

Short note

Photochemical decomposition of amidobiphenyls in highly excited triplet states studied by stepwise two-color laser photolysis

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Abstract

Photochemical decomposition of amidobiphenyls (R-AN; R = Me, Et and PhCH₂) in highly excited triplet states (T_n with n over 2) was investigated in solution by using stepwise two-color laser photolysis techniques. Upon direct excitation, R-ANs underwent photodecomposition in excited singlet states (S_1) with a quantum yield (Φ_{254}) of ca. 0.015. Triplet sensitization using acetone (Ac) was employed for efficient formation of the lowest triplet states (T_1) of R-AN and for determining molar absorption coefficients of the $T_n \leftarrow T_1$ absorption. No photochemical reactions were found in the T_1 state. Upon 355-nm laser flash photolysis of the T_1 states of R-ANs, they underwent decomposition. The quantum yields (Φ_{dec}) for the decomposition of the molecules in the T_1 states were determined to be ca. 0.08. The photodecomposition of the T_1 state was proposed to be responsible for CO–N bond cleavage in the T_n state.
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Keywords: Amide bond cleavage; Photodecomposition; Laser flash photolysis; Higher triplet state

1. Introduction

Photoinduced bond dissociation of aromatic carbonyl compounds is one of well-known reactions in photochemistry and photobiology. Norrish types I and II reactions, and carbon-heteroatom bond dissociation that occurs at the α - and β -positions of aromatic carbonyl compounds have been widely studied by means of product analysis and time-resolved transient measurements [1–9]. Shizuka et al. reported that anilide compounds undergo CO–N amide bond dissociation at the α -position of the carbonyl group [10]. It was shown that this bond dissociation proceeds in the excited singlet state, which is followed by photo-fries rearrangements [10–12]. However, less attention has been paid to bond dissociation processes in the triplet states since the triplet states would not be formed upon direct photoexcitation of amide compounds due to the occurrence of efficient photoreactions in excited singlet states.

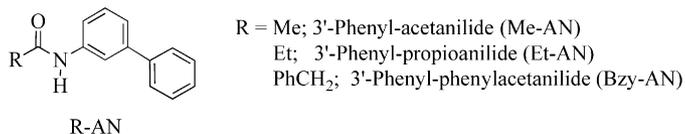
Triplet sensitization technique using triplet energy transfer has been widely used to investigate photochemical properties in the triplet state of molecules showing small triplet yields. Ace-

tone, acetophenone or benzophenone whose triplet energies are ca. 78, 74 or 69 kcal mol⁻¹, respectively, have been used as typical triplet sensitizers [13]. However, we are unable to investigate photoreactions of triplet acetanilide by using those sensitizers due to the large triplet energy of acetanilide (78 kcal mol⁻¹). One of the methods to produce triplet anilides by using these triplet sensitizers would be to keep the triplet energy of the anilides lower than that of a triplet sensitizer by modifying the aromatic rings. That is, a phenyl group has been attached to acetanilide to make biphenyl derivatives whose triplet energies of biphenyls are known to be ca. 65 kcal mol⁻¹ [13,14].

In this context, we have investigated photochemical reactions of triplet anilides having a biphenyl moiety (R-AN). Recently, bond dissociation processes in highly excited triplet (T_n) states of aromatic compounds are surveyed by means of two-color two-laser photolysis techniques [15–17]. The method of multi-step excitation has been widely used to study photophysical and photochemical processes in highly excited states [18–23]. In the present note, the photochemical properties not only in the lowest triplet (T_1) state but also in the T_n state are studied using sequential excitation with 308 and 355-nm laser pulses. The first 308-nm laser photolysis was performed to efficiently create the T_1 states by triplet sensitization of acetone (Ac). Upon the second 355-nm laser pulsing, the molecule

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in the T_1 state was further excited into the higher triplet states.



