Rates of Addition of Phenylthio Radicals to Vinyl Sulphide, Sulphoxide, Sulphone, and Ether Groups

Osamu Ito,* Shigeru Furuya, and Minoru Matsuda
Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Katahira, Sendai, 980 Japan

The rate constants for addition of *para*-substituted phenylthio radicals to vinyl sulphide, sulphoxide, sulphone, and ether groups have been determined by flash photolysis. The polar nature of the vinyl monomers was examined by constructing Hammett plots *vs.* σ^+ of the substituents on the phenylthio radicals; the reaction constants (ρ^+) are 2.0—2.2 for sulphides, 1.7—1.8 for ethers, 1.2 for sulphoxide, and 0.8 for sulphone, suggesting that the ρ^+ values increase with the electron density of the double bond. For phenylthio radical, the rate constants (in $dm^3 \, mol^{-1} \, s^{-1}$) of the vinyl sulphides [(2.6—4.8) × 10^6] are greater than those of the vinyl ethers [(0.8—1.0) × 10^5], the sulphoxide (1.4 × 10^4), and the sulphone (1.6 × 10^4), suggesting that stabilization of the carbon-centred radical adduct is a characteristic of the adjacent sulphide group.

The effect of the oxidation state of sulphur on the polymerization reactivity of vinyl monomers attached to sulphur groups can be estimated from *Q*–*e* values calculated from copolymer compositions,[1-3] where *e* refers to the electron density of the double bond and *Q* to the stability of the propagating radical [$-CH_2C^{\cdot}H(SO_nR)$]. The rates for hydrogen abstraction producing the carbon-centred radical substituted by the sulphur groups are compatible with observed *Q* values.[4] These findings, however, are derived from relative rate parameters; it is desirable to compare these findings with those devived from absolute rate parameters.

We have applied the flash photolysis technique to obtain absolute rates for the addition of phenylthio radicals to vinyl monomers substituted by sulphide, sulphoxide, sulphone, and ether groups. Although the addition of the thio radicals is reversible, the absolute rate constants and relative equilibrium constants can be obtained by the addition of a selective radical trap which reacts only with the adduct radical in the product. Thus, it becomes possible to discuss rate parameters on the basis of the equilibrium parameters which correlate with the stability of the adduct radical.[5,6] In order to estimate polar effects, the substituent effects of the phenylthio radicals have also been examined.

Results and Discussion

The flash photodecomposition of diphenyl disulphides in benzene solution generates transient absorption spectra in the range 460—525 nm which are attributable to *para*-substituted phenylthio radicals ($PhS^{\cdot}$); the corresponding thiols give similar absorption bands.[7] The transient bands begin to decay after the flash with second-order kinetics, suggesting that the thio radicals return to disulphides by recombination. The reactivity of the phenylthio radicals towards molecular oxygen was found to be low: the decay rate was not accelerated on addition of oxygen. The low hydrogen-abstraction ability of the phenylthio radicals was also confirmed from the decay profiles in hydrogen-donor solvents.[5] Since the slopes of the second-order plots, *i.e.* the ratios of the recombination rate constants (k_r) to the molar extinction coefficients (ε) of the phenylthio radicals, depend upon solvent viscosity, recombination is determined by the diffusion-controlled limit;[8] thus, the initial concentrations of the phenylthio radicals generated by one flash exposure can be calculated to be *ca.* 10^{-6} mol dm^{-3} by substituting the diffusion-controlled rate constant calculated from the Debye equation.[9]

Figure 1 shows the decay profiles of *p*-t-butylphenylthio radical in the presence of phenyl vinyl sulphide. In degassed solution the decay rate of the thio radical was not accelerated by the addition of the vinyl sulphide (curve b) in comparison with that in the absence of the vinyl sulphide (curve a). Only when both oxygen and the vinyl sulphide coexist are the decay rates accelerated, and the decay kinetics changed to first order (curves c—f); decay rates increase with concentrations of both species. This suggests that the addition of the phenylthio radicals is reversible and that oxygen acts as a selective radical trap for the carbon-centred radical adduct as shown in the Scheme. Addition of phenylthio radicals to alkenes is

