Cation-radical Transfer: Transfer Efficiency in Photosensitized Isomerization Reactions

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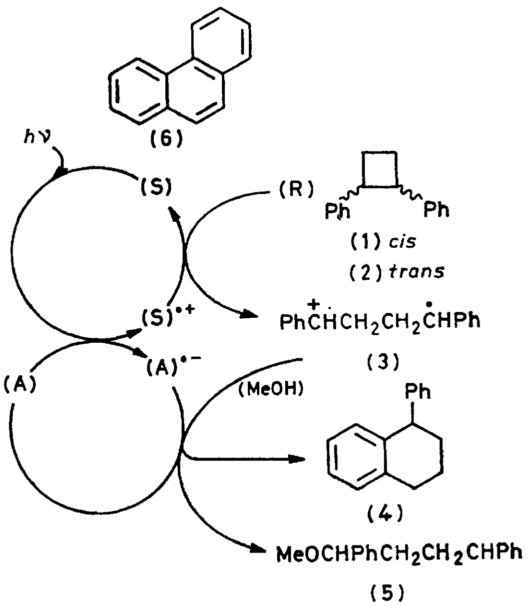
Summary The efficiency of cation-radical transfer was studied by photosensitized isomerization of cyclobutanes; the exothermic photosensitized isomerization occurs efficiently, while the rate of the endothermic isomerization decreases drastically with increase in the electron-transfer barrier.

RECENTLY a cation-radical transfer mechanism has been reported for the photochemical dimerization of olefins,[1–3] and cis–trans-isomerization[4] and cleavage reaction[5] of cyclobutane derivatives. However, the transfer efficiency has not yet been studied quantitatively. For charge separation and its utilization, the development of efficient electron-transfer systems is required[6] and, therefore, studies on electron-transfer processes are fundamentally important. We have investigated the efficiency of cation-radical transfer for various combinations of aromatic hydrocarbons [sensitizer: (S)] and 1,2-diphenylcyclobutanes [reactants: (R); *cis*-form (**1**) and *trans*-form (**2**)] by monitoring the quantum yields of their photosensitized isomerization reactions.



SCHEME. A = electron acceptor.

Irradiation of the system phenanthrene (**6**) (20 mM)–*m*-dicyanobenzene (20 mM)–(**1**) (10 mM) in MeCN and in MeCN–MeOH (1:1) by a mercury lamp (Toshiba 300H) through Pyrex glass gave 1-phenyl-1,2,3,4-tetrahydronaphthalene (**4**) (15% after 10 h irradiation) and 1-methoxy-1,4-diphenylbutane (**5**) (14%), respectively.† As shown in the Scheme, these are the characteristic products *via* the cation-radical intermediate (**3**) produced by the opening of the 1–2 bond of (**1**). In this system, the sensitizer (**6**) is selectively photoexcited‡ and $(\mathbf{1})^{\cdot+}$ is formed by the

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† Alternatively, the reaction could be performed when the charge-transfer band of (**1**) with 1,2,4,5-tetracyanobenzene was photoexcited, but considerable addition of the acceptor to (**1**) occurred in this system.

‡ Absorption of (**1**): $\lambda < 275$ nm.

cation radical-transfer mechanism, *i.e.*, electron-transfer from (**1**) to (**6**)$\cdot^+$. Use of the *trans*-form (**2**) in the above system led to a similar reaction to that of (**1**).

