ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 3, pp. 439–441. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © G.G. Midyana, R.G. Makitra, E.Ya. Pal'chikova, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 3, pp. 454–456.

Solvent Effect on the Reactivity of Trichloromethylperoxy Radicals

G. G. Midyana[a], R. G. Makitra[b], and E. Ya. Pal'chikova[b]

[a] *Division of Physical Chemistry of Fossil Fuels, Litvinenko Institute of Physical Organic and Coal Fuel Chemistry, National Academy of Sciences of Ukraine, ul. Nauchnaya 3a, Lviv, 79053 Ukraine*
e-mail: midstr@mail.lviv.ua
[b] *Institute of Geology and Geochemistry of Fossil Fuels, National Academy of Sciences of Ukraine, Lviv, Ukraine*

Received June 28, 2007

Abstract—The solvent effect on the rate of reaction of organic reductants with trichloromethylperoxy radicals can be adequaetly described by multiparameter linear equations. The major factor affecting the reaction rate is the solvent cohesion, enhancing the cage effect.

DOI: 10.1134/S1070363208030171

The solvent effect on the rate of heterolytic reactions depends on the total effect of solvation involving specific and nonspecific interactions of the components and reaction complex with the solvent. Therefore, generally the reaction rate constants do not show good linear correlations with any single solvent characteristic, and adequate description can be attained on the basis of the linear free energy relationship using multiparameter equations. The most widely used are the Koppel–Palm and Taft–Abraham equations [1, 2].

In the case of heterolytic reactions, this approach is beyond doubt, and several hundreds correlation equations have been reported for such reaction systems [3]. At the same time, homolytic reactions have been studied less extensively, in particular, because of the fact that the rate constants of radical reactions in different solvents vary in relatively narrow ranges.

Furthermore, the Koppel–Palm equation in most cases fits the overall rate constants unsatisfactorily, primarily because of complex and multistep mechanisms of these processes which can occur along different pathways. We found, however, that, as far as the rate of a particular elementary step of a homolytic process is concerned, its dependence on the solvent can be satisfactorily described by the extended Koppel–Palm equation supplemented by terms taking into account the solvent molar volume V_m and its self-association characterized by the Hildebrand solubility parameter squared, δ^2:

$$\log k = a_0 + a_1\frac{n^2-1}{n^2+2} + a_2\frac{\varepsilon-1}{2\varepsilon+1} + a_3\delta^2 + a_4B + a_5E_T + a_5V_M. \quad (1)$$

This approach proved to be efficient as applied to such reactions as initiated and molecular decomposition of peroxides, oxidation, etc. [4–6]. Therefore, it was interesting to check whether it is applicable to radical reactions of other types.

Relatively recently Alfassi et al. [7] examined the solvent effect on the reaction of trichloromethylperoxy radicals Cl_2C–OO. generated by radiolysis of CCl_4 in the presence of oxygen with chlorpromazine {2-chloro-10-[3-(dimethylamino)propyl]phenothiazine hydrochloride} and Trolox [6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid]. The choice of the investigation objects, especially of Trolox which is an analog of vitamin E, was governed by the importance of peroxy radicals in biological processes, including the processes responsible for the toxicity of CCl_4. The second-order rate constants obtained in [7] are given in the table. Alfassi et al. [7] found that the solvent effect on the rate of Trolox oxidation cannot be adequately described using a single solvent characteristics.

Rate constants of reactions of $Cl_3COO^{\cdot}$ radicals with Trolox and chlorpromazine

