

The Effect of the Hydrogen Bonding on the Photoinduced Electron Transfer Reaction of a Naphthalene-Triethylamine System in the Presence of Alcohols

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The effect of the addition of alcohols on the photoinduced electron transfer reaction of a naphthalene-triethylamine system has been studied. The results show that the addition of alcohol reduces both bimolecular rate constants for the quenching of the naphthalene fluorescence by triethylamine and the quantum yields for the formation of products, in the order of 2-methyl-2-propanol < 2-propanol < ethanol < methanol. These results are explained in terms of hydrogen-bonding interactions between the amine and alcohols, which suppress the electron transfer process.

Photoinduced electron-transfer reactions have been the subject of recent extensive studies. Among the studies, the effects of the addition of proton donors such as methanol on photoinduced electron-transfer reactions have been a subject of interest.<sup>1-3)</sup> Photochemical reactions of aromatic compounds with amines are known to proceed via ion-radical intermediates generated by photochemical electron-transfer, yielding reduction products and aminated adducts of aromatic compounds.<sup>4,5)</sup> It has been reported that the addition of methanol accelerates the reaction or increases the yields of the reduction products in the benzene-triethylamine<sup>2)</sup> and styrene-triethylamine<sup>3)</sup> systems owing to its role as a proton donor. On the other hand, such a case has also been reported as the addition of methanol quenches the reaction of, e.g., dicyanobenzene-amine system because of its role as a proton donor in competition with proton transfer from the amine cation radical.<sup>1)</sup> The addition of alcohol will cause hydrogen-bonding interactions with amines. Then, a question arises how hydrogen-bonding interactions affect the photochemical reactions of aromatic compounds with amines; however, there have been few detailed studies on this problem.<sup>6)</sup> From this viewpoint, we have studied the effect of the addition of alcohols on photochemical reaction of aromatic compounds with amines, in the naphthalene-triethylamine (TEA) system.

The fluorescence of naphthalene was sharply quenched by the addition of TEA, but the extent of the quenching was found to decrease distinctly in the presence of alcohols. The Stern-Volmer plots for the fluorescence quenching gave straight lines both in the absence and in the presence of varying amounts of alcohols as expected from Eq. 1 described later. Table 1 shows Stern-Volmer quenching constants ( $K_{SV}$ ) obtained from the slopes of the linear plots for the system

Table 1. Stern-Volmer Constants ( $K_{SV}$ ) for the Quenching of the Naphthalene Fluorescence by TEA in Acetonitrile in the Presence of Varying Amounts of Alcohols

Alcohol/vol%	$K_{SV}/\text{dm}^3 \text{ mol}^{-1}$ a)			
	MeOH	EtOH	i-PrOH	t-BuOH
10	51.2	90.5	111.2	112.0
20	39.0	62.2	90.0	109.5
50	19.2	40.5	54.5	92.9
100	10.2	21.2	33.0	63.3

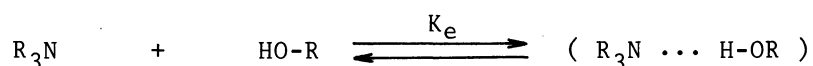
a) In the absence of alcohol :  $K_{SV} = 127.8 \text{ dm}^3 \text{ mol}^{-1}$ .

Table 2. Lifetimes ( $\tau_0$ ) of Naphthalene Fluorescence and the Apparent Bimolecular Rate Constants ( $k_q^{\text{obsd}}$ ) for the Quenching of the Naphthalene Fluorescence by TEA in Acetonitrile and Various Alcohols

Solvent	$\tau_0/\text{ns}$ a)	$K_{SV}/\text{dm}^3 \text{ mol}^{-1}$	$k_q^{\text{obsd}}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
Acetonitrile	13.6	127.8	$9.40 \times 10^9$
MeOH	14.9	10.2	$0.68 \times 10^9$
EtOH	15.6	21.2	$1.36 \times 10^9$
i-PrOH	15.8	33.0	$2.09 \times 10^9$
t-BuOH	19.3	63.3	$3.28 \times 10^9$

a) Lifetimes were measured in air by a single photon counting method.

