediate as suggested by Asensio and co-workers,[20] and that the earlier inference of a concerted mechanism as in Scheme 2a is most probably correct. Furthermore, the absence of any sulfone product when reaction does proceed via a betaine intermediate shows that betaine formation does not necessarily lead to the formation of a dioxathietane intermediate that is more easily oxidised than the initial sulfide. Conceivably, as suggested in Scheme 3, a dioxathietane (**D**) might form reversibly in aqueous acetone and prove to be inert to oxidation by **1** but, more probably we suggest, no dioxathietane is produced on account of solvation of the ionic centres of the betaine by water (see below). The solvent-dependence of the behaviour of **2** as an oxidant of sulfides supports this suggestion.[20b] The sulfone/sulfoxide product ratio characteristic of reaction in polar aprotic solvents (CH₂Cl₂, MeCN, Me₂CO) is increased by admixture of non-polar aprotic additives (e.g. CCl₄) but markedly decreased by admixture of

protic additives (CF$_3$CH$_2$OH, t-BuOH, CF$_3$CO$_2$H, MeCO$_2$H). Since sulfones derive from a dioxathietane whereas sulfoxides derive from a betaine (Scheme 2b), it is evident that the effect produced by an additive depends on its ability to influence the relative stability of the betaine and the dioxathietane.§ When both **1** and **2** oxidise sulfides in conditions involving intermediate betaines, the course of reaction depends crucially on the solvation of the betaine: protic nucleophilic solvent components solvate the betaine, thus favouring the formation of sulfoxide over sulfone.

(iv) The solvent dependence of the concerted mechanisms

It is now clear that the oxidations of the sulfides investigated here proceeded by a concerted mechanism with the exception of the reaction in 20% v/v H$_2$O in acetone. The oxidations of sulfoxides showed no evidence of a change in mechanism as a result of variation in the medium and we conclude that, for them, reaction was concerted in all the media studied. As the regression coefficients for both kinds of substrate show variation with the medium, differences in transition state character might be inferable from them.

Sulfides. Activation to the transition state for the single-step oxidation of sulfides by **1** involves a separation of partial charges (Scheme 2a). This process is, in principle, dependent on the relative permittivity, ε_r, of the medium. Above [see (ii)], it was found that the Hammett reaction constant for the oxidation of sulfides increases two-fold from its value in acetone ($\varepsilon_r = 21.01^{30a}$), when ε_r is reduced to 7.92 by admixture of 60% v/v hexane ($\varepsilon_r = 1.89^{30b,31a}$) (see ESI, Section S2†). We suggested the reason to be that, in the mixed solvent, where the effectiveness of the medium in stabilising charge-separation is reduced, there is a greater demand upon the substituents for electron density than in acetone alone. By contrast, it was found that an increase in ε_r to 33.60 caused by admixture of 80% v/v DMF ($\varepsilon_r = 38.25^{30a,31b}$) (see ESI, Section S2) had little effect: the measured reaction constant changed in the opposite sense to that caused by reduction in ε_r, but the decrease was small and not statistically significant. Evidently, the *absolute* rate constants for the oxidation of all the sulfides examined change by an approximately constant factor in response to increase in ε_r and the reaction constant, determined from the *relative* rate constants, k_X/k_H, thus remains virtually unchanged. An alternative explanation considered is that, in the 80% v/v DMF mixture, the transition states are preferentially solvated by acetone and are thereby shielded from the effects of change in the composition of the outer solvent shell. This, however, begs the question as to why a similar situation does not occur in the hexane–acetone mixture where the strength of dipole–dipole interaction between the transition state and acetone molecules would be expected to be greater than that in the DMF–acetone mixture; preferential solvation therefore seems unlikely.

It was found that significant increases in the Hammett reaction constant occur on addition of small amounts of water (1% and 5% v/v ($\varepsilon_r = 80.10^{30c}$) to acetone [see (iii) above]. These small

additions increase ε_r to 21.24 and 24.08, respectively[31c–e] (see ESI, Section S2†), which are less than that caused by addition of 80% v/v DMF; hence, in view of the latter having scant effect on the reaction constant, the observed behaviour must derive from another property of the aqueous solvent. The most obvious is the ability of water to interact with the transition state both by lone-pair donation at the electron-deficient sulfur centre and by hydrogen-bonding to the distal oxygen atom as shown in **6**.
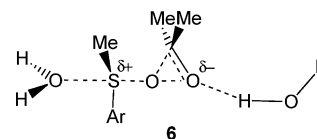
Interactions such as these serve to stabilise *individually* the partially charged centres and bring about an increased weakening of the O–O bond in the dioxirane moiety relative to that in neat acetone. The bond-weakening results in increased magnitudes of partial charge with a consequent increase in the demand for electron density from the substituents. Their differential abilities to supply it results in the larger reaction constants observed. Progressive increase in the proportion of water leads to a combination of these effects with an increase in ε_r, resulting in such O–O bond weakening that formation of a betaine intermediate becomes viable and a change of mechanism ensues as was observed for 20% v/v H$_2$O ($\varepsilon_r = 34.30$).[31c–e]

