

PHOTOINDUCED ELECTRON TRANSFER REACTIONS OF 1,4-DIPHENYL-1,3-BUTADIENE

BANG DUK KIM and SANG CHUL SHIM*

Department of Chemistry, The Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea

(Received 30 January 1998; accepted 20 February 1998)

Abstract – Irradiation of diphenylbutadiene (DPB) in methanol with 9,10-dicyanoanthracene (DCA) yields four methanol adducts, two more than the products obtained in the absence of DCA. Laser flash photolysis studies indicate the reaction to proceed through a photoinduced electron transfer mechanism involving DPB cation radical and DCA anion radical.

INTRODUCTION

We have been interested in the photochemistry of diphenylbutadiene (DPB) for some time.^{1–6} Irradiation of DPB with methanol gives 1:1 photoadducts as major products along with minor photoreduction products. The 1:1 photoadducts are formed from the singlet excited state of DPB, while the photoreduction products are generated from the triplet state.⁵ The lowest singlet excited state of the DPB shows a high degree of charge transfer character like zwitterion, while the triplet state behaves like a biradical.⁶ The charge seems to be delocalized throughout the conjugated system in the excited singlet state.

However, the mechanism of the photoreaction of DPB is not firmly established and radical ion pair mechanism is suspected to participate in the reaction. To make insight into the mechanism, the photoreaction was carried out with 9,10-dicyanoanthracene (DCA) as an electron acceptor (Fig. 1).

MATERIALS AND METHODS

Materials and Solvents. DPB was synthesized as reported.⁷ 9,10-Dicyanoanthracene (DCA) (Eastman Kodak) was recrystallized from pyridine. Azulene (Aldrich) was used after vacuum sublimation.⁸ Distilled methanol from calcium hydride was used for photoreactions. Chromatographic and spectroscopic grade solvents were used for high-performance liquid chromatography (HPLC), UV-visible absorption, and photoluminescence spectra, respectively. Doubly distilled water was used for HPLC.

Instruments. ¹H NMR and ¹³C NMR spectra were recorded on Bruker AM-300, and AM-200 MHz spectrometers. Infrared (FT-IR) spectra were recorded on a Bomem MB-100 Series FT-IR spectrophotometer. UV-visible absorption spectra were recorded on a Shimadzu 3100S spectrophotometer.

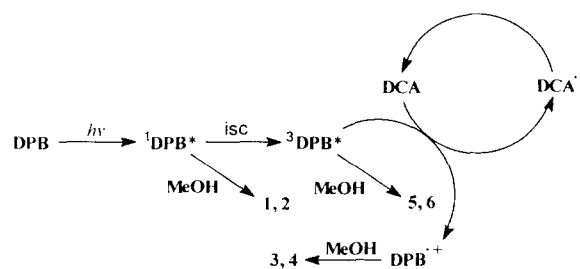


Figure 1. A plausible mechanism of photoinduced electron transfer reactions of DPB with methanol in the presence of DCA.

Fluorescence and phosphorescence spectra were recorded on a Perkin-Elmer LS-50 luminescence spectrophotometer with a gated photomultiplier tube detector at room temperature and 77K with modification of cell compartment. Mass spectra were determined at 70 eV with V.G. AutoSpec Ultra by the electron impact (EI) method. HPLC was performed on a Waters Associates Model 712 WISP HPLC equipped with a Waters 510 solvent delivery system, Waters 486 tunable absorbance detector fixed at 254 nm. Time resolved laser flash photolysis was performed on Nd:YAG laser (Spectron SL803G) equipped with a cw Xe-arc lamp (Atago Bussan Co. XC-150), monochromator (Jovin-Yvon HR320), and 500 MHz digital storage oscilloscope (DSO, Hewlett Packard HP54503A).

Photolysis of DPB in Methanol. Degassed 4 mM methanol solution of DPB (154 mg) was irradiated with 300 nm UV light in a Rayonet Photochemical Reactor Model RPR-208 equipped with RUL-3000 Å lamps. After the irradiation for 60 h, the resulting photoreaction mixture was concentrated in vacuum. The photoadducts, **1** and **2**, were isolated by column chromatography using diethyl ether : *n*-hexane (v/v, 1:60) as an eluting solvent, followed by HPLC using diethyl ether : *n*-hexane (v/v, 1:50) as eluent.

Compound **1** : IR (NaCl) 3054, 2850, 2190, 1609 cm⁻¹; ¹H NMR (CDCl₃) δ 3.92(s, 3H, OCH₃), 5.95(s, 1H, =CH), 7.20–7.64(m, 10H, aromatic); ¹³C NMR (CDCl₃) δ 57.0, 84.2, 92.6, 115.2, 122.3, 126.6, 128.3, 128.4, 128.7, 128.8, 131.5, 135.7,

* To whom correspondence should be addressed.

