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Photopolymerization and photocycloaddition reactions in the 2-vinylnaphthalene – Maleic anhydride system

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SUMMARY

Photochemical reaction of the 2-vinylnaphthalene (VN) (electron-donor monomer) - maleic anhydride (MAn) (electron-acceptor monomer) system has been studied in order to elucidate reaction pathways and the correlation between them and the multiplicity of an excited-state molecule. It was found that direct irradiation of the VN - MAn system both in benzene and acetonitrile produces predominantly copolymers probably via ion radicals generated by electron transfer in the electronically excited singlet state, whereas benzophenone-sensitized reaction yields a cycloadduct of VN with MAn as a main product via the electronically excited triplet state.

INTRODUCTION

The photochemical reaction of vinyl monomers containing pendant aromatic hydrocarbons tends to yield cyclodimers of vinyl monomers. For example, the photochemical reaction of styrene and 2-vinylnaphthalene (VN) produces mainly head-to-head cyclodimers, namely, cis- and trans-1,2-disubstituted cyclobutanes (1, 2). On the other hand, it has been reported that the photochemical reaction of some aryl vinyl monomer - electron-acceptor monomer systems, where the aryl vinyl monomer acts as an electron-donor monomer, gives copolymers probably via the intermediacy of ion radicals. For example, styrene - maleic anhydride (MAn) and VN - fumaronitrile (FN) systems reportedly undergo photopolymerization to give copolymers (3-5). However, few studies have been made of the correlation between the multiplicity of an excited-state molecule and reaction pathways in the electron-donor monomer - electron-acceptor monomer system (5). In the present study, we have studied this problem in the photochemical reaction of VN (donor monomer) - MAn (acceptor monomer) system.

EXPERIMENTAL

2-Vinylnaphthalene (Aldrich Chem. Co. Inc. U.S.A.) was chromatographed on a silica-gel column (Wakogel C-300, Wako Pure Chem. Ind. Ltd. Japan) with hexane as an eluent, then recrystallized from hexane and dried in vacuo, mp 65.5 - 66.0°C. Maleic anhydride (Wako Pure Chem. Ind. Ltd. Japan) was recrystallized twice from benzene and then sublimed twice in vacuo immediately before use, mp 51.5 - 52.5°C.

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, sealed off, and irradiated with a 500 W high-pressure mercury lamp at 15 - 20°C through an aqueous filter solution of $NaNO_3$ (1 g/10 ml) or $Cu(NO_3)_2 3H_2O$ (5 g/10 ml). After irradiation of a solution of VN (0.30 mol dm^{-3}) and MAn (0.30 mol dm^{-3}) in benzene or acetonitrile for 10 h, tetrahydrofuran (THF) was added to the reaction solution to dissolve reaction products deposited. Then the solvent was evaporated in vacuo, and again THF was added to dissolve the residue. The solution was poured into 20-fold excess of hexane to precipitate copolymers. Copolymers were redissolved in THF and precipitated from hexane. In the case of the photochemical reaction sensitized with benzophenone (0.10 mol dm^{-3}), the precipitates contained copolymers and cycloadducts of VN with MAn. A cycloadduct of VN with MAn, 3-(2-naphthyl)cyclobutane-1,2-dicarboxylic anhydride, was separated from the copolymer as a soluble part in hot benzene, and recrystallized from acetone, mp 186.0-188.0°C.

The structures of the products were identified by IR, UV, mass, and NMR spectra, molecular weight determination, and elemental analysis. Molecular weights of copolymers were determined by means of GPC using polystyrene as a standard sample.

Copolymer of VN with MAn: IR spectrum, 1850, 1775 cm^{-1} ($\nu_{C=O}$); composition (mole ratio) as determined from carbon analysis, 1:1 (VN:MAn); solubility: soluble in THF and acetone, insoluble in benzene and hexane. 3-(2-Naphthyl) cyclobutane-1,2-dicarboxylic anhydride: IR spectrum; 1860, 1780 cm^{-1}($\nu_{C=O}$); mass spectrum, m/e 252(M^+), 154(M^+-98); ^{1}H-NMR spectrum (in $CDCl_3$), δ 2.90-3.08(2H, m, methylene), 3.60-3.65(1H, m, methine), 3.70-3.75(1H, m, methine), 4.08-4.15(1H, m, methine), 7.35-7.90(7H, m, aromatic); elemental analysis, Found: C,75.97, H,4.72; Calcd. for $C_{16}H_{12}O_3$: C,76.18, H,4.79.

