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Cation-Recognized Photosensitization in *E*−*Z* Isomerization of 1,2-Dichloroethylene by Crowned Benzophenones

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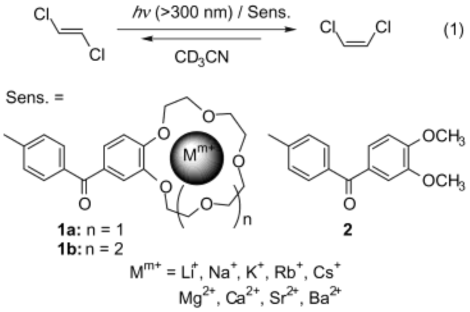
The triplet photosensitizer opens a new pathway for many attractive photoreactions by transferring the excited triplet energy (E_T) into a ground-state substrate to produce the active triplet substrate.[1] In connection with the development of a new versatile sensitizer capable of varying E_T continuously, molecular recognition[2] is one of the most promising techniques in that such noncovalent interaction will produce the delicate electronic and structural perturbation upon the conjunct chromophore function.[3] Here, we report that the photosensitized isomerization of 1,2-dichloroethylene (DCE) as a model olefin by using 15- and 18-membered crowned benzophenones[4] **1a** and **1b** causes the marked increase of the *Z*/*E* ratio on photostationary state (PSS) up to ca. 10 by complexation of alkaline earth or alkali metal ions in comparison with metal-free reaction as well as the reference dimethoxybenzophenone **2** (eq 1).



(1)

DCE is transparent for the Pyrex-filtered light and can be easily identifiable by ^{1}H NMR for each isomer: the *Z*-form resonates at 6.60 ppm and the *E*-form at 6.54 ppm in acetonitrile-d_3, respectively. A preliminary experiment with a solution of either *Z*- or *E*-DCE (10 mM) with equimolar **1a** in a NMR tube was carried out by irradiation of the filtered monochromated light (365 nm) from a 500 W ultrahigh-pressure mercury lamp in the absence or presence of Mg(ClO$_4$)$_2$ under argon atmosphere. Both isomers reached essentially the same value of $Z/E = 1.5$ in the metal-free PSS, while the presence of 5 equiv of Mg(ClO$_4$)$_2$ (50 mM) raised the isomer ratio up to the asymptotic value of 5.3 (inset in Figure 1).

Keeping this in mind, we hereinafter carried out the photosensitized isomerization using a 1:1 isomer mixture of DCE (10 mM) and a Pyrex-filtered light ($\lambda > 300$ nm). First, we investigated the dependence of *Z*/*E* ratios on the concentration of added Mg(ClO$_4$)$_2$ and found that the apparent saturation of *Z*/*E* value (~5.3) was satisfactorily attained at 2−5 equiv excess of Mg^{2+} with respect to **1a** (10 mM), while **2** brought about no increase in the isomer ratio (1.6−1.7) in the presence of Mg^{2+} (5 equiv) (Figure 1). These observations obviously indicate that the cation recognition of **1a** plays a crucial role in the rise of the *Z*/*E* value in PSS in light of the well-known cation complexation of crown compounds.

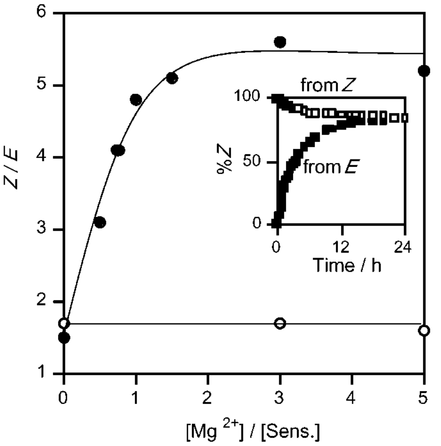


Figure 1. Dependence of the *Z*/*E* ratio of DCE (10 mM) in the photostationary state ($\lambda > 300$ nm) on the concentration of Mg(ClO$_4$)$_2$ for photosensitizer **1a** (●) and reference **2** (○) (10 mM) in acetonitrile-d_3 under argon atmosphere. Time course of the photosensitized irradiation ($\lambda = 365$ nm) of *Z*- (□) or *E*-DCE (■) by **1a** with 5 equiv of Mg(ClO$_4$)$_2$ is shown in the inset.

