FLUORESCENCE AND EXCITATION STUDIES

OF SOME MULTICOMPONENT SYSTEMS

My thanks go to Dr Ben Belanger for his guidance, encouragement and above all his infectious enthusiasm.

to Professor Ian Anderson for helpful discussions throughout the course of this work; and to the technical staff of the Department of Chemistry, without whom the experimental work would have been considerably hampered.

This work was carried out with the support of a Commonwealth Postgraduate Scholarship.

by

R.J. McDonald

Canberra
1972
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“Microcrystals in frozen solutions: the luminescence spectra”
J. Mol. Spectrosc.

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J. Mol. Specry. 40, 137.

McDonald, R.J. and Selinger, B.K. 1971
"Reabsorption effects in excitation spectra"

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"The detection of excited state intermolecular electron transfer by fluorescence spectroscopy"
43rd ANZAAS Congress, Brisbane.

McDonald, R.J. and Selinger, B.K. 1971
"Fact and fallacy in fluorescence quenching. II. Exciplex formation"

Selinger, B.K. and McDonald, R.J. 1972
"Exciplex formation in polar solvents"
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INTRODUCTION

Studies in photophysics and photochemistry are unified by the need to identify both permanent and transient species existing in solution. With this broad theme in mind two separate investigations have been pursued in this thesis.

Because of the wide use of glasses and frozen solutions as media for spectroscopic measurements, the nature of species present in such samples is important. Neglect of the separate contributions of the emission spectra of solute, solid and impurities has led, in the past, to incorrect interpretations and assignments of spectra. For this reason the spectral properties of frozen and glassy solutions of several aromatic hydrocarbons have been examined, and the species present identified.

The second investigation is concerned with clarifying the mechanism by which exciplexes are formed and destroyed. Despite the advances in photochemistry over the last decade, little is known of the physical processes involved in the formation and destruction of the photoassociated species which act as precursors to photoproduct formation. By studying the behaviour of
emissive photoassociated species (exciplexes) it is possible to gain some insight into the nature of the intermediates involved in photochemical reactions.

The two investigations are linked by the methods used in both. Fluorescence and phosphorescence spectra have been supplemented by the use of excitation spectra under different limiting conditions. Together these methods allow the characterisation of the species present in a given sample, and also permit the migration of excitation between different species to be traced.

When a fluorescent sample is excited with radiation of wavelength \( \lambda \) and intensity \( I_0(\lambda) \), the total intensity of fluorescence produced, \( F(\lambda) \), is given by

\[
F(\lambda) = I_0(\lambda) (1 - e^{-2.3A(\lambda)}) \gamma_f
\]

where \( A(\lambda) \) is the absorbance of the sample and \( \gamma_f \) its fluorescence quantum yield (see for example Parker 1968a). The measured fluorescence intensity \( F'(\lambda) \) is a function of \( F(\lambda) \) and geometrical and instrumental factors which are independent of excitation wavelength, with the modification that \( A(\lambda) \) measures the absorbance of the sample only over the field of view of the detection system.

A fluorescence excitation spectrum is a plot of the measured fluorescence intensity \( F'(\lambda) \) against the wavelength of excitation \( \lambda \).
CHAPTER 1

FLUORESCENCE EXCITATION SPECTRA

When a fluorescent sample is excited with radiation of wavelength \( \lambda \) and intensity \( I_0(\lambda) \), the total intensity of fluorescence produced, \( F(\lambda) \) is given by

\[
F(\lambda) = I_0(\lambda) \left( 1 - 10^{-A(\lambda)} \right) \phi_f
\]

where \( A(\lambda) \) is the absorbance of the sample and \( \phi_f \) its fluorescence quantum yield (see for example Parker 1968a). The measured fluorescence intensity \( F'(\lambda) \) is a function of \( F(\lambda) \) and geometrical and instrumental factors which are independent of excitation wavelength, with the modification that \( A(\lambda) \) measures the absorbance of the sample only over the field of view of the detection system.

