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.



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 $E_{\rm T}$ 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** (\bigcirc), **5** (\square); (*a*) benzene, (*b*) THF, (*c*) dichloromethane, (*d*) n-butyronitrile, (*e*) propionitrile and (*f*) acetonitrile



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

	Product				
Solvent	1	2	3	4	5
C ₆ H ₆ MeCN	0.014 0.040	0.008 0.009	0.004 0.015	0.030 0.150	0.200 ~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 K₂CrO₄ (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 dm³ 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 freeenergy 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 equation⁶ (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 electrontransfer 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 -CH₂ 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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[‡] Preliminary results show that the addition of a salt, *e.g.* tetra-nbutylammonium 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}

 $[\]dagger$ 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.