DYNAMICS OF EXCIPLEX FORMATION BETWEEN PERFLUORONAPHTHALENE AND EXCITED ANTHRACENE+

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The dynamics of the exciplex formation between electronically excited anthracene and perfluoronaphthalene was investigated in 2-methyltetrahydrofuran. Analysis of the fluorescence decay curves obtained by single photon counting technique indicate that the exciplex formation and decay follow the standard exciplex mechanism. The rate constant associated with this type of mechanism was evaluated. From their temperature dependence $E_a$, $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ for the exciplex equilibrium reaction were determined. The large values of $\Delta H^\circ$ and $\Delta S^\circ$ indicate a strong binding energy and the formation of a rigid structure in the exciplex state. The unusual negative value for $E_a$ ($-1.48$ kcal/mol), the ground state repulsion energy at the exciplex configuration, is attributed to be due to the unique electron density distribution in perfluoronaphthalene such that the ground state of perfluoronaphthalene-anthracene system at the exciplex configuration has favourable electrostatic interaction.

Key Words: Exciplex Configuration: Perfluoronaphthalene; Anthracene; 2-Methyltetrahydrofuran.

INTRODUCTION

Excited state complexes are the key intermediates in many cycloaddition reactions.\textsuperscript{1–3} The excimers and the exciplexes are the excited state molecular complexes with a well-defined stoichiometry which are dissociative in the ground state.\textsuperscript{4} The equilibrium geometry for the excimers formed from planar aromatic hydrocarbons is known to have plane parallel sandwich structure.\textsuperscript{5} This geometry is similar to that of the dimer cations of planar aromatic compounds.\textsuperscript{6,7} It has been observed that the dimer cations are readily formed from the salts of aromatic hydrocarbon cations. Recently, Bartlett \textit{et al.}\textsuperscript{8} have prepared the cationic salts of a number of planar perfluoroaromatic compounds. However, unlike their aromatic hydrocarbon counterpart no evidence could be found for dimer or polymer formation in these systems. They reasoned that the face-to-face bonding in the system, for example, in $\text{C}_{10}\text{F}_8^+$ and $\text{C}_{10}\text{F}_8$ is energetically not favourable because of the repulsive interaction of the highly electronegative and electron rich fluorine ligands. This indicates that similar face-to-face bonding requirements in the excimers/exciplexes in aromatic perfluorocarbons will be energetically

\textsuperscript{+}Dedicated to Professor Jagdish Shankar on the occasion of his 75th birthday.
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unfavourable and hence suggesting that excited state complex would play a minor role in the photochemistry of aromatic perfluorocarbons.

However it is interesting to note that although dimeric cations are not observed, dimeric anions such as perfluorobenzene dimer anion \((\text{C}_6\text{F}_6)_2^-\), has been observed in the gas phase high pressure electron mass spectrometer\(^9\) and also in the condensed phase at low temperature in isopentane matrix\(^10\) on gamma radiolysis at 77 K. Perfluorobenzene has also been reported to form cluster with the halide anions\(^9\)\(^11\) and the binding energy of such clusters for example, \(\text{F}^-\)\((\text{C}_6\text{F}_6)\), was estimated to be very large \((\Delta H^0 = -27.5\text{kcal/mol})\). This is significantly higher than the binding energy of the similar cluster formed from benzene, \(\text{F}^-\)\((\text{C}_6\text{H}_6)\), \((\Delta H^0 = -15.2\text{kcal/mol})\). These results indicate that polymeric aromatic perfluorocarbons could be formed under favourable energetic and geometrical condition.

Interestingly, Freeman and Srinivasa\(^12\) have recently reported photochemical evidences for the formation of excimers in the photochemical fluoride elimination of pentafluorobenzene and exciplex formation in the presence of triethylamine \((A)\). From the steady state assumption on the quantum yield \((\phi)\) for the photochemical fluoride elimination on the standard excimer/exciplex mechanism,

\[
\frac{1}{\phi} = \frac{k_p + k_4}{k_p} + \frac{k_M (k_p + k_4)}{k_2 k_3 [A]},
\]

they concluded that the excimer formation is the key intermediate in the product formation in the photolysis of pentafluorobenzene in acetonitrile and pentane. They also observed that the main route to the photochemical defluorination in the presence of triethylamine proceeds via the formation of pentafluorobenzene-triethylamine exciplex. However they did not observe fluorescence either from the excimer or the exciplex.

