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Action of Electron-Accepting Quenchers in Photoisomerization of Naphthylethylenes in Polar and Nonpolar Solvents

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The quantum yield of trans-cis isomerization of 3,3-dimethyl-1-(2-naphthyl)-1-butene was measured in the presence of various electron-accepting quenchers in benzene or in acetonitrile. In benzene the quantum yield was increased by addition of some of the quenchers; however, in acetonitrile it was decreased under similar conditions. This was attributed to more efficient formation of olefin triplets through an exciplex in benzene than through radical ion pairs in acetonitrile.

Recently, much attention has been paid to photoinduced electron transfer leading to characteristic reactions.[1-5] Among these reactions, isomerization of olefins by charge-transfer (CT) interaction with electron donors or acceptors were reported for stilbenes,[6-8] styrylnaphthalene,[9,10] and 1,2-dicyanoethylene.[11] Most studies on stilbenes in the presence of electron acceptors were carried out in very high concentrations of both components, and thus the reaction is usually initiated by excitation of ground state CT complexes. In these cases excitation of the CT complexes gives, by way of radical ion pairs, olefin triplets which play an important role in the isomerization. However, the reaction mechanism upon excitation of monomer olefins without exciting their ground state CT complex has scarcely been explored because of the short lifetime of the singlet excited state of most olefins. It has been reported that photochemical reactions on ground state CT excitation were often different from those on direct excitation of free molecules followed by diffusional CT quenching.[12] Since we have found that the singlet lifetime of an aromatic olefin, *trans*-3,3-dimethyl-1-(2-naphthyl)-1-butene (*trans*-DMNB), is as long as 63 ns in both polar and nonpolar solvents, we attempted to investigate the quenching effects of acceptors on behavior of the excited singlet *trans*-DMNB and also 2-styrylnaphthalene (SN) in acetonitrile and in benzene.

Experimental

Materials. *cis*- and *trans*-DMNB were obtained by the same method as described.[13] *cis*- and *trans*-SN were prepared and isolated as reported.[14] 1,2-Dicyanoethylene (FN) was purified by recrystallization in benzene followed by sublimation. Dimethyl terephthalate (TM), and *o*- (*o*-DCB), *m*- (*m*-DCB), and *p*-dicyanobenzene (*p*-DCB) were purified by recrystallization in ethanol. Benzene was distilled over calcium hydride. Acetonitrile was distilled over diphosphorus pentoxide followed by distillation over potassium carbonate.

Quantum Yield Measurements. Benzene or acetonitrile solutions of pure *trans*-DMNB (0.01 mol dm^{-3}) in the presence or absence of electron acceptors (0—0.02 mol dm^{-3}) in Pyrex tubes were degassed by bubbling argon for more than thirty minutes or by freeze-thaw cycles and were irradiated with 313-nm line of a 400 W high-pressure mercury lamp. The 313-nm mercury line was isolated by a Toshiba UV-D33S glass filter and a filter solution of potassium chromate.[15] Light intensity was determined by potassium tris(oxalato)ferrate(III) actinometry.[15] After irradiating for 1—2 h the conversion was determined by gas chromatography, a Shimadzu GC-4CM-PF gas chromatograph equipped with an FID. The experiments of *trans*-SN were carried out under similar conditions except olefin concentration (5×10^{-4} mol dm^{-3}) and an analytical procedure. The conversion was determined by both gas chromatography and by high-pressure liquid chromatography, a Shimadzu LC-6A and a spectro multichannel photodetector MCPD-350PC (Otsuka electronics).

Photostationary State Isomer Ratios. Photostationary state isomer ratios were determined in the presence of desired concentrations of a quencher and a sensitizer. The solutions were degassed using freeze-thaw cycles and irradiated with a 400W high-pressure mercury lamp. The compositions of the isomer were determined by gas chromatoraphy.

Fluorescence and Laser Photolysis Studies. Fluorescence spectra were obtained on a Hitachi MPF-2A or a Hitachi F-4000 fluorescence spectrophotometer. Fluorescence quantum yields were determined using anthracene (ϕ_f=0.27)[15] as a standard. Laser flash photolyses were performed as described elsewhere.[13] Sample solutions containing *trans*-DMNB (0.01 mol dm^{-3}) and acceptors (0.05 mol dm^{-3}) were deaerated by bubbling argon for 30 min. Fluorescence lifetimes of monomer and exciplex species were measured using a single photon counting apparatus, Applied Photophysics Model SP-3X.

