# Excited Complex Formation Between Styrenes and Tertiary Amines

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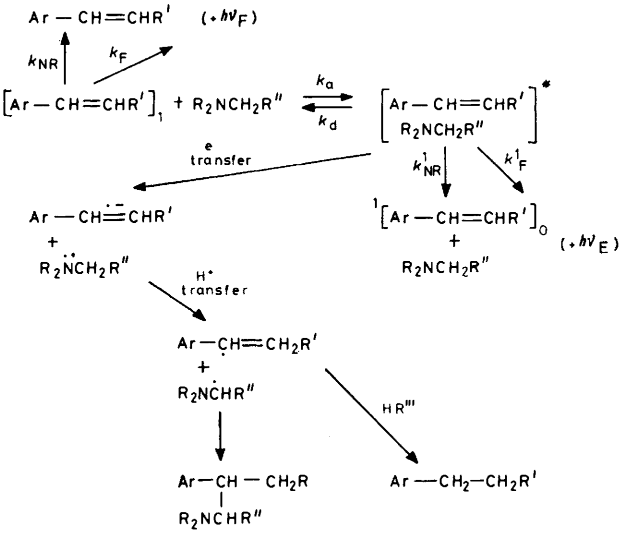
Fluorescence quenching by tertiary amines of a series of aromatic olefins all having the same styryl π-electron system leads to the formation of fluorescent exciplexes. The detection of these fluorescent exciplexes suggests a mechanism for the formation of addition products on irradiation of styrene derivatives in the presence of tertiary amines. Rate constants for styrene fluorescence quenching using a range of styrenes indicate the charge-transfer nature of the exciplex. *NN*-Dimethylaniline fluorescence is quenched by styrene with a rate near to the diffusion rate. However, exciplex emission was not observed.

OUR continuing programme of investigation of the photochemistry and photophysics of styrenes [1] has led us to examine the interactions of electronically excited styrenes and tertiary amines. In particular our interest was aroused by the observations made some time ago, that irradiation of mixtures of tertiary amines and styrene derivatives gave addition products.[2] No mechanism for product formation was given at the time of this earlier work. However, since that time the importance of excited state charge-transfer interactions leading to exciplex formation has been recognized [3] and it was realized that exciplex formation followed by electron transfer, proton transfer, and free radical combination may provide a reasonable mechanism for product formation (Scheme). A radical anion radical cation pair may also be formed directly on collisions between donor and acceptor.



SCHEME

It is always very difficult to provide unambiguous evidence for the formation of photochemical reaction products *via* a route involving exciplex formation and decay. There is the possibility that exciplex and product formation involves separate competitive pathways for the relaxation of a system. We report here the progress that has been made in understanding the photophysics of exciplex formation and decay in styrene–amine systems. The detailed relationship between exciplex decay and product formation will be the subject of a future publication.

## EXPERIMENTAL

*Materials*.—Styrene, *o*-methylstyrene, and indene were purchased from Koch–Light. 1-Phenylcyclopentene (a viscous oil) was synthesized from cyclopentanone *via* a Grignard reaction and dehydration. Its structure was confirmed by mass spectroscopy and n.m.r. and by comparison with published spectroscopic data; *trans*-1-phenylpropene was synthesized in a similar way from benzaldehyde. All the styrenes were purified by distillation and preparative g.l.c. with a Pye 104 g.l.c. using a 20% QF 1 on diatomite C column. The amines, triethylamine, tri-n-butylamine, and *NN*-dimethylaniline, were carefully distilled before use. Koch–Light cyclohexane was purified by passing it twice through a silica column. Acetonitrile was Aldrich Gold Label.

*Fluorescence Spectra*.—All fluorescence spectra were measured on a Farrand Mark 1 spectrofluorimeter fitted with correction modules or on a home-made spectrofluorimeter.

*Fluorescence Lifetime Measurements*.—Fluorescence lifetime measurements were made using a single-photon-counting apparatus constructed in this laboratory. It consists of (i) a free running $H_2$ lamp operated at 3—5 kV, (ii) a high intensity Bausch and Lomb excitation monochromator, (iii) a 56 DUVP photomultiplier tube, and (iv) Ortec electronics and an Ino. Tech. multi-channel analyser (S/5000). Deconvolution of decay curves was achieved using the SXFIT programme kindly supplied by W. R. Ware, University of Western Ontario. The instrument was calibrated using deoxygenated $10^{-5}$M solutions of 9,10-diphenylanthracene in cyclohexane ($\lambda_{excitation}$ 376 nm) and the value of the fluorescence lifetime taken as 7.58 ns.[4]

*Stern–Volmer Plots*.—Stern–Volmer plots were obtained using the Farrand spectrofluorimeter by measuring relative fluorescence spectra peak heights. No changes in the structure of the emissions (apart from the development of exciplex emission) were noted.

