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ARTICLES

Specific Solvent Effects on the Structure and Reaction Dynamics of Benzophenone Ketyl Radical

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Complex formation reaction between benzophenone ketyl (BPK) radical and triethylamine was investigated by means of transient absorption and time-resolved ESR methods. The formation constants (K_f's) in benzene, toluene, *o*-xylene, and anisole were measured by a transient absorption method. The enthalpy and entropy changes upon the complex formation were determined by van't Hoff plots of K_f values around 300 K. The ΔG values in the complex formation reaction at 298 K were calculated from these thermodynamic parameters, which show notable difference from those in aliphatic solvents and chlorotoluenes previously reported. The BPK conformation in these solvents was investigated by analyzing the time-resolved ESR spectra of BPK and by the DFT calculation. The hyperfine coupling constant of hydroxy-proton (a_{OH}) was found to depend on solvent as well and there exists a clear correlation between the a_{OH} and K_f (or ΔG) values. It was concluded that the conformation of BPK, especially the conformation between OH and two phenyl groups, depends on the solvation and is an important factor to control the complex formation reaction.

Introduction

Benzophenone ketyl (BPK) radical is one of the important intermediates in the well-known photoreduction of benzophenone (BP) and its spectroscopic property and photochemistry were widely studied.[1−6] BPK has the D_1-D_0 absorption starting at 545 nm and the D_1 state at room-temperature fluoresces with the quantum yield of 0.16 which is higher than those of other aromatic ketyl radicals.[3] The ESR spectrum of BPK shows significant dependence on the solvent, which was understood by considering slightly flexible internal motions of two phenyl and OH groups in BPK.[7] The complex formation reaction of BPK with TEA has recently been studied by a transient absorption method in various solvents and the thermodynamic analysis was carried out to reveal the complex formation dynamics.[8,9] According to the previous reports,[8−10] the BPK-TEA complex is formed through hydrogen-bonding interaction between the OH and amino groups of BPK and TEA, respectively, and the formation constant (K_f) significantly depends on the dielectric constant of solvent. The solvent dependence of K_f values was explained by introducing solvation energy which was calculated based on the reaction field model for solvation.

Since BPK and the BPK-TEA complex are open shell species, ESR spectroscopy is a powerful method to study these radicals selectively. Hyperfine coupling constants (hfcc) of ketyl-type radicals are known to be sensitive to the conformation of radical and we could describe the complex formation of ketyl radical through the conformational difference between uncoupled ketyl and the complex obtained by analysis of their ESR spectra.[10,11] In the present study, we have focused our attention on the conformation of BPK in various solvents and revealed the solvent dependence of K_f and ΔG values for the complex formation reaction. From the analysis of ESR spectra, we propose a few different conformations of uncoupled BPK stabilized by the solvent cage. The different conformations of OH and two phenyl rings of BPK are essential to distinguish them. The conformations of OH and two phenyl rings were derived from the hfcc of hydroxy-proton (a_{OH}) of uncoupled BPK. In relatively nonpolar solvents, the hydroxy-proton sits almost on the molecular plane of BPK.[12] In alcohol, the hydroxy-proton does not seem to locate on the molecular plane. The structure of the BPK-TEA complex is also derived from ESR spectra and it is found that the hydroxy-proton locates far over the molecular plane. A good correlation between the ΔG value for the complex formation reaction and the a_{OH} value of uncoupled BPK is recognized. This correlation suggests that the conformation of uncoupled BPK is strongly related to the ΔG value. The complex formation in the BPK-TEA system will be widely discussed on the basis of the solvent dependence of ΔG and the conformation of uncoupled BPK and the complex in each solvent derived from ESR spectra.

Experimental Section

Time-Resolved (TR) ESR Measurement. The TR-ESR detection system consists of an X-band ESR spectrometer (Varian E-112) and a boxcar integrator (Stanford SR-250) to extract transient ESR signals synchronized with laser pulses. The excitation light source was a XeCl excimer laser (Lambda Physik LPX 100, 308 nm) of 20 ns duration time and of 100 mJ/pulse laser power. The laser pulse of about 20 mJ was

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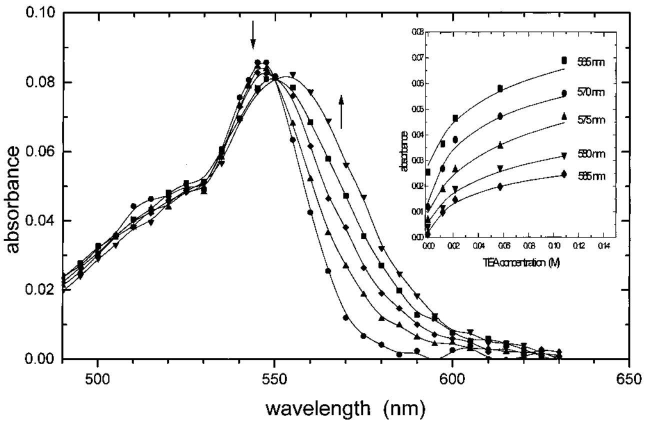


Figure 1. Transient absorption spectra of BPK and the BPK-TEA complex in toluene measured at 0.8−1.4 μs after 355 nm laser excitation at 295 K. The concentrations of TEA were 0, 11.8, 21.7, 57.8, and 108.4 mM. The inset shows fitting curves of eq 1 for absorbance changes against TEA concentration at various wavelengths.

introduced into a photoreaction cell in the microwave cavity. The gate of the boxcar integrator was opened from 1.5 to 2.0 μs after the laser pulse. The signals were collected at the repetition rate of 10 Hz. The microwave power was 15 mW.

Transient Absorption Measurement. The transient absorption detection system has already been described elsewhere.[13] The excitation light source was the third harmonics of a Nd^{3+}-YAG laser (Continuum Powerlight 8010, 8 ns duration time) and the laser power was attenuated to 10 mJ or less at the reaction cell. The laser was operated at Q-switch repetition frequency of 1 Hz under 10 Hz flash lamp operation by using a homemade frequency control unit for Q-switch.

Samples. All the samples, except α-phenylbenzoin, were purchased from Tokyo Kasei and mostly used as received. Benzophenone was recrystallized twice from *n*-heptane. α-Phenylbenzoin was synthesized by the Grignard reaction of phenylmagnesium bromide with benzil in tetrahydrofurane at 245 K and recrystallized from *n*-hexane. Sample solutions were degassed by bubbling of nitrogen or Ar gas and were flowed through the cell. Sample cells were (1) a quartz flat cell with 0.5 mm optical path length attached in the microwave cavity for the TR-ESR measurement and (2) a quartz cell with optical path lengths of 3 mm for excitation laser and 10 mm for monitor lights, respectively, for the transient absorption measurement.

