Primary Photochemical Process of Thiobenzophenone as Studied by Laser Flash Photolysis

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Self-quenching of the triplet excited state of thiobenzophenone (TBP) was suppressed in a viscous alcoholic solution, an SDS micellar solution and an ionic liquid of TMPA TFSA. In those solutions, the photochemical primary process of TBP could be studied by ns laser flash photolysis. Thiobenzophenone ketyl and phenylsulfanyl radicals were found to be generated from hydrogen abstraction of benzenethiol by TBP. The rate constant for the reaction was observed to be $1.1 \times 10^7 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$.

Benzophenone (BP) is the most commonly used molecule in photochemical studies¹⁻³ and its primary photophysical and photochemical processes have been well investigated by direct measurement of intermediates with the aid of ns laser flash photolysis^{2,3} and time-resolved ESR.⁴ However, the primary process of thiobenzophenone (TBP, Ph₂C=S), which is a sulfur analogue of BP, has scarcely been studied.^{5,6} de Mayo reported on the laser flash photolysis of TBP in cyclohexane and observed a short-lived transient absorption at 400–600 nm ($\lambda_{\text{max}} = 475$ nm).⁵ The absorption was tentatively assigned to the triplettriplet (T-T) absorption of TBP. Das carried out more quantitative studies of the triplet excited state of TBP ($\lambda_{max} = 400$ and 515 nm in benzene).⁶ Since the triplet excited state of TBP disappears by fast self-quenching due to the large spin-orbital coupling of sulfur, to the best of our knowledge, there has been no detailed study of its reactivity. Moreover, TBP contains a heavy sulfur atom. Thus, its photochemical primary process is attractive to compare with that of BP.

In this letter, we study the laser flash photolysis of TBP in a viscous alcoholic solution [1/25 (v/v) mixture of 2-methyl-1propanol (*i*-BuOH) and cyclohexanol (*c*-HexOH), 49.7 cP], a sodium dodecyl sulfate (SDS, $1.60 \times 10^{-1} \text{ mol dm}^{-3}$) micellar solution, and an ionic liquid of *N*,*N*,*N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)amide (TMPA TFSA, 72.6 cP). The ns laser flash photolysis apparatus was essentially the same as an apparatus described elsewhere.⁷ The third harmonic (355 nm) of a Nd:YAG laser was used as an excitation light source. TBP was synthesized as described in the literature.^{8,9} The concentration of TBP in the employed solution was $2.0 \times 10^{-3} \text{ mol dm}^{-3}$.

Laser flash photolysis was performed at 296 K. Time profiles of the transient absorption, A(t), were measured at 515 nm in the presence of TBP only, because the triplet excited state of TBP shows the T–T absorption around 515 nm.⁶

$$TBP + h\nu(355 \,\mathrm{nm}) \to {}^{1}TBP^{*} \to {}^{3}TBP^{*}$$
(1)

Here, ¹TBP* and ³TBP* represent the singlet and triplet excited states of TBP, respectively. The lifetimes of ³TBP* observed in each solution were as follows: 662 ns (in 1/25 mixture of *i*-BuOH/*c*-HexOH), 821 ns (in SDS) and 559 ns (in TMPA TFSA). On the other hand, the lifetime of ³TBP* in benzene

was observed to be as short as 77 ns ($k = 4.2 \times 10^9$ s⁻¹ mol⁻¹ dm³). Such a short lifetime is due to the diffusion-controlled self-quenching reaction of ³TBP*. Thus, we conclude that the self-quenching of ³TBP* is suppressed in the viscous alcoholic solution, SDS micellar solution and the ionic liquid, and the photochemical primary process of TBP can be studied in those solutions.

