Direct Observation of Two Different Types of TMM Intermediates in the Photoinduced Electron-Transfer Degenerate Methylenecyclopropane Rearrangement

Hiroshi Ikeda,† Tatsuo Nakamura,† Tsutomu Miyashi,*,†
Joshua L. Goodman,‡ Kimio Akiyama,§ Shozo Tero-Kubota,§
Abdelaziz Houmam,⊥ and Danial D. M. Wayner⊥

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
Department of Chemistry, University of Rochester
Rochester, New York 14627
Institute for Chemical Reaction Science
Tohoku University, Sendai 980-8577, Japan
Steacie Institute for Molecular Sciences
National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R6

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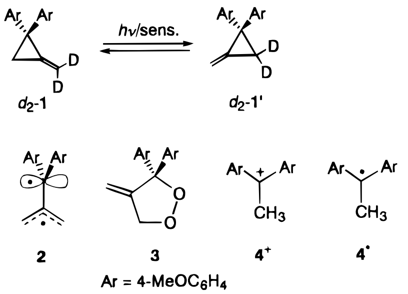
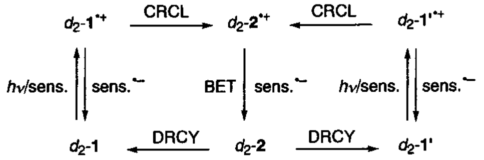
We previously reported that 4,4-dideuterio-2,2-bis(4-methoxyphenyl)-1-methylenecyclopropane (d_2-**1**)[1] undergoes the degenerate methylenecyclopropane (MCP) rearrangement, involving the bisected trimethylenemethane (TMM) cation radical intermediate (d_2-**2**$^{\bullet+}$)[4] under the triplet-sensitized photoinduced electron-transfer (PET) conditions (Chart 1). We now report further mechanistic studies based on nanosecond laser flash photolysis (LFP), EPR spectroscopy, and time-resolved photoacoustic calorimetry (PAC) that support a new, energetically favorable mechanism that requires both TMM cation radical d_2-**2**$^{\bullet+}$ and TMM d_2-**2** as key intermediates in the rearrangement sequence.

Table 1 shows photostationary ratios (d_2-**1**:d_2-**1′**) of the degenerate MCP rearrangement of d_2-**1**, yields of dioxolane (**3**) in oxygenation of **1** and transient absorption maxima (λ_{max}) observed in LFP of **1** under the 9,10-dicyanoanthracene (DCA)-, 1,2,4,5-tetracyanobenzene (TCNB)-, or *N*-methylquinolinium tetrafluoroborate (NMQ$^+$BF$_4^-$)-sensitized conditions. A mechanistic connection among rearrangement, oxygenation, and transient absorption provides evidence for the participation of TMM cation radical **2**$^{\bullet+}$ and TMM **2** in the degenerate rearrangement sequence. Relevant results were obtained under the TCNB- and NMQ$^+$-BF$_4^-$-sensitized conditions (entries 3−6). Oxygenation of **1** to give **3**[1,5] and the degenerate rearrangement of d_2-**1** occur efficiently under the sensitized conditions in which two transient absorptions at $\lambda_{max} = 351$ and 500 nm were observed by LFP (entry 3 or 5). Interestingly, under the sensitized conditions in which only the transient absorption at $\lambda_{max} = 354$ nm was observed the degenerate rearrangement occurs efficiently but not oxygenation (entry 4). Conversely, oxygenation proceeds rapidly but not rearrangement under the sensitized conditions in which the transient, $\lambda_{max} = 498$ nm was predominant (entry 6). These results suggest that the air-sensitive,[6] longer wavelength transient is a precursor for oxygenation product **3**, whereas the shorter wavelength transient species is a precursor for rearrangement product **1**. The identities of the 350 and 500 nm transients may be inferred from the absorption spectra of cation **4**$^+$ (484 nm in CH$_3$CN and 499 nm in CH$_2$Cl$_2$[7]) and radical **4**$^\bullet$ (349 nm in CH$_3$CN and 352 nm in CH$_2$Cl$_2$[8]). Thus, the λ_{max} around at 500 and 350 nm can be unambiguously assigned to the 1,1-bis(4-methoxyphenyl)ethyl cation moiety of the bisected TMM cation radical **2**$^{\bullet+}$ and the 1,1-bis(4-methoxyphenyl)ethyl radical moiety of the bisected TMM **2**.[9] The most reasonable process to form **2** is back electron transfer (BET)[11] from the sensitizer anion radical to **2**$^{\bullet+}$ within a contact or solvent separated ion radical pair [**2**$^{\bullet+}$/sens.$^{\bullet-}$].

