PCCP

# Laser photolysis studies of the carbon–sulfur bond cleavage induced in the triplet exciplex of benzylnaphthyl sulfide and aromatic ketones

**Minoru Yamaji,* Shin-ichi Ueda, Haruo Shizuka and Seiji Tobita**

*Department of Chemistry, Gunma University, Kiryu, Gunma 376-8515, Japan.*
*E-mail: yamaji@chem.gunma-u.ac.jp*

***Received 4th April 2001, Accepted 12th June 2001***
***First published as an Advance Article on the web 11th July 2001***

The photoinduced dissociation of the carbon–sulfur bond in benzyl-α-naphthyl sulfide (BNS) in acetonitrile has been studied by laser flash photolysis. Upon direct photoexcitation of BNS, C–S bond fission occurs in the excited singlet state, resulting in the formation of the α-naphthylthiyl and benzyl radicals with a quantum yield of 0.22. Triplet sensitization of BNS by xanthone and benzophenone causes the simultaneous formation of the lowest triplet state ($T_1$) of BNS and the radicals. The efficiencies of the formations of the $T_1$ state and the radicals are 0.53 and 0.41, respectively. When triplet BNS decays, further formation of the radicals is observed with an efficiency of 0.95. The decay rate of triplet BNS is enhanced non-linearly with increasing concentration of the ketone. The second cleavage can be interpreted by considering the formation of the triplet exciplex which consists of triplet BNS and ketone. The mechanism of the efficient C–S bond dissociation *via* the triplet exciplex is discussed.

## 1. Introduction

Much attention has been paid to H-atom, electron and triplet energy transfer processes of triplet carbonyl compounds in solution since they are of importance in understanding photochemical and photobiological phenomena. By using transient measurement techniques, the mechanisms of these fundamental reactions of triplet ketones have been revealed.[1–3] In this decade, we have vigorously investigated, with nanosecond laser photolysis techniques, the mechanism of a new type of H-atom and electron transfer reactions: H-atom and electron transfer reactions *via* the triplet exciplex of aromatic ketones (AK) and triplet naphthalene derivatives (ND) in solution.[4] The formation processes of the triplet exciplex are as follows. For efficient production of triplet ND, triplet sensitization by AK has been employed. The triplet energy of AK, thus, should be larger than that of ND. By choice of an appropriate wavelength of laser light for excitation, selective photoexcitation of the ketone in the presence of ND in solution enables production of triplet AK only. Triplet energy transfer from triplet AK to ND in solution yields triplet ND in the nanosecond timescale.

$$^3\mathrm{AK}^* + \mathrm{ND} \rightarrow \mathrm{AK} + {}^3\mathrm{ND}^* \qquad (1)$$

In the microsecond timescale, triplet ND encounters the ketone in a diffusion process to form a triplet exciplex, $^3(\mathrm{ND}\cdots\mathrm{AK})^*$ in an equilibrium.

$$^3\mathrm{ND}^* + \mathrm{AK} \rightleftharpoons {}^3(\mathrm{ND}\cdots\mathrm{AK})^* \qquad (2)$$

The triplet exciplex has been considered to have electronic character related to weak charge transfer from the carbonyl site to ND, $^3(\mathrm{ND}^{\delta+}\cdots\mathrm{AK}^{\delta-})^*$ since little difference is observed in the absorption spectra between the triplet exciplex and triplet ND. When the NDs are naphthol and naphthyl ammonium ion derivatives, the triplet exciplexes deactivate by H-atom transfer to form the triplet biradical in the solvent cage, resulting in the yield of free radicals without geminate recombination. With methoxynaphthalene and naphthylamine derivatives, electron transfer proceeds *via* the triplet exciplexes in the presence of proton and water. When the ND is inert for chemical reactions, *e.g.*, naphthalene, non-radiative deactivation *via* the triplet exciplex has been found. However, none of the chemical reactions except for H-atom and electron transfer *via* triplet exciplexes has been reported.

In the present paper, we report a new type of chemical reaction induced in the triplet exciplex; chemical bond cleavage between carbon and sulfur atoms. Triplet benzylnaphthyl sulfide is found to undergo dissociation of the carbon–sulfur bond in the presence of xanthone and benzophenone in acetonitrile to give the naphthylthiyl and benzyl radicals. The mechanism of the C–S bond cleavage *via* the triplet exciplex is discussed.