Recently, Kano et al.\(^13\) have studied the fluorescence quenching of naphthalene and perfluoronaphthalene by triethylamine in many solvents including cyclohexane and perfluorohexane. They observed the exciplex fluorescence from naphthalene-triethylamine exciplex but not from perfluoronaphthalene-triethylamine system although quenching proceeds quite efficiently \((k_q = 1.1 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}\) for perfluoronaphthalene and \(5.5 \times 10^9 \text{ M}^{-1} \text{ls}^{-1}\) for naphthalene). They concluded that the electron transfer from triethylamine to the excited perfluoronaphthalene takes place in the excited state prior to the exciplex formation.

Till recently studies on the photophysics and the photochemistry of aromatic perfluorocarbons have been very few\(^12\)\(^14\)\(^15\) and to our knowledge there has not been any report so far on the excimer/exciplex fluorescent from aromatic perfluorcarbon.

In the present work, we have demonstrated the first direct evidence for exciplex formation between perfluoronaphthalene and excited anthracene using steady state and time correlated single photon counting technique. The kinetics and the thermodynamic parameters thus obtained from these studies led us to
conclude that exciplex can play an important role in the photochemistry of aromatic perfluorocarbons.

**Experimental**

The absorption spectra were recorded on a Hitachi-330 spectrophotometer. The fluorescence, the excitation spectra and the steady state quenching studies were carried out on Aminco-Bowman 4-8202B spectrofluorophotometer. Edinburgh Instrument-199, time domain fluorescence spectrometer fitted with variable temperature control unit (Eurotherm) was used for lifetime measurements. The fluorescence lifetime measurements were based on the time correlated single photon counting technique. A thyatron gated flash lamp filled with hydrogen (0.5atm.) was used as the excitation light source. A sequence of light pulses from this lamp (ca. 1.2ns pulse width with a repetition rate of 30kHz) were passed through a monochromator and were focussed on a rectangular sample cell made of quartz. Emitted photons from the sample were passed through a second monochromator and were fed to a photomultiplier (XP-2020Q). The signal pulses thus generated were subjected to constant fraction discriminator with an ORTEC 584 discriminator and was finally fed into an ORTEC 567 TAC as the stop pulses. These time correlated pulses were accumulated and stored on an EG and G 7150 multichannel analyser. In the present case 512 channels were used to store a single decay curve on an excitation pulse profile. The channel width was 0.2ns. A set of data comprising a decay curve and a pulse profile thus obtained was fed into a microcomputer and analysed by the deconvolution method with a program specially written for multicomponent analysis.

Perfluoronaphthalene (PCR Research Inc.) was recrystallized from cyclohexane and anthracene (Fluka Scintillation grade) was used as received. Acetonitrile (Merch spectral grade) was used as received. 2-Methyltetrahydrofuran (Fluka Puriss) was treated with sodium hydroxide and was distilled over metallic sodium under nitrogen atmosphere. The samples were purged with nitrogen (AR) for about 45 minutes.

**Results and Discussion**

The absorption spectra of perfluoronaphthalene (PFN) and anthracene (AN) in 2-methyltetrahydrofuran (MTHF) are shown in Fig. 1. The 0-0 absorption band of AN at 376 nm is well separated from that of PFN band at 320nm, hence it is possible to selectively excite AN in a solution containing both AN and PFN. PFN fluoresce with a low quantum yield ($\phi \approx 0.01$)$^{13}$ and the broad band emission spectrum has maximum at 348nm as shown in the Fig. 2a. On the other hand anthracene fluoresce with relatively high quantum yield ($\phi \approx 0.3$)$^5$ with the characteristic structured emission spectrum with bands at 382, 404 and 424nm as shown in Fig. 2b. PFN quenches AN fluorescence in MTHF solution. The quenching was accompanied by a concomitant formation of a new emission band at 422nm. In a MTHF solution containing $5 \times 10^{-5}$M AN and 0.2M PFN,
excitation of AN band at 376nm yields a structureless fluorescence spectrum with emission maximum at 422nm, characteristic of an exciplex formation as shown in the Fig. 2c.

