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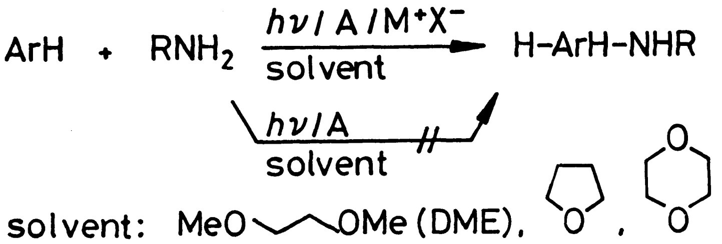
Salt-Induced Photoamination of Arenes by Aliphatic Amines via Arene/p-Dicyanobenzene Exciplexes. A Mechanism for Salt Effects on Charge Separation of Exciplexes

Masahide YASUDA,* Yoriaki MATSUZAKI, Toshiaki YAMASHITA,† and Kensuke SHIMA
Department of Industrial Chemistry, Faculty of Engineering, Miyazaki University,
Gakuen-Kibanadai, Miyazaki 889-21
† Department of Industrial Chemistry, Miyakonojo National College of Technology,
Yoshio, Miyakonojo, Miyazaki 885

Salt Effects on arene/p-dicyanobenzene exciplexes which undergo photoamination of arenes with aliphatic amines in the presence of tetra-n-butylammonium tetrafluoroborate are investigated. From a kinetic analysis it is found that the photoamination proceeds via charge-separation of the exciplexes with the salt followed by nucleophilic addition of aliphatic amines.

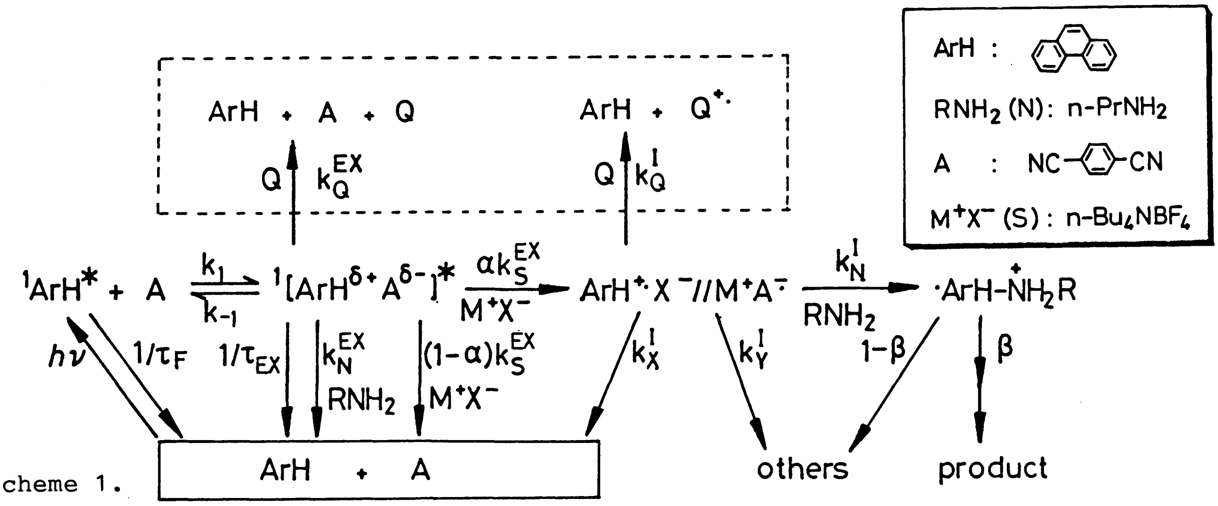
Exciplexes play an important role for the formation of ion radicals as well as for fluorescence quenching and such chemical reactions as cycloadditions.$^{1)}$ Charge-separation of exciplexes into ion radicals is well known to occur in polar solvents.$^{1,2)}$ Recently much attention has been paid to the interactions between exciplexes and salts since it is found that salts can induce the charge separation even in solvents of low polarity.$^{3-6)}$ Herein we wish to report the results of salt effects on arene/p-dicyanobenzene exciplexes which undergo photoamination of arenes with aliphatic amines in the presence of tetra-n-butylammonium tetrafluoroborate (M^+X^-).

