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# The effect of intermolecular hydrogen bonding on the photoinduced electron transfer reaction of a naphthalene–triethylamine–alcohol system: estimation of the equilibrium constant for hydrogen bond formation from fluorescence quenching and reaction pathways

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## Abstract

The effect of intermolecular hydrogen bonding on the photophysical and photochemical processes of a naphthalene–triethylamine system in the absence and presence of alcohols was studied. It is shown that the presence of alcohols reduces both the apparent bimolecular rate constant for the quenching of naphthalene fluorescence by triethylamine and the quantum yields of the products in the order 2-methyl-2-propanol < 2-propanol < ethanol < methanol. It is concluded that the hydrogen bonding interaction between the amine and the alcohol suppresses the electron transfer process from triethylamine to the excited singlet state of naphthalene due to the decrease in the concentration of the free amine, and the alcohol acts as a proton donor leading to a strong decrease in the yield of the adduct of naphthalene with triethylamine. The equilibrium constants for the intermolecular hydrogen bonding of triethylamine with alcohols were estimated from the quenching of the naphthalene fluorescence by triethylamine in the absence and presence of alcohols.

*Keywords:* Intermolecular hydrogen bonding; Naphthalene–triethylamine–alcohol system; Equilibrium constant; Fluorescence quenching

## 1. Introduction

Photoinduced charge transfer reactions have been the subject of extensive studies in recent years [1,2]. Using the 2-vinylnaphthalene (2-VN)–amine system in benzene, we have shown that exciplex formation between 2-VN in the excited singlet state and the amine in the ground state significantly alters the product distribution, resulting in an increase in the trans/cis ratio of 1,2-di(2-naphthyl)cyclobutane relative to that in the absence of the amine. It was concluded that the reaction proceeding through the 2-VN triplet state, which favours the formation of the trans cyclodimer, is enhanced via exciplex formation [3]. We have also reported that the photoinduced electron transfer reaction between naphthalene and 2-(diethylamino)ethanol is strongly affected by the solvent polarity, and that the results are most reasonably explained in terms of the difference between the reactivity of the geminate radical ion pair and the free radical ion [4]. We also studied the correlation between the spin multiplicity of an excited molecule and electron transfer reactions in electron donor–acceptor systems, and showed that the photochemical reactions of 2-VN–dichloromaleic anhydride and 1-vinylnaphthalene (1-VN)–pyromellitic dianhydride systems by direct irradiation and by triplet sensitization exhibit a striking contrast. It was concluded that the radical ion pair generated in the electronically excited singlet state undergoes back electron transfer, whereas that generated in the triplet state leads to the formation of products [5,6].

In this paper, we study the effect of intermolecular hydrogen bonding on photoinduced electron transfer reactions. The effect of the addition of proton donors, such as methanol, on photoinduced electron transfer reactions has been reported in Refs. [7–9]. The addition of methanol, which acts as a proton donor, accelerates the reactions, increasing the yields of the reduction products, in the benzene–triethylamine (TEA) [8] and styrene–TEA [9] systems. In contrast, the addition of methanol has been reported to quench the reaction in a dicyanobenzene–amine system, because it acts as a proton donor and interferes with the proton transfer from the amine radical cation [7]. The addition of an alcohol in a bimolecular photochemical reaction system containing an amine as one component is thought to cause hydrogen bonding interaction with the amine; however, few detailed studies have been reported on how the intermolecular hydrogen bonding interaction

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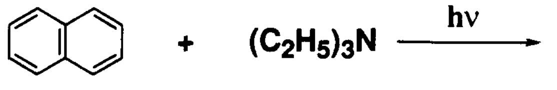
affects the photophysical and photochemical processes of electron transfer. With regard to this question, Lewis and Ho [10], in an investigation of the photochemical reactions of *trans*-stilbene with tertiary amines, briefly reported that hydrogen bonding of the amine with methanol or ethanol appears to hinder exciplex and product formation.

In this study, we have investigated the effect of intermolecular hydrogen bonding on the photophysical and photochemical processes of a naphthalene–TEA system in the absence and presence of alcohols. Part of this work has been reported previously [11].



