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Solvent Effect on the Rate of Decomposition of Peroxy Compounds

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Abstract—Solvent effect on the rate of decomposition of peroxy compounds was described by multiparameter equations based on the linear Gibbs energy relationship. In the decomposition of dialkyl peroxides, the determining factors are the cohesion energy density of solvents and their ability to electrophilic solvation, which accelerate the process. In the case of hydroperoxides, the nonspecific solvation factor should additionally be taken into account.

Solvent effects on the rate of heterolytic reactions can be described on the basis of the linear Gibbs energy relationship using multiparameter linear equations. Analysis of the significance of particular solvation terms in these equations could give valuable information on the reaction mechanism [1–3]. The number of analogous studies in the field of homolytic reactions is considerably smaller. A probable reason is relatively low sensitivity of homolytic reactions to solvent effects; moreover, these reactions can involve a number of steps and are characterized by a high probability of side processes. The above stated also applies to decomposition of peroxy compounds in various media. This process usually takes two concurrent pathways: unimolecular homolytic and initiated decomposition, whose rates differently depend on the solvent properties. Therefore, appropriate analysis of the apparent rate constants is impossible.

However, inhibition of the initiated decomposition makes it possible to analyze solvent effects on a quantitative level. An almost classical example is the publication by Pincock [4], where decomposition of *tert*-butyl peroxyformate in the presence of pyridine was studied in 20 solvents [5, 6]. Analogous general conclusions can be drawn for the inhibited decomposition of diacyl peroxides: in all cases, the rate of the process is determined only by solvation factors, primarily by nucleophilic solvation but not by self-association of the medium. These data confirm the absence of cage effect (i.e., initiated decomposition) [7].

Study of the decomposition of benzoyl peroxide in various solvents showed that the main factor determining initiated decomposition is the cohesion energy density of the medium while the rate of homolytic uninitiated decomposition depends mostly on the solvation ability which originates from the polarity and basicity of the solvent [8]. The effect of self-association becomes significant in the inhibited decomposition of *tert*-butyl peroxybenzoate and *tert*-butyl *o*-phenylsulfanylperoxybenzoate.

Up to now, solvent effects on the decomposition of only two groups of peroxy compounds, diacyl peroxides and peroxyacid esters, have been studied on a quantitative level. Moreover, the conclusions drawn on the basis of these studies cannot be regarded as strictly unambiguous. Therefore, we thought it reasonable to perform analogous correlations for other classes of peroxy compounds. As previously [6–9], the correlations were based on the extended Koppel'–Pal'm equation:

$$\log k = a_0 + a_1\frac{n^2-1}{n^2+2} + a_2\frac{\varepsilon-1}{2\varepsilon+1} + a_3B + a_4E_\mathrm{T} + \mathrm{a}_5\delta^2 + a_6V_\mathrm{M}. \qquad (1)$$

Here, n and ε are, respectively, the refractive index and dielectric constant which determine the polarizability and polarity of a solvent and are responsible for nonspecific solvation; V is the basicity according to Pal'm; and E_T is the Reichardt electrophilicity

Table 1. Logarithms of the experimental first-order rate constants for decomposition of di-*tert*-butyl peroxide $\log k \times 10^{-6}$, s^{-1}, in different solvents at 120 and 130°C [13] and $\log k$ values calculated by Eqs. (3) and (4)