Results and Discussion

Thermodynamic Parameters of Complex Formation Reaction. Figure 1 shows a series of transient absorption spectra of BPK obtained by the laser flash photolysis of benzophenone in toluene with different TEA concentrations. The absorption spectrum characteristic of BPK in the D_1-D_0 transition region is clearly seen in the spectrum without TEA, while the spectra measured in the presence of TEA consist of those due to uncoupled BPK and the BPK-TEA complex with an isosbestic point at 550 nm. The complex formation proceeds according to an equilibrium reaction; BPK + TEA $\rightleftarrows$ complex. From these spectra, we determined the formation constant (K_f) in toluene. The details of the procedures to determine a K_f value have been described in the previous papers.[8,9] The K_f value follows the equation, $K_f = [\mathrm{Com}]/[\mathrm{BPK}][\mathrm{TEA}]$, where Com represents the complex. Absorbance at a wavelength λ is given by $\mathrm{Abs}(\lambda) = \epsilon_k[\mathrm{BPK}] + \epsilon_c[\mathrm{Com}]$ where ϵ_k and ϵ_c are the molar extinction coefficients of BPK and the complex, respectively. We introduce a constant α, which equals to the concentration of [BPK] + [Com]. The α was kept constant during a series of measurements. Hence, the final form of Abs(λ) is given by the eq 1:

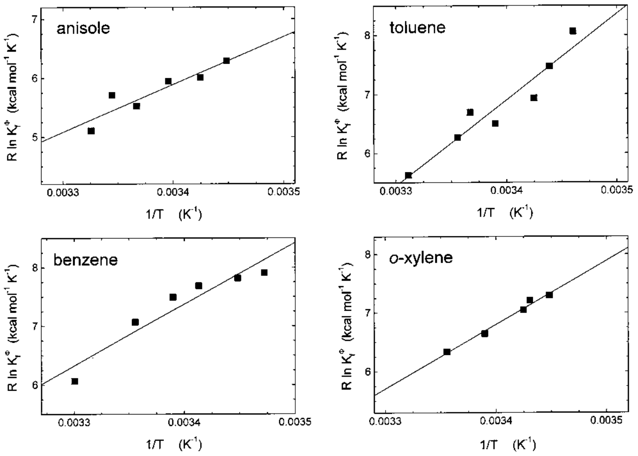


Figure 2. Van't Hoff plots of the complex formation reaction in benzene, toluene, *o*-xylene, or anisole.

$$\mathrm{Abs}(\lambda) = \alpha\epsilon_C \frac{K_f[\mathrm{TEA}] + \dfrac{\epsilon_k}{\epsilon_C}}{1 + K_f[\mathrm{TEA}]} \tag{1}$$

To determine the K_f value from eq 1, we measured Abs(λ) at five wavelengths against TEA concentration. The K_f value for the BPK/TEA system was determined from the least-squares fit of the eq 1 as shown in the inset of Figure 1 using the molar extinction coefficient, $\epsilon_k = 4600\ \mathrm{M^{-1}\ cm^{-1}}$ at the BPK absorption peak (545 nm)[14] and ϵ_c value[8] reported previously. The averaged value of five K_f's (17.1, 25.8, 30.8, 28.0, 30.3 $\mathrm{M^{-1}}$ at 295 K) was adopted as the final K_f value (26.4 $\mathrm{M^{-1}}$). Similar experiments were carried out to determine K_f values in benzene, *o*-xylene, or anisole. Thermodynamic parameters, namely enthalpy and entropy changes (ΔH and ΔS, respectively) of the complex formation reaction in benzene, toluene, *o*-xylene, or anisole were determined by the van't Hoff plot of dimensionless formation constants, K_f^{Φ} values ($= K_f \times \mathbf{c}^{\Phi}$, where $\mathbf{c}^{\Phi}$ is the standard concentration, 1 mol/dm^3) at different temperatures around 300 K as shown in Figure 2. From the slope and intercept values of four fitted lines in Figure 2, the ΔH and ΔS values were determined and are listed in Table 1. According to these values, ΔG values at 298 K were calculated by the equation, $\Delta G = \Delta H - T\Delta S$ and were listed in Table 1. The K_f values and thermodynamic parameters in other solvents reported previously[8,9] are also summarized in Table 1.

The transient absorption spectra of BPK with different TEA concentrations were also measured in tetrahydrofurane and in methanol as shown in Figure 3. In both systems, an absorption band around 550 nm appears in the spectra, which suggests the formation of BPK. In tetrahydrofuran, no drastic red-shift was seen even under the very high TEA concentration (361 mM). Therefore, we consider that the K_f vlaue in tetrahydrofurane must be very small compared to those in benzene, toluene, *o*-xylene, or anisole. It is noteworthy that BPK yield (BPK absorbance) seems to decrease when the TEA concentration becomes higher. It has been known that BP forms a complex with amines and that the rapid S_1 quenching occurs in the BP-TEA complex.[15] This may be why the relative BPK yield slightly depends on the TEA concentration. In methanol, it has been reported that BP anion as well as BPK is formed in the photoreduction of BP with TEA.[16] A largely red-shifted broad band appearing around 625 nm in the spectra is attributed to

TABLE 1: Thermodynamic Parameters for Complex Formation Reaction at 298 K and Hyperfine Coupling Constants of BPK in Various Solvents

group	solvent	η^a cp	$\epsilon_r{}^b$	$n_D{}^b$	K_f M^{-1}	ΔG kcal mol^{-1}	ΔH kcal mol^{-1}	ΔS cal K^{-1} mol^{-1}	hfcc^c G a_{OH}	a_m	a_p	a_o
A^d	*n*-hexane	0.30	1.89	1.37486	103	−2.70			2.08 ±0.04	1.23 ±0.03	3.69 ±0.05	3.27 ±0.04
	n-heptane	0.39	1.92	1.38764	101	−2.69	−6.6	−13.2				
	cyclohexane	0.89	2.02	1.42623	99	−2.68	−7.5	−16.5				
	o-chlorotoluene	0.96	4.45	1.5238	83	−2.57	−4.1	−5.2				
	p-chlorotoluene	0.84	6.08	1.5199	70	−2.47	−3.5	−3.4				
	1,2-dichloroethane	0.78	10.7	1.4448	60	−2.38	−2.0	+1.3				
B	benzene	0.60	2.28	1.50112	32^e	−2.06	−10.5 ± 1.72	−28.3 ± 5.8	2.45 ±0.10	1.21 ±0.04	3.58 ±0.03	3.28 ±0.02
	toluene	0.56	2.38	1.49693	23^e	−1.86	−14.6 ± 1.99	−42.8 ± 6.8		1.22 ±0.05	3.68 ±0.05	3.26 ±0.05
	o-xylene	0.63	2.57	1.50545	24^e	−1.88	−10.9 ± 0.78	−30.3 ± 2.7				
	anisole	1.15	4.33	1.51700	16^e	−1.65	−8.06 ± 1.71	−21.5 ± 5.8				
C^f	tetrahydrofurane	0.47	7.58	1.40716					2.78	1.23	3.64	3.20
	methanol	0.54	32.7	1.32840					2.91	1.23	3.64	3.21
	ethanol	1.07	24.6	1.36143					3.03	1.23	3.66	3.23
	2-propanol	2.04	19.9	1.3772					3.42	1.24	3.69	3.23

[a] Values at 298 K.[28] [b] Reference 28. [c] a_o, a_m, and a_p denote *hfcc's* of *ortho, meta,* and *para* protons, respectively. [d] K_f and thermodynamic parameters are from ref 9. [e] Calculated from thermodynamic parameters at 298 K. [f] hfcc's are from ref 7.