Sulfoxides. The Hammett reaction constants for the oxidation of sulfoxides by **1** are similar for reactions in acetone alone and in 1% v/v and 20% v/v water in acetone, $\rho_{mean} = -0.751 \pm 0.044$ (*cf.* Table 4 entry 7, Table 8a entries 5 and 7). Evidently, neither the smaller nor the larger increase in water content of the solvent has much effect on the relative rate constants. The changes in ε_r and hydrogen-bonding capacity of the solvent, which necessarily accompany the addition of water, must either negate one another or affect the absolute rate constants by similar combined factors across the substituent range, and so cancel in the relative rate constants. (The following paper examines the effect of solvent variation on absolute rate constants). For oxidation of sulfoxides in 60% v/v hexane in acetone, the Hammett correlation was poor (Table 6 entry 3); a correlation was found by using σ_p^+ (Table 6 entry 5) that was only fair by Exner's criterion despite a reduced data set. Comparison of the reaction constants (Table 4 entry 7 and Table 6 entry 5) reveals a 59% reduction on transfer of the oxidation from acetone to 60% v/v hexane in acetone, indicating that the reaction becomes less selective in the solvent of lower polarity. Although standardisation of the variables in multiple regression facilitates comparison of the coefficients derived from those having different scales, the comparisons for sulfoxides are uninformative as, for all the solvent systems examined, $|\beta_R| > |\beta_I|$ and λ_{st} does not show systematic variation. The notable finding is that, whereas ζ_R^+ (*i.e.* standardised σ_R^+) is the best mesomeric scale for the standardised dual parameter correlation of reactions in 60% v/v hexane in acetone (consistent with σ_p^+ in single parameter correlation), in acetone alone and in aqueous acetone mixtures, the best mesomeric scale is ζ_R^- (*cf.* Table 6 entry 6, Table 4 entry 10 and Table 8a entries 6 and 8).

Fig. 5 compares the relative rate constants for oxidations of sulfoxides by **1** in acetone and 60% v/v hexane in acetone (*cf.* Tables 3 and 5). The striking feature is that, in the less

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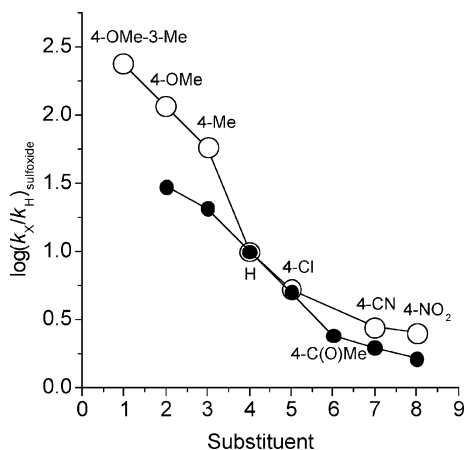
Org. Biomol. Chem., 2008, **6**, 745–761 | 755

Fig. 5 Illustration of the disposition of the logarithms of relative rate constants of aryl methyl sulfoxides when oxidised by **1** in different solvents: ●, neat acetone; ○, 60% v/v hexane in acetone.

polar solvent, both electron-withdrawing groups and electron-donating groups increase the relative rate constants in comparison to their values in acetone (the curves necessarily have the point for the unsubstituted substrate in common). This fact implies the operation of a solvent-dependent effect that varies across the range of substituents. Sulfoxides have a polarised $S^{\delta+}$–$O^{\delta-}$ bond (see below) which may be represented by the canonical structures **7a** ↔ **7b**. The dipolar positive charge on S results in the S(O)Me group exerting a strong electron-attracting effect that polarises an attached phenyl ring. This is demonstrated by its positive substituent constants: $\sigma_m = 0.52$, $\sigma_p = 0.49$, $\sigma_I = 0.50$.[22,24] The near equality of σ_m and σ_p shows that, despite possession of a lone-pair of electrons on S, the S(O)Me group exerts no significant +M effect, and the similar value for σ_I shows its electronic effect is essentially inductive. Structure **8** can therefore be envisaged to contribute to the overall hybrid of methyl phenyl sulfoxide. Placing a heteroatom-containing substituent *para* to the sulfoxide group will introduce an opposing I_π polarisation of the ring. However, of the substituents used, only CN and NO_2 (σ_I 0.56 and 0.65, respectively[24]) exert −I effects stronger than S(O)Me; thus, for all the other substituents, the direction of net polarisation of the ring will be the same as in **8**. Furthermore, a +M substituent such as 4-OMe should enhance the net polarisation (see **9a–b**). This expectation is based on the fact that S(O)Me has a substituent constant $\sigma_p^- = 0.72$,[22] which implies that it can accept π-electron density mesomerically from a conjugated strong donor. Given the pyramidal disposition of the attachments to S, it is unlikely that this 'mesomeric acceptance' involves an increased C(1)–S bond order but rather that the relative weighting of canonical structures **7a** and **7b** is adjusted in favour of **7a** as a result of increased negative charge at C(1). Strongly electron-withdrawing substituents such as CN and NO_2 will have the opposite effect. Their combined −I and −M effects are sufficient to reverse the polarisation of the aromatic ring caused by the S(O)Me group and to deplete C(1) of π-electron density, leading to adjustment of the relative weighting of canonical structures **7a** and **7b** in favour of the latter (see **10a–c**). It is thus clear that aryl methyl sulfoxides are polarised molecules in which the net charge-separation depends on the substitution and is expected to be most marked for the most strongly acting substituents, whether electron-donating or
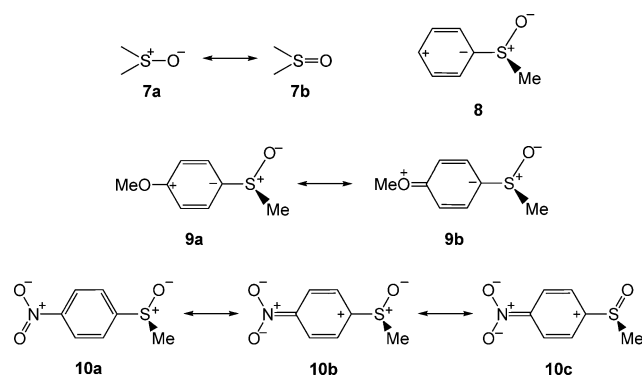
electron-accepting. The ground-states of such species are expected to be less well stabilised in solvents of low polarity than in more polar solvents. If ground-state stabilities were to be the dominant factor in determining the pattern of activation energies for oxidations of sulfoxides, the relative disposition of the curves of Fig. 5 would be explained.

