CHEMISTRY LETTERS, pp. 1889-1892, 1986.

Triplet States of Cyclic Olefins and Dienes. On the Lifetimes and Chemical Reactivities Studied by Pulse Radiolysis

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Triplet lifetimes of cyclic olefins and dienes measured by pulse radiolysis are dependent on the ring size which affects the most stable conformation of the triplet. In the case of cyclic nonconjugated dienes, an intramolecular biradical formation is an important decay process when the reaction is sterically allowed.

The cis-trans photoisomerization of cyclic and acyclic olefins via triplet state is one of the most studied photochemical reactions. With cyclic olefins, where the most stable orthogonal triplet is geometrically inhibited, the energy gap between T_1 and S_0 surface becomes relatively large which leads to a long lifetime and a specific chemical reactivity.[1)] For such a small or medium ring, dimerization and hydrogen abstraction, instead of cis-trans isomerization, become main type of reactions. In the case of cyclohexene and cycloheptene, the orthogonal triplet and highly strained trans ground state become close in energy.[2)] Thus, it is extremely difficult to distinguish them. Consideration of the lifetime of the active species seems to be very useful for the elucidation of the reaction mechanism. However, little is known about the information on the triplet lifetimes of simple olefins and the factors which affect the conformation and the chemical reactivity.

Recently, studies on such a transient triplet state have been successfully carried out by using laser flash photolysis[3)] and pulse radiolysis.[4)] In the present paper, we would like to report the lifetimes and the chemical reactivities of triplet states of cyclic olefins and dienes by a pulse radiolysis technique.

Pulse radiolysis of a benzene solution of cyclic olefin in the presence of perylene as a triplet monitor was carried out with an 8-ns electron pulse of high energy.[5)] Sample solutions were prepared freshly before irradiation and were degassed under high vacuum in a suprasil cell. The primary active species resulting from the irradiation of benzene solutions are excited singlet and triplet states of benzene ($^1B^*$, $^3B^*$) and benzene excimer which are quenched by cyclic olefin added in a high concentration ($\approx$0.3 mol dm^{-3}) to form excited singlet and triplet states of cyclic olefin ($^1Ol^*$, $^3Ol^*$). If the lifetime of $^3Ol^*$ is long enough, triplet energy transfer to perylene added in a very low concentraion ($\approx$1.0 mmol dm^{-3}) should occur in competition with dimerization. Since the triplet energy of perylene (35.1 kcal/mol)[6)] is lower than those of usual olefins and dienes, near the diffusion controlled rates are expected for the energy transfer reaction.

$$\begin{array}{lcl}
\mathrm{B} & \rightsquigarrow & {}^1\mathrm{B}^*\ ,\quad {}^3\mathrm{B}^*\ ,\quad \text{Excimer}\\
{}^1\mathrm{B}^* + \mathrm{Ol} & \longrightarrow & \mathrm{B} + {}^1\mathrm{Ol}^*\\
{}^3\mathrm{B}^* + \mathrm{Ol} & \longrightarrow & \mathrm{B} + {}^3\mathrm{Ol}^*\\
{}^3\mathrm{Ol}^* & \xrightarrow{k_d} & \mathrm{Ol}\\
{}^3\mathrm{Ol}^* + \mathrm{Ol} & \xrightarrow{k_{dd}} & \text{Dimers}\\
{}^3\mathrm{Ol}^* + \mathrm{Pe} & \xrightarrow{k_{et}} & \mathrm{Ol} + {}^3\mathrm{Pe}^*
\end{array}$$

Perylene triplet has a strong absorption band at 485 nm and is easily detectable. The formation of perylene triplet (k_{rise}) should follow pseudo-first-order kinetics which is related to the triplet lifetime of cyclic olefin ($\tau = k_d^{-1}$) and rate constants of energy transfer (k_{et}) and dimerization (k_{dd}) according to Eq. 1.

$$k_{rise} = k_d + k_{et}[\mathrm{Pe}] + k_{dd}[\mathrm{Ol}] \qquad (1)$$

Thus, plots of k_{rise} vs. [Pe] and of k_{rise} vs. [Ol] would allow determination of k_d, k_{et}, and k_{dd}. Typical examples are shown in Fig. 1.