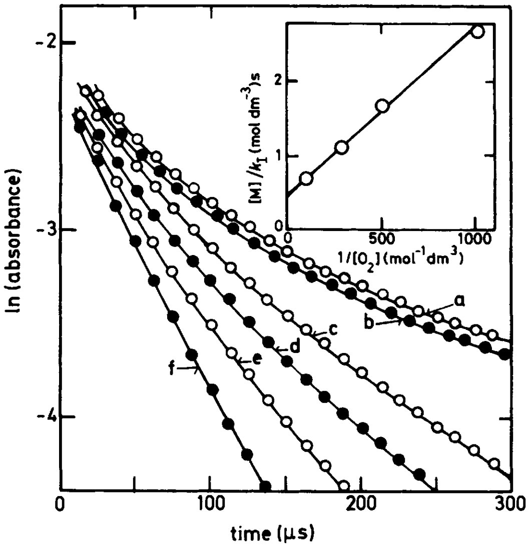


Figure 1. The effect of oxygen concentrations on the first-order plots for decay of the *p*-t-butylphenylthio radical (at 505 nm) generated by the flash photodecomposition of the disulphide (10^{-4} mol dm^{-3}) in benzene at 23 °C: (*a*) in degassed solution, (*b*) in degassed solution in the presence of phenyl vinyl sulphide (9.0 × 10^{-3} mol dm^{-3}), (*c*) with added O_2 concentration 1.0 × 10^{-3}, (*d*) 2.1 × 10^{-3}, (*e*) 3.4 × 10^{-3}, and (*f*) 9.5 × 10^{-3} mol dm^{-3}. Insert: Plots of equation (3)

$$p\text{-}XC_6H_4S^{\cdot} + CH_2{=}CHY \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} p\text{-}XC_6H_4SCH_2\dot{C}HY \xrightarrow[+[O_2]]{k_2} \text{peroxyl radical}$$

Scheme.

Table 1. Values of k_1 (in dm^3 mol^{-1} s^{-1}) and Kk_2 (in dm^6 mol^{-2} s^{-1}) for the reactions of p-$XC_6H_4S^\cdot$ with vinyl sulphides in benzene at 23 °C

		Ethyl vinyl sulphide		Phenyl vinyl sulphide	
X	$\lambda_{max.}$/nm	$10^{-5}k_1$	$10^{-9}Kk_2$	$10^{-5}k_1$	$10^{-9}Kk_2$
Br	515	790	3.7	170	3.2
Cl	515	620	3.9	150	2.5
H	495	260	3.4	48	1.7
Bu^t	505	57	0.76	22	0.56
CH_3	505	61	0.72	17	0.58
OCH_3	525	4.0	0.038	2.2	0.030

Estimated errors ±10%.

Table 2. Values of k_1 and Kk_2 for vinyl ethers in benzene at 23 °C

		Ethyl vinyl ether		Phenyl vinyl ether	
X	σ^+	$10^{-5}k_1$	$10^{-7}Kk_2$	$10^{-5}k_1$	$10^{-7}Kk_2$
Br	0.15	1.8	2.9	2.5	2.9
Cl	0.114	1.1	6.6	2.6	2.3
H	0.0	0.76	2.6	1.0	1.6
Bu^t	−0.256	0.24	0.74	0.65	0.28
CH_3	−0.311	0.19	0.76	0.69	0.33
OCH_3	−0.778	0.045	0.14	0.041	0.09

Table 3. Values of k_1 and Kk_2 for phenyl vinyl sulphoxide and ethyl vinyl sulphone