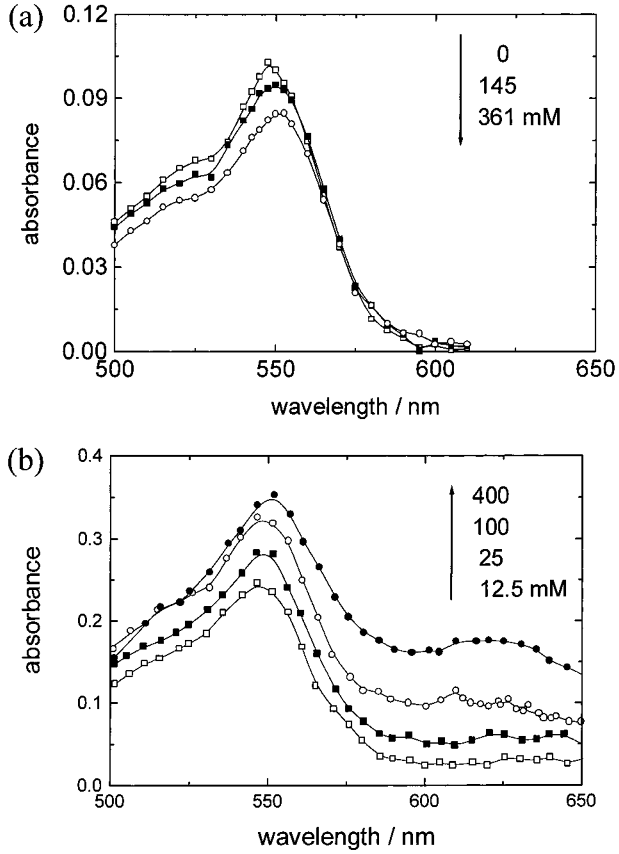


Figure 3. Transient absorption spectra of BPK in (a) tetrahydrofurane and (b) methanol measured at 0.8−1.4 μs after 355 nm laser excitation at 298 K. The concentrations of TEA were described in the figure.

the BP anion. If an appreciable amount of BPK forms a complex with TEA in methanol, we expect that the red-shifted band of the complex appears around 560 nm with an isosbestic point near 550 nm as observed in toluene (Figure 1). However, no such red-shifted band of BPK-TEA complex is recognized in the spectrum even at the very high TEA concentration (400 mM), which indicates that the K_f value in methanol is also very small. It is noteworthy that red-shifts in the BPK absorption band at high TEA concentration are only about 3.5 and 2 nm in tetrahydrofurane and in methanol, respectively, as seen in Figure 3. These red-shifts are very small compared to the red-shifts of ca. 10 nm due to the BPK-TEA complex formation. Similar small red-shifts were also observed in ethanol and in 2-propanol. Therefore, we conclude that the small red-shifts in these solvents are not due to complex formation but due to solvent effect on the $\pi\pi^*$ transition of BPK caused by an addition of TEA into these solvents. As no complex formation was recognized in these solvents even at very high TEA concentrations (>300 mM), we conclude that the K_f values in these solvents are much smaller than 16~32 M^{-1} in benzene, toluene, *o*-xylene, or anisole.

In our previous report, we showed that the solvent dependence of K_f and the thermodynamic parameters ΔG, ΔH, and ΔS in the complex formation reaction (BPK + TEA $\rightleftarrows$ complex) is well explained by considering the solvation effect due to the reaction field model. The thermodynamic parameter is expressed by the following equations:

$$G_{re} = G^0_{re} + \Delta G^s_{re}$$

$$G_{com} = G^0_{com} + \Delta G^s_{com}$$

where G_{re} and G_{com} represent Gibbs free energies of reactants and complex, respectively. G^0_{re} and G^0_{com} mean Gibbs free energies of nonsolvated reactants and complex, respectively. ΔG^s_{re} and ΔG^s_{com} represent Gibbs free energy changes for the solvation of reactants and complex, respectively. Then, Gibbs free energy change of the complex formation reaction, ΔG is given by[9]

$$\Delta G = (\Delta G^0_{com} - \Delta G^0_{re}) + (\Delta G^S_{com} - \Delta G^S_{re})$$

The first term ($\Delta G^0_{com} - \Delta G^0_{re}$) is constant for all solvents. The second term ($\Delta G^S_{com} - \Delta G^S_{re}$) arises upon solvation and the solvent dependence of this energy could be qualitatively explained by considering solvation energy based on the reaction field model.[17] According to the reaction field model, solvation energy, ΔE, is expressed by the following equation:

$$\Delta E = \frac{M^2}{R^3} g(n,\epsilon_r)$$

$$\text{where } g(n,\epsilon_r) = \frac{n^2-1}{2n^2+1} + 2\left(\frac{\epsilon_r - 1}{2n^2+1} - \frac{n^2-1}{n^2+2}\right) \quad (2)$$

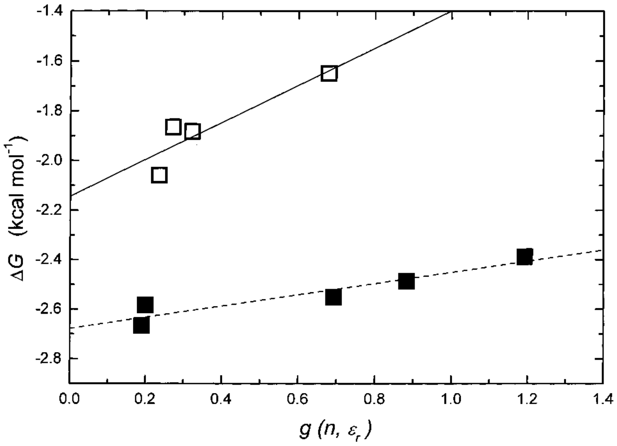


Figure 4. A correlation between the $g(n,\epsilon_r)$ value of solvent and the ΔG values in the BPK-TEA complex formation reaction at 298 K. Closed marks correspond to the ΔG values in *n*-hexane, *n*-heptane, cyclohexane, *o*-chlorotoluene, *p*-chlorotoluene, or 1,2-dichloroethane from ref 9. Open marks correspond to the ΔG values in benzene, toluene, *o*-xylene, or anisole.