We extended the cation-recognized photosensitization to all the combinations of **1a** or **1b** (10 mM) with alkali and alkaline earth metal perchlorates under the presence of a 5-fold excess of metal salts (50 mM) except for less soluble alkali metal ions K$^+$ (7 mM), Rb$^+$ (9 mM), and Cs$^+$ (10 mM). The PSS for the isomerization was attained within 4−24 h on monitoring by ^{1}H NMR. In these cation excess conditions (except above K$^+$, Rb$^+$, and Cs$^+$), most of the crown-metal systems with high binding constants are thought to be in the significant 1:1 complexation of crown function with metal ion.[5,6]

The saturated *Z*/*E* values for **1a** and **1b** were plotted against the metal ion radius along with the metal-free values (=1.5 and 2.1, respectively) for convenience at ion radius zero (Figure 2). On the photosensitization by 15-membered **1a**, the similar sized Li$^+$ (0.60 Å) and Mg^{2+} (0.65 Å) gave the highest *Z*/*E* values of 2.9 and 5.3, respectively, among each family of alkali and alkaline earth metal ions. These ions are rather smaller than the reported cavity size (0.86−1.1 Å) of 15-membered-ring benzocrown ethers like **1a**.[2] A similar photosensitization by 18-membered **1b** provided the more enhanced and more acute peaks ($Z/E = 8.2$ and 9.8, respectively) at almost the same size but smaller Na$^+$ (0.95 Å) and Ca^{2+} (0.99 Å). Thus, the observed ion-size selectivities in *Z*/*E* isomerization are inconsistent with the expectation from the ion-in-the-hole concepts.[7] This is probably because in the present cation excess conditions the *Z*/*E* ratios are governed by not the binding constants[3a] but the efficiency of the differential energy transfer to each isomer.

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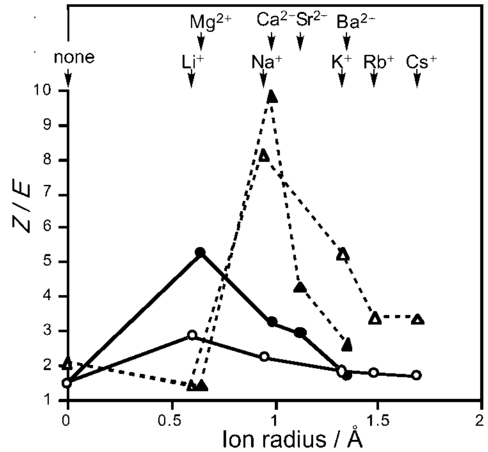

Figure 2. Plots of Z/E ratios of DCE (10 mM) at the PSS vs the ion radius of alkali (○, △) and alkaline earth metal (●, ▲) ions added (each 50 mM; except $[K^+] = 7$, $[Rb^+] = 9$, $[Cs^+] = 10$ mM) in the presence of photosensitizer 15-membered-ring **1a** (solid line) and 18-membered-ring **1b** (dotted line) (10 mM) in acetonitrile-d_3 under argon atmosphere.

Table 1. Quantum Yield (Φ) for the Photoisomerization of DCE and Triplet Energy (E_T) in the Presence of Sensitizer **1a** and **1b** with or without Mg^{2+} or Na^+

		Φ^a				
sensitizer	cation	Z	E	Φ_E/Φ_Z	$E_T{}^b$/kJ mol^{-1}	Z/E
1a	−	0.0010	0.0043	4.2	276	1.5
1a	Mg^{2+}	0.015	0.17	12	289	5.3
1b	−	0.0011	0.0067	6.2	271	2.1
1b	Na^+	0.0014	0.047	34	275	8.2

[a] Φ_Z: Quantum yield for the isomerization from Z to E. Irradiated with monochromated light (365 nm) using $K_3[Fe(C_2O_4)_3]$ as an actinometer; the conversion of the each alkene was determined by ^1H NMR. [b] Estimated by phosphorescence spectra.[9]

The quantum yields were obtained for the photoisomerization of Z- (Φ_z) and E- DCE (Φ_E) in the presence or absence of the peak-top Mg^{2+} for **1a** and Na^+ for **1b**, respectively, together with the estimated E_T (Table 1). A survey of Table 1 gives some observations: (1) both **1a** and **1b** yielded almost equal Φ_Z values (~0.001) for the Z-isomer in the absence of metal ion (2) but the E-isomer suffered 4- (for **1a**) and 6-times (for **1b**) more efficient photoisomerization than the Z-isomer, reflecting the higher Z/E ratio for **1b** than **1a**, (3) interestingly, the addition of Mg^{2+} into a solution of **1a** dramatically enlarged the quantum yield ca. 40-times for the E-isomer and only 15-times for the Z-isomer, leading to the considerably increased isomer ratio of 5.3, (4) however, the **1b**-Na^+ sensitizer raised the quantum yield slightly 1.3- and moderately 7-times, respectively, for Z- and E-isomers, although the highest Z/E ratio (=8.2) is a result of the largest Φ_E/Φ_Z (=34). With respect to the increase of Φ in the presence of metal ions, possible reduction of the radiationless process due to cation complexation can be ruled out by almost the same lifetime of the triplet state of **1a** (0.1 mM): $\tau = 24.7$ μs for metal free and 23.7 μs for the presence of Mg^{2+} (3 mM) in acetonitrile, respectively. As expected, the addition of DCE (10 mM) to the above Mg^{2+} solution shortened the lifetime (9.5 μs) due to the efficient energy transfer to DCE, although the lack of Mg^{2+} ion resulted in almost the same lifetime (23.5 μs) as in the above metal free experiment.

