A Laser Flash Photolysis Study of the Intramolecular Energy Transfer Reaction from Benzophenone to Norbornadiene Covalently Bonded by a Rigid Steroid Bridge

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(Received July 10, 1995)

The photoinduced intramolecular energy-transfer (ET) reaction between benzophenone (BP) and norbornadiene (N) covalently bonded by a rigid steroid bridge in acetonitrile has been studied by laser flash photolysis. The ET rate constant for the excited triplet BP (^{3}BP*) to N is 6.1×10^4 s^{-1}, whereas the constant for the intramolecular hydrogen atom abstraction of ^{3}BP* from the steroid is 1.91×10^5 s^{-1}.

Photochemistry of supramolecules is an emerging and growing research area, which is attractive from both fundamental and applied points of view.1) Many supramolecular systems have been synthesized artificially in order to increase the efficiencies of photoinduced energy- and electron-transfer processes in them.

The photoisomerization of norbornadiene (N) to its higher energy valence isomer, quadricyclane (Q), is a well-known system for solar energy storage and has been studied widely.2) The spectrum of solar irradiation has a maximum at about 500 nm, covering the 300—2600 nm region. Norbornadiene has an absorption band at the wavelengths shorter than 300 nm, and, therefore, it cannot harvest solar energy directly. To solve this problem, a lot of investigations have been carried out by introducing intra- and intermolecular photosensitizers. Gorman et al.3) reported the sensitized conversion of norbornadiene to quadricyclane by adding substituted benzophenones to a solution of norbornadiene. Ketones such as benzophenone and acetophenone are often used as triplet sensitizers.4)

In this research, a norbornadiene and benzophenone system covalently bonded by a rigid steroid bridge (N–S–BP) has been studied by laser flash photolysis. In this molecule, the intramolecular energy-transfer reaction (ET) and the hydrogen abstraction reaction (HA) take place simultaneously. The ET rate constant for the excited triplet BP (^{3}BP*) to N (k_{ET}) is 6.1×10^4 s^{-1}, whereas the HA rate constant for ^{3}BP* from the steroid bridge (k_{HA}) is 1.91×10^5 s^{-1}.

Experimental

Materials: The purest grade of benzophenone, 1-naphthol, and acetonitrile were purchased from Nacalai Tesque, Inc. and were used as supplied. Supramolecules N–S–BP, M–S–BP, and M–10–BP shown in Chart 1 were synthesized and identified by ^{1}H NMR spectroscopy.5) All sample solutions were deaerated by several freeze-pump-thaw cycles.

Apparatus: The absorption spectra were measured with a Hitachi U-3210 spectrophotometer. The transient absorption spectra were measured with a laser flash photolysis system described elsewhere.6) The pump light source was the third harmonic (355 nm) of an Nd : YAG laser (Spectra-Physics, GCR-11-1). The probe light source was a xenon arc lamp (Ushio, UXL-500-O). The probe light, transmitted through the sample cell, was fed to a 10 cm monochromator (Ritsu, MC-10L)–photomultiplier (Hamamatsu, R928)–digital oscilloscope (Tektronix, 2440)–microcomputer (NEC, PC-9801) detection system.

Results and Discussion

1. Assignment of Transient Absorption Spectra. Figure 1 shows time-resolved transient absorption spectra of N–S–BP in acetonitrile at room temperature. A transient spectrum immediately after laser excitation has a maximum at 560 nm and the peak moves to 580 nm at a 2 μs delay.

In order to assign the transient absorption spectra of N–S–BP, transient absorption spectra of related molecules were further examined. Firstly, transient absorption spectra of M–S–BP, which has no norbornadiene moiety, were examined. The transient spectra of M–S–BP in Fig. 2 are very similar to those of N–S–BP,

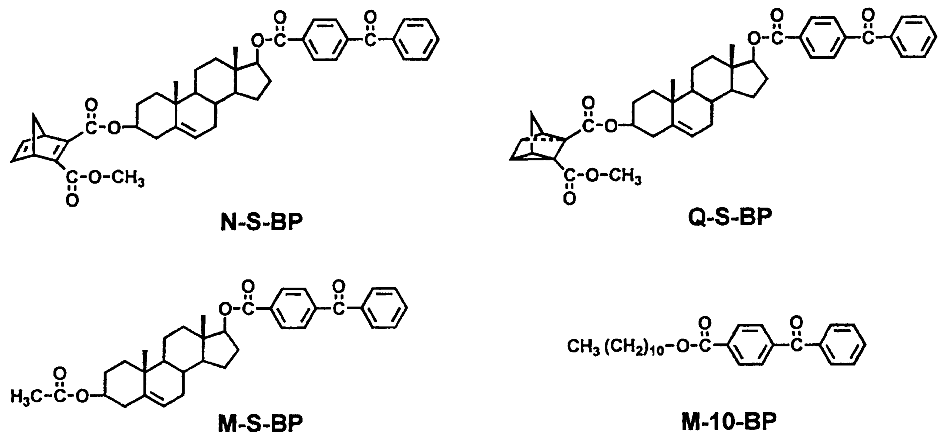


Chart 1.