Here, M and R denote dipole moment and cavity radius of solute, ϵ_r and n mean dielectric constant and refractive index of solvent, respectively. It has already been demonstrated in our previous study that the plots of the ΔG values (see Table 1) against $g(n, \epsilon_r)$ show good linear correlation. This feature is demonstrated in Figure 4 with the plots shown by rectangular closed marks fitted by a broken line. In the present study, we added the plots of ΔG values in benzene, toluene, *o*-xylene, or anisole with rectangular open marks in Figure 4. It is noteworthy that the plots of the ΔG values in benzene, toluene, *o*-xylene, or anisole are not on the broken straight lines but seem to show another linear dependence on $g(n, \epsilon_r)$ as indicated by a solid line. The slopes and intercepts of the broken and solid straight lines are fairly different. These plots strongly suggest that there must be something different in complex formation reaction between the solvents in our previous work and in the present work.

ESR Spectroscopy of BPK and the Complex in Various Solvents. Since thermodynamic parameters for the complex formation reaction in benzene, toluene, *o*-xylene, or anisole seem different from those in other general solvents, a certain property in the former solvents must be different from that in the latter solvents. BPK has two phenyl rings and a hydroxy group which could rotate depending on the solvent. Therefore, we assume that the conformation of BPK depends on the solvent and plays an important role in the complex formation reaction. To obtain information of the BPK conformation, we performed TR-ESR measurements of BPK in various solvents. Figure 5 shows TR-ESR spectra of BPK in *n*-heptane, *o*-chlorotoluene, or 1,2-dichloroethane together with the simulated spectrum. In a series of TR-ESR measurements, BPK was generated by the laser photolysis of α-phenylbenzoin instead of the photoreduction of benzophenone because (1) no hydrogen abstraction of benzophenone occurs in some of the solvents used in the present study, (2) the photolysis of α-phenylbenzoin efficiently produces BPK ($\Phi_{BPK} = 0.24$ in benzene),[18] and (3) CIDEP (chemically induced dynamic electron polarization)[19] of BPK produced by the photolysis of α-phenylbenzoin shows net emission without remarkable hyperfine dependent CIDEP. Though the S/N ratio and the line width depend on the case, no significant difference of hyperfine structure was found among these spectra. Figure 6 shows TR-ESR and simulated spectra of BPK in benzene, toluene, or *o*-xylene obtained by the same procedure as those in Figure 5. The hyperfine structure of BPK in Figure 6 is very different from that in Figure 5. The a_{OH} value determined from Figure 5 is about 2.08 G while that from Figure 6 is about 2.45 G. As for the remaining hfcc's of BPK, no remarkable difference was found, which is in good agreement with the previous ESR study by Wilson.[7a] Similar experiments were carried out for BPK in various solvents and the resultant hfcc values are listed in Table 1. The hfcc's of BPK in tetrahydrofurane and in alcohols reported by Wilson are also listed in Table 1.

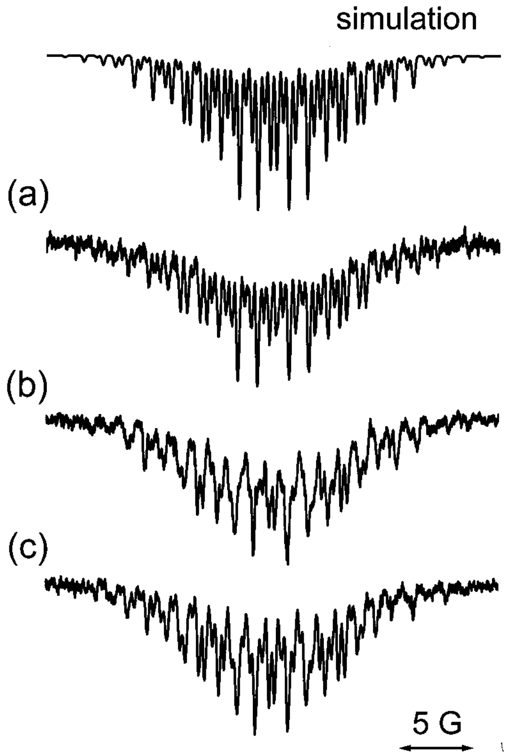


Figure 5. Time-resolved ESR spectra of BPK in (a) *n*-heptane, (b) 1,2-dichloroethane, and (c) *o*-chlorotoluene at 298 K. BPK was produced by the 308 nm laser photolysis of α-phenylbenzoin (12 mM) and the gate was opened from 1.5 to 2.0 μs after the laser pulse. In the simulation, the parameters of $a_{OH} = 2.08$ G, $a_o = 3.27$ G, $a_m = 1.23$ G, $a_p = 3.60$ G are employed and the line shape is Lorentzian with a line width of 0.20 G.

Figure 7 shows TR-ESR spectra of BPK in the presence of TEA (100 mM) in toluene and in *n*-hexane together with simulated spectra. Reflecting the complex formation of BPK in the presence of TEA, TR-ESR spectra with TEA and without TEA (see Figures 5 and 6) show significant difference. In Figure 7, parts a and b, the concentration ratio of the BPK-TEA complex to uncoupled BPK is about 3 and 5, respectively, which are calculated from K_f values, and the carrier of the spectra should be dominated by the BPK-TEA complex. The simulated spectrum of BPK-TEA complex well reproduced the observed ones and the hfcc of the complex was determined as shown in Table 2. The spectrum of the complex is characterized by a large a_{OH} value of about 4.95 G. Similar experiments were carried out for the complexes in various solvents and the hfcc of the complex are almost the same. In accordance with the previous work by Davidson and Wilson, the a_{OH} value of BPK in neat TEA was determined to be 5.48 G which is even larger than the a_{OH} value of the BPK-TEA complex determined in the present study (see Table 2). When we increased the concentration of TEA, the a_{OH} value of BPK slightly increased up to about 5.5 G in various solvents. This may be due to a sort of solvent effect of TEA because the TEA concentration more than 100 mM should be considered more likely as a mixture of two solvents than a solvent with dissolved TEA.

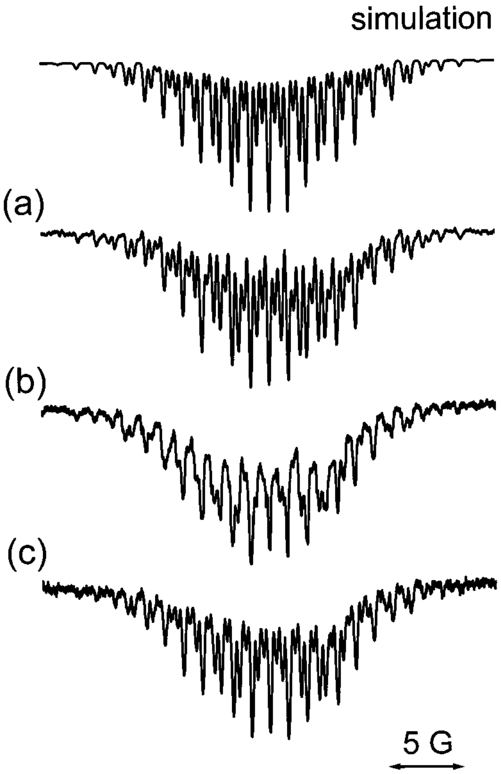


Figure 6. Time-resolved ESR spectra of BPK in (a) toluene, (b) benzene, and (c) *o*-xylene at 298 K. BPK was produced by the 308 nm laser photolysis of α-phenylbenzoin (12 mM) and the gate was opened from 1.5 to 2.0 μs after the laser pulse. In the simulation, the parameters of $a_{OH} = 2.45$ G, $a_o = 3.26$ G, $a_m = 1.22$ G, $a_p = 3.68$ G are employed and the line shape is Lorentzian with a line width of 0.20 G.