Redox Potentials. Redox potentials were measured by cyclic voltammetry with a Hokuto-Denko Function Generator HB-104 and a Potentiostat/Galvanostat HA-201. Electrochemical measurements were carried out using a three-electrode cyclic voltammetric cell. The working electrode was a platinum wire. Tetraethylammonium perchlorate was used as a supporting electrolyte. The reference electrode was Ag/AgNO$_3$ (0.1 mol dm^{-3}) under an atmosphere of dried argon. The voltammograms were scanned at 100 mV s^{-1}. In some cases, the voltammograms showed no reversible peaks. In such cases, half-peak potentials were employed as half-wave redox potentials. Substrate concentrations were 5×10^{-3} mol dm^{-3}.

Results and Discussion

Fluorescence Quenching of DMNB by Various Electron Acceptors. The fluorescence quantum yield of *trans*-DMNB was determined as 0.61 in benzene and 0.60 in acetonitrile. The fluorescence lifetime of *trans*-DMNB was as long as 63 ns in both benzene and acetonitrile in contrast with those reported for other olefins, for example, 52 ps for *trans*-stilbene,[16] and the fluorescence of *trans*-DMNB was quenched efficiently by electron acceptors. In benzene, a new weak emission of exciplex appeared in longer wavelength. A typical example is shown in Fig. 1 for the case of *trans*-DMNB and *p*-dicyanobenzene. The emission maxima were in the range of 385—485 nm and the emission lifetimes were 5.2 to 27 ns as determined by single photon counting (Table 1). The exciplex lifetime in the case of a methoxycarbonyl-substituted acceptor, TM, is shorter than those in the cases of cyano-substituted acceptors, *o*-DCB, *m*-DCB, *p*-DCB, and FN.

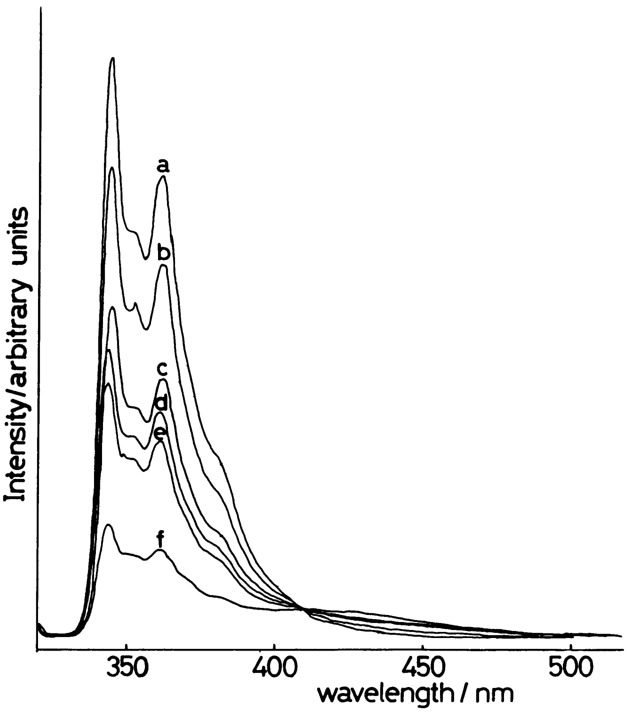


Fig. 1. Fluorescence spectra of *trans*-DMNB in the presence of different concentrations of *p*-DCB in benzene. The concentrations of *p*-DCB are a) 0, b) 4.7× 10^{-3}, c) 1.4×10^{-2}, d) 1.9×10^{-2}, e) 2.4×10^{-2}, f) 8.2× 10^{-2} mol dm^{-3}.

The rate constants for quenching by electron transfer in acetonitrile usually obey the well-known Weller equation (Eq. 1),[1,17] where ΔG° is the standard change of Gibbs free energy for the electron transfer from a singlet excited state to an electron acceptor calculated according to Eq. 2 and $\Delta G^{\circ *}$ denotes the Gibbs free energy of activation obtained from Eq. 3. The value $\Delta G^{\circ *}(0)$ is the Gibbs free energy of activation at $\Delta G^\circ=0$ kcal mol^{-1} (1 cal=4.184 J). The values for E_{red} and E_{ox} are the reduction potential of acceptors and the oxidation potential (1.23 V) of *trans*-DMNB, respectively, determined in acetonitrile and $E_{0,0}$ stands for the singlet excitation energy (83.6 kcal mol^{-1}) of *trans*-DMNB.