though the decay rate of the former is slower than that of the latter. Since in both molecules BP is the only chromophore which can be excited by a 355 nm pulse, it is reasonable to consider that the 560 nm band might be the T–T absorption band of the BP part. However it is not clear why N–S–BP and M–S–BP exhibit the 580 nm band at a 2 μs delay and what the role of the steroid spacer in the reaction is, though the 580 nm band might be either the absorption of a BP ketyl radical or of a BP anion radical.

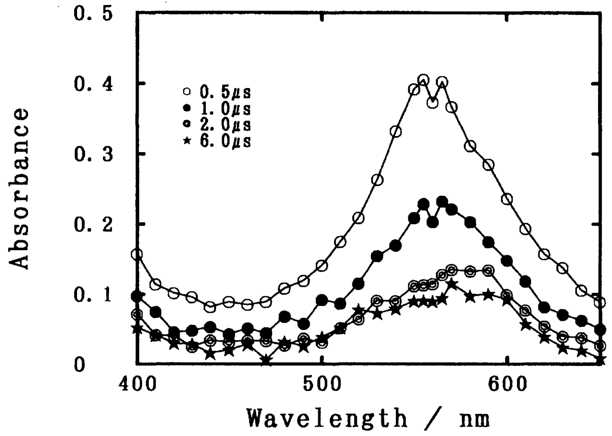


Fig. 1. Transient absorption spectra of N–S–BP (2.4×10^{-3} mol dm^{-3}) in acetonitrile.

In order to make this point clear, transient spectra of undecyl benzophenone-4-carboxylate (M–10–BP), which has no steroid spacer, was further studied. Figure 3 shows transient absorption spectra of M–10–BP in acetonitrile. In this case an absorption band is observed only at 560 nm. The phosphorescence lifetimes of normal alkyl esters of benzophenone-4-carboxylic acid at room temperature have been well-studied by Winnik et al.[7] The rate constant of intramolecular hydrogen abstraction reaction of M–10–BP from its undecyl group is estimated to be (3—9)$\times10^3$ s^{-1}. Therefore, the 560 nm absorption band of M–10–BP (lifetime 4.50 μs) is assigned to the T–T band of BP. The T–T absorption band of M–10–BP is red-shifted by 25 nm compared with that of unsubstituted benzophenone.[8] This spectral shift might be caused by substitution of the alkoxycarbonyl group.

Next, the effect of 1-naphthol (1-NAOH) addition to a solution of M–10–BP was examined. This was possible because the hydrogen abstraction of the excited triplet

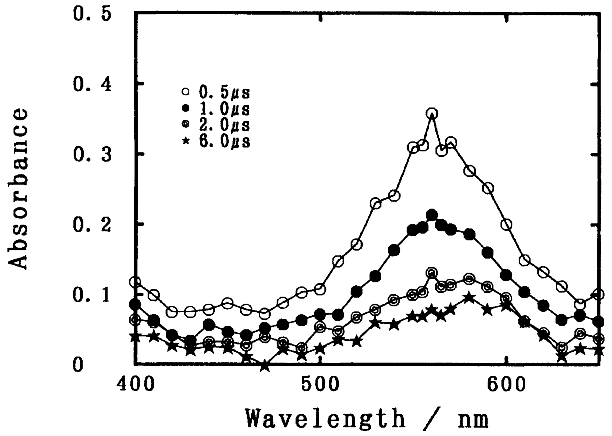


Fig. 2. Transient absorption spectra of M–S–BP (2.3×10^{-3} mol dm^{-3}) in acetonitrile.

