CHEMISTRY LETTERS, pp. 1855-1858, 1985.

DIVERGENT SOLVENT EFFECTS ON PHOTOSENSITIZED REACTIONS OF cis-1,2-DIPHENYLCYCLOBUTANE BY AROMATIC NITRILES[1)]

Chyongjin PAC,* Tomohito OHTSUKI, Takao FUKUNAGA,
Shozo YANAGIDA, and Hiroshi SAKURAI
Department of Chemical Process Engineering, Faculty of Engineering,
Osaka University, Suita, Osaka 565

Photosensitized reactions of cis-1,2-diphenylcyclobutane by aromatic nitriles, which mainly give styrene along with the trans isomer and 1-phenyltetralin revealed divergent solvent effects depending on the sensitizers.

Solvent effects on photochemistry of electron donor-acceptor pairs reveal interesting features in kinetics and product distributions, usually arising from a solvent-induced change of electronic properties of an exciplex[2,3)] or from a switching of an exciplex mechanism in nonpolar or less polar solvents to an electron-transfer mechanism in polar solvents.[2-5)] Therefore, such solvent effects may provide a clue to explore mechanisms of photoreactions as well as reactivities of exciplexes, ion-radical pairs, and free ion radicals. We have found that the photosensitized reactions of cis-1,2-diphenylcyclobutane (1) by some aromatic nitriles (S) reveal divergent solvent effects depending on the nitriles. In this paper, we wish to report the essential results and to discuss the mechanistic origin as well as reactivity differences of postulated intermediates.

The photoreactions mainly gave styrene (2) along with the trans isomer (3) and, in some cases, 1-phenyltetralin (4). Table 1 summarizes the results, revealing that the change of solvent from benzene (BZ) to acetonitrile (AN) led to decreases of the quantum yields as well as to the lack of the formation of 4 in the cases of 1,4-dicyanonaphthalene (DCN) and 9,10-dicyanoanthracene (DCA), whereas converse solvent effects on both the quantum yields and the formation of 4 were observed in the case of 1-cyanonaphtalene (CN). We reported that the photoreactions in benzene proceed via singlet exciplexes.[6)] Therefore, electron transfer might occur in AN, particularly in the cases of DCN and DCA where the calculated free-energy changes (ΔG) are considerably negative. In these cases, however, the lack of formation of 4 in AN suggests that the participation of the free cation radical of 1 is unlikely since this species exclusively gives 4.[7)] In each case, moreover, both the product ratio and the quantum yields of the photoreaction in 9:1 (v/v) AN/MeOH were identical with those in neat AN, and no indication was obtained at all on the formation of other products expected from the nucleophilic additions of methanol to $1^{+\cdot}$[7)] and $2^{+\cdot}$.[4,5,8)] It is therefore evident that free $1^{+\cdot}$ plays no important role in the photoreactions in AN.

