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Solvent Effect on the Rate of *β*-Scission of the *tert*-Butoxyl Radical

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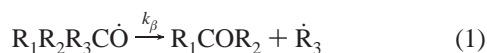
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The transient absorption spectrum of the *tert*-butoxyl radical in the UV region was obtained by the laser flash photolysis technique. The rate constants for *β*-scission and self-termination reactions of *tert*-butoxyl radicals were measured in five solvents; the Arrhenius parameters of the rate constant for *β*-scission k_β were determined. It was shown that both the solvent polarity and ability for hydrogen bonding accelerate the reaction of *β*-scission. The solvent effect on the rate constant of the *β*-scission reaction is discussed in terms of a simple Onzager−Betcher model, a point dipole model, and a model of the H-bonded complex of the radical with the solvent molecule.

Introduction

Spectroscopy and reaction kinetics of alkoxyl radicals have been extensively studied over the past decade. In these studies, special attention was given to the solvent effect on the main reactions of alkoxyl radicals: the *β*-scission and hydrogen abstraction:

$$R_1R_2R_3C\dot{O} \xrightarrow{k_\beta} R_1COR_2 + \dot{R}_3 \qquad (1)$$

$$R_1R_2R_3C\dot{O} + RH \xrightarrow{k_a} R_1R_2R_3COH + \dot{R} \qquad (2)$$

The first observation of the effect of media on the reaction rate constants of alkoxyl radicals has been made in pioneering works of Walling and Wagner.[1,2] Studying the distribution of the products of the reactions of *tert*-butoxyl radicals generated during the photolysis of *tert*-butyl hypochlorite, they found[1,2] that the ratio of the rate constants for hydrogen abstraction and *β*-scission, k_a/k_β, strongly depends on the polarity of the solvent. This effect could be attributed to either an increase in k_β with increasing solvent polarity or a decrease in k_a, or both.[3] To separate the contributions of these two processes, direct measurements of the rate constants for *β*-scission and hydrogen abstraction were required.

A recent investigation of the solvent effect on the rate constant for hydrogen abstraction by alkoxyl radicals has been performed by Ingold, Lusztyk, and co-workers.[3−8] It has been shown that the solvent effect on the hydrogen abstraction from substrates RH is mainly determined by hydrogen bonding between RH and solvent molecules and, in general, does not depend on the nature of the attacking radical.

The solvent effect on the rate constants of radical fragmentation is usually negligibly small;[9] that is why this reaction was often considered as a kinetic standard ("chemical clock") for the quantitative determination of the rate constants of competitive reactions.[10,11] Nevertheless, if the solvent stabilization (due to solvent polarity or hydrogen bonding) of the transition state

for the fragmentation differs significantly from that of the initial radical, the activation energy of this reaction becomes solvent dependent. Direct evidence of the solvent effect was obtained for *β*-scission of 2-phenylethoxyl,[12] cumyloxyl,[3,13] and decarbonylation of some acyl radicals.[14,15] However, to the best of our knowledge, direct measurements of the rate constant for *β*-scission in different solvents have never been performed for one of the most important alkoxyl radicals, *tert*-butoxyl. Most likely, it is mainly caused by experimental difficulties. *tert*-Butoxyl has no absorption bands in the visible,[16−18] and its absorption in the near-UV is rather small. To our knowledge, only weak "tail-end" absorption of *tert*-butoxyl radicals at wavelengths above 300 nm has been published[17,18] until now. Additionally, as follows from indirect measurements,[2,19] the rate constant of *β*-scission for *tert*-butoxyl is rather low, and at the high radical concentrations this reaction is strongly suppressed by the second-order reactions.

In the present work we are pleased to report the electronic absorption spectrum of the *tert*-butoxyl radical in the UV region and the measurements of the rate constant for its *β*-scission in variety of solvents. To decrease the contribution of the second-order reactions, we carried out the flash photolysis measurements at the lowest possible initial radical concentrations. Despite this, for some solvents at room temperature the radical recombination still remained the main channel of radical decay. Thus, for all solvents the measurements were performed at temperatures ranging from 295 to 345 K, and the rate constants of *β*-scission at room temperature were determined from the Arrhenius parameters obtained.