No.	Solvent	120°C			130°C		
		$\log k_{exp}$	$\log k_{calc}$	$\Delta \log k$	$\log k_{exp}$	$\log k_{calc}$	$\Delta \log k$
1	Cyclohexane	–0.2007	–0.1430	0.0577	0.4133	0.4334	0.0201
2	Triethylamine	–0.1024	–0.1507	–0.0483	0.4983	0.4466	–0.0517
3	Dimethylaniline	–0.0177	–0.0118	0.0059	0.5328	0.5334	0.0007
4	Cyclohexene	–0.1192	–0.1277	–0.0085	0.4487	0.4544	0.0057
5	Tetrahydrofuran	–0.0132	0.0211	0.0343	0.5302	0.5522	0.0220
6	*tert*-Pentyl alcohol	0.1004	0.1386	0.0383	0.6503	0.6329	–0.0174
7	Nitrobenzene	0.1173	0.1478	0.0305	0.6314	0.6288	–0.0027
8	Ethyl benzoate	0.0294	0.0476	0.0182	0.5302	0.5671	0.0369
9	Benzene	0.0414	–0.0457	–0.0871	0.5079	0.4982	–0.0096
10	*tert*-Butyl alcohol	0.1492	0.1806	0.0314	0.6335	0.6625	0.0290
11	Acetic acid	0.3404	0.3283	–0.0122	0.7987	0.8012	0.0025
12	Acetonitrile	0.3444	0.2841	–0.0602	0.7505	0.7150	–0.0355

parameter (V and E_T determine the acid–base properties of a solvent, i.e., its ability to specific solvation [1]); δ is the Hildebrandt solubility parameter (δ^2 is proportional to the cohesion energy density); and V_M is the molar volume (which reflects possible effect of structural factors). The solvent parameters were taken from [1, 10, 11], and the calculations were performed according to the IUPAC recommendations in the field of correlation analysis in chemistry [12].

Huyser and Van Scoy [13] studied the thermal unimolecular decomposition of the simplest dialkyl peroxide, di-*tert*-butyl peroxide, at 120–135°C in 10 solvents which are incapable of assisting initiated decomposition. According to the authors, the formation of transition state is affected by the energy consumed for formation of a cavity in liquid medium (self-association), as well by the solvation factors; however, no quantitative treatment of the results was performed.

Table 1 contains the corresponding logarithms of the rate constants at 120 and 130°C together with the enthalpies of activation (kcal/mol). The data obtained at 120°C give rise to the following six-parameter equation:

$$\log k = -0.978 + (0.64 \pm 0.35) f(n^2) - (0.76 \pm 0.25) f(\varepsilon) + (0.24 \pm 0.08) \times 10^{-3} B + (0.020 \pm 0.003) E_T + (1.08 \pm 0.25) \times 10^{-3} \delta^2 + (1.00 \pm 0.55) \times 10^{-3} V_M. \quad (2)$$

The multiple correlation coefficient R is equal to 0.985; the pair correlation coefficients are as follows: $r_{O1} = 0.374$, $r_{O2} = 0.745$, $r_{O3} = 0.137$, $r_{O4} = 0.948$, $r_{O5} = 0.862$, $r_{O6} = 0.687$; and the mean-square deviation s is ±0.129. It is seen that the rate of decomposition of di-*tert*-butyl peroxide is determined mainly by electrophilic solvation (E_T); obviously, the effect of cohesion energy density δ^2 is also significant. In keeping with the recommentations given in [12], we determined the significance of each particular term by excluding it from the correlation and calculating R each time. In this way, we have found that the V_M term is insignificant. On the other hand, quite proper description of the effect of the medium on the rate of decomposition of di-*tert*-butyl peroxide is given by Eq. (3) which includes only two terms, E_T and δ^2, both these favoring the process:

$$\log k = -0.872 + (0.019 \pm 0.004) E_T + (0.456 \pm 0.212) \times 10^{-3} \delta^2; \quad (3)$$

$$R = 0.964,\ s = 0.087.$$

The $\log k$ values calculated by Eq. (3) and the differences between the experimental and calculated values ($\Delta \log k = \log k_{calc} - \log k_{exp}$) are given in Table 1. The values of $\Delta \log k$ conform to $s = 0.087$ or exceed the latter only slightly. Analogous and even statistically better results were obtained for the decomposition rate constants at 130°C. The six-parameter equation is characterized by $R = 0.990$ and $s = 0.030$, and it can be reduced to two-parameter equation (4):

$$\log k = -0.120 + (0.017 \pm 0.002) E_T + (0.105 \pm 0.123) \times 10^{-3} \delta^2; \quad (4)$$

$$R = 0.975,\ s = 0.026.$$

Table 2. Experimental [13] and calculated [Eq. (6)] enthalpies of activation for decomposition of di-*tert*-butyl hydroperoxide in organic solvents and the corresponding experimental and calculated [Eq. (8)] enthalpies of dissolution (ΔH, kcal/mol)