2. Experimental

3'-Phenyl-acetanilide (Me-AN), 3'-phenyl-propioanilide (Et-AN) and 3'-phenyl-phenylacetanilide (Bzy-AN) were synthesized by a reaction of *m*-phenyl aniline with acetyl chloride, propionyl chloride and phenylacetyl chloride in benzene, respectively. Acetanilide was commercially purchased. These compounds were purified by repeated recrystallizations from hexane. Acetonitrile (ACN), methanol and ethanol were distilled for purification. ACN was used as the solvent while a mixture of methanol and ethanol (1:1, v/v) was used as a matrix at 77 K. Absorption and emission spectra were recorded on a U-best 50 spectrophotometer (JASCO) and a Hitachi F-4010 fluorescence spectrophotometer, respectively. A XeCl excimer laser (308 nm, Lambda Physik, Lextra 50) was used as the first excitation light source while the third (355 nm) harmonics of a Nd³⁺:YAG laser (JK Lasers HY-500; pulse width 8 ns) was as the second excitation light source. The fourth harmonics (266 nm) from the Nd³⁺:YAG laser was used as a light source for direct excitation. The details of the detection system for the time profiles of the transient absorption have been reported elsewhere [24]. The incidence direction of the second 355-nm laser beam was kept parallel to that of the first 308-nm laser light. The transient data obtained by laser flash photolysis were analyzed by using the least-squares best-fitting method. The transient absorption spectra were taken with a USP-554 system from Unisoku with which can provide a transient absorption spectrum with one laser pulse.

Steady-state photolysis was carried out by using a low-pressured mercury lamp (254 nm). The photonflux at 254 nm was determined by using *N*-methyl-diphenylamine in aerated methylcyclohexane as a chemical actinometer. The quantum yield for the formation of *N*-methylcarbazol from *N*-methyl-diphenylamine has been established as 0.42 [25]. The procedure to determine the quantum yields of photodecomposition of R-AN was the same as that described in the literature [26].

All the samples for transient absorption measurements were prepared in darkness, and degassed in a quartz cell with a path length of 1 cm using several freeze-pump-thaw cycles on a high vacuum line. The concentration of R-AN for 266 nm laser photolysis was adjusted to maintain the optical density at 266-nm being ca. 0.8 in ACN. Usual measurements were carried out at 295 K. The number of the repetition of laser pulsing was kept less than four pulses to avoid excess exposure. Several transient data obtained at the same concentration systems were averaged, and the experimental errors in the values were kept within $\pm 5\%$ deviation.

3. Results and discussion

3.1. Absorption and emission measurements

Fig. 1 shows absorption and fluorescence spectra of Me-AN and acetanilide in ACN at 295 K and phosphorescence spectra in a glass matrix of a mixture of methanol and ethanol (1:1, v/v) at 77 K. It was confirmed that the excitation spectra for the emission agreed well with the corresponding absorption spectra. The absorption and fluorescence spectra of R-ANs used in the present work were very similar to each other in the shape and maximum wavelengths. The energy levels of the lowest triplet (T_1) state were determined to be 65.3 kcal mol⁻¹ for R-AN and 78.1 kcal mol⁻¹ for acetanilide from the phosphorescence origins while those of the lowest excited singlet states of R-ANs were evaluated as 93.1 kcal mol⁻¹ by averaging the energy values of the 0–0 origins of absorption and fluorescence spectra. Fluorescence from acetanilide was not observed at 295 K. From the similarity in the fluorescence and phosphorescence spectral shapes of R-ANs with those of biphenyl derivatives [14,16], it is inferred that the excited energies of the lowest singlet (S_1) and triplet states (T_1) are localized on the phenylanilino moiety, and that the electronic configurations of the S_1 and T_1 are of π, π^* .