## 2. Experimental details

### 2.1. Materials

Naphthalene of extra pure grade (Wako Pure Ind., Ltd.) was recrystallized from ethanol and sublimated in vacuo before use. TEA was fractionally distilled over calcium hydride. Acetonitrile was passed through a column using basic, neutral and acidic alumina and then distilled over calcium hydride. Methanol, ethanol and 2-propanol were first dried over molecular sieves (3A) for several days and then fractionally distilled immediately before use. 2-Methyl-2-propanol was purified by fractional distillation over calcium hydride.

### 2.2. Reaction procedures

The photochemical reaction was carried out in a Pyrex tube of 2 cm in diameter using a merry-go-round apparatus. The reaction solution was degassed to $10^{-3}$ Torr using freeze–pump–thaw cycles, sealed and irradiated with a 500 W high-pressure mercury lamp at 15–20 °C. The quantum yield was measured with a potassium ferrioxalate actinometer by irradiation with 313 nm monochromatic light (obtained by a combination of a cut-off glass filter (Toshiba UV D33S) and an aqueous solution of $K_2CrO_4$ (0.2 g $dm^{-3}$)). The quantitative measurement of the product yields was carried out using a Hitachi 164 gas chromatograph with columns of silicone OV-17 (2% on Uniport HP, 1 m) and diethylene glycol succinate polyester (15% on Neopac AS, 1 m).

### 2.3. Identification of products

The reaction products were isolated by column chromatography over silica gel (Wako Gel C-300). 1,4-Dihydronaphthalene and 1,2,3,4-tetrahydronaphthalene were identified by comparison with commercially available authentic samples and by elemental analysis. 1,1′,4,4′-Tetrahydro-1,1′-binaphthyl [12,13] and 1-(2-*N*,*N*-diethylaminoethyl)-1,4-dihydronaphthalene were identified by various spectroscopies, mass spectrometry (MS) and elemental analysis.

1,1′,4,4′-Tetrahydro-1,1′-binaphthyl: MS $m/z$ 258 ($M^+$), 129 ($M^+/2$); proton nuclear magnetic resonance ($^1$H NMR) ($CDCl_3$) $\delta$ 2.78 (2H, d), 3.05 (2H, dd), 3.78 (2H, m), 5.89 (2H, m), 6.00 (2H, m), 6.66 (2H, d), 6.99–7.12 (6H, m); analysis: calculated for $C_{20}H_{18}$: C, 93.02%; H, 6.98%; found: C, 92.64%; H, 6.96%.

1-(2-*N*,*N*-Diethylaminoethyl)-1,4-dihydronaphthalene: MS $m/z$ 229 ($M^+$), 129 ($M^+ - 100$), 100 ($M^+ - 129$); $^1$H NMR (100 MHz, $CDCl_3$) $\delta$ 0.78 (3H, d), 1.02 (6H, t), 2.64 (4H, q), 2.90–3.10 (1H, m), 2.92–3.16 (1H, m), 3.28–3.39 (2H, m), 3.61–3.76 (1H, m), 5.88–6.10 (2H, m), 7.02–7.20 (4H, m); analysis: calculated for $C_{16}H_{23}N$: C, 83.84%; H, 10.04%; N, 6.11%; found: C, 84.09%; H, 10.08%; N, 5.80%.

### 2.4. Measurements

Electronic absorption and fluorescence spectra were measured in air for dilute solutions. The Stern–Volmer constant for fluorescence quenching and the lifetime of naphthalene fluorescence were also measured in air.

Electronic absorption spectra were obtained with a Hitachi U-3200 spectrophotometer. Fluorescence spectra were measured with a Hitachi 850 spectrofluorometer. The fluorescence lifetime was measured with a Horiba NAES-1100 time-resolved spectrofluorometer.

## 3. Results and discussion

### 3.1. Fluorescence quenching

The fluorescence of naphthalene was found to be sharply quenched by the addition of TEA in acetonitrile, but the extent of quenching decreased in the presence of alcohol. Fig. 1 shows the Stern–Volmer plots for the quenching of the naphthalene fluorescence by TEA in the absence and presence of varying amounts of methanol in acetonitrile. The Stern–Volmer plots for the fluorescence quenching gave straight lines in both the absence and presence of alcohol, as expected from Eq. (1) (described later). Table 1 shows the Stern–Volmer constants ($K_{sv}$) for the fluorescence quenching of the naphthalene–TEA system containing varying amounts of alcohols in acetonitrile. The $K_{sv}$ values decrease with increasing amounts of alcohol and in the order 2-methyl-2-propanol (t-BuOH) < 2-propanol (i-PrOH) < ethanol (EtOH) < methanol (MeOH). The addition of alcohol reduces the polarity of the medium in the order MeOH ($\epsilon = 32.6$) < EtOH ($\epsilon = 24.3$) < i-PrOH ($\epsilon = 18.3$) < t-BuOH ($\epsilon = 10.9$), where $\epsilon$ represents the dielectric constant, and hence leads to a decrease in the quenching constant in this order. However, the decreasing order of $K_{sv}$ observed for the alcohols is opposite to that expected from the decrease in the polarity of the medium.