The SO bonds in sulfones are less polar than those in sulfoxides. For example, the molecular dipole moment of Me_2S ($\mu = 1.47$ D; 4.900×10^{-30} C m)[33] is markedly increased on oxidation to Me_2SO ($\mu = 3.90$ D; 1.300×10^{-29} C m),[33] whereas the second oxidation to Me_2SO_2 produces a much smaller increment ($\mu = 4.49$ D; 1.498×10^{-29} C m).[33] Assuming the differences in molecular dipole moment between that of Me_2S and those of its two oxidation products are essentially due to the SO bond moment(s) and, allowing for the angular separation of the SO bonds in the sulfone (121°),[34] it is clear that the SO bonds of the sulfone are much less polarised than that of the sulfoxide. An analogous situation is expected for any triad ArSMe, ArS(O)Me and ArS(O)₂Me. That being the case, it is expected that the transition state for the oxidation of any sulfoxide to the sulfone, in which the properties of the latter are developing, will be less polarised than the initial sulfoxide, particularly so the later the transition state occurs in the reaction coordinate. Theoretical calculations bear out this expectation.[35] Transfer of the oxidation reaction from a polar medium to one less polar should therefore lead to a relative stabilisation of the transition state irrespective of the nature of Ar.

Three factors therefore appear to influence the relative reactivities of ring-substituted methyl phenyl sulfoxides: (1) the electronic character of the substituent, which governs the availability of the sulfur lone-pair to the electrophilic oxidant and hence determines the order of reactivities in any solvent; (2) the effect of solvent on the energy of the ground state of the sulfoxides, which is strongly substituent-dependent; and (3) the effect of solvent on the energy of the transition states, which largely depends on the bonding changes occurring at S. These factors combine to produce the relative reactivities illustrated in Fig. 5 and the reduced selectivity observed on transfer to a less polar solvent. They also produce the predominance of −M effects in polar solvents (acetone and aqueous acetone) and, by contrast, of +M effects in less polar 60% v/v hexane in acetone.

In the polar solvents, the effect of substituents is dominated by the ability of −M substituents to impede the electrophilic attack of **1**. The operation of a −M effect serves to increase dipolar positive charge at C(1) whereas the electrophilic attack increases electron-demand at the adjacent S atom. The former effect must impede the latter change and, if solvation is more

effective in stabilising the substituent-induced polarisation in the ground state of the sulfoxide than in stabilisation of the transition state for oxidation, the dominant effect of $-M$ substituents can be understood. It appears that hydrogen bonding is not important in the solvation process, as the $-M$ effect predominates in acetone alone, which at best would form weak H-bonds with the sulfoxidic oxygen and the relative reactivities show only slight decrease in the presence of added water. (In the following paper it is shown that the dominant property in determining the effect of solvent on the rates of oxidation of methyl 4-nitrophenyl sulfoxide in aqueous acetone is its polarity/polarisability). By contrast, in the less polar solvent, the substituent-dependent polarisations caused by M effects of either kind are not as well stabilised by solvation, and ground-state energies are consequently raised. The less polar solvent also facilitates excitation to the transition states for oxidation on account of the decrease in SO bond dipolarity relative to that of the substrates. There is, nevertheless, partial positive charge at S in the transition states that is stabilised by electron-donation from $+M$ substituents accumulating negative charge at C(1), so accounting for their predominance in this medium.

Comparison between sulfides and sulfoxides. In the Introduction it was noted that, on reaction with both hydroperoxidic oxidants and dimethyldioxirane, sulfides and sulfoxides do not follow the reactivity-selectivity principle: although, experimentally, sulfoxides are generally less reactive than sulfides, the oxidants do not discriminate more between substituted sulfoxides than between substituted sulfides. Theoretical studies indicate sulfoxides to be intrinsically *more* reactive than sulfides towards electrophilic oxidants in the gas-phase but that the relative reactivity is inverted by solvation.[35] The discussion above attests to the importance of solvation in determining the reactivity of sulfoxides and the following paper demonstrates the relative reactivity of sulfides and sulfoxides to be solvent-dependent. Why sulfoxides should have a high intrinsic reactivity in the gas phase which is maintained between substituted sulfoxides in solution, leading to the failure of the reactivity-selectivity principle, can be understood qualitatively as follows. The separation of the partial charges of the $S^{\delta+}$–$O^{\delta-}$ bond requires a notional input of energy. Suppose this is compensated by a concomitant stabilisation of the lone-pair orbital on S as a consequence of the increase in the electronegativity of S due to its increased positive charge. The energy of the lone-pair orbital also depends on the substituent. For each sulfoxide there is thus a substituent-dependent 'balance' between the extent of charge separation and the energy level of the lone-pair orbital on S. When the lone-pair orbital interacts with the LUMO of an electrophile on forming a transition state this balance is perturbed. Collapse of the charge separation raises the energy of the lone-pair orbital, hence increasing the strength of its interaction with the LUMO and facilitating the formation of the new bond to the electrophile. The sulfoxide SO bond thus activates the electrophilic attack by providing electron density, and the extent to which it does so is governed by the particular substituent.

Conclusions

1. The Hammett reaction constant found for the oxidation of aryl methyl sulfides by dimethyldioxirane, **1**, in acetone is in good agreement with that previously reported by Murray and co-workers[19] for a smaller data set. The reaction constant was increased two-fold, *i.e.* the selectivity of reaction increased, when the oxidations were carried out in 60% v/v hexane in acetone. Since partial charges separate in the transition state for oxidation of a sulfide by **1** and the sulfoxide reaction product is highly polarised, both the transition state and, particularly, the product will be relatively less well solvated than the reactants in a solvent of lower polarity. A shift of transition state to a position later in the reaction coordinate, with resultant increased selectivity, is therefore consistent with the Hammond postulate.

