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Study of the Rotational Barrier in the Hindered Bisphenoxyl A Radical

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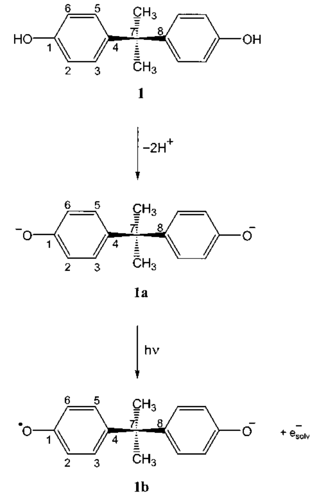
The bulky para substituent of bisphenol A (**1**) restricts rotation around the C4−C7 bond in the phenol, phenoxide, and phenoxyl radical. This hindered rotation is responsible for modulation of the hyperfine interaction between the unpaired electron and the meta protons on the phenoxyl ring. The modulation manifests itself in the time-resolved electron paramagnetic resonance (TREPR) spectrum of the bisphenol A phenoxyl radical as selective broadening of certain transitions. Line widths of the broadened transitions of the bisphenoxyl A TREPR spectrum at different temperatures were obtained by simulation of the TREPR spectra, and an energy barrier of 6.2 ± 1 kcal mol^{-1} for this rotation was estimated using a simple two-state model for rotation around the C4−C7 bond.

Introduction

The structure and reactivity of phenols and phenoxides are of interest in many areas of chemistry. Bisphenol A, structure **1** in Scheme 1, is a popular monomer and polymer constituent and is used, for example, to synthesize dimethacrylates,[1] epoxy resins,[2] and poly(arylene ether ketones).[3,4] Previously in our laboratory, the photoionization of bisphenol A has been used to create a phenoxyl radical and a solvated electron as a model system to study the inhibition of polymer chain growth in step-growth polymerizations.[5] In the course of that work, it became important to understand the chemical and photochemical behavior of bisphenol A and its anion (conjugate base) and the detailed structures of the ensuing free radicals from photochemical reactions. We present here the results of further studies on radical **1b**, in particular, which focus on dynamic effects and their manifestation in time-resolved electron paramagnetic resonance (TREPR) spectra.

Photoexcitation of the *n*-*π** transition in the phenol chromophore, followed by intersystem crossing from the first excited singlet to the triplet state, can result in the ejection of an electron. The triplet radical pair created by this photoionization process is phenoxyl/solvated electron ($\mathrm{PhO^{\bullet}/e_{solv}^{-}}$). As we have shown in a previous study of tyrosyl radicals,[6,7] TREPR is an excellent tool with which to study the phenoxyl radicals produced by these photoionization processes because it is fast enough to directly detect the radicals with high structural resolution. The magnitudes and line widths of the hyperfine splittings in the TREPR spectra provide information about the structure and, in some cases, the dynamics of the phenoxyl radical. The phenoxyl TREPR signal is split into multiple transitions by hyperfine interaction between the unpaired electron spin and magnetic nuclei in the phenoxyl molecule. Rotational motion in the molecule can affect these transitions via modulation of hyperfine interactions. It is clear that there should exist a significant barrier for rotation in phenoxyl radical **1b**, and the purpose of this study is to estimate this barrier by simulation of the observed line-broadening effects due to hindered rotation.

SCHEME 1



Experimental Section

1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (dimethylpropyleneurea, DMPU), bisphenol A, and 4-*tert*-butylphenol were used as received from Aldrich. Sodium hydroxide (NaOH) was used as received from Mallinckrodt. Water with a resistance of 18.2 MΩ/cm from a Millipore Milli-Q system was used in all experiments. The TREPR data were collected using a JEOL-USA, Inc. RE-1X X-band (9.5 GHz) spectrometer modified for time-resolved direct detection in a manner described elsewhere.[8] The gatewidths of the boxcar integrator were 100 ns. Samples were photolyzed with a Lambda Physik LPX-100i excimer laser operated at 308 nm (XeCl) at a repetition rate of 60 Hz with pulse energies between 14 and 28 mJ at the sample and a pulse width of approximately 17 ns. Samples were prepared by dissolving bisphenol A in basic water, followed by addition of the appropriate volume of DMPU to achieve a molar DMPU concentration (X_{DMPU}) of ~0.20. Aqueous phenoxide solutions were prepared with the final pH ≈ 11, which is basic enough to ensure that the phenols (pK_a ≈ 10) are deprotonated. Samples were bubbled with nitrogen before and during the experiment, and sample volumes of ~50−80 mL

