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Features of Solvent Effects on Styrene Oxidation

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Abstract—Correlation analysis of solvent effects on the rate of styrene oxidation showed that the uninhibited process is favored by nonspecific solvation of the substrate and enhanced cohesive energy density of the medium, that both assist the cage effect. The phenol-inhibited oxidation is much contributed by specific solvation as the result of inhibitor–solvent binding.

Solvent effects in homolytic reactions are poorer understood that in heterolytic. However, it is known that solvents may appreciably affect the rates of oxidation of organic compounds [1, 2], such as hydrocarbons [3–5] or aldehydes [6]. Solvent effects are intricate in nature, but, based on the linear free energy principle, one can fairly correlate them with the rate of oxidation of hydrocarbons in terms of the five-parameter equation (1) that takes account of the ability of solvents to nonspecific and specific solvation of a substrate, as well as their cohesive energy density [7, 8].

$$\log V \text{ or } \log (k_2/k_6^{1/2}) = a_0 + a_1 \frac{n^2 - 1}{n^2 + 2} + a_2 \frac{\varepsilon - 1}{2\varepsilon + 1} + a_4 E_T + a_5 \delta^2. \qquad (1)$$

Here V is the rate of the process, k_2 and k_6, rate constants of chain propagation and termination, n_D^{20} and ε, refractive indices and dielectric constants of solvents, B and E_T, Palm's basicity [9] and Reichard's electrophilicity [10], and δ, Hildebrand's solubility parameter. The first two terms of the equation, that characterize solvent polarizability and polarity, relate to nonspecilific solvation, B and E_T relate to specific solvation (acid–base interaction), and δ^2 is proportional to the energy of cavity formation in the liquid. Analysis of the equations obtained in [7, 8] showed that the rate of uninhibited oxidation is mostly contributed by nonspecific solvation of substrates. Therefore, we considered it important to compare the effects on noninhibited and inhibited hydrocarbon oxidation.

We took into consideration data on the oxidation of styrene in 18 solvents at 65°C [11]. The concentration of styrene and initiator (AIBN) were 0.42 and 0.07 M, respectively. According to Howard and Ingold [11], the reaction rate V is determined primarily by the $k_2/k_6^{1/2}$ ratio, and it decreases in low-polarity solvents (hydrocarbons, CCl_4) and increases in polar solvent, varying ~3 times (Table 1). However, attempted direct correlation between reaction rate and such functions of medium polarity as (ε – 1)/(2ε + 1) or (ε – 1)/(2ε + 1)d/M (d, density, and M, molecular weight of the solvent) failed: With certain solvents, especially aromatic, these values varied in parallel, but considerable deviations for linearity were observed. The referees [11] related these deviations to nonelectrostatic interactions, specifically, nonspecific solvation that depends both on the high polarizability of CCl_4 and on the presence of π electrons in the aromatic rings; however, no quantitative treatment of these deviations was performed. Therefore, we considered it of interest to consider the possibility of generalization of these data in terms of an equation like (1) and to compare the resulting data with those for other hydrocarbons, primarily for the structurally related cumene and α-methylstyrene [7, 8]. Table 1 lists the rate constants of uninhibited oxidation $V \times 10^6$, mol l^{-1} s^{-1}, and their logarithms, as well as the $(k_2/k_6^{1/2}) \times {}^{102}$ ratios (l mol s^{-1}) and their logarithms, obtained on the basis of data in [11]. The required solvent characteristics were taken from the reviews [12, 13]; the calculation procedure was consistent with recommendations of the Group for Correlation Analysis at IUPAC [14].

Treatment of the rate constants for all the 18 solvents gives an equation with an unsatisfactorily low multiple correlation coefficient R 0.874. However, by omitting one solvent, p-xylene, we obtain a five-parameter equation (2) with an acceptable R value of 0.950 (s –0.46).

$$\log V = -5.96 + (1.33 \pm 0.61) f_1(n^2) + (0.82 \pm 0.29) f_2(\varepsilon) + (0.19 \pm 0.32) \times 10^{-3} B + (2.72 \pm 4.60) \times 10^{-3} E_T + (0.46 \pm 0.28) \times 10^{-3} \delta^2. \qquad (2)$$

Table 1. Experimental [11] and calculated rate constant of uninhibited styrene oxidation