containing varying amounts of alcohols. The results show that the values of  $K_{SV}$  decrease with increasing amounts of alcohols and in the order of 2-methyl-2-propanol (t-BuOH) < 2-propanol (i-PrOH) < ethanol (EtOH) < methanol (MeOH). The addition of alcohols will reduce the polarity of the medium; however, the observed order of the alcohols is opposite to the one expected from the decrease in the polarity of the medium. Table 2 lists the apparent bimolecular rate constants ( $k_q^{\text{obsd}}$ ) for the quenching of the naphthalene fluorescence by TEA in acetonitrile and in various alcohols, together with the lifetimes of the naphthalene fluorescence. The value of  $k_q^{\text{obsd}}$  decreases in the order of t-BuOH < i-PrOH < EtOH < MeOH, and the value of  $k_q^{\text{obsd}}$  for the system in MeOH is one order of magnitude smaller than that for the system in acetonitrile. The order of the alcohols observed is in good agreement with the order of hydrogen-bonding ability of the alcohols.<sup>8)</sup> It is most reasonable to attribute the decrease of  $K_{SV}$  and  $k_q^{\text{obsd}}$  caused by the addition of alcohols to hydrogen-bonding interactions between the amine and alcohols.



Here, let the bimolecular rate constants for the naphthalene fluorescence quenching by the free TEA and by the hydrogen-bonded TEA be  $k_{qf}$  and  $k_{qc}$ , respectively, then Eq. 1 holds, and  $k_q^{\text{obsd}}$  is expressed by Eq. 2;

$$\phi_f^0 / \phi_f = 1 + \frac{1}{1 + K_e[A]} (k_{qf} + k_{qc}K_e[A])\tau_0[\text{TEA}] \quad (1)$$

$$k_q^{\text{obsd}} = K_{sv}/\tau_0 = \frac{k_{qf} + k_{qc}K_e[A]}{1 + K_e[A]} \quad (2)$$

where  $\phi_f^0$  and  $\phi_f$  are the fluorescence intensities in the absence and presence of TEA, respectively,  $K_e$  is the equilibrium constant for the hydrogen-bond formation,  $[A]$  is the concentration of alcohols added,  $\tau_0$  is the lifetime of the naphthalene fluorescence in the absence of TEA, and  $k_{qf}$  is thought to be much larger than  $k_{qc}$ .

If it is simply assumed that the fluorescence quenching takes place only by the free TEA in view of the fact that a quarternary ammonium salt, triethylamine hydrochloride, does not quench the naphthalene fluorescence, Eq. 2 is simplified as Eq. 3, from which the value of  $K_e$  can be calculated by putting the value of  $k_q^{\text{obsd}}$  in the system in acetonitrile as the value of  $k_{qf}$ .

$$k_q^{\text{obsd}} = \frac{k_{qf}}{1 + K_e[A]} \quad (3)$$

The values of  $K_e$  calculated from Eq. 3 for the TEA-alcohol systems in acetonitrile were 0.52, 0.30, 0.21, and 0.13  $\text{dm}^3 \text{mol}^{-1}$  for MeOH, EtOH, *i*-PrOH, and *t*-BuOH, respectively. Since the literature values of  $K_e$  for the TEA-alcohol systems have been determined for the systems in nonpolar solvents,<sup>8)</sup> comparison of the data is not pertinent. However, the  $K_e$  values obtained in the present study are comparable with the literature value of  $K_e$ , 0.37, for the 1,4-diazabicyclo[2,2,2]octane-EtOH system in acetonitrile.<sup>9)</sup> The value of  $K_e(\text{H})/K_e(\text{D})$  obtained for the TEA-MeOH system containing 10 vol% MeOH and MeOD was 0.58, which is in accord with the literature value of 0.60.<sup>10)</sup>

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. Quantum yields were measured with a potassium ferrioxalate actinometer by the irradiation of a 313 nm monochromatic light, which was obtained by a combination of a cut-off glass filter (Toshiba UV D-33S) and an aqueous solution of  $\text{K}_2\text{CrO}_4$  (0.2 g/1000 ml).