## 2. Experimental

Benzyl-α-naphthyl sulfide (BNS) was synthesized as follows. α-Naphthalenethiol (NpSH; Across) and excess α-chlorotoluene (Aldrich) were refluxed overnight in a mixture of toluene and water (1 : 1 v/v) with KOH in the presence of 18-crown-6-ether as a phase-transfer catalysis. The organic layer was washed with water, and evaporated to give the crude product, which was chromatographed by passing through a silica-gel column with a mixture of n-hexane–benzene (5 : 1 v/v). BNS was purified by recrystallizations from n-hexane. α-Naphthylmethyl sulfide (NMS) was synthesized by mixing NpSH and iodomethane (IMe) (1 : 0.7 mol/mol) in a mixture of ethanol and water (1 : 1 v/v) with KOH at room temperature. IMe was added dropwise to the solution of NpSH over 0.5 h. After complete addition, the mixture was stirred at room temperature for 0.5 h. Benzene was added to the product. The organic layer was separated, washed several times with water containing sodium thiosulfate to remove iodide, and evaporated. The crude product was purified by passing through a silica-gel column with a mixture of n-

DOI: 10.1039/b103026b

hexane–benzene (5 : 1 v/v) as eluent. BNS and NMS were identified by NMR spectroscopy. Xanthone (XT) and benzophenone (BP) were purified by sublimation *in vacuo*. Acetonitrile (ACN) was purified by distillation, and used as the solvent. All samples in a quartz cell with a 10 mm or 1 mm path length were degassed by several freeze–pump–thaw cycles on a high vacuum line.

Absorption and emission spectra were recorded by a JASCO U-best 50 UV–VIS spectrophotometer and a Hitachi F-4010 fluorescence spectrophotometer. Laser flash photolysis was carried out at 295 K. Third harmonics (355 nm) of a nanosecond $Nd^{3+}$ : YAG laser (JK Lasers HY-500) and a XeCl excimer laser (Lambda Physik, Lextra 50) at 308 nm were used for flash photolysis. The transient absorption spectra were taken with a USP-554 system from Unisoku which enabled us to take a transient absorption spectrum with one-shot laser pulse. The detection system for the time profiles of the transient absorption has been reported elsewhere.[5] The kinetic analysis of the transient data obtained by laser photolysis was carried out by the least-squares best-fitting method. The calculations for the heats of formation ($\Delta_f H$) were performed with the PM3 method by using the MOPAC '97 program.

## 3. Results and discussion

### 3.1 Absorption and emission spectra of BNS

Fig. 1 shows the absorption spectrum of BNS along with that of NMS in ACN. The shape of the absorption band of BNS in the wavelength region 260–350 nm is very similar to that of NMS. A very weak fluorescence of BNS was observed in ACN at 295 K. The fluorescence yield was less than $10^{-3}$. In methanol–ethanol (1 : 1 v/v) glass at 77 K, phosphorescence of BNS together with fluorescence was recorded. From the 0–0 origins of the fluorescence and phosphorescence spectra of BNS, the lowest excited singlet ($E_S$) and triplet energies ($E_T$) were, respectively, determined to be 86.0 and 57.3 kcal $mol^{-1}$.

### 3.2 Direct excitation at 308 nm

Fig. 2 shows the transient absorption spectrum obtained at 500 ns after 308 nm laser pulsing in a degassed ACN solution of BNS ($1.3 \times 10^{-4}$ mol $dm^{-3}$) at 295 K. The absorption spectrum with peaks at 410 and 670 nm is ascribed to that of the naphthylthiyl radical (NTR).[6] No other absorption spectrum than that of NTR was observed in the wavelength region, 370–740 nm. The formation of NTR upon photolysis of BNS demonstrates the dissociation of the carbon–sulfur bond in BNS. The counter radical to be formed, benzyl radical (BR) which has an absorption band at 310 nm,[7] was unable to be detected owing to the ground-state absorption of BNS. When a quartz cell with a 1 cm optical path length is used, the quantum yield ($\Phi_{rad}$) of the radical formation is determined by:

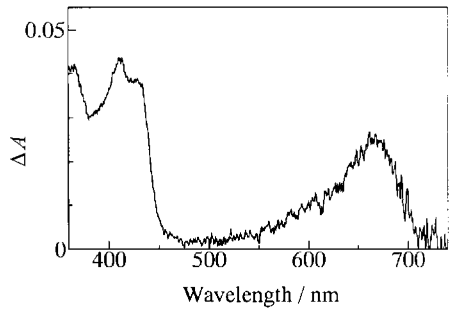


**Fig. 2** The transient absorption spectrum obtained at 500 ns after 308 nm laser pulsing in the degassed ACN solution of BNS ($1.3 \times 10^{-4}$ mol $dm^{-3}$) at 295 K.