3.2. Photochemical profiles in the S_1 and T_1 states

To elucidate the photochemical profiles of R-ANs, stationary-photolysis was carried out in degassed ACN, and the photochemical features were compared with that of acetanilide. Fig. 2 shows changes of absorption spectra of Me-AN and acetanilide upon 254-nm light irradiation of the ACN solutions. With an increase of irradiation time, the absorption spectrum of Me-AN changes showing an isosbestic point at 267 nm to provide a broad absorption band at 300 nm. We were unable to identify the final products from the absorption spectra. Similar changes in absorption spectra of Et- and Bzy-ANs were obtained. In contrast, photoproducts of acetanilide are known

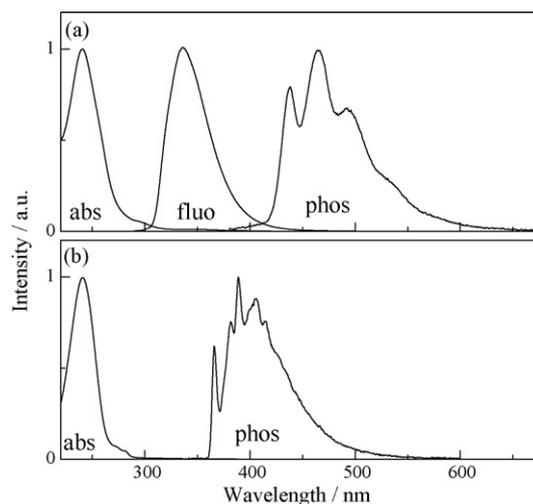
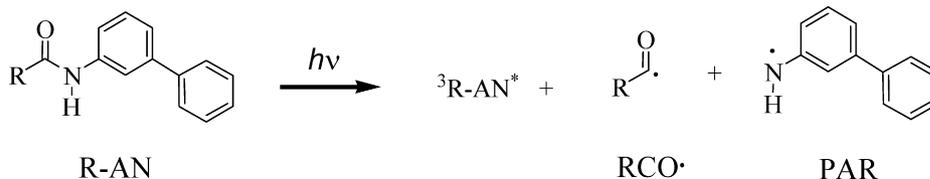


Fig. 1. Absorption and fluorescence spectra in ACN at 295 K and phosphorescence spectra in a mixture of methanol and ethanol (1:1, v/v) at 77 K for Me-AN (a) and acetanilide (b).

to be 4-amino and 2-aminoacetophenones (λ_{max} at 303 and 355 nm, respectively) due to photo-fries rearrangement of radicals produced upon the CO–N bond cleavage in the lowest excited singlet (S_1) state [10]. The quantum yields, Φ_{254} of photodecomposition upon 254-nm light irradiation were determined to be 0.015 ± 0.001 for Me–AN, 0.017 ± 0.001 for Et–AN and 0.015 ± 0.001 for Bzy–AN, which are comparable with that in ethanol (0.03) or smaller than that of acetanilide in cyclohexane (0.15) [10a,b]. The yields thus determined were not affected by the amount of dissolved oxygen. Since the initial reaction of acetanilide is reported to be the CO–N bond dissociation in the S_1 state [10], it is plausible that the decomposition of R–AN is due to the corresponding CO–N bond rupture in the S_1 state.

Fig. 3a shows transient absorption spectra at 100 ns after 266-nm laser pulsing in the ACN solution of Me–AN. The shape of the transient absorption spectrum at 375 nm resembles those of triplet biphenyl derivatives and the intensity of the absorption band was decreased in the presence of dissolved oxygen. Therefore, the obtained absorption spectrum can be ascribed to the $T_n \leftarrow T_1$ absorption of Me–AN. Similar triplet absorption spectra were obtained for Et- and Bzy-ANs.



After decay of the triplet absorption, appreciable absorption spectra were not seen at wavelengths longer than 330 nm although the formation of *m*-phenylanilino radical (PAR) and the corresponding radical (RCO•) due to the CO–N bond rupture was expected. This may be because of the very small yield ($\Phi_{254} = 0.015$) and small molar absorption coefficients of the radicals. Based on these observations, it seems that photoexcited R–ANs undergo the CO–N bond cleavage in the excited singlet states and the triplet formation.

