

## Heats of formation of intermediate radicals in solution

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### Abstract

The heats of formation of radicals in solution were measured by using transient absorption and time-resolved thermal lensing methods. The heat of formation of benzophenone ketyl radical (BPK) in benzene solution was determined to be  $21 \pm 2$  kcal/mol. Using this value, the heats of formation of several radicals, which were generated as the counter radicals of BPK in the hydrogen abstraction reaction of triplet benzophenone, were also determined. The solvation energies of radicals are compared with those of their parent molecules and discussed in light of solvation mechanism. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Heats of formation; Intermediate radicals; Solvation mechanism

### 1. Introduction

Many photoreactions are understood as consecutive steps in which several reaction intermediates are involved. To understand the overall photoreaction processes, it is necessary to obtain information about these reaction intermediates, such as radicals and excited states. However, only several studies have been done to determine the physical properties of intermediate radicals, such as diffusion coefficients, heats of formation in solution, and so on. Recently, Terazima et al. [1,2] and Okamoto et al. [3] studied the diffusion processes of radicals by using the transient grating method. They found that the translational diffusion coefficients of the radicals were 2–4 times smaller than those of the parent molecules. They suggested some specific radical–solvent interaction to occur.

To elucidate the interaction mechanism between intermediate radical and solvent molecule, it is experimentally difficult but necessary to determine the heats of formation of reaction intermediates in solution. Most radicals in solution are chemically unstable: they normally disappear through the association/disproportion reactions between radicals or the addition to and abstraction from other molecules. Since these radical reactions also release the heat, it is necessary to measure the heat generated by a single reaction step of interest in order to determine the accurate heat of formation of inter-

mediate radicals. A few groups have so far attempted such types of experiments. Castelhana and Griller [4] measured the heats of formation of some simple alkyl radicals by electron paramagnetic resonance spectroscopy. From the equilibrium constants for a series of systems,  $R \cdot + R'I \rightleftharpoons RI + R' \cdot$ , the C–H bond dissociation energies were determined to be  $\sim 100$  (primary C–H bonds),  $\sim 96$  (secondary C–H), and  $\sim 94$  (tertiary C–H) in units of kcal/mol. The C–H bond dissociation energies in nonpolar solvents were found to be in good agreement with the corresponding gas-phase data, which suggests that the solvation energies of alkyl radicals and their parent alkanes are essentially same. Kanabus-Kaminska et al. [5] tackled the problem of solvation effects by measuring the heats of radical reactions in an extremely polar solvent, water, by using the photoacoustic method. Their result implies that the solvation energies of organic radicals and their parent molecules are almost the same even in the extremely polar solvent.

Benzophenone ketyl radical (BPK) is known to be an important intermediate in the photoreduction of benzophenone (BP). Although many studies have been done on the photoreduction of BP, only a few papers have treated the energetics. Poston and Harris [6] and Cambron and Harris [7] measured the heat of this reaction by the time-resolved photothermal method. They estimated the O–H bond dissociation energy of BPK in acetonitrile to be 34 kcal/mol. The heat of formation of BPK was recently reported by Arnaut and Caldwell [8]. They measured the heat released by the hydrogen atom transfer reaction between benzophenone and benzhydrol (BH) in benzene;  $BP + BH \rightarrow 2BPK$ . The heat

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of formation and the O–H bond dissociation energy of BPK in benzene were determined to be 5.3 and 41.6 kcal/mol, respectively. There is a large discrepancy between reported O–H bond energies of BPK.

In this work, we carefully determined the heat of formation and O–H bond dissociation energy of BPK in benzene, and the heats of formation of other radicals ( $R\cdot$ ) generated as the counter radicals of BPK in the hydrogen atom transfer reactions,  $BP + RH \rightarrow BPK + R\cdot$ . We discuss the solvation effects on radicals, and the role of unpaired electron on solvation.

## 2. Experiment

A transient absorption apparatus was reported previously [9]. A XeF excimer laser (Lambda Physik EMG101) was used as an excitation light source. A Xe flash lamp (Ushio UXL150DS, 150 W), which was synchronously fired with the excimer laser, was used as the monitoring light. The monitoring light was detected with a monochromator (Nikon P250)/photomultiplier tube (Hamamatsu Photonics R928) combination system, which had a spectral resolution of 2 nm. The transient absorption signals were digitized with a digital storage oscilloscope (Sony Tektronics TDS350) and analyzed with a personal computer. The transient signals were accumulated over 30 times to improve the S/N ratio.

