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Solvent Effects on the Decomposition Kinetics of Peracid Esters

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Abstract—Electrophilic solvation that operates to weaken the oxygen-oxygen bond is shown to a factor relating to the effect of the media on the decomposition rate of peracid esters. However, an adequate correlation between reaction rate and solvent properties can only be obtained by means of multiparameter linear equations including various characteristics simultaneously.

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Peracid esters are widely used initiators of radical processes. Due to that their decomposition features and, in particular, solvent effects on the decomposition kinetics, are well documented (for example see the review [1]). It is known that peracid esters can decompose, depending on structure and conditions, by different mechanisms involving homolytic cleavage of either O–O bonds exclusively or both O–O and C–O bonds, the second mechanism prevailing [2].

As shown in a classical Pincock's research on the pyridine-catalyzed decomposition of *tert*-butyl performate in 20 solvents at 90°C [3], in going from *n*-heptane to the polar nitrobenzene the reaction rate increases two orders of magnitude, but there is no clear correlation between log (reaction rate constant) and Kirkwood function. According to more recent findings, the effect of the medium on the rate of this process can be described exclusively in terms of a multiparameter linear free energy relationship (LFER) equation whose prevailing terms are those relating to the ability of solvents to nonspecific and electrophilic solvation [4]. This conclusion was confirmed in [5].

The effect of the medium on the decomposition rate of *tert*-butyl *o*-(phenylsufanyl)perbenzoate in 11 solvents at 25°C and 40°C [6], too, could only be generalized in terms of multiparameter equations, and in this case, too, the above two factors proved to be the most significant [7]. The results of Blomquist and Ferris [8] for the decomposition of *tert*-butyl perbenzoate in 8 aromatic solvents gave evidence in favor of the significance of the same solvation factors. However, in the inhibited decomposition of the same compound in 15 aliphatic and aromatic solvents basicity and cohesion energy density were fount to take force along with polarizability [7]. Such a difference in the significance of separate solvation factors in the decomposition of *tert*-butyl performate and perbenzoate is probably explained by the presence of hydrogen on the carbonyl carbon atom in the former compound.

In view of the fact that the effect of electrophilic solvation on the decomposition of peresters is still not quite clear, we considered it expedient to take a broader look at this issue by means of LFER equations.

Ruchardt and Quadbeck-Seeger [9] have studied the inhibited decomposition of decalyl phenylperacetate at 80°C in seven solvents to show that the decomposition rate increases with increasing Reichardt electrophilicity parameter E_t (ability to electrophilic solvation), but this dependence is not linear. No clear correlation was also revealed between log k and the viscosity of the medium, which made the referees to conclude that the cage effect is insignificant.

The effect of the medium on the kinetcs of chemical reactions, including hemolytic, is expedient to descried in terms of a six-parameter Eq. (1) which includes, together with solvation factors, solvent cohesion and molar volume.

$$\log k = a_0 + a_1(n^2 - 1)/(n^2 + 2) + a_2(\varepsilon - 1)/(2\varepsilon + 1) + a_3E_t + a_4B + a_5\delta^2 + a_6V_m. \quad (1)$$

Table 1. Experimental [9] and calculated [Eq. (2)] log k values for the decomposition of *trans*-decalyl phenylperacetate

Solvent	log k_{exp}	log k_{calc}	Δlog k
Ethylbenzene	–4.199	–4.182	–0.017
Chlorobenzene	–4.039	–4.100	0.061
Methanol	–2.708	–2.806	0.098
Propan-2-ol	–3.416	–3.346	–0.070
n-Butanol	–3.264	–3.195	–0.069
Acetonitrile	–3.642	–3.596	–0.046
Benzonitrile	–3.830	–3.872	0.042

Here n is the refraction index and ε, dielectric constant, parameters relating to solvent polarizability and polarity, that control nonspecific interactions; B, Koppel–Palm basicity, and E_t, Reichardt electrophilicity, parameters relating to specific (acid–base) interactions; δ^2, squared Hildebrandt solubility parameter which is proportional to the cohesion energy of the organic phase; and V_m, molar volume of the organic phase.

However, the number of solvents considered in the works [9, 10] considered below is too small for generalization by Eq. (1). Therefore, in what follows we made use of two- to four-parameter equations, excluding selectively insignificant and then repeated generalization using an equation including significant characteristics only.

The generalization of data in [9] by LFER equations including various solvents parameters gave evidence showing that the perester decomposition rate is controlled by the electrophilicity parameter E_t. Additional inclusion of the Kirkwood parameter, that is medium polarity factor, leads to a two-parameter Eq. (2) with an excellent multiple correlation coefficient R 0.991 and the mean square error s ±0.0813.

$$\log k = -6.56 - 1.45f(\varepsilon) + 0.0804E_t. \quad (2)$$

The log k values calculated by this equation are presented in Table 1 together with their deviations from the experimental values $\Delta\log k = \log k_{calc} - \log k_{exp}$.