No.	Solvent	$\Delta H^{\neq}_{\text{exp.}}$	Equation (6)		ΔH_{dis}(exp.)	Equation (8)	
			$\Delta H^{\neq}_{\text{calc}}$	$\Delta\Delta H^{\neq}$		ΔH_{dis}	$\Delta\Delta H_{\text{dis}}$
1	Triethylamine	40.600	39.910	–0.690	0.000	0.109	0.109
2	Dimethylaniline	37.600	37.589	–0.011	0.866	0.653	–0.213
3	Cyclohexene	37.300	38.010	0.710	0.000	0.012	0.012
4	Tetrahydrofuran	37.100	37.544	0.444	0.236	0.483	0.247
5	*tert*-Pentyl alcohol	35.700	34.405	–1.295	0.949	1.139	0.190
6	Nitrobenzene	35.600	35.038	–0.562	1.150	1.250	0.100
7	Ethyl benzoate	35.500	36.244	0.744	0.575	1.086	0.511
8	Benzene	35.300	35.175	–0.125	0.400[a]	0.381	–0.019
9	*tert*-Butyl alcohol	34.300	34.611	0.311	1.330	1.192	–0.138
10	Acetic acid	33.400	33.566	0.166	1.080	1.034	–0.046
11	Acetonitrile	31.000	31.309	0.309	1.550	1.489	–0.061
12	Cyclohexane	40.800[a]	37.063	–3.737	0.307	0.127	–0.180

[a] Data were excluded from the calculation.

A slightly impaired correlation was obtained for the enthalpies of activation $\Delta H^{\neq}$ (Table 2). The correlation including all 12 solvents was unsatisfactory, $R = 0.928$. Exclusion of the most deviating data for cyclohexane afforded Eqs. (5) and (6) which properly reflect the effect of the medium on $\Delta H^{\neq}$ (kcal/mol):

$$\Delta H^{\neq} = 41.403 + (5.598 \pm 7.015) f(n^2) + (11.867 \pm 4.603) f(\varepsilon) + (2.700 \pm 1.572) \times 10^{-3} B - (0.094 \pm 0.053) E_T - (0.022 \pm 0.005) \delta^2 + (0.004 \pm 0.010) V_M; \quad (5)$$

$$R = 0.977,\ s = 0.526;$$

$$\Delta H^{\neq} = 45.427 + (17.940 \pm 4.223) f(\varepsilon) - (0.127 \pm 0.054) E_T - (0.029 \pm 0.004) \delta^2; \quad (6)$$

$$R = 0.967,\ s = 0.629.$$

In this case we observe consistent action of solvation factors: increase in E_T and δ^2, which favor the decomposition process, is accompanied by decrease in $\Delta H^{\neq}$, i.e., in the energy barrier.

Presumably, electrophilic solvation involves oxygen atoms of the peroxy group, thus weakening the O–O bond. This is consistent with the data obtained in [13] for the heats of dissolution (ΔH_{dis}, kcal/mol) of di-*tert*-butyl peroxide in the same solvents: the maximal values of ΔH_{dis} were observed for hydroxyl-containing solvents and electrophilic nitrobenzene and acetonitrile (Table 2). The corresponding correlation in terms of Eq. (1) was characterized by a poor correlation coefficient ($R = 0.949$), but exclusion of the most deviating data for ethyl benzoate gave fairly satisfactory correlations (7) and (8) in which the E_T and δ^2 parameters were the most significant ($r = 0.822$ and 0.920, respectively).