A TRTL experimental setup was described elsewhere [10]. The excitation light source was a XeF excimer laser (351 nm). A He–Ne laser beam (NEC GLG-5380; 1.5 mW) was used as an analyzing beam of TRTL signals. The laser power was monitored by a silicon photodiode (Hamamatsu Photonics S1336-5BQ) calibrated with a pyroelectric detector (Gentec ED 100). The He–Ne laser beam, sampled through a pinhole with 300- $\mu$ m diameter and the monochromator, was detected by the photomultiplier tube.

An on-line controlled calorimetry system to measure solution heat was reported previously [11]. Benzophenone (Kanto Chemical; GR grade) and benzhydrol (Tokyo Kasei; TLC grade) were purified by recrystallization for several times in hexane. 8-Quinolinol (Tokyo Kasei; GC grade) was used as a calorimetric standard for the TRTL measurement in the UV region without further purification. Benzene, *n*-hexane, cyclohexane, ethanol, 2-propanol (Kanto; GR grade), and 1,4-cyclohexadiene (Tokyo Kasei; TLC grade) were used without further purification. All sample solutions at 293 K were deoxygenated by bubbling argon gas (purity 99.95%) saturated with solvent for half an hour before use and flowed through a cuvette to eliminate the influence of photoproducts.

## 3. Results and discussion

### 3.1. Hydrogen abstraction reaction

Laser-excited BP rapidly dissipates the vibrational energy to the surrounding medium and relaxes to the bottom of the

lowest excited singlet state ( $S_1$ ), followed by the  $S_1 \rightarrow T_1$  intersystem crossing with a quantum yield of unity ( $\Phi_{ISC} = 1$ ). In the presence of hydrogen donor (RH), triplet benzophenone ( $^3BP^*$ ) abstracts hydrogen atom from RH and yields benzophenone ketyl radical (BPK) and the counter radical ( $R\cdot$ ).



In order to determine the heats of formation of transient radicals, it is necessary to obtain the quantum efficiency of reaction sequence (1a) and (1b),  $\phi_a$ . The  $\phi_a$  value is actually a conversion efficiency of  $^3BP^*$  into BPK and defined as

$$\phi_a = \Phi_{ISC} \times \frac{[BPK]/n}{[^3BP^*]} = \frac{1}{n} \times \frac{[BPK]}{[^3BP^*]} \quad (\because \Phi_{ISC} = 1) \quad (2)$$

where [BPK] and [ $^3BP^*$ ] represent the molar concentrations of BPK and  $^3BP^*$  generated by the reactions (1a) and (1b), respectively, and  $n$  is unity in general. The  $n$  value of 2 was adopted in the special case of the BP/benzhydrol system, because two BPK radicals are formed from one  $^3BP^*$ . The concentrations of [BPK] and [ $^3BP^*$ ] were determined from the absorbances obtained by the transient absorption experiments. Using Lambert-Beer's law, Eq. (2) is converted to Eq. (3).

$$\phi_a = \frac{1}{n} \times \frac{\varepsilon_T^{525}}{\varepsilon_{BPK}^{545}} \times \frac{OD_{BPK}^{545}}{OD_T^{525}} \quad (3)$$

Here, the symbols of OD and  $\varepsilon$  represent the absorbance and molar extinction coefficient, respectively. The superscripts denote the wavelength used for transient absorption, and the subscripts the absorbers. The molar extinction coefficients are adopted from literature [12],  $\varepsilon_{BPK}^{545} = 4600 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\varepsilon_T^{525} = 6500 \text{ M}^{-1} \text{ cm}^{-1}$ . The coefficients are assumed to be independent of solvents as in Ref. [7].

In the presence of 50-mM benzhydrol (BH), the transient absorption exhibits two components: the fast and slow ones are due to triplet benzophenone and BPK, respectively. Triplet benzophenone was almost quenched at 4  $\mu$ s after the excitation. The values of  $OD_{BPK}^{545}$  and  $OD_T^{525}$  were obtained from the transient spectra measured at the delay time of 4  $\mu$ s and immediately after the excitation, respectively. Fig. 1 displays the laser intensity dependences of  $OD_{BPK}^{545}$  and  $OD_T^{525}$ . We obtain the  $OD_{BPK}^{545}/OD_T^{525}$  ratio in Eq. (3) to be 0.71 from slopes of two lines. By introducing all the necessary values into Eq. (3), the  $\phi_a$  value is determined to be  $0.50 \pm 0.02$  in the BP/BH(50 mM) system.