$$k_{\mathrm{q}} = \frac{20 \times 10^9\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}}{1 + 0.25\{\exp(\Delta G^{\circ *}/RT) + \exp(\Delta G^\circ/RT)\}} \tag{1}$$

$$\Delta G^\circ = E_{\mathrm{ox}} - E_{\mathrm{red}} - 0.06 - E_{0,0}/\mathrm{eV} \tag{2}$$

$$\Delta G^{\circ *} = \{(\Delta G^\circ/2)^2 + (\Delta G^{\circ *}(0))^2\}^{1/2} + \Delta G^\circ/2 \tag{3}$$

$$\Delta G^{\circ *}(0) = 2.4\ \mathrm{kcal\,mol^{-1}} \tag{4}$$

Table 1 lists the observed quenching rate constants (k_{q}) of the fluorescence of *trans*-DMNB in both deaerated solvents, the reduction potentials (E_{red}), and ΔG° calculated by Eq. 2. Figure 2 plots the energies ($E^{\mathrm{ex}}_{\mathrm{max}}$) corresponding to the maximum wavelength of the exciplex emission ($\lambda^{\mathrm{ex}}_{\mathrm{max}}$) in benzene vs. ΔG°, and shows that the energies of the exciplexes over the ground state nearly linearly decrease with the decrease of ΔG°. This result shows that the larger the extent of charge transfer as revealed by the amount of ΔG°, the more stabilized the resulting exciplex.

In Fig. 3, the plot of the quenching rate constants of monomer fluorescence of *trans*-DMNB by electron acceptors in acetonitrile against ΔG° well fit the curve (curve a) calculated from Eqs. 1—4.[1,17] On the other hand, the plot of the quenching rate constants in benzene is shifted considerably from curve a, and best fit curve b, which is depicted

Table 1. Quenching Rate Constants, Exciplex Lifetimes, and Some Kinetic Values

Quencher	In acetonitrile				In benzene			
	E_{red}[a)]	ΔG°[b)]	$k_{\mathrm{q}}\tau_0$[c)]	k_{q}[d)]$/10^9$	$k_{\mathrm{q}}\tau_0$[c)]	k_{q}[d)]$/10^9$	$\lambda^{\mathrm{ex}}_{\mathrm{max}}$[e)]	τ_{ex}[f)]
m-DCB	−2.19	−6.12	535	8.49	71	1.13	385	12.6
TM	−2.11	−7.96	780	12.4	370	5.87	400	5.2
o-DCB	−2.09	−8.42	826	13.1	466	7.40	435	16.2
p-DCB	−2.07	−10.27	870	13.8	540	8.60	415	26.9
FN	−1.64	−18.80	1000	15.9	880	14.0	485	14.9

a) In V. b) In kcal mol^{-1}. c) In dm^3 mol^{-1}. d) In dm^3 mol^{-1} s^{-1}. e) In nm. f) In ns.

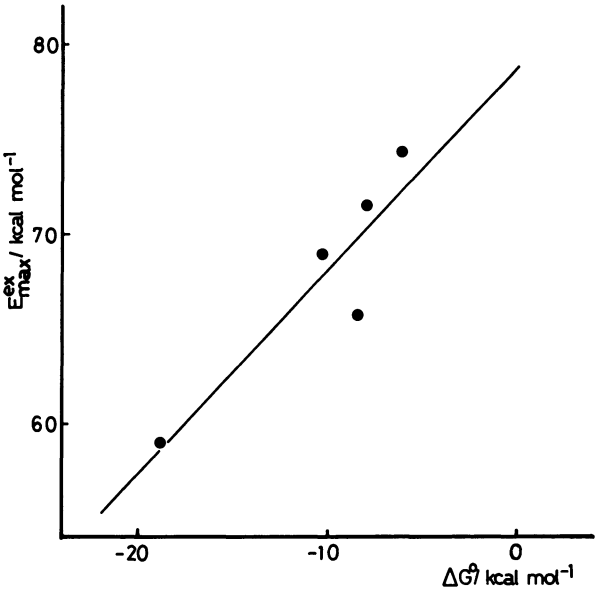


Fig. 2. The linear dependence of the exciplex emission maximum vs. the change of Gibbs free energy.