Chart 1



Scheme 1



The most reasonable mechanism, based on the spectroscopic evidence and the product analysis, that accounts for the participation of two different types of TMM intermediates is a cation radical cleavage-diradical cyclization (CRCL-DRCY) mechanism shown in Scheme 1. Cation radical d_2-**2**$^{\bullet+}$ formed by the CRCL of d_2-**1**$^{\bullet+}$ or d_2-**1′**$^{\bullet+}$ does not directly recyclize to d_2-**1**$^{\bullet+}$ and d_2-**1′**$^{\bullet+}$ but undergoes BET to form d_2-**2**. The degenerate MCP rearrangement is then completed by the DRCY of d_2-**2** to d_2-**1** and d_2-**1′**. This mechanism is supported by time-resolved PAC.[12] Using PAC for the **1**-DCA-biphenyl (BP) system, ΔH^{irp}([**2**$^{\bullet+}$/DCA$^{\bullet-}$]) was determined to be 37.0 ± 0.8 kcal/mol. This result indicates that recyclization of d_2-**2**$^{\bullet+}$ to d_2-**1**$^{\bullet+}$ and d_2-**1′**$^{\bullet+}$ is at least 16 kcal/mol endothermic because ΔH^{irp}([**1**$^{\bullet+}$/DCA$^{\bullet-}$]) is calculated to be 53.0 kcal/mol.[13,15] A MNDO UHF calculation[16] also supports the suggestion that the recyclization of d_2-**2**$^{\bullet+}$ at the cation radical stage is significantly endothermic: at this level

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† Graduate School of Science, Tohoku University.

‡ University of Rochester.

§ Institute for Chemical Reaction Science, Tohoku University.

⊥ National Research Council of Canada.

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(6) Under the DCA-BP-cosensitized conditions in CH$_3$CN in the presence of oxygen, LFP of **1** exhibited a new transient absorption with λ_{max} at 518 nm. The observed transient species may be assigned to a peroxy cation radical, a precursor of dioxolane **3**.

(7) Heublein, G.; Helbig, M. *Tetrahedron* **1974**, *30*, 2533−2536.

(8) Radical **4**$^\bullet$ was generated by photolysis of bis(4-methoxyphenyl)methane with di-*tert*-butyl peroxide (0.5 M) in CH$_3$CN and CH$_2$Cl$_2$.

(9) Intersystem crossing (ISC) of diradicals with small spin−orbit coupling interaction[10] proceeds generally with small Arrhenius *A* factor. From the Arrhenius plot of the decay rate constants of TMM **2** in the TCNB-sensitized LFP between 266.7 and 299.5 K in CH$_2$Cl$_2$, an activation energy (E_a) was determined to be 2.9 kcal/mol and small *A* factor ($10^{7.2}$ s^{-1}) was obtained. If the observed small *A* factor may be explained by ISC and large structural change from triplet TMM **2** to singlet **1**, TMM **2** observed in LFP is triplet and gives the singlet **1** via a surface crossing mechanism.

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Table 1. Results of the Degenerate MCP Rearrangement of d_2-**1**,[a] Oxygenation of **1**,[b] and LFP of **1**[c] under Various PET Conditions

entry	conditions	d_2-**1**:d_2-**1′** (time/h)	yield of **3**/% (time/min)	$\lambda_{max}(\mathbf{2})$/nm	$\lambda_{max}(\mathbf{2}^{\bullet+})$/nm	$\Delta OD(\mathbf{2}^{\bullet+})/\Delta OD(\mathbf{2})$[d]
1	DCA/CH_3CN	58:42 (4.5)	100 (15)	*e*	*f*	
2	DCA-BP/CH_3CN	slow	100 (15)	*e*	494[g]	
3	TCNB/CH_3CN	54:46 (4.5)	100 (20)	351	500	1.3
4	TCNB/CH_2Cl_2	56:44 (3)	4 (30)	354	*f*	~0
5	TCNB-BP/CH_2Cl_2	56:44 (2)	96 (15)	354	508	2
6	$NMQ^+BF_4^-$-toluene/CH_3CN	slow	100 (5)	350[h]	498[h]	>10

[a] Under N_2. [d_2-**1**] = 100 mM. Deuterated solvent and cosensitizer were used. [b] Under O_2. [**1**] = 10 mM. [c] Under N_2. [**1**] = 1 mM. [d] Ratio of ΔOD of $\mathbf{2}^{\bullet+}$ to that of **2** at 200 ns after excitation. [e] Not observable. [f] No transient absorption was observed. [g] See footnote 6. [h] Under air.

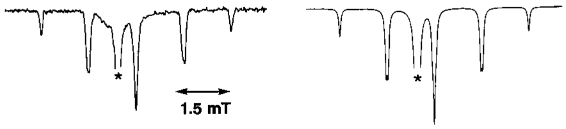

Figure 1. CIDEP spectrum (left) and its simulation (right) of $\mathbf{2}^{\bullet+}$. An asterisk, *, represents an emission due to chloranil anion radical.

$\mathbf{2}^{\bullet+}$ is located 18 kcal/mol lower in energy than $\mathbf{1}^{\bullet+}$. In contrast, BET from $DCA^{\bullet-}$ to d_2-$\mathbf{2}^{\bullet+}$ is estimated to be about 20.5 kcal/mol exothermic using the oxidation potential of $\mathbf{4}^{\bullet}$ ($E^{ox}_{1/2} = -0.06$ V vs SCE in CH_3CN) as determined by photomodulation voltammetry.[18] Thus the highly exothermic BET presumably occurs rapidly[19] to form d_2-**2**, which is 16.5 kcal/mol higher in energy than either d_2-**1** or d_2-**1′**.