When hydrogen donor was used as a solvent, all  $^3BP$  were quenched out within 0.5–2  $\mu$ s. Then, appropriate gate time was selected to measure  $OD_{BPK}^{545}$  in the different hydrogen donor systems.

The quantum efficiencies of the reaction sequence, (1a) and (1b), and the quenching rate constants of  $^3BP^*$  are

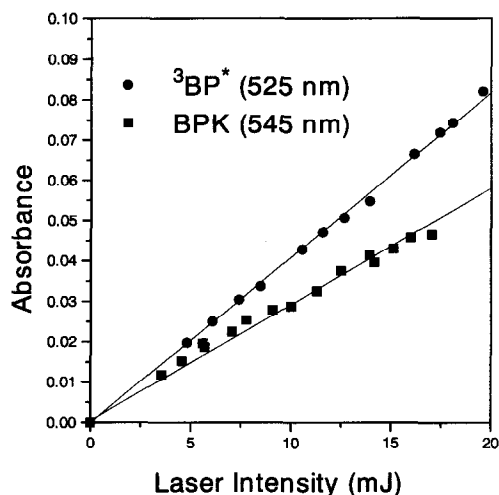


Fig. 1. Laser intensity dependence of absorbance of  $^3\text{BP}^*$  and BPK.

summarized in Table 1. As recognized in this table, the  $\Delta H_r$  values (the heats of reaction for  $\text{BP} + \text{RH} \rightarrow \text{BPK} + \text{R}\cdot$ ), which will be derived later, are comparable to the triplet energy of BP (about 69 kcal/mol) except for the 1,4-cyclohexadiene system. The quenching rate constant in the 1,4-cyclohexadiene system is 3 orders of magnitude larger than those in other systems. This result is consistent with the fact that the  $\Delta H_r$  value in the 1,4-cyclohexadiene system is about 40 kcal/mol smaller than those in other hydrogen donor systems. In the benzhydrol (50 mM) system, about half of  $^3\text{BP}^*$  is estimated to be quenched by benzhydrol using the quenching rate constant ( $7.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) and triplet lifetime ( $3.1 \mu\text{s}$  in benzene [10]). Therefore, the net quenching process of  $^3\text{BP}^*$  by benzhydrol is dominated by hydrogen abstraction. In the other systems, almost all  $^3\text{BP}^*$  are quenched by hydrogen donors. Among them, *n*-hexane gives rather low quantum efficiency ( $\phi_a = 0.70$ ). The H-atom abstraction from *n*-hexane seems less effective than that from cyclohexane. While the six carbon positions in cyclohexane are equivalent, *n*-hexane has three-types of carbon positions. The H-atom abstraction efficiency at the primary positions, which have the strongest C–H bonds in *n*-hexane, would be

reduced than those at the secondary positions of *n*-hexane and six equivalent positions of cyclohexane.

### 3.2. Heat of formation of BPK

It is well-known that BP is non-radiative species at room temperature. If no chemical reaction occurs, all the photon energy absorbed by BP is released as heat. On the other hand, in the presence of hydrogen donor, the photon energy is partially stored as chemical energy in the system through reactions. The heat conversion efficiency ( $\alpha$ ), the ratio of released heat to photon energy absorbed, is given by Eq. (4)

$$\alpha = \frac{E_{\text{ex}} - \phi_a \times \Delta H_r}{E_{\text{ex}}} \quad \text{or} \quad \Delta H_r = \frac{(1 - \alpha) \times E_{\text{ex}}}{\phi_a} \quad (4)$$

where  $\Delta H_r$  is the enthalpy change in the reaction,  $\text{BP} + \text{BH} \rightarrow \text{BPK} + \text{R}\cdot$ . We need to have the  $\alpha$  values to obtain  $\Delta H_r$ .