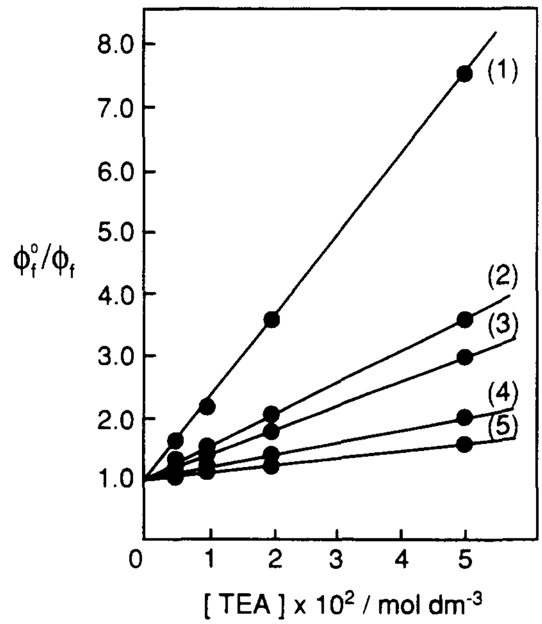


Fig. 1. Stern–Volmer plots for the quenching of naphthalene fluorescence in acetonitrile in the absence and presence of varying amounts of MeOH in air: (1) 0 vol.%; (2) 10 vol.%; (3) 20 vol.%; (4) 50 vol.%; (5) 100 vol.%. [Naphthalene] = $1.0 \times 10^{-4}$ mol dm$^{-3}$.

Table 1
Stern–Volmer constants ($K_{sv}$) for the quenching of naphthalene fluorescence by TEA in acetonitrile in the presence of varying amounts of alcohol

| Alcohol (vol.%) | $K_{sv}$ (dm$^3$ 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 |

[a] In acetonitrile: $K_{sv} = 127.8$ dm$^3$ mol$^{-1}$.

Table 2
Apparent bimolecular rate constants ($k_q^{obsd}$) for the quenching of naphthalene fluorescence by TEA in acetonitrile and various alcohols

| Solvent | $k_q^{obsd}$ (dm$^3$ mol$^{-1}$ s$^{-1}$) |
|---|---|
| Acetonitrile | $9.40 \times 10^9$ |
| MeOH | $0.68 \times 10^9$ |
| EtOH | $1.36 \times 10^9$ |
| i-PrOH | $2.09 \times 10^9$ |
| t-BuOH | $3.28 \times 10^9$ |

Table 2 lists the apparent bimolecular rate constants ($k_q^{obsd}$) for the quenching of naphthalene fluorescence by TEA in acetonitrile and in various alcohols, calculated from the values of $K_{sv}$ and the lifetime of naphthalene fluorescence. The value of $k_q^{obsd}$ decreases significantly in the order t-BuOH < i-PrOH < EtOH < MeOH; the $k_q^{obsd}$ value for the system in MeOH is approximately one order of magnitude smaller than that for the system in acetonitrile. The decreasing order of the $k_q^{obsd}$ values observed for the alcohols is in good agreement with the order of the hydrogen bonding ability of the alcohols [14]. It is therefore reasonable to attribute the decrease in $K_{sv}$ and $k_q^{obsd}$ caused by the addition of alcohols to a hydrogen bonding interaction between the amine and the alcohol. Gebecki [15] has reported that the Stern–Volmer constants for the quenching of anthracene fluorescence by TEA in alcohols are lower than those in aprotic solvents of the same dielectric constant, and that this anomalous behaviour in alcoholic solutions may be explained by the specific interaction between the hydroxyl group of the solvent and the lone pair electrons on the nitrogen atom. It is understood that the decrease in $K_{sv}$ and $k_q^{obsd}$ results from a decrease in the concentration of free TEA and the much smaller bimolecular rate constant for naphthalene fluorescence quenching by hydrogen-bonded TEA relative to that by free TEA.