The participation of two types of TMM intermediates in the degenerate MCP rearrangement of d_2-**1** was further directly confirmed by EPR spectroscopy using chloranil or anthraquinone as sensitizers.[1] Figure 1 (left) shows the time-resolved EPR spectrum of $\mathbf{2}^{\bullet+}$ observed at a delay time of 1 μs after the laser excitation of chloranil (10 mM) with **1** (50 mM) in DMSO[22] at ambient temperature. The hyperfine structure (hfs) was analyzed with two splitting constants corresponding to $\mathbf{2}^{\bullet+}$ [a_H (2H) = 1.38 mT, a_H (2H) = 1.44 mT, and g = 2.0026]. The observed spectrum was well reproduced by simulation, in which both the triplet (E) and radical pair mechanisms (E/A)[23] are taken into account [Figure 1 (right)]. Since the hfs constants and g-value of $\mathbf{2}^{\bullet+}$ are close to those of the neutral allyl radical,[24] it follows that the unpaired electron is mainly distributed over the allyl part and the positive charge is localized on the bis(4-methoxyphenyl)-methyl moiety. The structure of bisected TMM cation radical $\mathbf{2}^{\bullet+}$ elucidated by time-resolved EPR well agrees with that from LFP and CIDNP.[4]

On the other hand, irradiation of anthraquinone with **1** in a CH_2Cl_2 matrix at 20 K provided a characteristic EPR spectrum of randomly oriented triplet species ascribed to **2** along with $\mathbf{2}^{\bullet+}$. In addition to the $|\Delta M_s| = 1$ transition signals, a weak $|\Delta M_s| = 2$ transition was observed at 0.1673 T. The zero-field splitting parameters were estimated to be $|D/hc| = 0.0116$ and $|E/hc| = 0.0038$ cm^{-1} from the spectrum. The $|D/hc|$ value is small[25] compared with those of other phenyl-substituted TMM derivatives.[27] The triplet EPR signal of **2** persisted at cryogenic temperature, and the Curie plot of the $|\Delta M_s| = 2$ transition line intensity gave a straight line between 4.2 and 50 K, indicating that the ground state of **2** is triplet as usual TMMs. It is noteworthy that while the ground state of the parent TMM[28] is triplet with a planar structure in accord with calculation,[28b] the structure of TMM **2** is bisected regardless of its triplet ground state. Since **2** is formed by BET without significant conformational change, the bisected structure[29] of **2** is most likely due to that of $\mathbf{2}^{\bullet+}$ formed by the least motion ring cleavage[4] of $\mathbf{1}^{\bullet+}$ which requires only the rotation of the methylene group but not of the bulkier diarylmethylene group of $\mathbf{1}^{\bullet+}$.

The proposed rearrangement sequence including a diradical-forming BET process[30] was also suggested to similar PET MCP rearrangements of 2-aryl-1-methylenecyclopropane, 2,2-diaryl-1-methylenespiropentane,[32] and 1-cyclopropylidene-2,2-diarylcyclopropane.[32] The results herein provide the first observation of the interconversion of the relevant intermediates.

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Supporting Information Available: Transient absorption spectrum ($\mathbf{2}^{\bullet+}$ and **2**), deconvolution fitting parameters for the PAC waveforms (**1**-DCA-BP), and the Curie plot for **2** (4 pages, print/PDF). See any current masthead page for ordering and Web access instructions.

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(13) $\Delta H^{irp}([\mathbf{1}^{\bullet+}/sens.^{\bullet-}]) = 23.06\,[E^{ox}_{1/2}(\mathbf{1}) - E^{red}_{1/2}(sens.)\,] - C$ (in kcal/mol), where $E^{ox}_{1/2}(\mathbf{1}) = +1.35$ V vs SCE, $E^{red}_{1/2}(DCA) = -0.95$ V, and $E^{red}_{1/2}(NMQ^+PF_6^-) = -0.90$ V in CH_3CN and the Coulomb term (C) was ignored after Farid's example.[14]

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(15) For the **1**−$NMQ^+PF_6^-$−toluene system in CH_3CN, $\Delta H^{irp}([\mathbf{2}^{\bullet+}/NMQ^{\bullet}PF_6^-])$ was determined to be 35.0 ± 0.7 kcal/mol by PAC, and thus endothermicity for the *cation radical cyclization* of d_2-$\mathbf{2}^{\bullet+}$ is suggested to be about 17 kcal/mol endothermic based on $\Delta H^{irp}([\mathbf{1}^{\bullet+}/NMQ^{\bullet}PF_6^-])$, 51.9 kcal/mol.[13]

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(25) A small $|D/hc|$ value of **2** can be ascribed to its bisected form. If diphenylmethylenecyclopentane-1,3-diyl is planar,[26a] a decrease in $|D/hc|$ value of **2** is probably caused by molecular distortion of **2** as exemplified by a series of biphenyl derivatives,[26b] conjugated enones,[26c] and conjugated TMMs.[26d]

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