The  $\alpha$  value was determined from the thermal lensing measurement. In the BH system, the gate time for data acquisition was set at about 4  $\mu\text{s}$  after the excitation, corresponding to the delay time when  $^3\text{BP}$  was quenched out. Fig. 2 plots the TRTL signals against laser intensity at the various concentrations of BP. Two-photon absorption is not expected to occur, since the absorption due to BPK and  $^3\text{BP}$  is weak at 351 nm. In fact, each plot gives a straight line, which clarifies the multiphoton process and the recombination reaction of radicals can be neglected. Therefore, the kinetics of the photothermal system employed in this work has become much simpler than that employed in Cambron and Harris [7]. The TRTL signal intensity,  $U$ , is proportional to the heat emitted into the surrounding solvent and expressed as

$$U = K\alpha(1 - 10^{-\text{OD}})I \quad (5)$$

where  $K$  is an apparatus factor governed by both the experimental alignment and thermoelastic properties of solvent. Symbols of  $I$  and OD are the excitation light intensity and the absorbance due to BP at 351 nm, respectively. Terazima et al. [14] mentioned the lens signal deviates due to 'population

Table 1

Kinetic and photothermal parameters for the reaction of  $^3\text{BP}^* + \text{RH} \rightarrow \text{BPK} + \text{R}\cdot$ .

Hydrogen donor (RH)	Solvent	$\phi_a^a$	Quenching rate constant <sup>b</sup> ( $10^6 \text{ M}^{-1} \text{ s}^{-1}$ )	$\alpha^c$	$\Delta H_r^d$ (kcal/mol)
Benzhydrol (50 mM)	Benzene	$0.50 \pm 0.02$	7.5 <sup>e</sup>	$0.59 \pm 0.03$	$67 \pm 3$
Cyclohexane	Cyclohexane	$0.93 \pm 0.03$	0.31	$0.23 \pm 0.02$	$67 \pm 3$
Hexane	Hexane	$0.70 \pm 0.02$	0.14	$0.38 \pm 0.03$	$73 \pm 3$
Ethanol	Ethanol	$0.93 \pm 0.02$	0.34	$0.20 \pm 0.02$	$70 \pm 2$
2-Propanol	2-Propanol	$1.0 \pm 0.02$	0.55	$0.15 \pm 0.02$	$69 \pm 2$
1,4-Cyclohexadiene (50 mM)	Benzene	$1.0 \pm 0.02$	290 <sup>e</sup>	$0.65 \pm 0.03$	$29 \pm 3$

<sup>a</sup>Quantum efficiency determined Eq. (3).

<sup>b</sup>Quenching rate constants of  $^3\text{BP}^*$ .

<sup>c</sup>Heat conversion efficiencies ( $\lambda = 351 \text{ nm}$ ).

<sup>d</sup>Heats of reaction of  $\text{BP} + \text{RH} \rightarrow \text{BPK} + \text{R}\cdot$ .

<sup>e</sup>Ref. [13].

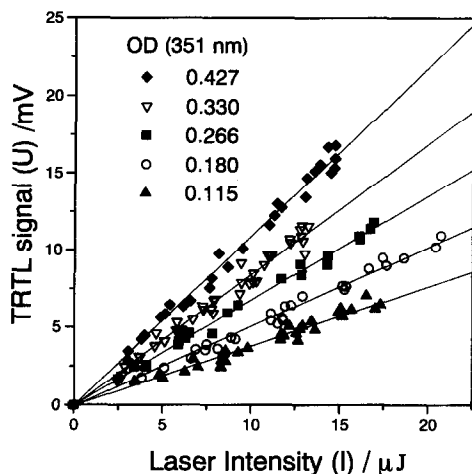


Fig. 2. TRTL signals against laser intensity at the various concentration of BP.

lens effect' when the wavelength of an analyzing He–Ne laser beam (633 nm) is close to the absorption bands of reaction products or transients. As the reaction products or transients in our systems, only  $^3\text{BP}^*$  and BPK have the absorption bands in the spectral region near 633 nm and might deserve the consideration of the effect. Terazima et al. reported that the population lens effect due to  $^3\text{BP}^*$  is small in the photo-physical system of benzophenone. In fact, the intersystem crossing yield of BP could be measured to  $1.00 \pm 0.01$  from the TRTL experiment using the He–Ne laser [15]. The population lens effect due to BPK is expected to be even smaller than that due to  $^3\text{BP}^*$ , because the visible absorption spectra of BPK and  $^3\text{BP}^*$  are similar each other in shape and the absorption coefficients of BPK are smaller than those of  $^3\text{BP}^*$  [12]. The population lens effect can be neglected in the other photoreaction systems employed in this work, where the product radicals absorb the light much shorter than 633 nm.