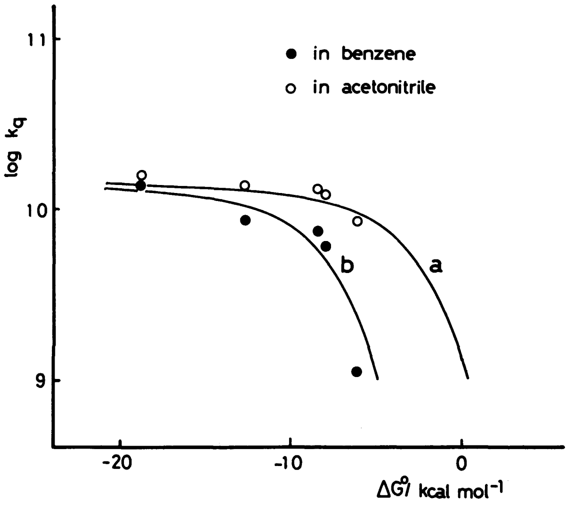


Fig. 3. The relation of the quenching rate constants vs. the change of Gibbs free energy. The curve a (in acetonitrile) is depicted according to Eqs. 1 and 2 (after Weller[17]) and the curve b (in benzene) is the best fitting one according to Eqs. 1 and 5.

by using Eq. 5 instead of Eq. 2. In Eq. 5, the value of 0.16 was chosen to give the best fitting. The energy of

$$\Delta G^\circ = E_{ox} - E_{red} + 0.16 - E_{0,0}/\text{eV} \qquad (5)$$

$$E_e = E_{ox} - E_{red} + 0.15 \pm 0.10/\text{eV} \qquad (6)$$

an exciplex (E_e) in nonpolar solvents can be generally expressed by Eq. 6,[1,17] which can lead to an equation similar to Eq. 5 showing the Gibbs free energy change in the electron transfer reaction in a nonpolar solvent. The above result means that the stabilization energy of the resulting radical ion pair solvated in acetonitrile is 0.22 eV larger than that in benzene. Therefore, it is safely concluded that the quenching of singlet excited state of *trans*-DMNB by electron acceptors proceeds by electron transfer.

Table 2. The Effect of Ferrocene on the Photostationary State Isomer Ratios $([t]/[c])_{pss}$ of DMNB on 2-Acetylnaphthalene Sensitization[a)]

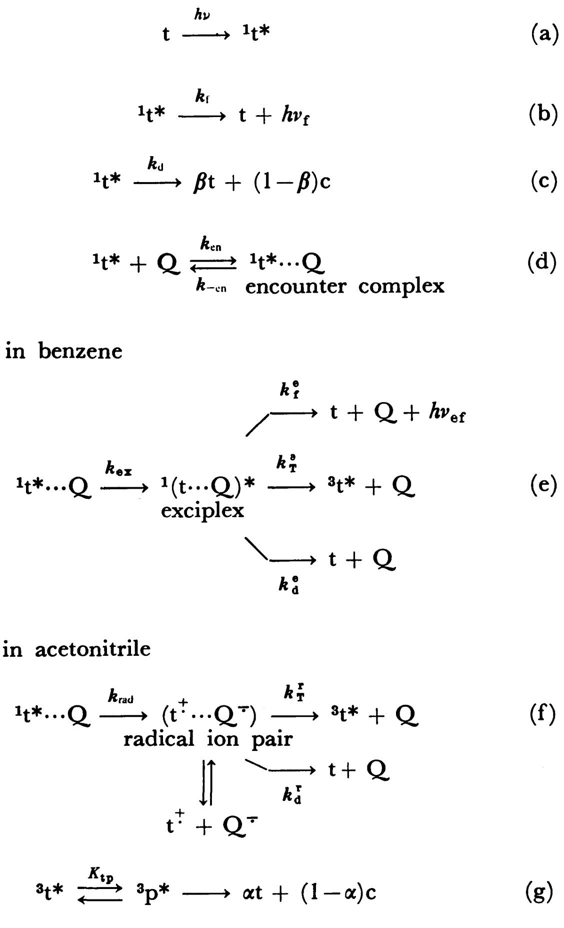
[ferrocene] / 10^{-3}mol dm^{-3}	Trans$_{pss}$ / %	$([t]/[c])_{pss}$
0	43.6±0.4	0.77±0.01
1.0	49.7±0.2	0.99±0.01
2.0	54.0±1.2	1.18±0.06
3.0	57.8±0.2	1.37±0.01

a) In the presence of 0.2 mol dm^{-3} of 2-acetylnaphthalene in benzene.