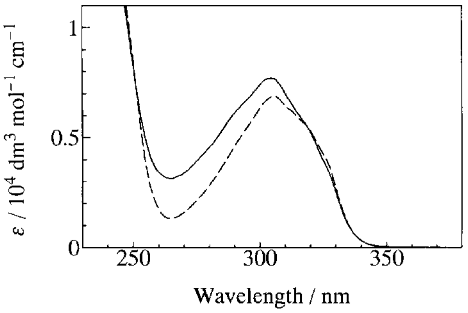


**Fig. 1** Absorption spectra of BNS (solid line) and NMS (broken line) in ACN at 295 K.

$$\Phi_{rad} = \Delta A_{\lambda} \varepsilon_{\lambda}^{-1} I_{abs}^{-1} \qquad (3)$$

where $\Delta A_{\lambda}$, $\varepsilon_{\lambda}$ and $I_{abs}$ are, respectively, the absorbance change due to the formation of NTR at a wavelength, $\lambda$, the molar absorption coefficient of NTR (7200 $dm^3$ $mol^{-1}$ $cm^{-1}$ at 410 and 3400 $dm^3$ $mol^{-1}$ $cm^{-1}$ at 670 nm)† and the absorbed photon flux by BNS.

The value of $I_{abs}$ was determined by using the triplet absorption of benzophenone in a cell with a 1 cm optical path length as an actinometer.[8] The value of $\Phi_{rad}$ was determined to be $0.22 \pm 0.01$ in ACN at 295 K. In the presence of 2,3-dimethylbuta-1,4-diene (0.5 mol $dm^{-3}$) as a triplet quencher, this value of $\Phi_{rad}$ was not affected. Therefore, the triplet state of BNS is not involved in the bond cleavage upon direct excitation. Considering the observation of fluorescence at 295 K ($\Phi_f < 10^{-3}$), it is presumed that the reactive state for the homolysis of BNS is the lowest excited singlet state ($S_1$) of BNS. The deactivation of the $S_1$ state of BNS seems to be virtually governed by the chemical reaction with a high efficiency ($=1 - \Phi_f$), which may be close to unity. The value of $\Phi_{rad}$ ($=0.22$) can be interpreted by considering the conservation rule of spin multiplicity. Immediately after bond dissociation occurs in the $S_1$ state of BNS, a singlet radical pair of NTR and BR, $^1(NTR + BR)_{cage}$ may be formed in the solvent cage according to the conservation rule of spin multiplicity.

$$^1BNS^* \rightarrow {}^1(NTR + BR)_{cage} \qquad (4)$$

The singlet radical pair is fated to follow two processes; geminate recombination to the parent molecule, BNS in the solvent cage and escape from the solvent cage to exist as free radicals.

$$^1(NTR + BR)_{cage} \rightarrow BNS \qquad (5)$$

$$^1(NTR + BR)_{cage} \rightarrow NTR + BR \qquad (6)$$

The determined value of $\Phi_{rad}$ is for the yield of the free radicals. The residual value ($1 - \Phi_{rad} = 0.78$) would be for the geminate recombination in the singlet radical pair.

The bond energy, $D$(C–S) between the naphthylthiyl and benzyl groups is calculated by:

$$\Delta_f H(BNS) = \Delta_f H(NTR) + \Delta_f H(BR) - D(C{-}S) \qquad (7)$$

---

† The ε value of NTR was determined by comparing with that of the α-naphthylmethyl radical (5500 $dm^3$ $mol^{-1}$ $cm^{-1}$ at 364 nm in acetonitrile) produced 308 nm laser photolysis of α-nathyl-α-naphthylmethyl sulfide in acetonitrile.

where $\Delta_f H$(BNS), $\Delta_f H$(NTR) and $\Delta_f H$(BR) are, respectively, the heats of formation for BNS, NTR and BR, found to be 71.8, 72.2 and 52.5 kcal mol$^{-1}$ by computation. The value of $D$(C–S) was determined to be 52.9 kcal mol$^{-1}$, which was sufficiently smaller than those of $E_S$ (86.0 kcal mol$^{-1}$) and $E_T$ (57.3 kcal mol$^{-1}$) of BNS for bond cleavage to occur in the excited states. To investigate the reactivity in the triplet state of BNS, triplet sensitization was carried out by using aromatic ketones.