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were recirculated through the EPR cavity at a rate of ~0.5−1 mL per second. Sample temperature was controlled by passing the Teflon flow line through a copper coil immediately before it entered the cavity. For high-temperature experiments, the coil was wrapped in heating tape regulated by a temperature control box. For low-temperature experiments, the sample reservoir, the pump head, and the coil were all immersed in ice or an ice bath. Thermocouples were placed where the tubing exited from the copper coil (before the cavity) and at the top of the sample cell (after the cavity). At high temperatures (~55 °C), the temperature difference between the thermocouples was approximately 4 °C. At intermediate temperatures (~40 °C), the difference was about 2.5 °C. At room temperature, with no use of the heating apparatus, the thermocouple readings were usually identical, though some heating from the laser light (~0.2 °C) was occasionally observed. At low temperatures (~10 °C), the difference between the thermocouple readings varied from 4 to 6 °C. The temperatures given in the text represent the average temperature between these two readings.

Simulations of TREPR spectra were based on a spin Hamiltonian that includes the Zeeman interaction, the *g* factor difference of the two radicals, and any hyperfine interactions that the radicals experience from $I = {}^1/_2$ or $I = 1$ nuclei. One line width may be input for all transitions for each radical. Hyperfine modulation is simulated by inputting two parameters: A_{MOD}, which is the magnitude of the modulation of the hyperfine interaction, and τ, which is the time constant for the modulation. These parameters will be discussed further below in relation to well-established models for hyperfine modulation.

Results and Discussion

Photoionization of bisphenol A in a basic water/DMPU mixture with a mole fraction in DMPU of ~0.20 resulted in the corresponding phenoxyl radical. DMPU was used as a cosolvent because the basic water/DMPU mixture has a very high viscosity (~7−8 cP) which produces enhanced radical pair mechanism (RPM) polarization and lengthens T_1 of the phenoxyl radical. These characteristics allow for the collection of highly resolved phenoxyl TREPR spectra.[9,6] The use of DMPU is also relevant, as it is a safe dipolar and aprotic solvent used as a cosolvent in many reactions of **1** and other phenols performed under basic and nucleophilic conditions.[10−15]

Figure 1 shows the TREPR experimental spectra of the bisphenol A phenoxyl radical in basic water/DMPU at three temperatures, along with one simulation. The hyperfine coupling constants used in the simulation of the phenoxyl radical are listed in Table 1. In general, a change of ±0.05 G in any hyperfine coupling constant had a significant impact on the quality of the simulation. The line width applied to every phenoxyl line in the simulation is 0.2 G. The broad absorptive transition right of center is assigned to the solvated electron but is not included in the simulation. The simulation fits the positions and intensities of the bisphenol A phenoxyl transitions. However, there is a significant broadening of three groups of lines observed in the experimental spectrum which cannot be reproduced. This failure occurs because the simulation program assigns the same line width to every line in the spectrum, but different transitions clearly have different line widths. Restricted rotational motion has been shown to modulate hyperfine interactions, and this modulation results in the broadening of certain EPR lines.[16−24] Under conditions of fast motion, all of these line widths would be equal, but the modulation of one set of equivalent hyperfine interactions results in an alternating line width pattern. For radical **1b**, it is likely that the observed broadening in the TREPR spectrum is due to restricted rotation around the bonds between C4 and C7 and also between C7 and C8 due to the bulky phenoxide group on the C7 carbon. This hypothesis is supported by the TREPR spectrum of the photoionization of 4-*tert*-butylphenol in basic water/DMPU. Replacement of the bulky phenoxide group by a methyl group should make rotation less restricted, and less broadening should occur. This is in fact the case, because even at room temperature the TREPR spectrum of 4-*tert*-butylphenoxyl shows narrow line widths for each transition (Figure 2).