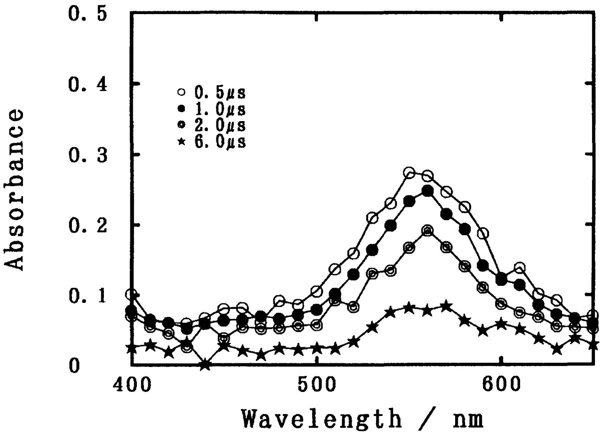


Fig. 3. Transient absorption spectra of M–10–BP (2.9×10^{-3} mol dm^{-3}) in acetonitrile.

benzophenone from 1–NAOH is well-studied by Shizuka et al.[9] Figure 4 shows the transient absorption spectra of M–10–BP (2.9×10^{-3} mol dm^{-3}) in the presence of 1-NAOH (3.0×10^{-3} mol dm^{-3}). Immediately after laser excitation, the T–T absorption of BP appears at 560 nm; then a new band at 430 nm grows up as the 560 nm band decays. Furthermore, an absorption band at 580 nm appears concomitant with the decrease in the intensity of the 430 nm band. By analogy with the reported reaction of benzophenone and 1-NAOH,[9] the transient spectra shown in Fig. 4 were interpreted as follows. The absorption band at 430 nm is the T–T absorption of 1-NAOH generated by the energy transfer from the excited triplet of M–10–BP (M–10–^{3}BP*) to 1-NAOH. The excited triplet 1-NAOH (^{3}1-NAOH*) and M–10–BP undergo a hydrogen abstraction reaction in addition to the usual hydrogen abstraction of ^{3}BP* from 1-NAOH:

$$\text{M–10–}^3\text{BP}^* + \text{1-NAOH} \rightarrow \text{M–10–BP} + {}^3\text{1-NAOH}^*$$

$$^3\text{1-NAOH}^* + \text{M–10–BP} \rightarrow \text{1-}\dot{\text{N}}\text{AO} + \text{M–10–}\dot{\text{B}}\text{PH}$$

1-Naphthyloxyl radical (1-$\dot{\text{N}}$AO) has a sharp absorption band at 400 nm ($\varepsilon=4020$ M^{-1} cm^{-1}) and a broad one at 545 nm ($\varepsilon=830$ M^{-1} cm^{-1}) in methanol (1 M=1 mol dm^{-3}),[9] the intensity ratio of the latter to the former being 0.2. In Fig. 4B, maximal contribution of the absorbance of 1-$\dot{\text{N}}$AO to the transient spectrum at a 0.7 µs delay was estimated to be only 1/2 of the intensity at 545 nm and 1/3 of that at 580 nm, assuming that the absorbance at 400 nm is completely due to 1-$\dot{\text{N}}$AO. Thus the 580 nm band observed in the spectrum at a 0.7 µs delay shown in Fig. 4B is assigned mainly to that of BP ketyl radical ($\dot{\text{B}}$PH). Based on the observations mentioned above, the 580 nm absorption bands of N–S–BP and M–S–BP shown in Figs. 1 and 2 are then assigned to the BP ketyl radical.