Solvent	$(\varepsilon - 1)/(2\varepsilon + 1)$	Experiment, $-\log V$	Calculation by Eq. (3)		Experiment, $-\log(k_2/k_6^{1/2})$	Calculation by Eq. (5)	
			$-\log V$	$\Delta\log V$		$-\log(k_2/k_6^{1/2})$	$\Delta[-\log(k_2/k_6^{1/2})]$
Styrene	0.244	5.009	5.083	–0.074	1.633	1.656	–0.023
Decane	0.195	5.337	5.250	0.087	1.870	1.819	0.051
CCl_4	0.226	5.215	5.162	0.053	1.747	1.739	0.008
tert-Butylbenzene	0.238	5.167	5.150	0.017	1.780	1.730	0.050
p-Xylene	0.229	5.523[a]	5.442	0.081	1.710	1.723	–1.013
Toluene	0.240	5.086	5.124	–0.038	1.678	1.705	–0.027
Benzene	0.231	5.061	5.123	–0.062	1.652	1.702	–0.050
Propionic acid	0.297	5.046	5.044	0.002	1.658	1.638	0.020
Chlorobenzene	0.379	4.979	4.957	0.022	1.580	1.568	0.012
Bromobenzene	0.373	4.951	4.925	0.026	1.564	1.536	0.028
Acetic acid	0.398	4.921	4.998	–0.077	1.533	1.608	–0.075
o-Dichlorobenzene	0.428	4.907	4.877	0.030	1.509	1.499	0.010
2-Propanol	0.463	4.903	4.854	0.049	1.516	1.483	0.033
2-Methyl-2-propanol	0.472	4.886	4.921	–0.035	1.520	1.544	–0.024
Ethanol	0.471	4.857	4.796	0.061	1.470	1.428	0.042
Nitrobenzene	0.479	4.801	4.800	0.001	1.435	1.434	0.001
Nitromethane	0.481	4.787	4.777	0.010	1.379	1.411	–0.032
Acetonitrile	0.480	4.770	4.841	–0.071	1.338[b]	1.473	–0.135

Excluded from the calculation [a] by Eq. (3) and [b] by Eq. (5).

Here and hereafter, the adequacy of the equation is tested, according to [14], by Fisher's test at a confidence level α of 0.95. The positive signs at all terms of the equation suggest that solvation of the styrene molecule and the cage effect determined by the cohesion of the medium favor oxidation. According to [14], significance of each term was estimated by their successive exclusion from the equation and subsequent calculation of R. Thus we revealed insignificance of specific solvation factors: For 17 solvents, exclusion of B decreases R to 0.949 only and subsequent exclusion of E_T, to 0.946. Thus, the solvent effects on the rate of styrene oxidation can to a reasonable accuracy described in terms of athree-parameter equation (3) with R 0.946 and s –0.06.

$$\log V = -5.79 + (0.92 \pm 0.45) f_1(n^2) + (0.92 \pm 0.26) f_2(\varepsilon) + (0.52 \pm 0.25) \times 10^{-3}\delta^2. \tag{3}$$

Further exclusions appreciably deteriorate the correlation: Two-parameter equations without δ^2 or without $f_1(n)$ have R 0.926, and that without $f_2(\varepsilon)$ has R 0.890. The rate of styrene oxidation in various media is primarily controlled by solvent polarity, as evidenced by the high pair correlation coefficient r between $\log V$ and $f_2(\varepsilon)$: 0.921 (without *p*-xylene). At the same time, the effects of polarizability and cohesive energy density are less significant but still appreciable. Table 1 lists the $\log V$ values calculated by Eq. (3) and their differences with experimental values ($\Delta\log V$). As seen, the differences are either within the error corridor s –0.06 or fall slightly beyond this corridor (styrene, decane, acetic acid); an exception is *p*-xylene that was excluded from the calculations.