A fluorescence excitation spectrum is a plot of the measured fluorescence intensity \( F'(\lambda) \) against the wavelength of excitation \( \lambda \).
1.1 EXCITATION SPECTRA AT LOW ABSORBANCE

Excitation spectra of low-absorbance samples are

If the absorbance $A(\lambda)$ of the sample is small, higher terms in the expansion

$$F(\lambda) = I_0(\lambda) \left\{ 2.3A(\lambda) - \frac{(2.3A(\lambda))^2}{2} + \frac{(2.3A(\lambda))^3}{(2)(3)} - \ldots \right\}$$

(1-2)

can be neglected and eq. (1-1) reduces to

$$F(\lambda) = 2.3 I_0(\lambda) A(\lambda) \phi_f$$

(1-3)

If $\phi_f$ is invariant to excitation wavelength, the observed fluorescence intensity corrected for the spectral distribution of the exciting light is given by

$$\frac{F'(\lambda)}{I_0(\lambda)} \propto A(\lambda).$$

Invoking the Beer-Lambert law:

$$A(\lambda) = \varepsilon(\lambda) c,$$

this means that for a given sample under conditions of low-absorbance,

$$\frac{F'(\lambda)}{I_0(\lambda)} = \varepsilon(\lambda)$$

(1-4)

and the fluorescence intensity is proportional to the square of the ratio of absorbance of excitation (Eather and Natchard 1963). The excitation spectrum in this case would have more pronounced peaks and minima than the corresponding absorption spectrum, as the fluorescence intensity at a given wavelength is proportional to the square of the extinction coefficient.
Excitation spectra of low-absorbance samples are usually recorded using right-angle geometry. In practice, the excitation spectrum is identical to the absorption spectrum only when $A(\lambda) \ll 1$ (for all $\lambda$ in the region of interest), the condition that was invoked to obtain eq. (1-3). Higher solute concentrations result in unequal illumination throughout the cell, causing a diminution of the intensity of exciting radiation available to produce fluorescence in the field of view. This "inner filter" effect is represented mathematically by the further terms in eq. (1-2). Under these condit-

*This is only true for "single-photon" processes. For delayed fluorescence from, for example, phenanthrene or anthracene, the kinetics is represented by

\[
M + h\nu \rightarrow M^* + h\nu
\]

\[
1M^* + 1M^* \rightarrow \frac{3M^* + 3M^* + 1M^* + M}{h\nu'}
\]

\[
M
\]

and the fluorescence intensity is proportional to the square of the rate of absorption of excitation (Parker and Hatchard 1962). The excitation spectrum in this case would have more pronounced "peaks" and "troughs" than the corresponding absorption spectrum, as the fluorescence intensity at a given wavelength is proportional to the square of the extinction coefficient.
ions eq. (1-4) no longer holds and the excitation spectrum does not accurately represent the absorption spectrum. A point that has been made by Phillips, Gray and Al-Ani (1971) concerning vapour-phase measurements, which is relevant to this discussion, is that if the excitation bandwidth is not small enough to fully resolve the spectrum, a system may appear to be in "low-absorbance" conditions when in fact it is not. The criterion 
\[ A(\lambda) << 1 \]
refers to the actual physical properties of the sample, irrespective of whether the instrument has the resolving power to measure these properties accurately.

The equivalence of the excitation spectrum of a low-absorbance sample and its absorption spectrum has found several applications. Parker and Barnes (1957) noted that a fluorescence excitation spectrum allows separate measurement of the absorption spectra of all species in a mixture, whose fluorescence spectra can be separated. In this context excitation spectra offer a more powerful method of analysis than absorption spectra.

Weber and Teale (1958) and Børrensen (1967) have used excitation spectra to study a number of compounds. They measured the total emission from a sample as a function of excitation wavelength, and attributed deviations from the absorption spectrum in different cases to impurities, the existence of tautomers and ground state association. However, it is worth noting that these deviations were only observed because the separate emissions from more than one species could not
be separated. If it is possible to detect the emission from any one solute selectively, the presence of other absorbing and emitting species should not affect its excitation spectrum, provided that the criterion
\[ \sum_i A_i(\lambda) \ll 1 \]
is met. This result is obtained because under these conditions the probability of absorption is so low that a photon absorbed by a second species would not otherwise have been absorbed.