In more polar acetonitrile solution, the quenching of AN fluorescence by PFN does not lead to the formation of exciplex band as shown in Fig. 3. The quenching follows a simple Stern-Volmer equation:

\[ \frac{I_0}{I_q} = k_q \tau_c [Q] + 1. \]  

The quenching rate constant obtained \( k_q = 9.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \) is close to the diffusion controlled rate constant \( 2.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \) in acetonitrile as shown in Fig. 4 and Table I. The high electron affinity of aromatic perfluorocarbons (\( \sim 1\text{eV} \)) and the low ionization potential of AN (7.38eV) indicate that AN-PFN system would form an attractive electron donor-acceptor pair for the excited state electron transfer from excited AN to the ground state PFN. In highly polar acetonitrile (\( \epsilon = 37.5 \)) medium such an excited electron transfer is likely to lead to the formation of free AN cation and PFN anions as follows

\[ \text{hv} + \text{AN} \rightarrow \text{AN}^* \]

\[ \text{AN}^* + \text{PFN} \rightarrow \text{AN}^+ + \text{PFN}^- \]
Fig. 2: Fluorescence spectra in MTHF of (a) PFN ($\lambda_{\text{exc}}$ = 320 nm), (b) AN ($\lambda_{\text{exc}}$ = 376 nm) and (c) [AN-PFN] exciplex ($\lambda_{\text{exc}}$ = 376 nm).

Fig. 3: Quenching of AN fluorescence by PFN in acetonitrile containing $5 \times 10^{-4}$ M AN (a) [PFN] = 0 M (b) [PFN] = $3.5 \times 10^{-4}$ M and (c) [PFN] = $8.1 \times 10^{-4}$ M.
Fig 4  Stern-Volmer plot for the fluorescence quenching of AN by PFN in acetonitrile

Table I

<table>
<thead>
<tr>
<th>$h_v M$ (eV)</th>
<th>$h_v^{max}$ (eV)</th>
<th>$k_d$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_d$ ($k_d = 8RT/(2000\eta_1)$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.33</td>
<td>2.96</td>
<td>$9.3 \times 10^9$</td>
<td>$2.9 \times 10^{10}$</td>
</tr>
</tbody>
</table>

However, in the less polar medium such as cyclohexane ($\varepsilon = 2.02$) and MTHF ($\varepsilon = 6.24$), there is only a partial charge transfer in the excited state, thus leading to the formation of [AN-PFN] exciplex.

In order to evaluate the complete kinetic parameters for the exciplex formation and decay the following standard exciplex mechanism$^{18,19}$ was assumed as follows in scheme 1:

$$h_v + AN \rightarrow AN^*$$

$$AN^* + PFN \rightleftharpoons [AN-PFN]^* \rightarrow \text{product}$$

$$AN + h_v M \quad AN \quad AN + PFN + h_v E$$
The exciplex mechanism above leads to the following time-dependent equation for a δ pulse excitation:

$$[\text{AN}^\ast](t) = c_1 e^{-\lambda_1 t} + c_2 e^{-\lambda_2 t}$$

...(3)

and

$$[\text{AN-PFN}^\ast](t) = c_3 (e^{-\lambda_1 t} - e^{-\lambda_2 t}),$$

...(4)

where

$$\lambda_{1,2} = \frac{1}{2} [k_1 + k_2 + k_3 [\text{PFN}] + k_4 + k_7 \pm \{(k_1 + k_2

k_3 [\text{PFN}] - k_4 - k_7)^2 + 4k_3 k_4 [\text{PFN}]\}^{1/2}]$$

$$k_7 = k_5 + k_6$$

...(5)

Hence,

$$\lambda_1 + \lambda_2 = k_1 + k_2 + k_3 [\text{PFN}] + k_4 + k_5 + k_6$$

...(6)

$$\lambda_1 \lambda_2 = (k_1 + k_2)(k_4 + k_5 + k_6) + (k_5 + k_6) K_3 [\text{PFN}]$$

...(7)

It is seen from the equations (3-7) that although the [AN-PFN] exciplex fluorescence overlaps considerably with that of the monomer AN fluorescence, it should not affect the measurement of the lifetimes, $\tau_1$ and $\tau_2$.

