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Formation and Properties of Enyne Radical Cation

Bang Duk Kim[1], Sang Chul Shim*[1], Noboyuki Ichinose[2], Sachiko Tojo[2], and Tetsuro Majima[2]
[1]Department of Chemistry, School of Molecular Science-BK21, Korea Advanced Institute of Science and Technology, Yusung-Gu, Taejon 305-701, South Korea
[2]The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

Radical cations of DPBEY and PPCB were generated by γ-radiolysis and pulse radiolysis in halogenated solvents. The radical cation $PPCB^{\bullet+}$ shows 505 (shoulder) and 520 nm absorption peaks with 700 ns lifetime in agreement with the laser flash photolysis work and strongly support the exciplex mechanism proposed for the photoreaction of PPCB and dimethylfumarate.

key words: Radical cation, exciplex, ^{60}Co γ - radiolysis, pulse radiolysis, enyne

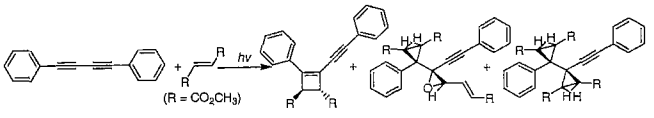
INTRODUCTION

Photolysis of conjugated polyalkynes with simple olefins normally yields [2+2] type cycloaddition products, cyclobutenes, through cumulene-type triplet excited states [1]. The regio- and site-selectivity of the reaction are dependent upon the kind of terminal groups and the number of conjugated triple bonds of polyalkynes, and on the electronic character of the substrate olefins. The electron deficient olefins are more reactive than the electron rich olefins.

Irradiation of 1,4-diphenylbutadiyne (DPB) with dimethyl fumarate (DMFu), however, yields unexpected oxirane and cyclopropane adducts along with a normal cyclobutene adduct [2,3] (Scheme 1.).

The formation of oxirane and cyclopropane adducts is very interesting and the mechanism of the reaction is proposed to involve a geminate radical ion pair type exciplex of PPCB and DMFu [4].

Enynes are compounds having neighboring C=C double bond and C≡C triple bond. Six electrons are conjugated in the skeleton including four carbon atoms. Radical cations of enynes can be generated from one electron oxidation with electrochemical, photochemical, and radiation chemical reactions, although their formation and transient behaviors have not been reported.



Scheme 1.

*To whom correspondence should be addressed.
E-mail : scshim@mail.kaist.ac.kr
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Radiolysis of a halogenated solution including an organic compound (M) is a convenient method to generate the radical cation ($M^{\bullet+}$). We have studied formation and absorption of radical cations of enynes such as 1,4-diphenylbutenyne (DPBEY) and a enyne derivative (PPCB), dimethyl 1-phenyl-2-phenylethynyl-3,4-dicarboxylate with γ-radiolyses of DPBEY and PPCB in n-butyl chloride rigid matrices at 77 K and pulse radiolyses of DPBEY and PPCB in 1,2-dichloroethane (DCE) at room temperature to prove the geminate radical ion pair type exciplex mechanism for the photoreaction of DPB and DMFu.

MATERIALS AND METHODS

Materials and Solvents

DPB and DPBEY were synthesized by the reported methods. PPCB was synthesized by photolysis of DPB with DMFu. Chromatographic and spectroscopic grade solvents were used for radiolyses.

Methods

Pulse radiolyses were performed, as described previously [5], using an electron pulse (28 MeV, 8 ns, 0.7 kGy per pulse) from a linear accelerator at Osaka University. γ-Radiolyses were carried out using a ^{60}Co γ source (dose, 2.6×10^2 to 1.0×10^3 Gy) [5]. Optical absorption spectra were taken by a Shimadzu 3011S spectrophotometer and a multichannel photodetector. n-Butyl chloride rigid matrix containing DPBEY or PPCB with 5.0 mM were used for the γ-radiolyses at 77 K 1,2-Dichloroethane (DCE) solution containing DPBEY or PPCB with 5-7.2 mM were used for the pulse radiolyses at room temperature. The solutions were prepared freshly in 1 cm × 1 cm rectangular Suprasil cells for the pulse radiolyses and in 1.5 mm thick Suprasil cells for UV-vis absorption measurements at 77 K before irradiation and were degassed by freeze-pump-thaw cycles.

RESULTS AND DISCUSSION

γ-Radiolysis at 77 K

An absorption spectrum with peaks at 530 nm and 770 nm and serveral shoulder peaks at 470 and 500 nm was observed after γ-radiolyses of DPBEY in n-butyl chloride rigid matrix at 77 K (5.0 mM) (Fig. 1a). The spectrum assigned to $DPBEY^{\bullet+}$ disappeared without formation of other absorption peaks with warming up to 80 K. The disappearance corresponds to the neutralization of $DPBEY^{\bullet+}$ with Cl^- generated in the initial radiolytic processes of n-butyl chloride. It is considered that $DPBEY^{\bullet+}$ is unimolecularly stable and decays through the neutralization with Cl^-.

