J. Phys. Chem. **1996,** *100,* 10021−10026

Time-Resolved ESR Studies on Ketyl Type Radical−Amine Complexes

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Received: March 7, 1996[⊗]

Time-resolved (TR) ESR spectra were measured for α-hydroxybenzyl−amine (α-HB) and α-hydroxydiphenylmethyl−amine complexes. Hyperfine coupling constants (hfcc) of the complexes were determined, and considerable increase in hfcc was recognized on the hydrogen of hydroxy group of both radical complexes, which suggests that the complexes are produced through the hydrogen bond formation between hydroxy group of the radical and amino group of amines. Complex formation constants were determined for various α-HB−amine complexes by monitoring TR-ESR signals of the complexes against amine concentrations. It has been noticed that the degree of hydrogen substitution on nitrogen atom of aliphatic amine roughly determines the complex formation constant: complexes with primary amines show the largest value of the complex formation constant while tertiary amines show the smallest value. This result is interpreted based on the structure of the amine.

Introduction

The hyperfine structure (hfs) of radicals usually shows various dependence on the solvent polarity, viscosity, and temperature and also reflects the reactions such as proton and electron exchanges,[1−7] which allows us to elucidate the structure and properties of radicals. Ketyl type radicals are known to have drastic change in their hyperfine coupling constant (hfcc) of hydroxy group, a_{OH}, especially its dependence on the polarity is of considerable interest.[1−6]

In the previous study, we have demonstrated that the α-hydroxybenzyl (α-HB) radical in benzene shows dependence of hfs on the concentrations of amine or alcohol.[8] Increasing the concentration of solute, the spectra showed drastic increase of a_{OH} value resulting in the appearance of an extra doublet on each hyperfine line. Previously, we have reported the complex formation between α-HB radical and triethylamine (TEA) in benzene by taking time-resolved ESR (TR-ESR) spectra at various TEA concentrations.[8] We should point out that an idea of radical−molecule complex formation itself is not brand new but quite few works have been done on this subject while a large number of studies are found on the complex formation reaction among stable species.[9] In the present report, we have studied complex formation reactions of α-HB and α-hydroxydiphenylmethyl (HDPM) with aliphatic amines by means of TR-ESR spectroscopy.

Kajii et al. have reported the complex formation between HDPM and TEA in benzene and cyclohexane by utilizing laser flash photolysis technique.[10] They observed the slightly red-shifted transient absorption spectra of the HDPM−TEA complex compared with that of HDPM and suggested that the complex was formed via hydrogen bonding between HDPM and amine. This observation is in good agreement with the conclusion of our previous work that α-HB forms a complex with TEA. The formation constant of the HDPM−TEA complex is found to be 37 M^{-1} while that of α-HB-TEA is 450 M^{-1}. This difference of the formation constants is tentatively explained in terms of the difference in acidity or structural constrain of ketyl radicals. However, further measurements of hfcc and formation constants of various complexes are needed to elucidate the mechanism of complex formation and the structures of the complexes.

We adopted the following simple methods of radical production to study the radical−amine complex and its formation dynamics. We use widely known α-photocleavage reactions of benzoins as a source reaction of ketyl type radicals of present interest.[11−13] α-HB produced from benzoin and HDPM from α-phenylbenzoin are chosen as the representative of ketyl type radicals to be studied. The formation constants of α-HB with various aliphatic amines were determined by means of the TR-ESR technique. The formation constants depend on the degree of hydrogen substitution on nitrogen atom of amines; they are the largest for primary amines and the smallest for tertiary amines. The dependence of the formation constants is discussed on the basis of the structure of aliphatic amine.

Experimental Section

As our TR-ESR equipment has already been described previously, we briefly explain it below. TR-ESR spectra were measured by an X-band ESR spectrometer (Varian E-112) with some modification.[14] An excitation light source was a XeCl excimer laser (Lambda Physik LPX 100) of 20 ns duration time and of 100 mJ/pulse laser power. The gate of a boxcar integrator (Stanford SR-250) was opened from 1.5 to 2.0 μs after laser pulse unless otherwise mentioned. The signals were collected at the repetition rate of 10 Hz. The microwave power was 15 mW. For the temperature dependence experiment, temperature-controlled N_2 gas was flowed outside of the cell to cool the solution.