RESULTS AND DISCUSSION

The VN - MAn system shows charge-transfer interactions both in the ground and electronically excited states. The fluorescence of VN in a dilute solution was found to be sharply quenched by the addition of MAn both in benzene and in acetonitrile. No exciplex fluorescence was observed. The bimolecular rate constants for the quenching of the VN fluorescence by MAn in benzene and acetonitrile were almost diffusion-controlled. Since the singlet-energy transfer from VN to MAn is energetically unfavorable, the dynamic quenching of the VN fluorescence by MAn is attributed to charge transfer, probably electron transfer from the excited singlet-state VN to the ground-state MAn. The formation of a ground-state charge-transfer complex in the VN - MAn system is evidenced from the electronic absorption spectrum of the reaction solution, which is distinctly red-shifted compared with that of VN or MAn alone of the same concentration, as shown in Figure 1.

Direct irradiation of the VN - MAn system with light of

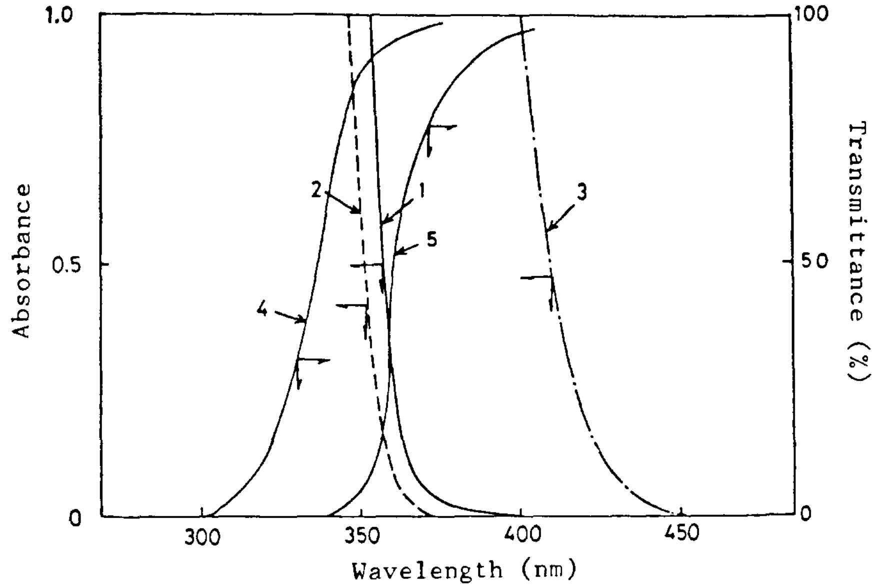


Fig. 1. Electronic absorption spectra of VN, MAn, and VN - MAn system in benzene and transmittance of aqueous filter solutions. (1) VN (0.30 mol dm^{-3}); (2) MAn (0.30 mol dm^{-3}); (3) VN (0.30 mol dm^{-3}) + MAn (0.30 mol dm^{-3}); (4) aqueous solution of $NaNO_3$ (1 g/10 ml); (5) aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (5 g/10 ml).

the wavelength longer than 334 nm both in benzene and in acetonitrile produced a copolymer of VN with MAn (1) as a main product and a small amount of cycloadducts of VN with MAn (2). Trace amounts of 1,2,3,4-tetrahydro-4-(2-naphthyl)phenanthrene (3) and trans- and cis-1,2-di(2-naphthyl)cyclobutanes (4 and 5) were also formed: these products were detected by gas chromatography and identified by comparison with the authentic samples. Selective excitation in the charge-transfer band of the VN - MAn system in benzene with light of the wavelength longer than 366 nm or 405 nm resulted in the formation of the same products with decreased yields. By contrast, the benzophenone (BP)-sensitized reaction of the VN - MAn system in benzene by irradiation with light of the wavelength longer than 366 nm gave a cycloadduct of VN with MAn, either cis- or trans-3-(2-naphthyl)cyclobutane-1,2-dicarboxylic anhydride, as a main product together with the copolymer of VN with MAn and trace amounts of 3, 4 and 5. The gas chromatogram of the irradiated solution suggested the formation of a trace amount of the other stereoisomeric cycloadduct. The identification of the cis- or trans-form for the isolated cycloadduct 2 was difficult from the present data available. The copolymer of VN with MAn, 1, obtained by the photochemical reaction of the VN - MAn system is similar to that obtained by the 2,2'-azobisisobutyronitrile-initiated copolymerization of VN with MAn, in the IR, UV, and NMR spectra and copolymer compositions. Table 1 shows product distributions in the photochemical reaction of the VN - MAn system by direct irradiation and by triplet sensitization.