2. The reaction constant measured when sulfide oxidations were carried out in 80% v/v DMF in acetone was scarcely different from that measured in acetone alone, indicating that increasing the relative permittivity of the solvent does not shift transition states to positions in the reaction coordinate significantly earlier than those in acetone. This is consistent with the extent of transition state dipolarity being maximised for each sulfide in acetone so that, although increasing solvent polarity will stabilise each individual maximally-polarised transition state, there is no differential substituent-dependent stabilisation and the relative rate constants, and hence the reaction constant, remain unchanged.

3. In aqueous acetone mixtures (1% v/v H_2O and 5% v/v H_2O) Hammett reaction constants for oxidation of sulfides were increased (by 57% and 75%, respectively) relative to that in acetone alone. Since the relative permittivities of these solvent mixtures are less than that of 80% v/v DMF in acetone (where the effect was negligible) it is clear that factors specific to the water co-solvent are operative. It is suggested these are solvation of the individual centres of charge: lone-pair donation to $S^{\delta+}$ and hydrogen bonding to $O^{\delta-}$ (*cf.* **6**), which allows a greater extent of charge separation than can occur under the influence of increased relative permittivity alone.

4. Increasing the water content further to 20% by volume results in a change of kinetic behaviour, although the relative permittivity is very similar to that of 80% v/v DMF in acetone. The solvation by water of the separate centres of charge and the raised relative permittivity together enable the electrophilic attack of dimethyldioxirane upon a sulfide to produce an intermediate sulfonium betaine, a process that is rate-determining for sulfides with electron-withdrawing substituents and for which a characteristic Hammett reaction constant of -3.0 can be deduced. There is no evidence of the betaine cyclising to a dioxathietane as reported for sulfide oxidations by (trifluoromethyl)methyldioxirane.[20]

5. The oxidation of aryl methyl sulfoxides to the corresponding sulfones by dimethyldioxirane occurs *via* a single-step concerted mechanism irrespective of the solvent composition. The behaviour of sulfoxides can be understood in terms that stem from their high and variable polarity, arising from their polarised SO bond and its interaction with substituents and solvent. The reaction constant is only slightly diminished (by 11%) between acetone and 20% v/v aqueous acetone as reaction media, which indicates that the substituent effect on the oxidation of sulfoxides to sulfones is rather insensitive to the specific solvating properties of water. Although solvation reduces the reactivity of sulfoxides relative to sulfides, sulfoxides are activated to electrophilic attack by their polarised SO bonds, a fact which accounts for the failure of the reactivity-selectivity principle when they are compared with sulfides reacting with the same electrophile.

Experimental

General

Infra-red spectra, obtained for solutions in CH_2Cl_2, were recorded on an Ati Mattson Genesis Series FTIR instrument. NMR spectra, obtained for solutions in $CDCl_3$, were recorded using a JEOL JNM-EX270 (270 MHz) spectrometer and are referenced to residual $CHCl_3$. GC analysis was performed on a Varian 3000 CX chromatograph served by a Varian Star Workstation 4.5; the column used was an Econocap FFAP column from Alltech (30 m, 0.32 mm, 0.25 μm). For column chromatography, ICN Silica 32–63, 60 Å, was used and thin layer chromatography was performed using DC-Alufolien Kieselgel 60 F_{254} tlc plates supplied by Merck. Data processing for correlation analysis was carried out using SPSS 10 for Windows and the Excel add-in Essential Regression 2.219.[28]

Materials

Solvents (Fisher) were of either analytical or HPLC grade and were used as supplied. Methyl phenyl sulfide and its 4-substituted derivatives were sourced commercially (Aldrich, Fluka or Lancaster) in the highest available purity. Methyl phenyl sulfoxide and sulfone (Aldrich) were further purified by column chromatography (silica, 10% v/v acetone in CH_2Cl_2).

Methyl 3-substituted-phenyl sulfides

Methyl 3-substituted-phenyl sulfides were synthesised from the corresponding anilines by adaptation of the procedure of Oae, Shinhama and Kim[36] to use *tert*-butyl nitrite in place of *tert*-butyl thionitrate. The appropriate aniline (20 mmol) was added to dimethyl disulfide (20 cm³) and the mixture stirred magnetically. After heating to *ca.* 100 °C, *tert*-BuONO (3.10 g, 30 mmol) was added in five portions over 10 min (*Vigorous evolution of N_2!*). After a further 20 min stirring, the mixture was cooled to room temperature and the solvent removed *in vacuo* (*Stench!*). The reaction mixture was purified by column chromatography (silica, 5% v/v diethyl ether in hexane); after rotary evaporation of the bulk of eluting solvent, vestigial amounts were removed by pumping under vacuum at ambient temperature.

3-Methoxyphenyl methyl sulfide

Colourless oil (0.31 g, 10%); *m/z* 154 (100%, M⁺), 121 (47); v_{max}/cm⁻¹(CH_2Cl_2) 2926 (CH) and 1248s (CO); δ_H (270 MHz, CDCl₃) 2.47 (s, 3H), 3.79 (s, 3H), 6.68 (ddd, *J* 8.0, 2.4 and 0.7, 1H), 6.75–6.86 (m, 2H) and 7.20 (t, *J* 8.0, 1H); δ_C (67.9 MHz, CDCl₃) 15.7, 55.2, 110.5, 112.1, 118.7, 129.6, 139.8 and 159.8.[37,38]

3-Chlorophenyl methyl sulfide

Colourless oil (1.17 g, 37%); *m/z* 158 (100%, M⁺), 143 (18), 125 (33) and 108 (32); v_{max}/cm⁻¹(CH_2Cl_2) 2926 (CH) and 768 (CCl); δ_H (270 MHz, CDCl₃) 2.49, (s, 3H) and 7.05–7.27 (m, 4H); δ_C (67.9 MHz, CDCl₃) 15.5, 124.4, 124.9, 125.7, 129.7, 134.7 and 146.6.[38]