Benzoin (Tokyo Kasei) was used as received. α-Phenylbenzoin was synthesized by the Grignard reaction of phenylmagnesium bromide with benzil in tetrahydrofuran at 245 K and recrystallized from *n*-hexane. Benzene (Tokyo Kasei) was used as a solvent. Sample solutions were degassed by bubbling Ar gas and were flowed through a quartz flat cell with 0.5 mm interior space attached in a microwave cavity.

Results

Formation of Ketyl−Amine Complexes. Figure 1 shows TR-ESR spectra obtained by the laser photolysis of (a) benzoin and (b) α-phenylbenzoin in benzene. Almost totally net emissive polarized radicals were detected with good S/N ratio, which allows us to analyze intensity pattern of hyperfine lines as well as to determine hfcc. The photolysis of benzoins is

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[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1996.

S0022-3654(96)00715-0 CCC: $12.00

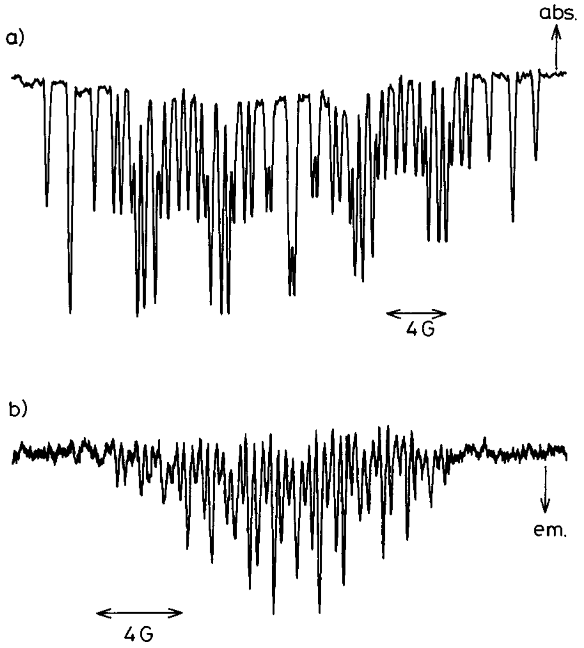

Figure 1. TR-ESR spectra measured by 308 nm laser photolysis of (a) benzoin and (b) α-phenylbenzoin in benzene. The radicals in the spectra are assigned to (a) α-HB and (b) HDPM. See the text for the details of assignments.

known to produce the corresponding ketyl type radical and benzoyl.[11,12] The radicals in Figure 1, a and b, were assigned to α-HB and HDPM, respectively, in comparison to the reported spectra[12] of the radicals. The hfcc of α-HB in neat benzene has been reported in a TR-ESR study of the radical produced by the photoreaction of benzaldehyde in benzene.[15] There is good agreement between the hfcc of α-HB produced by the present method and those of the photoreaction of benzaldehyde. The hfcc of HDPM in benzene has not been reported previously. However, the ESR spectrum of the photolyzed benzophenone in cyclohexane has been reported.[4] We used this hfcc in nonpolar solvent for our assignment. Since no other products were detected, we conclude that no other reactions of benzoins such as hydrogen transfer reaction from amine occur in the present system.

So far, the ketyl type radicals were produced by hydrogen atom transfer reaction, in the photoexcited aromatic ketones such as benzophenone where relatively high concentration of hydrogen donors is present.[4,14−16] In this case, donor molecules with very high polarity should affect the hfs of ketyl type radicals. Our goal is to study the role of polar solute like amines in the complex formation reaction with ketyl type radicals. Thus, we choose photoinduced α-cleavage reactions as a source of radicals in both measurements of the spectra of the complex and determination of complex formation constants.

The net emissive polarization is attributed to the triplet mechanism (TM) in the dissociation of benzoins. Benzoyl radicals, the countered part of both α-HB and HDPM, did not appear in the spectra in the interval of 1.5−2.0 μs after the laser shot though they were detected at the time of 0.5−1.5 μs and later than 2.0 μs. The former spectrum shows net emissive polarization due to TM while the microwave absorption signals of benzoyl is observed in the later due to thermalization or α-HB-benzoyl free radical pair mechanism. Fortunately, the accidental cancellation of emission and absorption signals at the window time of 1.5−2.0 μs enables us to extract only the ketyl radical signals.