### *3.2. Estimation of the equilibrium constants for the formation of hydrogen bonds from fluorescence quenching*

Assuming a 1:1 stoichiometry, the equilibrium constant for the formation of a hydrogen bond between TEA and alcohol is expressed by Eq. (1) under the condition of [ROH] ≫ [C]

$$K_e = \frac{[C]}{([ROH]-[C])([TEA]-[C])} \approx \frac{[C]}{[ROH]([TEA]-[C])} \qquad (1)$$

where [C] represents the concentration of hydrogen-bonded TEA. Let the bimolecular rate constants for naphthalene fluorescence quenching by free TEA and by hydrogen-bonded TEA be represented by $k_{qf}$ and $k_{qc}$ respectively; then Eq. (2) holds

$$\phi_f^0/\phi_f = 1 + \frac{1}{1+K_e[ROH]}(k_{qf}+k_{qc}K_e[ROH])\tau_0[TEA] \qquad (2)$$

and $k_q^{obsd}$ is expressed by Eq. (3)

$$k_q^{obsd} = K_{sv}/\tau_0 = \frac{k_{qf}+k_{qc}K_e[ROH]}{1+K_e[ROH]} \qquad (3)$$

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 hydrogen bond formation, [ROH] is the concentration of alcohol and $\tau_0$ is the lifetime of naphthalene fluorescence in the absence of TEA. $k_{qf}$ is thought to be much larger than $k_{qc}$.

If it is simply assumed that the fluorescence quenching takes place mostly by free TEA, i.e. $k_{qf} \gg k_{qc}$, in view of the fact that quaternary ammonium salts, e.g. TEA hydrochloride, do not quench the naphthalene fluorescence, Eq. (3) can be simplified to Eq. (4)

$$k_q^{obsd} = \frac{k_{qf}}{1+K_e[ROH]} \qquad (4)$$

Then the value of $K_e$ can be calculated by substituting the value of $k_q^{obsd}$ obtained for the acetonitrile solution without alcohol as $k_{qf}$. The values of $K_e$ calculated from Eq. (4) for the TEA–alcohol systems in acetonitrile were 0.52, 0.30, 0.21 and 0.13 $dm^3 mol^{-1}$ for MeOH, EtOH, i-PrOH and t-BuOH respectively.

Since the equilibrium constants for the formation of hydrogen bonds for TEA–alcohol systems have been determined for non- polar solutions [14], the fluorescence quenching in a non-polar solvent was examined in order to determine the $K_e$ values for comparison.

Fig. 2 shows the Stern–Volmer plots for fluorescence quenching in the presence of 5 vol.% alcohol in benzene. The Stern–Volmer plots for fluorescence quenching gave straight lines in both the absence and presence of the alcohols t-BuOH, i-PrOH, EtOH and MeOH. The values of $K_e$ for the TEA–alcohol systems in benzene were calculated from Eq. (4) in the same manner as for the TEA–alcohol systems in acetonitrile. The results are summarized in Table 3. The $K_e$ values obtained for the TEA–alcohol systems in benzene are in accord with the literature values of $K_e$ determined from the solvent effects on the $n \rightarrow \sigma^*$ absorption bands of the amine for the TEA–alcohol systems in isooctane [14], taking the different solvents used into account. The results indicate that it is reasonable to assume that the fluorescence quenching takes place mostly by the free amine. Simon and Peters [16] have reported the equilibrium constant for hydrogen bonding between 1,4-diazabicyclo[2.2.2]octane and EtOH in acetonitrile, as estimated from the electron transfer rates determined by laser photolysis during an investigation of the dynamics of interconversion between the solvent-separated ion pair and the contact ion pair. The present results show that the fluorescence quenching technique can serve as a new, convenient method for estimating the equilibrium constants of hydrogen bond formation.

### 3.3. Photochemical reaction pathways

Photochemical reactions of aromatic compounds with amines in polar solvents yield reduction products of the aromatic compounds and adducts via ion radicals generated by photochemical electron transfer [10,17,18]. Thus the photochemical reaction of naphthalene with TEA in aqueous acetonitrile has been reported to give reduction products of naphthalene and an adduct of naphthalene with TEA [17,18]; however, the chemical yields and quantum yields of the products have not been quantified. Spectroscopic evidence for electron transfer from the electronically excited singlet state of naphthalene to TEA has been presented [19].