Quantum Yields of Trans–Cis Isomerization. The quantum yields ($\phi_{t\text{-}c}$) for the isomerization of *trans*- to *cis*-DMNB were 0.13 in benzene and 0.14 in acetonitrile, respectively, in the absence of quenchers. In benzene, $\phi_{t\text{-}c}$ increased with increasing concentration of TM, *o*-DCB, and *p*-DCB, but slightly decreased with *m*-DCB and FN. The trans-cis isomerization was most effective through the exciplex with a quencher having moderate electron acceptability in benzene. On the other hand, in acetonitrile $\phi_{t\text{-}c}$ was decreased on addition of any quenchers examined. These results indicate that behavior of the exciplex considerably changes with electron acceptors which control critically the efficiency of the isomerization.

Mechanism of Trans–Cis Isomerization in the Presence of Electron Acceptors. The isomerization of *trans*-DMNB on direct irradiation can occur in the singlet excited state as well as in the triplet excited state. If the isomerization proceeds on the triplet manifold, $\phi_{t\text{-}c}$ should decrease with the increase of the concentration of an added triplet quencher such as ferrocene, because ferrocene can quench the transoid triplet state of DMNB. Actually, on benzophenone sensitization, the composition of the trans-isomer at the photostationary state of DMNB increased with the increase of ferrocene concentration (Table 2). However, $\phi_{t\text{-}c}$ on direct excitation was not changed on addition of ferrocene. Therefore, it is clear that the isomerization of *trans*-DMNB on direct irradiation proceeds on the singlet manifold.

In view of the fact that $\phi_{t\text{-}c}$ is much higher for triplet sensitization (0.46)[18] than $\phi_{t\text{-}c}$ for direct irradiation, the increase of $\phi_{t\text{-}c}$ in benzene by addition of some quenchers suggests that the triplet state of DMNB is produced in benzene possibly from the exciplex formed from the excited singlet DMNB and the acceptors. Actually, nitrogen laser excitation of *trans*-



$$\mathrm{t} \xrightarrow{h\nu} {}^1\mathrm{t}^* \qquad \text{(a)}$$

$$ {}^1\mathrm{t}^* \xrightarrow{k_f} \mathrm{t} + h\nu_f \qquad \text{(b)}$$

$$ {}^1\mathrm{t}^* \xrightarrow{k_d} \beta\mathrm{t} + (1-\beta)\mathrm{c} \qquad \text{(c)}$$

$$ {}^1\mathrm{t}^* + \mathrm{Q} \underset{k_{-en}}{\overset{k_{en}}{\rightleftarrows}} \underset{\text{encounter complex}}{{}^1\mathrm{t}^*\cdots\mathrm{Q}} \qquad \text{(d)}$$

A) in benzene

$$ {}^1\mathrm{t}^*\cdots\mathrm{Q} \xrightarrow{k_{ex}} \underset{\text{exciplex}}{{}^1(\mathrm{t}\cdots\mathrm{Q})^*} \xrightarrow{k_T^e} {}^3\mathrm{t}^* + \mathrm{Q} \qquad \text{(e)}$$

$$ {}^1(\mathrm{t}\cdots\mathrm{Q})^* \xrightarrow{k_f^e} \mathrm{t} + \mathrm{Q} + h\nu_{ef}$$

$$ {}^1(\mathrm{t}\cdots\mathrm{Q})^* \xrightarrow[k_d^e]{} \mathrm{t} + \mathrm{Q}$$

B) in acetonitrile

$$ {}^1\mathrm{t}^*\cdots\mathrm{Q} \xrightarrow{k_{rad}} \underset{\text{radical ion pair}}{(\overset{+}{\mathrm{t}}{}^{\cdot}\cdots\mathrm{Q}^{\overline{\cdot}})} \xrightarrow{k_T^r} {}^3\mathrm{t}^* + \mathrm{Q} \qquad \text{(f)}$$

$$ (\overset{+}{\mathrm{t}}{}^{\cdot}\cdots\mathrm{Q}^{\overline{\cdot}}) \xrightarrow[k_d^r]{} \mathrm{t} + \mathrm{Q}$$

$$ (\overset{+}{\mathrm{t}}{}^{\cdot}\cdots\mathrm{Q}^{\overline{\cdot}}) \rightleftarrows \overset{+}{\mathrm{t}}{}^{\cdot} + \mathrm{Q}^{\overline{\cdot}}$$

$$ {}^3\mathrm{t}^* \underset{}{\overset{K_{tp}}{\rightleftarrows}} {}^3\mathrm{p}^* \longrightarrow \alpha\mathrm{t} + (1-\alpha)\mathrm{c} \qquad \text{(g)}$$

Scheme 1.