Irradiation of some arenes in the presence of aliphatic amines, p-dicyanobenzene (A), and M^+X^- gave dihydroaminoarenes in solvents with relatively low polarity such as 1,2-dimethoxyethane (DME), teterahydrofuran, and 1,4-dioxane.$^{7)}$ In the absence of M^+X^-, however, no photoamination occur at all. In order to investigate the participation of salts on the photoamination, we performed a kinetic analysis for the photoamination of phenanthrene (ArH) with n-propylamine (RNH_2) in the presence of A and M^+X^- in DME.[8)]



Excited-singlet phenanthrene forms emissive exciplex with A in DME.[9)] Though the exciplex emission was quenched by RNH_2, the charge-transfer character of the exciplex is not so large to allow the addition of RNH_2 since no photoamination occur in the absence of M^+X^-. As shown in Fig. 1, Stern-Volmer plot for lifetime quenching of the emission by M^+X^- reveals a linear relationship and shows a good agreement with that for intensity quenching within experimental errors, thus demonstrating that the quenching takes place by dynamic process between exciplexes and dipolar salt. For kinetic analysis, therefore, we assume Scheme 1 involving salt-induced charge separation of exciplexes followed by nucleophilic addition of RNH_2 as a key pathway.

In the absence of quencher (Q), the quantum yield (ϕ) for the formation of the aminated product are given as Eq. 1 by usual steady state analysis where lifetime of ion radicals (τ_I) equals $1/(k_X^I + k_Y^I)$. Equation 2 represents the Stern-Volmer relationship for quenching of the photoamination using p-dimethoxybenzene (Q) as quencher of $ArH^{+\bullet}$. According to Eq. 1, the intercept-to-slope ratio (I/S) of double-reciprocal plot ϕ vs. [S] equals $k_S^{EX}\tau_{EX}/(1+k_N^{EX}\tau_{EX}[N])$. The I/S value of



Scheme 1.

$$\frac{1}{\phi} = \frac{1}{\alpha\beta}\left(1 + \frac{1 + k_N^{EX}\tau_{EX}[N]}{k_S^{EX}\tau_{EX}[S]}\right)\left(1 + \frac{1}{k_N^{I}\tau_I[N]}\right) \qquad (1)$$

$$\frac{1}{\phi^Q} = \frac{1}{\alpha\beta\gamma}\left(1 + \frac{1}{k_N^{I}\tau_I[N]} + \frac{k_Q^{I}[Q]}{k_N^{I}[N]}\right) \qquad (2)$$

$$\gamma = \frac{k_S^{EX}[S]}{1/\tau_{EX} + k_N^{EX}[N] + k_S^{EX}[S] + k_Q^{EX}[Q]}$$

Table 1. Kinetic data

$\lambda_{max}/nm^{a)}$	427
$\tau_{EX}/ns^{b)}$	49
$k_N^{EX}/mol^{-1}dm^3s^{-1}$ c)	4.8×10^9
$k_S^{EX}/mol^{-1}dm^3s^{-1}$ c)	5.6×10^9
$k_Q^{EX}/mol^{-1}dm^3s^{-1}$	8.1×10^9
$\alpha\beta$	0.19
$k_N^I\tau_I/mol^{-1}dm^3$	43
$k_N^I/mol^{-1}dm^3s^{-1}$	6.3×10^9
τ_I/ns	7

a) Emission maxima. b) Emission lifetime. c) Determined from Stern-Volmer constants for exciplex quenching using τ_{EX}.

