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Temperature-Dependent Photostationary trans/cis Ratio in Photosensitized Isomerization of Cyclooctene

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In the triplet-sensitized photoisomerization, the photostationary trans/cis ratio of cyclooctene doubled upon lowering irradiation temperature from 25 to -78 °C, whereas the ratio of 2-octene stayed unchanged.

Stilbene and its derivatives have long been known to show temperature-dependent quantum yields of photoisomerization or photostationary state trans/cis ratios, for which the complicated excited-state potential-energy surfaces of these aromatic alkenes are responsible.[1,2] Possessing much simplified U-shaped excited-state surfaces, nonconjugated aliphatic alkenes have never been presumed to behave similarly.[3,4] In the present communication we report the first temperature-dependent photostationary trans/cis ratio in the triplet-sensitized photoisomerization of cyclooctene.

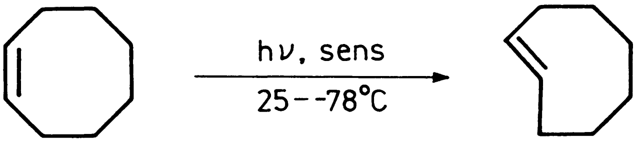

Table 1. Temperature-dependent Photostationary trans/cis Ratio upon Sensitized Photoisomerization of Cyclooctene in Pentane[a)]

Temp °C	Sensitizer(E_T)[b)] Benzene (84.3)	Toluene (82.8)	p-Xylene (80.3)
25	0.20	0.16	0.089
0	0.24	0.18	0.098
-78	0.48	0.33	0.17

a) Irradiated with a 30-W mercury resonance lamp (Vycor filter).
b) Triplet energy of sensitizer in kcal/mol (Ref. 6).

Triplet-sensitized photoisomerization of cyclooctene (2 mM) was performed at 254 nm in pentane solution containing an aromatic sensitizer (0.1 M) under a nitrogen atmosphere in a transparent quartz Dewar vessel thermostated at 25 to -78 °C. The low concentration in cyclooctene was employed in order to avoid possible operation of singlet mechanism.[5] With all sensitizers and at all temperatures employed, the major photoreaction was the geometrical isomerization. The photostationary state trans/cis ratios, $(t/c)_{pss}$, at various temperatures were determined as reported;[5] see Table 1. As has been reported,[5] the $(t/c)_{pss}$ ratio upon triplet sensitization decreased with lowering triplet energy (E_T)[6] of the sensitizer employed, which has been attributed to the endothermic energy transfer process and also to the large E_T difference[7,8] between cis- and trans-cyclooctenes.[5] Unexpectedly, the $(t/c)_{pss}$ ratio increased significantly with lowering irradiation temperature. Analogous temperature dependences were observed for all sensitizers; the value at 25 °C approximately doubled at -78 °C in each case. By contrast, no evident difference in $(t/c)_{pss}$ was observed with 2-octene upon triplet photosensitization at 25 and -78 °C under similar photochemical conditions. Since there is no precedent of such a temperature-dependent photochemical isomerization of simple alkenes,[3,4] and the present photobehavior is of theoretical as well as practical interest. Synthetically this result indicates that this and probably other highly strained trans-isomers of cycloalkenes[9] or cycloalkadienes[10] can be prepared in much higher efficiency just by performing photosensitization at low temperature rather than room temperature[11] without using vacuum UV light.[12]

The origin and the mechanistic features of this temperature-dependent photochemistry are not necessarily clear at present. Usual triplet-sensitized photoisomerization sequence assuming a common perpendicular triplet leads to the equation,[5] $(t/c)_{pss} = (k_{qc}/k_{qt})(k_{dt}/k_{dc})$, where the photostationary trans/cis ratio is expressed by a product of the excitation ratio for cis- and trans-isomers by sensitizer triplet, k_{qc}/k_{qt}, and the decay ratio from the common triplet, k_{dt}/k_{dc}. For most simple alkenes, quenching as well as decay rate constants do not substantially differ with cis- and trans-isomers, and therefore both ratios are usually very close to unity.[13] However, in the cyclooctene case, the decay ratio, though reduced to 0.5 mostly owing to the strain in the trans-form, is invariant for these three sensitizers, whereas the excitation ratio, which is also much smaller than unity, is sensitive to the sensitizer E_T and is responsible for the E_T-dependent photostationary state ratio at room temperature.[5] Although there are several suspected temperature-dependent factors which may affect the excitation and/or the decay ratios, one interesting observation is that the profile of the temperature-dependence of $(t/c)_{pss}$ ratio is very close with each sensitizer irrespective of E_T. This may suggest that the decay, rather than excitation, ratio is affected by varying irradiation temperature to give the temperature-dependent $(t/c)_{pss}$ ratios. Further kinetic study on this unique temperature-dependent photochemistry is currently in progress.

References

1) D. Gegiou, K. A. Muszkat, and E. Fischer, J. Am. Chem. Soc., 90, 3907 (1968).
2) J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, Org. Photochem., 3, 1 (1973).
3) P. J. Kropp, Org. Photochem., 4, 1 (1979).
4) M. G. Steinmetz, Org. Photochem., 8, 67 (1987).
5) Y. Inoue, T. Kobata, and T. Hakushi, J. Phys. Chem. 89, 1973 (1985).
6) S. L. Murov, "Handbook of Photochemistry," Dekker, New York (1973), p. 3.
7) R. S. Mulliken, J. Chem. Phys., 16, 87 (1977).
8) I. Sauers, L. A. Gresso, S. W. Staley, and J. H. Moore, Jr., J. Am. Chem. Soc., 98, 4218 (1976).
9) Y. Inoue, T. Ueoka, T. Kuroda, and T. Hakushi, J. Chem. Soc., Perkin Trans. 2, 1983, 983.
10) Y. Daino, S. Hagiwara, T. Hakushi, Y. Inoue, and A. Tai, J. Chem. Soc., Perkin Trans. 2, 1989, 275.
11) J. S. Swenton, J. Org. Chem., 38, 1178 (1969).
12) Y. Inoue, S. Takamuku, and H. Sakurai, Synthesis, 1977, 111.
13) Small deviation from unity has been reported: J. J. Snyder, F. P. Tise, R. D. Davis, and P. J. Kropp, J. Org. Chem., 46, 3609 (1981).

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