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Electron Transfer vs. Excited-State Reactions in the Photochemical Reaction of the 2-Vinylnaphthalene - Fumaronitrile System

Kentaro YAMAGUCHI, Shin-Chol OH, and Yasuhiko SHIROTA*
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadaoka, Suita, Osaka 565

Photochemical reaction of the 2-vinylnaphthalene (VN) - fumaronitrile (FN) system by direct irradiation, which proceeds probably via ion radicals generated by electron transfer in the excited singlet state of VN to yield a VN-FN copolymer and VN cyclodimers, contrasts with the benzophenone-sensitized reaction, which proceeds via the triplet states of VN and FN with no dominant contribution of electron transfer leading to the formation of VN-FN cycloadducts as main products.

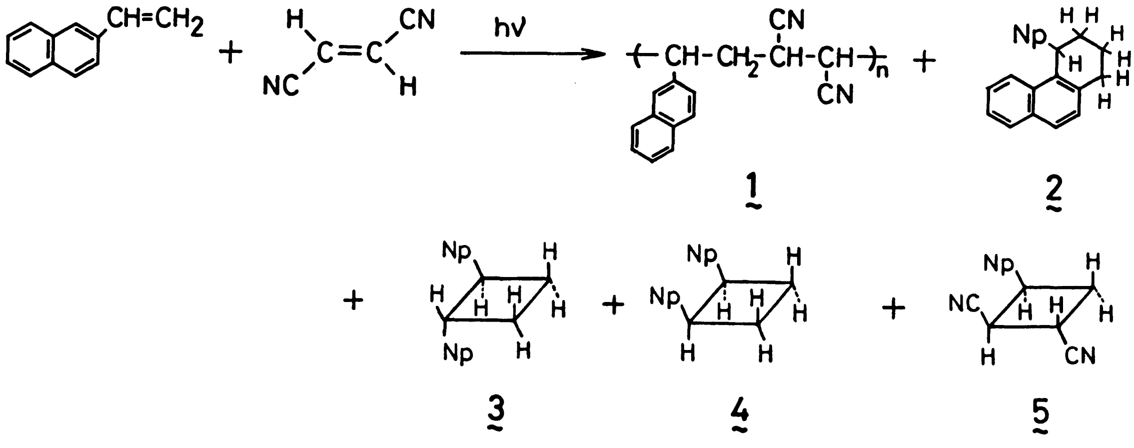
Recently there have been extensive studies of photochemical reactions of electron donor - acceptor systems that involve the formation of exciplexes or ion radicals.1) It is known that photochemical electron transfer in the electron donor - acceptor system takes place in the excited singlet or triplet state depending on reaction systems. For example, electron transfer usually occurs in the excited singlet state in such systems as the fluorescence is sharply quenched,2) whereas it takes place in the excited triplet state in the systems using a molecule with highly efficient intersystem crossing, e.g., benzophenone - amine systems.3) However, few studies have been made of the correlation between the multiplicity of an excited-state molecule and reaction pathways including the problem of the occurrence of electron transfer in the electron donor - acceptor system. In the present study, we have studied this problem in the photochemical reaction of the 2-vinylnaphthalene (VN) (donor) - fumaronitrile (FN) (acceptor) system, and found that the reaction by direct irradiation, which proceeds via the VN excited singlet state, greatly differs from the triplet-sensitized reaction.

First, the photochemical reaction of VN alone should be mentioned. We have reported that the photochemical reaction of VN alone by direct irradiation with a 334 nm light proceeds predominantly via the excited singlet state to produce cis- and trans-1,2-di(2-naphthyl)cyclobutanes in the ratio of 10:1, whereas the bezophenone-sensitized reaction of VN by the irradiation of a 365 nm light, which proceeds exclusively via the VN triplet state, yields cis- and trans-1,2-di(2-naphthyl)cyclobutanes in the ratio of 1:4.4) Fumaronitrile (FN) absorbs the light of a shorter wavelength than VN. Thus the VN - FN reaction system will be suitable for studying the problem descrived above. Although it has been briefly reported that the VN - FN system produces a copolymer by the irradiation with a nitrogen-pulsed laser,5) no study has been made from the viewpoint described above.

The fluorescence of VN was found to be sharply quenched by the addition of FN. A week, broad exciplex fluorescence band peaking at ca. 460 nm was observed in a nonpolar solvent, benzene, but in a polar solvent, acetonitrile, only strong quenching of the VN fluorescence occurred. The Stern-Volmer plots for the fluorescence quenching in both solvents gave straight lines, and the bimolecular rate constants for the quenching of the VN fluorescence by FN in benzene and acetonitrile were determined to be 1.2×10^{10} and 2.0×10^{10} $dm^3\ mol^{-1}\ s^{-1}$, respectively (the fluorescence lifetimes of VN in benzene and acetonitrile solutions in air were 24 and 13 ns, respectively).

The photochemical reaction was carried out in a pyrex-glass tube of 2 cm in diameter by using a merry-go-round apparatus. The reaction solution was evacuated at 10^{-3} Torr (1 Torr = 133.322 Pa), sealed off, and irradiated with a 500 W high-pressure mercury lamp at 15–20 °C through a filter solution. Quantum yields were measured with a potassium ferrioxalate actinometer by the irradiation of the monochromatic light of 334 and 365 nm, which were obtained, respectively, by combinations of cut-off glass filters and an aqueous solution of $NiSO_4$ (5 g/100 ml).