A profitable variation of fluorescence excitation spectra has been used by Rothman, Case and Kearns (1965) and Borkman and Kearns (1966) in an investigation of singlet-triplet transitions using phosphorescence excitation spectra. The method is naturally restricted to systems from which phosphorescence can be observed. Since it possesses the usual advantage of detecting an emission process rather than a corresponding weak absorption, it is only limited by the intensity of the exciting light and not by the precision with which a difference in light intensity can be measured. By studying the phosphorescence excitation spectra obtained by exciting into both the singlet and triplet manifolds, and knowing the intersystem crossing yield, absolute values have been obtained for the molar extinction coefficient of the singlet-triplet transitions of several molecules. Similar information has been obtained from the excitation spectrum of delayed fluorescence following excitation directly into the triplet manifold (Avakian, Abramson, Kepler and Caris 1963; Avakian and Abramson 1965).
1.2 EXCITATION SPECTRA AT HIGH ABSORBANCE

The usefulness of excitation spectra in the past has stemmed from the fact that the "low-absorbance" excitation spectrum of a compound corresponds to its absorption spectrum. The use of such spectra has tended to obscure the importance of the completely different spectra which are obtained with strongly absorbing samples. In the present work it has been found that study of "high-absorbance" fluorescence excitation spectra can be a valuable aid in elucidating the composition of samples containing more than one species, and in studying the transfer of energy between them.

Under conditions of high-absorbance ($A(\lambda) \gg 1$) eq. (1-1) becomes

$$F(\lambda) = I_0(\lambda) \cdot \Phi_f$$  (1-5)

Under these conditions the fluorescence intensity is independent of the absorbance of the sample; for a sample with fluorescence quantum yield independent of excitation wavelength, the fluorescence intensity depends only on the intensity of the excitation. A fluorescence excitation spectrum which is corrected for the intensity distribution of the excitation source should be flat within the wavelength range in which eq. (1-5) holds.

Right-angle geometry is clearly unsuitable for measuring fluorescence excitation spectra under these conditions, and front-surface illumination is more appropriate. The result given by eq. (1-5) can then be intuitively obtained by considering that for high ab-
sorbances, all the exciting light is absorbed in a small volume within the field of view of the detector: the observed fluorescence intensity is then only a function of the quantum yield of the sample, the intensity of the exciting light, and instrumental factors.

The change from "low-absorbance" to "high-absorbance" conditions achieved by changing the concentration of a solution of 9-methylanthracene in benzene is shown in Fig. 1-1. "Low-absorbance" conditions are only reached in solutions of $10^{-5}$ mole l$^{-1}$ and below, at which concentrations the excitation and absorption spectra agree to within the resolution of the excitation. However, the excitation spectrum retains a qualitative similarity to the absorption spectrum at much higher concentrations, and it is only in solutions containing $10^{-2}$ mole l$^{-1}$ that conditions of "high-absorbance" are met.

An important way in which fluorescence excitation spectra at high absorbance differ from their low-absorbance counterparts is in the spectra of samples containing more than one absorbing species. In low-absorbance samples absorption of light by any one species does not subtract a significant proportion of light from that available for absorption by other species. However, when all the light is absorbed this is clearly not the case, and the fluorescence excitation spectra of high-absorbance samples reflect the competition by each species for the available excitation energy.

In a mixture of more than one absorbing species the amount of absorption ($dI_{abs}$) by any one species, in
**Fig. 1-1.** Corrected fluorescence excitation spectra of different concentrations of 9-methyllanthracene in benzene.

(Excitation bandwidth 0.5 nm)
a thickness $dl$, is given by a form of the Beer-Lambert law:

$$dI_{\text{abs}}(\lambda) = I_0(\lambda) \cdot 2.3\varepsilon(\lambda) \cdot c \cdot dl \quad (1-6)$$

The total amount of light absorbed ($=I_0(\lambda)$) is equal to the sum of $dI_{\text{abs}}$ for all absorbing species. As all the incident light is absorbed, the intensity of fluorescence from a species $i$ is proportional to the fraction of the incident light it absorbs, and therefore from eq. (1-6):

$$F_i(\lambda) = \frac{dI_{\text{abs},i}(\lambda)}{\sum_i dI_{\text{abs},i}(\lambda)} = \frac{\varepsilon_i(\lambda) c_i}{\sum_i \varepsilon_i(\lambda) c_i} \quad (1-7)$$