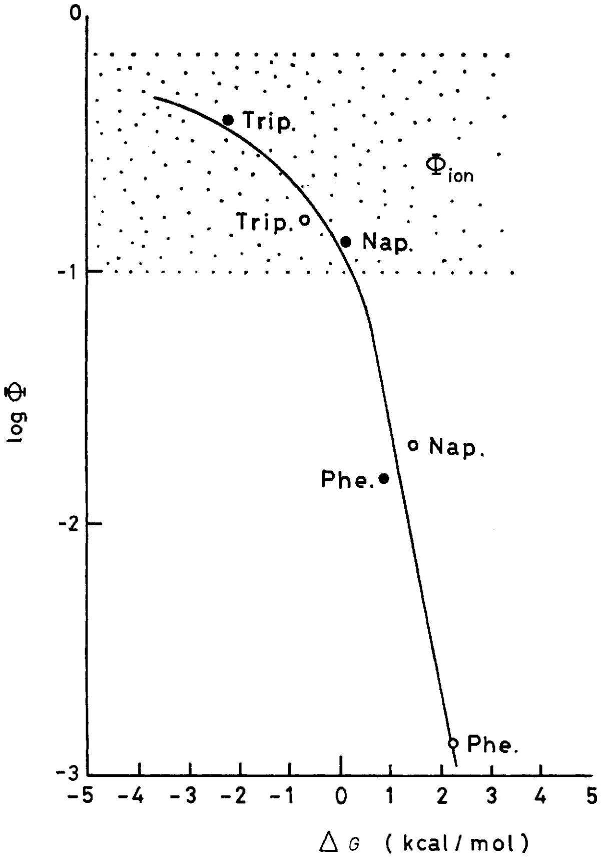

FIGURE. Plots of log Φ vs. ΔG for the photosensitized isomerizations of (**1**) and (**2**) by a cation-radical transfer mechanism. (●): (**1**) (10 mM), (○): (**2**) (10 mM); Phe: phenanthrene (20 mM), Nap: naphthalene (20 mM), Trip: triphenylene (10 mM).

The relationship between the photoisomerization quantum yield Φ and the free-energy change ΔG is shown in the Figure. Quantum yields were measured at 313 nm. ΔG values were calculated from the half-peak oxidation potentials of the sensitizers and reactants shown in the Table by the use of the equation ΔG(kcal/mol) = 23·06 $[E_{p/2}(R)/(R^+) - E_{p/2}(S)/(S^+)]$. In the exothermic region, the photoisomerization occurs efficiently and Φ may be approximated by $\Phi_{ion.}$, where $\Phi_{ion.}$ is the ionization quantum yield of (*S*); in the endothermic region the reaction still occurs but Φ decreases and approaches the value given by $\Phi \propto \Phi_{ion.} \exp(-\Delta G/RT)$. These relationships seem to indicate that the rate-determining step is electron transfer rather than the subsequent reactions.

TABLE. Half-peak oxidation potentials[a] of (S) and (R).

	$E_{p/2}(S/S^+)$/V		$E_{p/2}(R/R^+)$/V
Triphenylene	1·42	(**2**)	1·39
Naphthalene	1·32	(**1**)	1·33
Phenanthrene	1·29		
Pyrene[b]	1·06		

[a] Measured *vs.* Ag/Ag$^+$ (0·01 M) in MeCN using $Et_4N^+ClO_4^-$ as supporting electrolyte at 0·1 V s^{-1} scan speed. [b] Almost no reaction was observed.

As a whole, this photoisomerization by a cation radical-transfer mechanism is similar to the fluorescence quenching by electron transfer studied extensively by Rehm and Weller.[7] Hence, it is considered that the reaction may be limited by the mutual diffusion rate of (S)$\cdot^+$ and (R) in the exothermic region, and by the cation radical-transfer (electron-transfer) rate in the endothermic region.

The cation radical-transfer process could be followed spectroscopically by ruby-laser photolysis (347 nm excitation, 20 ns pulse) of the endothermic system: (**6**) (20 mM)–*p*-dicyanobenzene (80 mM)–(**1**) (200 mM) in MeCN solvent. Addition of (**1**) to the mixture of (**6**) and *p*-dicyanobenzene led to a decrease in the absorptions of (**3**)$\cdot^+$ at 400, 430, and 900 nm, and a new peak appeared at around 460—480 nm, which can be assigned to a type of cation radical species of (**1**); the spectrum is comparable with the cation-radical spectra of (**1**) obtained in an isopentane–Bu^{n}Cl glass matrix by γ-irradiation. A slow increase (*ca.* 120 ns) in the intensity of the 460—480 nm peak and a corresponding decay of the 430 nm peak were observed; this indicates that the rate of the cation radical transfer in the endothermic system is rather slow compared to that of the ordinary diffusion-controlled process.

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[1] S. Farid, S. E. Hartman, and T. R. Evans in 'The Exciplex,' ed. M. Gordon and W. R. Ware, Academic Press, New York, 1975, p. 327.
[2] T. Asanuma, T. Gotoh, A. Tsuchida, M. Yamamoto, and Y. Nishijima, *J. Chem. Soc., Chem. Commun.*, 1977, 485.
[3] S. Tazuke and N. Kitamura, *J. Chem. Soc., Chem. Commun.*, 1977, 515.
[4] T. R. Evans, R. W. Wake, and O. Jaenicke in reference 1, p. 345.
[5] T. Majima, C. Pac, A. Nakasone, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 1978, 490. In their work, a different scheme proceeding *via* a π complex (SR)$\cdot^+$ has been proposed.
[6] See for example: M. Calvin, *Kagaku* (*Kyoto*), 1978, **33**, 254; K. Sauer, *Acc. Chem. Res.*, 1978, **11**, 257.
[7] D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259.