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Solvent Effect on the Reactivity of Arylsulfanyl Radicals

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Abstract—The rate of reaction of *p*-aminophenylsulfanyl radicals with styrenes decreases as a result of solvation of the initial reactants. The determining factor in the reaction with styrene is specific solvation, and in the reaction with α-methylstyrene, nonspecific solvation.

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Unlike heterolytic reactions, homolytic processes are considerably less sensitive to parameters of liquid medium; as a rule, the rate constants for reactions involving free radicals (k) change within no more than one or two orders of magnitude upon variation of solvent [1, 2]. The kinetics of such processes were the subject of a number of studies. However, attempts to reveal quantitative relations between k and physicochemical parameters of solvents, in particular with the aid of multiparameter Koppel'–Pal'm or Kamlet–Taft–Abraham equations, were unsuccessful, which may be due to relatively weak solvation of radical species. On the other hand, radical reactions can be influenced to an appreciable extent by the ability of solvent molecules to undergo self-association (so-called cage effect). We previously showed that an appropriate correlation between the rate constants k for decomposition of peroxy or azo compounds, as well as for some oxidation or halogenation processes, and solvent parameters may be obtained in terms of the six-parameter linear free energy relationship [Eq. (1)] [3].

$$\log k = a_0 + a_1 \frac{n^2 - 1}{n^2 + 2} + a_2 \frac{\varepsilon - 1}{2\varepsilon + 1} + a_3 E_T + a_4 B + a_5 \delta^2 + a_6 V_M. \quad (1)$$

The terms $f(n^2) = (n^2 - 1)/(n^2 + 2)$ and $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$ in Eq. (1) characterize the ability of solvent to solvate a substrate in nonspecific mode, which is determined by solvent polarizability and polarity; B is the basicity according to Pal'm, and E_T is the Reichardt electrophilicity parameter, which describe possible acid–base (specific) interaction; The squared Hildebrand solubility parameter δ^2 is proportional to the self-association energy; and the molar volume V_M characterizes possible effect of steric factors on solvation.

In the present work we made an attempt to apply Eq. (1) to describe the effect of solvent properties on the reactivity of arylsulfanyl radicals ArS$^{\cdot}$. The results of kinetic study on the reversible addition of *p*-aminophenylsulfanyl radicals to styrene in 26 solvents were reported in [4].

$$p\text{-}H_2NC_6H_4S^{\cdot} + PhCH{=}CH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} n\text{-}H_2NC_6H_4CH_2CH\text{–}Ph$$

$$+ O_2 \xrightarrow{k_2} \text{Peroxy radicals.}$$

p-Aminophenylsulfanyl radicals *p*-$H_2NC_6H_4S^{\cdot}$ are generated by photolysis of bis(*p*-aminophenyl)disulfide prepared by reaction of aniline with S_2Cl_2. Due to the presence of an amino group in the *para* position with respect to the radical center, *p*-$H_2NC_6H_4S^{\cdot}$ is characterized by enhanced polarizability, so that the rate constants k can be determined by flash photolysis. The resulting radicals with unpaired electron on the carbon atom react then with oxygen (k_2) to give the corresponding peroxyl radicals [4].

Both styrene and oxygen are present in large excess with respect to sulfanyl radicals; therefore, the addition

Table 1. Rate constants for the addition of $NH_2C_6H_4S^{\cdot}$ radicals to styrene $k_1 \times 10^{-4}$ (l mol^{-1} s^{-1}), rate constants for the overall process $K_{eq}\, k_2\, [O_2] \times 10^{-4}$, relative equilibrium constants $K_{eq} = k_1/k_{-1}$, and the corresponding frequencies ν