The photochemical reaction of naphthalene with TEA in acetonitrile yielded an adduct of naphthalene with TEA, i.e., 1-(2-N,N-diethylaminoethyl)-1,4-dihydronaphthalene (1), as a main product and reduction products of naphthalene, i.e., 1,4-dihydronaphthalene (2), 1,2,3,4-tetrahydronaphthalene (3), and bis-1,1'-(1,4-dihydronaphthalene) (4), the products being in agreement with those reported earlier.<sup>4)</sup> The addition of alcohols to the reaction system was found to suppress the formation of the products, particularly the adduct of naphthalene with TEA. Figure 1 shows the quantum yields ( $\phi_r$ ) for the formation of the products in the absence and presence of varying amounts of MeOH. As seen in Fig. 1, the values of

$\phi_r$  for the products decreases with increasing amounts of MeOH, and particularly the decrease in  $\phi_r$  for the adduct (1) formation is striking. The decrease in  $\phi_r$  is parallel to the decrease in  $k_q^{\text{obsd}}$ . Similar results were obtained for the other alcohols, and the extent of the decrease in  $\phi_r$  follows the same order as observed for the fluorescence quenching. It is understood that the occurrence of the hydrogen-bonding interaction between the amine and alcohols added hinder the electron transfer process from TEA to the naphthalene in its electronically excited singlet state because of the decrease in the amount of free TEA and  $k_{qf} > k_{qc}$ , leading to the decrease of both  $k_q^{\text{obsd}}$  and  $\phi_r$ . On the other hand, once the ion radicals are generated, alcohols act as good proton donors to the naphthalene anion radical, and hence  $\phi_r$  for the reduction products 2, 3, and 4 results in slight decrease. It is conceivable that in the case of photochemical reactions in neat or in nonpolar solvents, where electron transfer hardly occurs or back electron transfer occurs rapidly, the acceleration of the reaction by the addition of alcohols may be observed.

In summary, the present study has clearly shown that the addition of alcohols hinders the photochemical reaction of naphthalene with triethylamine in a polar solvent, acetonitrile, and that this is due to the hydrogen-bonding interaction between the amine and alcohols. This concept seems to be extended to other reaction systems.

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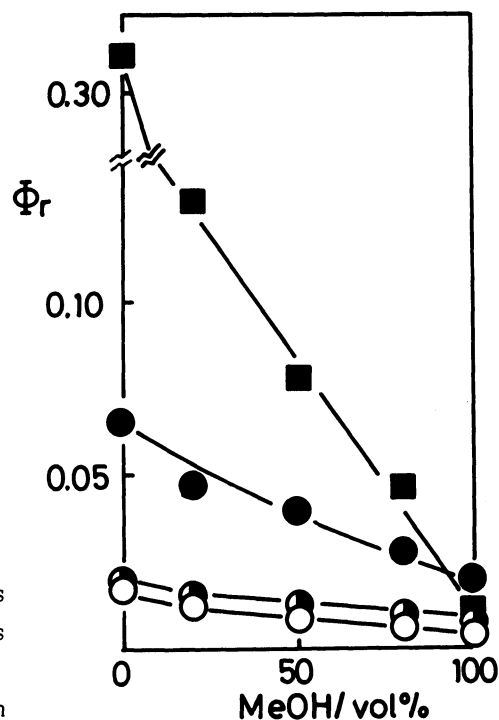


Fig. 1. Quantum yields for the formation of the products in the absence and presence of MeOH. [naphthalene]=[TEA]=0.10 mol dm<sup>-3</sup> (■);  $\phi_1$ , (●);  $\phi_2$ , (○);  $\phi_3$ , (⊙);  $\phi_4$

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