1.3 DEPENDENCE OF FLUORESCENCE QUANTUM YIELD ON EXCITATION WAVELENGTH

The preceding discussion assumes that the fluorescence quantum yield of a compound in a condensed phase is independent of the excitation wavelength. This has been observed for many compounds, and is embodied in Vavilov's law. It arises from extremely fast intramolecular (or possibly intermolecular (Birks 1970a)) radiationless transitions between different electronic states, followed by rapid dissipation of vibrational energy to bring a molecule into thermal equilibrium with its environment. For the same reasons the shape of the fluorescence spectrum and the decay time are also independent of ex-
citation wavelength.

The relationships between fluorescence excitation spectra and absorption spectra (as in eqs. (1-4) and (1-7)) rely on the constancy of quantum yield with excitation wavelength. Thus it is worthwhile to consider exceptions to this general rule.

$S_2 \rightarrow S_0$ fluorescence

The fluorescence of azulene and its derivatives was for some time the only example of fluorescence from any but the lowest excited state of a molecule. Other examples of this violation of Kasha's rule (and, by implication, of Vavilov's law) have been sought but until recently no examples have remained unchallenged. In 1969 Geldorf, Rettschnick and Hoytink reported emission from the second excited singlet state of pyrene vapour, and this has been followed by reports of fluorescence from the $S_2$ states of 1,2-benzanthracene and 3,4-benzopyrene in solution (Easterly, Christophorou, Blaunstein and Carter 1970) and the decacycline mononegative ion (Brugman, Rettschnick and Hoytink 1971). In all cases the effect is small.

Two chromophores connected by a saturated alkane chain

In molecules of this type the absorption spectrum is very nearly the sum of that of the two chromophores. The observed fluorescence spectrum and quantum yield depends on the quantum yields of the two chromophores and their relative extinction coefficients in the same way as it would for an equimolar mixture of the two chromophores, considered as separate molecules. If the
system is considered in this way its photophysical properties are not anomalous. Some energy transfer takes place between the chromophores, but the transfer is in no case complete, as would be required in order that the molecule as a whole obey Vavilov's law.

**Benzene**

In concentrated solutions of benzene the fluorescence quantum yield depends on excitation wavelength (Braun, Kato and Lipsky 1963). However, studies using added quenchers indicate that this is due to the production of a photochemical product which then acts as a quencher (Lawson, Hirayama and Lipsky 1969). The concentration of quencher produced is a function of the extinction coefficient, leading to the apparent dependence of $\phi_f$ on the excitation wavelength.

**Quinine sulphate**

The fluorescence quantum yield and excitation spectra of this compound have been the subject of much detailed study, because it possesses many characteristics desirable in a fluorescence standard. Previous reports that the quantum yield depends on the excitation wavelength (Børrensen 1965; Chen 1967; Dawson and Windsor 1968) have recently been discounted by Fletcher (1969). He found that if exciting radiation of the same spectral bandwidth was used when recording both the absorption and excitation spectra, the fluorescence quantum yield was constant to within 5% over a large wavelength range. (The caution that valid comparisons can only be made between spectra obtained using the same spectral band-
width, was also given by Weber and Teale in 1958). Fletcher has suggested that the dependence of the observed quantum yield on excitation wavelength may be due to this being disregarded, and possibly also to the use of absorption spectrophotometers in which fluorescence of the sample can contribute to the observed measurement.

In another study, the fluorescence excitation spectrum of a low-absorbance solution of quinine sulphate has been found to agree with its absorption spectrum to within less than 5% (Gill 1969). From these results and others (Eastman 1967; Turner 1971), Demas and Crosby (1971) have concluded that the quantum yield of quinine sulphate in acid solution is constant over a wide range of excitation wavelengths.

Although the shape of the emission spectrum of quinine sulphate is independent of exciting wavelength below 350 nm, it exhibits a progressive red shift when excited at longer wavelengths (Chen 1967). This has been interpreted in terms of the existence of at least two different "average" conformations, each with its own distinct excited state (Fletcher 1968).