Run no.	Solvent	$k_1 \times 10^{-4}$, l mol^{-1} s^{-1}	$K_{eq}\, k_2 \times 10^{-4}$, l mol^{-1} s^{-1}	K_{eq}	ν, kK
1	Cyclohexane	21.70	2.93	0.74	18.35
2	Benzene	5.88	0.87	0.68	17.54
3	Toluene	5.00	1.04	0.48	17.54
4	Ethylbenzene	6.33	1.17	0.54	17.54
5	Mesitylene	5.12	1.16	0.44	17.54
6	Methylene chloride	1.86	–	–	17.33
7	Chloroform	3.93	–	–	17.54
8	Carbon tetrachloride	20.00	2.22	0.90	18.18
9	Dichloroethane	1.05	–	–	17.33
10	*o*-Dichlorobenzene	2.63	0.20	1.34	17.30
11	Fluorobenzene	4.35	0.93	0.47	17.54
12	Pentan-3-ol	0.20	–	–	16.39
13	Dioxane	1.74	0.19	0.92	17.33
14	Tetrahydrofuran	1.04	0.15	0.68	17.24
15	Ethyl acetate	1.00	0.14	0.72	17.30
16	Ethyl benzoate	1.03	0.10	1.08	17.30
17	Anisole	2.00	0.45	0.52	17.39
18	Acetonitrile	1.12	0.08	1.34	16.39
19	Benzonitrile	0.40	–	–	17.24
20	Butylamine	0.07	–	–	16.67
21	Dibutylamine	0.67	0.07	0.96	17.24
22	Triethylamine	1.38	0.17	0.83	17.39
23	Pyridine	0.33	0.03	1.32	16.67
24	Dimethylformamide	0.07	–	–	16.39
25	Dimethyl sulfoxide	0.03	–	–	16.39

process may be treated as a pseudofirst-order reaction. Table 1 contains the values of $k_1 \times 10^{-4}$ (l mol^{-1} s^{-1}) at 23°C in 25 solvents [4], as well as the rate constants for the overall process $[k_1/(k_{-1})]\, k_2[O_2] = K_{eq}\, k_2\, [O_2] \times 10^{-4}$ (l mol^{-1} s^{-1}), the relative equilibrium constants $K_{eq} = k_1/k_{-1}$, and the corresponding frequencies of light absorption maxima $\nu = 10^4/\lambda$ (kK).

Ito and Matsuda [4] presumed that the rate of the process considerably depends on the solvent polarity. It is seen that that the maximal rate ($k_1 \approx 20.0 \times 10^{-4}$ l mol^{-1} s^{-1}) is observed in nonpolar cyclohexane and carbon tetrachloride; in most other solvents, the reaction rate is lower by an order of magnitude [$k_1 \approx (1–6) \times 10^{-4}$ l mol^{-1} s^{-1}], whereas polar dimethylformamide and dimethyl sulfoxide, as well as alcohols, are characterized by more considerable reduction of the rate constant [$k_1 \approx (0.05–0.5) \times 10^{-4}$ l mol^{-1} s^{-1}]. However, there is no reliable correlation between log$k$ and the Kirkwood parameter (Fig. 1). Likewise, no correlation exists between log$k$, on the one hand, and such solvent polarity parameters as Reischardt electrophilicity parameter E_T and Kosower parameter Z (Fig. 2). It is now believed that the above parameters

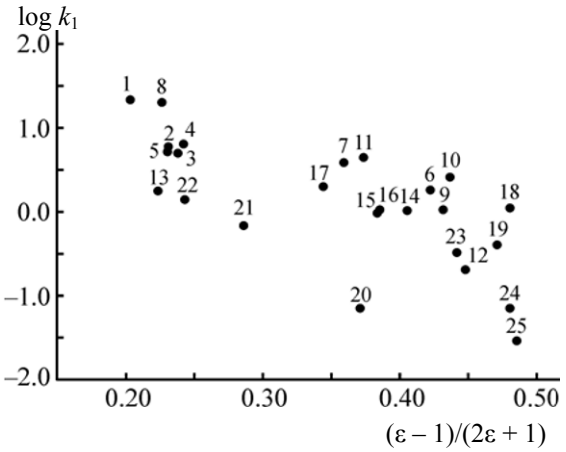

Fig. 1. Correlation between log k_1 and Kirkwood parameter (ε – 1)/(2ε + 1). For solvent numbering, see Table 1.