### 3.3 Triplet sensitization by aromatic ketones

In order to investigate the chemical reactions in the triplet state of BNS, triplet sensitization of xanthone (XT) and benzophenone (BP) was performed. Since the triplet energies of XT and BP are, respectively, 74.1 and 69.1 kcal mol$^{-1}$,[9] triplet energy transfer to BNS is possible. Fig. 3(a) shows the absorption spectrum obtained at 800 ns upon 355 nm laser pulsing in the XT (1.5 × 10$^{-3}$ mol dm$^{-3}$)–BNS (4.8 × 10$^{-4}$ mol dm$^{-3}$) mixture in ACN. Three absorption bands appear at 410, 520 and 670 nm. The reference absorption spectra of NTR and triplet naphthylmethyl sulfide (NMS) having an absorption maximum at 520 nm are shown in Fig. 3(b). The obtained transient absorption spectrum in Fig. 3(a) resembles a superposition of those of NTR and triplet NMS. We, thus, identify the absorption band at 520 nm in Fig. 3(a) with that of triplet BNS by similarity. In short, the formation of both triplet BNS and NTR is simultaneously observed upon triplet sensitization.

Fig. 4 shows the temporal absorption changes at 625 nm for triplet XT,[10] at 410 and 670 nm for NTR and at 520 nm for triplet BNS obtained by 355 nm laser pulsing in the XT (1.5 × 10$^{-3}$ mol dm$^{-3}$)–BNS (4.8 × 10$^{-4}$ mol dm$^{-3}$) mixture in ACN. The observed decay rate ($k^{XT}_{obsd}$) of triplet XT at 625 nm (6.2 × 10$^6$ s$^{-1}$) was in agreement with the decay rate at 670 nm and the rise rate at 520 nm.‡

Consequently, the following concomitant reactions are revealed by triplet sensitization of BNS; (1) the formation of the lowest triplet state ($T_1$) of BNS and (2) the homolysis of BNS resulting in the formation of NTR. The quantum yields

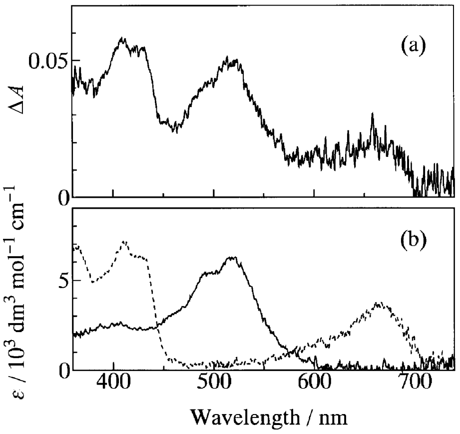


**Fig. 3** (a) The absorption spectrum at 400 ns obtained by 355 nm laser pulsing in the XT (1.5 × 10$^{-3}$ mol dm$^{-3}$)–BNS (4.8 × 10$^{-4}$ mol dm$^{-3}$) system in ACN. (b) The reference absorption spectra of triplet NMS (solid line) and NTR (broken line) in ACN. See text for details.

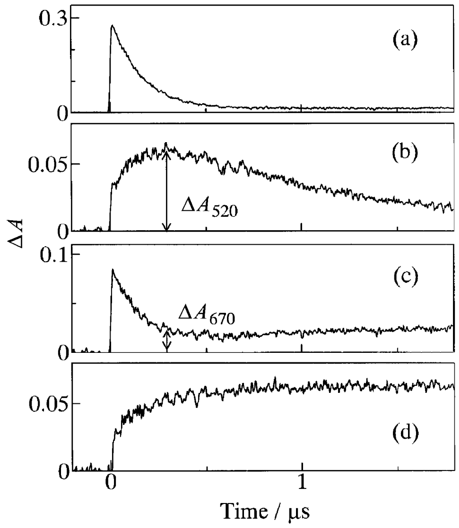


**Fig. 4** The time-resolved absorption changes at (a) 625, (b) 520, (c) 670 and (d) 410 nm obtained by 355 nm laser pulsing in the XT (1.5 × 10$^{-3}$ mol dm$^{-3}$)–BNS (4.8 × 10$^{-4}$ mol dm$^{-3}$) system in ACN.