Similar results were obtained with data in [10] for the thermolysis of *tert*-butyl (2,5-dioxopyrrolidin-1-yl) performate in 7 solvents at 100°C (Table 2). The key effect here is the electrophilic solvation of the substrate (log k–E_t pair correlation coefficient 0.961), but additional inclusion of the polarity of the medium improves the R value.

Table 2. Experimental [10] and calculated [Eq. (3)] log k values for the decomposition of *tert*-butyl (2,5-dioxopyrrolidin-1-yl) performate

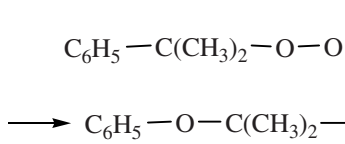
Solvent	log k_{exp}	log k_{calc}	Δlog k
Cyclohexene	–5.046	–4.890	–0.156
Benzene	–4.421	–4.697	0.276
Chlorobenzene	–4.309	–3.996	–0.313
Methanol	–2.222	–2.157	–0.065
Benzonitrile	–3.004	–3.342	0.338
Nitrobenzene	–3.467	–3.388	–0.079

$$\log k = -8.33 + 2.85f(\varepsilon) + 0.0869E_t, \quad (3)$$

$$R\ 0.970;\ s\ \pm 0.238.$$

Contrary to the previous case, the $f(\varepsilon)$ term has a positive sign. That means that the decomposition rate increases with increasing polarity of the medium.

The acid-catalyzed thermolysis of cumyl perbenzoate is a more complicated case [11]. At 50–80°C, in the presence of halocarboxylic acids, benzenesulfonic acid, or $AlCl_3$, this compound undergoes protonation followed by heterolytic rearrangement.



$$C_6H_5{-}C(CH_3)_2{-}O{-}O{-}C(=O){-}C_6H_5 \longrightarrow C_6H_5{-}O{-}C(CH_3)_2{-}O{-}C(=O){-}C_6H_5. \quad (4)$$

The rate of the perester rearrangement to benzoate is described by a first-order equation and is strongly depends on the solvent but not directly related to its polarity (Table 3). At the same time, the experimental data [11] are excellently generalized by a six-parameter equation (5).

$$\log k = 6.37 + (4.45\pm2.78)f(n^2) - (9.16\pm4.00)f(\varepsilon) - (0.843\pm0.893)\times10^{-3}B + (0.129\pm0.014)E_t - (0.259\pm1.17)\times10^{-3}\delta^2 - (7.15\pm6.02)\cdot10^{-3}V_m, \quad (5)$$

$$N\ 8;\ R\ 0.999;\ s\ \pm 0.0807.$$

The pair correlation coefficients r between log k and separate characteristics are equal to 0.684, 0.471, 0.393, 0.009, 0.920, and 0.784, respectively. The low r values and large standard deviations of the coefficients at some terms in Eq. (5) show that most of the terms are insignificant, and the reaction rate is controlled by one parameter, specifically electrophilic solvation of the transition state. The three-parameter equation

Table 3. Experimental [11] and calculated [Eq. (6)] log k values for the rearrangement of cumyl perbenzoate

Solvent	log k_{exp}	log k_{calc}	Δlog k
Methanol	–3.405	–3.367	–0.038
Ethanol	–3.750	–3.742	–0.008
n-Butanol	–4.027	–3.846	–0.181
tert-Butanol	–4.721	–4.571	–0.150
Cyclohexanone	–5.357	–5.172	–0.185
Acetic acid	–2.883	–3.027	0.144
Nitromethane	–4.387	–4.538	0.151
Nitrobenzene	–4.903	–5.167	0.264

Table 4. Yields of t-Bu_2O_2 in the decomposition of di(*tert*-butyl) peroxalate in various solvents

Solvent	Viscosity, η, sP	Yield of t-Bu_2O_2		
		log P_{exp}	log P_{calc}	Δlog P
n-Dodecane	1.01	1.1040	1.4170	–0.3130
Hexadecane	2.09	1.3580	1.1590	0.1990
Cyclohexene	0.505	0.7634	0.5561	0.2073
Benzene	0.473	0.6532	0.9236	–0.2704
Toluene	0.472	0.6902	0.7602	–0.0700
Ethylbenzene	0.528	0.7924	0.7272	0.0652
Cumene	0.598	0.8325	0.7101	0.1224
Tetraline	1.61	1.0570	1.1470	–0.0900
o-Dichlorobenzene	1.00	1.0130	0.8505	0.1625
2-Butanol	1.56	–1.0000	–0.8118	–0.1882
Acetic acid	0.865	0.6721	0.5597	0.1124
Acetonitrile	0.310	0.3222	0.2587	0.0635

including $f(\varepsilon)$, B, and E_t very well describes the effect of the medium (R 0.997), but a two-parameter equation including polarity and electrophilic solvation, too, provides quite an adequate generalization.

$$\log k = -6.08 - (8.94\pm2.48)f(\varepsilon) + (0.126\pm0.014)E_t, \quad (6)$$

$$R\ 0.978;\ s\ \pm0.201.$$

The log k values obtained by Eq. (6) and their deviations from experiment (Δlog k) are also presented in Table 3. As seen, the Δlog k values, except for that for nitrobenzene, are smaller than the standard deviation s ±0.20.