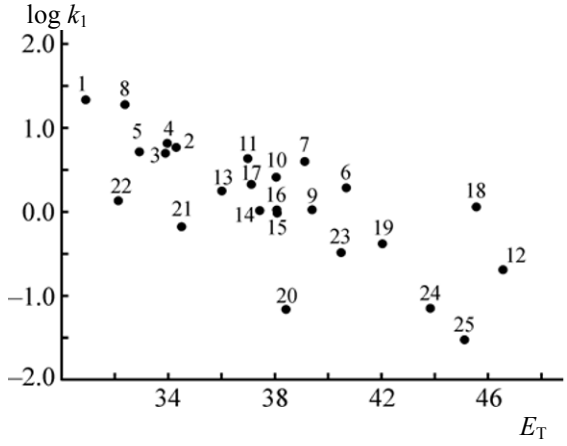

Fig. 2. Correlation between log k_1 and Reichardt electrophilicity parameter E_T. For solvent numbering, see Table 1.

reflect the ability of solvents for electrophilic solvation rather than their polarity.

Obviously, like other radical reactions, the rate of the reaction of sulfanyl radicals with styrene is determined by overall effect of different solvation factors [3]. Therefore, the rate constants given in Table 1 were involved in six-parameter correlation according to Eq. (1). The data were treated in keeping with the IUPAC recommendations for correlation analysis in chemistry [5]. The obtained correlations were considered to be appropriate when the multiple correlation coefficient R was equal to or higher than 0.95; the required solvent parameters were taken from reviews [6, 7]. Taking into account different dimensions of different scales of parameter, the significance of particular terms (i.e., their effect on the process) was determined [5] by successive exclusion of the corresponding term from correlation, each time the multiple correlation coefficient R being calculated; if the R value decreased insignificantly, the corresponding term was considered to be inessential.

Table 2 contains log k_1 values. Generalization of these data using Eq. (1) gives a correlation with R = 0.936; after exclusion of the most deviating data for one solvent (acetonitrile), we obtained satisfactory six-parameter correlation (2):

$$\log (k_1\times 10^{-4}) = 4.145 + (1.338\pm2.243)f(n^2) - (0.093\pm1.108)f(\varepsilon) - (0.0020\pm0.0003)B - (0.080\pm0.032)E_T - (0.002\pm0.001)10^{-3}\delta^2 - (0.0005\pm0.0022)V_M; \quad (2)$$

$$R = 0.964, \text{ mean-square deviation } s = \pm0.196.$$

It is seen that all terms in Eq. (2), except for $f(n^2)$, reduce k_1, indicating stabilization of ArS$^{\cdot}$ radical due to solvation or self-association of solvent molecules around radical species. This is consistent with the fact that the reaction rate is maximal in weakly polar carbon tetrachloride and cyclohexane. However, the low pair correlation coefficients r for log k_1 and particular terms of Eq. (2), 0.207, 0.732, 0.620, 0.776, 0.648, and 0.193, respectively, do not allow us to reliably estimate their effect on k_1, whereas large standard deviations for some terms (which sometimes exceed the corresponding regression coefficients) imply their low signifycance or insignificance at all. In fact, exclusion of the $f(\varepsilon)$, V_M, and $f(n^2)$ terms almost does not affect the R value for the resulting three-parameter equation (3):

$$\log (k_1\times 10^{-4}) = 4.5656 - (0.0021\pm0.0002)B - (0.0861\pm0.0185)E_T - (0.0021\pm0.0008)\times 10^{-3}\delta^2; \quad (3)$$

$$R = 0.963, s = \pm0.198.$$

The effect of self-association is also insignificant; only specific solvation of radical species really affects the rate of the process:

$$\log (k_1\times 10^{-4}) = 5.2871 - (0.0020\pm0.0002)B - (0.1269\pm0.0112)E_T; \quad (4)$$

$$R = 0.952, s = \pm0.225.$$

As follows from Eq. (4), the rate of addition of arylsulfanyl radical to styrene molecule is determined only by specific solvation of the former. Electrophilic solvation of amino group, as well as nucleophilic solvation of the whole structure, promotes withdrawal of unpaired electron from the sulfur atom, so that the radical species is stabilized. Self-association exerts some weak inhibitory effect: solvent cage appearing around radical species hampers its contact with styrene molecule.