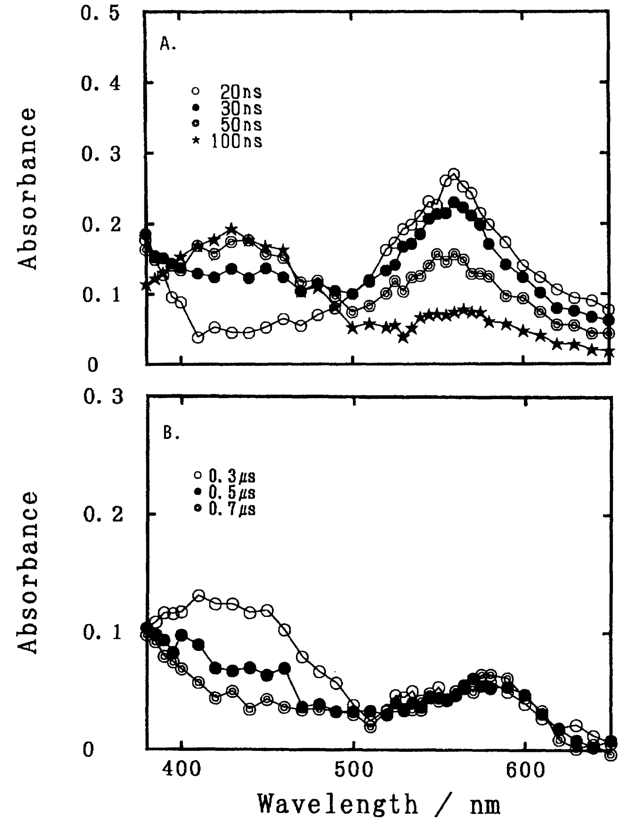


Fig. 4. Transient absorption spectra of M–10–BP (2.9×10^{-3} mol dm^{-3}) in the presence of 1-naphthol (3.0×10^{-3} mol dm^{-3}) in acetonitrile.

2. Determination of Decay Rate Constants. In the present experiment, an intense laser pulse was used as the pumping light. Decay curves of the T–T absorption bands were affected by triplet–triplet annihilation. In order to avoid the effect of laser intensity, we calculated the decay rate constants from the initial slope of the transient decay curves as a function of laser intensity and extrapolated to zero laser intensity. Figure 5 shows a typical example of this analysis. From the plot shown in Fig. 5, the decay rate constant of the excited triplet BP (k_{T}(N–S–BP)) in N–S–BP was obtained to be 4.19×10^5 s^{-1}. Analogously, k_{T}(M–S–BP) and k_{T}(M–10–BP) were obtained to be 3.58×10^5 and 1.67×10^5 s^{-1}, respectively. Uncertainties in these values were estimated to be about 10%.

3. Primary Processes in N–S–BP. Now let's consider the reaction mechanism of N–S–BP. M–S–BP and N–S–BP exhibit a transient absorption due to the BP ketyl radical, whereas M–10–BP exhibits no absorption due to the radical. These facts lead to the conclusion that intramolecular hydrogen abstraction of the excited triplet BP from the steroid spacer takes place in M–S–BP and N–S–BP.

Moreover, the decay rate constant of the excited triplet BP in N–S–BP (4.19×10^5 s^{-1}) is faster than that in M–S–BP (3.58×10^5 s^{-1}). This means that norbornadiene is intervening in the deactivation of the excited BP in N–S–BP. In a previous work,[5] it was shown

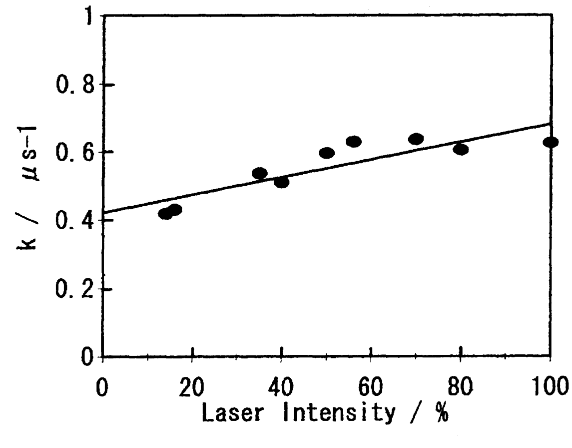
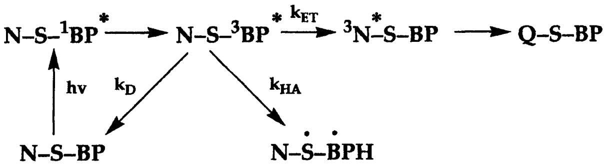


Fig. 5. Plot of k_{T} vs. relative laser intensity for N–S–BP. A laser intensity of 100% was roughly estimated to be ca. 40 mJ/pulse.

that steady-state photoirradiation ($\lambda > 350$ nm) of an acetonitrile solution of N–S–BP results in formation of a photoproduct characterized as Q–S–BP by IR and ^{1}H NMR. Accordingly it is most reasonable to consider that one of the deactivation process from the excited BP in N–S–BP is the intramolecular energy transfer to norbornadiene, followed by isomerization of norbornadiene into quadricyclane.

If an electron transfer reaction takes place in the reaction of N–S–BP, a broad transient band due to BP anion radical whose intensity may be analogous to or stronger than that of $\dot{\mathrm{B}}\mathrm{PH}$, should be detected in the 600—800 nm region.[10] However, we could not detect such an absorption band attributable to the BP anion radical. Although intramolecular electron transfer reaction might be an another possible process for energy dissipation of ^{3}BP*, the contribution of this process to the decay of ^{3}BP* seems to be less than 10%, if any.