($\Phi_T$ and $\Phi_{rad}$) for the formation of triplet BNS and NTR were, respectively, determined by:

$$\Phi_T = \Delta A_{520}(\varepsilon_{520}(^3\mathrm{BNS}^*) + \varepsilon_{520}(\mathrm{NTR}))^{-1} I_{abs}^{-1} \quad (8)$$

$$\Phi_{rad} = \Delta A_{670}\, \varepsilon_{670}(\mathrm{NTR})^{-1} I_{abs}^{-1} \quad (9)$$

where $\Delta A_{520}$ and $\Delta A_{670}$ are the absorbance changes for the formations of triplet BNS at 520 nm and of NTR at 670 nm, respectively (*cf.* Figs. 4(b) and (c)). Since the value of the molar absorption coefficient of triplet BNS, $\varepsilon_{520}(^3\mathrm{BNS}^*)$ was unknown, that of triplet NMS ($\varepsilon_{520}(^3\mathrm{NMS}^*)$ = 6400 dm$^3$ mol$^{-1}$ cm$^{-1}$)§ was used.

The term $\varepsilon_{520}$(NTR) in eqn. (8) was negligible compared to $\varepsilon_{520}(^3\mathrm{NMS}^*)$ (see Fig. 3(b)). The values of $\Phi_T$ and $\Phi_{rad}$ at [BNS] = 4.8 × 10$^{-4}$ mol dm$^{-3}$ were determined to be 0.44 and 0.33, respectively.

The $k^{XT}_{obsd}$ values at various [BNS] are plotted in Fig. 5. Since the plots show a straight line, $k^{XT}_{obsd}$ can be expressed as:

$$k^{XT}_{obsd} = k_0 + k_q[\mathrm{BNS}] \quad (10)$$

where $k_0$ and $k_q$ are the decay rate of triplet XT in the absence of BNS and the quenching rate constant of triplet XT by BNS,

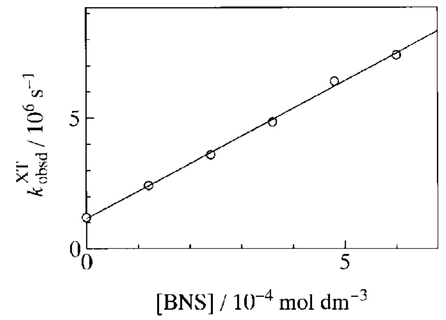


**Fig. 5** Plots of the decay rate, $k^{XT}_{obsd}$ of triplet XT in ACN as a function of [BNS].

---

‡ The decay profile at 670 nm originates from the molar absorption coefficient of triplet XT being larger than that of NTR at 670 nm. The precise value of the rise rate at 410 nm could not to be determined due to the small absorbance change.

§ Based on the triplet yield (0.95) of NMS determined by time-resolved thermal lensing techniques, the ε value of triplet NMS was determined by the method described in an earlier paper.[8]

respectively. From the slope of the line, $k_0$ and $k_q$ were determined to be $1.2 \times 10^6$ s$^{-1}$ and $1.0 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively. The $k_q$ value obtained is close to the diffusion limit of ACN ($2.0 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 20 °C).[9]

According to the spin-conservation rule, the spin multiplicity of the radical pair caged by the solvent molecules should be the triplet manifold when the cleavage occurs in the triplet state of BNS. In general, recombination between radicals requires singlet spin-multiplicity. Intersystem crossing from a triplet radical pair to a singlet one would take longer than the time to escape from the solvent cage to exist as free radicals. Thus, once bond fission occurs in the triplet manifold in fluid solutions, free radicals are efficiently yielded without geminate recombination. Therefore, the efficiency, $\alpha_{dis}$ of the bond cleavage by triplet sensitization can be calculated by using the $\Phi_{rad}$ value obtained experimentally as well as that of the $T_1$ state of BNS, $\alpha_T$ as follows:

$$\Phi_{rad} = \alpha_{dia} k_q[BNS]\Phi_{isc}(k_0 + k_q[BNS])^{-1} \qquad (11)$$

$$\Phi_T = \alpha_T k_q[BNS]\Phi_{isc}(k_0 + k_q[BNS])^{-1} \qquad (12)$$

where $\Phi_{isc}$ is the triplet yield of XT (1.0).[9] By using the obtained values of $k_0$, $k_q$, $\Phi_{rad}$ and $\Phi_T$ at [BNS] = $4.8 \times 10^{-4}$ mol dm$^{-3}$, $\alpha_{dis}$ and $\alpha_T$ were determined to be 0.41 and 0.55, respectively. These values indicate that the probability ratio of the bond cleavage to the triplet formation upon triplet sensitization of BNS by XT is 0.75. The sum of $\alpha_{dis}$ and $\alpha_T$ is considered to be the efficiency of triplet energy transfer from triplet XT to BNS. The residual value ($1 - \alpha_{dis} - \alpha_T = 0.04$) is interpreted in terms of the efficiency for induced-quenching of triplet BNS by XT.[4]