Solvent	Trolox			Chlorpromazine		
	log ($k_{exp}\times10^6$)	log ($k_{calc}\times10^6$)	$\Delta\log k$	log ($k_{exp}\times10^6$)	log ($k_{calc}\times10^6$)	$\Delta\log k$
Water	8. 7634	8. 7801	0. 0167	9. 0414	9. 0696	0. 0282
N-Methylformamide	7. 7324	7. 7217	–0. 0107	8. 2304	7. 9580	–0. 2725
Ethylene glycol	7. 6628	7. 6868	0. 0241	7. 6902	7. 9725	0. 2823
Methanol	7. 4914	7. 3849	–0. 1065	7. 9345	7. 9741	0. 0396
Dimethylformamide	7. 3222	7. 4948	0. 1726	7. 5798	7. 5534	–0. 0264
Acetonitrile	7. 0792	7. 0884	0. 0093	7. 7634	7. 6980	–0. 0654
Isopropanol	7. 3222	7. 2729	–0. 0493	7. 4914	7. 4223	–0.0691
Pyridine	7. 9031	7. 8242	–0. 0789	7. 2553	7. 5189	0. 2637
tert-Butanol	7. 3222	7. 2642	–0. 0580	7. 1761	7. 1433	–0. 0328
Acetone	6. 9638	6. 9869	0. 0231	7. 1461	7. 3346	0. 1884
Tetrachloromethane	7. 6628	7. 6419	–0. 0209	–	–	–
Triethylamine	7. 9777	7. 9865	0. 0088	–	–	–
Diethyl ether	7. 1461	7. 2159	0. 0698	–	–	–
1,4-Dioxane[a]	7. 1761	7. 8697	0. 6936	7. 1761	7. 1105	–0. 0655
Formamide[a]	8. 4314	7. 2244	–1. 2070	8. 0000	7. 9479	–0. 0521
Dimethyl sulfoxide	–	–	–	7. 9494	7. 7309	–0. 2185

[a] Solvents excluded from the calculation for Trolox.

The best correlation (correlation coefficient squared r^2 0.60) was obtained with δ^2, but even in this case the data for triethylamine, CCl_4, pyridine, and formamide strongly deviated from the linear correlation.

A two-parameter equation including, along with δ^2, also p*K* of solvents, provided a better description. An attempt to describe data from the table on the Trolox oxidation by six-parameter equation (1) also failed (multiple correlation coefficient *R* 0.847). However, exclusion, in accordance with IUPAC recommendations [8], of the most outlying rate constants (namely, those in formamide and dioxane) increased *R* to 0.943 and 0.992, respectively. Thus, for 13 solvents we obtained adequate correlation equation (2):

$$\log (k\times10^6) = 6.649 + (5.361\pm0.646)f(n^2) - (3.530\pm0.439)f(e) + (1.287\pm0.169)\cdot10^{-3}B + (7.957\pm5.801)\cdot10^{-3}E_T + (0.903\pm0.078)10^{-3}\delta^2 + (2.288\pm2.0083)\times10^{-3}V_m, \quad (2)$$
$$N\ 13;\ R\ 0.992;\ s\ \pm0.060,$$

where *s* is the root-mean-square deviation.

Low pair correlation coefficients (the maximal *r*, 0.699, is observed with δ^2) do not allow reliable conclusions about the contributions of the corresponding factors to log *k*. Large rms deviations of coefficients at certain terms of regression equation (2) suggest probable insignificance of these factors. A check of the significance of terms, following the IUPAC recommendations, by the leave-one-out procedure with the calculation of *R* for equations with the smaller number of terms showed insignificance of E_T and V_m and led to four-parameter equation (3), also adequate:

$$\log (k\times10^6) = 6.431 + (5.423\pm0.758)f(n^2) - (2.725\pm0.264)f(\varepsilon) + (1.117\pm0.139)\times10^{-3}B + (1.047\pm0.047)\times10^{-3}\delta^2, \quad (3)$$
$$R\ 0.989;\ s\ \pm0.071.$$

The subsequent exclusion of any term from Eq. (3) decreases R to undesirably low value (<0.95). The effect of the solvent polarizability, $f(n^2)$, is also of relatively low significance: For the three-parameter equation obtained upon exclusion of this term, *R* is 0.940. The decisive factor is the self-association of solvents: Exclusion of δ^2 from Eq. (3) fully breaks the correlation (*R* 0.212). Thus, in agreement with the opinion of Alfassi et al. [7], the solvent effect on the rate of radical oxidation of Trolox is determined by the cohesion energy of the medium. With an increase in

the cohesion, the so-called cage effect favoring an increase in the number of effective collisions of the reacting particles is enhanced. The effect of solvent basicity B is also significant, though to a lesser extent. This effect is apparently due to donor–acceptor interaction of solvents with electrophilic chlorine atoms of the $Cl_3COO^{\cdot}$ radical, facilitating cleavage of the C–O bond.