## RESULTS

Monomer fluorescence from cyclohexane solutions of styrene (1), *o*-methylstyrene (2), *trans*-1-phenylpropene (3), 1-phenylcyclopentene (4), and indene (5), were all quenched by triethylamine (TEA) and in each case a new, long wave-

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[1] (*a*) M. G. Rockley and K. Salisbury, *J.C.S. Perkin II*, 1973, 1582; (*b*) P. M. Crosby and K. Salisbury, *J.C.S. Chem. Comm.*, 1975, 477; (*c*) R. P. Steer, M. D. Swords, P. M. Crosby, D. Phillips, and K. Salisbury, *Chem. Phys. Letters*, 1976, **43**, 461.

[2] R. C. Cookson, S. M. de B. Costa, and J. Hudec, *Chem. Comm.*, 1969, 753.

[3] R. S. Davidson, 'Molecular Association,' ed. R. Foster, Academic Press, London, 1975, vol. I, p. 215.

[4] D. J. S. Birch and R. E. Imhof, *Chem. Phys. Letters*, 1975, **32**, 56; J. V. Morris, M. A. Mahaney, and J. R. Huber, *J. Phys. Chem.*, 1976, **80**, 969.

TABLE 1

Styrene fluorescence lifetimes and quenching rate constant for quenching by tertiary amines [a] ($\lambda_{\text{excitation}}$ 280 nm)

| | Amine | Solvent | $\tau_F$/ns | $k_q\tau$/l mol$^{-1}$ | $10^{-9}k_q$/ l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| Styrene (1) | $Et_3N$ | $C_6H_{12}$ | 8.4 | 76.9 | 9.2 |
| *o*-Methylstyrene (2) | $Et_3N$ | $C_6H_{12}$ | 7.5 [b] | 62.5 | 8.3 |
| *trans*-1-Phenylpropene (3) | $Et_3N$ | $C_6H_{12}$ | 7.5 [b] | 36.0 | 4.8 |
| | $Et_3N$ | $C_6H_{12}$ | 12.3 [c] | | |
| | $Et_3N$ | $CH_3CN$ | Quenching but no exciplex emission | | |
| | $Bu^n_3N$ | $C_6H_{12}$ | 7.5 [b] | 36.0 | 4.8 |
| Phenylcyclopentene (4) | $Et_3N$ | $C_6H_{12}$ | 7.0 [b] | 42.0 | 6.0 |
| Indene (5) | $Et_3N$ | $C_6H_{12}$ | 15.9 [c] | 12.9 | 0.81 |
| | $Et_3N$ | $C_6H_{12}$ | 8.8 [b] | 6.5 | 0.74 |
| | $Et_3N$ | $CH_3CN$ | 11.0 [c] | 64.2 | 5.8 |
| | $Bu^n_3N$ | $C_6H_{12}$ | 8.8 [b] | 23.0 | 2.6 |

[a] *NN*-Dimethylaniline [$\tau_F$ ($C_6H_{12}$) 2.4 ns] [5] is quenched by styrene; $k_q = 1.4 \times 10^{10}$ l mol$^{-1}$ s$^{-1}$ but no exciplex emission was observed. [b] Aerated solutions. [c] Deaerated solutions.

length emission was observed. Quenching by tri-n-butylamine was examined in the case of (3) and (5) and again new, long wavelength emissions were observed. Although efficient fluorescence quenching occurred in acetonitrile no new emissions were detected. See Table 1 for the monomer fluorescence lifetimes in the absence of amine and quenching rate constants ($k_q$) of the different systems. Table 2 provides data on the maxima of the long-wavelength

TABLE 2

Styrene–triethylamine exciplex emissions in cyclohexane solutions

| Compound | I.p.[6]/eV | log $k_q$ | Exciplex emission [a] $\lambda_{max.}$/nm (eV) |
|---|---|---|---|
| (1) | 8.5 | 9.93 | 399 (3.11) |
| (2) | 8.5 | 9.92 | 410 (3.02) |
| (3) | 8.37 | 9.68 | 389 (3.19) |
| (4) | | | 376 (3.30) |
| (5) | 8.2 | 8.90 | 395 ($C_6H_{12}$–$CH_2Cl_2$ 9 : 1) [b] |
| | | | 400 ($C_6H_{12}$–$CH_2Cl_2$ 4 : 1) [b] |

[a] The accuracy of determining $\lambda_{max.}$ is limited by the broad structureless nature of the emission. [b] Not only did a red shift occur on using a more polar solvent, but a marked decrease in the exciplex emission yield was also noted.