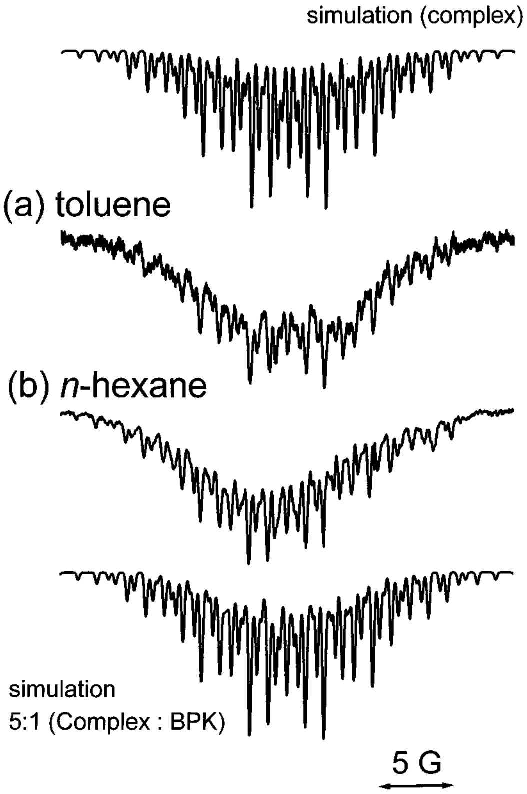


Figure 7. Time-resolved ESR spectra of BPK in the presence of TEA (100 mM) in (a) toluene and (b) *n*-hexane at 298 K. BPK was produced by the 308 nm laser photolysis of α-phenylbenzoin (12 mM) and the gate was opened from 1.5 to 2.0 μs after the laser pulse. The simulated spectra; the top is for the BPK-TEA complex in toluene or in *n*-hexane, and the bottom is for the spectrum of a 5:1 mixture of the complex and uncoupled BPK.

TABLE 2: Hyperfine Coupling Constants of BPK-TEA Complex in Toluene and BPK in Neat TEA

	hfcc G			
	a_{OH}	a_m	a_p	a_o
BPK-TEA complex in toluene or *n*-hexane (298 K)	4.95 ±0.10	1.22 ±0.03	3.67 ±0.05	3.22 ±0.03
BPK in neat TEA (295 K)	5.48	1.22	3.66	3.21

The broadening of the spectra is seen in Figure 7, which may be partly due to the blend of different spectra of uncoupled BPK and BPK-TEA complex coexisting. This feature is demonstrated in Figure 7 by the simulation of the spectrum for 5:1 mixture of uncoupled BPK and the complex.

It is noteworthy that the a_{OH} value of the complex is about 4.95 G which is remarkably larger than that of BPK of 2.08 or 2.45 G while the hfcc's of the complex except the a_{OH} value are almost the same with the corresponding hfcc's of BPK. Figure 8 shows plots of hfcc's of uncoupled BPK and of the complex against ΔG for the complex formation. This plots clearly suggests that there is a correlation between ΔG for the complex formation reaction and the a_{OH} value of BPK. Therefore, we focus on the a_{OH} value in the following. According to the a_{OH} value of BPK, we divide the solvents into three groups as indicated in Table 1. Groups A, B, and C include the solvents in which the a_{OH} values of BPK are about 2.08, 2.45, and >2.7 G, respectively. The solvents belonging to each group are marked in Table 1; Group A includes *n*-hexane, *n*-heptane, cyclohexane, 1,2-dichloroethane, *o*- and *p*-chlorotoluene; group B includes benzene, toluene, *o*-xylene, and anisole; and group C includes tetrahydrofurane and aliphatic alcohols such as ethanol and 2-propanol. It is interesting to mention that the linear dependence of the ΔG value on $g(n, \epsilon_r)$ are found within group A and within group B as shown in Figure 4. No correlation is found between the solvent properties and the a_{OH} value of the complex which is constant at about 4.95 G.

Factors Determining a_{OH} Values of BPK and the Complex. There are a number of ESR studies on BPK in various solvents where the conformation and internal motion of BPK were discussed on the basis of the hfcc's and line width of BPK and their temperature dependence.[7,18] According to the calculation by Wilson, the a_{OH} value due to the coupling between oxygen of CO and the 1s orbital of hydroxy-proton (H_{1s}) is only −0.64 G assuming a planer conformation of BPK.[7a] This is much smaller than observed values in the solvents of groups A, B, and C. In the ESR study by Wilson, it was concluded that the a_{OH} value of BPK is dominantly determined by the overlap between the H_{1s} and the *2p* orbital of C_{13} in the COH group together with the overlaps between H_{1s} and *2p* orbital of C_1 and C_7 in C−CO. The numbers of carbon atoms is referenced to Scheme 1.

These overlaps are characterized by two different dihedral angles, θ and ϕ, which are described in Figure 9. The former is the angle between OH bond axis and the plane through the $C_{1,7}-C_{13}-O$ group and the latter is the angle between phenyl ring and the plane through the $C_{1,7}-C_{13}-O$ group. Larger overlaps of H_{1s} and *2p* orbitals of C_{13}, C_1, and C_7 results in a larger a_{OH} value and thus, these angles are the important factors to control the a_{OH} value. In the following, we discuss these angles with respect to possible BPK conformation.

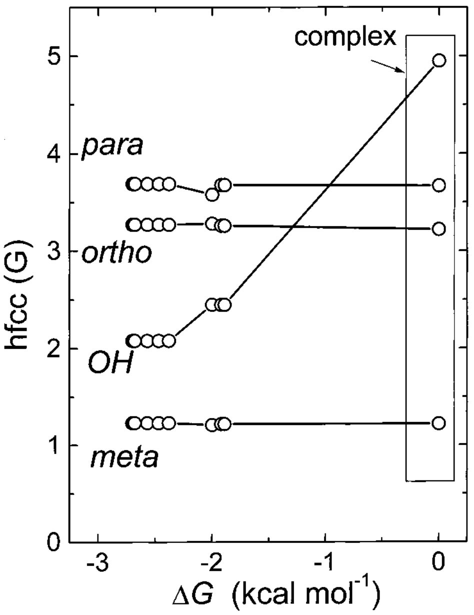


Figure 8. Plots of hfcc's of BPK and the complex against the ΔG for the complex formation reaction.