138.8 ppm; Mass (EI), m/e 235.107 (M^+)

Compound **2**: IR (NaCl) 3055, 2850, 2208, 1612 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.78(s, 3H, OCH_3), 6.24(s, 1H, =CH), 7.19-7.71(m, 10H, aromatic); ^{13}C NMR (CDCl_3) δ 56.1, 83.8, 95.0, 113.2, 122.2, 126.7, 127.9, 128.2, 128.5, 129.0, 131.6, 135.1, 139.1 ppm; Mass (EI), m/e 235.108 (M^+)

Photolysis of DPB in Methanol in the presence of DCA. Solution of DPB in methanol containing 0.1 mM DCA was photolyzed by following the procedures described above.

Compound **3**: IR (NaCl) 3053, 2849, 2204, 1614 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.18(s, 3H, OCH_3), 5.55(s, 1H, =CH), 7.21-7.62(m, 10H, aromatic); ^{13}C NMR (CD_3COCD_3) δ 60.1, 86.9, 87.4, 94.3, 125.0, 126.6, 128.8, 129.3, 129.4, 130.1, 131.6, 136.6, 164.7 ppm; Mass (EI), m/e 235.109 (M^+)

Compound **4**: IR (NaCl) 3054, 2835, 2196, 1613 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.80(s, 3H, OCH_3), 5.17(s, 1H, =CH), 7.29-7.41(m, 8H, aromatic), 7.93-7.98(m, 2H, aromatic); ^{13}C NMR (CDCl_3) δ 55.9, 80.9, 87.6, 91.2, 124.3, 127.3, 127.7, 128.0, 128.2, 129.3, 130.8, 134.9, 164.8 ppm; Mass (EI), m/e 235.108 (M^+)

Time-resolved Laser Flash Photolysis Experiments. The fourth harmonic (266nm) output from a Q-switched Nd:YAG laser was used as an excitation source. The time duration of the excitation pulse was *ca.* 5 ns, and the pulse energy was typically 55 mJ. A cw Xe-arc lamp was used as a probe light source for the transient absorption measurements. The probe light after the reaction cell was focused into the entrance slit of a 320 nm monochromator. The slit width of the monochromator was adjusted to obtain the spectral resolution of *ca.* 1 nm in the 200 ~ 600 nm range. A photomultiplier tube (PMT) was attached to the exit slit of the monochromator for the signal detection.

Typically, signals from *ca.* 100 ~ 150 shots of the laser pulses were averaged. The temporal profile of the transient absorption signal was monitored by a 500 MHz digital storage oscilloscope.

The concentration of solution was adjusted to give *ca.* 1.0

absorbance at 266 nm. The I-L sample solution was circulated through a quartz cuvette with a 10 mm pathlength (Hwima QS 1.0) to reduce effects caused by the accumulation of the reaction products.

Relative Quantum Yield Measurements. The sample solutions were degassed by three freeze-pump-thaw cycles with cooling in liquid nitrogen and were sealed. These samples were irradiated with 300 nm light for 30 min in a merry-go-round apparatus. Quantitative analysis was carried out by integration of the peak areas of photoproducts on HPLC. Diphenylacetylene as an internal standard, Merck Lichrosorb RP-18 ($5\mu\text{m}$) column, and methanol : water : tetrahydrofuran (v/v/v, 10:3:1) eluent were used.

Quenching Experiment with Azulene. Degassed solutions of DPB (4 mM), DCA (0.1 mM), and azulene (4 mM) in methanol were irradiated with 300 nm light for 6 h. The qualitative analysis was carried out by measuring the ^1H NMR peak ratio of methanol on photoadducts.

RESULTS AND DISCUSSION

Irradiation of a methanol solutions of DPB with 300 nm light yields products **1** and **2** as major photoadducts probably through a zwitterion-like excited singlet state, and minor photoreduction products **5** and **6** from the biradical-like triplet excited state. The *Z*-isomer **2** was obtained as the major addition product while *E*-isomer **6** was the major reduction product (Fig. 2).

Photolysis of methanol solutions of DPB in the presence of DCA results in the formation of major methanol photoadducts **1-4** and minor photoreduction products **5** and **6** (Fig. 2, Table 1). Higher yields of products **1** and **2** are expected in the presence of DCA if **1** and **2** are formed through a radical ion pair. Photolysis of DPB with DCA, however, did not enhance the yields