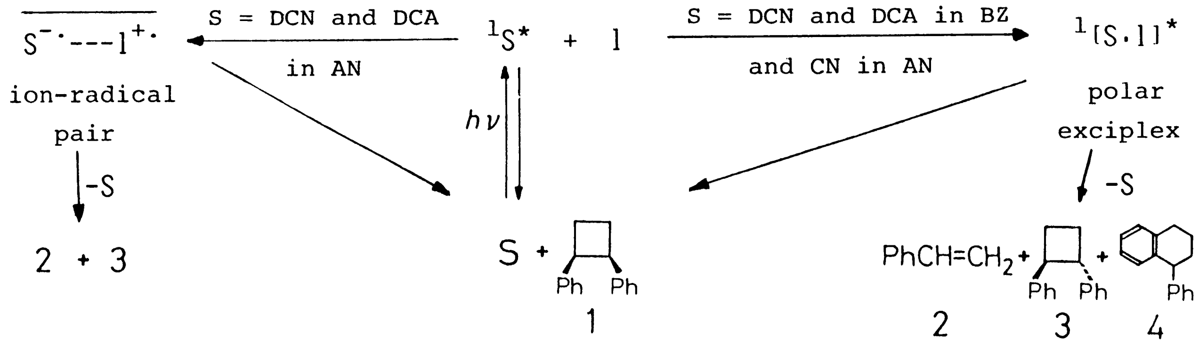


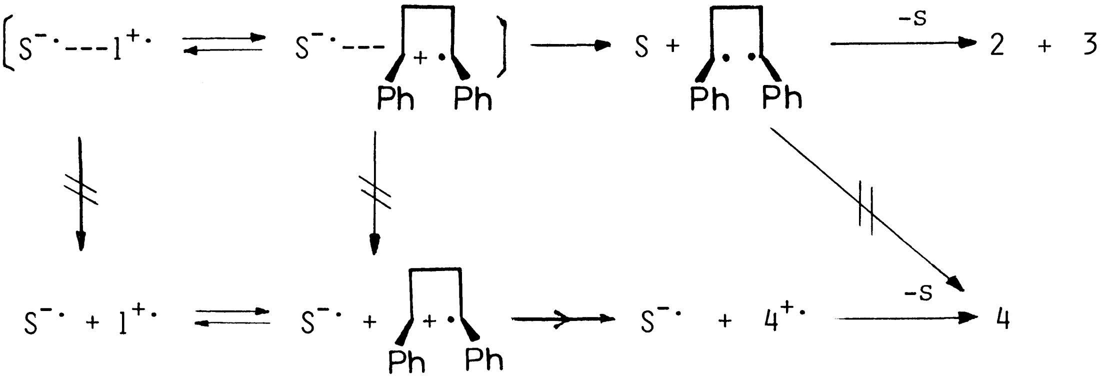
Table 1. Quantum yields for photosensitized reactions of 1 by aromatic nitriles

Aromatic nitriles ($*E$[a)]/eV; $*E^{red}$[b)]/V)	Solvents	Quantum yields[c)] 2	3	4	$10^{-9}k_q$[d)] $dm^3 mol^{-1} s^{-1}$	$-\Delta G$[e)] $kJ\ mol^{-1}$
1-Cyanonaphthalene (CN)	BZ	0.072 (0.10)	0.0065	$<10^{-4}$	0.86	
(3.75; 1.42)	AN	0.43 (0.53)	0.024	0.005	3.2	13.4
1,4-Dicaynonaphthalene (DCN)	BZ	0.90 (0.90)[f)]	0.10	0.025	4.4	
(3.45; 2.40)	AN	0.20 (0.20)[f)]	0.04	$<10^{-4}$	12.4	108
9,10-Dicyanoanthracene (DCA)	BZ	0.11 (0.25)	0.008	0.007	0.97	
(2.88; 1.76)	AN	0.11 (0.11)[f)]	0.005	$<10^{-4}$	8.0	46

a) Excitation energies of the excited-singlet nitriles in AN cited in reference 5, p. 237. b) Reduction potentials of the excited singlet nitriles vs. Ag/Ag^+ in AN calculated from *E plus ground-state reduction potentials determined by cyclic voltammetry. c) Values at 0.2 or 0.3 mol dm^{-3} at 313 nm for CN and DCN runs and at 366 nm for DCA runs. In parentheses are the limiting quantum yields obtained from double-reciprocal plots of quantum yields vs. concentrations of 1 unless otherwise noted. d) Rate constants for quenching of the aromatic nitrile fluorescence by 1. e) Free-energy changes for an electron transfer process calculated from $*E^{red}$ minus the oxidation potential of 1 (1.28 V vs. Ag/Ag^+ in AN. f) Values at 0.3 mol dm^{-3} where the fluorescence quenching was complete.