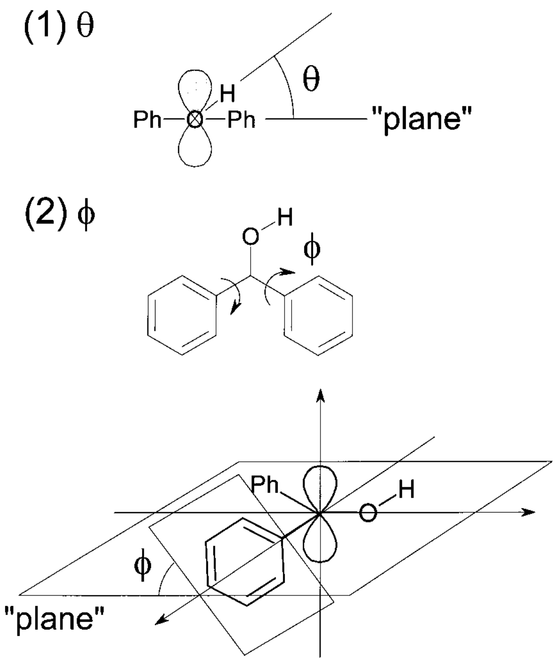
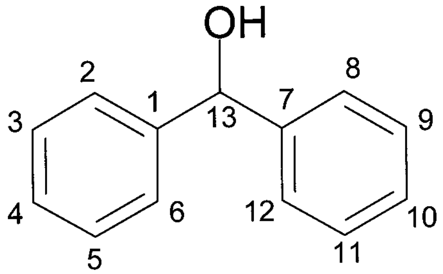


Figure 9. Schematic representation of BPK with two characteristic angles, θ and ϕ. "Plane" = the plane through the $C_{1,7}-C_{13}-O$ group.

SCHEME 1



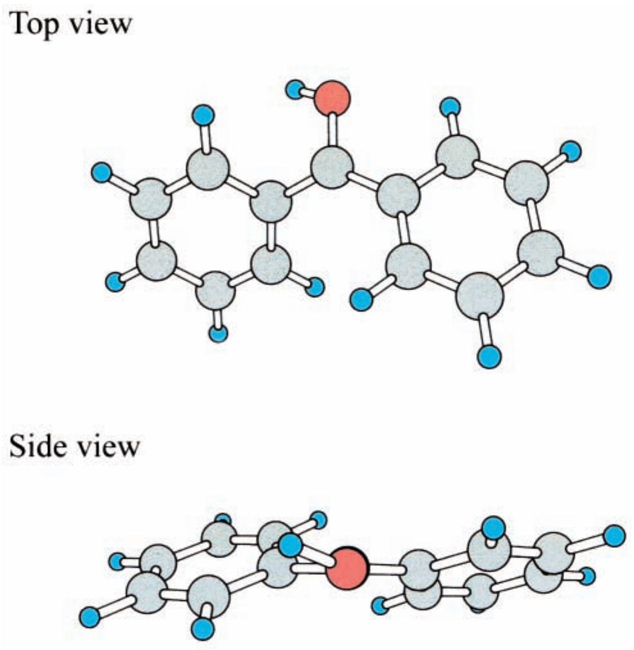


Figure 10. Schematic drawing of the BPK structure at the minimum energy. The bond lengths and angles are determined by DFT calculation with B3LYP/6-31G* level of theory. See text for details.

TABLE 3: The Calculated Results for BPK with B3LYP/6-31G* Level of Theory

atom and position	atomic spin density (ρ)	atomic charge[a]
carbon		
1	−0.123	0.0803
2	0.155	−0.153
3	−0.0817	−0.0855
4	0.165	−0.0878
5	−0.0782	−0.0926
6	0.146	−0.121
7	−0.143	0.0904
8	0.174	−0.106
9	−0.0923	−0.0894
10	0.187	−0.0866
11	−0.0918	−0.0945
12	0.169	−0.130
13	0.563	0.190
hydrogen		
2	−0.00737	0.0887
3	0.00329	0.0878
4	−0.00773	0.0864
5	0.00306	0.0887
6	−0.00658	0.100
8	−0.00769	0.0989
9	0.00350	0.0838
10	−0.00875	0.0823
11	0.00347	0.0836
12	−0.00738	0.0933
hydroxy hydrogen	0.00261	0.316
oxygen	0.0785	−0.525

[a] Atomic charges were obtained by Mulliken population analysis and sum of Mulliken charges equals zero.

The most stable conformation of isolated BPK in the gas phase was calculated by B3LYP/6-31G* level of theory provided by the *Gaussian 94* program.[21] The schematic drawing of the conformation of BPK by this calculation is shown in Figure 10 and the charge and spin densities of this conformation are summarized in Table 3. According to the DFT calculation, energy minimum conformation requires that a hydroxy-proton locates over the $C_{1,7}-C_{13}-O$ plane with $\theta = 23°$ ($\theta = 0$ means OH axis is on the plane through $C_{1,7}-C_{13}-O$ group) and that two phenyl rings twist by 48° with $\phi = 22$ and 26° ($\phi = 0$ means that phenyl ring is on the plane through the $C_{1,7}-C_{13}-O$ group) and hydroxy-proton is facing to the phenyl with the larger ϕ. This result is qualitatively understood as follows. If hydroxy-

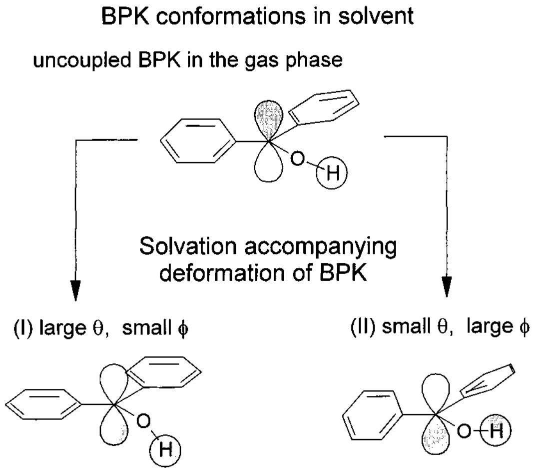


Figure 11. Schematic drawing of the possible conformations of BPK in various solvents and in the BPK-TEA complex.

proton of BPK was on the plane through $C_{1,7}-C_{13}-O$ group and the BPK was almost planer, the steric hinderence between hydroxy- and *ortho* protons must be large. This requires θ and ϕ with nonzero values. The DFT calculation suggests that the BPK is not planer and supports that overlaps of H_{1s} and *2p* orbital of C_{13}, C_1, and C_7 is not zero to give nonzero a_{OH} value.