Experimental Section

The detailed description of our LFP setup has been published earlier.[20] Solutions placed in a rectangular cell 10 × 10 mm² were irradiated by the light pulses of a Lambda Physik EMG 101 excimer laser (308 nm, pulse energy up to 100 mJ). The dimensions of the laser beam at the cell front are 4 × 9 mm². The monitoring system includes a xenon short-arc lamp DKSh-120 connected to a high-current pulser, two monochromators, a Hamamatsu R955 photomultiplier, a digitizer LeCroy 9310A, and sets of filters and shutters. The monochromator placed between the lamp and the cell allows to completely avoid

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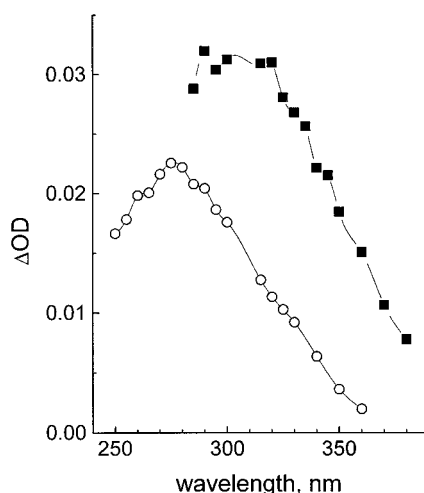
Figure 1. Absorption spectrum of the *tert*-butoxyl radical: open circles, solvent acetonitrile; solid squares, solvent benzene.

depletion of the solution by the monitoring light and increases the spectral selectivity of the monitoring system; besides, it easily allows to compensate for the wavelength-dependent shift of the focus caused by the lens chromatic aberration and to form the monitoring beam inside the cell into a distinct rectangle of area 3×1 mm^2.

All solutions were purged with argon for 15 min prior to use and during the irradiation. For high-temperature measurements the cell was warmed by a hot air flow; the temperature was controlled by a thermocouple placed inside the cell just above the irradiated zone.

Quantum chemical calculations of the geometry and enthalpy of formation of the reactants, products, and transition states were performed using AM1[21] and PM3[22,33] methods based on a modified MNDO-85 program.[24] Properties of the radical species were determined by both unrestricted (UHF) and restricted (RHF) Hartree–Fock techniques in a "half-electron" approximation.[25] The transition states were found according to ref 26. The free energies of solvation were estimated using a simple Onzager–Betcher model or a point dipole model.[27,28] Since the PM3 method is better adopted to the calculation of the geometry and enthalpy of formation of H-bonded complexes,[23,29] we used only this technique for the study of the influence of the protic solvents on the activation energy of the β-scission reaction.

The UV–vis absorption spectrum of the *tert*-butyl radical was calculated using a single excitation configuration interaction (CIS) method[30] with 6-311+G* basis set. The geometry was optimized by a DFT method[31] (B3LYP/6-31G*). Free energy of solvation of *tert*-butyl was calculated in terms of the UHF approximation (UHF/6-31G*) using an Onsager model[32] and a polarized continuum model[33] (PCM). The calculations were performed using the GAUSSIAN94 program.[34]

Results

Spectral Data. Figure 1 shows the transient absorption spectra obtained during the photolysis of 0.07 M di-*tert*-butyl peroxide (DTBP) in different solvents 300 ns after the laser flash. For four solvents, tetrachloromethane, acetonitrile, *tert*-butyl alcohol, and acetic acid, the transient spectra were practically identical (open circles in Figure 1, only spectrum for acetonitrile solvent is shown), and the time profiles of the signal decay in all solvents were wavelength-independent. The spectrum at wavelengths above 320 nm well coincides with the