On the basis of the experimental results mentioned above, the primary photophysical and photochemical processes in N–S–BP can be expressed by Scheme 1: In N–S–BP, BP is selectively photoexcited by a 355 nm pulse, since it is the only chromophore that has an absorption band longer than 300 nm. Subsequently, the excited triplet BP (^{3}BP*) is efficiently generated by fast intersystem crossing from the singlet excited BP (^{1}BP*). The deactivation channels of ^{3}BP* can be described by (1) energy transfer from ^{3}BP* to N (triplet energy of N$=70.7$ kcal mol^{-1}) [3] (the rate constant, k_{ET}), followed by isomerization to Q–S–BP; (2) hydrogen atom abstraction reaction of ^{3}BP* from the steroid moiety (k_{HA}); and (3) nonradiative decay of ^{3}BP* to the ground state BP (k_{D}).



Scheme 1.

Now we can determine the respective rate constants by using the decay rate constants of M–10–BP, M–S–BP and N–S–BP. The decay rate of the excited triplet BP increases in the order of N–S–BP>M–S–BP>M–10–BP. The decay rate constant of M–10–BP is considered to be attributable chiefly to the non-radiative decay process, since intramolecular hydrogen abstraction of ^{3}BP* from its methylene chain is not significant.[7] Consequently, an increase in the decay rate of M–S–BP is attributable to the substitution of a M–S moiety for a M–10 moiety. As shown in Fig. 2, an absorption band of $\dot{\mathrm{B}}\mathrm{PH}$ was observed in the transient spectra of M–S–BP, whereas it was not detected in the spectra of M–10–BP (Fig. 3). Taking these findings into account, we conclude that an increase in the decay rate of M–S–BP is due to intervention of the intramolecular hydrogen abstraction of BP from the S moiety. Analogously, a further increase in the decay rate in N–S–BP is attributable to the intramolecular process caused by the existence of the N moiety, i.e., intramolecular energy transfer one. Consequently, the decay rate constants of ^{3}BP* in M–10–BP, M–S–BP, and N–S–BP can be presented by the following equations:

$$k_{\mathrm{T}}(\text{M–10–BP}) = k_{\mathrm{D}} \tag{1}$$

$$k_{\mathrm{T}}(\text{M–S–BP}) = k_{\mathrm{HA}} + k_{\mathrm{D}} \tag{2}$$

$$k_{\mathrm{T}}(\text{N–S–BP}) = k_{\mathrm{ET}} + k_{\mathrm{HA}} + k_{\mathrm{D}} \tag{3}$$

From Eq. 1, $k_{\mathrm{D}} = 1.67 \times 10^5$ s^{-1}. By subtracting Eq. 1 from Eq. 2, k_{HA} was obtained to be 1.91×10^5 s^{-1}. Analogously, k_{ET} was obtained to be 0.61×10^5 s^{-1}. From these rate constants the quantum yield of ET reaction from ^{3}BP* was obtained as 0.14 in N–S–BP, whereas that of HA was 0.46. Owing to the presence of the intramolecular HA reaction, the quantum yield of ET leading to the isomerization was reduced by about 50%. Present results indicate that it is better to use a less-reactive ketone as a sensitizer so as to improve the ET efficiency.

Finally, let us consider briefly the mechanism of the intramolecular ET process. The distance between energy donor (^{3}BP*) and acceptor (N) attached to a rigid steroid spacer was estimated to be about 15 Å. The ET rate constant obtained (6.1×10^4 s^{-1}) corresponds to that for the transfer at a distance of 15 Å. There are two main mechanisms for the ET reaction. The first is a through-space exchange mechanism and the second is a through-bond mechanism. Energy transfer via a through-space exchange mechanism would be quite inefficient when two groups are separated by 11.6 Å.[11] Therefore, a long distance energy transfer in N–S–BP may be explained by a through-bond mechanism, in which the bridging C–C σ bonds play an important role.[12—15]

In conclusion, the photoinduced ET reaction in N–S–BP seems to take place via the through-bond mechanism. The ET rate constant from ^{3}BP* to N is 6.1×10^4 s^{-1} and its quantum yield is 0.14. Intramolecular hydrogen abstraction of ^{3}BP* from the steroid spacer, competing with the ET reaction, reduces the ET efficiency by ca. 50%.

This work was in part supported by Grants-in-Aid for Scientific Research Nos. 06NP0301 and 04242107 from the Ministry of Education, Science, Sports and Culture. H.C. thanks the Heiwa Nakajima Foundation for a scholarship.

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