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Short note

Photophysical and photochemical properties of an aromatic carbonyl compound for a moderate triplet energy sensitizer studied by steady state and laser flash photolysis

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ABSTRACT

1-Benzoyl-2-phenylacetylene (BPA) having a moderate triplet energy (65 kcal mol^{-1}) was prepared, and steady state and laser photolysis techniques were conducted to characterize the photochemical features of the triplet state and the BPA ketyl radical that was formed via H-abstraction of the triplet n,π* from alcohol and phenol. The photophysical and photochemical properties of BPA similar to those of benzophenone may encourage photochemists to use it as an *n*, π* triplet sensitizer scheduled for triplet-energy-tuned experiments upon laser flash photolysis in solution.

1. Introduction

Benzophenone (BP) is one of the most important and useful compounds in photochemical studies in solution. The photophysical properties of BP have been revealed in details [1]. The excited lowest singlet (S_1) n, π* state has the lifetime of ~10 ps, and undergoes fast intersystem crossing to the lowest triplet (T_1) n,π* state with the unity efficiency (Φ_{isc} = 1.0) via the second excited triplet (T_2) π, π* state according to El-Sayed rule. The T_1 (n,π*) state undergoes H-abstraction from hydrocarbons, alcohols and amines. BP with the triplet energy (E_T) being 69.1 kcal mol^{-1} has been used on triplet sensitization experiments in solution as a triplet energy donor to aromatic compounds having triplet energies smaller than that of BP, such as biphenyl (E_T = 65 kcal mol^{-1}) and naphthalene (E_T = 60 kcal mol^{-1}) [2]. These fundamental photochemical reactions in inter- and intramolecular systems have been vigorously studied by using steady state and laser photolysis techniques in solution [3]. It is known that as the phenyl ring of BP is replaced with expanded π-electron rings, *eg*, on going from BP to 4-phenylbenzophenone (E_T = 61 kcal mol^{-1}) and 2-(benzoyl) naphthalene (E_T = 59 kcal mol^{-1}) (The data for the E_T are deposited in Supplementary data.), the T_1 energies become lower than that of BP, and the electronic character of the T_1 state alters from n,π* to π,π*. To our knowledge, there are few *proper* triplet sensitizers that have E_T values between 62–69 kcal mol^{-1} although triplet energy transfer experiments in solution require tuning the energy gaps between the triplet energy donors and acceptors. Aromatic carbonyl molecules having moderate E_T values (63–69 kcal mol^{-1}) have been, thus, sought for better performance of energy transfer experiments to understand the relationship between the energy gap and the transfer rates according to the Sandros's equation [4,5].

Finally, we found that 1-benzoyl-2-phenylacetylene (BPA, see Chart 1) has a desired E_T value of 65 kcal mol^{-1}. In this research note, we report the preparation of BPA from 1.3-diphenylpropagyl alcohol (DPPA in Chart 1) as well as the photophysical and photochemical properties of BPA and the corresponding ketyl radical in solution by using steady state and laser photolysis techniques.

2. Experimental

The preparation procedure and the NMR data of BPA, and experimental details for the present work are deposited in Supplementary data.

3. Result and Discussion

Fig. 1a shows the absorption and phosphorescence spectra of BPA in solution.The molar absorption coefficient (ε) of BPA is

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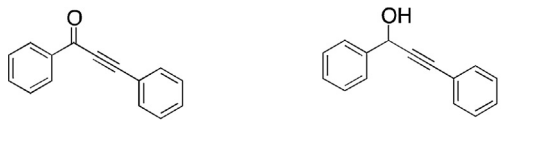

1-Benzoyl-2-phenylacetylene (BPA) 1,3-Diphenylpropagyl alcohol (DPPA)

Chart 1. The molecular structures of BPA and DPPA.

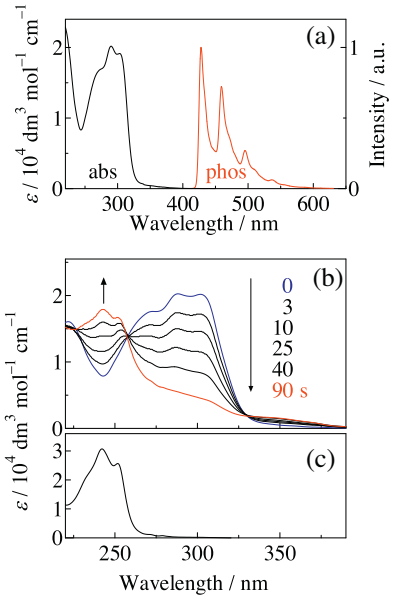

Fig. 1. (a) Absorption spectrum of BPA in ACN at 295 K and phosphorescence spectrum in EtOH at 77 K. (b) Absorption spectral changes upon 254 nm photolysis of BPA in Ar-purged EtOH at 295 K. (c) The absorption spectrum of DPPA in EtOH.