	Phenyl vinyl sulphoxide		Ethyl vinyl sulphone	
X	$10^{-5}k_1$	$10^{-7}Kk_2$	$10^{-5}k_1$	$10^{-7}Kk_2$
Br	0.42	1.3	0.37	1.3
Cl	0.36	1.2	0.26	0.92
H	0.14	0.97	0.16	0.40
Bu^t	0.08	0.22	0.15	0.20
CH_3	0.08	0.20	0.15	0.25
OCH_3	0.03		0.05	

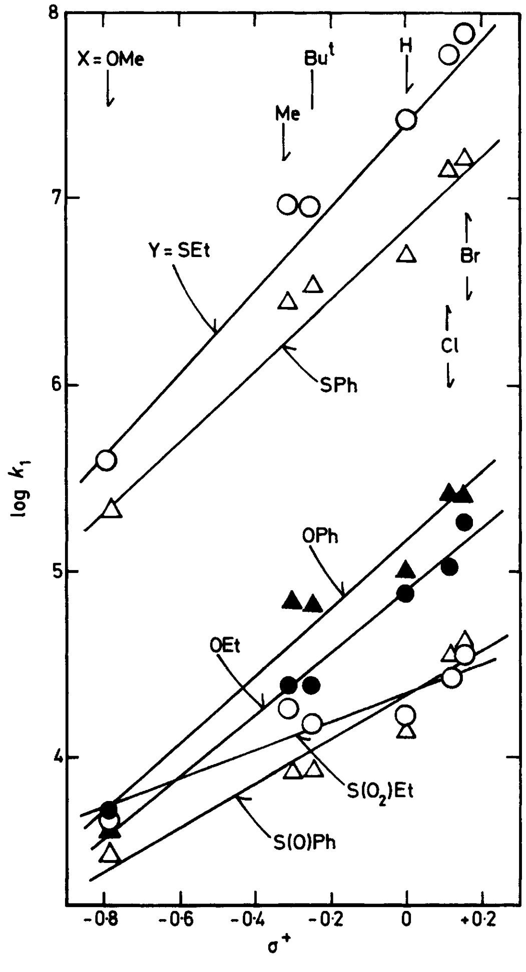


Figure 2. The Hammett plots of log k_1 *vs.* σ^+ of X for the reaction of p-$XC_6H_4S\cdot$ with CH_2=CHY

known to be anti-Markovnikov; the high reactivity of oxygen towards the carbon-centred radicals is also well known and the resulting peroxy compounds have been identified by Oswald *et al.*[10]

Under our experimental conditions, with concentrations of both vinyl monomer (10^{-3}—10^{-1} mol dm^{-3}) and oxygen (10^{-3}—10^{-2} mol dm^{-3}) in large excess of that of the thio radical (*ca.* 10^{-6} mol dm^{-3}), the pseudo-first-order relation can be expected to hold. When decay kinetics are mixed-order, *i.e.* first order ($k_1[PhS^\cdot]$) and second order ($k_r[PhS^\cdot]^2$), the first-order parts can be separated by a graphic method or by computer simulation using $2k_r/\varepsilon$ values estimated from the second-order plots in the absence of vinyl monomer.[5,11,12] The first-order rate constants thus estimated can be expressed as in equation (2), which is derived from the rate expression (1) by assuming a steady-state concentration of the carbon-centred radical adduct. Equation (3) can be derived from the reciprocal of equation (2).[5]

$$-d[PhS^\cdot]/dt = 2k_r[PhS^\cdot]^2 + k_1[PhS^\cdot][CH_2{=}CHY] - k_{-1}[PhSCH_2\dot{C}HY] \quad (1)$$

$$k_1 = k_1\{1 - k_{-1}/(k_{-1} + k_2[O_2])\}[CH_2{=}CHY] \quad (2)$$

$$[CH_2{=}CHY]/k_1 = 1/k_1 + k_{-1}/k_1k_2[O_2] \quad (3)$$

The insert in Figure 1 shows the plot of equation (3); a straight line is obtained. From the intercept, the absolute addition rate constant (k_1) can be directly estimated. The slope yields k_{-1}/k_1k_2, from which the equilibrium constant ($K = k_1/k_{-1}$) is estimated in the form Kk_2. For other reaction systems the rate parameters are obtained in a similar manner. The k_1 and Kk_2 values thus obtained are summarized in Table 1 for vinyl sulphides, in Table 2 for vinyl ethers, and in Table 3 for vinyl sulphoxide and sulphone. The backward rate constants (k_{-1}) are estimated in the form k_{-1}/k_2 from k_1/Kk_2.