"tail-end" absorption of *tert*-butoxyl reported by Avila et al.[17] Ab initio calculations show that the *tert*-butoxyl radical has two absorption bands, the first one being in a vacuum-UV region (141 nm, oscillator strength $f = 2.6 \times 10^{-2}$) and the second, of rather low intensity ($f = 4 \times 10^{-4}$), at 277 nm. This band very well coincides with the experimental spectrum (Figure 1). Thus, the obtained spectrum can be reliably attributed to the *tert*-butoxyl radical (BO$^\bullet$). The spectrum obtained in benzene is more intensive (solid squares) and demonstrates a red shift as compared with the case of nonaromatic solvents. The red shift in spectra of alkoxyl radicals in aromatic solvents has been observed earlier[18] and was attributed to the formation of π-complexes between radicals and solvent.

To determine the absolute values of absorption coefficient of BO$^\bullet$ in different solvents, for every solvent carefully matched pairs of experiments[17,18,35] have been performed: (1) during the photolysis of 0.11 M DTBP, the kinetics of BO$^\bullet$ at the absorption maximum (300 nm for benzene and 275 nm for other solvents) were measured; (2) during the photolysis of 0.11 M DTBP and 0.3 M diphenylmethanol (DPH) the kinetic traces of ketyl radicals DP were obtained at 545 nm, where the absorption coefficient of these radicals $\epsilon_{DP} = 3220$ M^{-1} cm^{-1} is well-known.[36] In these experimental conditions, the rise time of the signal at 545 nm (in experiment 2) was more than 10 times shorter than the decay of BO$^\bullet$ (in experiment 1). Thus, most of BO$^\bullet$ abstracts the hydrogen atom from diphenylmethanol forming benzophenone ketyl radicals:
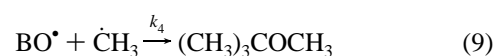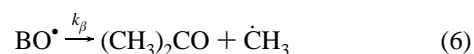
$$(CH_3)_3C\dot{O} + DPH \rightarrow (CH_3)_3COH + D\dot{P} \qquad (3)$$

The absorption coefficient of BO$^\bullet$ was determined from the ratio

$$\epsilon_{BO} = \epsilon_{DP} \frac{OD_{in}^{BO}}{OD_{max}^{DP}} \frac{C_{max}^{DP}}{C_{in}^{BO}} \qquad (4)$$

where C_{in}^{BO} and OD_{in}^{BO} are the initial concentration and optical absorption of BO$^\bullet$ at 275 nm (300 nm in benzene); C_{max}^{DP} and OD_{max}^{DP} are the maximal concentration and optical absorption of DP at 545 nm. The actual ratio C_{max}^{DP}/C_{in}^{BO} was determined taking into account the rate of initial growth of absorption at 545 nm and the rate of BO$^\bullet$ decay in absence of diphenylmethanol. The small absorption of DPH at 308 nm was also taken into account. For every solvent, these sets of experiments were carried out for 3–5 different laser energies (in the range 10–70 mJ per pulse), and the results were averaged. For four nonaromatic solvents, the absorption coefficient of BO$^\bullet$ at 275 nm was the same within the experimental error, $\epsilon_{BO} = 560 \pm 70$ M^{-1} cm^{-1}; for benzene solvent at 300 nm $\epsilon_{BO} = 800 \pm 50$ M^{-1} cm^{-1}.

Kinetic Data. The general scheme of DTBP photolysis can be presented as follows:

$$DTBP \xrightarrow{h\nu} 2BO^\bullet \qquad (5)$$

$$BO^\bullet \xrightarrow{k_\beta} (CH_3)_2CO + \dot{C}H_3 \qquad (6)$$

$$2BO^\bullet \xrightarrow{2k_2} DTBP \qquad (7)$$

$$2\dot{C}H_3 \xrightarrow{2k_3} C_2H_6 \qquad (8)$$

$$BO^\bullet + \dot{C}H_3 \xrightarrow{k_4} (CH_3)_3COCH_3 \qquad (9)$$

Besides, BO$^\bullet$ can abstract a hydrogen atom from a solvent or

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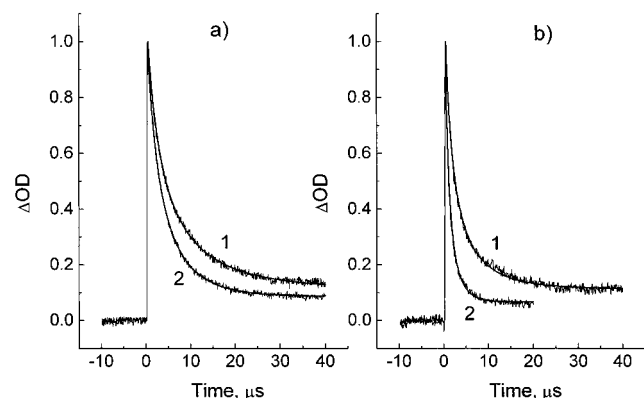
Figure 2. Transient absorption kinetics of the *tert*-butoxyl radical in benzene (trace 1) and acetonitrile (trace 2): (a) at $T = 295$ K, (b) at $T = 335$ K. For the fitting procedure, see text.

from the parent peroxide:

$$BO^\bullet + RH \xrightarrow{k_a} (CH_3)_3COH + \dot{R} \qquad (10)$$

Figure 2a shows the kinetics of BO$^\bullet$ decay obtained at room temperature for two solvents, benzene (trace 1) and acetonitrile (trace 2); both traces are scaled to unity. For benzene solvent, the absorption of BO$^\bullet$ decays practically by pure second-order law until the lowest detectable initial concentrations of radicals. It means that the rate of β-scission (6) is too small to compete with the reaction (7) of radical termination. On the other hand, the BO$^\bullet$ decay in acetonitrile presents a mixture of the first-order and second-order reactions. When the same experiments were carried out at $T = 61$ °C, the admixture of the first-order reaction was observed for both benzene and acetonitrile (Figure 2b).

The rate constants for β-scission k_β of BO$^\bullet$ at different temperatures were determined in the following way. For every given temperature, the kinetics of BO$^\bullet$ decay have been obtained for at least three different laser energies (typical values are 50, 35, and 20 mJ per pulse). These kinetic data were treated simultaneously according to the reaction scheme (5)−(9), taking into account the known absorption coefficient of BO$^\bullet$ (see above). Thus, the contribution of the first-order reaction into the radical decay was determined.

In an additional experiment, the dependence of radical decay on the concentration of the initial substrate has been measured. The independence of the first-order component of decay on DTBP concentration testifies that the hydrogen abstraction from DTBP is negligibly small.

The temperature dependencies of the first-order rate constant for five solvents in Arrhenius coordinates are shown in Figure 3. For all solvents, the data lay on a straight line fairly well. The corresponding frequency factors and activation energies are collected in Table 1. This table also presents the rate constants for BO$^\bullet$ self-termination reaction at room temperature and the first-order rate constants at room temperature. (For nonpolar solvents the last is an extrapolation from the higher temperatures.)

Product Yields. The analysis of the product yields at different temperatures was carried out by means of NMR spectroscopy. The 0.11 M solution of DTBP in deuterated acetonitrile placed in a quartz cell was irradiated by an excimer laser under exactly the same experimental conditions as in LFP measurements, and then the ^{1}H NMR spectra of the irradiated samples were obtained. For every temperature, 3−4 samples with the different dose of irradiation were taken. In all
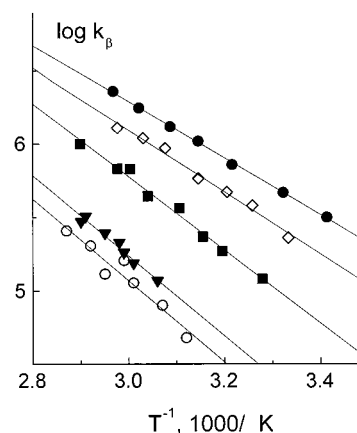

Figure 3. Arrhenius plots for the β-scission rate constant of the *tert*-butoxyl radical. Solvents: open circles, tetrachloromethane; triangles, benzene; squares, acetonitrile; diamonds, *tert*-butyl alcohol; solid circles, acetic acid.