The theoretical values of log ($k \times 10^6$), calculated with Eq. (3), and their deviations from the experimental values, $\Delta\log k$, are given in the table. As can be seen, these values are mostly either lower than the rms error (s ±0.071) or only slightly exceed it (methanol, DMF). Certainly, larger deviations are observed for dioxane and formamide, which were excluded from the general calculation.

Still better results were obtained for the rates of oxidation of chlorpromazine in 13 solvents (see table). All the data without exceptions are described by a six-parameter equation with R 0.951, and in this case the maximal pair correlation coefficient r is observed with δ^2: r 0.849. As for the previous reaction, the factor of specific electrophilic solvation is insignificant here, but the effect of B is insignificant also. Exclusion of these factors leads to four-parameter equation (4) adequately describing the solvent effect on radical oxidation of chlorpromazine with $Cl_3COO^{\cdot}$ radicals:

$$\log (k\times10^7) = 6.888 + (3.525\pm1.785)f(n^2) + (0.857\pm0.779)f(\varepsilon) + (0.554\pm0.138)\times10^{-3}\delta^2 - (1.288\pm0.352)\times10^{-2}{}_m \quad (4)$$

N 13; R 0.951; s ±0.165.

Thus, as in the reaction of $Cl_3COO^{\cdot}$ radicals with Trolox, the cohesion factor is decisive: For the pair correlation of log k with δ^2, r 0.880. However, in contrast to the first reaction, the factor of possible nucleophilic solvation is also of low significance. The molar volume of solvents exerts a noticeable decelerating effect. Apparently, with an increase in the volume of solvent molecules their aggregation into a cage around the reaction complex becomes complicated. The capability of solvents for nonspecific solvation favors the reaction.

The primary experimental values of log ($k \times 10^6$) and those calculated by Eq. (4) are given in the table. As in the previous system, in most cases the deviations are smaller than s ±0.165, and even the maximal deviations observed in ethylene glycol, pyridine, and DMSO do not exceed ±2s.

Thus, we quantitatively confirmed the qualitative conclusion made in [7] that the cohesion energy density of solvents exerts a decisive effect on the rates of reactions of organic reductants with $Cl_3COO^{\cdot}$ radicals, and for Trolox the effect of solvent basicity is also significant. High rate of such radical reactions in associated solvents, especially in water, accounts for the low stability of radicals in biological systems, including living bodies.

REFERENCES

1. Koppel, I.A. and Palm, V.A., *Advances in Linear Free Energy Relationships,* Chapman, N.B. and Shorter, J.L., Eds., New York: Plenum, 1972.
2. Kamlet, M.J., Abboud, J.L.M., and Taft, R.W., *Prog. Phys. Org. Chem*., 1981, vol. 13, p. 485.
3. Pytela, O., *Coll. Czech. Chem. Commun*., 1988, vol. 53, no. 7, p. 1333.
4. Makitra, R.G., Pirig, Ya.N., and Gavryliv, E.M., Available from VINITI, Moscow, 1988, no. 8418-V-88.
5. Pirig, Ya.N., Makitra, R.G., and Yatchishin, I.I., *Kinet. Katal*., 1991, vol. 32, no. 5, p. 104.
6. Makitra, R.G., Polyuzhin, I.P., and Golovata, I.N., *Zh. Obshch. Khim*., 2005, vol. 75, no. 2, p. 196.
7. Alfassi, Z.B., Huie, R.E., and Neta, P., *J. Phys. Chem*., 1993, vol. 97, p. 7253.
8. *Recommendations for Reporting the Results of Correlation Analysis in Chemistry Using Regression Analysis, Quant. Struct. Act. Relat.*, 1985, vol. 4, no. 1, p. 29.