A typical double exponential decay curve obtained in MTHF solution containing $5 \times 10^{-5}$ M AN and $1.1 \times 10^{-2}$ M PFN at 20 °C is shown in Fig. 5.

![Graph showing decay profile](image)

**Fig. 5** Typical decay profile obtained for MTHF solution containing $[\text{AN}] = 5 \times 10^{-5}$M and $[\text{PFN}] = 1.11 \times 10^{-2}$M and the standard deviation obtained for two component analysis (temperature = 20 °C)
Analysis of the decay profile for two components yields $\tau_1 = 3.17$ and $\tau_2 = 7.41$ ns with CHISQ = 1.01.

Fig. 6b shows $\lambda_1 + \lambda_2$ vs. [PFN] plot of equation 6, for MTHF solution containing $5 \times 10^{-5}$ M AN at 26°C. The slope yields the rate constant ($k_3 = 5.56 \times 10^9$ M$^{-1}$ s$^{-1}$) for the exciplex formation and is close to the diffusion controlled rate constant in MTHF ($2.2 \times 10^{10}$ M$^{-1}$ s$^{-1}$). The exciplex dissociation rate constant ($k_4$) can be obtained by plotting $\lambda_1 \lambda_2$ vs [PFN] using equation 7. The slope ($k_p k_3$) yields $k_p$ since $k_3$ is known. The excited state lifetime of AN ($\tau_\text{M} = 1/(k_1 + k_2)$) can be obtained independently. Hence, the intercept of the $\lambda_1 \lambda_2$ vs [PFN] plot yields the rate constant $k_4$ for the exciplex dissociation.

Fig. 7b shows a typical $\lambda_1 \lambda_2$ vs [PFN] plot for MTHF solution containing $5 \times 10^{-5}$M AN at 26°C. It is interesting to note that the rate constant for the exciplex formation ($k_3 = 5.56 \times 10^9$ M$^{-1}$ s$^{-1}$) is nearly two orders of magnitude higher than the rate constant ($k_4 = 8.59 \times 10^7$ s$^{-1}$) for the exciplex dissociation and the rate constant $k_p$ ($9.6 \times 10^7$ s$^{-1}$) $\approx k_4$ ($8.59 \times 10^7$ s$^{-1}$) indicating that the Steven-Ban$^{4-20}$ equation (8):

$$\log \frac{\phi_{\text{EF}}}{\phi_{\text{MF}}} = \text{constant} - \frac{\Delta H^0}{RT}$$

...(8)

cannot be applied to obtain the thermodynamic parameters such as enthalpy ($\Delta H^0$) of the exciplex formation by steady state measurements.
The activation energies involved in exciplex formation and dissociation were obtained from studies of the exciplex dynamics as a function of temperature as shown in Figs. 6 and 7. Table II lists the rate constants obtained at different temperatures. The activation energies obtained from the Arrhenius plot: $\ln k$ vs. $1/T$, as shown in Fig. 8 are listed in Table III. The activation energy for $k_3(E_3 = 2.94\text{kcal/mol})$ is close to what would be expected from the temperature coefficient ($E_{\text{viscosity}} = 2.3\text{kcal/mol}$) of the viscous flow in MTHF solution. The dissociation rate constant on the other hand involved a high activation energy ($E_4 = 12.92\text{kcal/mol}$), indicating that there is considerable stabilization ($\Delta E = 9.98\text{kcal/mol}$) upon exciplex formation.