TABLE 1: Rate Constants for the Reactions of β-Scission and Self-Termination of *tert*-Butoxyl Radicals at $T = 295$ K and Arrhenius Parameters for k_β

solvent	$\log(A/\mathrm{s}^{-1})$	E_a, kJ/mol	k_β(295 K) $\times 10^4$,[a] s^{-1}	$2k_2$(295 K) $\times 10^9$, M^{-1} s^{-1}
gas phase[b]	14.04	62.5	0.163[c]	
CCl$_4$	13.4 ± 0.5	53 ± 4	1.0 ± 0.2	2.8 ± 0.4
C$_6$H$_6$	13.4 ± 0.6	52 ± 4	1.4 ± 0.3	3.4 ± 0.3
CH$_3$CN	13.2 ± 0.4	48 ± 3	6.4 ± 1.1	4.1 ± 0.8
(CH$_3$)$_3$COH	12.4 ± 0.6	40 ± 5	19 ± 4[c]	1.5 ± 0.4[c]
CH$_3$COOH	12.1 ± 0.3	37 ± 3	34 ± 6	2.7 ± 0.6
H$_2$O[d]			140 ± 15	

[a] Values of the observed rate constant for first-order decay. [b] Data from ref 50. [c] For $T = 303$ K. [d] Data from ref 49.
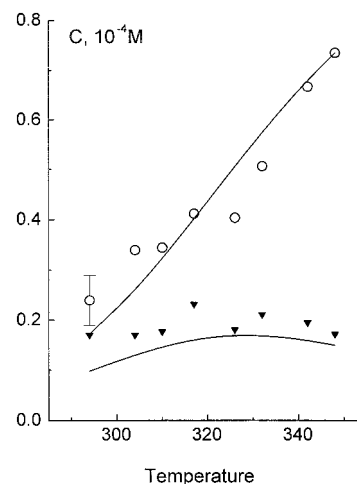
Figure 4. Calculated (solid lines) and experimental yields of acetone (circles) and *tert*-butyl methyl ether (triangles) during the photolysis of 0.11 M DTBP in deuterated acetonitrile. In calculations, the kinetic parameters were taken from Table 1; the initial radical concentration was 1×10^{-4} M.

measurements, the depletion of the parent peroxide was kept below 5%. The formation of the main reaction products, acetone and *tert*-butyl methyl ether, was linear with respect to the irradiation dose. The concentrations of the reaction products have been determined from the integration of NMR spectra and then recalculated into the product yield per laser shot in the irradiated volume. The results are shown in Figure 4.

We tried to carry out the same experiment using deuturated benzene as a solvent. However, in testing experiments, we revealed that under our experimental conditions during the

irradiation at temperatures above 50 °C a significant amount of the forming acetone evaporates from the cell. (In the associating solvent acetonitrile the evaporation of acetone was below 10% at highest temperatures used.) Thus, the results obtained for benzene solvent were disregarded.

Solid lines in Figure 4 show the calculated temperature dependence of the product yield according to the reaction scheme (5)−(9). The Arrhenius parameters for the rate constant of β-scission were taken from the kinetic measurements. For radical termination reactions, two reasonable assumptions have been made:

(i) The radical termination rate constants k_t are close to the diffusional limit, $k_t \sim D$, where D is the diffusion coefficient.[37,38] The dependence of the diffusion coefficient on the solvent viscosity η and temperature T can be expressed[39,40] as $D = kT/6\pi r\eta f$, where r is the radical hydrodynamic radius and f is the microfriction factor. Thus, in our calculations, we used the relation $k_t \sim T/\eta$.

