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SINGLET SENSITIZATION OF THE NORBORNADIENE REARRANGEMENT: EXCITATION ENERGY CASCADE POTENTIALLY INVOLVING TRIPLET EXCIPLEXES

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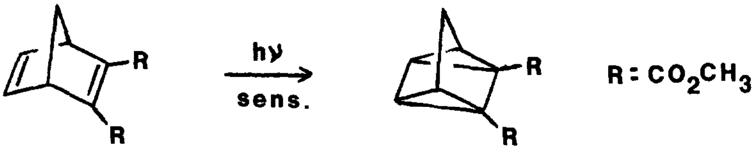
Summary: Valence isomerization of dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate is induced on quenching the fluorescence of a variety of sensitizers. Quantum efficiencies for rearrangement depend on the triplet energy of of the sensitizer.

Triplet energy transfer from a sensitizer to a reactive substrate is a common means of photosensitization which has found wide application.[1] Promotion of a reaction through interaction with the singlet state of a sensitizer is less well established, although a number of examples including ring opening processes and geometrical isomerization have appeared.[2]

Interest in our laboratory in new mechanisms[3] of photosensitization has focused substantially on singlet quenching, where in principle the full measure of photochemical driving force for an excited sensitizer can be deployed to bring about reaction. Several variations of reaction mechanism have been identified, all involving an electron donor-acceptor interaction between sensitizer and reactive substrate. In the event that a low-lying vertical excited state of the substrate is unavailable for population, the encounter with sensitizer leads to bond order changes and subsequent decay along a reactive path (e.g., the rearrangements of quadricyclene[4] and hexamethyl(Dewar benzene)[5] in non-polar solvent). For strong electron donor-acceptor quenching in a polar medium, reaction may proceed through radical ions,[6,7] with the sensitizer acting as a reservoir for electrons or holes for catalytic activation of the substrate. In this paper we wish to report yet another mode of behavior apparent in the rearrangement of norbornadiene derivative 1, induced by singlet sensitizers in a non-polar solvent.

The emission of a series of fluorescent sensitizers was readily quenched on addition of 1 in cyclohexane or benzene solution. Stern-Volmer analysis of the data for undegassed samples provided values for $k_q\tau$ (Table), which were corrected for the competitive quenching by oxygen by measuring sensitizer fluorescence intensities before and after purging with argon. The corrected values of $k_q\tau$, along with lifetime data (τ) from the literature[9] permitted calculation of quenching rate constants (k_q). These values (Table) were generally high and above the range for which one customarily finds correlation with the excitation energy and oxidation potential of the sensitizer;[10,11] i.e., near diffusion-limited rates are obtained and a substantial donor-acceptor interaction can be inferred, since outright electron transfer can be observed for similar quenching by 1 in a polar solvent (acetonitrile).[6] Along with conventional aromatic donors, sensitizers included a coumarin laser dye, Eastman C102. In the case of pyrene quenching, a high concentration of the sensitizer was used, so that the dominant excited species was the excimer.[12]



1 2

Rearrangement 1 → 2 could be driven by some sensitizers with relatively high efficiency. The dependence of quantum yield was most readily related to the triplet energy of the sensitizer, even under circumstances in which sensitizer singlets were nearly completely quenched. Singlet sensitized isomerization was not observed for sensitizers whose triplet energies appear below the value estimated for the triplet of 1($\sim$53 kcal/mol[3]). Rearrangement persisted at lower concentration of 1 for sensitizers having higher triplet energies and reasonable intersystem crossing efficiencies (phenanthrene and chrysene),[13,14] presumably via the more conventional energy transfer mechanism. Covalent interaction of 1 with sensitizers was not indicated by any measureable sensitizer disappearance.

The results are reminiscent of the findings for singlet sensitization of 1 by electron donors in a polar solvent. For reaction in acetonitrile, the evidence favored formation of radical-ions followed by ion recombination yielding triplets of 1.[6] Although the dependence on sensitizer triplet energy is manifest again for reaction in cyclohexane, other tests suggest a different type of mechanism. Flash photolysis of phenanthrene and 1 in non-polar solvent (frequency doubled ruby laser, 347 nm) resulted in no transient absorption, unlike the previous result in which the phenanthrene radical-cation could be observed in the microsecond time regime.[6] Moreover, CIDNP effects associated with formation of radical-ion pairs for sensitizer and 1[6] were not obtained on irradiation of donors and 1 in C_6D_6.