Fig. 2 shows a satisfactory agreement with the value calculated from Stern-Volmer constants for the exciplex quenching,[10] clearly demonstrating that salt is responsible for charge separation of exciplexes. Moreover $1/\alpha\beta$ and $k_N^I\tau_I$ can be obtained from respective intercept and I/S of plots of $\phi^{-1}[k_S^{EX}[S]/(\tau_{EX}^{-1} + k_N^{EX}[N] + k_S^{EX}[S])]$ vs. $[N]^{-1}$. Since the slope (K_{SV}) of a Stern-Volmer plot of γ/ϕ^Q vs. [Q] at given concentration of RNH_2 equals $k_Q^I/\alpha\beta k_N^I[N]$, $k_Q^I/\alpha\beta k_N^I$ can be obtained from the slope of the plots of K_{SV} vs. [N]. Thus we determined k_N^I and τ_I as listed in Table 1.[11] The formation of ion pair separated by M^+X^- is suggested,[3] since τ_I is much smaller than that of photo-

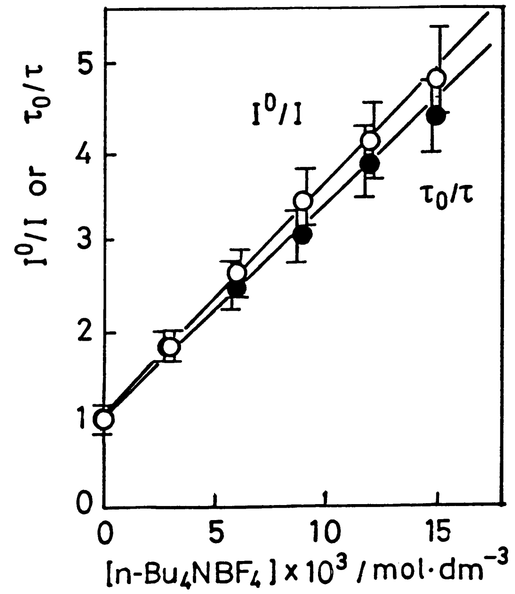


Fig. 1. Stern-Volmer plots for lifetimes quenching (●) and intensities quenching (○) of the phenanthrene/p-dicyanobenzene exciplex with M^+X^- in DME.

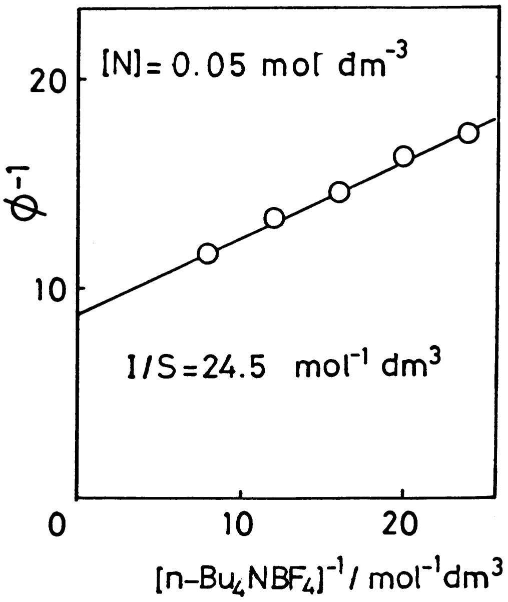


Fig. 2. Double-reciprocal plot of ϕ vs. [S] for photoamination.

generated free cation radicals of ArH.[12)]

In summary, the quenching of exciplexes with dipolar salt bring the charge-separation of exciplexes and the resulting salt-separated ion pairs allow nucleophilic addition of RNH_2.

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7) The photoamination of phenanthrene, anthracene, naphthalene, and 2,3-dimethylnaphthalene were investigated. Details will be published elsewhere.

8) 9-n-Propyl-9,10-dihydrophenanthrene was isolated in a 76% yield.

9) It was cofirmed that the fluorescence of ArH was not quenched by RNH_2, M^+X^- or p-dimethoxybenzene.

10) From Stern-Volmer constants, $k_S^{EX}\tau_{EX}/(1 + k_N^{EX}\tau_{EX}[N])$ is calculated to be 21.2 $mol^{-1}dm^3$ at $[N]= 0.05\ mol^{-1}dm^3$.

11) We reasonably assume that $k_Q^I = 2x10^{10}\ dm^3mol^{-1}s^{-1}$, since the quenching process should be largely exothermic.

12) Lifetime of cation radical of phenanthrene was determined to be ca. 30 ns in $MeCN-H_2O$, see: M. Yasuda, Y. Matsuzaki, K. Shima, and C. Pac, J. Chem. Soc., Perkin Trans. 2, 1988, 745.

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