20,000 $dm^3\,mol^{-1}\,cm^{-1}$ at 290 nm in acetonitrile (ACN). Fluorescence was absent at 295 K, indicating that the electronic character of the S_1 state is of n,π*. The phosphorescence spectrum in ethanol (EtOH) at 77 K shows vibrational structures due the carbonyl group. From the 0–0 origin of the phosphorescence spectrum, the E_T value was determined to be 65.2 kcal mol^{-1}. Fig. 1b shows absorption spectral changes upon 254 nm steady state photolysis of BPA in Ar-purged EtOH at 295 K. With the lapse of irradiation time, the intensity of BPA at 290 nm decreased with isosbestic points at 227, 258 and 330 nm while those of absorbance at 242 and 350 nm increased. The photodecomposition rate of BPA was delayed in aerated EtOH. The grown-up absorption spectrum at 242 nm is similar to that of DPPA (ε = 30,800 $dm^3\,mol^{-1}\,cm^{-1}$ at 242 nm in EtOH) shown in Fig. 1c, indicating that the $T_1(n,\pi^*)$ of BPA undergoes H-atom abstraction from the EtOH molecule forming the corresponding BPA ketyl radical as the initial photoproduct, resulting in producing DPPA. The absorption band at 350 nm was unable to identify from the absorption spectrum. The quantum yield for the photodecomposition of BPA in EtOH was determined to be 0.28. It is revealed that the photophysical and photochemical features of BPA resemble those of BP except the E_T value.

Laser flash photolysis of BPA was carried out to investigate the photochemical features of the intermediates upon photolysis of BPA in ACN. Fig. 2a shows a transient absorption spectrum obtained upon 308 nm laser pulsing in Ar-purged ACN solution of BPA at 295 K.

The transient absorption spectrum having the maximum at 485 nm decayed according to the first-order kinetics with a lifetime of 2.3 μs. The decay was accelerated by the amount of the dissolved oxygen. This fact indicates that the observed transient absorption is due to the triplet–triplet (T–T) absorption of BPA.

We have recognized H-abstraction of triplet BPA from EtOH. Photochemical features of the BPA kethyl radical (BPAK) were investigated by laser photolysis techniques. Fig. 2b shows transient absorption spectra obtained upon 308 nm laser pulsing in BPA in the presence of EtOH as a H-atom donor in ACN at 295 K. The intensity of triplet BPA at 485 nm decreased with a rate (k_{obsd}) of $2.5 \times 10^6\,s^{-1}$ while an absorption band at 357 nm and a small band at 572 nm, both of which are ascribable to the BPAK formed by H-abstraction by n,π* triplet BPA, appeared with the same rate as the k_{obsd} value. The quenching rate constant (k_q) of triplet BPA by EtOH was determined to be $1.4 \times 10^6\,dm^3\,mol^{-1}\,s^{-1}$, which is in the same magnitude of order as those for triplet BP by alcohols [6]. The procedure determining the k_q is described in Supplementary data. The ε values of the BPAK were determined to be 21,000 ± 2000 $dm^3\,mol^{-1}\,cm^{-1}$ at 357 nm and 2400 ± 200 $dm^3\,mol^{-1}\,cm^{-1}$ at 572 nm by using laser photolysis techniques on H-abstraction of triplet BPA from phenol (PhOH), based on the ε value of the phenoxy radical. The determining processes for these ε values are also described in Supplementary data.

4. Conclusion

We report a synthesis procedure 1-benzoyl-2-phenylacetylene (BPA) readily prepared from DPPA, and have studied the photochemical features of BPA using steady state and laser flash photolysis techniques in solution. BPA shows a desired value of 65.2 kcal mol^{-1} that locates in the blank range (62–69 kcal mol^{-1}) of E_T values for triplet sensitizers. The photophysical and photochemical features of BPA are very similar to those of BP except for the E_T values. The present report would provide

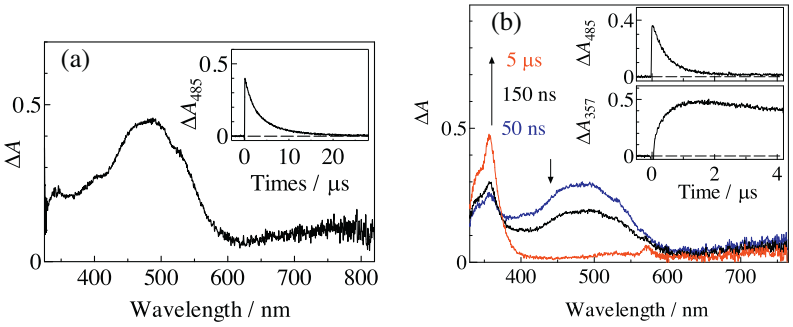

Fig. 2. (a) A transient absorption spectrum obtained at 50 ns upon 308 nm laser pulsing in BPA in Ar-purged ACN at 295 K. Inset; a trace at 485 nm. (b) Absorption spectral changes upon 308 nm laser pulsing in BPA in the presence of [EtOH] = 1.2 mol dm^{-3} in Ar-purged ACN at 295 K. Insets; traces at 485 nm (upper) and 357 nm (lower).