The similar absorption spectrum with peaks at 530 and 770 nm and several shoulder peaks at 470 and 500 nm was observed after γ-radiolyses of PPCB in n-butyl chloride rigid matrix at 77 K (5.0 mM) (Fig. 1b). The spectrum assigned to $PPCB^{\bullet+}$ disappeared without formation of other absorption peaks on warming up to 80 K. The disappearance corresponds to the neutralization of $PPCB^{\bullet+}$ with Cl^- generated in the initial radiolytic processes of n-butyl chloride. It is considered that $PPCB^{\bullet+}$ is unimolecularly stable and decays through the neutralization with Cl^-.

Pulse radiolysis at room temperature

A transient absorption spectrum with peaks at 505 (shoulder) and 520 nm was observed immediately after the pulse radiolysis of DPBEY in DCE (5.0 mM) at room temperature (Fig. 2a). The spectrum assigned to $DPBEY^{\bullet+}$ decayed according to the second-order reaction rate equation with the half-lifetime of 700 ns. No formation of a new peak was observed during the decay. The decay corresponds to the neutralization of $DPBEY^{\bullet+}$ with chlorine anion generated in the initial radiolytic processes of DCE. It is considered that

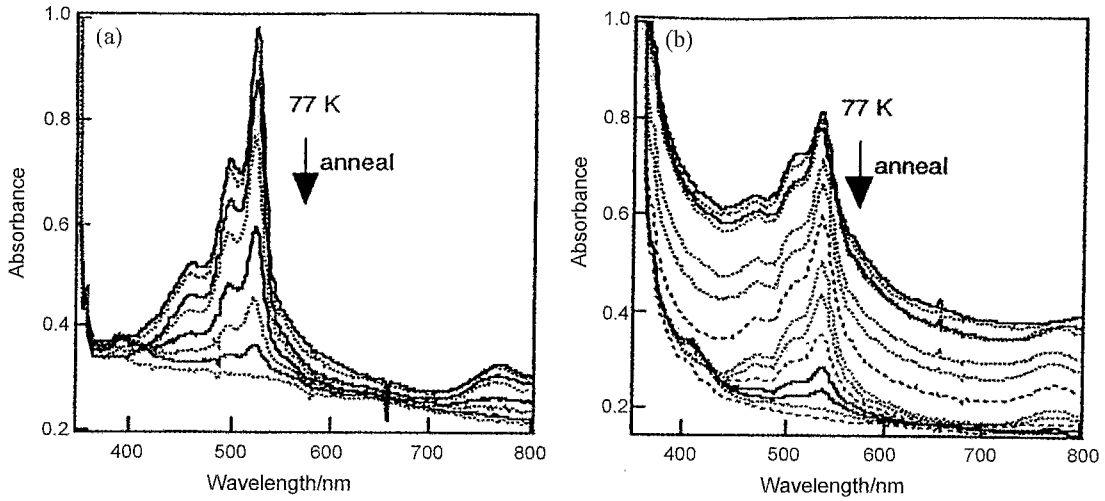

Figure 1. Absorption spectral changes observed with annealing from 77 K up to 80 K after γ-radiolyses of DPBEY (5.0 mM) (a) and PPCB (5.0 mM), (b) in n-butyl chloride rigid matrices at 77 K.