Direct irradiation of the VN - FN system both in benzene and acetonitrile with a 334 nm light by the use of a filter solution of aqueous $NaNO_3$ (1 g/10 ml) produced a copolymer of VN with FN (1) (copolymer molar composition; FN:VN = 0.6:0.4), and two kinds of cyclodimers of VN, i.e., 1,2,3,4-tetrahydro-4-(2-naphthyl)phenanthrene (2) and trans-1,2-di(2-naphthyl)cyclobutane (3), as main products. By contrast, the benzophenone (BP)-sensitized reaction of the VN - FN system in benzene by selective excitation of BP with a 365 nm light by using an aqueous $Cu(NO_3)_2 \cdot 3H_2O$ (5 g/10 ml) as a filter solution yielded four isomeric cycloadducts of VN with FN, 1-naphthyl-2,3-dicyanocyclobutanes (5), as main products together with minor amounts of the copolymer (1) and cis- and trans-1,2-di(2-naphthyl)cyclobutanes (4 and 3) in the ratio of 1:4. The structures of these products were identified by IR, UV, mass, and NMR spestra, molecular-weight determination, and elemental analysis. Table 1 shows product distributions and quantum yields for the formation of the products in the photochemical



Np = Naphthyl group

reactions of the VN - FN system by direct irradiation and by triplet sensitization.

Table 1. Product Distributions and Quantum Yields for the Products in the Photochemical Reaction of 2-Vinylnaphthalene (VN) - Fumaronitrile (FN) System

Reaction system	Product yields/%[a] and Quantum yields[b]				
	1	2	3	4	5
VN - FN in Benzene[c]	47.9[e]	20.9 (0.085)[b]	4.1 (0.016)[b]	0.2	3.6 (0.010)[b]
VN - FN in Acetonitrile[c]	75.9[f]	1.2 (0.002)[b]	6.4 (0.015)[b]	0.3	0.5 (0.002)[b]
VN - FN - BP in Benzene[d]	5.5[g]	2.3 (0.010)[b]	4.1 (0.006)[b]	1.0	31.5 (0.048)[b]

a) Irradiated for 10 h. Product distributions were determined by means of glc. Yields were calculated on the basis of the quantity of the starting materials. b) Quantum yields were measured at low conversions. c) Irradiated with light of 334 nm, [VN] = [FN] = 0.30 mol dm^{-3}. d) Irradiated with light of 365 nm, [VN] = [FN] = 0.30 mol dm^{-3}, [BP] = 0.10 mol dm^{-3}. e) $\bar{M}n$ = 2430, $\bar{M}w$ = 5990 (GPC with polystyrene as a standard). f) $\bar{M}n$ = 1080, $\bar{M}w$ = 1380 g) $\bar{M}n$ = 8560, $\bar{M}w$ = 9280

These results indicate that reaction mechanisms greatly differ between the reactions by direct irradiation and by triplet sensitization. The formation of 1,2,3,4-tetrahydro-4-(2-naphthyl)phenanthrene (2) and the predominant formation of the trans-isomer (3) of 1,2-di(2-naphthyl)cyclobutane in the reaction of the VN - FN system by direct irradiation both in benzene and acetonitrile can be explained neither by the VN excited singlet-state reaction nor by the VN excited triplet-state reaction in view of the results of the photochemical reactions of VN alone descrived above. Instead, these products are most reasonably explained in terms of the intermediacy of the VN cation radical. It has been reported that the photochemical reactions of 1,1-diphenylethylene, methylstyrenes, and N-vinylcarbazole in the presence of an electron acceptor produce the products analogous to 2 for the former olefins[6,7] and the trans-cyclobutane dimer corresponding to 3 for the latter olefin.[8] The formation of the copolymer of VN with FN is also understood as being initiated via the ion radicals.[5,9] The experimental fact that the photochemical reactions of the VN-styrene system by direct irradiation and by BP sensitization both in benzene and in acetonitrile produced no appreciable amounts of a VN-styrene copolymer, giving almost the same results with those of the photochemical reactions of VN alone, supports the intermediacy of ion radicals in the initiation of the VN-FN radical copolymerization. The occurrence of electron transfer from VN in the excited singlet state to the ground-state FN is supported from highly exothermic free energy change for electron transfer as estimated from the Rehm-Weller equation,10) the value being -75 kJ mol^{-1}. It is strongly suggested that the photochemical reaction of the VN - FN system by direct irradiation proceeds mainly via the VN cation radical and FN anion radical generated by electron transfer from VN in the excited singlet state to the ground-state FN both in benzene and acetonitrile, leading to the formation of the products **1**, **2**, and **3** as main products. Considering the number-average molecular weights of copolymers **1**, the ratios leading to the formation of the copolymer to that of the cyclodimers (**2**, **3**, **4**) from the ion radicals are comparable or do not greatly differ between them.

On the other hand, it is suggested that the electron-transfer process does not contribute dominantly in the BP-sensitized reaction. In the BP-sensitized reaction, triplet-energy transfer will occur from BP (E_T = 288 kJ mol^{-1}) to both VN (E_T = 288 kJ mol^{-1}) and FN (E_T = 209 kJ mol^{-1}).11) The formation of the cis- and trans-cyclobutane dimers of VN in the ratio of 1:4 is in accord with the VN triplet-state reaction. The formation of the four isomeric 2+2 cycloadducts of VN with FN is suggested to result from the reactions of the triplet-state VN and FN with the ground-state FN and VN, which proceed probably via the triplet exciplex as reported for the photocycloaddition of phenanthrene to dimethyl fumarate.12) The BP-sensitized reaction of the VN - diethyl maleate (E_T = 301 - 322 kJ mol^{-1}) system also produces 2+2 cycloadducts similar to **5** together with the cis- and trans-cyclobutane dimers of VN in the ratio of 1:4 via the triplet-state VN.13)

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