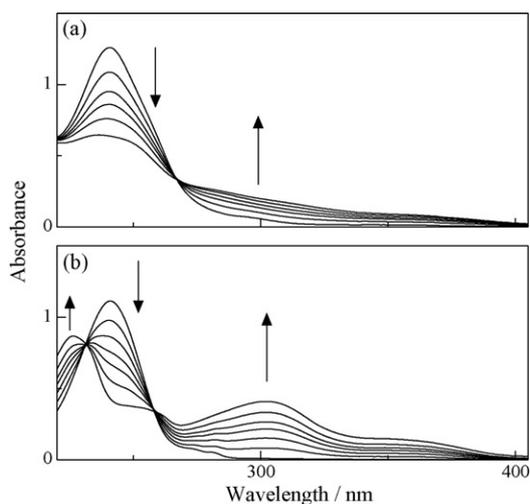


Fig. 2. Absorption spectral changes upon 254 nm photoirradiation of ACN solutions of Me–AN at 0, 1, 2, 3, 5 and 18 min (a) and acetanilide at 0, 20, 40, 60, 80, 120 and 240 s (b).

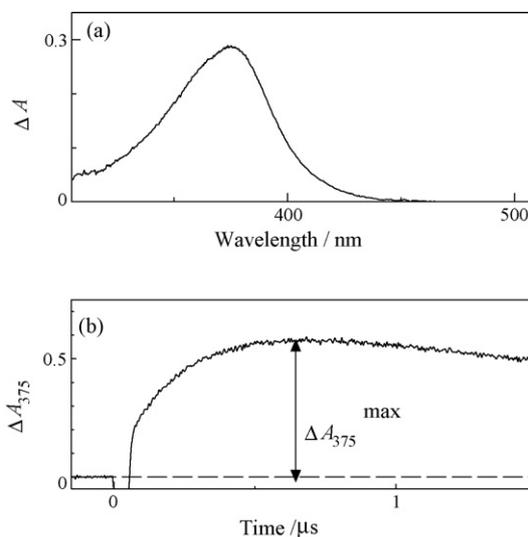


Fig. 3. (a) A transient absorption spectrum at 100 ns obtained upon 266-nm laser pulsing in ACN solutions of Me–AN. (b) A time profile of absorbance at 375 nm obtained upon 308-nm laser pulsing in an Ac (0.6 mol dm⁻³)/Me–AN (2.0 × 10⁻³ mol dm⁻³) system in ACN.

In order to efficiently produce triplet states of R–ANs, we performed triplet sensitization by using acetone (Ac) as a triplet energy donor upon 308-nm laser photolysis. Since the triplet energy of Ac is higher by 74.0 kcal mol⁻¹ than those (ca. 65 kcal mol⁻¹) of the used compounds [13], R–AN possibly gains the energy from triplet Ac. Fig. 3b shows a time profile of absorbance at 375 nm obtained upon 308-nm laser pulsing in a Ac(0.6 mol dm⁻³)/Me–AN(2.0 × 10⁻³ mol dm⁻³) system. The intensity of the absorbance increases with a first-order rate, k_{obsd} of $3.8 \times 10^6 \text{ s}^{-1}$. A transient absorption spectrum obtained at 850 ns after laser pulsing in the Ac/Me–AN system was due to the presence of triplet Me–AN. The growth of the absorption in Fig. 3b, therefore, is caused by the triplet energy transfer from triplet acetone to Me–AN, resulting in the formation of triplet Me–AN. The transient absorption spectra obtained upon 308-nm laser photolysis of Ac/Et–AN and Ac/Bzy–AN systems were the same as those of the corresponding triplet R–AN. The similarity in the shape of the triplet absorption spectra of R–ANs indicates that triplet exciton is localized on the *m*-phenylanilino moiety, irrespective of the substituents, R.