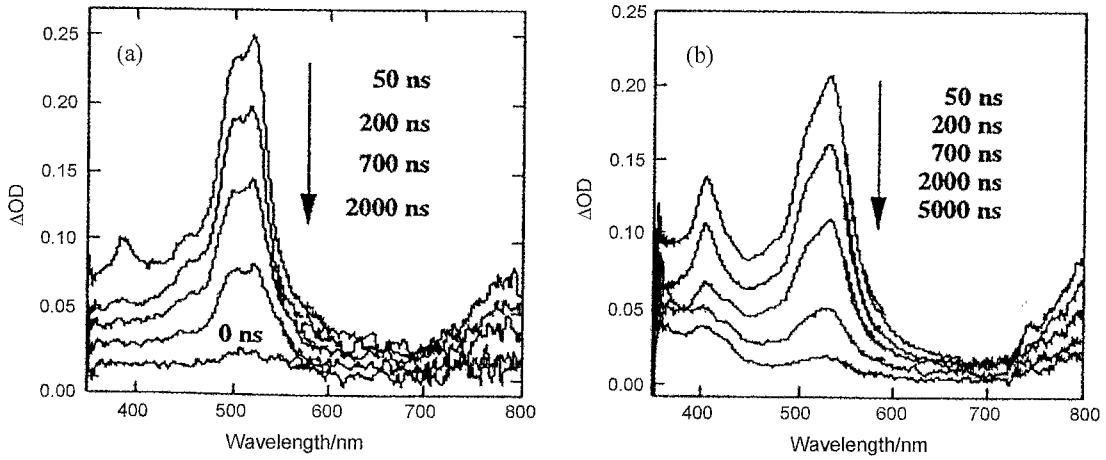

Figure 2. Transient absorption spectral changes observed during the pulse radiolyses of DPBEY (5.0 mM) (a) and PPCB (7.2 mM), (b) in DCE at room temperature. Time after the electron pulse.

DPBEY$^{\bullet+}$ is unimolecularly stable and decays through the neutralization with Cl^-.

A similar transient absorption spectrum with peaks at 505 (shoulder) and 520 nm was observed immediately after the pulse radiolysis of PPCB in DCE (7.2 mM) at room temperature (Fig. 2b). The spectrum assigned to PPCB$^{\bullet+}$ decayed according to the second-order reaction rate equation with the half-lifetime of 700 ns. No Formation of a new peak was observed during the decay. The decay corresponds to the neutralization of PPCB$^{\bullet+}$ with Cl^-. It is considered that PPCB$^{\bullet+}$ is unimolecularly stable and decays through the neutralization with Cl^-.

The results strongly support the laser flsh photolysis work. Laser flash photolysis of PPCB in dichloromethane or acetonitrile shows triplet-triplet absorption at 440 nm while the mixture of PPCB and DMFu shows peaks at 510, 440, and 410 nm which are attributed to PPCB$^{\bullet+}$, triplet state of PPCB, and DMFu$^{\bullet-}$, respectively. The peak at 410 nm was identified as the radical anion of DMFu as reported [6] and 440 nm peak is due to the triplet-triplet absorption as observed in the photolysis of PPCB alone in dichloromethane. The peak at *ca.* 510 nm can be assigned to PPCB$^{\bullet+}$ which is formed by electron transfer from PPCB* to DMFu leading to the exciplex [PPCB$^{\bullet+}$-DMFu$^{\bullet-}$]*. Excitation of PPCB-DMFu solution in acetonitrile showed stronger absorption peak at 510 nm by PPCB$^{\bullet+}$ due to the extensive charge separation and stabilization of radical ion pair, [PPCB$^{\bullet+}$-DMFu$^{\bullet-}$]*, in polar solvents. These results strongly indecate that 510 nm peak in laser flash photolysis and pulse radiolysis is due to PPCB$^{\bullet+}$, and an exciplex is formed along with the triplet excited state of PPCB in the photolysis of PPCB with DMFu [4], and an exciplex mechanism is unequivocally proven for the photo-addition of PPCB to DMFu.

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3. **Compound 1**: ^{1}H-NMR(300 MHz, $CDCl_3$), δ=7.37-7.26(m, 10H), 6.80/6.27(d/d, J=15.6 Hz, 1H/1H), 4.28/4.19(d/d, J=9 Hz, 1H/1H), 3.77(s, 3H), 3.72(s, 3H), 3.36(s, 3H), 3.26(s, 3H); ^{13}C-NMR(75 MHz, $CDCl_3$) δ=170.86, 169.41, 165.79, 143.27, 136.30, 131.73, 128.56, 128.15, 127.97, 127.65, 125.97, 124.50, 122.28, 105.81, 92.16, 85.60, 82.44, 54.96, 52.04, 51.90, 51.77, 51.66, 51.27,42.34 ppm; MS(70 eV), m/e=490(M^+,1.5%) **Compound 2**: ^{1}H-NMR(300 MHz, $CDCl_3$), δ=7.44-7.11(m, 10H), 4.03/3.97(d/d, J=9.10 Hz, 1H/1H), 4.23/3.97(d/d, J=9.43 Hz, 1H/1H), 3.75(s, 3H), 3.73(s, 3H), 3.73(s, 3H), 3.67(s, 3H), 3.10(s, 3H); ^{13}C-NMR(75 MHz, $CDCl_3$) δ=171.66, 170.87, 170.72, 170.58, 137.90, 132.30, 132.21, 129.12, 128.93, 128.76, 128.44, 128.09, 127.43, 122.96, 91.50, 85.14, 55.64, 52.96, 52.82, 52.35,47.78, 46.45, 46.14, 44.70, 44.25 ppm; MS(70 eV), m/e=490(M^+, 3.1%)
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