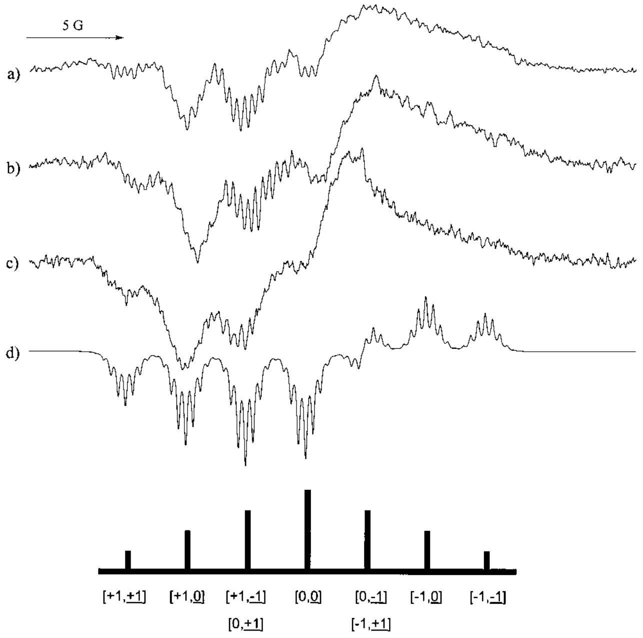
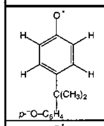
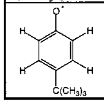


Figure 1. TREPR experimental spectra of bisphenol A phenoxyl radical/e_{solv}^- in basic water/DMPU with $X_{\mathrm{DMPU}} = 0.20$ at a delay time of 0.8 μs and (a) 54 °C, (b) 41 °C, and (c) 24 °C and (d) simulation of the bisphenol A phenoxyl radical. Simulation parameters are listed in the table.

TABLE 1: Simulation Parameters for Bisphenoxyl A and 4-*tert*-Butylphenoxyl Radicals

Phenoxyl	Figure	A_H ortho, G	A_H meta, G	A_H para, G	A_H para, G	Phenoxyl linewidth, G	Sweep Width, G	Delay time (μs)
	1d	5.9	2.95	0.36, β $(CH_3)_2$	0.36 –PhO⁻meta protons	0.2	30	0.8
	2b	6.72	1.9	0.5	–	0.2	50	0.6

The temperature dependence of the TREPR spectrum of radical **1b** is shown in Figure 1. The phenoxyl spectrum may be broken down into seven groupings, each corresponding to the sums, *M*, of the quantum number for the *z* projections of the nuclear spins (m_I) of the ortho and meta protons. These seven groupings are, from low field to high field [*M*(ortho), *M*(meta)], (1) [+1,+1], (2) [+1,0], (3) [+1,−1] and [0,+1], (4) [0,0], (5) [0,−1] and [−1,+1], (6) [−1,0], and (7) [−1,−1]; these transitions are labeled on a stick plot in Figure 1. It is clear that in the room-temperature spectrum the second and fourth groups of lines are broadened in comparison to the first and third sets and the sixth group is not even detected, while the first and third groups are fairly well-resolved. The fifth and seventh groups are not detected both because of their low intensities and because of the presence of the overlapping e_{solv}^- signal.