$$\Delta H_{\text{dis}} = -3.53 + (0.947 \pm 1.652) f(n^2) - (1.566 \pm 1.166) f(\varepsilon) - (3.955 \pm 0.035) \times 10^{-3} B + (0.043 \pm 0.013) E_T + (5.293 \pm 1.142) \times 10^{-3} E_T + (8.825 \pm 3.444) \times 10^{-3} V_M; \quad (7)$$

$$R = 0.971,\ s = 0.132;$$

$$\Delta H_{\text{dis}} = -2.866 + (0.032 \pm 0.013) E_T + (4.217 \pm 0.744) \times 10^{3} \delta^2 + (7.471 \pm 2.634) \times 10^{-3} V_M; \quad (8)$$

$$R = 0.962,\ s = 0.150.$$

Table 2 contains the values of ΔH_{dis} calculated by Eq. (8) and the corresponding deviations from the experimental values.

Analogous effect of solvation factors was revealed by treatment of the kinetic data given in [14] for decomposition of lithium *tert*-butyl peroxide in 8 solvents at 80°C (Table 3). It was found that the rate of decomposition of lithium *tert*-butyl peroxide in weakly polar media is determined mainly by nonspecific solvation and that in aromatic hydrocarbons the main factor is specific solvation: the correlation between $\log k$ and the Pal'm basicity parameter was characterized by a partial coefficient r of 0.990. Almost the same value of r was obtained for the Hammett parameter E_S which takes into account steric hindrances. However, in the two cases, the required parameters

Table 3. Logarithms of the experimental first-order rate constants for decomposition of lithium *tert*-butyl peroxide ($\log k \times 10^{-6}$, s^{-1} [14]) and $\log k$ values calculated by Eq. (10)

No.	Solvent	$\log k_{exp}$	$\log k_{calc}$	$\Delta \log k$
1	Benzene	0.8633	0.8652	0.0019
2	Cumene	0.9445	0.9328	–0.0117
3	Ethylbenzene	0.9823	0.9841	0.0019
4	Toluene	1.0000	1.0083	0.0083
5	*p*-Xylene	1.0682	1.0699	0.0017
6	Mesitylene	1.1614	1.1592	–0.0022
7	Butylbenzene	0.9731	0.9560	–0.0171
8	*tert*-Butylbenzene	0.9191	0.9364	0.0173

Table 4. Logarithms of the experimental first-order rate constants for decomposition of tetrahydronaphthyl hydroperoxide ($\log k \times 10^{-6}$, s^{-1} [15]) and $\log k$ values calculated by Eq. (12)

No.	Solvent	$\log k_{exp}$	$\log k_{calc}$	$\Delta \log k$
1	Cumene	–0.1192	–0.2001	–0.0809
2	Tetrahydronaphthalene	–0.1135	–0.0700	0.0435
3	Decane	0.2304	0.2557	0.0252
4	Decahydronaphthalene	0.3010	0.2527	–0.0483
5	*p*-Methoxybenzene	0.2041	0.3380	0.1339
6	Acetophenone	0.3617	0.4237	0.0620
7	Nitrobenzene	0.6532	0.5539	–0.0993
8	Chlorobenzene	0.6990	0.6629	–0.0361
9	Quinoline[a]	0.7482	–0.4067	–1.1549

[a] The data for quinoline were excluded from the calculation.

were available only for 5–6 solvents. Therefore, we recalculated $\log k$ from [14] using Eq. (1) and obtained the following correlation:

$$\log k = 10.317 - (9.253 \pm 5.141) f(n^2) + (9.246 \pm 1.400) f(\varepsilon) - (0.977 \pm 2.393) \times 10^{-3} B + (0.293 \pm 0.046) E_T + (3.416 \pm 0.316) \delta^2 + (0.147 \pm 0.339) \times 10^{-3} V_M; \quad (9)$$

$$R = 0.998,\ s = 0.006,\ r_{O1} = 0.352,\ r_{O2} = 0.377,\ r_{O3} = 0.942,\ r_{O4} = 0.899,\ r_{O5} = 0.026,\ r_{O6} = 0.230.$$