Theoretically, the rate of radical processes is proportional to $k_2/k_6^{1/2}$, but actually, as noted in [11], solvent exerts a certain effect of the rate of initiator decomposition, i.e. on the k_1 value, and, since V varies in parallel to k_2/k_6, these values are not strictly proportional. Therefore, we also treated in a similar way the $k_2/k_6^{1/2}$ values in [11] (Table 1). With all the 18 solvents, an adequate correlation with R 0.947 was obtained, and, R could be improved to 0.963 by excluding acetonitrile [Eq. (4), s ±0.04].

$$\log(k_2/k_6^{1/2}) = -2.41 + (1.03 \pm 0.96) f_1(n^2) + (0.68 \pm 0.21) f_2(\varepsilon) - (0.07 \pm 0.23) \times 10^{-3} B + (2.84 \pm 3.52) \times 10^{-3} E_T + (0.45 \pm 0.28) \times 10^{-3}\delta^2. \tag{4}$$

Like with V, specific solvation factors proved to contribute little [Eq. (5), R 0.961, s ±0.04].

$$\log(k_2/k_6^{1/2}) = -2.31 + (0.89 \pm 0.33) f_1(n^2) + (0.72 \pm 0.19) f_2(\varepsilon) + (0.51 \pm 0.18) \times 10^{-3}\delta^2. \tag{5}$$

Table 2. Experimental [11] and calculated [Eq. (7)] rate constants of inhibited styrene oxidation

Solvent	Basicity B [9]	Experiment, $-\log(k_2/k_6)$	Calculation	
			$-\log(k_2/k_6)$	$\Delta\log(k_2/k_6)$
Styrene	43	2.072	2.239	–0.167
Decane	0	2.509	2.505	0.004
CCl_4	0	2.424	2.410	0.014
p-Xylene	68	2.294	2.219	0.075
Chlorobenzene	38	2.300	2.285	0.015
Bromobenzene	40	2.308	2.191	0.117
Acetic acid	139	2.266	2.265	0.001
o-Dichlorobenzene	28	2.184	2.239	–0.055
2-Methyl-2-Propanol[a]	247	2.175	1.640	0.535
Nitrobenzene	67	2.087	2.089	–0.002
Nitromethane	65	1.831	1.818	0.013
Acetonitrile	178	1.624	1.638	–0.014

[a] Excluded from the calculation.

Here, again, the k_2/k_6 value is most contributed by the polarity of the medium (r 0.929), and the contributions of polarizability and cohesive energy density, like with V, are no more than corrective: Exclusion of any of these two parameters renders R for the corresponding two-parameter equations only slightly lower (0.935–0.937). Table 1 lists the corresponding $\log(k_2/k_6^{1/2})$ values calculated by Eq. (5) and their deviations from the experimental values.

Thus, we obtained quantitative evidence for the qualitative conclusions in [11] that the rate of styrene oxidation is controlled by the polarity of the medium, whose increase favors dipole formation in the substrate, as well as for the considerable contribution of polarizability. However, the suggestion of Howard and Ingold [11] about significance of specific solvation in the case of aromatic hydrocarbons is contrary to fact; here, probably, their enhanced polarizability matters. Of significance is also the self-association effect of the medium, whose enhancement affects the oxidation rate via the cage effect that favors radical processes.

With cumene [8], too, the most significant factors are solvent polarity and cohesive energy density, rather than their ability to specific solvation. Comparing Eq. (5) with the corresponding equation for the structurally related α-methylstyrene in [7] one can see that specific solvation factors are also insignificant, but, even though the rate–polarity pair correlation coefficient is fairlt high (r 0.875), for adequate correlation in the case of α-methylstyrene two significant parameters, polarizability and cohesive energy density, both favoring faster oxidation, would suffice. Thus, one can speak about a uniform solvent effect on oxidation of these three hydrocarbons, that is underlain by nonspecific solvation of the substrate, associated with the polarity of the medium. Of importance is also the cage effect.

Howard and Ingold [11] have studied the kinetics of phenol-inhibited styrene oxidation. Table 2 lists the k_2/k_6 values for oxidation of 1.74 M solutions of styrene in 12 solvents in the presence of 4.8×10^{-4} mole l^{-1} of AIBN and 9.8×10^{-5} mole l^{-1} of inhibitor aninhibitor, di-2,6-*tert*-butyl-4-methylphenol. The process is generally much decelerated, but its rate in polar solvents is relatively higher, on account of hydrogen bonding between the solvent and phenol, and the resulting decrease in the effective concentration of the latter. However, both data for aromatic solvents and for MeCN and $MeNO_2$ deviate from the linear correlation with the Kirkwood function. At the same time, k_2/k_6 was found to vary in parallel with the shift of the phenol OH absorption frequency in the corresponding solvents. According to Palm [9], this shift was taken as a characteristic of solvent basicity, which points to significance in this case of specific B_{PhOH} interaction.

