The Effect of Charge-transfer Interactions on the Photochemical Reaction of 2-Vinylnaphthalene

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Charge-transfer interactions between 2-vinylnaphthalene (VN) in the excited singlet state and amines in the ground state significantly alter the product distribution in the photochemical reaction of VN, increasing the *trans* : *cis* ratio of 1,2-di(2-naphthyl)cyclobutane from 1 : 10 in the absence of amines to *ca.* 2 : 1 in the presence of 1,4-diazabicyclo[2.2.2]octane.

There have been numerous studies of bimolecular photochemical reactions *via* emitting or non-emitting exciplexes where electron donor and acceptor molecules react with each other.[1] However, little attention has been paid to how the photochemical reaction of a single molecule is affected by charge-transfer interactions in the presence of a second molecule.[2,3] We report here a clear-cut example of the effect of charge-transfer interactions on photochemical reactions, in the 2-vinylnaphthalene (VN)–amine system.

The fluorescence of VN was found to be sharply quenched by the addition of triethylamine (TEA) or 1,4-diazabicyclo[2.2.2]octane (DABCO). The VN–TEA system forms an emitting exciplex in benzene, exhibiting a broad exciplex fluorescence band peaking at *ca.* 455 nm, while no exciplex fluorescence is observed for the VN–DABCO system. The bimolecular rate constants for the quenching of the VN fluorescence by TEA and DABCO in benzene were determined to be 1.4×10^9 and $6.5 \times 10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, respectively.†

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† The fluorescence quenching experiment was carried out in benzene solutions in air ($[\mathrm{VN}] = 9.9 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$). The fluorescence lifetime of VN in the absence of amines is 24 ns.

Direct irradiation of a benzene solution of VN with light of 334 nm from a high pressure mercury lamp produced predominantly *cis*-1,2-di(2-naphthyl)cyclobutane and the *trans*-isomer in the ratio of 10 : 1, together with a small amount of VN oligomers.‡ On the other hand, the benzophenone-sensitized photochemical reaction *via* the VN triplet state yielded the *cis*- and *trans*-1,2-di(2-naphthyl)cyclobutanes in the ratio of 1 : 4. These results indicate that the photochemical reaction of VN by direct irradiation proceeds predominantly *via* the VN singlet state, which reacts with the ground state VN to give the *cis*-cyclodimer probably *via* a *cis*-pairwise excimer.§ In contrast, it is suggested that the reaction *via* the VN triplet state proceeds as a stepwise process involving the intermediacy of the dimeric biradical species, leading to the formation of cyclodimers rich in the thermodynamically more stable *trans*-isomer.

The addition of TEA or DABCO was found to alter the product distribution significantly, increasing the *trans* : *cis* ratio of the cyclodimer, as shown in Table 1, where the quantum yields for the formation of *cis*- and *trans*-cyclodimers in the absence and presence of amines are summarized. The results show that charge-transfer interactions between VN in the excited singlet state and the amines in the ground state quench the reaction *via* the VN singlet state which gives the *cis*-cyclodimer, enhancing deactivation to the ground state and population of the VN triplet state particularly for the VN–DABCO system. That is, the reaction *via* the excited triplet state is enhanced in the reaction system where the fluorescence is strongly quenched. The enhanced generation of the triplet states of aromatic hydrocarbons *via* charge-transfer interactions has been shown spectroscopically in a few systems.[4–6] The present study presents a clear-cut example demonstrating the involvement of this phenomenon in chemical reactions.

Table 1. Quantum yields (Φ) for the formation of *cis*- and *trans*-1,2-di(2-naphthyl)cyclobutane in the photochemical reaction of 2-vinylnaphthalene (VN) in the absence and presence of amines.[a]

Reaction system (mole ratio)	Φ (*cis*)	Φ (*trans*)	*trans*/*cis* Ratio
VN only	0.230	0.022	0.10
VN–BP[b]	0.016	0.064	4.00
VN–TEA (1 : 1)	0.043	0.022	0.51
VN–TEA (1 : 2)	0.029	0.022	0.76
VN–TEA (1 : 3)	0.021	0.021	1.00
VN–DABCO (1 : 0.5)	0.033	0.038	1.15
VN–DABCO (1 : 1)	0.022	0.043	1.95

[a] Quantum yields were measured with a potassium ferrioxalate actinometer. Irradiated with light of 334 nm from a high pressure mercury lamp (the products do not absorb the light) in benzene at 10^{-3} Torr. [VN] = 0.2 mol dm^{-3}. [b] Benzophenone (BP)-sensitized reaction with light of 365 nm. [BP] = 0.2 mol dm^{-3}.

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‡ The structures of the products were identified by i.r., u.v., mass, and n.m.r. spectra, molecular weight determination, and elemental analysis.

§ The fluorescence lifetime of VN in relatively concentrated solutions decreases with increasing concentration of VN. The kinetic treatment of the quantum yields for the *cis*-cyclodimer formation as a function of the concentration of VN indicates the involvement of an intermediate *via* the VN excited singlet state leading to the *cis*-cyclodimer, which is thought to be an excimer.

References

1 For example, see F. D. Lewis, *Acc. Chem. Res.*, 1979, **12**, 152.
2 R. S. Davidson, *Chem. Commun.*, 1969, 1450.
3 J. Saltiel, D. E. Townsend, B. D. Watson, P. Shannon, and S. L. Finson, *J. Am. Chem. Soc.*, 1977, **99**, 884.
4 M. Ottolenghi, *Acc. Chem. Res.*, 1973, **6**, 153.
5 J. F. Delouis, J. A. Delaire, and N. Ivanoff, *Chem. Phys. Lett.*, 1979, **61**, 343.
6 T. Okada, I. Karaki, E. Matsuzawa, N. Mataga, Y. Sakata, and S. Misumi, *J. Phys. Chem.*, 1981, **85**, 3957.