Table 2. Experimental log ($k \times 10^{-4}$) values and those calculated by Eq. (4)

Run no.	Solvent	log k_{exp}	log k_{calc}	Δ log k
1	Cyclohexane	1.3365	1.3660	0.0295
2	Benzene	0.7694	0.8402	0.0708
3	Toluene	0.6990	0.8713	0.1723
4	Ethylbenzene	0.8014	0.8586	0.0572
5	Mesitylene	0.7093	0.9609	0.2516
6	Methylene chloride	0.2695	0.0772	–0.1923
7	Chloroform	0.5944	0.2979	–0.2965
8	Carbon tetrachloride	1.3010	1.1756	–0.1254
9	Dichloroethane	0.0212	–0.1085	–0.1297
10	*o*-Dichlorobenzene	0.4200	0.3973	–0.0227
11	Fluorobenzene	0.6385	0.5172	–0.1213
12	Pentan-3-ol	–0.6990	–1.0656	–0.3666
13	Dioxane	0.2405	0.2550	0.0145
14	Tetrahydrofuran	0.0170	–0.0582	–0.0752
15	Ethyl acetate	0.0000	0.1300	0.1300
16	Ethyl benzoate	0.0128	0.1733	0.1605
17	Anisole	0.3010	0.2746	–0.0264
18	Acetonitrile[a]	0.0492	–0.8492	–0.8984
19	Benzonitrile	–0.3979	–0.3472	0.0507
20	*n*-Butylamine	–1.1549	–0.6410	0.5139
21	Dibutylamine	–0.1739	–0.4488	–0.2749
22	Triethylamine	0.1399	–0.0636	–0.2035
23	Pyridine	–0.4815	–0.7798	–0.2983
24	Dimethylformamide	–1.1549	–0.8487	0.3062
25	Dimethyl sulfoxide	–1.5229	–1.1473	0.3756

[a] Excluded.

The calculated values of log k_1 and their deviations from the experimental values $\Delta \log k$ are given in Table 2, and Figure 3 shows a correlation between the calculated and experimental log k_1 values. Except for acetonitrile (which was excluded from correlation), all other $\Delta \log k$ values either do not exceed $s = \pm 0.225$ or exceed it insignificantly (polar pentan-3-ol, chloroform, butan-1-amine, DMSO, DMF); these deviations are lower than $\pm 2s$.

It should be noted that an attempt to correlate the data of [4] was made by Forg et al. [8] using different parameters of liquids, in particular their ability to act as hydrogen bond acceptor (β) and donor (α) and bipolarity factor π. However, the corresponding parameters are available for a smaller number of solvents; therefore, all data of [4] cannot be taken into consideration. The bipolarity factor π reflects a combination of polarity and polarizability, and in some cases introduction of an arbitrary "polarizability correction" term γ is necessary. Correspondingly, the quality of the correlations obtained with the above scale is generally worse, and the effect of solvation could not be interpreted properly in all cases. The data for 21 solvents (ethylbenzene, benzonitrile, pentan-3-ol, and methylene chloride were excluded) gave rise to Eq. (5):

$$\log k_1 = 5.47 - 1.64(\pi^* - 0.20\gamma) - 1.43\beta; \quad (5)$$
$$R = 0.968.$$

The calculation with the use of the Kamlet–Tafta–Abraham scale led us to conclude that solvation reduces the reactivity of arylsulfanyl radical; however,