The correlation analysis of data for all the 12 solvents in Table 2 in terms of a five-parameter equation (1) results in a poor correlation (R 0.907), and acceptable correlation [Eq. (6), R 0.964, s –0.10] could only be obtained upon exclusion of 1-methyl-2-propanol.

$$\log(k_2/k_6) = -2.44 + (0.56\pm1.15)f_1(n^2) - (0.43\pm0.79)f_2(\varepsilon) + (3.09\pm0.98)\times10^{-3}B - (0.02\pm0.01)\times10^{-3}E_T + (2.37\pm0.61)\times10^{-3}\delta^2. \quad (6)$$

Analysis of the individual contributions reveals insignificance of nonspecific solvation in this case, and, the rate of inhibited styrene oxidation can be fairly correlated with solvent properties in terms of a three-parameter equation (7) (R 0.961, s ±0.09).

$$\log(k_2/k_6) = -2.20 + (3.01 \pm 0.81) \times 10^{-3}B - (2.69 \pm 0.85) \times 10^{-2}E_T + (2.11 \pm 0.34) \times 10^{-3}\delta^2. \quad (7)$$

The $\log(k_2/k_6)$ values calculated by Eq. (7) and their deviations from experiment are listed in Table 2.

Comparison of Eqs. (5) and (7) for uninhibited and inhibited styrene oxidations points to a radically different roles of solvents in these two processes. The rate of the inhibited oxidation depends on specific binding of an inhibitor, phenol, with basic solvents, which is consistent with data of Howard and Ingold [11]. However, even though the reaction rate is controlled by solvent basicity, the rate–basicity pair correlation coefficient is as low as 0.704 and adequate description is impossible without inclusion of the electrophilicity of solvents, that, in its turn, operates to decelerate the reaction, probably, by weakening their ability to hydrogen bonding. The role of the cohesive energy density of the medium is also of significance.

Specific solvation also controls the heterolytic oxidative dinmerization of styrene under the action of $Pd_3(OAc)_6$ trimer [15]. The reaction kinetics in 12 solvents have been studied (Table 3). The reaction rate has been found to increase 1.5 orders of magnitude, from ~10^{-6} mol l^{-1} s^{-1} in heptane and DMSO to ~60×10^{-6} mol l^{-1} s^{-1} in acetic acid, but no quantitative treatment of these data has been given. Later on these data have been generalized in [16] in terms of a four-parameter Koppel–Palm equation and a three-parameter Kamplet–Taft equation. However, the R values for all the solvents used proved to be unsatisfactorily low, and acceptable R values, 0.990 and 0.995, respectively, could only be obtained after exclusion of many solvents, specifically, for 8 or 5 of 14. According to [16], the most significant terms in the Koppel–Palm equation relate to specific solvation and in the Kamplet–Taft equation, to electrophilicity and dipolarity of πsolvents, in consistency with the fairly high pair correlation coefficient between the log rate constant with E_T (–0.921) for 8 solvent.

By treatment of data in [15] in terms of a five-parameter equation (1) for all the 12 solvents, too, resulted in unsatisfactory correlation (R 0.925). However, by consecutive exclusion of the most deviating points for heptane and acetonitrile we could impove R to 0.923 and 0.983, respectively, i.e. to obtain already for 10 solvents a good correlation [Eq. (8), R 0.983, s ±0.153].

Table 3. Experimental [15] and calculated [Eq. (9)] rate constants of oxidative dimerization of styrene

Solvent	Experiment, –log *k*	Calculation	
		–log *k*	Δlog *k*
DMSO	6.040	5.870	0.176
Heptane	5.921	5.471	0.450
Ethyl acetate	5.886	5.672	0.214
Dioxane	5.796	5.945	–0.149
DMF	5.602	5.732	–0.130
Benzene	5.553	5.390	0.163
Acetone	5.398	5.483	–0.085
Acetonitrile[a]	5.328	5.102	0.226
CCl_4	5.222	5.390	–0.168
$CHCl_3$	5.137	4.954	0.183
Acetic anhydride	4.721	4.950	–0.229
Acetic acid	4.229	4.204	0.025

[a] Excluded from the calculation.