A calorimetric standard is required to determine the  $\alpha$  value, because it is rather difficult to measure directly the absolute  $K$  factor. We chose 8-quinolinol as a calorimetric standard [16]. The slopes of straight lines in Fig. 2,  $U/I$ , are plotted against the absorptivity,  $1-10^{-\text{OD}}$ , in Fig. 3. The same procedures were applied to the data analysis in the 8-quinolinol system, and the results are shown in Fig. 3. From the ratio of two slopes, the heat conversion efficiency ( $\alpha_{\text{BP}}$ ) for BH (50 mM) system was determined to be  $0.59 \pm 0.03$ . The heat of reaction ( $\Delta H_r$ ) for the reaction,  $\text{BP} + \text{BH} \rightarrow 2\text{BPK}$ , is determined to be  $67 \pm 3$  kcal/mol by introducing the values of  $E_{\text{ex}}$  (81.4 kcal/mol),  $\alpha_{\text{BP}}$  ( $0.59 \pm 0.03$ ) and  $\phi_a$  ( $0.50 \pm 0.02$ ) into Eq. (4). These values are listed in Table 1.

The total heat of formation of BPK and  $R\cdot$  generated by the reaction sequence (1a) and (1b) is expressed as

$$\begin{aligned} & \Delta H_f^{293}(\text{BPK}) + \Delta H_f^{293}(R\cdot) \\ &= \Delta H_f^{293}(\text{BP}) + \Delta H_f^{293}(\text{RH}) + \Delta H_r \end{aligned} \quad (6)$$

where  $\Delta H_f^{293}$  represents the heat of formation of chemical

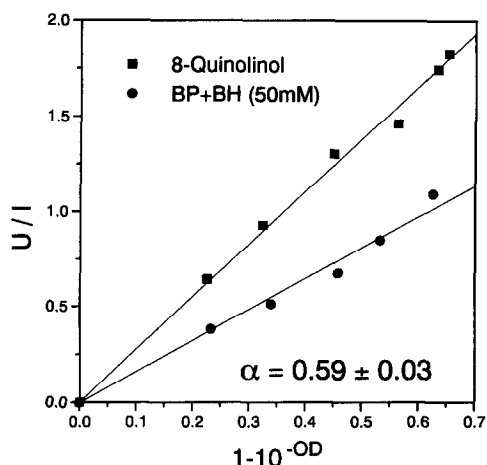


Fig. 3. Plots of  $U/I$  vs.  $(1-10^{-\text{OD}})$ . Data are fitted to Eq. (5).

species (BPK,  $R\cdot$ , BP or RH) at 293 K. The formation heats of crystalline BP and BH are  $-8.1$  and  $-25.1$  kcal/mol, respectively [17]. The solution heat of BP in benzene was measured to be 4.7 kcal/mol, which was independent on the BP concentration. On the other hand, the solution heat of BH in benzene depended on the BH concentration and was measured to be 3.5 kcal/mol at 50 mM. Thus,  $\Delta H_f^{293}(\text{BP})$  and  $\Delta H_f^{293}(\text{BH})$  are determined to be  $-3.4$  and  $-21.6$  kcal/mol, respectively, under the present experimental conditions. The value of  $\Delta H_f^{293}(\text{BPK}) + \Delta H_f^{293}(R\cdot)$  is derived to be 42 kcal/mol using Eq. (6). In the particular BH system, two BPK radicals are formed, and hence the  $\Delta H_f^\circ(\text{BPK})$  value in benzene is determined to be  $21 \pm 2$  kcal/mol. The values of  $\Delta H_f^{293}(\text{BP})$ ,  $\Delta H_f^{293}(\text{BH})$ , and  $\Delta H_f^{293}(\text{BPK})$  are listed in Table 2.

The  $\Delta H_f^{293}(\text{BPK})$  value of 21 kcal/mol is larger than 5.3 kcal/mol reported by Arnaut and Caldwell [8] using the photoacoustic method. The reason of the discrepancy between two  $\Delta H_f^{293}(\text{BPK})$  values is not clear yet, but we point out uncertainty in their experiment. The solution heat of benzhydrol (BH) was found to be considerably dependent on its concentration. The solution heat decreased as the BH concentration increased. Specific solute–solute interaction, like dimerization, would be expected to act in the higher concentrations of 300–600 mM Arnaut and Caldwell employed.