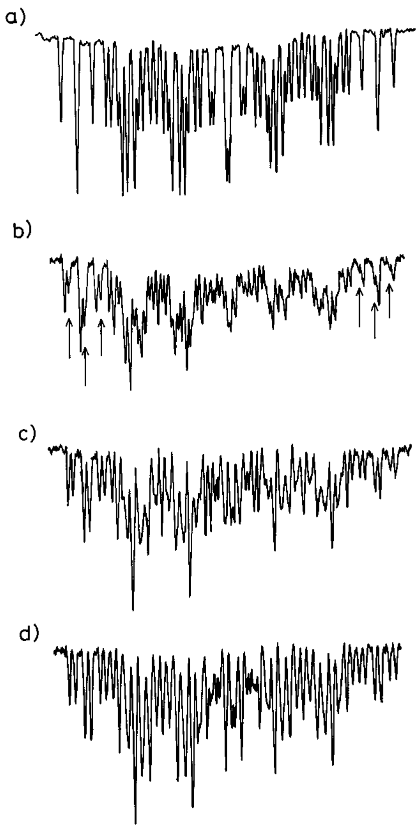

Figure 2. TR-ESR spectra of α-HB obtained by laser photolysis of benzoin in benzene in the presence of CHA. The concentrations of the amine are (a) 0 mM, (b) 3.02 mM, (c) 6.86 mM, and (d) 27.7 mM. The inhomogeneous spectra change suggests the formation of α-HB-CHA complex.

Complex formation of ketyl type radicals with aliphatic amine, such as α-HB-TEA and HDPM-TEA, has been reported in the previous studies.[8,10] Here, we report the TR-ESR spectra of the complex of α-HB with other amines. First of all, we adduce the evidence of the complex formation by taking the spectra at various amine concentrations. Figure 2 shows TR-ESR spectra of α-HB at different cyclohexylamine (CHA) concentrations. When we increased the CHA concentration, we observed that additional small peaks, indicated with arrows, appear beside each peak of α-HB. Furthermore, the additional peaks become stronger as the amine concentration is increased. This suggests the formation of the complex in this system by analogy with our previous study[8] in which we observed similar spectral change of α-HB as a function of TEA concentration. The spectrum shown in Figure 2d is almost the same as that of pure α-HB−TEA complex. We therefore assign this spectrum to the α-HB−CHA complex. According to this assignment, the spectra in Figure 2, b and c, must arise from the mixture of bare ketyl radical and the complex. In this study, several aliphatic amines have been found to form complexes with the ketyl radical from the measurement of TR-ESR spectra as a function of amine concentrations. We determined the values of a_{OH} of the complexes for several amines from the splitting of the peaks since this doublet structure is due to hyperfine coupling of hydrogen in hydroxy group. The measured values are summarized in Table 1. It is quite clear that the a_{OH} value is about 0.5 G for the complex of amines studied and is fairly larger than that of bare α-HB ketyl of which a_{OH} is nearly zero.

Figure 3 shows the TR-ESR spectra of HDPM in benzene in the presence of (a) TEA and (b) *sec*-butylamine (SBA). The formation constants of the HDPM−TEA and HDPM−SBA complexes are reported to be 37 and 50 M^{-1},[10] respectively. In our spectra of Figure 3, the concentrations of the complexes are estimated to be about 5 times larger than that of bare HDPM