3-(Trifluoromethyl)phenyl methyl sulfide

Colourless oil (2.20 g, 57%); *m/z* 192 (100%, M⁺), 177 (13), and 159 (18); v_{max}/cm⁻¹(CH_2Cl_2) 2926 (CH), 1169s and 1105s (CF); δ_H (270 MHz, CDCl₃) 2.52 (s, 3H) and 7.35–7.54 (m, 4H); δ_C (67.9 MHz, CDCl₃) 16.4, 122.4, 122.8, 124.4 (q, *J* 249.9, 1C), 130.0, 130.3, 133.2 (q, *J* 33.3, 1C) and 141.0.[39]

3-Cyanophenyl methyl sulfide

Colourless solid (1.64 g, 55%), mp 39.8–41.0 °C (lit.[40] 40 °C); *m/z* 149 (100%, M⁺), 134 (22), 116 (30); v_{max}/cm⁻¹(CH_2Cl_2) 2926 (CH) and 2231s C≡N; δ_H (270 MHz, CDCl₃) 2.50 (s, 3H), and 7.31–7.48 (m, 4H); δ_C (67.9 MHz, CDCl₃) 15.3, 113.0, 118.4, 128.2, 128.7, 129.2, 130.3 and 140.9.

Methyl 3-nitrophenyl sulfide

Pale yellow solid (2.03 g, 60%), mp 89.1–90.3 °C (lit.[41] 90 °C); *m/z* 169 (100%, M⁺), 123 (30), 108 (31) and 45 (44); v_{max}/cm⁻¹(CH_2Cl_2) 2952 (CH), 1519s and 1349s (NO_2); δ_H (270 MHz, CDCl₃) 2.54 (s, 3H), 7.42 (t, *J* 7.7, 1H), 7.52 (ddd, *J* 7.9, 1.7 and 1.2, 1H), 7.96 (ddd, *J* 7.9, 2.2, 1.0, 1H) and 8.03 (t, *J* 1.9, 1H); δ_C (67.9 MHz, CDCl₃) 15.3, 119.6, 120.0, 129.3, 131.9, 141.5 and 148.5.[42]

Oxidations

Sulfoxides and sulfones were prepared by oxidation of the corresponding sulfides in procedures which differed only in the stoichiometric proportion of oxidant used. The sulfide (*ca.* 12 mmol) was oxidised in chilled (ice-water bath) aqueous acetone (50% v/v, 40 cm³) by addition, with stirring, of Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) (0.55 or 1.5 mol equiv. depending on the product required). Reactions were normally stirred overnight. On completion, the reaction mixtures were diluted with water (30 cm³) and extracted with CH_2Cl_2 (3 × 30 cm³). The extracts were washed with water (50 cm³) and dried (Na_2SO_4). Evaporation of the solvent gave the required products, which were purified by column chromatography. In all cases gradient elution was used; initially CH_2Cl_2 (100%), and finally acetone (10% v/v) in CH_2Cl_2.

3-Methoxyphenyl methyl sulfoxide

Colourless oil (72%); *m/z* 170 (61%, M⁺), 155 (100), 92 (25) and 76 (26); v_{max}/cm⁻¹(CH_2Cl_2) 3051 and 2966 (CH), 1250 (CO) and 1068s (SO); δ_H (270 MHz, CDCl₃) 2.76 (s, 3H), 3.82 (s, 3H), 6.96 (ddd, *J* 8.2, 2.4 and 0.7, 1H), 7.08 (dd, *J* 7.7, and 2.4, 1H), 7.10–7.25 (m, 1H) and 7.36 (t, *J* 8.0, 1H); δ_C (67.9 MHz, CDCl₃) 43.9, 55.4, 107.8, 115.4, 117.2, 130.2, 147.0 and 160.3.[37]

3-Methoxyphenyl methyl sulfone

Colourless solid (83%), mp 46.1–47.3 °C (lit.[43] 47 °C); *m/z* 186 (39%, M⁺), 171 (46) and 107 (100); v_{max}/cm⁻¹(CH_2Cl_2) 3066 and 2965 (CH), 1322s and 1152s (SO_2); δ_H (270 MHz, CDCl₃) 2.96 (s, 3H), 3.85 (s, 3H), 7.05 (t, *J* 8.1, 1H), 7.16 (dt, *J* 7.9 and 2.1, 1H) 7.28 (dt, 7.9 and 1.9, 1H), and 7.46 (t, *J* 2.1, 1H); δ_C (67.9 MHz, CDCl₃) 44.3, 57.4, 109.8, 115.4, 118.6, 131.2, 148.0 and 161.2.[37]

3-Chlorophenyl methyl sulfoxide

Colourless solid (86%), mp 42.2–43.4 °C (lit.[44] 43–44 °C); m/z 174 (76%, M[+]), 159 (100), 131 (41), 111 (37), 84 (82) and 74 (42); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3052 and 2983 (CH), 1089s (SO) and 782 m (CCl); δ_H (270 MHz, CDCl$_3$) 2.69 (s, 3H), 7.40–7.48 (m, 3H) and 7.62 (m, 1H); δ_C (67.9 MHz, CDCl$_3$) 44.6, 122.2, 124.2, 131.2, 131.8, 136.3 and 148.4.[45]

3-Chlorophenyl methyl sulfone

Colourless solid (54%), mp 105.2–106.4 °C (lit.[46] 106 °C); m/z 190 (63%, M[+]), 175 (56), 128 (57), 111 (100) and 74 (56); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3066 and 2929 (CH), 1321s and 1157s (SO$_2$); δ_H (270 MHz, CDCl$_3$) 3.05 (3H), 7.51 (t, J 7.7, 1H), 7.62 (ddd, J 8.0, 2.2 and 1.2, 1H), 7.82 (ddd, J 7.8, 2.9 and 1.2, 1H) and 7.91 (t, J 1.9, 1H); δ_C (67.9 MHz, CDCl$_3$) 45.0, 126.1, 128.2, 131.4, 134.5, 136.2 and 142.8.