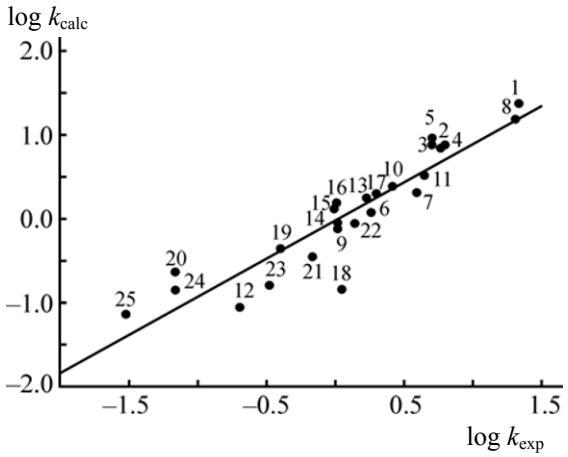

Fig. 3. Correlation between the experimental log k_1 values and those calculated by Eq. (4). For solvent numbering, see Table 2.

in this case neither electrophilic solvation of the amino group [as follows from Eqs. (3) and (4)] nor cohesion energy density effect (though not very strong) is taken into account. On the other hand, electrophilic solvation is undoubtedly significant. This follows from both appreciable pair correlation coefficient (r = 0.776) for log k_1 and E_T and systematic reduction of log k_1 with rise in E_T which was found in [4]. Moreover, division of the solvent set into three groups, electron donors (*I*), halogen derivatives, nitriles, and alcohols (*II*), and aliphatic amines (*III*) gives almost strictly linear dependences for each group. A probable reason for the observed discrepancy between our results and those reported in [8] is that the Kamlet–Taft–Abraham solvent parameters are composite quantities as compared to the Koppel'–Pal'm scale; in the first case, only solvation via hydrogen bonding is taken into account, whereas interaction with π-electrons in the substrate is not [9].

Other parameters of the addition of arylsulfanyl radical to styrene [4] are also reliably generalized using Eq. (1). The product of the equilibrium constant K for the formation of $ArSCH_2\dot{C}HPh$ radical and the rate constant k_2 for the addition of oxygen thereto (Table 1) in 17 solvents may be described by a six-parameter equation with R = 0.893; after exclusion of the most deviating data for acetonitrile (as with k_1), R reaches a value of 0.965. As above, the terms characterizing nonspecific solvation and molar volume turned out to be insignificant, and Eqs. (6) and (7) are appropriate:

$$\log (K k_2 \times 10^{-4}) = 4.4379 - (0.0018\pm0.0003)B - (0.1180\pm0.0348)E_T - (0.0010\pm0.0017)\delta^2; \quad (6)$$
$$R = 0.9649,\ s = \pm0.1525;$$

$$\log (K k_2 \times 10^{-4}) = 4.7201 - (0.0017\pm0.0002)B - (0.1361\pm0.0148)V_M; \quad (7)$$
$$R = 0.9641,\ s = \pm0.1541.$$

The correlation for $K = k_1/k_{-1}$ (Table 1) in 17 solvents was characterized by a low coefficient R (0.693); the correlation may be improved by exclusion of the data for four solvents: carbon tetrachloride, cyclohexane, *o*-dichlorobenzene, and ethyl acetate, presumably due to inaccurate determination of k_{-1}. A correlation with R = 0.980 was obtained for 13 solvents, and elimination of insignificant terms gave three-parameter Eq. (8) where the solvent polarity factor was significant together with the specific solvation factors.

$$\log (k_1/k_{-1}) \times 10 = -2.0985 - (1.5144\pm0.3639)f(\varepsilon) + (0.0006\pm0.0001)B + (0.0631\pm0.0090)E_T; \quad (8)$$
$$R = 0.9546,\ s = \pm0.0487.$$

Clearly, specific solvation of initial radical species favors the reverse reaction. The frequencies of absorption maxima of sulfanyl radicals (Table 1) can be described satisfactorily using Eq. (1). For 25 solvents we obtained a correlation with R = 0.950 and the maximal pair correlation coefficient with E_T (r = 0.832). After exclusion of the data for benzonitrile we arrived at Eq. (9):

$$\nu = 21.6616 - (1.5035\pm1.4428)f(n^2) + (1.0513\pm0.8411)f(\varepsilon) - (0.0012\pm0.0002)B - (0.0963\pm0.0232)E_T - (0.0012\pm0.0006)\delta^2 - (0.0004\pm0.0016)V_M; \quad (9)$$
$$R = 0.9616,\ s = \pm0.1434.$$

Exclusion of insignificant parameters gives appropriate Eq. (10) with the same significant terms as in the preceding correlations:

$$\nu = 20.566 - (0.0012\pm0.0002)B - (0.0676\pm0.0142)E_T - (0.0014\pm0.0006)\delta^2; \quad (10)$$
$$R = 0.957,\ s = \pm0.1517.$$

Subsequent elimination of any of the three terms either considerably impairs the correlation (without δ^2, R = 0.947) or destroys it at all.