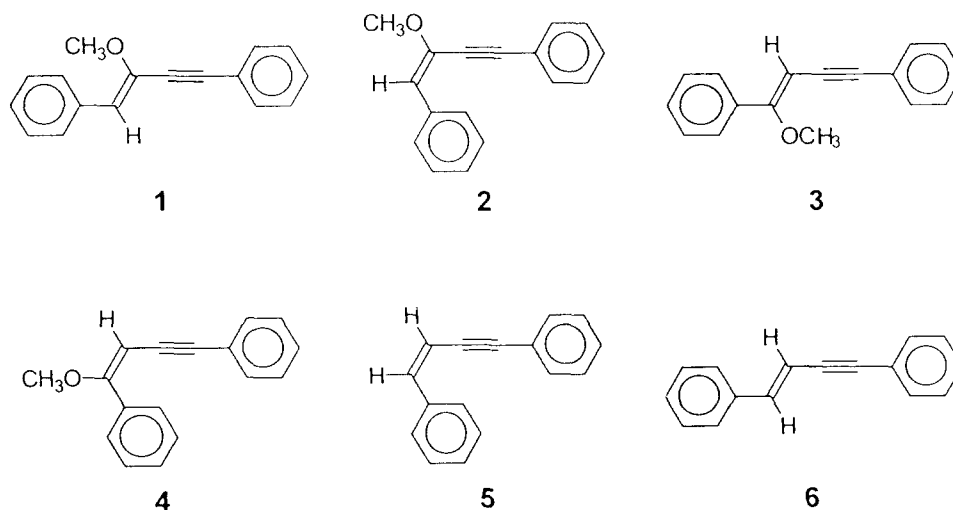


Figure 2. The methanol photoadducts and photoreduction products.

Table 1. Relative quantum yields and isolation yields. Most of the unreacted DPB was recovered intact ($> ca. 80\%$).

Isolation yield	1, 2		3, 4	
-	6.0		-	
DCA	5.7		3.6	
Quantum yield	1	2	3	4
-	1.1	1.0	-	-
DCA	1.0	0.6	0.4	0.2

of **1** and **2** and gave almost the same amounts of **1** and **2** in addition to new methanol photoadducts **3** and **4**. The relative quantum yields of **1** and **2** are slightly decreased in the presence of DCA on the contrary to our expectation. The quantum yields of **3** and **4** are smaller than those of **1** and **2** (Table 1). A 2:1 methanol photoadduct was also obtained in trace amounts, structure of which could not be determined. The results suggest that **1** and **2** are not generated through a radical ion pair but the new methanol photoadducts **3** and **4** are formed through a radical ion pair as proposed in Fig.1.⁹ In this mechanism, DCA anion radical and DPB cation radical pair is formed where DCA plays a role as an electron acceptor.

DPB shows intense absorption peak at 300 nm, while DCA does not absorb the light at this wavelength indicating the excited DPB transfers an electron to the ground state DCA to form a radical ion pair.

Laser flash photolysis was carried out under argon atmosphere to test the proposed mechanism. Oxygen is removed by bubbling the solution with argon to avoid the quenching of triplet states. Fig. 3 (a) shows a strong triplet-triplet absorption of DPB at 435 nm after excitation of DPB methanol solution. The λ_{max} of DCA anion radical appears at 470 nm as reported earlier.^{10, 11} A small absorption band at 400 nm appears as the triplet-triplet absorption of DPB at 435 nm decreases as shown in Fig. 3 (b). This band can be assigned to a DPB

Table 2. Azulene quenching of transients.

Detection Wavelength	Life Time (τ)	
	No azulene	Azulene (0.04 mM)
400 nm	1.9 μ s	-
435 nm	2.3 μ s	1.9 μ s
470 nm	3.5 μ s	-

cation radical because 400 nm and 470 nm bands always appear simultaneously while the intensity of the band at 435 nm is decreased. All the absorption bands show only the first order decay. The lifetime of every species is shown in Table 2. Azulene quenching experiment was carried out to identify the excited state, singlet or triplet excited state, which is responsible for the formation of the radical ion pair of DPB and DCA. The lifetime of DPB triplet state decreased from 2.3 μ s to 1.9 μ s in the presence of azulene due to the efficient quenching of the triplet state of DPB by azulene. DCA anion radical was not generated in the presence of azulene strongly indicating that the triplet state of DPB transfers an electron to the ground state DCA molecule. Consequently, photoadducts **3** and **4** formed through the radical ion pair of DPB and DCA were not formed in the presence of azulene. The products **3** and **4** are, therefore, generated through a radical ion pair which is formed *via* photoinduced electron transfer from DPB to DCA.

CONCLUSION

The 9,10-dicyanoanthracene (DCA) leads to the formation of radical ion pair which gives new methanol photoadducts, **3** and **4**, in the photolysis of 1,4-diphenyl-1,3-butadiyne (DPB) in methanol.