Fig. 4a shows rates (k_{obsd}) of the growth of triplet Me–AN plotted as a function of the concentration, [Me–AN] of Me–AN. Since the plots give a straight line, the k_{obsd} can be formulated by Eq. (1):

$$k_{\text{obsd}} = k_0 + k_q[\text{Me-AN}] \quad (1)$$

where k_0 and k_q , respectively, represent the decay rate of triplet Me–AN in the absence of Me–AN and the rate constant for

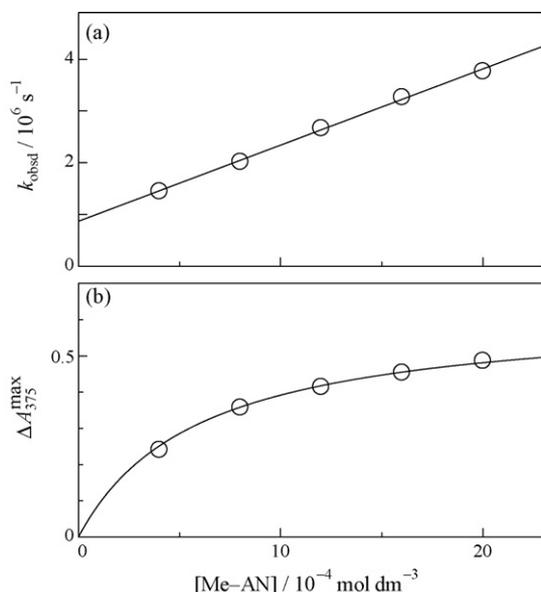


Fig. 4. (a) The rate (k_{obsd}) for the growth of triplet Me–AN plotted as a function of [Me–AN] upon 308-nm laser photolysis in Ac (0.6 mol dm^{-3})/Me–AN systems in ACN. (b) Plots of the maximum absorbance at 375 nm ($\Delta A_{375}^{\text{max}}$) as a function of [Me–AN] obtained upon 308-nm laser photolysis in Ac (0.6 mol dm^{-3})/Me–AN systems in ACN. The solid curve was drawn by Eq. (2).

quenching of triplet Ac by Me–AN. From the intercept and the slope of the line, the values of k_0 and k_q were determined to be $8.7 \times 10^5 \text{ s}^{-1}$ and $1.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively.

Fig. 4b shows the maximum absorbance, $\Delta A_{375}^{\text{max}}$ of triplet Me–AN produced by triplet sensitization plotted as a function of [Me–AN]. The value of $\Delta A_{375}^{\text{max}}$ increases with increasing [Me–AN], but the increase is not linear with [Me–AN]. The quantity of $\Delta A_{375}^{\text{max}}$ triplet Me–AN produced by triplet sensitization can be formulated by Eq. (2):

$$\Delta A_{375}^{\text{max}} = k_q [\text{Me-AN}] \alpha_{\text{TET}} \varepsilon_{375}^{\text{T-T}} \Phi_{\text{ISC}}^{\text{Ac}} I_{\text{abs}}^{\text{Ac}} (k_0 + k_q [\text{Me-AN}])^{-1} \quad (2)$$

where α_{TET} , $\varepsilon_{375}^{\text{T-T}}$, $\Phi_{\text{ISC}}^{\text{Ac}}$ and $I_{\text{abs}}^{\text{Ac}}$ are, respectively, an efficiency of triplet energy transfer from triplet acetone to Me–AN, the molar absorption coefficients of triplet Me–AN at 375 nm, the triplet yield of acetone (1.0 [13]) and the number of photon flux of an incident 308-nm laser pulse absorbed by Ac. The quantity

of I_{abs} was determined by Eq. (3) [27]:

$$\Delta A_{\text{T}}^{\text{BP}} = \varepsilon_{\text{T}}^{\text{BP}} \Phi_{\text{ISC}}^{\text{BP}} I_{\text{abs}}^{\text{BP}} \quad (3)$$

where $\Delta A_{\text{T}}^{\text{BP}}$, $\varepsilon_{\text{T}}^{\text{BP}}$ and $\Phi_{\text{ISC}}^{\text{BP}}$ are, respectively, the initial absorbance at 520 nm for the formation of triplet benzophenone obtained immediately after laser pulsing, the molar absorption coefficient of triplet BP at 520 nm in ACN ($6500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ [28]) and triplet yield of benzophenone (1.0 [13]). By using Eqs. (1)–(3), and assuming the efficiency of α_{TET} being unity, the $\varepsilon_{375}^{\text{T-T}}$ value of triplet Me–AN was determined to be $16,000 \pm 800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 375 nm. By using the same procedures, the quenching rate constants, k_q for triplet sensitization of acetone and the molar absorption coefficients, $\varepsilon_{375}^{\text{T-T}}$ of the triplets of Et- and Bzy-ANs at 375 nm were determined, as listed in Table 1. The obtained k_q and $\varepsilon_{375}^{\text{T-T}}$ values are the same or close to each other. Upon triplet sensitization, only the formation of triplet R–ANs was seen in transient absorption spectra. These observations indicate that CO–N bonds in R–ANs do not cleave in the T_1 states.

3.3. Photolysis of triplet R–AN upon the second laser pulsing

Since triplet R–ANs show the absorption at 355 nm, it is possible to excite the triplets to R–AN in the higher triplet states by using the second 355-nm laser pulsing. Fig. 5 shows transient absorption spectra at 850 ns upon 308-nm laser photolysis of an Ac(0.6 mol dm^{-3})/Me–AN($2.0 \times 10^{-3} \text{ mol dm}^{-3}$) system in the absence and the presence of the second 355 nm laser pulsing at 700 ns after the first laser pulsing. The transient absorption spectrum in the absence of the second laser pulse is due to triplet Me–AN. By employing the second laser pulse, the intensity of the absorption of the triplet at 375 nm was found to decrease without showing the recovery to the initial intensity before the second laser pulsing (see inset in Fig. 5). Any appreciable transient absorption spectra of photoproducts upon the second laser pulsing were not seen in the transient absorption. Decomposition of triplet Et- and Bzy-ANs was also recognized upon the second 355-nm laser photolysis in Ac/Et-AN and Ac/Bzy-AN systems, respectively.

A quantum yield (Φ_{dec}) for the decomposition in the T_n state of R–AN upon the second 355-nm laser pulsing was determined

Table 1
Photophysical and photochemical parameters for R–AN obtained in the present work

| R | E_{T} (kcal mol ⁻¹ ^a) | Φ_{254}^{b} | $\varepsilon_{375}^{\text{T-T}}$ (dm ³ mol ⁻¹ cm ⁻¹ ^b) | k_q (10 ⁹ dm ³ mol ⁻¹ s ⁻¹ ^b) | Φ_{dec} | $\Delta_{\text{f}}H$ (R–AN) (kcal mol ⁻¹) | $\Delta_{\text{f}}H$ (RCO [•]) (kcal mol ⁻¹) | BDE(CO–N) (kcal mol ⁻¹ ^c) |
|-----|---|-------------------------|---|---|---------------------|---|--|--|
| Me | 65.1 | 0.015 | 16,000 | 1.5 | 0.086 ^d | 5.1 | –19.0 | 61.0 |
| Et | 65.2 | 0.017 | 15,600 | 1.5 | 0.084 ^d | 1.2 | –24.1 | 59.8 |
| Bzy | 65.2 | 0.015 | 17,300 | 1.4 | 0.069 ^e | 32.9 | 10.5 | 62.7 |

^a Determined from 0 to 0 origin of the phosphorescence spectrum obtained in a mixture of methanol and ethanol (1:1, v/v) at 77 K.