DMNB in the presence of the quenchers, e.g. *p*-DCB, gave the transient absorption due to the DMNB triplet (λ_{max}: around 420 and 580 nm)[13] in benzene. In acetonitrile the absorption due to DMNB radical cation (λ_{max}: 430, 640, and 700 nm)[19] was observed, although that of triplet DMNB was escaped from detection by interference of the absorption due to the radical ions. However, the intermediacy of the excited triplet state of DMNB was supported by the magnetic field effect on the photoisomerization in acetonitrile.[20] Therefore, it is reasonable to propose the preceding mechanism (Scheme 1) for photoisomerization of the olefin in the presence of the electron acceptors. According to Scheme 1, the quantum yield for trans-cis isomerization is described as Eq. 7 (in benzene) or 8 (in acetonitrile).

$$\phi_{t\to c} = \frac{(1-\beta)k_d + k_q[\mathrm{Q}]\mathrm{x}\dfrac{(1-\alpha)k_T^e}{k_f^e + k_T^e + k_d^e}}{k_f + k_d + k_q[\mathrm{Q}]}$$

$$= \frac{(1-\alpha)k_T^e}{k_f^e + k_T^e + k_d^e} + \frac{(1-\beta)k_d\tau_0 - \dfrac{(1-\alpha)k_T^e}{k_f^e + k_T^e + k_d^e}}{1 + k_q\tau_0[\mathrm{Q}]}$$

$$\left(1/\tau_0 = k_f + k_d,\ k_q = \frac{k_{en}k_{ex}}{k_{-en} + k_{ex}}\right) \qquad (7)$$

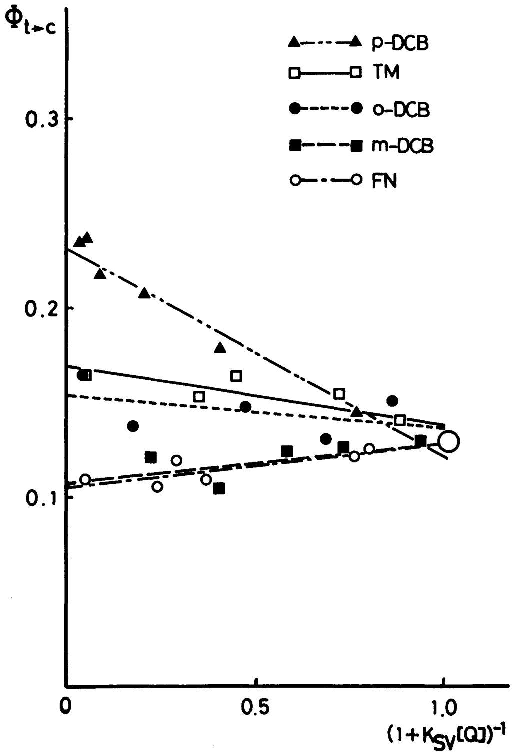


Fig. 4. Plots of the quantum yields for trans-cis isomerization vs. $(1+k_q\tau_0[\mathrm{Q}])^{-1}$ in benzene.

Table 3. Quantum Yields for Trans-Cis Isomerization ($\phi_{t\to c}$) and Some Rate Constants

Quencher	In benzene			In acetonitrile
	$\phi^{\infty}_{t\to c}$	k_T^{e} a)	$k_d^e + k_f^e$ a)	$\phi^{\infty}_{t\to c}$
m-DCB	0.11	1.7	6.3	0.06
TM	0.17	6.3	12	0.02
o-DCB	0.16	1.9	4.3	0.05
p-DCB	0.23	1.6	2.1	0.04
FN	0.11	1.4	5.3	0.01

a) In $10^7\,\mathrm{s}^{-1}$.