Interestingly, further formation of NTR was found after the completion of energy transfer from triplet XT to BNS. This second bond-fission was observed not only for XT but also for benzophenone (BP). Fig. 6 shows the transient absorption spectra obtained after 355 nm laser pulsing in the BP ($1.2 \times 10^{-2}$ mol dm$^{-3}$)–BNS ($2.0 \times 10^{-3}$ mol dm$^{-3}$) mixture in ACN. As the absorption band of triplet BNS produced by triplet energy transfer from triplet BP decays in intensity, an increase in the band at 670 nm for NTR can be seen. The time-resolved absorbance changes at 520 and 670 nm are shown in Fig. 7. The first-order decay rate ($k^T_{obsd}$) of triplet BNS at 520 nm ($1.2 \times 10^6$ s$^{-1}$) was identical with the rise rate of NTR at 670 nm. The agreement between the rise and decay rates indicates that the $T_1$ state of BNS is reactive for the C–S bond cleavage. The efficiency for the second formation of the radical, $\phi_{rad}$, *via* triplet-sensitized BNS is evaluated by:

$$\phi_{rad} = \Delta A_{670}\,\varepsilon_{520}\,\Delta A_{520}^{-1}\,\varepsilon_{670}^{-1} \qquad (13)$$

Here, $\Delta A_{670}$, $\Delta A_{520}$, $\varepsilon_{520}$, $\varepsilon_{670}$ are, respectively, the absorbance changes at 670 and 520 nm due to the formation of NTR and the decay of triplet BNS (*cf.* Fig. 7), and the molar absorption coefficients of triplet BNS at 520 nm and NTR at 670 nm (3400 dm$^3$ mol$^{-1}$ cm$^{-1}$). Since the value of $\varepsilon_{520}$ was unknown, the molar absorption coefficient of triplet NMS at 520 nm (6400 dm$^3$ mol$^{-1}$ cm$^{-1}$) was used instead of that of triplet BNS. For the BP ($1.2 \times 10^{-2}$ mol dm$^{-3}$)–BNS ($2.0 \times 10^{-3}$ mol dm$^{-3}$) system, the value of $\phi_{rad}$ was determined to be 0.56 ± 0.03.

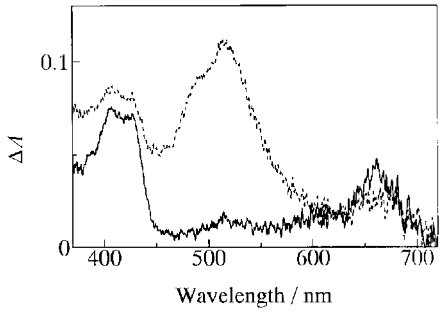


**Fig. 6** The transient absorption spectra at 300 ns (dotted line) and 1.9 μs (solid line) obtained after 355 nm laser pulsing in the BP ($1.2 \times 10^{-2}$ mol dm$^{-3}$)–BNS ($2.0 \times 10^{-3}$ mol dm$^{-3}$) system in ACN.

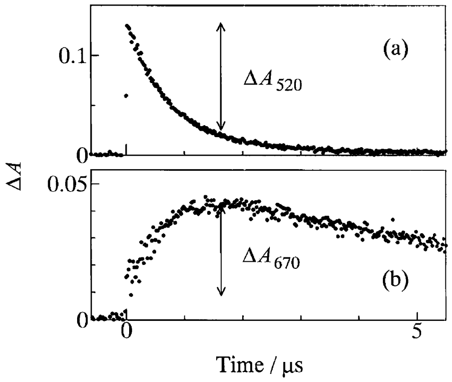


**Fig. 7** The temporal absorbance changes at (a) 520 and (b) 670 nm observed after 355 nm laser pulsing in the BP ($1.2 \times 10^{-2}$ mol dm$^{-3}$)–BNS ($2.0 \times 10^{-3}$ mol dm$^{-3}$) system in ACN.