The transient intermediates, DPB cation radical and DCA anion radical, were detected at 400 nm and 470

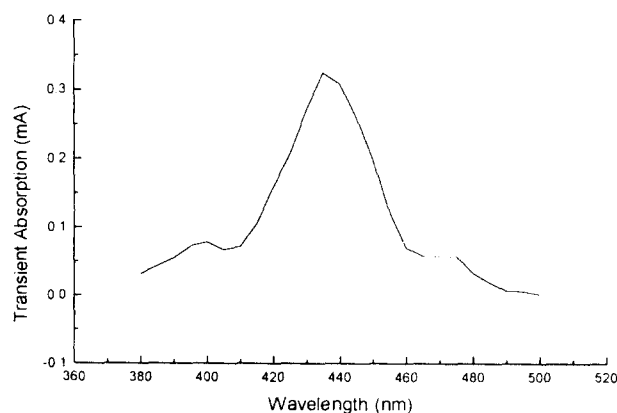
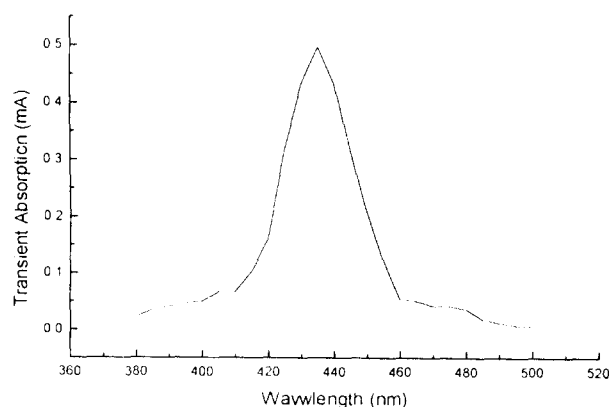


Figure 3. Transient absorption spectra of (a) DPB (b) a mixture of DPB, DCA. The concentration of solutions was adjusted to give ca 1.0 absorbance at 266 nm.

nm, respectively, in the laser flash photolysis. The triplet-triplet absorption of DPB was detected at 435 nm. The triplet state of DPB was quenched by azulene, and photoadducts **3** and **4** were not generated in the presence of azulene indicating that **3** and **4** are formed through a radical ion pair intermediate formed through the excited triplet state of DPB.

Acknowledgement – This investigation was supported by OCRC-KOSEF, Ministry of Education (BSRI-97-3406) and the Korea Advanced Institute of Science and Technology. We thank Dr. Nam Woong Song and Dr. Dongho Kim at the Korea Research Institute of Standards and Science for laser flash photolysis experiments.

REFERENCES

1. Lee, T. S., S. J. Lee, S. C. Shim (1990) [2+2] Photocycloaddition reaction of aryl-1,3-butadiynes with some olefins. *J. Org. Chem.* **55**, 4544-4549.
2. Lee, S. J. and S. C. Shim (1990) Photochemistry of conjugated polyacetylenes: Photoreaction of 1,4-diphenyl-1,3-butadiyne with dimethyl fumarate. *Tetrahedron Letters* **31**(43), 6197-6120.
3. Lee, S. J., J. H. Kwon and S. C. Shim (1991) Photochemistry of conjugated polyacetylenes. Photoreaction of 1,4-diphenyl-1,3-butadiyne with unsymmetrical olefins. *Chemistry Letters* 1767-1770.
4. Lee, T. S., S. C. Shim and S. S. Kim (1986) The Photoaddition reaction of 1,4-diphenyl-1,3-butadiyne with 5-fluorouracil. *Bull. Korean Chem. Soc.* **7**(3), 228-230.
5. Lee, T. S. and S. C. Kim (1986) Photoreaction of 1,4-disubstituted-1,3-butadiyne with alcohol. *Bull. Korean Chem. Soc.* **7**(2), 116-120.
6. Shim, S. C. and T. S. Lee (1990) Photoreaction of 1-(1-naphthyl)-1,3-butadiynes with methanol. *J. Photochem. Photobiol. A: Chem* **53**, 323-334.
7. Shim, S. C. and T. S. Lee (1986) Synthesis of some conjugated polyynes. *Bull. Korean Chem. Soc.* **7**(5), 357-362.
8. Perrin, D. D., W. L. F. Armarego and B. R. Perrin (1980) *Purification of Laboratory Chemicals*, p. 147, Pergamon Press, Oxford.
9. Fagnoni, M. and M. Mella (1995) Radical addition to alkenes via electron transfer photosensitization. *J. Am. Chem. Soc.* **117**, 7877-7881.
10. Brown-Wensley, K. A., S. L. Mattes and S. Farid (1978) Photochemical electron-transfer and triplet reactions of 1,2-diphenylcyclopropene-3-carboxylate. *J. Am. Chem. Soc.* **100**, 4162-4172.
11. Spada, L.T. and C. S. Foote (1979) Electron-transfer photooxidation. 3. Detection of radical-ion intermediates in the cyanoaromatic-sensitized photooxidation of trans- and cis-stilbene. *J. Am. Chem. Soc.* **102**, 391-393.