$$\phi_{t\to c} = \frac{(1-\beta)k_d + k_q[\mathrm{Q}]\mathrm{x}\dfrac{(1-\alpha)k_T^r}{k_d^r + k_T^r}}{k_f + k_d + k_q[\mathrm{Q}]}$$

$$= \frac{(1-\alpha)k_T^r}{k_d^r + k_T^r} + \frac{(1-\beta)k_d\tau_0 - \dfrac{(1-\alpha)k_T^r}{k_d^r + k_T^r}}{1 + k_q\tau_0[\mathrm{Q}]}$$

$$\left(1/\tau_0 = k_f + k_d,\ k_q = \frac{k_{en}k_{rad}}{k_{-en} + k_{rad}}\right) \qquad (8)$$

Dependence of Charge-Transfer Interaction and Subsequent Steps on Quencher Properties. As Figs. 4 and 5 show, the quantum yields depend linearly upon $(1+k_q\tau_0[\mathrm{Q}])^{-1}$. By extrapolating to the infinite quencher concentration, i.e. $(1+k_q\tau_0[\mathrm{Q}])^{-1}\to 0$, one can obtain the quantum yields of trans-cis

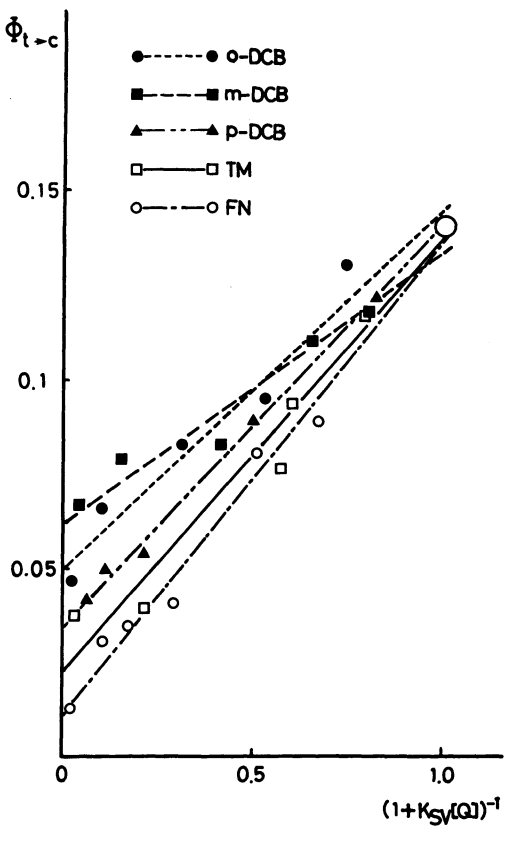


Fig. 5. Plots of the quantum yields for trans–cis isomerization vs. $(1+k_q\tau_0[\mathrm{Q}])^{-1}$ in acetonitrile.

isomerization taking place solely through the exciplex or radical ion pairs ($\phi_{\mathrm{t\to c}}^{\infty}$), as listed in Table 3. The $\phi_{\mathrm{t\to c}}^{\infty}$ values are larger in benzene (0.11—0.23) than in acetonitrile (0.01—0.06). According to the Scheme 1, the quantum yield of triplet formation, ϕ_{T}, is expressed as $\phi_{\mathrm{T}}=\phi_{\mathrm{t\to c}}^{\infty}/(1-\alpha)$ where α, the decay fraction of the triplet DMNB producing the trans-isomer, is 0.48.[18] Accordingly, ϕ_{T} is obtained as 0.21—0.44 in benzene and 0.02—0.12 in acetonitrile varied with quenchers employed.

The trans–cis isomerization of 2-styrylnaphthalene (SN) was reported to be efficient in the presence of *p*-DCB in acetonitrile ($\phi_{\mathrm{t\to c}}=0.53$) as well as in dichloromethane ($\phi_{\mathrm{t\to c}}=0.25$).[10] The quantum yields for stilbene isomerization were also reported in the presence of FN in benzene ($\phi_{\mathrm{t\to c}}=0.11$) and in acetonitrile ($\phi_{\mathrm{t\to c}}=0.22$).[21] In those cases the quantum yields of the trans–cis isomerization increased with the increase of solvent polarity. This is in contrast with the present findings for DMNB. The reason for the difference in exciplex behavior is not certain. In the case of stilbene, however, because of the short lifetime of its excited singlet state, the experiments were done in very high concentrations of both stilbene and acceptors. Therefore, the excitation of a ground state CT complex cannot be ruled out at any wavelength and the isomerization mechanism must be rather complicated. For 2-styrylnaphthalene we have measured the quantum yields of the trans–cis isomerization at 313-nm irradiation and found that with the increase of *p*-DCB concentration in acetonitrile $\phi_{\mathrm{t\to c}}$ decreased, while in benzene $\phi_{\mathrm{t\to c}}$ increased. The $\phi_{\mathrm{t\to c}}^{\infty}$ value was obtained from similar treatments using Eqs. 7 and 8 to be 0.18 (in benzene) and 0.04 (in acetonitrile).[22] The present results in acetonitrile are different from the previous one[10] in which irradiation was performed at 335 nm and trans–cis conversions were analyzed by a UV spectrometer. For analysis we used a gas chromatograph and a high-pressure liquid chromatograph with a multichannel photodiode detector to avoid contamination of side products. Actually, we observed in acetonitrile an unknown product which absorbs at similar wavelengths to *cis*- and *trans*-SN and this may be the reason of an overestimation of the quantum yield for its trans–cis isomerization.[10] Of course, the effect of the irradiation wavelength on the $\phi_{\mathrm{t\to c}}^{\infty}$ value can also explain the above difference.