The enthalpy ($\Delta H^0$) of the exciplex formation was obtained from the van’t Hoff plot, $\ln K$ vs $1/T$, as shown in Fig. 9 and other thermodynamic parameters such as $\Delta G^0$ and $\Delta S^0$ were evaluated from equations 9 and 10.

$$\Delta G^0 = RT \ln K$$

$$\Delta G^0 = \Delta H^0 + T \Delta S^0$$

Table III lists the thermodynamic parameters obtained for [AN-PFN] exciplex. Interestingly, the exciplex has a strong binding energy ($\Delta H^0 = -9.94\text{kcal/mol}$)
Fig 6(c) Standard $\lambda_1 + \lambda_8$ vs [PFN] plots for MTHF containing $5 \times 10^{-4}$M AN at various temperatures (30 °C).

**TABLE II**

*Rate and equilibrium constants in MTHF at various temperature*

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$k_d \times 10^{-9}$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_d \times 10^{-7}$ (s$^{-1}$)</th>
<th>$k_p \times 10^{-7}$ (s$^{-1}$)</th>
<th>$K$ (M$^{-1}$)</th>
</tr>
</thead>
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<tr>
<td>293</td>
<td>5.0</td>
<td>5.50</td>
<td>11.43</td>
<td>90.90</td>
</tr>
<tr>
<td>299</td>
<td>5.56</td>
<td>8.59</td>
<td>9.60</td>
<td>64.69</td>
</tr>
<tr>
<td>303</td>
<td>5.92</td>
<td>11.51</td>
<td>9.01</td>
<td>51.42</td>
</tr>
</tbody>
</table>

**TABLE III**

*Activation energies and thermodynamic properties of [AN-PFN] exciplex in MTHF*

<table>
<thead>
<tr>
<th>$E_a$ (kcal/mol)</th>
<th>$E_d$ (kcal/mol)</th>
<th>$-\Delta H^0$ (kcal/mol)</th>
<th>$-\Delta G^0$ (kcal/mol)</th>
<th>$-\Delta S^0$ (eu)</th>
<th>$E_R$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.94</td>
<td>12.92</td>
<td>9.94</td>
<td>2.49</td>
<td>24.96</td>
<td>-1.48</td>
</tr>
</tbody>
</table>

and the large negative entropy change ($\Delta S^0 = -24.96$ kcal/mol) indicating the formation of a rigid structure in the exciplex.
Fig 7(a) Standard $\lambda_1, \lambda_2$ vs [PFN] plots for MTHF solution containing $5 \times 10^{-4}$M AN at various temperatures (20 °C).

The binding energy of the [AN-PFN] exciplex is close in value to that of anthracene-diethylamline exciplex ($\Delta H^0 > -10$ kcal/mol) but is considerably higher than that of most excimers\(^{18, 21-25}\) ($\Delta H^0 < -8$ kcal/mol) where the stabilization is mostly due to exciton resonance (AN*-PFN $\leftrightarrow$ AN-PFN*). This indicates that the charge transfer configuration ([AN-PFN]* $\leftrightarrow$ [AN+-PFN-]) contributes considerably to the binding energy in the [AN-PFN] exciplex. The importance of the charge transfer configuration is also demonstrated by the fluorescence quenching in acetonitrile where solvent separated ion pairs are formed (vide infra).

Interestingly, the exciplex emission maximum at 422nm is only slightly redshifted from the AN emission maximum (404nm). The small redshift (1065cm$^{-1}$) of the exciplex emission and the large enthalpy change ($-9.94$ kcal/mol) on its formation indicate a weak ground state repulsion energy, $E_R$, in the exciplex configuration. The value of $E_R$ can be obtained from equation 11, assuming the conservation of energy as follows:
Fig 7(b) Standard $\lambda_{\lambda_2}$ vs $[PFN]$ plots for MTHF solution containing $5 \times 10^{-5}$M AN at various temperatures (26 °C).