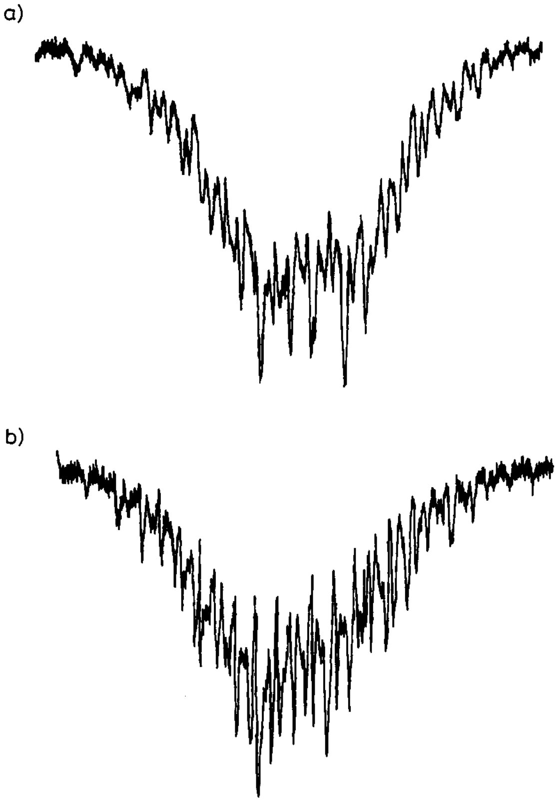

Figure 3. TR-ESR spectra of HDPM obtained by laser photolysis of α-phenylbenzoin in benzene in the presence of (a) TEA (160 mM) and (b) SBA (100 mM). According to the value of K_e reported previously, the main species observed in the spectra are considered to be (a) HDPM−TEA complex and (b) HDPM−SBA complex rather than bare HDPM.

TABLE 1: Values of a_{OH} of Several α-HB−Amine Complexes

	amines	a_{OH} (G)
primary	cyclohexyl	0.55
	n-hexyl	0.61
	sec-butyl	0.57
secondary	dipropyl	0.51
	methylbutyl	0.50
tertiary	triethyl	0.47
	dimethylethyl	0.50
	tri-*n*-butyl	0.42

TABLE 2: Hyperfine Coupling Constants (G) of Bare HDPM, HDPM−TEA, and HDPM−SBA Complexes in Benzene

	bare	TEA	SBA
a_o	3.27	3.27	3.27
a_m	1.25	1.25	1.25
a_p	3.69	3.69	3.69
a_{OH}	2.40	5.30	3.90

using the above formation constants. This indicates that both TR-ESR spectra are mainly due to the complexes rather than the bare HDPM. Actually, the hfs of the spectra are different from that of bare HDPM shown in Figure 1b. The hfcc of HDPM and complexes were determined by spectral simulation and are summarized in Table 2. It is clear that the value of a_{OH} becomes large when the HDPM forms the complex with amine. This is the same behavior as α-HB where a_{OH} is increased by complex formation.

Temperature Dependence of a_{OH} Value of α-HB. Since the a_{OH} value of α-HB increased by complex formation with amine, we examined the temperature dependence of a_{OH} of bare α-HB to see if the increase of a_{OH} value is explained by the viscosity effect. Figure 4 shows plots of a_{OH} of α-HB against solvent temperature, where toluene was used as a solvent. No significant difference was found between hyperfine structures in toluene and in benzene. No changes were found on the other hfcc. The plot clearly suggests negative dependence of a_{OH}: The value of a_{OH} increases from about 0.1 to 0.5 G with decreasing temperature. This result suggests that the a_{OH} value increases at least up to 0.5 G by the suppression of the motion of α-HB. According to the present results, a_{OH} of the complex is around 0.5 G as seen in Table 1. These results indicate that the restricted motion of α-HB in the complex would result in the increase of a_{OH} value.

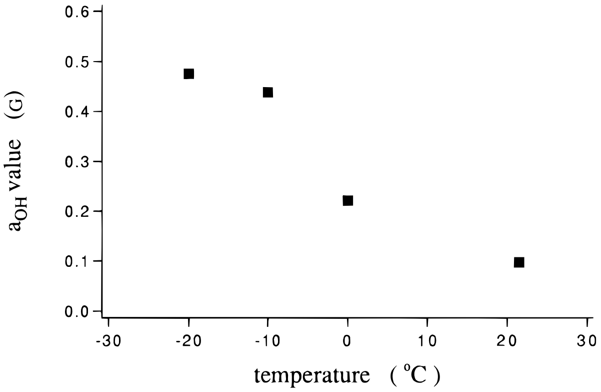

Figure 4. Temperature dependence of a_{OH} value of α-HB in toluene.