The experiments in this work were performed at a low and constant concentration of 50 mM to exclude the solute–solute interaction effect mentioned above. In this condition, the BPK–BH interaction is also neglected by the following reasons. The hydrogen-bonded 1:1 complex of BPK and TEA exhibits a red-shifted spectrum [19–21]. However, the visible absorption spectrum of BPK did not show any variation by changing [BH]. Furthermore, it is safely neglected radical–radical interaction because of its low concentration ( $< 10^{-6}$  M). Therefore, it seems reasonable to suppose that  $\Delta H_f^{293}(\text{BPK})$  in this system would be constant against the BH concentration.

Table 2  
Heats of formation and solvation energies of BP, BPK, RH and  $R\cdot$  in solution<sup>a</sup>

RH/ $R\cdot$	Solvent	$\Delta H_f^{293}(\text{BP})$	RH <sup>b</sup>		$\Delta H_f^{293}(\text{BPK})$	$R\cdot$ <sup>b</sup>	
			$\Delta H_f^{293}(\text{RH})$	$E^{\text{sol}}(\text{RH})$		$\Delta H_f^{293}(R\cdot)$	$E^{\text{sol}}(R\cdot)$
Benzhydrol/BPK	Benzene	-3.4	-21.6		21 ± 2	21 ± 2	15
Cyclohexane/Cyclohexyl	Cyclohexane	-0.7	-37.4	7.9	24 ± 2	5.2 ± 3	8.7
<i>n</i> -Hexane/Hexyl	<i>n</i> -Hexane	-0.9	-47.5		24 ± 2	1.1 ± 3	
Ethanol/CH <sub>3</sub> CHOH	Ethanol	-1.6	-66.2	10.1	23 ± 2	-21 ± 2	5.8
2-Propanol/CH <sub>3</sub> C(OH)CH <sub>3</sub>	2-Propanol	-1.6	-76.0	10.9	23 ± 2	-31 ± 2	4.4
1,4-Cyclohexadiene/ Cyclohexadienyl	Benzene	-3.4	18.2	8.1	21 ± 2	23 ± 3	21

<sup>a</sup>All the values are in units of kcal/mol.

<sup>b</sup>The  $\Delta H_f^{293}$  values in the gas phase are taken from Refs. [17,18]; cyclohexane = -29.5, *n*-hexane = -39.9, ethanol = -56.1, 2-propanol = -65.1, 1,4-cyclohexadiene = 26.3, BPK = 36.1, cyclohexyl = 13.9, CH<sub>3</sub>CHOH = -15.2, CH<sub>3</sub>C(OH)CH<sub>3</sub> = -26.6, cyclohexadienyl = 44.0.

From  $\Delta H_f^{293}(\text{BPK})$  of 21 kcal/mol, the bond dissociation energy (BDE) value of Ph<sub>2</sub>CO-H can be evaluated by the following equation.

$$\text{BDE}(\text{Ph}_2\text{CO-H}) = \{\Delta H_f^{293}(\text{BP}) + \Delta H_f^{293}(\text{H}\cdot)\} - \Delta H_f^{293}(\text{BPK}) \quad (7)$$

The BDE (Ph<sub>2</sub>CO-H) value is determined to be 28 kcal/mol in this work, which is inconsistent with 41.6 kcal/mol reported by Arnault and Caldwell. The reasons for the inconsistency have already been discussed above. Cambron and Harris reported BDE (Ph<sub>2</sub>CO-H) to be 34 kcal/mol [6,7], which was derived under the high laser power conditions that triplet-triplet annihilation and two-photon process occur to appreciable content. They simulated the photothermal signal assuming the internal conversion efficiency of <sup>3</sup>BP\*\* → <sup>3</sup>BP\* to be unity, where <sup>3</sup>BP\*\* is the highly excited triplet state. Kajiji et al. [22] and Takatori et al. [23,24] found that <sup>3</sup>BP\*\* dissociates into two phenyl radicals and a carbon monoxide with the quantum yield of 0.39. Possibly, Cambron and Harris would overestimate the BDE(Ph<sub>2</sub>CO-H) value. In order to eliminate the two-photon process, we choose the wavelength of 351 nm for the excitation, at which the T-T absorption is very weak.

