A Striking Solvent Effect on the Photochemical Reaction of Naphthalene with 2-(Diethylamino)ethanol

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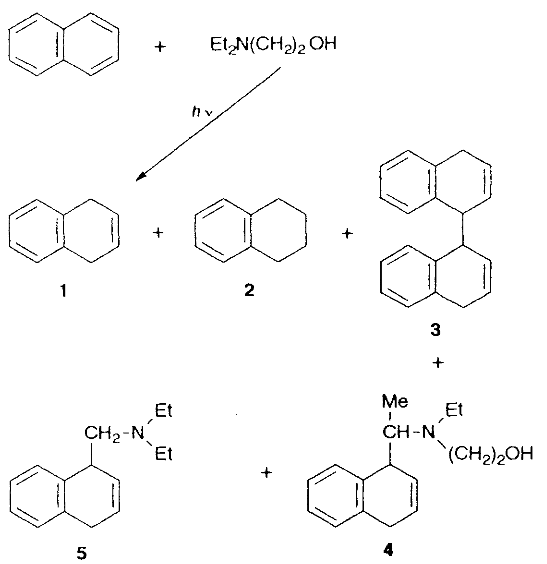
Photochemical reaction of naphthalene with 2-(diethylamino)ethanol shows a striking effect of solvent polarity on the reaction course, which is explained in terms of the intermediacy of a geminate radical ion pair in benzene and free radical ions in acetonitrile.

Photoinduced charge-transfer reactions are the subject of recent extensive studies.[1] A subject matter of interest in this field is the effect of solvent on reaction courses. It has been reported for certain systems that the reaction in nonpolar solvents proceeds *via* an exciplex, while the reaction in polar solvents involves the intermediacy of radical ions. Nucleophilic addition of solvent to radical cations has also been reported.[1,2]

We report here a striking effect of solvent polarity on the photoinduced electron-transfer reaction of naphthalene with 2-(diethylamino)ethanol (2-DEAE), which can be most reasonably explained as resulting from the difference in reactivity between a geminate radical ion pair and free radical ions.



Scheme 1

The fluorescence of naphthalene is quenched by 2-DEAE by a charge-transfer mechanism. The bimolecular rate constant for the quenching of the naphthalene fluorescence by

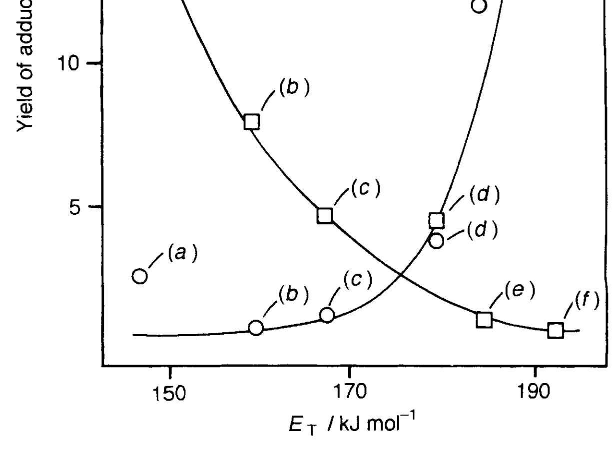
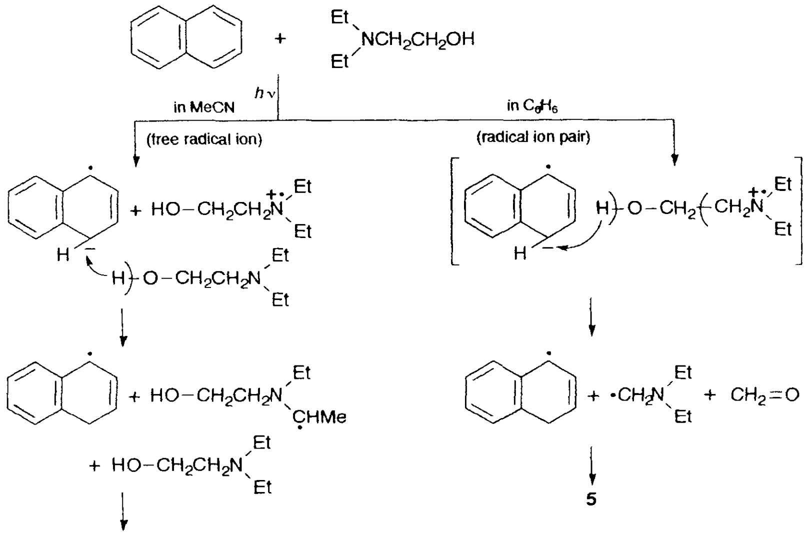


Fig. 1 Dependence of yields of the adducts, **4** and **5**, on the E_T value of solvents;[10] [naphthalene] = [2-DEAE] = 0.10 mol dm^{-3}; irradiated for 10 h with light of wavelength longer than 313 nm from a 500 W high-pressure mercury lamp at room temp.; **4** (○), **5** (□); (*a*) benzene, (*b*) THF, (*c*) dichloromethane, (*d*) n-butyronitrile, (*e*) propionitrile and (*f*) acetonitrile



Scheme 2

Table 1 Quantum yields for the products of photochemical reaction of naphthalene–2-DEAE system[a]

	Product				
Solvent	1	2	3	4	5
C_6H_6	0.014	0.008	0.004	0.030	0.200
MeCN	0.040	0.009	0.015	0.150	~0

[a] Quantum yields were measured with a potassium ferrioxalate actinometer on irradiation with monochromatic light (313 nm), obtained by a combination of an interference filter UV-D33S and an aqueous solution of K_2CrO_4 (0.2 g dm^{-3}). [naphthalene] = 0.10 mol dm^{-3}, [2-DEAE] = 0.10 mol dm^{-3}.