Determination of the Formation Constants. Since α-HB was found to form the complex with various aliphatic amines, we determined the formation constants of several complexes of α-HB. We failed to determine formation constants for HDPM complex by measuring the TR-ESR spectra of the complex versus various amine concentrations because of their poor S/N ratio. Hence, below we described the study for α-HB complex only. The method we used to determine chemical formula and formation constants has already been reported in our previous paper and we will briefly introduce the method. The formation constant, K_e, is represented by the following equation:

$$\log [C] = \log [K] + \log [A] + \log K_e \tag{1}$$

where [C], [K], and [A] refer to the concentrations of the complex, ketyl radical (α-HB), and amine, respectively. Since α-HB has been reported to form a 1:1 complex with TEA, we checked whether it is a good assumption that α-HB forms a 1:1 complex with various aliphatic amines. We regard that the concentrations of radical and the complex are in proportion to the corresponding CIDEP intensities, and hence introduce the equations $[C] = 2f_CI_C$ and $[K] = f_KI_K$, where f and I are enhancement factor of CIDEP for each molecule and intensity of CIDEP of single line, respectively. Since the peaks of α-HB split into a doublet by forming a complex with amine, we introduce the cofactor 2. The intensity ratio, I_C/I_K, is extracted from the lines in the lower field side of the TR-ESR spectra according to the manner shown in Figure 5. The ratios of enhancement factors, f_C/f_K, are thought to be unity because TM is the origin of the CIDEP which depends only on the dissociation of parent molecules.[17] Experimentally, the ratio of enhancement factors was measured to be close to unity in α-HB and TEA system.[8] Thus, eq 1 is rewritten as

$$\log 2\, I_C = \log I_K + \log [A] + \log K_e \tag{2}$$

The intensities are measured from the spectra at the interval of 1.5−2.0 μs for the following reasons: (1) the ratio of I_C/I_K is

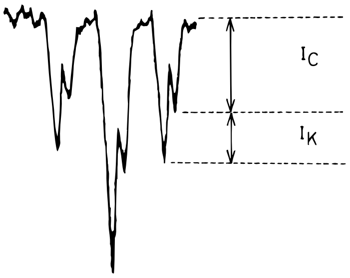

Figure 5. Schematic explanation of the contribution of α-HB and its complex CIDEP I_K and I_c, respectively, to the total spectrum of the mixture.

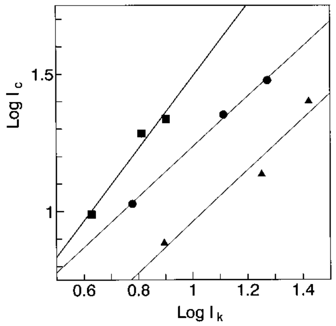

Figure 6. Plot of log [I_C] against log [I_K] after eq 2 for SBA (■), CHA (●), and TEA (▲). The slopes of fitted lines are 1.3 for SBA, 0.91 for CHA, and 0.92 for TEA.

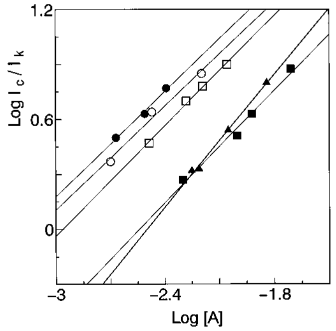

Figure 7. Plot of log [I_c] against log [A] after eq 2 for CHA (●), *n*-hexylamine (○), SBA (□), methylbutylamine (▲), and dimethylamine (■). The slopes of fitted lines are 0.95 for CHA, 0.93 for *n*-hexylamine, 1.0 for SBA, 1.21 for methylbutylamine, and 1.02 for dimethylethylamine. The straight line with the slope of almost unity suggests the 1:1 complex formation in the systems of α-HB and amines in benzene.

almost constant from 0.5 to 3.0 μs, which means that the equilibrium condition is already established at this interval time, and (2) the lifetime of the radical is relatively long, i.e., more than 10 μs according to the transient absorption measurement, which suggests that the concentrations of α-HB and its complex are presumably constant during TR-ESR detection. It should be noticed that spectrum of the complex partially overlaps with that of bare ketyl. Hence, we omitted the data at relatively low concentrations of amines. The concentration of amines is assumed to be constant since the concentration of amines is at least 10 times higher than that of the ketyl radical which is controlled to be about 10^{-4} M or less by the intensity of the photolysis laser. To confirm the 1:1 ratio of ketyl and amine in the complex, we plotted $\log(I_C/I_K)$ against log [A] by changing the amine concentration as well as log [I_C] against log [I_K] by changing the photolysis laser power. Examples of the plots are shown in Figures 6 and 7. Taking into account the S/N ratio of CIDEP signals, the slopes of the plots are nearly unity in both plots, which suggests that ketyl forms the complex with amine at the ratio of 1:1.