3-(Trifluoromethyl)phenyl methyl sulfoxide

Colourless oil (58%); m/z 208 (87%, M[+]), 193 (100), 165 (28), 145 (50) and 75 (26); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3062 and 2983 (CH), 1168s and 1105s (CF) and 1091s (SO); δ_H (270 MHz, CDCl$_3$) 2.72 (s, 3H), 7.60–7.79 (m, 3H) and 7.89 (t, J 0.7, 1H); δ_C (67.9 MHz, CDCl$_3$) 43.8, 120.5, 123.9 (q, J 244.4, 1C), 126.7, 127.6, 128.8, 131.6 (q, J 27.4, 1C) and 147.2.[39]

3-(Trifluoromethyl)phenyl methyl sulfone

Colourless solid (67%), mp 58.3–59.5 °C (lit.[47] 58–60 °C); m/z 224 (17%, M[+]), 209 (19), 162 (42) and 145 (100); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3019 and 2967 (CH), 1327s and 1153s (SO$_2$); δ_H (270 MHz, CDCl$_3$) 3.10 (s, 3H), 7.75 (t, J 7.8, 1H), 7.93 (d, J 7.7, 1H) and 8.13–8.22 (m, 2H); δ_C (67.9 MHz, CDCl$_3$) 44.4, 123.7 (q, J 240.3, 1C), 124.5, 130.2, 130.5, 130.7, 133.2 (m, 1C), 141.5.[47]

3-Cyanophenyl methyl sulfoxide

Colourless solid (72%), mp 69.0–69.8 °C (lit.[48] 69–70 °C); m/z 165 (85%, M[+]), 150 (100); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 2983 (CH), 2235s (C≡N) and 1080s (SO); δ_H (270 MHz, CDCl$_3$) 2.76 (s, 3H), 7.67 (t, J 7.7, 1H)), 7.79 (dt, J 7.7 and 1.2, 1H), 7.86 (dt, J 7.7 and 1.5, 1H) and 7.95 (t, J 1.7, 1H); δ_C (67.9 MHz, CDCl$_3$) 43.9, 113.8, 117.5, 127.2, 127.6, 130.2, 134.3 and 147.8.

3-Cyanophenyl methyl sulfone

Colourless solid (87%), mp 100.9–101.6 °C (lit.[49] 101–103 °C); m/z 181 (28%, M[+]), 166 (37), 119 (53), and 102 (100); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3066 and 2929 (CH), 2237 (C≡N), 1327s and 1149s (SO$_2$); δ_H (270 MHz, CDCl$_3$) 3.09 (s, 3H), 7.74 (t, J 7.8, 1H), 7.94 (dt, J 7.8 and 1.5, 1H), 8.17 (dt, J 7.8 and 1.0, 1H) and 8.23 (t, J 0.7, 1H); δ_C (67.9 MHz, CDCl$_3$) 44.4, 114.0, 116.8, 130.5, 131.1, 131.4, 136.8 and 142.0.

Methyl 3-nitrophenyl sulfoxide

Pale yellow solid (72%), mp 114.3–115.7 °C (lit.[50] 115–116 °C); m/z 185 (96%, M[+]), 170 (100), 139 (12), 124 (40), 75 (27) and 48 (29); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3068 and 2873 (CH), 1535s and 1351s (NO$_2$) and 1076s (SO); δ_H (270 MHz, CDCl$_3$) 2.79 (s, 3H), 7.75 (t,

J 7.7, 1H), 7.99 (ddd, J 7.7, 1.5 and 1, 1H), 8.34 (ddd, J 8.2, 2.4 and 1.2, 1H) and 8.49 (t, J 1.9, 1H); δ_C (67.9 MHz, CDCl$_3$) 43.9, 118.9, 125.7, 129.2, 130.6, 148.5 and 148.6.

Methyl 3-nitrophenyl sulfone

Pale yellow solid (82%), mp 147.5–148.2 °C (lit.[46] 147–148 °C); m/z 201 (33%, M[+]), 186 (39), 139 (100), and 122 (60); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3080 and 2987 (CH), 1537s and 1353s (NO$_2$), 1327s and 1161s (SO$_2$); δ_H (270 MHz, CDCl$_3$) 3.14 (s, 1H), 7.83 (t, J 7.7, 1H), 8.30 (dt, J 7.7 and 1.2, 1H), 8.53 (ddd, J 8.2, 2.2 and 1.2, 1H) and 8,81 (t, J 1.7, 1H); δ_C (67.9 MHz, CDCl$_3$) 44.3, 122.9, 128.3, 130.9, 133.0, 142.3 and 148.7.

4-Methoxy-3-methylphenyl methyl sulfoxide

Colourless oil (85%), m/z 184 (16%, M[+]), 169 (100); v_{max}/cm^{-1} (CH$_2$Cl$_2$) 3049 and 2966 (CH), 1255s (CO) and 1047s (SO); δ_H (270 MHz, CDCl$_3$) 2.20 (s, 3H), 2.65 (s, 3H), 3.81 (s, 3H), 6.86 (d, J 8.1, 1H), and 7.30–7.45 (m, 2H): δ_C (67.9 MHz, CDCl$_3$) 16.3, 44.0, 55.5, 110.2, 123.1, 125.6, 128.4, 135.8 and 160.0.[51]

4-Methoxy-3-methylphenyl methyl sulfone

Colourless solid (68%), mp 64.2–64.9 °C (lit.[52] 64–65 °C); m/z 200 (95%, M[+]), 185 (100), 137 (51), 121 (84), 91 (95) and 77 (34); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 2969 (CH), 1307s and 1130s (SO$_2$) and 1260 (CO); δ_H (270 MHz, CDCl$_3$) 2.20 (s, 3H), 2.96 (s, 3H), 3.82 (s, 3H), 6.86 (d, J 8.9, 1H), 7.62 (dd, J 2.2 and 1.6, 1H) and 7.70 (d, J 8.6, 1H); δ_C (67.9 MHz, CDCl$_3$) 16.2, 44.9, 55.7, 109.7, 127.2, 128.1, 129.4, 131.5 and 161.9.