Hammond and Saltiel et al. argued that the photosensitizer having an appropriate E_T value causes the most enhanced increase of Z/E ratio on account of the far more discriminating energy transfer on each isomer.[8] A preliminary experiment with 13 common triplet sensitizers with a wide range of E_T (227−311 kJ mol^{-1}) provided the Saltiel plots in which DCE was found to suffer the most pronounced differential isomerization around 290 kJ mol^{-1}, although some sensitizers deviated from the ideal line (Figure 3). The present cation-recognized sensitizers which scattered only at a narrow range of E_T (276−289 kJ mol^{-1})[9] are rather separated into each family of **1a** and **1b** on the left side slope, but both show the abrupt increasing tendency of Z/E values with the increase of E_T by cation complexation (see also Table 1).[10]

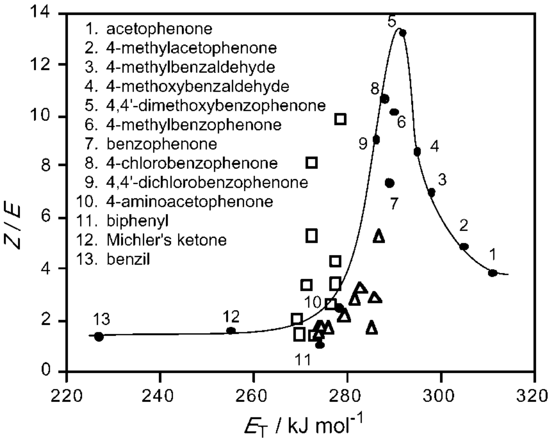

Figure 3. Saltiel plot of the Z/E ratio on PSS of 1,2-DCE vs various triplet energies of sensitizers: common sensitizers 1−13 (●), **1a** metals (△), and **1b** metals (□).

In summary, photosensitization of 1,2-dichloroethylene with the crowned benzophenones **1a** and **1b** resulted in the cation-dependent increase in the Z/E isomer ratios up to ca. 10 by addition of alkali and alkaline earth metal ions compared with the metal-free reactions ($Z/E = 1.5−2.1$).

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References

(1) (a) Turro, N. J.; Dalton, J. C.; Weiss, D. S. In *Organic Photochemistry*; Chapman, O. L., Ed.; Marcel Dekker: New York, 1969; Vol. 2, p 1. (b) Engel, P. S.; Monroe, B. M. In *Advances in Photochemistry*; Pitts, J. N., Jr., Hammond, G. S., Noyes, W. A., Jr., Eds.; John Wiley & Sons: New York, 1971; Vol. 8, p 245.
(2) Steed, J. W.; Atwood, J. L. In *Supramolecular Chemistry*; John Wiley & Sons: Chichester, UK, 2000.
(3) (a) Tsuda, A.; Oshima, T. *J. Org. Chem.* **2002**, *67*, 1282. (b) Kokubo, K.; Kanematsu, Y.; Oshima, T. *Chem. Lett.* **2000**, 1284.
(4) Prepared by the method in the following: Stott, P. E.; Bradshaw, J. S.; Parish, W. W.; Copper, J. W. *J. Org. Chem.* **1980**, *45*, 4716.
(5) (a) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271. (b) Izatt, R. M.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, *91*, 1721.
(6) The alkali metal ions, $K^+−Cs^+$, do not fit in the small cavity of **1a** and are to be appreciably sandwiched between two crown rings. However, no noticeable effect of such complexation was found in the Z/E ratios (Figure 2). The smaller Li^+ and Mg^{2+} are also poorly complexed by larger **1b**.
(7) Pedersen, C. J.; Frensdorff, H. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 16.
(8) (a) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. *J. Am. Chem. Soc.* **1964**, *86*, 3197. (b) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769.
(9) Phosphorescence spectra were measured at 77 K in frozen acetonitrile containing **1** (0.1 mM) in the absence or presence of 30 equiv of metal perchlorates by 300 nm excitation. These measurements gave the structureless broad spectra regardless of the absence or presence of metal ions, so the adopted E_T values were obtained from the onset ones by subtracting 10.5 kJ mol^{-1}, which was the average energy difference between the peak onset and the apparent 0−0 band of the above common sensitizers (1, 5, 7, and 9 in Figure 3).
(10) This means that the present sensitizer **1** with the E_T around 280 ± 10 kJ mol^{-1} is not useful for the differential isomerization of olefins with relatively too large or too small E_T value like stilbene (206 kJ mol^{-1}).

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