The photochemical reaction of naphthalene with TEA in acetonitrile yielded the adduct of naphthalene with TEA (1-(1-(*N,N*-diethylamino)ethyl)-1,4-dihydronaphthalene (**1**)) as the main product, together with the reduction products of naphthalene (1,4-dihydronaphthalene (**2**), 1,2,3,4-tetrahydronaphthalene (**3**) and 1,1′,4,4′-tetrahydro-1,1′-binaphthyl (**4**)) (Scheme 1).

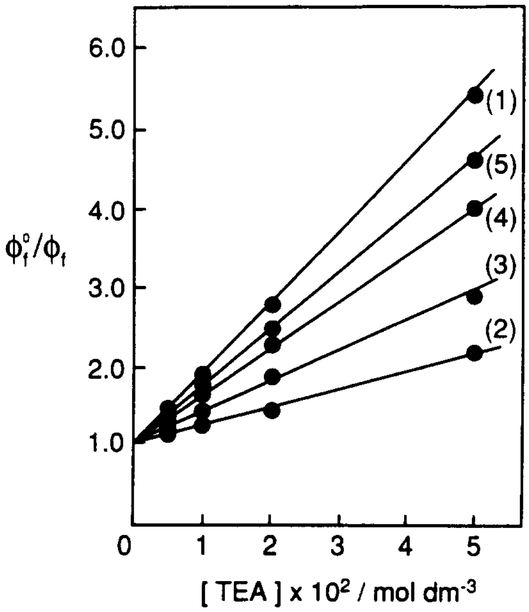


Fig. 2. Stern–Volmer plots for the quenching of naphthalene fluorescence in benzene in the absence and presence of 5 vol.% alcohols in air: (1) benzene only; (2) MeOH; (3) EtOH; (4) i-PrOH; (5) t-BuOH. [Naphthalene] = $1.0 \times 10^{-4}$ mol $dm^{-3}$.

Table 3
Equilibrium constants ($K_e$) for the formation of hydrogen bonds between triethylamine and alcohol in benzene [a]

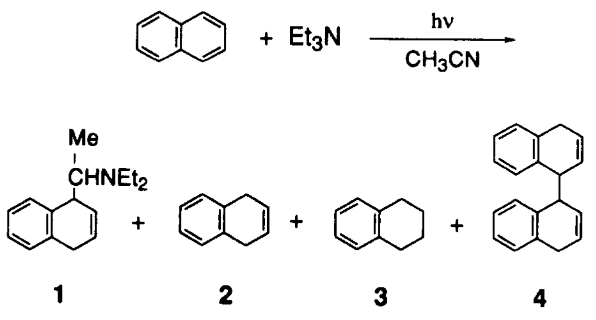
| Alcohol (5 vol.%) [b] | $k_q^{obsd}$ ($dm^3 mol^{-1} s^{-1}$) | $K_e$ ($dm^3 mol^{-1}$) |
|---|---|---|
| MeOH | $1.40 \times 10^9$ | 2.2 (3.4) [c] |
| EtOH | $2.09 \times 10^9$ | 1.8 (2.6) [c] |
| i-PrOH | $3.45 \times 10^9$ | 0.8 (1.4) [c] |
| t-BuOH | $3.85 \times 10^9$ | 0.7 (1.1) [c] |

[a] In the absence of alcohols: $k_q^{obsd} = 5.23 \times 10^9$ $dm^3 mol^{-1} s^{-1}$.

[b] Density of alcohols at 20 °C: MeOH, 0.80; EtOH, 0.79; i-PrOH, 0.79; t-BuOH (25 °C), 0.78 g $cm^{-3}$.

[c] The values in parentheses show the literature values in isooctane [14].

The addition of alcohols to the reaction system was found to suppress the formation of the products, particularly adduct **1**. Fig. 3 shows the quantum yields ($\phi_r$) of formation of the products as a function of the concentration of EtOH in acetonitrile. The quantum yields of the products decreased with increasing amounts of EtOH. In particular, the decrease in $\phi_r$



Scheme 1. Photochemical reaction of naphthalene with TEA in acetonitrile.