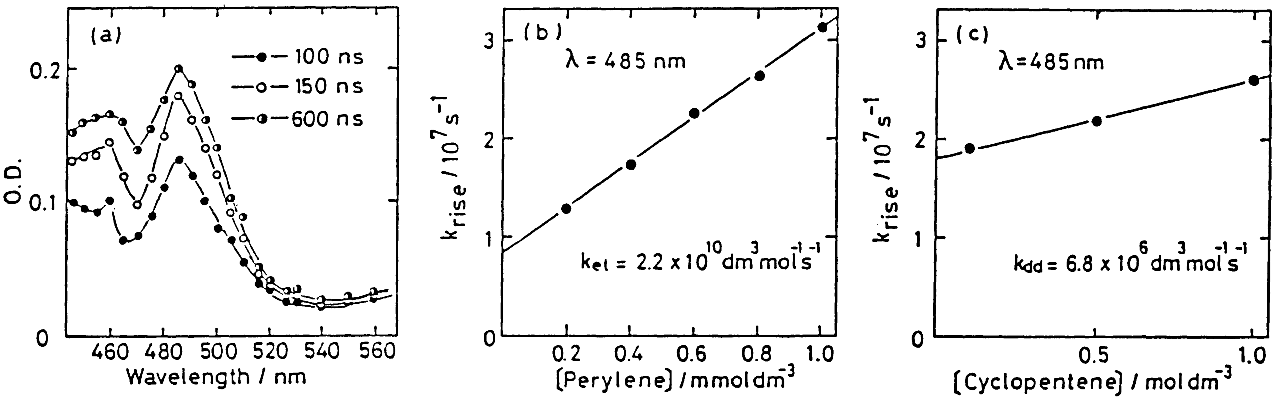
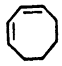
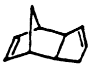
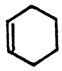
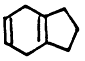


Fig. 1. (a) Transient absorption spectra of a benzene solution of cyclopentene containing perylene (cyclopentene, 0.3 mol dm^{-3}, perylene, 0.5 mmol dm^{-3}).
(b) Plot of k_{rise} vs. perylene concentration (cyclopentene, 0.3 mol dm^{-3}).
(c) Plot of k_{rise} vs. cyclopentene concentration (perylene, 0.5 mmol dm^{-3}).

In the case of cyclopentene, as shown in Fig. 1, k_{et} and k_{dd} were determined as 2.2×10^{10} and 6.8×10^6 $dm^3 mol^{-1} s^{-1}$, respectively, which provide the triplet lifetime of cyclopentene to be 150 ns. These kinetic parameters obtained with other cyclic olefins and dienes are summarized in Table 1.

In the case of cyclic olefins (**1**-**5**), triplet states were detected only in cyclobutene (**3**) and cyclopentene (**1**, **2**) derivatives, the lifetimes of which were in the range of 150 - 230 ns. The build-up of perylene triplets could not be detected for cyclohexene and cycloheptene. This fact is compatible with previous understandings that triplet states of cyclohexene and cycloheptene relax into a twisted form which undergoes a rather rapid intersystem crossing leading to the formation of a highly strained trans isomer. Such a decay path is not allowed for small-ring olefins where the triplet lifetime becomes long enough to subject dimerization. The dimerization of **1** and **2** via triplet has been previously reported.[7,8]

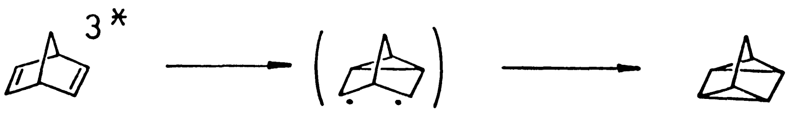
Table 1. Kinetic Parameters for Cyclic Olefins and Dienes