Assuming $k_2 = 10^9$ dm^3 mol^{-1} s^{-1},[13] the K and k_{-1} values are calculated to be 10^{-3}—10 dm^3 mol^{-1} and 10^6—10^7 s^{-1}, respectively. The k_{-1} values suggest that the backward reactions occur within *ca.* 1 μs, which is shorter than the flash-duration of the xenon-flash lamp used in this study (*ca.* 10 μs); our finding that the decay curves a and b in Figure 1 are practically identical indicates that the equilibrium in the Scheme is established during the flash duration. This method was first reported by the present authors,[5] and recently confirmed by Kuntz *et al.*[14]

Hammett plots of log k_1 *vs.* σ of the *para*-substituents of the phenylthio radicals show upward curvatures, suggesting that the substituent effect on log k_1 arises from both inductive and resonance effects, as many investigators have found for radical addition reactions.[15–19] Hammett plots *vs.* σ^+, however, show linear correlations as seen in Figure 2; the substituent constant,

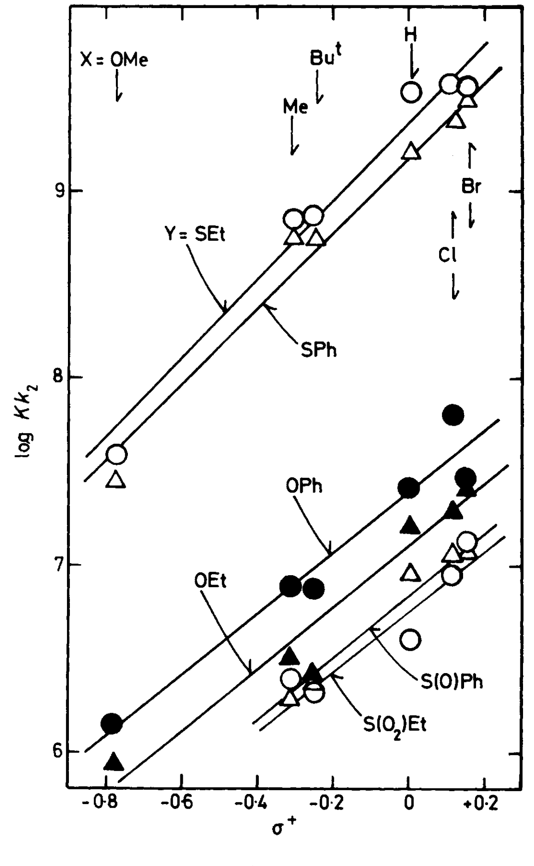


Figure 3. The Hammett plots of log Kk_2 *vs.* σ^+ of X

Table 4. Observed $\rho^+(k_1)$ and $\rho^+(Kk_2)$ for $CH_2=CHY$

Y =	SEt	SPh	OEt	OPh	S(O)Ph	S(O$_2$)Et
$\rho^+(k_1)$	2.23	1.99	1.67	1.84	1.20	0.81
$\rho^+(Kk_2)$	2.09	2.04	1.65	1.73	1.62	1.56
e [a]	−1.2	−1.4	−1.2	−1.2	0.69	1.2
Q [a]	0.37	0.34	0.03	0.08	0.13	0.07

[a] Ref. 22.