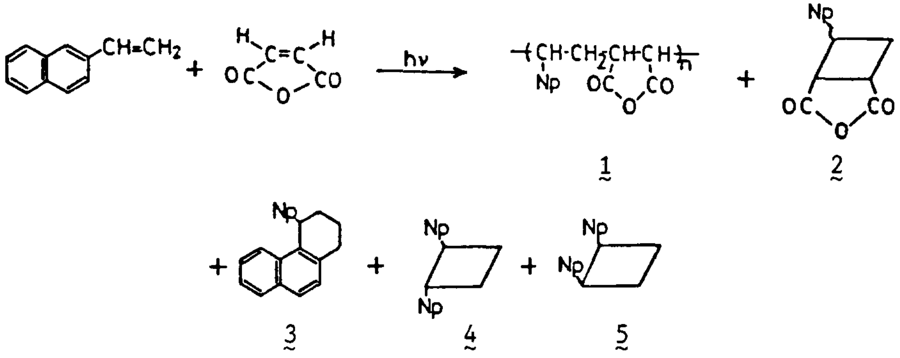


Table 1. Product distributions in the photochemical reaction of the 2-vinylnaphthalene (VN) - maleic anhydride (MAn) system.[a]

Reaction System / Yield(%)	Direct Irrad. in Benzene hν >334 nm	Direct Irrad. in Benzene hν >366 nm	Direct Irrad. in CH_3CN hν >334 nm	Benzophenone-Sensitization in Benzene hν >366 nm
Copolymer 1	41.8[c]	31.0	72.7[d]	17.8[e]
Cycloadduct 2	1.5	1.0	0.8	41.3 (0.075)[b]

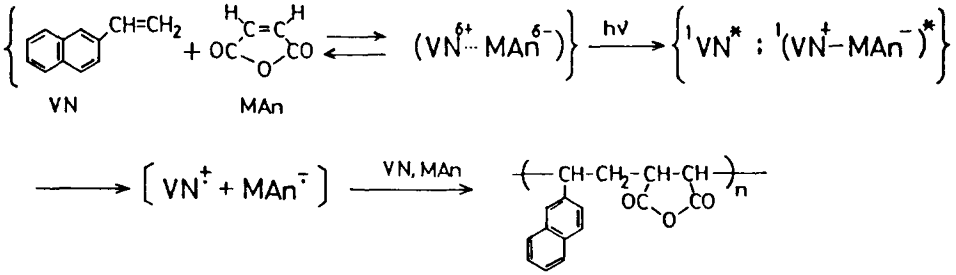
a) Irradiated for 10 h. [VN] = [MAn] = 0.30 mol dm^{-3}. [BP] = 0.10 mol dm^{-3}. The molar extinction coefficients (dm^{3} mol^{-1} cm^{-1}) at 366 nm in benzene: 68 for BP, 267 for the VN-MAn CT-complex (association constant: K = 0.37 dm^{3} mol^{-1}). The products 2, 3, 4 and 5 were quantified by means of glc. Yields of 3, 4 and 5: trace. b) The quantum yield was measured with a potassium ferrioxalate actinometer. c) $\bar{M}n$ = 5200, $\bar{M}w$ = 14700. d) $\bar{M}n$ = 2700, $\bar{M}w$ = 5100. e) $\bar{M}n$ = 5000, $\bar{M}w$ = 11500.