Our quantitative results agree with the qualitative conclusion of Yablokova et al. [11] that the effect of permittivity is weaker than the specific effect ofsolvent salvation described by the Grunewald–Winstein parameter Y. Agreement with Eqs. (2) and (3) is also observed, implying that the rate-determining factor in the decomposition of peracid esters is the ability of the medium to effect electrophilic solvation of the substrate, probably by the acid carbonyl oxygen, and thus weaken the peroxide O–O bond.

Our conclusions are also consistent with published data on the thermolysis of *tert*-butyl *o*-(phenylsulfanyl) perbenzoate whose thermolysis rate in 11 solvents is determined exclusively by electrophilic solvation (pair correlation coefficient r 0.985) [12]. But in general the effect of solvation factors is substrate-dependent. Hence, data on *tert*-butyl perbenzoate decomposition are generalized by equations where the determining factors are the energy density, polarizability, and basicity of the medium [7]. The first of these factors is analogous to the cage effect which is significant in radical reactions.

The inhibited decomposition of di(*tert*-butyl) peroxalate proceeds specifically. Here one of the main reaction products is *tert*-butyl peroxide *t*-Bu–OO–*t*-Bu. Niki and Kamiya [13] have considered the contribution of the cage effect in the recombination of the $(CH_3)_3CO^{\cdot}$ radicals formed together with *tert*-butanol and acetone in the inhibited decomposition of this compound at 45°C. Table 4 lists the yields of t-Bu_2O_2 (%), in a series of solvents, and also the viscosities of the latter (η, sP; of the 25 media studied in [14], the required characteristics are available for 12 only). The referees obtained evidence in favor of the Noyes's hypothesis that the reciprocal probability of radical recombination $1/P$ is proportional to the viscosity of the medium $1/\eta$, but only for some binary low-molecular solvent–polymer mixtures, which agrees with data of other workers. However, considering the yields of t-Bu_2O_2 in various individual solvents we can only note a significant difference between aliphatic solvents, where the peroxide yields vary in parallel (not linearly) with their viscosity, and aromatic ones, where the peroxide yields are much lower and almost invariable (Table 4). Niki and Kamiya [13] explained this feature by the possible formation of π complexes between the components and the resulting complication of radical recombination.

The H-bond formation between *t*-BuO$^{\cdot}$ and hydroxyl is explained by the absence of recombination in alcohols (except for *tert*-butanol). As a result, the authors of the cited work repudiate the conclusion that the peroxide yield in the recombination reaction correlates with physicochemical properties of the medium.

We made an attempt to generalize the results of Niki and Kamiya [13] by means of a six-parameter equation (1). The *R* value for all the 15 solvents was unsatisfactorily low (0.706), but after exclusion of the most deviating data for *tert*-butanol, anisole, and *n*-decane, we obtained Eq. (7) with a fair correlation coefficient.

$$\log P = 5.09 - (9.97\pm4.02)f(n^2) + (2.79\pm2.43)f(\varepsilon) - (12.0\pm2.16)\times10^{-3}B - (6.27\pm28.10)\times10^{-3}E_t - (2.54\pm2.13)\times10^{-3}\delta^2 - (3.65\pm1.92)\times10^{-3}V_m, \quad (7)$$

$$N\ 12;\ R\ 0.964;\ s\ \pm0.235.$$

Noteworthy are negative signs at the specific solvation parameters (*B* and E_t) and cohesion factor (δ^2) in this equation. Since there are no reasons to suggest that this perester decompose by a mechanism different from that for other peresters whose electrophilic solvation accelerates the process, it is logical to suggest that here specific solvation stabilizes *t*-BuO$^{\cdot}$ radicals and thus prevents their dimerization.

The low pair correlation coefficients between log *P* and separate parameters of the equation and large deviations in the coefficients at some terms make the most significant factors difficult to determine and point to an intricate *t*-Bu_2O_2 formation kinetics. Therefore, as recommended in [14], to assess significance of separate terms of the equation we excluded them one after another and calculated *R* for the resulting equation with a smaller number of terms. If *R* decreased only slightly, the contribution of the excluded parameter was considered negligible. Thus we found that E_t is insignificant, $f(\varepsilon)$ and δ^2 are of low significance, and the dependence of the *t*-Bu_2O_2 yield on the parameters of the medium is satisfactory described by a three-parameter equation (8).

$$\log P = 4.37 - (8.95\pm3.06)f(n^2) - (11.60\pm1.79)\times10^{-3}B - (3.00\pm1.45)\times10^{-3}V_m, \quad (8)$$

$$R\ 0.952;\ s\ \pm0.213.$$

In this equation, the determining factor is specific nucleophilic solvation. When the *B* term is excluded, *R* decreases to 0.647, while on the exclusion $f(n^2)$ or V_m the decrease in *R* is much smaller (to about 0.9). Hence, it is evident that basic solvents effect solvation of *t*-BuO$^{\cdot}$. radicals formed by the decomposition of di-(*tert*-butyl) peroxalate and thus prevent their dimerization.

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