$$h_{VM} = -\Delta H^0 + h_{VE}^{\text{max}} + E_R,$$

...(11)

where, $E_R$ is the ground state repulsion energy between AN and PFN in the geometrical configuration of the exciplex, $h_{VM}$ and $h_{VE}^{\text{max}}$ are the energies at 0-0 fluorescence of AN and the maximum of the exciplex fluorescence respectively. Equation 11 yields $E_R = -1.48$ kcal/mol, indicating that the ground state is stabilised in the exciplex configuration. This is in marked contrast to the hitherto known excimers/exciplexes systems where the $E_R$ values are positive, indicating repulsive destabilization in the ground state with the excimer/exciplex configuration. The equilibrium excimer/exciplex geometry is believed to arise from the balance between the ground state repulsion and the excited state attraction. Typical $E_R$ values for benzene and pyrene excimers are 11.3 and 8.1 kcal/mol respectively and somewhat smaller values are observed for exciplexes, for example, anthracene-diethylamidine and perylene-diethylamidine have $E_R$ values 4.4 kcal/mol and 3.0 kcal/mol respectively.\textsuperscript{21}
**Fig 7(c)** Standard $\lambda_1\lambda_2$ vs [PFN] plots for MTHF solution containing $5 \times 10^{-5}$M AN at various temperatures (30 °C).

**Fig 8(a)** Arrhenius plots for [AN-PFN] exciplex formation ($k_3$).
Fig 8 Arrhenius plots for [AN-PFN] dissociation (kₐ) in MTHF solution: ln k vs 1/T

The negative Eₐ value for [AN-PFN] exciplex we believe could presumably be due to the unique electron density distribution in perfluoronaphthalene such that a sandwich configuration between PFN and AN has an attractive potential. Recently, Hiraoka et al. have theoretically evaluated the electron density distribution of totally symmetric D₆h benzene and perfluorobenzene. The values in the parentheses are the electron densities thus obtained and are shown in the diagram below.

The net charge distribution in the free benzene and perfluorobenzene semi-ion pairs in C-H and C-F bonds are estimated to be C⁰⁻²⁻⁻⁻⁻ H⁰⁻⁻⁺⁺ and C⁰⁺⁺⁺⁺ F⁻⁻⁻⁻⁻ respectively. Flygare et al. calculated the electric dipole and quadrupole moments of a large number of molecules. The quadrupole moments, Qₓₓ, Qᵧᵧ and Qزاد (where Z is the component perpendicular to the molecular plane) of C₆F₆ are −8.6, −8.6 and + 17.2 × 10⁻²⁶ cgs esu respectively and the corresponding values for C₆H₆ are +2.8, +2.8 and −5.6 × 10⁻²⁶ cgs esu. The quadrupole moments for C₆F₆ are opposite to that of C₆H₆. That results indicate that a
sandwich configuration between C₆F₆ and C₆H₆ molecules would have an attractive potential. We believe that similar charge distribution in C₁₀F₈ and C₁₄H₁₀ could be responsible for the stabilization in the ground state with the exciplex configuration for [AN-PFN] system and hence a negative value of $E_R$.

In exciplexes with considerable charge transfer character, the oxidation potential of the donor $E(D/D^+)$ and the reduction potential of the acceptor $E(A^-/A)$ are related by the empirical Weller equation as follows:

$$hνE_{max} = E(D/D^+) - E(A^-/A) - 0.15$$

...(12)

This correlation has been observed to be valid for many donor and acceptor pairs. From the exciplex fluorescence maximum of 422nm and the literature value of $E(D/D^+) = 1.16$ V for anthracene, equation 12 yields an estimated $E(A^-/A) = -1.952$ V for the reduction potential of perfluoronaphthalene.

CONCLUSION

The exciplex formation and decay in perfluoronaphthalene-anthracene system follow the standard exciplex mechanism. The enthalpy ($ΔH^0$) and the entropy
(ΔS°) changes accompanying the exciplex formation indicate strong binding energy and the formation of rigid structure. The negative value obtained for ER is unusual because it indicate stabilization instead of the normally expected destabilization in the ground state with the exciplex configuration. This is presumed to be due to the unique electron density distribution in perfluoronaphthalene and anthracene such that the exciplex configuration has attractive potential. However, only appropriate theoretical investigation could lead to a reasonable interpretation for the negative value obtained for ER. The kinetics and the thermodynamic properties obtained in this system indicate that exciplexes may play an important role in the photochemistry of aromatic perfluorocarbons.

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