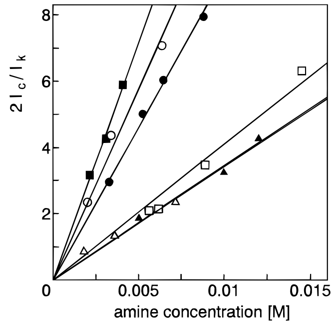

Figure 8. Plot of $2I_C/I_K$ against [A] for CHA (■), *n*-hexylamine (○), SBA (●), methylbutylamine (□), dimethylethylamine (▲), and TEA (△). K_e values were determined from the slope of each plot assuming eq $2I_C/I_K = K_e[A]$.

TABLE 3: Formation Constants of α-HB−Amine Complexes in Benzene

	amines	formation const (M^{-1})
primary	cyclohexyl	1430 ± 28
	n-hexyl	1150 ± 59
	sec-butyl	919 ± 13
secondary	dipropyl	663 ± 71
	methylbutyl	410 ± 23
tertiary	dimethylethyl	345 ± 14
	triethyl	342 ± 58[a]
	tri-*n*-butyl	167 ± 5

[a] This value was determined by the present method using reported data of our previous paper.

We determined the K_e value for various amines. We plotted $2I_c/I_k$ against [A] according to the equation $2I_C/I_K = K_e[A]$, as shown in Figure 8, and the K_e values were obtained from the slope. K_e values for various complexes are summarized in Table 3.

Discussion

Hydrogen Bond between Ketyl and Amine. The previous reports have suggested[8,10] that the complex formation between ketyl type radical and amine proceeds through the hydrogen-bonding interaction. The red shift of absorption spectrum of HDPM complex is quite small, about 330 cm^{-1},[10] which is one piece of evidence to show that the interaction of complex formation is due to the hydrogen bonding. In the present study, we found marked difference in a_{OH} values between the bare ketyl radical and the complex, which should be a key to reveal the nature of bonding of the complex. The a_{OH} of α-HB changed about twice when it formed complex, while no significant changes were observed on other hfcc. Besides, the a_{OH} value of the complex depends on the amine. Thus, we plotted a_{OH} values against the free energy difference between α-HB and complex in Figure 9 to examine the relation between complex formation and the a_{OH} value. The free energy differences were obtained from the K_e values according to the equation, $\Delta G = -RT \ln K_e$. The plot exhibits the linear relation between a_{OH} and $\Delta G/RT$, which indicates that a_{OH} of the α-HB complex depends on the stabilization energy. This plot suggests that α-HB complex is formed through the hydrogen bond between amino and OH groups.

There may be a few possible mechanisms to explain the drastic change of the a_{OH} value due to the complex formation. Two mechanisms of hyperfine interactions should be considered in the present case: one is due to hyperfine interaction between carbon atom and H(β proton), which contributes to a_{OH} with positive sign, and the other is between oxygen atom and H(α proton), which does with negative sign. According to the theory

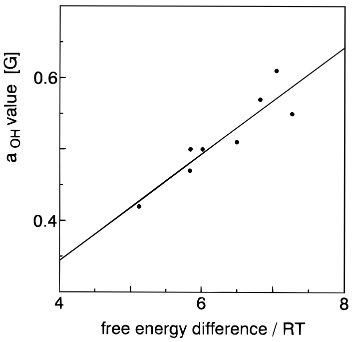

Figure 9. Plots of a_{OH} value vs free energy difference of complex formation reaction.

of hfcc of β proton,[7] a_{OH} follows the equation $a_{OH} = (B_0 + B_2 \cos^2 \theta)\rho^C{}_\alpha$, where B_2 is the coefficient reflecting the spin density arising from hyperconjugation, B_0 is due to other mechanism and is generally negligible compared to B_2, $\rho^C{}_\alpha$ is the spin population at the carbon atom, and θ is the dihedral angle between the plane through C−O bond and the p orbital at carbon atom and the plane through COH. According to this mechanism, the a_{OH} value depends on the averaged position of H against molecular plane. On the other hand, the second mechanism does not depend on the orientation between H and the molecular plane. Since the a_{OH} value of α-HB is close to zero, it may be concluded that positive and negative contributions from C and O atoms cancel one another in bare α-HB. This was confirmed by the temperature dependence of the a_{OH} value. The OH group may be torsionally oscillating out of the molecular plane and the decrease of temperature restricts the torsional oscillation to reduce the contribution of the first mechanism. This mechanism was suggested for 9-hydroxyfluorenyl radical[2] whose a_{OH} showed similar negative temperature dependence. Thus, the a_{OH} value of negative sign increases with decreasing temperature. The complex formation may restrict the torsional motion of OH group similar to the decrease of temperature in the bare α-HB system and positive contribution decreases. This results in the increase of a_{OH} value in the complex formation.