The results obtained by the same authors while studying the kinetics of the reaction of *p*-dimethylaminophenylsulfanyl radical $Me_2NC_6H_4S^{\cdot}$ with α-methylstyrene [10] were satisfactorily described using Eq. (1). However, in this case the effect of solvation is

complicated, presumably due to some steric hindrances intrinsic to the α-methylstyrene molecule. The corresponding data are collected in Table 3. According to [10], the main factor determining the rate of the process is solvent polarity; however, unlike [4], the solvent polarity parameter was defined as the Kirkwood function. In fact, the dependence is only approximate: the pair correlation coefficient r for log k_1 and $(\varepsilon - 1)/(2\varepsilon + 1)$ is as low as 0.862. On the other hand, correlation of log k_1 values from Table 3 according to Eq. (1) involves some difficulty. To obtain a satisfactory correlation, data for six solvents (i.e., about 20%), dioxane, pentan-3-ol, *o*-dichlorobenzene, benzene, toluene, and ethylbenzene should be excluded. The remaining 23 solvents give rise to Eqs. (11) and (12):

$$\log (k_{-1} \times 10^{-4}) = 1.9608 - (1.0255 \pm 1.0121) f(n^2) - (5.3967 \pm 0.6238) f(\varepsilon) + (0.0001 \pm 0.0001) B + (0.0163 \pm 0.0178) E_T + (0.0000 \pm 0.0005) \delta^2 - (0.0016 \pm 0.0012) V_M; \quad (11)$$

$$R = 0.961, s = \pm 0.1119;$$

$$\log (k_{-1} \times 10^{-4}) = 1.2614 - (5.3912 \pm 0.6091) f(\varepsilon) + (0.0237 \pm 0.0094) E_T; \quad (12)$$

$$R = 0.9546, s = \pm 0.1208.$$

Thus, we observe fundamental differences from the attack by arylsulfanyl radical on styrene, namely positive effect of electrophilic solvation on the reaction rate, insensitivity of the latter to nucleophilic solvation, and determining role of solvent polarity ($r = 0.9404$ for 23 solvents involved). Obviously, this is related to differences in the structures of intermediate complexes and their dipole moments. According to [10], an important factor is difference in the nucleophilicities of the NH_2 and NMe_2 groups. In fact, their basicities B according to Pal'm are 346 and 422, respectively. However, we believe that more important factor is effect of the α-methyl group in α-methylstyrene, which hampers attack by arylsulfanyl radical at the double bond.

Analogous results were obtained for the rate of the reaction of complex sulfanyl radical with oxygen log $(K_{eq} k_2 \times 10^{-4})$ $[O_2]$ and frequencies of absorption maxima ν (Table 3). In the first case (28 solvents), the determining parameter was solvent polarity (r = 0.821), but the correlation was not satisfactory; the coefficient R for the six-parameter equation was as low as 0.8890. To obtain an acceptable correlation, exclusion of data for 4 solvents was necessary, mainly for the same solvents as in the preceding case, dioxane, chloroform, benzene, and *o*-dichlorobenzene.