4-Methoxyphenyl methyl sulfoxide

Colourless solid (65%), mp 42.0–43.6 °C (lit.[44] 44–45 °C); m/z 170 (15%, M[+]) and 155 (100); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3050 and 2966 (CH), 1250s (CO) and 1043 (SO); δ_H (270 MHz, CDCl$_3$) 2.70 (s, 3H), 3.85 (s, 3H), 7.03 (d, J 8.7, 2H) and 7.70 (d, J 8.7, 2H): δ_C (67.9 MHz, CDCl$_3$) 43.8, 55.4, 114.7 (2C), 125.3 (2C), 136.4 and 161.8.[53,54]

4-Methoxyphenyl methyl sulfone

Colourless solid (76%), mp 118.9–119.8 °C (lit.[47] 118–120 °C); m/z 186 (84%, M[+]), 171 (100), 123 (45), 107 (66), 92 (44) and 77 (65); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3056 and 2842 (CH), 1319 and 1145 (SO$_2$) and 1298 (CO); δ_H (270 MHz, CDCl$_3$) 2.99 (s, 3H), 3.85 (s, 3H), 6.98 (d, J 8.7, 2H) and 7.83 (d, J 8.7, 2H); δ_C (67.9 MHz, CDCl$_3$) 44.7, 55.6, 114.4 (2C), 129.4 (2C), 132.1 and 163.6.[47,55]

Methyl 4-methylphenyl sulfoxide

Colourless solid (68%), mp 41.9–42.9 °C (lit.[45] 40 °C); m/z 154 (54%, M[+]), 139 (100) and 91 (30); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3041 and 2981 (CH) and 1045 (SO); δ_H (270 MHz, CDCl$_3$) 2.41 (s, 3H), 2.70 (s, 3H), 7.33 (d, J 8.0, 2H) and 7.54 (d, J 8.0, 2H); δ_C (67.9 MHz, CDCl$_3$) 21.2, 43.8, 123.2 (2C), 129.8 (2C), 141.3 and 142.3.[45,53,54,56]

Methyl 4-methylphenyl sulfone

Colourless solid (86%), mp 86.1–86.7 °C (lit.[47] 85–87 °C); m/z 170 (35%, M[+]), 155 (36), 107 (30), and 91 (100); v_{max}/cm^{-1}(CH$_2$Cl$_2$)

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3056 and 2929 (CH), 1315s and 1149s (SO$_2$); δ_H (270 MHz, CDCl$_3$) 2.41 (s, 3H), 3.00 (s, 3H), 7.33 (d, J, 8.3, 2H), and 7.79 (d, J, 8.3, 2H); δ_C (67.9 MHz, CDCl$_3$) 21.5, 44.5, 127.2 (2C), 129.8 (2C), 137.5 and 144.5.[47]

4-Chlorophenyl methyl sulfoxide

Colourless solid (64%), mp 45.0–46.3 °C (lit.[44] 46–47 °C); m/z 174 (57%, M$^+$), 159 (100), 131 (27), 111 (22) and 75 (33); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 2981 (CH) and 1053s (SO); δ_H (270 MHz, CDCl$_3$) 2.73 (s, 3H), 7.51 (d, J 8.4, 2H) and 7.61 (d, J 8.4, 2H); δ_C (67.9 MHz, CDCl$_3$) 43.9, 124.8 (2C), 129.5 (2C), 137.0 and 144.1.[45,54,56]

4-Chlorophenyl methyl sulfone

Colourless solid (67%), mp 96.5–96.9 °C (lit.[57] 97 °C); m/z 190 (35%, M$^+$), 175 (45), 12 (37), 111 (100) and 75 (45); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3056 and 2934 (CH), 1319s and 1155s (SO$_2$) and 775 (CCl); δ_H (270 MHz, CDCl$_3$) 3.04 (s, 3H), 7.53 (d, J 8.5, 2H), 7.62 (d, J 8.5, 2H); δ_C (67.9 MHz, CDCl$_3$) 44.4, 128.8 (2C), 129.6 (2C), 138.9 and 140.4.[58]

4-Acetylphenyl methyl sulfoxide

Colourless solid (82%), mp 107.1–108.0 °C (lit.[56] 110 °C); m/z 182 (100%, M$^+$), 167 (98), 152 (75) and 139 (20); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3006 and 2979 (CH), 1689s (C=O) and 1052s (SO); δ_H (270 MHz, CDCl$_3$) 2.57 (s, 3H), 2.69 (s, 3H), 7.67 (d, J 8.6, 2H) and 8.02 (d, J 8.6, 2H); δ_C (67.9 MHz, CDCl$_3$) 26.6, 43.6, 123.5 (2C), 128.9 (2C), 138.8, 150.7 and 196.9.[56]

4-Acetylphenyl methyl sulfone

Colourless solid (73%), mp 128.9–129.3 °C (lit.[46] 127–128 °C); m/z 198 (22%, M$^+$), 183 (100) and 121 (30); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3064 (CH), 1693s (C=O), 1321s and 1153s (SO$_2$); δ_H (270 MHz, CDCl$_3$) 2.63 (s, 3H), 3.05 (s, 3H), 8.00 (d, J 8.6, 2H) and 8.09 (d, J 8.6, 2H); δ_C (67.9 MHz, CDCl$_3$) 26.8, 44.1, 127.7 (2C), 129.0 (2C), 140.7, 144.0 and 196.6.[55]