We favor a mechanism for sensitized rearrangement of 1 in which a polar (but nonionic[15]) exciplex results on bimolecular quenching in non-polar solvent. Exciplex intersystem crossing[16] leads to a triplet complex which can further degrade its energy through population of the triplet of 1 or the sensitizer. The important result here is the indication that the lowest triplet excited state available to the system is reached along the dominant non-radiative decay path.[17,18] Novel features also include the apparently high yield of norbornadiene triplets reached on singlet sensitization

Table. Rate data for the quenching of sensitizer fluorescence and quantum yields of isomerization, $\underline{1} \rightarrow \underline{2}^a$

Sensitizer (conc.)	E_T (kcal/mol)	$k_q\tau$ $(M^{-1})^b$	10^9 $k_q(M^{-1}s^{-1})$	Ø	$[\underline{1}]$	(%)^c
2-methoxynaphthalene	62	106.	6.1	0.28	0.11	(92)
(0.10 M)						
2,6-dimethoxynaphthalene	61	120.	10.	0.11	0.11	(93)
(0.15 M)						
phenanthrene	62	31.3	0.73	0.20	0.20	(89)
(0.20 M)				0.09	0.002	(8)
chrysene	57	60.7	3.8	0.24	0.20	(97)
(0.002 M)				0.15	0.002	(17)
C102		68.5	15.	0.04	0.20	(95)
(0.001 M)						
Pyrene^d	48	42.7	0.66	<0.01	0.10	(81)
(0.10 M)						
9,10-dimethylanthracene	∿40	14.1	1.3	<0.005	0.39	(85)
(0.016 M)						
1,4-dimethoxyanthracene	∿40	105.	11.	<0.005	0.10	(91)
(0.007 M)						

[a] Quantum yields were obtained using a monochromator apparatus (313 or 366 nm) or with parallel irradiation in a chamber reactor equipped with filter solution (340-370 nm) as previously described (ref. 8); cyclohexane solvent (degassed) except where noted. [b] Stern-Volmer constants for undegassed samples. [c] Concentration of $\underline{1}$ for quantum yield measurement and extent of singlet quenching (%). [d] Results for quenching pyrene excimer in benzene.

(∿ 40% in the case of chrysene[19]). The results are most readily related to the findings of singlet sensitized geometrical isomerization in non-polar solvent for which exciplex intersystem crossing and decay have been proposed, and a similar preference for reaction of a low-lying partner triplet has been observed.[20]

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References

(1) A. Albini, Synthesis, 249 (1981).

(2) See, for example, (a) K. Okada, K. Hisamitsu, and T. Mukai, Tetrahedron Lett., 1251 (1981); (b) A. Albini and D.R. Arnold, Can. J. Chem., 56, 2985 (1978); (c) F.D. Lewis, Accts. Chem. Res., 12, 152 (1979).

(3) G. Jones, II, S.-H. Chiang, and P.T. Xuan, J. Photochem., 10, 1 (1979).

(4) G. Jones, II, S.-H. Chiang, W.G. Becker, and D.P. Greenberg, J. C. S. Chem. 681 (1980).

(5) G. Jones, II and S.-H. Chiang, Tetrahedron, 37, 3397 (1981).

(6) G. Jones, II, W. Schwarz, and V. Malba, J. Phys. Chem., 86, 2286 (1982).

(7) (a) G. Jones, II, S.-H. Chiang, W.G. Becker, and J.A. Welch, J. Phys. Chem. 86, 2805 (1982); (b) H.D. Roth, M.L.M., Schilling, and G. Jones, II, J. Am. Chem. Soc., 103, 1246 (1981).

(8) W.R. Bergmark, G. Jones, II, T.E. Reinhardt, and A.M. Halpern, J. Am. Chem. Soc., 100, 6665 (1978).

(9) (a) S.L. Murov, "Handbook of Photochemistry," Marcel Dekker, Inc., New York, 1973; (b) D.A. Labianca, G.N. Taylor, and G.S. Hammond, J. Am. Chem. Soc., 94, 3679 (1972); (c) G. Jones, II, W.R. Jackson, and A.M. Halpern, Chem. Phys. Lett., 72, 391 (1980).

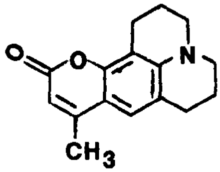
(10) L. Eberson, Adv. Phys. Org. Chem., 18, 79 (1982).

(11) The circumstances are analogous to the situation for polar solvent in which electron transfer from the sensitizer is exothermic.[6,10]

(12) J.B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, 1970, chp. 7.

(13) The triplet level for C102 is not known but likely to be near that of 1 since for unsubstituted coumarin, E_T = 62 kcal/mol: see W.M. Mantulin and P.-S. Song, J. Am. Chem. Soc., 95, 5122 (1973).

C102



(14) The quantum efficiency of isc for phenanthrene is 0.80.[9a]

(15) D.F. Eaton and D.A. Pensak, J. Phys. Chem., 85, 2760 (1981).

(16) N. Mataga and M. Ottolenghi, in "Molecular Association," vol 2, R. Foster, ed., Academic Press, New York, 1979.

(17) Sensitizer excited singlets in all cases lie in energy above the triplet of 1 (the lowest, the pyrene excimer, at about 65 kcal/mol).

(18) Our experiments do not distinguish selective population and decay of one partner triplet vs. population of both triplets followed by thermalization.

(19) The limiting yield of isomer 2 from triplet 1 is $\sim$ 60%.[3]

(20) (a) F.D. Lewis and J.T. Simpson, J. Phys. Chem., 15, 2015 (1979); (b) G.G. Aloisi, G. Bartocci, G. Favaro, and U. Mazzucato, ibid., 84, 2020 (1980)

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