In the cases of DCN and DCA, the photoreactions in AN might occur directly from ion-radical pairs without any dissociation into free ion radicals, a unique mechanism which has some precedents[9-11] though little has been investigated. The lower quantum yields in AN compared with those in BZ should arise from short lifetimes of the ion-radical pairs by rapid geminate recombination. In the case of CN, on the other hand, the converse solvent effect appears to be accomodated with a solvent-induced change of electronic properties of the exciplex from a minor charge-transfer contribution in BZ to a considerably polar state in AN;[2,3] more polar exciplexes are more reactive and 4 can be formed, even in part, from polar exciplexes.[6] Electron transfer from 1 to excited-singlet CN seems to play no important role as implied by the least negative value of ΔG.[12] The CN exciplex in AN would be as polar as those with DCN and DCA in BZ.

The above discussions imply different reactivities of less polar exciplexes, polar exciplexes, ion-radical pairs, and free $1^{+\cdot}$. In particular a crucial question arises as to why $1^{+\cdot}$ paired with $S^{-\cdot}$ does not undergo the rearrangement to 4 at all but the ring splitting to 2 and the isomerization to 3 unlike the reaction of free $1^{+\cdot}$.[7] This reactivity difference is reminiscent of a recent publication on the photosensitized dimerization of 1,1-diphenylethylene by aromatic nitriles, which describes that a cyclobutane is formed via a 1,4-biradical generated by back electron transfer from $S^{-\cdot}$ to the dimer cation radical of the olefin in a solvent cage, whereas the free cation radical undergoes the dimerization to a tetralin compound.[13] This mechanism can interpret chemical behaviors of the postulated ion-radical pairs as shown below; a 1,4-biradical is formed by back electron transfer from $S^{-\cdot}$ to $1^{+\cdot}$ and/or to a ring-opened cation radical in a solvent cage, thus undergoing the fragmentation to 2 and the cyclization to 3.



This work was supported by Grant-in-Aid for Scientific Research (No. 60045071) from the Ministry of Education, Science and Culture.

References

1) Part 41 of Photochemical Reactions of Aromatic Compounds. Part 40: M. Yasuda, Y. Yamashita, T. Matsumoto, K. Shima, and C. Pac, J. Org. Chem., 50, in press (1985).

2) C. Pac, M. Yasuda, K. Shima, and H. Sakurai, Bull. Chem. Soc. Jpn., 55, 1605 (1982).

3) F. D. Lewis and L. E. Hoyle, J. Am. Chem. Soc., 99, 2779 (1977).

4) H. Sakurai and C. Pac, Mem. Inst. Sci. Ind. Res., Osaka Univ., 37, 59 (1980); M. Yasuda, C. Pac, and H. Sakurai, Bull. Chem. Soc. Jpn., 53, 502 (1980).

5) S. L. Mattes and S. Farid, Org. Photochem., 6, 233 (1983).

6) C. Pac, T. Fukunaga, T. Ohtsuki, and H. Sakurai, Chem. Lett., 1984, 1847.

7) T. Gotoh, M. Kato, M. Yamamoto, and Y. Nishijima, J. Chem. Soc., Chem. Commun., 1981, 90. See also Ref. 13.

8) R. A. Neunteufel and D. R. Arnold, J. Am. Chem. Soc., 95, 4080 (1973); Y. Shigemitsu and D. R. Arnold, J. Chem. Soc., Chem. Commun., 1975, 407.

9) H. F. Davis, P. K. Das, L. W. Reichel, and D. W. Griffin, J. Am. Chem. Soc., 106, 6968 (1984); C. V. Kumar, S. K. Chattopadhyay, and P. K. Das, J. Chem. Soc., Chem. Commun., 1984, 1107.

10) G. Jones, II, S. -H. Chiang, W. G. Becker, and J. A. Welch, J. Phys. Chem., 86, 2805 (1982).

11) K. A. Bowen-Wensley, S. L. Mattes, and S. Farid., J. Am. Chem. Soc., 100, 4162 (1978).

12) The calcualted values of ΔG should be considered to be only of relative significance since the quantities used for the calculations are based on the observed irreversible redox potentials of 1 and S.

13) S. L. Mattes and S. Farid, J. Am. Chem. Soc., 105, 1386 (1983).

(Received September 17, 1985)