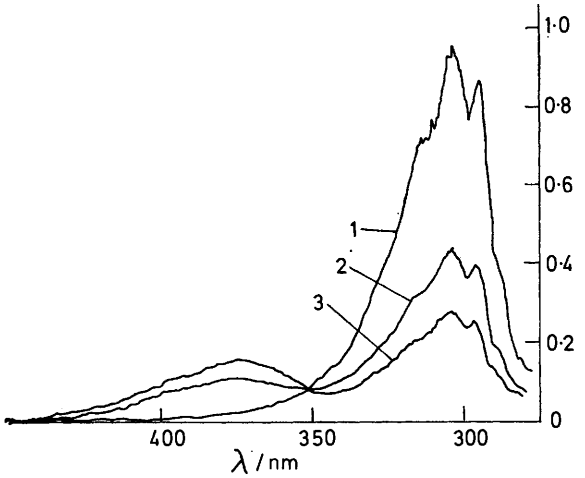

FIGURE 1 Exciplex emission in the indene–triethylamine system. Indene concentration = $3 \times 10^{-4}$M. Solvent; cyclohexane. 1, No triethylamine; 2, 0.1M-triethylamine; 3, 0.4M-triethylamine

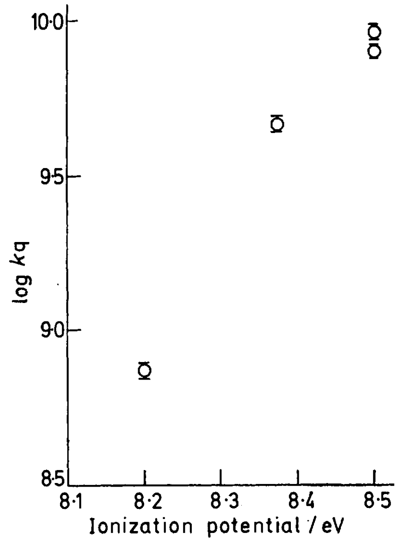

FIGURE 2 Plot of the fluorescence quenching rate constants for triethylamine quenching (cyclohexane solutions) *versus* ionization potential for a series of styrenes

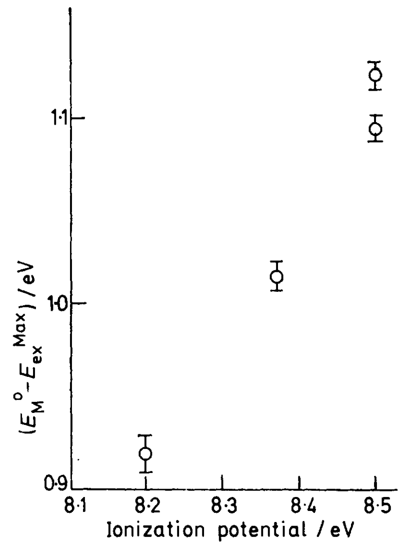

FIGURE 3 Plot of the difference between the energy of the $S_1$, 0–0 band ($E_M^0$) and the $\nu_{max.}$ ($E_{ex}^{max}$) for exciplex emission *versus* ionization potential for a series of styrenes

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[5] I. B. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Molecules,' Academic Press, New York, 1971, 2nd edn., p. 145.

[6] J. P. Maier and D. E. Turner, *J.C.S. Faraday II*, 1973, 196; A. Nakajima and H. Akamatu, *Bull. Chem. Soc. Japan*, 1969, **42**, 3030.

emissions and log $k_q$ and ionization potential values for the systems studied. Figure 1 shows the growth of exciplex emission for the triethylamine–indene system. The data for the quenching of *NN*-dimethylaniline fluorescence by styrene is given at the foot of Table 1.

In order to investigate the correlation between the excited state electron affinities of the styrenes and their $k_q$ and $\nu_{max.}$ (exciplex) emission values, Figures 2 and 3 were constructed.

## DISCUSSION

From the results in Table 1 it is clear that tertiary aliphatic amines efficiently quench the $S_1$ ($^1L_b$) states of styrenes. Since aliphatic amines cannot quench by energy transfer, charge transfer leading to exciplex formation or direct hydrogen abstraction by the styrene from the amine [$ArCH{=}CHR^* + N(CH_2CH_3)_3 \longrightarrow Ar\dot{C}H{-}CH_2R + (CH_3CH_2)_2N\dot{C}HCH_3$] are two possible explanations for the observations. However, in the non-polar solvent cyclohexane, exciplex formation is indicated by the appearance of new, long wavelength emission bands when the styrenes are excited in the presence of tertiary aliphatic amines (Table 2 and Figure 1). The charge-transfer character of the states responsible for the long wavelength emissions is shown by the effect of increasing solvent polarity on the $\lambda_{max.}$ (exciplex) of indene. That the primary quenching interaction is also charge-transfer in character is indicated by the increase in $k_q$ for indene quenching by triethylamine on changing the solvent from cyclohexane to acetonitrile. No exciplex emission was observed for acetonitrile solutions in any of the systems so far examined. However, this observation is consistent with the findings of studies of other exciplex forming systems[3] and has been attributed to increased rate constants of non-radiative relaxation of the exciplexes (*e.g.* to form radical anion–radical cation pairs).