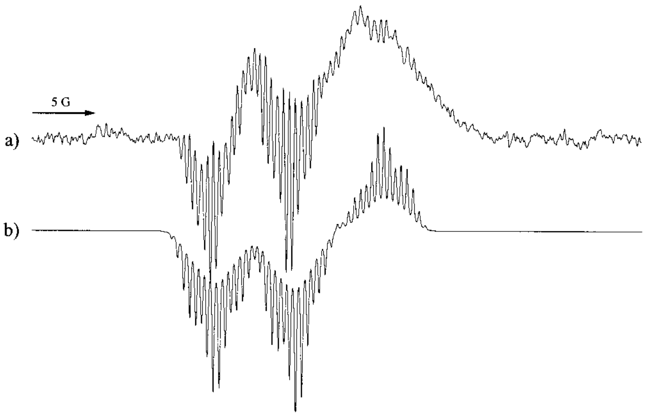
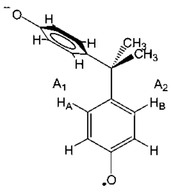
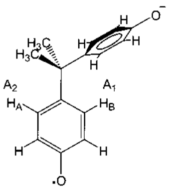


Figure 2. TREPR experimental spectrum (a) and simulation (b) of 4-*tert*-butylphenoxyl/e_{solv}^- in basic water/DMPU with $X_{DMPU} = 0.20$. Simulation parameters are listed in the table.

CHART 1



I



II

This alternating line width pattern is common in EPR spectra of radicals undergoing restricted motion or exchange between two environments of different nuclear spin symmetry.[17,25] Such a restricted rotation may be treated as a two-site problem with jumping occurring between two states, I and II, shown in Chart 1. The hyperfine coupling constant values of the two meta protons involved are A_1 and A_2, and these values are exchanged as the molecule “jumps” from state I to state II.[25] A theory to describe the effect of restricted rotation has been developed which describes line widths of hyperfine transitions as[17,25]

$$T_2(M)^{-1} = T_{2,0}^{-1} + [T_2(M)^{\mathrm{mod}}]^{-1} \tag{1}$$

where $M = \sum m_I$, $T_2(M)^{-1}$ is the total line width of the line, $T_{2,0}^{-1}$ is the line width due to contributions other than hyperfine modulation, and $[T_2(M)^{\mathrm{mod}}]^{-1}$ is the contribution to the line width from the modulation of hyperfine couplings. The latter term is expressed as

$$[T_2(M)^{\mathrm{mod}}]^{-1} = 1/8\tau\gamma_e^{\,2}(A_1 - A_2)^2(M_A - M_B)^2 \tag{2}$$

where τ is the average lifetime of the states I and II (assumed to be equal), γ_e is the magnetogyric ratio of the electron, A_1 and A_2 are the hyperfine coupling constants as defined above, and M_A and M_B are the individual $\sum m_I$ of the sets of protons involved in the modulation. The proton hyperfine couplings that are being modulated by the restricted rotation are the meta protons, H_A and H_B, located on C3 and C5 of the phenoxyl ring. According to eq 2, the contribution to the line width from hyperfine modulation will be largest for the largest values of $(M_A - M_B)$. Because we are dealing with the modulation of only two protons, there are only two possible values for M_A and M_B, $\pm^1/_2$. Therefore, there are only two possible values for $(M_A - M_B)$: a value of 0 (corresponding to $M(\mathrm{meta}) = \pm 1$) and a value of 1 (corresponding to $M(\mathrm{meta}) = 0$). Thus, according to eq 2, the lines corresponding to $M(\mathrm{meta}) = 0$ will be broadened relative to lines with $M = \pm 1$, as is the case (Figure 1).