### 3.3. Heats of formation of various counter radicals

The same procedures used in the BH system were applied to determine the heats of formation of counter radicals ( $R\cdot$ ) generated by the reactions of <sup>3</sup>BP\* + RH → BPK +  $R\cdot$ . The  $\alpha$  and  $\Delta H_f$  values determined by the transient absorption and thermal lensing experiments are listed in Table 1. We estimate  $\Delta H_f^{293}(\text{BPK})$  in various solvents. The reaction rates of <sup>3</sup>BP\* with the solvents except for benzene are faster than that with BH (50 mM). For example, the reaction of <sup>3</sup>BP\* and cyclohexane proceeds at the rate of  $3 \times 10^6 \text{ s}^{-1}$ , while the reaction of <sup>3</sup>BP\* and BH (50 mM) does at  $4 \times 10^5 \text{ s}^{-1}$ . Therefore, it is impossible directly to determine  $\Delta H_f^{293}(\text{BPK})$  in the cyclohexane. The situation is all the same for the other solvents except for benzene. Then, we assume that the BDE(Ph<sub>2</sub>CO-H) values are constant at 28

kcal/mol in all the solvents. Actually, Terazima et al. [1] reported that the diffusion coefficient ratios of BPK/BP measured in various solvents are constant around 0.4, which implies the BPK-solvent interaction does not depend on solvents, even if they are alcoholic or non-alcoholic. The  $\Delta H_f^{293}(R\cdot)$  values obtained by using Eq. (7) are listed in Table 2, together with  $\Delta H_f^{293}(\text{BPK})$ .

### 3.4. Solvation energies of radicals

All the radicals are stabilized by solvent to some extent. The solvation energy ( $E^{\text{sol}}$ ) is defined as

$$E^{\text{sol}}(R\cdot) = \Delta H_f(R\cdot) \text{ in the gas phase} - \Delta H_f(R\cdot) \text{ in solution.} \quad (8)$$

The calculated  $E^{\text{sol}}(R\cdot)$  values are listed in Table 2. The  $E^{\text{sol}}(\text{RH})$  are also estimated from the relation of Eq. (8) for RH and the literature data of  $\Delta H_f^{293}(\text{RH})$  in the gas phase, which are listed in Table 2. The  $E^{\text{sol}}(\text{RH})$  values are almost constant at about 8–11 kcal/mol. The  $E^{\text{sol}}(R\cdot)$  values are quite different depending on the kind of radical. Because  $R\cdot$  radical and the parent RH molecule possess almost the same volumes, weight and structures, variation in the solvation energies of  $R\cdot$  and RH is estimated to mainly come from the solvation effect of unpaired electron in  $R\cdot$ .

First, we consider the effect of dipole moment. Based on the Onsager's reaction field model [25], the solvation energy ( $E^{\text{Onsager}}$ ) in solvent which has the dielectric constant ( $\epsilon_r$ ) and the refractive index ( $n$ ) is represented by Eq. (9),

$$E^{\text{Onsager}}(\text{BP, RH or } R\cdot) = \frac{2\mu^2}{R^3} \left( \frac{\epsilon_r - 1}{\epsilon_r + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \quad (9)$$

where  $\mu$  and  $R$  represent the dipole moment and the diameter of solute, respectively. Since the refractive indexes are essentially the same ( $n = 1.4$ ), the second term of Eq. (9) is constant for all solvents. The  $E^{\text{Onsager}}$  values are controlled by the first term. Among BP and RH's, BP ( $\mu = 2.98 \text{ D}$  [26],  $R = 3.77 \text{ \AA}$  [1]) and ethanol ( $\mu = 1.69 \text{ D}$  [18],  $R = 2.58 \text{ \AA}$  [1]) give the maximum  $E^{\text{Onsager}}$  values of about 3.2 kcal/mol. The dipole moments of transient radicals have been