4-Cyanophenyl methyl sulfoxide

Colourless solid (58%), mp 86.3–87.9 °C (lit.[59] 86–88 °C); m/z 165 (73%, M$^+$), 150 (100), 122 (43) and 102 (48); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 2986 (CH), 2233s (C≡N) and 1075s (SO); δ_H (270 MHz, CDCl$_3$) 2.79 (s, 3H) and 7.75–7.95 (m, 4H); δ_C (67.9 MHz, CDCl$_3$) 43.6, 114.6, 117.6, 124.2 (2H), 132.8 (2H) and 151.3.[45]

4-Cyanophenyl methyl sulfone

Colourless solid (68%), mp 140.0–142.1 °C (lit.[47] 142–143 °C); m/z 181 (26%, M$^+$), 166 (28), 119 (75) and 102 (100); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3062 and 2929 (CH), 2235 (C≡N), 1322s and 1151s (SO$_2$); δ_H (270 MHz, CDCl$_3$) 3.08 (s, 1H), 7.88 (d, J 8.3, 2H) and 8.07 (d, J 8.3, 2H); δ_C (67.9 MHz, CDCl$_3$) 44.5, 117.4, 117.9, 128.5 (2C), 133.6 (2C) and 144.7.[47]

Methyl 4-nitrophenyl sulfoxide

Pale yellow solid (82%), mp 150.6–151.9 °C (lit.[60] 151–152 °C); m/z 185 (100, M$^+$), 170 (52) and 50 (41); v_{max}/cm^{-1}(CH$_2$Cl$_2$)

3099 and 2863 (CH), 1529s and 1346s (NO$_2$) and 1056s (SO); δ_H (270 MHz, CDCl$_3$) 2.78 (s, 3H), 7.82 (d, J 8.5, 2H) and 8.37 (d, J 8.5, 2H); δ_C (67.9 MHz, CDCl$_3$) 43.7, 124.4 (2H), 126.6 (2C), 149.5 and 153.2.[45,53,60]

Methyl 4-nitrophenyl sulfone

Pale yellow solid (74%), mp 141.5–141.8 °C (lit.[60] 142–144 °C); m/z 201 (31%, M$^+$), 186 (35), 139 (100) and 122 (60); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 3066 and 2967 (CH), 1535s and 1349s (NO$_2$), 1326 m and 1157s (SO$_2$); δ_H (270 MHz, CDCl$_3$) 3.12 (s, 3H), 8.16 (d, J 8.9, 2H) and 8.42 (d, J 8.9, 2H); δ_C (67.9 MHz, CDCl$_3$) 44.6, 124.9 (2C), 1.29.3 (2C), 164.2 and 151.2.[55,60]

Dimethyldioxirane, 1

The method adopted was that of Adam and co-workers.[61] Water (60 cm^3), acetone (50 cm^3) and NaHCO$_3$ (14.5 g, 0.17 mol) were added to a 1000 cm^3 two-necked, round-bottomed reaction flask equipped with a magnetic stirrer, and cooled (to 5–10 °C) by immersion in an ice-water bath. The reaction flask was connected by means of a U-tube to a Dewar condenser and thence to a two-necked receiving flask. The condenser and receiving flask were cooled to −78 °C by means of dry ice/acetone. With cooling and vigorous stirring, Oxone$^®$ (2KHSO$_5$·KHSO$_4$·K$_2$SO$_4$) (30 g, 48.7 mmol) was added in 5 portions at 3 min intervals. Three min after the last addition, the ice-water bath was removed, a moderate vacuum (80–100 Torr) was applied and, with vigorous stirring, the reaction mixture was distilled. Typically, 20–30 cm^3 of pale yellow dimethyldioxirane in acetone distillate was collected (*Caution: strained peroxide—but dilute and no hazards reported*). The concentration of **1** (0.04–0.10 mol dm^{-3}, 2–6%) was determined by oxidation of MeSPh and GC analysis of the MeS(O)Ph produced using 1,4-dibromobenzene as internal standard. The dried (Na$_2$SO$_4$) dimethyldioxirane/acetone solution was stored at −20 °C.

Competitive oxidations

Stock solutions in acetone of each of the reactant sulfides and sulfoxides and their respective product sulfoxides and sulfones were prepared freshly as required. Gas-chromatographic response factors were determined for each product using 1,4-dibromobenzene as internal standard. The chromatographic conditions for both the calibration and the analysis of reaction products employed the earlier mentioned FFAP capillary column with temperature programming: 1 min at 60 °C then increasing to 230 °C (the maximum for the column) at 16 °C min^{-1}. For all analyses the split injection mode was used with, normally, a 1 μl injection volume; the exceptions were mixtures containing the 3- and 4-nitrophenyl sulfoxides and sulfones where 3 μl was used to improve the response. For the competitive oxidations, measured volumes—around 1 cm^3 of stock solutions of the competing substrates in acetone (8×10^{-3} to 2×10^{-2} mol dm^{-3})—were added to a small reaction flask such that there was a 1–1.5-fold molar excess of the less reactive compound; in mixed solvent studies the co-solvent was added at this juncture. The mixtures were equilibrated at 20.0 ± 0.1 °C for 15 min. Standardised dimethyldioxirane solution (see above) was diluted to *ca.* 5×10^{-3} mol dm^{-3} with the appropriate solvent and also thermally equilibrated. An aliquot (0.1 cm^3) was

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added to the substrate mixture, which was shaken vigorously for *ca.* 10 s and then allowed to stand for 3 min before analysis. Each competitive oxidation was repeated three to five (*n*) times and the mean value of k_X/k_H and its standard deviation s_{mean} found from the molar product ratios and the known initial molar ratios (r_0) of competing substrates [see eqn (1)]. The standard error of the mean ($s_{mean}/\sqrt{n}$) was multiplied by the appropriate Student's *t*-factor for ($n - 1$) degrees of freedom to give the 95% confidence intervals.

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27 σ_R^0 measures the resonance component of σ_p^0 and σ_m^0, which were determined on systems lacking conjugation between the reaction centre

and the substituent, such as phenylethanoic acids and 3-substituted benzene derivatives (see ref. 23).
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