Table 3. Rate constants for the addition of $Me_2NC_6H_4S^{\cdot}$ radicals to α-methylstyrene $k_1 \times 10^{-4}$, relative equilibrium constants $K_{eq} k_2 [O_2]$, and frequencies of light absorption maxima ν

Solvent	$k_1 \times 10^{-4}$, l mol^{-1} s^{-1}	$K_{eq} k_2 \times 10^{-4}$, l mol^{-1} s^{-1}	ν, kK
Cyclohexane	14.00	140.0	16.81
Benzene	2.70[a]	9.7	16.00
Toluene	2.50[a]	13.0	15.87
Ethylbenzene	2.50[a]	13.0	16.00
Mesitylene	2.90	21.0	16.00
Chloroform	1.60	3.1	15.63
Carbon tetrachloride	7.50	52.0	16.53
Dichloroethane	0.89	3.2	15.38
Trichloroethylene	2.30	13.0	16.00
o-Dichlorobenzene	1.40[a]	3.7	15.50
Fluorobenzene	1.50	7.0	15.87
Pentan-3-ol	1.80[a]	6.4	15.75
Tetrahydrofuran	0.88	3.8	15.75
Dioxane	1.70[a]	5.2	15.75
Ethanol	1.10	5.0	15.75
Ethyl acetate	1.20	7.1	15.87
Ethyl benzoate	1.10	3.1	15.50
Anisole	1.20	4.5	15.50
Acetonitrile	0.68	2.3	15.15
Benzonitrile	0.75	1.3	15.27
Butylamine	1.70	5.2	16.00
Dibutylamine	3.40	26.0	16.26
Triethylamine	5.30	46.0	16.53
Tributylamine	5.90	46.0	–
Pyridine	0.71	2.1	15.15
Methylformamide	0.71	1.6	15.15
Dimethylformamide	0.43	1.6	15.15
Dimethyl sulfoxide	0.40	0.52	16.53
Carbon disulfide	5.00	7.4	15.87

[a] Excluded.

$$\log (K_{eq} k_2 [O_2] \times 10^{-4}) = 3.9020 - (6.0798 \pm 1.5334) f(n^2) - (6.2586 \pm 0.8995) f(\varepsilon) - (0.0002 \pm 0.0002) B + (0.0269 \pm 0.0250) E_T - (0.0006 \pm 0.0008) \delta^2 + (0.0006 \pm 0.0018) V_M; \quad (13)$$

$$R = 0.9528, s = \pm 0.1721;$$

$$\log (K_{eq} k_2 [O_2] \times 10^{-4}) = 4.4090 - (6.4186 \pm 1.2391) f(n^2) - (6.2866 \pm 0.8322) f(\varepsilon) + (0.0109 \pm 0.0136) E_T; \quad (14)$$

$$R = 0.9498, s = \pm 0.1774.$$

Here, the E_T term (i.e., electrophilic solvation) is almost insignificant: exclusion of E_T reduces R to 0.9498.

The absorption frequency of 4-dimethylaminophenylsulfanyl radical is determined primarily by solvent polarity, but polarizability factor should also be taken into account and some solvents should be excluded to obtain a satisfactory correlation. The correlation coefficient R for six-parameter equation like (1) is 0.710 (28 solvents), and only elimination of the data for DMSO, dioxane, acetonitrile, carbon disulfide, *o*-dichlorobenzene, and benzonitrile gave an acceptable correlation with $R = 0.951$. The pair correlation coefficient r with the Kirkwood parameter thus increases from 0.6521 to 0.8049.

$$\nu = 20.112 - (10.111\pm1.622)f(n^2) - (4.313\pm0.772)f(\varepsilon) - (0.0001\pm0.0002)B - (0.0023\pm0.0211)E_T - (0.0001\pm0.0006)\delta^2 + (0.0007\pm0.0016)V_M; \quad (15)$$

$$R = 0.951,\ s = \pm0.137.$$

Most coefficients in Eq. (15) are characterized by standard deviations that exceed their absolute values. In fact, exclusion of the corresponding terms showed that their effect is insignificant (except for nonspecific solvation).

$$\nu = 20.105 - (9.855\pm1.339)f(n^2) - (4.706\pm0.345)f(\varepsilon); \quad (16)$$

$$R = 0.950,\ s = \pm0.139.$$

Thus in this case we also observe a sharp difference from the addition of 4-aminophenylsulfanyl radical to styrene, where reduction of the absorption frequency is controlled by specific solvation.

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