To clarify the reactivity of ³TBP*, reaction with benzenethiol (PhSH, $0-100 \times 10^{-3}$ mol dm⁻³) was studied by laser flash photolysis. Upon irradiation of a 1/25 mixture of *i*-BuOH/ *c*-HexOH containing TBP and PhSH $(5 \times 10^{-3} \text{ mol dm}^{-3})$, a strong T-T absorption band of ³TBP* was observed at 515 nm. The decay of the T-T absorption accelerated with increasing concentration of PhSH. The PhSH concentration dependence of the ³TBP^{*} decay rate constant (k) observed at 515 nm is shown in Figure 1. A good linear relationship was observed between k and PhSH concentration. From the slope of the plots, the rate constant for the reaction between ³TBP* and PhSH was determined to be $1.1 \times 10^7 \,\text{s}^{-1} \,\text{mol}^{-1} \,\text{dm}^3$. This value is ten times smaller than that observed for the similar reaction between ³BP* and PhSH $(1.2 \times 10^8 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3)$ although the viscosity is slightly higher (37.3 cP) than that of the present study.¹⁰ Such a small rate constant of ³TBP* may be due to the lower triplet energy of ${}^{3}TBP^{*}$ (166 kJ mol⁻¹) than that of benzophenone $(290 \text{ kJ mol}^{-1}).$

The transient absorption spectra observed for the reaction between TBP and PhSH $(1 \times 10^{-1} \text{ mol dm}^{-3})$ at delay times of 0.1, 0.5, 1.0, and 1.5 µs after laser irradiation are shown in Figure 2. The transient absorption spectrum observed at a delay time of 0.1 µs after laser irradiation has three absorption peaks at 380, 490, and 515 nm. The A(t) curves observed at 490 and 515 nm showed single exponential decay, while the A(t) curve observed at 380 nm had a fast decay component and an almost



Figure 1. PhSH concentration dependence of the ³TBP* decay rate constant (k) observed in a 1/25 mixture of *i*-BuOH/ c-HexOH at 515 nm.



Figure 2. Transient absorption spectra observed for the reaction of TBP and PhSH $(1 \times 10^{-1} \text{ mol dm}^{-3})$ at delay times of 0.1 (•), 0.5 (\bigcirc), 1.0 (•), and 1.5 µs (\triangle) after laser irradiation.



Figure 3. The A(t) curves observed at 380 nm in the absence and presence of PhSH $(1 \times 10^{-1} \text{ mol dm}^{-3})$.

constant one. From the previous reports,^{5,6} the peaks observed at 490 and 515 nm can safely be assigned to the T-T absorption of ³TBP*. The A(t) curve observed at 380 nm is shown in Figure 3. Since the decay of the fast component was accelerated in the presence of PhSH and the lifetime was observed to be the same as that at 515 nm, the fast component could be assigned to the T-T absorption of ³TBP*. The almost constant value can be assigned to the transient absorption of thiobenzophenone ketyl radical for the following reasons: (1) the yields of this component increased with increasing concentration of PhSH, (2) the similar ketyl radical of benzophenone ketyl radical has a transient absorption band around 360 nm,¹¹ and (3) the product analysis of the photochemical reaction of TBP in THF suggests the formation of thiobenzophenone ketyl radical.¹² Moreover, a weak transient absorption band for phenylsulfanyl radical was observed at 450 nm.¹³ From these results, we can safely describe the present photochemical reaction of TBP with PhSH as follows:

$${}^{3}\text{TBP}^{*} + \text{PhSH} \rightarrow \text{TBPH} \bullet + \text{PhS} \bullet$$
 (2)

Here, TBPH• and PhS• represent thiobenzophenone ketyl and phenylsulfanyl radicals, respectively. These results indicate that the observed rate constant of $1.1 \times 10^7 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$ should be due to the hydrogen abstraction of ³TBP* from PhSH.

In the present study, the self-quenching of ³TBP* could successfully be suppressed in a viscous alcoholic solution of *i*-BuOH/*c*-HexOH, a SDS micellar solution, and an ionic liquid of TMPA TFSA. The reasons for suppressing the self-quenching of ³TBP* may be as follows: high viscosity of the alcoholic solution, ¹⁰ cage effects with the high microviscosity of SDS micellar solution, ^{14–17} and cage effects with the low microviscosity of ionic liquid.^{7,18,19} To elucidate the mechanism for suppressing the self-quenching, it is desirable to clarify the reaction field as a nanoscale structure. Along this way, further studies with the *MFE probe* (magnetic field effect as a probe of reaction field) are now in progress.

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