(ii) We presumed that the self-termination rate constants for the radicals of different size (e.g., BO• and methyl) are proportional to the microfriction factors:

$$k_2/k_3 = r_{BO}D_{BO}/r_{Me}D_{Me} = f_{BO}/f_{Me}$$

The microfriction factors were estimated as[39,40]

$$f = 0.16 + 0.4r/r_s$$

where r_s is the radius of the solvent molecule, which leads to the ratio $k_2/k_3 \approx 0.45$. The cross-termination rate constant can be described[40,41] by the geometric mean rule: $k_4 = 2(k_2k_3)^{1/2} \approx 1.3k_3$.

During the calculations, the initial radical concentration taken from the kinetic measurements was adjusted within 20% in order to obtain the best fit to the experimental results.

It is noteworthy that the product analysis in both solvents (acetonitrile and benzene) has revealed only the trace amounts of *tert*-butyl alcohol, the main product of the hydrogen abstraction reaction (10).

Discussion

Generally speaking, the first-order decay of BO• can be caused by two reactions: β-scission of BO• (reaction 6) and hydrogen abstraction from the solvent or from the starting peroxide (reaction 10). The independence of the first-order rate constant of radical decay on the concentration of initial compound testifies that under our experimental conditions (concentration of DTBP about 0.1 M, initial radical concentrations $10^{-5}-10^{-4}$ M) the hydrogen abstraction from DTBP is insignificant.

The reaction with solvents cannot be ruled out completely. Paul et al.[42] revealed that *tert*-butoxyl radicals can react with even such an inert solvent as acetonitrile. Avila and co-workers[3] reported the hydrogen abstraction by cumyloxyl radicals from *tert*-butyl alcohol. Here, we have only indirect evidence that, for the solvents used in the present work, the reactions with the solvents do not play a significant role. Table 1 shows that for all solvents the frequency factors for the first-order rate constant are similar, but the activation energy is solvent-dependent. The typical frequency factors for H abstraction are 10^8-10^9 M^{-1} s^{-1};[43,44] for the neat solvent it corresponds to 10^9-10^{10} s^{-1}, which is 2−3 orders of magnitude smaller than the frequency factors for the first-order rate constants determined in the present work. Somewhat smaller frequency factors in $(CH_3)_3COH$ and CH_3COOH, as compared with the other solvents, indicate that some radicals can be lost due to hydrogen

abstraction from acetic acid and *tert*-butyl alcohol. However, if for any of the solvent used the hydrogen abstraction was the main channel of BO• decay, one would expect a significantly smaller frequency factor for this solvent. This statement is also confirmed by the absence of *tert*-butyl alcohol formation during the photolysis of DTBP in acetonitrile and benzene. Unfortunately, it is difficult to provide the product analysis for the most probable hydrogen donor solvent *tert*-butyl alcohol, because in this case the product of the hydrogen abstraction coincides with the solvent. Thus, for this particular solvent the role of hydrogen abstraction remains somewhat uncertain.

The analysis of the product yield in acetonitrile confirms the reaction scheme (5)−(9). Solid lines in Figure 4 show the computer simulations of the yields of acetone and ether according to this scheme. Rather good agreement between calculated and experimental product yields has been achieved. The calculated ratio of acetone/ether concentrations also coincides well with the experimental data. From these results, the following conclusions could be extracted: (a) under our experimental conditions the hydrogen abstraction is of minor importance, and the main channels of BO• decay are the reactions of β-scission and radical termination; (b) the agreement between calculated and experimental temperature dependencies of the product yields is also a good confirmation of the kinetic results obtained by LFP.

The values of the rate constants k_β and k_2 reported in this work can be compared with the previous indirect measurements. Walling and Kurkov[45] estimated $2k_2$ as 2.8×10^9 M^{-1} s^{-1} at 313 K in CCl$_4$; Wong[19] reported $2k_2 = 1.6 \times 10^9$ M^{-1} s^{-1} measured by the EPR technique. However, since in the last work the measurement of $2k_2$ was based on a probably underestimated rate constant for hydrogen abstraction,[44] this value for $2k_2$ is likely underestimated as well.