Nature of the Bond of Complexes. As seen in Table 3, it is remarkable that the formation constant shows various values depending on aliphatic amines. It is very interesting that K_e is relatively large, 919−1430 M^{-1} for primary amines and 410−663 M^{-1} for secondary amines, and is small, 167−345 M^{-1}, for tertiary amines. This suggests that stabilization of the complex is the biggest in the complex with primary amines and the smallest with tertiary amines. Another remarkable result is that the value of a_{OH} of α-HB is the largest in the complex with primary amines while the smallest with tertiary amines. This indicates that the hydrogen bond between amine and α-HB depends on the degree of hydrogen substitution on the nitrogen atom of the amine. The pK_a value of amine might explain the dependence of K_e and a_{OH}. However, this is excluded because pK_a of cyclohexyl-, diethyl-, and triethylamines, which are typical of primary, secondary, and tertiary amines, are 10.64, 10.93, and 10.72 in aqueous solution, respectively, and no significant difference is found among the three. IP of amine is another possible factor to control the K_e and a_{OH} values. If charge transfer interaction contributes to the complex formation, tertiary amines should have larger K_e value than primary amines, because IP of tertiary amines is generally smaller than that of primary amines. However, the result is in the reverse of this prediction and IP is excluded from the factor. The remarkable difference among amines is the number of hydrogen (H) atoms attached on the nitrogen: two for primary, one for secondary, and zero for tertiary. We attributed the nubmer of H atoms of amine to the factor controlling the magnitude of K_e. The complex is produced through the hydrogen bond formation between N atom of amine and H atom of OH group in ketyl. Thus, the nonbonding electrons of N atom facing the H atom of OH group are important. It is well-known that the structure of amine depends on the degree of hydrogen substitution. Primary amine has more pyramidal geometry than does tertiary amine. This means that the electron density of nonbonding orbital of N atom on the side of α-HB is the richest in primary amine. Thus the bond is more tightly formed in α-HB−primary amine case. This is in good consistence with the dependence of K_e value.

Comparison of the Complexes of α-HB and HDPM. The value of K_e is found to be smaller for HDPM complexes (<100 M^{-1}) than that for α-HB complexes (167−1430 M^{-1}). The pK_a of HDPM and α-HB are considered to be very similar since the pK_a of HDPM is 9.25 and that of acetophenone ketyl radical, which has very similar chemical structure to that of α-HB, is about 10.[18] If the ability of proton donation controls the K_e value, HDPM complex should show larger K_e value than α-HB complexes. Thus, the difference in K_e value cannot be explained by the difference in the ability of proton donation. The small K_e value for HDPM may be interpreted by considering the structural hindrance: α-HB has one bulky phenyl group while HDPM has two. The extra phenyl group of HDPM will refuse to form the complex, which results in relatively small K_e vlaue in the HDPM complex.

The behavior of a_{OH} value of α-HB against amines is different from that of HDPM. a_{OH} of HDPM in benzene is 2.5 G while those in TEA and SBA complexes are 5.3 and 3.9 G, respectively. The value itself increases when HDPM forms the complex with TEA and SBA, which is the same result with α-HB case. However, the a_{OH} value of α-HB in the complexes decreases from primary to tertiary amines while a_{OH} for the HDPM complex with SBA is smaller than that with TEA. The behavior of a_{OH} of the HDPM complex is fairly complicated and no systematic explanation could be found. The extra phenyl ring of HDPM may generate the slight difference of the averaged position of the H atom in OH group depending on the structure of countered amine. This would result in different dependence of a_{OH} value of the HDPM−amine complex.

Acknowledgment. The present work is partly supported by the Grant-in-Aid on Priority-Area-Research on Photoreaction Dynamics from the Ministry of Education, Science, Sports, and Culture of Japan (No. 06239103).

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