It deserves short comment that there is the internal rotation of two phenyl rings of BPK. This was predicted by the fact that hfcc's of proton at *ortho* and *meta* positions are almost equivalent at room temperature. Though detail analysis of BPK internal rotation has not been reported as far as we know, some studies have mentioned the internal rotation of benzophenone anion. The rate of geometry change due to internal rotation of two phenyls was calculated from the line width changes of a series of ESR spectra at different temperatures and was estimated to proceed on the order of 10^6 s^{-1} around 200 K.[22] This report indicates that in BPK the internal rotation occurs along the C−CO bond. In the recent study of jet-cooled BPK by means of laser-induced fluorescence spectroscopy,[23] it has been concluded that BPK has a low frequency (74 cm^{-1}) torsional motion of these phenyls, which suggests that the potential of two phenyl rings of BPK along the internal rotation angle is shallow. According to these results, one can find that two phenyls of BPK rather freely rotate and it is very likely that the angle ϕ corresponding to the potential minimum conformation of BPK is easily changed depending on the solvent, which results in the slight difference in a_{OH} value.

Dependence of BPK Conformation on the Solvent. The a_{OH} values measured in the solvents of groups A and B are different by about 0.37 G, which implies that the BPK conformation in solvent group A is slightly different from that in the solvent group B. No dependence of a_{OH} value upon the static physical properties of solvent such as dielectric constant and viscosity are recognized (see Table 1). The two distinguished conformations of BPK in solvent groups A and B may be determined by the local solvent effect. When BPK dissolves into the solvent, BPK with the most stable conformation in the gas phase deforms to become stable solvated BPK in the solvent cage. The deformation due to solvation may be different between solvent groups A and B, which is illustrated in Figure 11. Two structural factors are responsible for slightly different a_{OH} values; One is the twisted angle, ϕ, of two phenyl rings and the other is the θ value. Theoretically, smaller a_{OH} is responsible for smaller θ and ϕ values. In the case of BPK, there is a steric hinderence between hydroxy- and *ortho* protons and thus, if BPK has a larger ϕ value, θ value must become smaller and if a smaller ϕ value, θ value must become larger. Hence, when one of these angles increases the a_{OH} value, the other must decrease the a_{OH} value. The difference of the a_{OH} value between the solvents of groups A and B is determined as a result of these two contributions. Either of the solvated BPK conformations (I) or (II) in Figure 11 corresponds to either of BPK in solvent group A or B. Since the difference of the a_{OH} value is very small (0.37 G), we could not tell which of ϕ and θ is dominate in the deviation of the a_{OH} value. Unfortunately, we could not have any experimental evidence to determine which conformations of (I) or (II) corresponds to BPK conformations in the solvent of group A or B.

The BPK conformation in the solvent group C (alcohol and tetrahydrofurane) may be different from those in solvent groups A and B. This is because BPK can form a H-bond with alcohol and tetrahydrofurane. In the solvent group C, the a_{OH} value is not constant and rather shows dependence on the solvent viscosity as already suggested by Wilson.[7a] For larger a_{OH} values observed in solvent group C (2.7∼3.1G) compared to those in solvent groups A and B (2.08 and 2.45G), the viscosity of the solvent may be an important key controlling the rotation of phenyl rings, but we cannot propose a clear mechanism at this moment.

Structure of the BPK-TEA Complex. The small difference in the a_{OH} value of BPK (2∼3G) among solvent groups A, B, and C has been discussed above. Now, we consider the large change in a_{OH} during complex formation (4.95 G). For the a_{OH} value of the complex, we again consider two factors, θ and ϕ. The ϕ factor is, however, unlikely to be important in this case. Usually, the hfcc of a γ proton is less than 1 G for carbon-centered radicals. In BPK, spin density on $C_{1,7}$ is ca. −0.12 to −0.14 according to the DFT calculation (see Table 3). For such a small spin density, hfcc may be much smaller than 1 G. This value is fairly smaller than the a_{OH} value of 4.95 G of the complex. On the other hand, hfcc due to a β proton usually could become such a large value. The equation for hfcc due to a β proton is approximately given by[22]

$$a_{OH} = \frac{H_\beta}{2}\rho_{13}\cos^2\left(\frac{\pi}{2} - \theta\right) \tag{3}$$

where ρ_{13} is the atomic spin density on C_{13} which is estimated to be ca. +0.56 according to the DFT calculation, and H_β is the coefficient for hfcc of a β proton whose typical value is 50 G.[22] The corresponding hfcc due to a β proton can be 14 G at the maximum under the assumption that spin density is constant for any θ value. This value is much larger than the a_{OH} value of the complex (4.95 G). Therefore, the a_{OH} value of the complex is dominantly controlled by the factor θ. Since uncoupled BPK is rather a planer structure with relatively small θ value as shown in Figure 10, a_{OH} value can easily be twice by taking a larger θ value. For example, a_{OH} value is ca. 2.14 and 5.07 G for $\theta = 23$ and 37°, respectively. With the a_{OH} values of uncoupled BPK (2.08 and 2.45 G) and BPK-TEA complex (4.95G), θ value was estimated to be 22.7, 24.7, and 36.5° according to eq 3. In the estimation of the θ value, we omitted the contribution to the a_{OH} value from the coupling between hydroxy proton and $C_{1,7}$ or O atoms. Contributions from these couplings are about −0.6 G for an O atom and on the order of +0.1 G for $C_{1,7}$ atoms (γ proton case) as mentioned above. These contributions may cancel out partially or totally and thus, we consider that the a_{OH} value can be estimated only by eq 3.

To make sure that the angle θ becomes larger when BPK forms a complex with TEA, we calculated the optimized

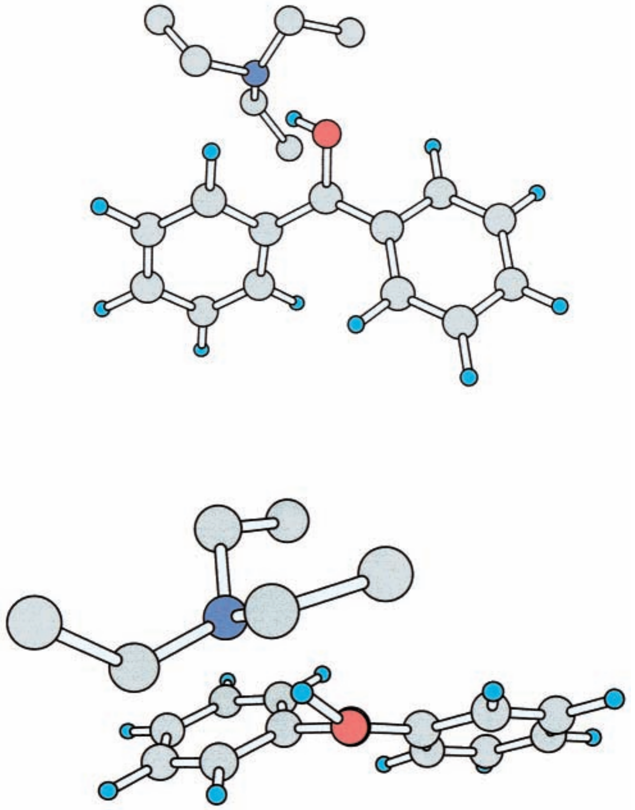


Figure 12. Schematic drawing of the BPK-TEA structure calculated by DFT method with B3LYP/6-31G* level of theory. Hydrogen atoms in TEA are excluded in order to simplify the figure.