σ^+, may contain both inductive and resonance factors in the cases of reactions of phenylthio radicals.[20] The slopes yield the reaction constants [$\rho^+(k_1)$] which are summarized in Table 4; the $\rho^+(k_1)$ values vary with the vinyl monomer. The $\rho^+(k_1)$ values are a measure of the polar nature of the reactions. The difference in reactivities amongst the vinyl monomers can be appreciated from the height of the lines in Figure 2; this is one of the advantages of using Hammett plots of the absolute rates.

Figure 3 shows the Hammett plots of log Kk_2 *vs.* σ^+ for each vinyl monomer; linear correlations are seen. The variation in the slopes is rather small; the $\rho^+(Kk_2)$ values are in the range 2.1—1.6 (Table 4). If we assume that the k_2 values are invariant with the substituent X, the positive $\rho^+(Kk_2)$ values suggest that the reaction for each vinyl monomer with a phenylthio radical having an electron-withdrawing substituent is more exothermic than in the case of an electron-donating substituent. We can also assume that the thermodynamic stabilities of the carbon-centred radical adducts (p-$XC_6H_4SCH_2\dot{C}HY$) are invariant with the change of the substituent X when Y is the same, because of the intermediacy of one methylene bond from the radical centre. Therefore, the $\rho^+(Kk_2)$ values observed (Figure 3) are attributed to the substituent effect of the thermodynamic stabilities of the phenylthio radicals in the reactant; from this effect, some part of the substituent effect in the reactivities arises from the linear free-energy relationship. In addition, there may be some contribution of the polar transition state to the reactivities. Thus, the substituent effect in the reactivities can be expressed by both terms as shown in equations (4) and (5), where α ($0 < \alpha < 1$) is a coefficient of the linear free-energy relationship and γ refers to the contribution of the polar transition state. When there is charge transfer in the transition state (CTTS) from the double bond of vinyl monomer to the thio radical, the sign of $\gamma\rho^+$ (CTTS) coincides with that of $\alpha\rho^+(Kk_2)$. These considerations are illustrated in Figure 4a.

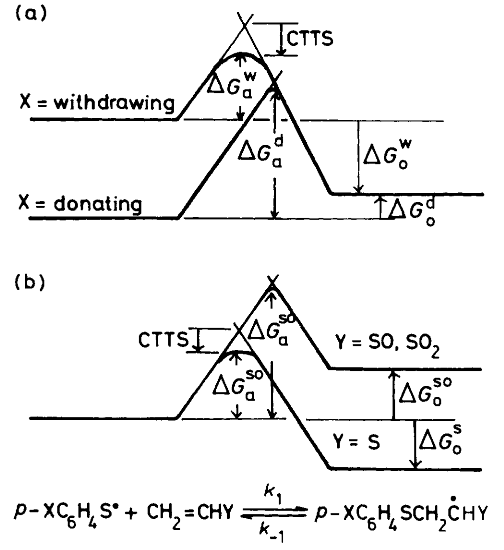


Figure 4. Energy diagrams for the reaction of p-$XC_6H_4S^\bullet$ with $CH_2=CHY$; (a) substituent effect of X; (b) substituent effect of Y; ΔG_a = free energy of activation and ΔG_o = difference in free energy between product and reactant; w and d refer to electron-withdrawing and -donating substituents, respectively. Superscript 'so' represents both SO and SO$_2$ groups

$$\Delta \log k_1 = \alpha \Delta \log Kk_2 + \gamma \Delta \mathrm{CTTS} \tag{4}$$

$$\rho^+(k_1) = \alpha\rho^+(Kk_2) + \gamma\rho^+(\mathrm{CTTS}) \tag{5}$$

The $\rho^+(k_1)$ values for vinyl sulphides are similar to those for vinyl ethers, even though there is a great difference in the log Kk_2 values between them for each phenylthio radical. This suggests that the α values do not vary with the exothermicity of the reactions. Thus, the variable part of the observed $\rho^+(k_1)$ values can be attributed to the γ values. Although it is quite difficult to estimate the α values, we can approach the γ values in the following way.