We have not found in the literature the data on the direct measurements of the rate constant for β-scission of the *tert*-butoxyl radical, so we can compare our results only with the related data from the different sources. Walling and Wagner[2] measured the yields of acetone and *tert*-butyl alcohol during the photolysis of mixtures of *tert*-butyl hypochlorite and cyclohexane and determined in this way the ratios of k_a/k_β (reactions 10 and 6, RH = cyclohexane) for the different solvents. In particular, the k_a/k_β ratios were equal 48.6 M^{-1} in benzene, 19.8 M^{-1} in acetonitrile, and 4.87 M^{-1} in acetic acid at temperature 298 K. The rate constants for hydrogen abstraction by alkoxyl radicals from cyclic hydrocarbons k_a were measured by different authors.[42−44,46,47] For the reaction of *tert*-butoxyl with cyclopentane the reported values of k_a are 3.45×10^5 M^{-1} s^{-1},[44] 8.57×10^5 M^{-1} s^{-1},[43] and 8.8×10^5 M^{-1} s^{-1},[42] and with cyclohexane $k_a = 1.6 \times 10^6$ M^{-1} s^{-1}.[47] Avila et al. reported $k_a = 1.2 \times 10^6$ M^{-1} s^{-1} for the reaction of cumyloxyl radical with cyclohexane;[3] besides, in this work[3] it was shown that the rate constant k_a for hydrogen abstraction from cyclohexane is solvent-independent. Thus, we can estimate the rate constant of the reaction of BO• with cyclohexane as $k_a \approx 1.0 \times 10^6$ M^{-1} s^{-1}. The combination of this value with k_a/k_β ratios reported by Walling and Wagner[2] (see above) gives $k_\beta = 2.0 \times 10^4$ s^{-1} in benzene, 5.0×10^4 s^{-1} in acetonitrile, and 2.0×10^5 s^{-1} in acetic acid, which is in good agreement with our results (Table 1).

For further analysis, our results can be presented as a correlation between the most commonly used solvent parameter $E_T(30)$[9,48] and the logarithm of the rate constant for β-scission (Figure 5). Figure 5 presents also the data reported by Erben-Russ et al.[49] for water solvent. The data for all solvents except

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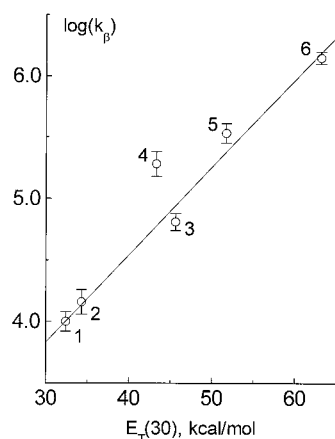
Figure 5. Correlation of $\log(k_\beta)$ with $E_T(30)$ (kcal/mol) in tetrachlormethane (1), benzene (2), acetonitrile (3), *tert*-butyl alcohol (4), acetic acid (5), and water[49] (6).

TABLE 2: Data of Semiempirical Quantum Chemical Calculations of the Activation Enthalpy ($\Delta H^\#$) for the Reaction of β-Scission of *tert*-Butoxyl Radical, Values of Dipole Moment of Reactant (μ_R) and Transition State (μ_{TS}), and Solvation Part of Free Energy of Activation in Benzene ($\Delta G_b^\#$) and Acetonitrile ($\Delta G_{ac}^\#$)

method	$\Delta H^\#$, kJ/mol	μ_R, D	μ_{TS}, D	$\Delta G_b^\#$, kJ/mol	$\Delta G_{ac}^\#$, kJ/mol
AM1 (RHF)	67.0	2.59	3.23	1.13	2.14
AM1 (UHF)	59.1	1.96	2.76	1.14	2.18
PM3 (RHF)	66.6	2.22	3.00	1.22	2.35
PM3 (UHF)	65.4	1.76	2.61	1.13	2.14

tert-butyl alcohol show a reasonably good linear relationship. The unexpectedly high value of k_β in *tert*-butyl alcohol points to the possible contribution of the hydrogen abstraction from this solvent into BO• decay.