In fact, aromatic hydrocarbons nos. 1–6 give rise to linear increase in the rate constant with increase in the solvent basicity, but the rate considerably decreases upon introduction of bulky butyl and *tert*-butyl groups into the aromatic ring. As a result, the correlation coefficient R decreases, the sign at the B term changes to the opposite (what is the most important), and its effect on $\log k$ becomes insignificant. The rate of the substrate decomposition is eventually determined by electrophilic solvation and cohesion energy density with some contribution of the polarity factor:

$$\log k = 6.741 + (9.316 \pm 1.195) f(\varepsilon) - (0.260 \pm 0.013) E_T + (9.316 \pm 1.195) \delta^2; \quad (10)$$

$$R = 0.993,\ s = 0.011.$$

Table 3 contains the $\log k$ values calculated by Eq. (10) and those found experimentally together with the corresponding deviations. Obviously, electrophilic solvation of the oxygen atoms in the HOO group reduces the rate of decomposition. On the other hand, taking into account that the substrate is the corresponding lithium salt, nucleophilic interaction postulated in [14] seems to be improbable.

A considerable effect of electrophilic solvation on the rate of decomposition of hydroperoxide also follows from the data of [15] where decomposition of tetrahydronaphthyl hydroperoxide in the presence *N*-phenyl-β-naphthylamine at 90°C was studied in 9 aromatic solvents. It was found that consumption of one molecule of the amine corresponds to decomposition of 2.5 to 19 molecules of the hydroperoxide. Therefore, the authors concluded that *N*-phenyl-β-naphthylamine acts mainly as catalyst which initially reacts with the hydroperoxide to give a complex like a contact ion pair. The reaction follows the first-order kinetics. However, the corresponding rate constants were determined only for some solvents, so that we took the rate of decomposition $W_{ROOH} \times 10^6$ (mol l^{-1} s^{-1}) (Table 4) as parameter for correlation. According to the authors, the rate of decomposition increases as the solvent polarity rises, but we observed no distinct relation between $\log W$ and ε.

Treatment of the data in Table 4 according to Eq. (1) gave a poor correlation (R = 0.922). An excellent correlation [Eq. (11)] was obtained by excluding the most deviating data for quinoline.

$$\log W = 12.730 - (25.217 \pm 5.125) f(n^2) + (8.153 \pm 2.360) f(\varepsilon) - (1.758 \pm 0.393) \times 10^{-3} B - (0.185 \pm 0.048) E_T + (2.653 \pm 2.091) \delta^2 - (0.014 \pm 0.002) \times 10^{-3} V_M; \quad (11)$$

$$R = 0.992,\ s = 0.039,\ r_{O1} = 0.229,\ r_{O2} = 0.654,\ r_{O3} = 0.154,\ r_{O4} = 0.589,\ r_{O5} = 0.482,\ r_{O6} = 0.447;$$

$$\log W = 14.690 - (18.620 \pm 3.187) f(n^2) - (13.346 \pm 2.088) f(\varepsilon) - (0.322 \pm 0.062) E_T - (0.013 \pm 0.003) \times 10^{-3} V_M; \quad (12)$$

$$R = 0.965,\ s = 0.080.$$

Here, unlike lithium *tert*-butyl peroxide, the cohesion energy density term is insignificant, whereas the molar volume is significant. The larger the solvent molecule, the weaker the solvation of the peroxy group surrounded by bulky tetrahydronaphthalene and phenylaminonaphthalene fragments. The observed deviation of the data obtained in quinoline from the general correlation is not surprising: the experimental rate of decomposition in quinoline is almost twice as large as the calculated value. Presumably, the reason is concurrent oxidation of quinoline to quinoline *N*-oxide.

Comparison of the results obtained in the present work and those reported in [6–9] led us to conclude that the main factors affecting decomposition of peroxy compounds in various solvents include both the cohesion energy density and solvation ability, their contribution depending on the substrate structure. Electrophilic solvation of the peroxy group may both favor and hamper the process.

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