To examine the effects of acceptors on the decay process of exciplex, we have calculated the rate constant of the triplet DMNB production from the exciplex ($k_{\mathrm{T}}^{\mathrm{e}}$) and the sum of the rate constants for nonfluorescent and fluorescent decay $k_{\mathrm{d}}^{\mathrm{e}}+k_{\mathrm{f}}^{\mathrm{e}}$ as described below. The quantum yields of the triplet formation are expressed as $\phi_{\mathrm{T}}=k_{\mathrm{T}}^{\mathrm{e}}\tau_{\mathrm{ex}}$ in benzene and $\phi_{\mathrm{T}}=k_{\mathrm{T}}^{\mathrm{i}}/(k_{\mathrm{d}}^{\mathrm{i}}+k_{\mathrm{T}}^{\mathrm{i}})$ in acetonitrile. In the case of cyano-substituted compounds, as shown in Table 3, the $k_{\mathrm{T}}^{\mathrm{e}}$ value seems constant regardless of the strength of charge-transfer interaction, $k_{\mathrm{T}}^{\mathrm{e}}=(1.7\pm0.3)\times10^{7}\ \mathrm{s}^{-1}$, while the $k_{\mathrm{d}}^{\mathrm{e}}+k_{\mathrm{f}}^{\mathrm{e}}$ value changed. To compare the efficiency of the isomerization among the isomeric cyanobenzenes for simplicity, it is to be noted that the apparent isomerization efficiency is not governed by the rate for triplet production from the exciplex ($k_{\mathrm{T}}^{\mathrm{e}}$) but by the rate for the deactivation of the exciplex ($k_{\mathrm{d}}^{\mathrm{e}}+k_{\mathrm{f}}^{\mathrm{e}}$). Among the dicyanobenzene isomers, the $k_{\mathrm{d}}^{\mathrm{e}}+k_{\mathrm{f}}^{\mathrm{e}}$ value tends to decrease as the exciplexes are more stabilized compared to the DMNB singlet excited state.

The low quantum yields in acetonitrile indicate that the ion pairs resulting from quenching of the singlet DMNB neither efficiently produce the triplet DMNB, though the radical ion pair (65—77 kcal mol^{-1}) lies sufficiently higher in energy than triplet-DMNB (52 kcal mol^{-1})[18], nor undergo isomerization in the form of the radical cation of DMNB. These results suggest that in acetonitrile the production of DMNB triplet by back electron transfer is not so efficient as in benzene. The radical ions of *cis*-β-methylstyrene and *cis*-stilbene were reported to isomerize effectively into the trans-isomer,[23,24] while the reverse process is inefficient. These facts are in accordance with our results and the assumption that $\mathrm{t}^{+\cdot}$ should be thermodynamically more stable than $\mathrm{c}^{+\cdot}$.

Conclusion

The quenching rate constants of the DMNB singlet state by various electron acceptors in acetonitrile and in benzene fit the curves for electron-transfer quenching mechanism. The electron-transfer process plays the key step for the trans–cis isomerization of *trans*-DMNB. However, once the exciplex is formed, the subsequent processes seem not to be linearly dependent on the reduction potentials of acceptors or the polarity of solvent. The trans–cis isomerization is more efficient in benzene than in acetonitrile, and also in benzene the exciplexes composed of the quenchers with moderate electron acceptability could efficiently produce the DMNB triplet state, the isomerization intermediate.

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