On the assumption that $\alpha \sim 0$, the γ value becomes positive even for vinyl monomers substituted by an electron-withdrawing group such as vinyl sulphoxide or sulphone; this case is improbable. On the assumption that $\alpha \sim 1$, the γ value becomes negative even for vinyl sulphide; however, it would also be expected from this assumption that k_1 for each thio radical with vinyl sulphoxide or sulphone becomes greater than (or close to) that of vinyl sulphide. Such an example is found in the relative reactivities of these vinyl monomers toward the styryl radical as shown in Table 5. Since the thio radicals are electrophilic, the reactivities are rather similar to

Table 5. Observed k_1 values relative to $CH_2=CH(SO)R$ and relative monomer reactivity ($1/r$)

Y =	SR	OR	S(O)R	$S(O_2)R$
k_1 (X = Cl)	400—1 700	5	1	0.7
k_1 (X = OCH_3)	100	2	1	2
$1/r$(styrene) [a]	2	0.05	1	3
$1/r$(AN) [a]	25—50	0.05	1	3

[a] $1/r$(styrene) = reactivity toward the styryl radical; $1/r$(AN) = reactivity toward the acrylonitrile radical (ref. 22).

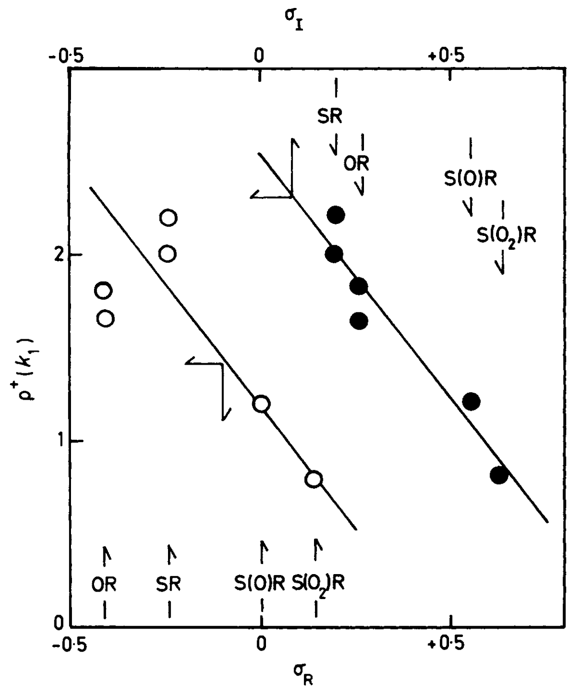
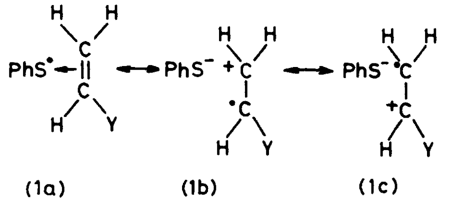


Figure 5. Plots of $\rho^+(k_1)$ vs. σ_R and σ_I

that of the acrylonitrile radical (Table 5). Thus, in the case of the thio radical, the γ values for vinyl sulphides and ethers are positive; for vinyl sulphoxide and sulphone the γ values may be close to zero or slightly negative. Then the α values may be estimated to be 0.5—0.75, close to Semenov's empirical value for endothermic radical reactions.[21] A positive γ value implies a contribution of the polar resonance structures (1a—c) to the transition state, which results in stabilization of the transition state.