We wished to examine quantitatively the relationship between the excited state electron affinities of the styrenes and the quenching rate constants and exciplex emission wavelengths. Since it was not possible to obtain either the ground state electron affinities or the ground state reduction potentials of the styrenes studied, we made use of their ground state ionization potentials.

The ionization potential of a molecule in its ground state is the energy of its highest occupied molecular orbital and the electron affinity of an excited molecule (in its $S_1$ state) is the energy of the lowest energy unoccupied or partially occupied molecular orbital.[7] Suitable corrections as discussed later must be considered for the latter cases. Thus the relationship between the ionization potential of a ground state molecule and the electron affinity of its $S_1$ state is given by equation (1)

$$(\mathrm{E.A.})^* = (\mathrm{I.P.}) + \mathrm{C} \qquad (1)$$

which holds for a series of structurally similar molecules; C is a constant to take into account molecular reorganization, exchange, and coulombic repulsion effects. A plot of log $k_q$ *versus* I.P. of the styrene should give a straight line for $k_{diff} \ll k_q$ or $k_{diff} \gg k_q$.[8] Since the $k_q$ values measured in this work lie in between these two extremes, only an approximate linear relationship is to be expected. Figure 2 demonstrates that the analysis is reasonably sound and provides further evidence for the charge-transfer nature of the quenching process.

If relationship (1) is accepted then for the simple picture relationship (2) holds, or for the same amine,

$$(\mathrm{I.P.})_{\mathrm{styrene}} - (\mathrm{I.P.})_{\mathrm{triethylamine}} = \mathrm{a}(E_{\mathrm{M}} - E_{\mathrm{ex}}) + \mathrm{b} \qquad (2)$$

$$(\mathrm{I.P.})_{\mathrm{styrene}} = \mathrm{a}(E_{\mathrm{M}} - E_{\mathrm{ex}}) + \mathrm{B} \qquad (3)$$

equation (3) where $E_{\mathrm{M}}$ is the energy of the $S_0 \longrightarrow S_1$ 0–0 transition for the styrene molecule, $E_{\mathrm{ex}}$ is the energy corresponding to the $\lambda_{max.}$ (exciplex) and B, a, and b are constants.

A plot of $(\mathrm{I.P.})_{\mathrm{styrene}}$ *versus* $(E_{\mathrm{M}}^{\circ} - E_{\mathrm{ex}}^{\mathrm{max.}})$ should give a straight line and as Figure 3 shows, this is the case, providing further qualitative support for the charge-transfer character of the emitting state. Thus we believe we have demonstrated that the formation of exciplexes on excitation of styrenes in the presence of tertiary aliphatic amines is an important process.

A further point to note from Table 1 is the effect on $k_q$ seen for decreasing the ionization potential of the tertiary amine. Thus in the case of quenching fluorescence from (**3**) changing the ionization potential of the amine [triethylamine (I.P. 7.5 eV) and tri-n-butylamine (I.P. 7.1 eV)] has no effect on $k_q$. On the other hand, in the case of indene [with a lower I.P. and therefore lower excited state electron affinity than (**3**)] there is a marked increase in $k_q$ when the amine, tri-n-butylamine, is used instead of triethylamine. Observations of this type may be understood in terms of a maximum in the charge-transfer nature of the collision complex, so that any further increase in the ionization potential of donor or electron affinity of acceptor has little effect on $k_q$. It is our intention to explore further the photophysics of exciplex formation and decay in these systems and to relate the processes to the efficiencies of product formation (Scheme).

In order to demonstrate the ability of styrenes to act as electron acceptors in their ground state we examined the fluorescence quenching of excited *NN*-dimethylaniline by styrene in cyclohexane. The fluorescence quenching rate constant so obtained is within experimental error of the diffusion rate ($1.1 \times 10^{10}$ l mol$^{-1}$ s$^{-1}$). However, in the solvent used no exciplex emission was observed.

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[7] G. Briegleb, *Angew. Chem. Internat. Edn.*, 1964, **3**, 617.

[8] B. Stevens, *Adv. Photochem.*, 1971, **8**, 161.