The determination of fluorescence quantum yields is fraught with such difficulty that some uncertainty in values obtained at different wavelengths of excitation can be expected. The current acceptance that the quantum yield of quinine sulphate is independent of excitation wavelength is significant, and follows the recent accumulation of sufficient data to enable previous contradictory
reports to be discounted. As a result, it seems reasonable to require corroboration of any reports of the variation of the quantum yield of any compound with excitation wavelength.

1.4 DISTORTION OF EXCITATION SPECTRA

1.41 Energy transfer

The initial distribution of excitation between different species in a mixture can be determined for the limiting cases of low- and high-absorbance samples. This population may then be altered by energy transfer, which will accentuate the emission from the energy acceptor at the expense of that from the donor. In high-absorbance solutions, energy transfer will cause the spectrum to deviate from eq. (1-7). Under conditions of low-absorbance, where excitation of one species does not take place at the expense of the other, energy transfer will tend to superimpose the absorption (or excitation) spectrum of the donor on that of the energy acceptor.

In both cases the shape of the normal fluorescence spectra of both species remains unchanged.

1.42 Differential absorption of exciting light ("inner-filter effect")

Parker and Rees (1962) have shown that the inner-filter effect can cause a large change in excitation spectra when right-angle illumination is used. The proportion of exciting light absorbed before it reaches the field of view of the detector depends on $\varepsilon(\lambda)$, and
therefore on the excitation wavelength. The result is to change the effective incident intensity and thus modify the excitation spectrum.

If a system is properly in the limit of low-absorbance, inner-filter effects are negligible and the excitation spectrum is not distorted.

1.43 Differential absorption of emitted light (re-absorption effects)

The phenomenon of reabsorption of fluorescence arises because fluorescence excited within the body of a solution has to pass through part of the sample before detection. Where the absorption spectrum of a species overlaps its fluorescence spectrum, the fluorescence in this wavelength region may be reabsorbed*. For a given concentration of a solute, the extent of reabsorption depends on the distance the fluorescence has to travel through the solution to the edge of the cell at the focus of the detection system. If the excitation spectrum is produced by monitoring the change with exciting wavelength of either

a fluorescence band which is partly overlapped by the absorption spectrum, or

*To avoid unnecessary confusion, the term "absorption" is reserved for the primary absorption of incident light. "Reabsorption" is used here to describe the absorption of fluorescence by the solution. While re-absorption is most commonly caused by the fluor itself, the arguments presented apply to any species present whose absorption spectrum overlaps the emission spectrum of the fluor.
the total fluorescence emission, part of which is overlapped by the absorption spectrum, the spectrum obtained will be modified by reabsorption.

If excitation takes place at a wavelength corresponding to a high molar extinction coefficient of the species, a given fraction of the incident light will be absorbed more closely to the front of the cell, than for excitation at a wavelength where the extinction coefficient is lower. Thus the higher the extinction coefficient, the closer to the front of the cell is the emission produced. From this reasoning it appears that the effect of reabsorption would depend on geometry. Three geometries are in use for the study of fluorescence spectra, and the effect of each is considered separately.

(i) High-Absorbance Samples

**Front-surface observation.** From the reasoning above, excitation at an absorption peak of the species will result in emission which has not as far to travel through the solution, as emission which is produced when the species is excited at an absorption trough. Emission produced by excitation at an absorption trough would suffer more from reabsorption than emission produced by excitation at a peak, resulting not in a "flat" spectrum, but in a spectrum with troughs at those wavelengths at which the compound absorbs least strongly.

**In-line observation.** In this geometry, the further the fluorescence is produced from the front of the cell, the shorter distance it will have to travel through the solution. Thus the emission will be
reabsorbed more strongly when excitation takes place at an absorption peak. This would be expected to produce a high-absorbance spectrum with troughs at those wavelengths at which the compound absorbs most strongly: the opposite result to the "front-surface" spectrum.

Right-angle observation. From section 1.42 above it is obvious that fluorimeters having "right-angle" geometry are not well suited to fluorescence measurement at high-absorbance. The effect of reabsorption on excitation spectra is expected to vary widely, depending on which region of the sample cuvette is viewed by the detection system, and the spectra obtained could vary between the two extreme results above.