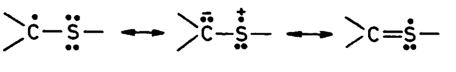
(1a) (1b) (1c)

The observed $\rho^+(k_1)$ values are linearly correlated with the e values of vinyl monomers,[22] which reflect the polar nature of the double bonds [equation (6)]. The negative slope suggests that the electron-donating power of Y, which is proportional to the negative e value, increases the contribution of the polar nature of the transition state (1a—c). Furthermore, as shown in Figure 5, the $\rho^+(k_1)$ values are correlated not only with σ_I but also with σ_R.[20] Since the groups RS and RO have slightly positive σ_I values, they do not have strong electron-donating power. Thus, the considerable electron-donating power of the vinyl sulphides and ethers may arise from the resonance effect when the electrophilic thio radical approaches the double bond of the vinyl monomer in the transition state.

$$\rho^+(k_1) = -0.50e + 1.44 \qquad (6)$$

The observed spacings between the lines in Figure 3 (log Kk_2 vs. σ^+) are a measure of the thermodynamic stabilities of the adduct radicals. The stabilities of $PhSCH_2\dot{C}HY$ increase in the order Y = SR $\gg$ OR > S(O)R ~ $S(O)_2R$. The k_1 values for one of the phenylthio radicals also show a similar order; thus, the reactivities of vinyl monomers with each thio radical are determined by the stabilities of the adduct radicals (Figure 4b). Although the polar nature of the transition state also affects the reactivity, the polar effect does not surpass the thermodynamic effect when we compare vinyl sulphides with other vinyl monomers. When we compare the reactivity of vinyl sulphones with those of sulphoxides and ethers, the polar effect becomes important; in Table 5 or in Figure 2, the reactivity ratio of sulphone to sulphoxide with respect to the p-chlorophenylthio radical is reversed when X is the methoxy group.

The stability of the carbon-centred radical attached to the sulphur atom is well interpreted by the canonical structures (2a—c). The structure (2b) may contribute more than (2c):



(2a) (2b) (2c)

e.s.r. studies indicate that the radical centre has a bent conformation.[23,24] The lesser contribution of (2c) may be ascribed to the weak $2p$–$3p$ bond.

In the case of the oxygen atom, although canonical structures similar to those of the sulphur atom can be written, the contribution of an electron transfer structure like (2b) is small because the ionization potentials of ethers are *ca.* 1 eV larger than those of sulphides.[25] An electron-sharing canonical structure like (2c) cannot contribute because the expansion of the octet is not permitted for the oxygen atom. Although the sulphoxide group also has a lone pair on the sulphur atom, the stability is the same as that of the sulphone group; thus, the lone pair of the sulphoxide group can participate neither in electron-transfer conjugation [like (2b)] nor in electron-sharing conjugation [like (2c)], because of the semipolar character of the S–O bond.

The effect of the ethyl and phenyl groups attached to the sulphur and oxygen atoms on the k_1, Kk_2, and $\rho^+(k_1)$ values appears likely to be small. If there were further stabilization of the canonical structure (2b) by the phenyl π systems, the lines of phenyl vinyl sulphide in the Hammett plots for both log k_1 and log Kk_2 should be higher than those of ethyl vinyl sulphide; however, the opposite tendency was found. Data for phenyl vinyl sulphone were not obtained because of its low solubility in benzene; in this case, we would expect the effect of the ethyl and phenyl groups to be small. Thus, comparison of data for ethyl vinyl sulphone with those for phenyl vinyl sulphoxide may be permitted.

When the lines in Figure 2 are extrapolated, a reactivity ratio similar to that of the acrylonitrile radical shown in Table 5 would be expected at the phenylthio radical substituted by X having $\sigma^+ = ca.\ -1.5$; the reactivity ratio similar to that of the styryl radical is at $\sigma^+ = ca.\ -2.5$.

Experimental

Commercially available ethyl vinyl sulphide, phenyl vinyl sulphoxide, and ethyl vinyl ether were used after purification by distillation in the usual manner. Phenyl vinyl sulphide, ethyl vinyl sulphone, and phenyl vinyl ether were prepared by the methods reported in the literature.[26-28] Benzene used as a solvent was of spectrophotometric grade.