To further investigate this phenomenon in the bisphenol A phenoxyl TREPR spectrum, TREPR spectra were collected during the photolysis of bisphenol A in basic water/DMPU at different temperatures. Higher temperatures lead to faster rotation around the relevant carbon−carbon bonds, which should result in an averaging of the hyperfine coupling constants, i.e., $A_1 = A_2$, and a decrease in the lifetime τ. The results are shown in Figure 1. The lines in the second, fourth, and sixth groups, where $M = 0$ and $(M_A - M_B)^2 = 1$, are expected to become more resolved as the temperature is increased, and this is indeed the case as the hyperfine splittings in the second and fourth groups become more resolved. However, the effect on the appearance of the sixth group is less obvious and is related to the solvated electron transition. In the experimental spectra, it appears that the solvated electron signal becomes broader at higher temperatures. However, in similar temperature studies of *p*-cresol and tyrosine in basic water/DMPU mixtures, the line width of the solvated electron remains unchanged or narrows only slightly within the same temperature range. It is proposed that this *apparent* broadening of the solvated electron signal is actually the growing in of the 6th group of lines as rotation around the C4−C7 and C7−C8 bonds becomes less restricted and the broadening of this group decreases.

The activation energy for rotation around the bonds, E_a, may be found by the following analysis. Rearranging eqs 1 and 2 and substituting LW(T) for $T_2(M)^{-1}$, LW$_{\mathrm{mod}}$(T) for $[T_2(M)^{\mathrm{mod}}]^{-1}$ and LW$_0$ for $T_{2,0}^{-1}$ give

$$\mathrm{LW_{mod}}(T) = \mathrm{LW}(T) - \mathrm{LW_0} \tag{3}$$

$$= 1/8\tau\gamma_e^{\,2}(A_1 - A_2)^2(M_A - M_B)^2 \tag{4}$$

which leads to an expression for the lifetime of the states I and II (Chart 1):

$$\tau(T) = 8[\mathrm{LW}(T) - \mathrm{LW_0}]/[\gamma_e^{\,2}A_{\mathrm{MOD}}^{\,2}(M_A - M_B)^2] \tag{5}$$

where $\tau(T)$ is in seconds and depends on the temperature, T, and the expression for the hyperfine coupling constant difference $(A_1 - A_2)$ has been replaced with A_{MOD}. For the bisphenol A radical, the only lines that are broadened are those for which $(M_A - M_B)^2$ is not equal to 0; this is only the case for $M_A = -M_B$ or $(M_A, M_B) = (^1/_2, -^1/_2), (-^1/_2, ^1/_2)$. Therefore, for the second, fourth, and sixth groups of lines, $(M_A - M_B)^2 = 1$, and eq 5 becomes

$$\tau(T) = 8[\mathrm{LW}(T) - \mathrm{LW_0}]/[\gamma_e^{\,2}A_{\mathrm{MOD}}^{\,2}] \tag{6}$$

This lifetime may be related to the activation energy for rotation through the rate constant described by the Arrhenius equation:

$$\tau(T) = k_T^{-1} \tag{7}$$

$$k_T = A\exp(-E_a/(RT)) \tag{8}$$

To obtain an activation energy for bond rotation, we must first assume that all other line broadening is equal for all transitions and may be reproduced with a single line width in the simulation program. This assumption is supported by the equal line widths found in the 4-*tert*-butylphenoxyl TREPR spectrum (Figure 2). The broad absorptive transition is attributed to the solvated electron created by photoionization of the phenoxide. Although its appearance obscures some of the upfield phenoxyl transitions, it is clear that the line widths of the phenoxyl transitions do not change with field position. The rates