$$\log k = -6.09 - (7.61 \pm 3.18)f_1(n^2) - (3.06 \pm 0.99)f_2(\varepsilon) - (4.74 \pm 0.66) \times 10^{-3}B + (0.08 \pm 0.01) \times 10^{-3}E_T + (2.63 \pm 1.04) \times 10^{-3}\delta^2. \quad (8)$$

Relatively insignificant in this case proved to be polarizability and cohesive energy density; their successive exclusion decreases R to 0.958 and 0.951. Finally, the effect of solvent properties on the rate of oxidative dimerization of styrene is generalized in terms of a three-parameter equation (9) [R 0.951, s ±0.210].

$$\log k = -8.35 - (1.41 \pm 1.07)f_2(\varepsilon) - (3.86 \pm 0.71) \times 10^{-3}B + (0.10 \pm 0.02)E_T. \quad (9)$$

Further exclusion of $f_2(\varepsilon)$ decreases R to 0.937, while exclusion of B or E_T destroys the correlation (R 0.65). These findings provide evidence in favor of the conclusion of Yatsimirski *et al.* [15], based on analysis of the $\Delta G^{\neq}$ values, that the rate of this reaction is controlled by specific solvation, and, therewith, the effects of basicity and electrophilicity have opposite signs. The log *k* values calculated by Eq. (9) and their deviations from experiment Δlog *k* are listed in Table 3.

Thus, correlation analysis allows quantitative generalization of data on the rates of styrene oxidation and assessment of the effects on this process of separate solvation factors.

REFERENCES

1. Emanuel’, N.M., Zaikov, G.E., and Maizus, Z.K., *Rol’ sredy v radikal’no-tsepnyh reaktsiyah okisleniya organicheskih soedinenii* (Role of Medium in Radical Chain Oxidation Reactions of Organic Compounds), Moscow: Nauka, 1973.
2. Emanuel, N.M., Zaikov, G.E., and Maizus, Z.K., *Oxidation of Organic Compounds. Medium Effect in Radical Reactions*, Oxford: Pergamon, 1984.
3. Niki, E., Kamiya, J., and Ohtu, N., *Bull. Chem. Soc. Jpn.*, 1969, vol. 42, no. 11, p. 3324.
4. Howard, I.A. and Ingold, K.U., *Can. J. Chem.*, 1964, vol. 42, no. 12, p. 1250.
5. Hendry, D.G. and Russel, G.A., *J. Am. Chem. Soc.*, 1969, vol. 86, no. 12, p. 2368.
6. Makitra, R.G., Pirig, Ya.N., and Yatchishin, I.I., *Reakts. Sposobn. Org. Soedin.*, 1987, vol. 24, no. 3, p. 336.
7. Makitra, R.G. and Pirig, Ya.N., *Zh. Org. Khim.*, 1996, vol. 32, no. 10, p. 1468.
8. Makitra, R.G., Pirig, Ya.N., and Yatchishin, I.I., *Zh. Org. Khim.*, 1999, vol. 35, no. 7, p. 1073.
9. Koppel’, N.A. and Payu, A.N., *Reakts. Sposobn. Org. Soedin.*, 1974, vol. 11, no. 1, p. 121.
10. Reichardt, C., *Solvent and Solvent Effects in Organic Chemistry*, Weinheim: VCH, 1988, p. 170.
11. Howard, I.A. and Ingold, K.U., *Can. J. Chem.*, 1964, vol. 42, no. 11, p. 1045.
12. Makitra, R.G., Pirig, Ya.N., and Kivelyuk, R.B., Available from VINITI, 1985, Moscow, no. 628-V86.
13. Abboud, J.L.M. and Notario, R., *Pure Appl. Chem.*, 1999, vol. 71, no. 4, p. 645.
14. *Quant. Struct. Act. Relat.*, 1985, vol. 4, no. 1, p. 29; Makitra, R.G., *Ukr. Khim. Zh.*, 1992, vol. 58, no. 3, p. 260.
15. Yatsimirski, A.K., Ryabov, A.D., Zagorodnikov, V.P., Sakodinskaya, I.K., Kavetskaya, O.I., and Berezin, I.V., *Inorg. Chim. Acta*, 1981, vol. 48, no. 2, p. 163.
16. Pytela, O., *Collect. Czech. Chem. Commun.*, 1988, vol. 53, no. 7, p. 1333.