2-DEAE was determined to be 2.4×10^9 in benzene and 5.7×10^9 dm^3 mol^{-1} s^{-1} in acetonitrile.

Photochemical reactions of aromatic hydrocarbons with tertiary aliphatic amines are known to proceed in polar solvents to yield aminated adducts and reduction products of aromatic hydrocarbons *via* radical ion intermediates.[3–5] The present naphthalene–2-DEAE system was found to undergo photochemical reaction even in a nonpolar solvent, benzene, producing an adduct **5** as a major product together with an adduct **4** and reduction products of naphthalene **1**–**3**. By contrast, the photochemical reaction in acetonitrile yielded the adduct **4** as the main product together with **1**–**3** (Scheme 1).† Table 1 summarizes product distributions in the photochemical reactions in benzene and acetonitrile.

The effect of solvent polarity on the reaction course is dramatic. As Fig. 1 shows, the ratio of **5** to **4** varies greatly with the change in solvent polarity. That is, as the solvent polarity decreases, the formation of the adduct **5** becomes more favoured at the expense of the formation of **4**.

The photochemical reactions of the naphthalene–2-DEAE system in both nonpolar and polar solvents are reasonably explained as involving radical ion intermediates. The free-energy change for photochemical electron transfer of this system is exothermic; the values of ΔG are *ca.* −65 kJ mol^{-1} as estimated from the Rehm–Weller equation[6] (E^{ox} 0.45 V for 2-DEAE, E^{red} for naphthalene −2.93 V *vs.* Ag/Ag$^+$ 0.01 mol dm^{-3}; excitation energy of naphthalene 385 kJ mol^{-1}).

The striking effect of solvent polarity on the reaction course in the naphthalene–2-DEAE system can be rationalized in terms of the intermediacy of a geminate radical ion pair in nonpolar solvents and free radical ions in polar solvents.‡ The presence of the hydroxy group in 2-DEAE, which acts as a good proton source to the naphthalene radical anion, seems to be essential for the occurrence of photoinduced electron-transfer reaction even in nonpolar solvents. That is, in nonpolar solvents, proton transfer takes place from the hydroxy group in the 2-DEAE radical cation to the naphthalene radical anion within the geminate ion pair, and the subsequent cleavage reaction of 2-DEAE radical cation leads to the formation of **5** as a main product.§ Scheme 2 describes the main reaction pathways in benzene and in acetonitrile. In polar solvents, proton transfer following electron transfer occurs in appearance from the α-CH_2 group of the 2-DEAE radical cation to the naphthalene radical anion, leading to the formation of **4**. It is suggested that the hydroxy group in the neutral 2-DEAE intervenes in the sequential proton transfer process (Scheme 2).

The present study provides a clear-cut example of different reaction pathways between geminate radical ion pair and free radical ions.

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References

1 *Photoinduced Electron Transfer*, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988.
2 J. J. McCullough, *Chem. Rev.*, 1987, **87**, 811, and references cited therein.
3 J. A. Barltrop, *Pure Appl. Chem.*, 1973, **33**, 179.
4 R. S. Davidson, *Adv. Phys. Org. Chem.*, 1983, **19**, 1.
5 S.-C. Oh, Y. Shirota, H. Mikawa and S. Kusabayashi, *Chem. Lett.*, 1986, 152.
6 D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259.
7 S. L. Mattes and S. Farid, *J. Am. Chem. Soc.*, 1986, **108**, 7356.
8 X. Ci, L. Y. Lee and D. G. Whitten, *J. Am. Chem. Soc.*, 1987, **109**, 2536.
9 X. Ci and D. G. Whitten, *J. Am. Chem. Soc.*, 1987, **109**, 7215.
10 *Solvents and Solvent Effects in Organic Chemistry*, ed. C. Reichardt, VCH, 1988, p. 365.

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† The products **1**–**3** were identified by comparison with authentic samples. The structures of **4** and **5** were identified by IR, UV, mass and NMR spectroscopy and elemental analysis.

‡ Preliminary results show that the addition of a salt, *e.g.* tetra-n-butylammonium perchlorate, to the reaction system in tetrahydrofuran (THF) strikingly reduces the formation of **5**, and instead increases the yield of **4**. Different reaction paths between geminate radical ion pair and free radical ions have also been reported recently on the basis of kinetic analysis for photoinduced electron-transfer dimerization of 1,1-diphenylethylene.[7]

§ Such a reaction did not take place for 3-(diethylamino)propanol containing the hydroxy group at the γ-position to the amino group. The C–C bond cleavage of the β-aminoalcohol radical cation has recently been reported for a hydroxyethyl morpholine derivative.[8,9]