More quantitatively, the solvent effect on the rate constant for β-scission can be explained in terms of different solvent stabilization of the radical and the transition state for radical fragmentation, caused by the different polarity of the solvents and their ability to form the hydrogen bonds. The influence of the solvent polarity can be accounted for as a dipole–dipole interaction of the parent radical and the transition state for β-scission with the solvent medium treated as a continuum of dielectric constant ϵ. According to Kirkwood's formula,[9] the solvent influence on the activation energy of the reaction can be considered as the difference of the solvation energies for the transition state (TS) and reactant (R):

$$\Delta G_{sol}^\# = \Delta G_{sol}^{TS} - \Delta G_{sol}^{R} \qquad (11)$$

$$\Delta G_{sol}^{TS,R} = \frac{\mu^2}{r^3} \frac{\epsilon - 1}{2\epsilon + 1} \qquad (12)$$

where μ is the dipole moment and r is the radical radius.

We performed the semiempirical calculations of the reaction and activation enthalpies and the dipole moments of the radical and the transition state using AM1 and PM3 methods. The results of the calculations are presented in Table 2. Our calculations show that the dipole moment of the transition state is greater than the dipole moment of the parent radical; hence, the solvent should more strongly stabilize the transition state, and the activation energy for β-scission should decrease with the solvent polarity increase. That coincides with the experimental results. The calculated value of the activation enthalpy for the β-scission also well coincides with the reported[50]

activation energy 62.5 kJ/mol for this reaction in the gas phase. However, the experimental difference in activation energies for the polar and nonpolar solvents is much larger than calculated. The same holds true for the activation energies in solutions and in the gas phase (compare Tables 1 and 2). We suppose that this discrepancy is probably connected with the simplicity of the model: a radical is considered as a dipole of radius r, whereas in the real radical the dipole moment is mainly concentrated along the C–O bond.

To account for the charge distribution in the molecule, we also used the more sophisticated point dipole model.[27,28] The empirical parameter of this model, the energy of interaction between two neighboring solvent molecule, was estimated as the energy of dipole–dipole interaction between acetonitrile molecules, 12.5 kJ/mol. In this model, the calculated value of activation energy in acetonitrile is 46 kJ/mol, which qualitatively agrees with the experimental value.

Ab initio calculations of the free energy of solvation of BO• confirm the importance of the charge distribution in radical. The calculations were performed using the GAUSSIAN94 program[34] and UHF approximation (UHF/6-31G*) in two models: an Onsager model[32] and a more sophisticated polarized continuum model (PCM).[33] In the Onsager model, the calculated value of free energy of BO• solvation in acetonitrile was only 3.1 kJ/mol, whereas PCM, which takes into account the charge distribution, gives 19.2 kJ/mol. Thus, the simple Onsager model significantly underestimates the solvent stabilization of molecules.

Formulas 11 and 12 and the point dipole model describe only the nonspecific interactions of the solute molecule with the solvent. To account for the effect of the hydrogen bonding, we performed the calculation of the activation enthalpy for the complex of *tert*-butoxyl radical with H_2O (as a typical example of protic solvent). The activation enthalpy of β-scission reaction in the H-bonded complex was estimated as 57.7 kJ/mol, which is 8.8 kJ/mol lower than for the reaction of nonbonded radical. The reason for this effect is the higher energy of H-bond formation for transition state (18.4 kJ/mol) compared with that of the radical (9.6 kJ/mol). The difference in the activation energies of the β-scission reaction in CH_3CN and in protic solvents (*tert*-butyl alcohol and acetic acid) can be attributed to the effect of H-bond formation in the latter solvents (Table 1). This difference (7–10 kJ/mol) is in a very good agreement with our theoretical estimation.

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