^b Errors $\pm 5\%$.

^c BDE values for the CO–N bond were determined by Eq. (5) by using the values of $\Delta_{\text{f}}H$ (PAR) = 85.1 kcal mol⁻¹.

^d Errors ± 0.006 .

^e Errors ± 0.005 .

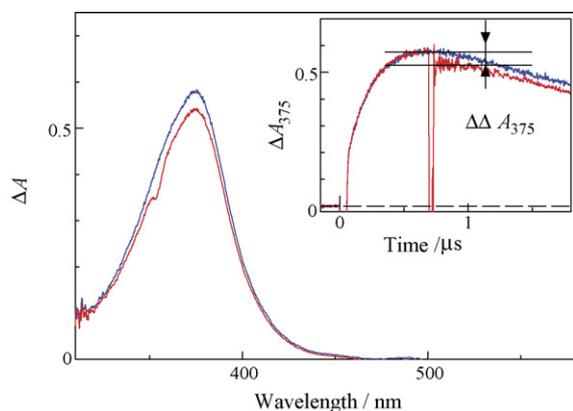


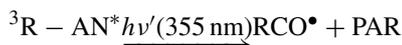
Fig. 5. Transient absorption spectra obtained at 850 ns upon 308-nm laser pulsing an Ac (0.6 mol dm^{-3})/Me-AN ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$) system in ACN in the absence (blue color) and the presence (red color) of the second 355 nm laser pulsing at 700 ns. A dimple at 355 nm in the transient absorption spectrum in red color is due to scattering of the second 355 nm laser pulse. Insets; time profiles at 375 nm in the absence (blue color) and the presence (red color) of the second 355-nm laser pulsing. The spike at 700 ns is due to scattering of the second 355-nm laser pulse.

by Eq. (4):

$$\Phi_{\text{dec}} = \Delta\Delta A_{375} I_0^{355} (1 - 10^{-\Delta A_{355}^{\text{TT}}}) \varepsilon_{375}^{\text{T-T}-1} \quad (4)$$

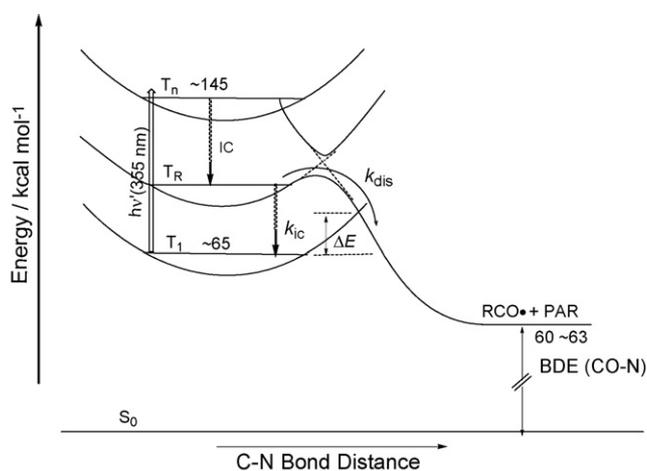
where $\Delta\Delta A_{375}$, I_0^{355} and $\Delta A_{355}^{\text{T-T}}$, respectively, represent an absorbance change at 375 nm for triplet R-AN due to decomposition upon the second 355-nm laser photolysis, the intensity of the incident second 355-nm laser pulse and the absorbance of triplet R-AN at 355 nm generated upon Ac sensitization. The quantity of I_0^{355} was determined as $3.7 \times 10^{-5} \text{ einstein dm}^{-3} \text{ pulse}^{-1}$ by using the triplet-triplet absorption of benzophenone formed upon 355-nm laser photolysis in the ACN solution as an actinometer (see Eq. (3)). By changing the intensity of the first 355-nm laser pulse, we obtained the $\Delta A_{355}^{\text{T-T}}$ values varied from ca. 0.2 to ca. 0.5. Since plots of $\Delta\Delta A_{375}$ as a function of the term of $1 - 10^{-\Delta A_{355}^{\text{TT}}}$ showed a straight line, it can be ruled out on our experimental conditions that multi-photon absorption of the T_1 state is involved upon CO-N bond cleavage in the T_n state. The Φ_{dec} value was thus determined to be 0.086 ± 0.006 for Me-AN, 0.084 ± 0.006 for Et-AN and 0.069 ± 0.005 for Bz-AN.