structure of the BPK-TEA complex as shown in Figure 12. The bulky alkyl group of amine interacting with twisted phenyl rings may control the equilibrium conformation of the complex, especially the position of hydroxy-proton. In TEA, there is a bulky ethyl group whose interaction with phenyl rings of BPK is not negligible and TEA is thus, encouraged to locate in an upper position over $C_{1,7}-C_{13}-O$ plane, which is accomplished by taking a larger θ value in the complex than in uncoupled BPK. Reflecting this feature for the complex, DFT calculation gave a θ value of 36° which is 1.6 times larger than that of uncoupled BPK ($\theta = 23°$). In the complex, the conformation of $C_{1,7}-C_{13}-O$ group becomes slightly pyramidal. Hence, we assume the planner $C_{1,7}-C_{13}-O$ conformation by using the $C_{1,7}-O$ plane for the calculation of the θ value.

In our previous study,[10] we reported that the complex of BPK with *sec*-butylamine (SBA) shows an a_{OH} value of about 3.9 G, which is smaller than 4.95 G of BPK-TEA complex and that any difference were found in the remaining hfcc's. This may suggest that the θ value of BPK-SBA complex is smaller than that of the BPK-TEA complex. With the a_{OH} value of the BPK-SBA complex under the assumption that ρ_{13} is +0.56 and H_β is 50 G, we estimated the θ value as 30.6° which is apparently smaller than that of the BPK-TEA complex (36.5°). The alkyl group of SBA is less bulky than that of TEA and the steric hindrance between alkyl and phenyl groups should be smaller in the BPK-SBA complex than in the BPK-TEA complex, which results in a smaller θ value of the BPK-SBA complex. DFT calculation of the BPK-SBA complex also shows that the θ value of the complex is 30° which is larger than that of BPK (23°) but smaller than that of the BPK-TEA complex (36°). These experimentally determined θ values from the a_{OH} values were summarized in Table 4, together with θ values in the energy minimum conformations of BPK or BPK−amine complexes given by DFT calculation. A good agreement between the θ values determined by the a_{OH} values and DFT calculation were seen for BPK and BPK complexes. This result strongly suggests that the θ value increases when BPK forms complex with amine while other parts of BPK conformations do not show significant change.

TABLE 4: The a_{OH} and θ Values of BPK and BPK−Amine Complexes in Benzene

radicals	a_{OH}	θ estimated by a_{OH} value assuming eq 3	θ determined by DFT calculation
BPK in solvent A)	2.08	22.7°	23°
BPK (in solvent B)	2.45	24.7°	23°
BPK/SBA	3.63	30.6°	30°
BPK/TEA	4.95	36.5°	36°

Solvation Effect on the Complex Formation. It is noteworthy that a good correlation between K_f (or ΔG) and a_{OH} values is seen as indicated in Table 1 and in Figure 8. When the a_{OH} value of BPK is 2.08 G (group A), the K_f value is in the range of 60∼103 M^{-1}. If a_{OH} of BPK is 2.45 G (group B), the K_f value is in the range of 16∼32 M^{-1}. For BPK with a_{OH} values of more than 2.7 G (group C), the K_f value is almost zero and complex formation was hardly recognized in the experiment. A smaller K_f value in group C solvents is easily understood because BPK is already stabilized by hydrogen bond formation between BPK and the solvent.

The BPK-TEA complex, TEA, and uncoupled BPK are involved in the complex formation reaction. We examine which of them mainly contributes to the solvent effects on the ΔG value. Solvation energy by the reaction field is given by the term, $M^2/R^3 g(n, \epsilon_r)$. Therefore, dipole moment (M) and mean radius (R) of the molecule are essentially important in the solvation energy. We estimate the M and R values of BPK, TEA, and the complex. The radii were calculated according to the equation of Spernol and Wirtz,[25]

$$R = \left(\frac{3 \times w}{4\pi\rho N_A}\chi\right)^{1/3}$$

where w, ρ, N_A, and χ are molecular weight, density, Avogadro's constant, and free volume, respectively. We adopted a free volume of 0.74 as used in their calculation. Since the density of BPK and the complex are unknown, we assume that the densities of them are unity. The M values were obtained from DFT calculation with the minimum energy conformations of BPK, TEA, and the complex. Since the θ value of the BPK-TEA complex obtained by DFT calculation agrees well with the experimentally determined θ value as shown in Table 4, we believe that the conformation of the BPK-TEA complex given by DFT calculation is close to the real conformation of the complex. According to these methods, the M and R values are obtained as 1.48 D and 3.77 Å for BPK, 0.55 D and 3.44 Å for TEA, and 3.53 D and 4.37 Å for the complex, respectively. The dipole moment of BPK is mainly generated by positively charged C_{13} and hydroxy-proton, and negatively charged oxygen (see Table 3). Dipole moment of TEA is due to negatively charged nitrogen and positively charged end-carbons of each ethyl part. The complex is formed by the H-bond between the hydroxy-proton of BPK and the nitrogen atom in TEA and two dipoles tends to locate rather parallel giving large total dipole moment of the complex. Calculated M values of BPK and TEA is close to the observed M values for BPK (1.5 D)[26] in benzene and for TEA (0.66 D).[27] Slight differences may be due to the deformation of these molecules in the solvent. According to the *M* and *R* values mentioned above, we obtained the relative solvation energy of three species as 149:41:7(complex:BPK: TEA). This means that contribution of TEA is almost negligible compared to BPK and the complex. Therefore, we consider that the solvation effect is mainly controlled by the complex and BPK. Since conformation of the complex is almost identical between the solvent groups A and B, it is unlikely that the solvation energy of the complex differs between the two. Thus, we conclude that the different solvent dependence of ΔG value between solvent group A and B as shown in Figure 4 is mainly due to the different conformation of uncoupled BPK.

Conclusion

We studied the complex formation reaction of BPK with TEA in various solvents by means of transient absorption and TR-ESR method. According to TR-ESR spectra of uncoupled BPK and the complex together with DFT calculation, we concluded that BPK has at least three different conformations depending on the solvent. The conformation of COH group and twisted angle of phenyls in BPK depends on the solvent. On the other hand, the conformation of the BPK-TEA complex does not depend on the solvent. Conformation of BPK is strongly controlled by the solvation while that of the BPK-TEA complex may be controlled only by the interaction between BPK and TEA.

The dihedral angle between OH bond axis and the plane through the $C_{1,7}-C_{13}-O$ group changes from 22.7° and 24.7° to 36.5° by the complex formation. A good correlation between BPK conformation and the ΔG value in the complex formation reaction was found, which suggests that the ΔG value is roughly controlled by the conformation of uncoupled BPK.

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