The results described above indicate that reaction mechanisms greatly differ between the reactions by direct irradiation and by triplet sensitization using BP. It has been shown that the photochemical reaction of VN alone by direct irradiation proceeds predominantly via the electronically excited singlet state to give 4 and 5 in the ratio of 1:10 (2). Direct irradiation of the VN - styrene system yielded no appreciable amount of a VN - styrene copolymer, giving almost the same result as observed for the photochemical reaction of VN alone. These results, together with the results of the dynamic quenching of the VN fluorescence by MAn and the copolymer formation by the selective excitation of the ground-state charge-transfer complex, indicate that the formation of the copolymer of VN with MAn is initiated by ion radicals, followed by free-radical propagation. The photochemical generation of ion radicals, i.e., VN cation radical and MAn anion radical, takes place by electron transfer from the excited singlet-state VN to the ground-state MAn and by the ionization of the charge-transfer complex in the electronically excited singlet state. The results indicate that the electron-transfer reaction proceeds in a nonpolar solvent, benzene, as well as in a polar solvent, acetonitrile, and that the reaction is accelerated in acetonitrile. The occurrence of the electron transfer from VN in the excited singlet state to the ground-state MAn is supported from highly exothermic free-energy change for electron transfer as estimated from the Rehm-Weller equation (6); the value is about -115 kJ mol^{-1}.

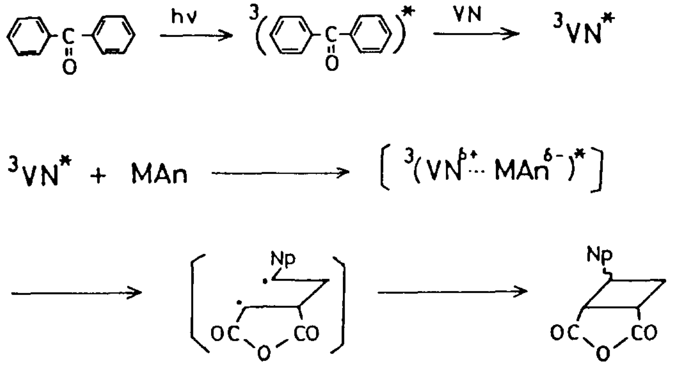
On the other hand, it is suggested that the electron-transfer process does not contribute dominantly in the BP-sensitized reaction, although the free-energy change for electron transfer from VN in the excited triplet state to the ground-state MAn is estimated to be -49 kJ mol^{-1}. It is

Scheme 1. Main Reaction Pathways

Direct Irradiation -Reaction via Excited Singlet State-



Benzophenone Sensitization -Reaction via Excited Triplet State-



understood that the cycloadduct of VN with MAn results from the reaction of VN in the excited triplet state with the ground-state MAn, possibly via the triplet exciplex as reported for the photocycloaddition of phenanthrene to dimethyl fumarate (7). Triplet-energy transfer occurs from BP (E_T = 288 kJ mol^{-1}) to VN (E_T = 288 kJ mol^{-1}) but not to MAn (E_T = 301 kJ mol^{-1}) (8). It is conceivable that triplet-energy transfer from BP or VN to the VN-MAn charge-transfer complex is also allowed to generate the excited triplet-state charge-transfer complex. It should be noted that in the BP-sensitized reaction, not only BP but also the ground-state charge-transfer complex of VN with MAn absorbs the photoenergy. Therefore, the formation of the copolymer of VN with MAn in the BP-sensitized reaction may result from the excitation of the ground-state charge-transfer complex. The main reaction pathways in the photochemical reaction of the VN - MAn system by direct irradiation and by BP sensitization are shown in Scheme 1.

The present study shows that the photochemical reaction of the VN - MAn system in the electronically excited singlet states of VN and VN-MAn charge-transfer complex produces the copolymer of VN with MAn as a main product probably via the ion radicals generated by electron transfer, whereas the reaction in the triplet state of VN yields the cycloadduct of VN with MAn as a main product possibly via the triplet exciplex. As compared with the VN - FN system (5), the photochemical reaction of the VN - MAn system is characteristic in that the yields of the products other than the copolymer and the cycloadduct of VN with MAn are negligibly low. The present VN - MAn system, where the triplet-energy transfer from BP to MAn is energetically unfavorable, provides a more definite result concerning the correlation between the reaction pathways and the multiplicity of an excited-state molecule than the VN - FN system, where triplet energy transfer occurs from BP to both VN and FN.

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