Fig. 8 shows plots of $k^T_{obsd}$ as a function of [BP]. With increasing [BP], the $k^T_{obsd}$ values are found to increase, but not linearly, giving a leveling off at higher [BP]. This behavior is responsible for the triplet exciplex formation between aromatic ketones and triplet naphthalene derivatives.[4] The mechanism of the triplet exciplex formation between BP and BNS is illustrated in Scheme 1. Here, $k_0$, $k'_0$, $k_{dis}$ and $K$ are, respectively, the rate constants of the decay rates of triplet BNS, $^3$BNS* and the triplet exciplex, $^3$(BP···BNS)* to BP plus BNS in the ground state, the bond cleavage in the triplet exciplex and the equilibrium constant for triplet exciplex formation. We denote that $k_f$ and $k_b$ are the rate constants for association and dissociation of the triplet exciplex. According

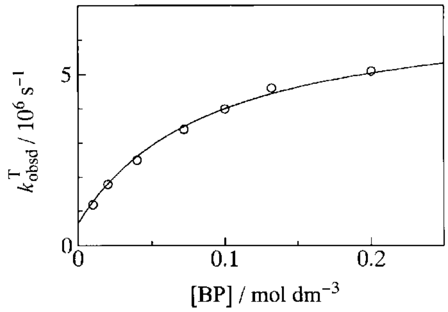
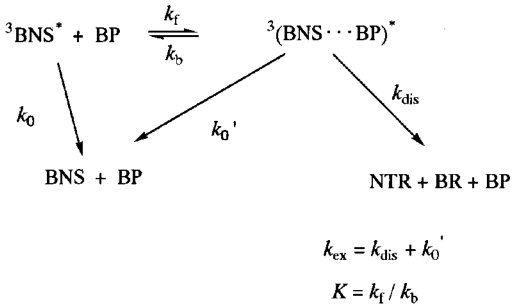
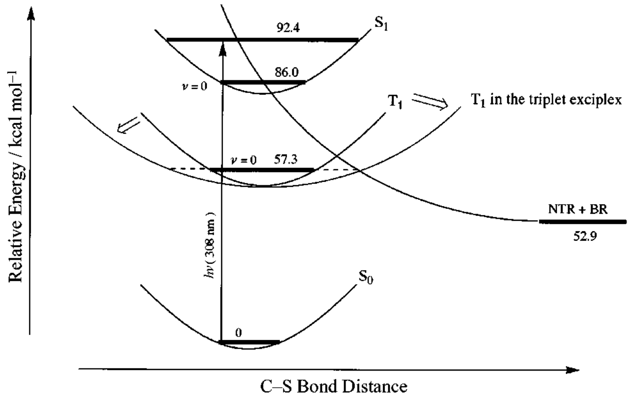


**Fig. 8** Plots of the decay rate, $k^T_{obsd}$ of triplet BNS *vs.* [BP]. The solid curve was calculated by eqn. (14). See text for details.



**Scheme 1**



**Scheme 2**

to the presented scheme, the $k^{T}_{Obsd}$ value can be formulated by:[4]

$$k^{T}_{obsd} = (k_0 + k_{ex}K[BP])(1 + K[BP])^{-1} \qquad (14)$$

where $k_{ex} = k'_0 + k_{dis}$ and $K = k_f/k_b$. The solid curve in Fig. 8 was calculated by using eqn. (14) and the best-fitted values of $k_0 = 6.5 \times 10^5$ s$^{-1}$, $k_{ex} = 7.0 \times 10^6$ s$^{-1}$ and $K = 11.2$ dm$^3$ mol$^{-1}$. The solubility of XT in ACN was so small that the parameters for the triplet exciplex of XT and BNS could not be determined.

The efficiency, $\beta_{dis}$ of the bond cleavage *via* the triplet exciplex can be calculated by using the $\phi_{rad}$ value obtained experimentally as follows:

$$\phi_{rad} = \beta_{dis} k_{ex} K[BP](k_0 + k_{ex}K[BP])^{-1} \qquad (15)$$

With the use of the obtained values of $k_0$, $k_{ex}$, $K$ and $\phi_{rad}$ ($=0.56$ at $[BP] = 1.2 \times 10^{-2}$ mol dm$^{-3}$), the value of $\beta_{dis}$ was determined to be $0.95 \pm 0.05$. This value, close to unity, indicates that bond dissociation in the triplet exciplex proceeds very efficiently.