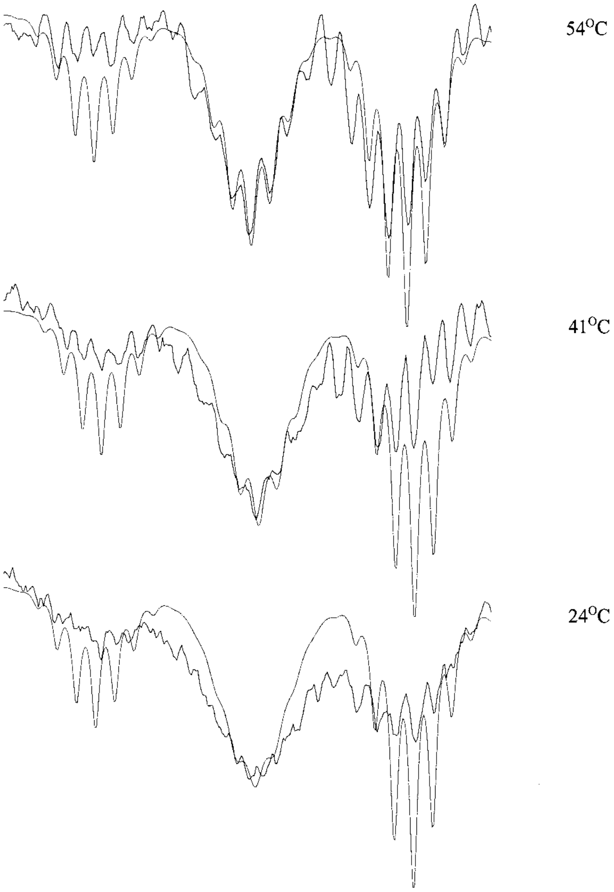


Figure 3. TREPR experimental (solid) and simulation (dashed) spectra of the second group of broadened lines at three temperatures. Simulation parameters are discussed in the text.

k_T may then be found by simulating the bisphenol A phenoxyl TREPR spectra from different temperatures with a simulation routine that takes into account hyperfine modulation of the meta protons on the phenoxyl ring. By fixing A_{MOD} and varying τ in the simulation program, we may obtain k_T for the three temperatures at which spectra were collected. Figure 3 shows the experimental and simulation spectra of the second group of broadened lines at three temperatures. Some comments should be made about the agreement between these experimental and simulation spectra. Most important is that the purpose of these simulations is to match the line widths of the second group of transitions (the middle group in the zoomed-in spectra in Figure 3) by including hyperfine modulation into the simulation routines. It is clear that this goal is achieved for all three temperatures. However, the intensities of the transitions in the other groups are not reproduced in any of the simulations in Figures 1 and 3. This lack of agreement is due to the difficulty in correctly reproducing intensities of TREPR transitions caused by one or more chemically induced dynamic electron polarization mechanisms. The presence of the absorptive transition of the solvated electron also obscures some of the transitions (as discussed above). However, neither of these conditions affects the validity of the physical parameters obtained by simulating the broadening due to hyperfine modulation in the second group of transitions. Values determined for k_T are 3.3×10^8 s^{-1} at 54 °C, 2.0×10^8 s^{-1} at 41 °C, and 1.3×10^8 s^{-1} at 24 °C. According to eq 8, a plot of the $\ln(k_T)$ versus inverse temperature yields a line with a slope equal to $-E_a/R$ and an intercept of $\ln(A)$.

When A_{MOD} is set equal to 1 G, lifetimes for states I and II on the order of 3−8 ns were obtained for the different spectra. This is physically reasonable, and a fit of the data provides a slope of −3130 K and an intercept of 29.2. These values provide $E_a = 6.2$ kcal mol^{-1} and $A = 4.8 \times 10^{13}$ s^{-1}. This is a reasonable value for the preexponential factor A and further justifies the time scale used for τ. This value is higher than those for sp^2−sp^3 bond rotation (generally 1−2.4 kcal mol^{-1}) but slightly lower than the range for unhindered sp^3−sp^3 bond rotation (7.2−9.6 kcal mol^{-1}).[16] Similarly, Sealy et al determined that the restricted motion temperature domain for rotation around the C7−C8 bond in tyrosyl is 278−334 K and that the activation energy for rotation around this bond is on the order of sp^3−sp^3 bond rotation.[16] However the bisphenoxyl A barrier is also lower than the barrier for rotation of 7.8 ± 1.0 kcal mol^{-1} found for the methoxy group in 1,3-methyl-4-methoxyphenoxyl radical, despite the bulk of the para group in the bisphenoxyl A radical.[25] This difference indicates that the double bond character in the C4−C7 bond in the bisphenoxyl A radical is relatively smaller than that in the 1,3-methyl-4-methoxyphenoxyl radical, leading to more facile rotation.

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