We propose that the decomposition upon photolysis of the T_1 state is responsible for CO-N bond cleavage in the T_n state of R-AN although we were unfortunately unable to observe the corresponding radicals formed upon the decomposition of the T_1 state, presumably due to the small molar absorption coefficients of the radicals or small Φ_{dec} values.



The bond dissociation energies (BDE) of the CO-N bonds in R-ANs were obtained by Eq. (5) on the basis of the heats of formation ($\Delta_f H$) for R-AN, RCO \bullet and PAR computed by using a semi-empirical PM3 program contained in MOPAC '97.

$$\Delta_f H(\text{R-AN}) = \Delta_f H(\text{RCO}^\bullet) + \Delta_f H(\text{PAR}) - \text{BDE}(\text{CO-N}) \quad (5)$$



Scheme 1. An energy diagram for excited R-AN including the dissociative potential.

The $\Delta_f H$ value for PAR was $85.1 \text{ kcal mol}^{-1}$ whereas those for R-AN and RCO \bullet are listed in Table 1 along the estimated BDE values. The BDE values vary in a small range of ca. $60\text{--}63 \text{ kcal mol}^{-1}$.

Assuming that the decomposition of the T_1 state is due to the CO-N bond cleavage, a schematic energy diagram for triplet R-AN is depicted in Scheme 1. Upon the second 355-nm laser photolysis of the T_1 (π, π^*) state of R-AN, the T_n (π, π^*) state whose state energy is located at $145 \text{ kcal mol}^{-1}$ is produced. The molecule in the T_n state will be deactivated through internal conversion to a dissociative state, T_R (π, π^*). It is originally suggested that the bond dissociation in excited states proceeds by avoided crossings between the reactive excited state with dissociative potential surfaces of the same overall symmetry [29]. In the present case, the electronic configuration of the dissociative potential for the CO-N bond rupture is of a σ, σ^* type which is allowed to strongly interact with the T_R (π, π^*) state, leading to free radical formation with little thermal activation energies. In contrast, the absence of fragmentation in the T_1 states can be interpreted by considering a large energy barrier, ΔE for the interaction between the T_1 (π, π^*) state and a dissociative triplet σ, σ^* potential [15d].

4. Conclusions

Photochemical features of R-AN in the S_1 , T_1 and T_n states have been studied. Upon steady-state photolysis, R-ANs undergo photodecomposition in the S_1 state with the yields, Φ_{254} of ca. 0.016. Transient absorption measurements upon 266-nm laser pulsing in R-AN revealed formation of triplet R-ANs, but intermediates formed as the result of the CO-N bond dissociation were not recognized in the transient absorption. Acetone sensitization of R-AN efficiently forms triplet R-AN, and enabled us to determine the molar absorption coefficients, $\varepsilon_{375}^{\text{T-T}}$. No photochemical reaction proceeds in the T_1 state whereas photodecomposition in the T_n state is found upon 355-nm laser photolysis of triplet R-AN. The quantum yields, Φ_{dec} of the decomposition in the T_n state are estimated to be ca.

0.08 which are five times greater than those in the S_1 state. The plausible photochemical reaction responsible for the decomposition of triplet R-ANs is suggested as the CO–N bond rupture in the T_n state. Further studies for direct evidence of CO–N bond dissociation in higher triplet states are in progress.

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