The energy diagram for the photoreaction of BNS is illustrated in Scheme 2. The energy level of the crossing point between the potential curves of the $S_1(\pi,\pi^*)$ state and the dissociative state of $\pi,\sigma^*$ character would be close to that of $S_1$ since the main deactivation channel of $S_1$ was the bond-cleavage process. On the other hand, the energy level of the crossing point between the potential surfaces of the $T_1$ state and the dissociation would be higher than the $T_1$ energy (57.3 kcal mol$^{-1}$) of BNS since the formation of triplet BNS and radicals was simultaneously observed upon triplet sensitization. In other words, there must be a thermal barrier at the branching point for the $T_1$ and the dissociative potential surfaces. When XT was used as a sensitizer, the branching ratio of the bond dissociation to the triplet formation was found to be 0.75. Unfortunately, since the absorption spectrum of triplet BNS was very similar to that of triplet BP, the branching ratio in the case of BP as a sensitizer could not be obtained. In the presence of aromatic ketones, triplet BNS was shown to undergo efficient homolysis due to triplet exciplex formation. The mechanism of the bond cleavage induced by the exciplex formation can be interpreted by considering the charge-transfer character of triplet exciplexes.[4] Due to the weak charge-transfer from BNS to the carbonyl site of ketone, the spin density on the C–S bond may be reduced. Since the weakened chemical bond would be elongated, the potential surface of triplet BNS as a function of the C–S atomic distance would become shallow (*cf.* Scheme 2). The thermal barrier on $T_1$ for the bond cleavage diminishes in energy, resulting in efficient fission *via* the triplet exciplex. It seems that aromatic ketone behaves not only as a triplet sensitizer but also as a catalyst for the bond cleavage of triplet BNS by forming the triplet exciplex.

## 4. Conclusion

The photoinduced dissociation of the carbon–sulfur bond in BNS in the absence and presence of XT and BP is studied by laser flash photolysis. The excited singlet state is reactive for C–S bond fission upon direct excitation. Triplet sensitization of BNS by XT and BP reveals bond dissociation in the triplet manifold as well as formation of the lowest triplet state of BNS. To understand the competitive reactions of triplet-sensitized BNS, the potential energy surfaces of BNS are suggested by considering a thermally activated crossing from the $T_1$ $(\pi,\pi^*)$ state to a dissociative $\pi,\sigma^*$ state. Following deactivation of triplet-sensitized BNS, the second cleavage of the C–S bond takes place. Based on the kinetic analysis of the decay rate of triplet BNS, the triplet exciplex of BNS and ketone is shown to be the precursor for the second fission. It is proposed for the mechanism of bond cleavage *via* the triplet exciplex that the weak charge-transfer character of the triplet exciplex is the origin of the weakening of the chemical bond between the carbon and sulfur atoms of BNS in the triplet exciplex, resulting in a decrease in the thermal barrier leading to the dissociative surface.

## References

1 N. J. Turro, in *Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, CA, 1978.
2 M. Hoshino and H. Shizuka, in *Photo-induced Electron Transfer*, ed. M. A. Fox and N. Chanon, Elsevier, Amsterdam, 1988, Part C, p. 313.
3 M. Hoshino and H. Shizuka, in *New Aspects of Radiation Curing in Polymer Science and Technology*, ed. J. P. Foussier and J. F. Rabek, Elsevier, London, 1993, vol. 2, p. 637.
4 H. Shizuka and M. Yamaji, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 267.
5 M. Yamaji, Y. Aihara, T. Itoh, S. Tobita and H. Shizuka, *J. Phys. Chem.*, 1994, **98**, 7014.
6 O. Ito and M. Matsuda, *J. Org. Chem.*, 1983, **48**, 2410.
7 K. Tokumura, T. Okazaki, H. Nosaka, Y. Saigusa and M. Itoh, *J. Am. Chem. Soc.*, 1991, **113**, 4974.
8 M. Yamaji, T. Sekiguchi, M. Hoshino and H. Shizuka, *J. Phys. Chem.*, 1992, **96**, 9353.
9 S. L. Murov, I. Carmichael and G. L. Hug, in *Handbook of Photochemistry*, Marcel Dekker, New York, 2nd edn., 1993.
10 C. H. Evans, N. Prud'homme, M. King and J. C. Scaiano, *J. Photochem. Photobiol. A*, 1999, **121**, 105.