Flash photolysis experiments were performed at 23 °C by using an apparatus of standard design;[29] the input energy into xenon-flash lamps was *ca.* 150 J and the half-duration of the flash lamps (Xenon Co. N-851C) was *ca.* 10 μs. The disulphides were flash-photodecomposed in a cylindrical cell with light of wavelength 350—420 nm, selected by appropriate light filters. Decay kinetics were monitored by continuous light with photomultiplier detection, connected to a differential amplifier (Textronics 7A13), a transient memory (Kawasaki Elec. 50 E), and a microcomputer.

The concentration of oxygen in benzene was controlled by dissolving oxygen in degassed solution under an appropriate partial pressure of oxygen; the oxygen concentrations were calculated from Henry's law using the Ostwald coefficient.[30]

References

1 C. C. Price and S. Oae, 'Sulfur Bonding,' Ronald Press, New York, 1962.
2 C. C. Price and J. Zomlefer, *J. Am. Chem. Soc.*, 1950, **72**, 14.
3 C. C. Price and R. D. Gilbert, *J. Am. Chem. Soc.*, 1952, **74**, 2073.
4 G. A. Russell in 'Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1972, vol. I, p. 275.
5 O. Ito and M. Matsuda, *J. Am. Chem. Soc.*, 1979, **101**, 1815.
6 O. Ito and M. Matsuda, *J. Am. Chem. Soc.*, 1982, **104**, 568.
7 F. C. Thyrion, *J. Phys. Chem.*, 1973, **77**, 1478.
8 M. Nakamura, O. Ito, and M. Matsuda, *J. Am. Chem. Soc.*, 1980, **102**, 698.
9 K. U. Ingold in 'Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1972, vol. I, p. 37.
10 A. A. Oswald, K. Griesbaum, and B. E. Hudson, *J. Org. Chem.*, 1963, **67**, 549.
11 E. F. Zwicker and L. I. Grossweiner, *J. Phys. Chem.*, 1963, **67**, 549.
12 G. L. Closs and B. E. Rabinow, *J. Am. Chem. Soc.*, 1976, **98**, 8190.
13 J. S. Howard in 'Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1972, vol. II, p. 4.
14 L. V. Natarajan, R. R. Lembke, and R. R. Kuntz, *J. Photochem.*, 1981, **15**, 13.
15 C. Walling, E. R. Briggs, K. B. Wolfstirn, and F. R. Mayo, *J. Am. Chem. Soc.*, 1948, **70**, 1537.
16 M. Imoto, M. Kinoshita, and M. Nishigaki, *Makromol. Chem.*, 1966, **94**, 238.
17 H. Sakurai, S. Hayashi, and A. Hosomi, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 1945.
18 J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc. B*, 1966, 1191.
19 S. Dincturk and R. A. Jackson, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1127.
20 C. D. Johnson, 'The Hammett Equation,' Cambridge University Press, Cambridge, 1973.
21 N. N. Semenov, 'Some Problems of Chemical Kinetics and Reactivity,' Pergamon, London, 1958.
22 J. Brandrup and E. H. Immergut, 'Polymer Handbook,' Wiley, New York, 1975.
23 D. Forrest, K. U. Ingold, and D. H. R. Barton, *J. Am. Chem. Soc.*, 1977, **81**, 915.
24 C. Gaze and B. C. Gilbert, *J. Chem. Soc., Perkin Trans. 2*, 1978, 503.
25 B. J. Gallegos and R. W. Kiser, *J. Phys. Chem.*, 1962, **66**, 136.
26 W. M. Lauer and M. A. Spielman, *J. Am. Chem. Soc.*, 1933, **55**, 1972.
27 E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, 1949, **71**, 237.
28 L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, 1970, **89**, 597.
29 G. Porter and M. A. West in 'Techniques of Chemistry,' ed. A. Weissberger, Wiley, New York, vol. 6, 1974, p. 367.
30 S. T. Murov 'Handbook of Photochemistry,' Dekker, New York, 1973.

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