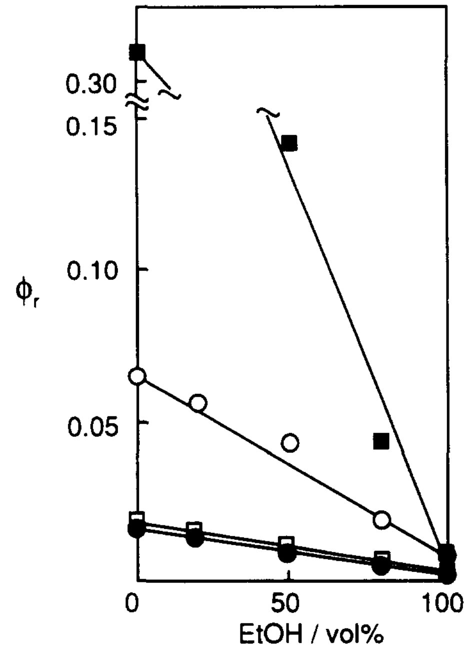
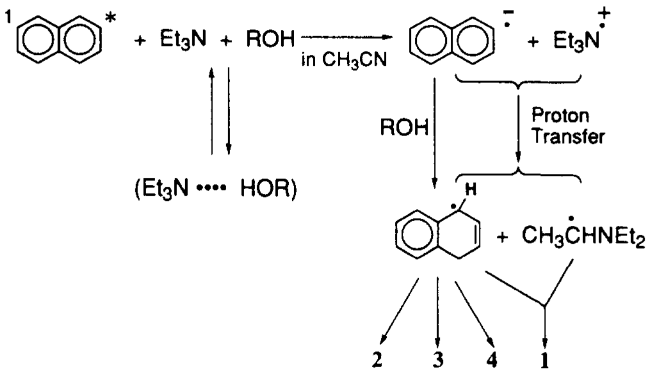


Fig. 3. Quantum yields of products 1–4 in acetonitrile as a function of the concentration of EtOH: ■, 1; ○, 2; □, 3; ●, 4. [Naphthalene] = [TEA] = $1.0 \times 10^{-4}$ mol $dm^{-3}$.

Table 4
Quantum yields of reaction products in acetonitrile in the presence of varying amounts of alcohol

| Alcohol (20 vol.%) | $\phi_r$ [a] | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Without alcohol | 0.310 | 0.065 | 0.017 | 0.016 |
| MeOH | 0.129 | 0.047 | 0.012 | 0.014 |
| EtOH | 0.205 | 0.056 | 0.015 | 0.014 |
| i-PrOH | 0.246 | 0.054 | 0.013 | 0.016 |
| t-BuOH | 0.286 | 0.063 | 0.016 | 0.018 |

[a] [Naphthalene] = [TEA] = 0.10 mol $dm^{-3}$.



Scheme 2. Reaction pathways in the photochemical reaction of the naphthalene–TEA–alcohol system in acetonitrile.

for adduct 1 was striking. The decrease in $\phi_r$ parallels the decrease in $k_q^{obsd}$. As shown in Table 4, similar results were obtained for the other alcohols, and the extent of the decrease in $\phi_r$ followed the same order as observed for fluorescence quenching. It is concluded that the hydrogen bonding interaction between the amine and the alcohol hinders the electron transfer process from ground state TEA to the electronically excited singlet state of naphthalene due to the decrease in the amount of free TEA and because $k_{qf} \gg k_{qc}$, leading to a decrease in $k_q^{obsd}$ and $\phi_r$. Alcohols act as good proton donors to the naphthalene radical anion, and hence $\phi_r$ for 1 shows a striking decrease. The reaction pathways are shown in Scheme 2.

## 4. Conclusions

The effect of intermolecular hydrogen bonding on the photoinduced electron transfer reaction of the naphthalene–TEA system in acetonitrile in the absence and presence of alcohols was studied. It was shown that the intermolecular hydrogen bonding interaction between TEA and alcohol significantly affects both the photophysical and photochemical processes, reducing the apparent bimolecular rate constant for naphthalene fluorescence quenching by TEA and the quantum yields of the products. This is a result of the suppression of the electron transfer process due to the decrease in the concentration of the free amine and $k_{qf} \gg k_{qc}$. It was suggested that the fluorescence quenching technique may serve as a new, convenient method for estimating the equilibrium constant of hydrogen bond formation. It was also shown that the alcohol acts as a good proton donor, causing a striking decrease in the quantum yield of the adduct.

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