Substrate	τ [a] / ns	ket / $dm^3mol^{-1}s^{-1}$	kdd / $dm^3mol^{-1}s^{-1}$	Substrate	τ [a] / ns	ket / $dm^3mol^{-1}s^{-1}$	kdd / $dm^3mol^{-1}s^{-1}$
 **1**	150	2.2×10^{10}	6.8×10^{6}	 **8**	120 (140)[d]	1.8×10^{10}	f
 **2**	260 (250)[b]	1.2×10^{10}	6.4×10^{6}	 **9**	e	e	e
 **3**	230	1.4×10^{10}	f	 **10**	180	1.2×10^{10}	f
 **4**	e	e	e	 **11**	e	e	e
 **5**	e	e	e	 **12**	e	e	e
 **6**	5000 (1300)[c] (5200)[d]	1.3×10^{10}	2.7×10^{6} (2.0×10^{6})[c]	 **13**	e	e	e
 **7**	550 (390)[d]	1.1×10^{10}	f				

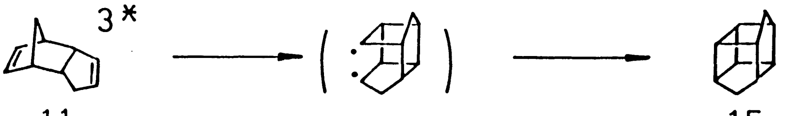
a) Triplet lifetime (kd^{-1}). b) Ref. 4a . c) Ref. 3c . d) Ref. 4c . e) The triplet formation of perylene was not detected. f) Dimer formation was not observed under these conditions.

Consideration of triplet lifetime of conjugated dienes (**6**-**8**) together with those of cyclopentadiene (1.7 μs)[4b] and 2,4-hexadiene (32 ns)[3c] indicates that the triplet lifetime of cyclic dienes are μs order for small rings and decreases for medium ring and finally approaches that of acyclic diene. Geometry of conjugated diene triplet has been estimated to be a twisted s-cis or s-trans allylmethylene.[3b,9] The very long lifetimes observed for small rings and **6** is consistent with their constraint to near planarity.

In the case of nonconjugated diene of small-rings(**9**-**13**), the triplet formation could not be detected except for exo-dicyclopentadiene (**10**) although the triplet formation of cyclopentene or norbornene itself was observed under the same reaction conditions.[10] Valence isomerization, on the other hand, was observed in these cyclic dienes, **9** and **11** as shown in Eqs. 2 and 3.[11]



9 14 (2)



11 15 (3)

These reactions are well-known in the triplet photosensitized reaction of **9** and **11** studied by Turro et al.[12)] and Schenck et al.,[13)] respectively. Therefore, the most important decay path of the triplet di-π-methane system is an intramolecular addition to form a 1,3-biradical which leads to a cage compound formation or backs to the starting compound. In the case of di-π-ethane system (**11**), the similar type of valence isomerization was observed as shown in Eq. 3. However, in the case of exo-dicyclopentadiene (**10**), where such an intramolecular reaction is sterically inhibited, the triplet state with relatively long lifetime (180 ns) was obsereved.

References

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5) The L-band linear accelerator at Osaka University was used as the source of electron pulse. The energy was 28 MeV and the dose was 0.74 kGy per pulse. A 450 W xenon pulse lamp (OPG-450, Osram), a monochromator (Nikon G-250), a photomultiplier tube (R-928), and a programmable digitizer (Tektronix 7912AD) were used.

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10) Exo-dicyclopentadiene (**10**) was synthesized by a literature procedure [G. L. Nerson and C. L. Kuo, Synthesis, 1975, 105].

11) Benzene solutions of **10** and **11** (10 mmol dm^{-3}) were irradiated with a ^{60}Co γ-ray source up to a dose of 81 kGy at room temperature. The product **15** was isolated and the spectral data were compared with those of the authentic sample.

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(Received August 22, 1986)