hardly reported. To the best of our knowledge, the ketyl radical of  $\alpha,\alpha,\alpha$ -trifluoroacetophenone was measured by a microwave dielectric absorption method [26]. The conversion of the  $\alpha,\alpha,\alpha$ -trifluoroacetophenone into the ketyl radical is accompanied by the decrease in the dipole moment. It seems reasonable to suppose that the dipole moment of ketyl type radicals are smaller than those of the parent molecules in the ground state. Since BPK, ethanol radical and propanol radical can be regarded as ketyl-type radicals, those radicals would have the smaller dipole moments than the corresponding parent molecules. The dipole moments of alkyl radicals are not so different from those of the parent molecules [26] and  $E^{\text{Onsager}}(R\cdot)$  would be close to  $E^{\text{Onsager}}(\text{RH})$ . Therefore, the difference in  $E^{\text{Onsager}}$  between  $R$  and  $\text{RH}$  is estimated to be less than 3 kcal/mol, which is recognized for cyclohexyl radical in cyclohexane. As seen in Table 2, we found that the differences are more than 3 kcal/mol in the cases of alcohol and  $\pi$  radicals. Thus, the Onsager's model is insufficient to explain our observation in this point. We discuss the solvation effect on these intermediate radicals below.

In the ethanol and 2-propanol systems, the solvation energies of  $\text{CH}_3\dot{\text{C}}\text{HOH}$  and  $\text{CH}_3\dot{\text{C}}(\text{OH})\text{CH}_3$  are smaller by 5–6 kcal/mol than the corresponding  $E^{\text{sol}}(\text{RH})$  values. Alcohols are known to form hydrogen bond with each other, and are stabilized by several kcal/mol [27]. Alcohol radicals may also form hydrogen bond with solvent alcohols. Nevertheless, we suppose that  $\text{CH}_3\dot{\text{C}}(\text{H})\text{OH}$  and  $\text{CH}_3\dot{\text{C}}(\text{OH})\text{CH}_3$  do not form hydrogen bond with alcohols based on the following reasons. (1) The solvation energies of these alcohol radicals studied in this work are 4–6 kcal/mol, which are smaller by several kcal/mol than those of the corresponding parent alcohols. (2) The diffusion rate constants of  $\text{CH}_3\dot{\text{C}}(\text{H})\text{OH}$  in ethanol and  $\text{CH}_3\dot{\text{C}}(\text{OH})\text{CH}_3$  in 2-propanol are larger than the self-diffusion rate constants of ethanol and 2-propanol, respectively [1]. These observations strongly suggest that the alcohol radicals do not form hydrogen bond with solvent alcohols. Alcohol radicals,  $\text{CH}_3\dot{\text{C}}(\text{H})\text{OH}$  and  $\text{CH}_3\dot{\text{C}}(\text{OH})\text{CH}_3$ , are carbon-centered radicals with the adjacent oxygen atom and the resonant formula,  $R-\dot{\text{C}}\text{H}-\text{OH} \leftrightarrow R-\dot{\text{C}}\text{H}=\text{OH}$ , might be expected. As a result, the electron density on the oxygen atom of the alcohol radicals would become lower than that of the parent alcohols. This seems the reason why the alcohol radicals do not form hydrogen bond with solvent alcohols.

The solvation energy of cyclohexadienyl radical is 11 kcal/mol larger than that of 1,4-cyclohexadiene. The characteristic of this radical lies in the possession of five conjugated  $\pi$  electrons and the unpaired electron are delocalized in the entire molecular frame. Due to this delocalization, the radical seems to interact with many solvent molecules, which may result in the large solvation energy (21 kcal/mol). Terazima et al. [1,2] and Okamoto et al. [3] also found that radicals with unpaired  $\pi$  electron diffuse more slowly than the parent molecules. The slow diffusion of radicals are interpreted in terms of a specific radical–solvent interaction. Our observation seems consistent with their interpretation. It is likely that

there is a specific attractive interaction between  $\pi$  radicals and solvent molecules.

#### 4. Conclusions

The TRTL method is useful for determining the heats of formation of reaction intermediates. In benzene, the heat of formation of BPK in benzene and the O–H bond dissociation energy of BPK were determined to be 21 and 28 kcal/mol, respectively. Measurements of the heats of reaction of triplet benzophenone with a variety of hydrogen donors led to the determination of the heats of formation of related radicals,  $\Delta H_f(R\cdot)$ . The  $\pi$  electron radical, cyclohexadienyl, is much stabilized by solvent than the parent molecule due to the delocalization of unpaired electron. On the other hand, the alcohol radicals are less stabilized by solvent than the parent molecule due to the unfavorable hydrogen bond.

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