The complete anticoincidence of the excitation spectra of high-absorbance solutions obtained using different geometries is verified experimentally using perylene. Fig. 1-2a shows the uncorrected excitation spectra of a solution of perylene, obtained by observing a section of the fluorescence spectrum which is not re-absorbed. For concentrations of $1.5 \times 10^{-4}$ mole l$^{-1}$ and above in cyclohexane and benzene, for which the absorbance is "high" ($>3$) in the region 440-370 nm, the excitation spectrum is independent of geometry. Fig. 1-2b shows the effect of reabsorption on the excitation spectra in the two geometries. For purposes of comparison, the absorption spectrum of perylene (Fig. 1-2c) is shown below each of the excitation spectra. It is emphasised
Fig. 1-2. Uncorrected fluorescence excitation spectra of perylene, $1.5 \times 10^{-4}$ mole l$^{-1}$ in benzene, using two different geometries. Spectra (a) were observed at 500 nm; spectra (b) were observed at 432 nm. For purposes of comparison the absorption spectrum (c) is shown under both sets of excitation spectra.

(Excitation bandwidth 2 nm)
that the excitation spectra in Fig. 1-2b are deviations from the spectra in Fig. 1-2a.

The reabsorbed front-surface excitation spectrum is diminished most strongly at those wavelengths where the extinction coefficient of perylene is least*, as it is at these wavelengths that the fluorescence is produced furthest from the front-surface of the cell. An almost opposite effect is observed on the in-line spectrum. The positions of the peaks in the excitation spectrum do not correspond to peaks in the absorption spectrum as in the front-surface method, but correspond more closely to the troughs.

This relatively simple experiment confirms the predicted result, and shows the dramatic effect that the geometrical arrangement may have on excitation spectra.

Excitation spectra of highly absorbing samples may be distorted not only by reabsorption of fluorescence but by the subsequent emission. Whereas the effect of reabsorption on the excitation spectrum can be minimised by a suitable choice of emission wavelength, the effect of emission following reabsorption is more insidious as it will be observed over the whole emission spectrum. Thus the excitation spectrum of a sample in which some reabsorption is occurring, taken at an emission wave-

*The high degree of similarity between the reabsorbed high-absorbance excitation spectrum and the absorption spectrum is to some extent a coincidence. Had a slightly shorter wavelength of observation been chosen the amount of reabsorption would have been greater, and the peaks and troughs would have been more accentuated.
length at which no reabsorption is obvious, may still be affected by re-emitted fluorescence. (The effect of re-emitted fluorescence on the observed fluorescence quantum yield has been analysed by Melhuish (1961).) In these experiments the fluorescence was collected over a small solid angle, and only an estimated 0.5% of the re-emitted fluorescence was detected. If it were detectable, it would appear in all the spectra in Fig. 1-2. From the absence of any effect on the spectra 1-2a, it is concluded that it did not affect the results.

(ii) Samples not in the limit of high absorbance

When in-line geometry is used, the excitation spectra of samples which are not optically dense is a function of two opposing drives. Unlike the previous case, more light is absorbed at wavelengths at which the extinction coefficient is greater, resulting in a greater fluorescence intensity. However, excitation into a strong absorption band results in the production of fluorescence near the front of the cell, and this is subject to more reabsorption than if it were produced more evenly throughout the cell. Similarly, excitation spectra obtained using right-angle geometry will reflect the competition between these two effects, whereas in a "front-surface" excitation spectrum the two drives reinforce each other. Thus the excitation spectra of samples which are not in the high-absorbance limit are expected to depend not only on the geometry of the system but on the absorbance of the sample.

In the limit of low-absorbance, fluorescence is produced evenly throughout the cell. The extent of re-absorption which occurs under these conditions depends
on the absorbance of the sample, not at the wavelength of excitation but at the wavelength of fluorescence. Thus when low-absorbance conditions are attained by the use of very dilute solutions the effect of reabsorption on the fluorescence excitation spectrum is small. In this context it is worth noting that excitation spectra of low-absorbance samples are most free of distortion when taken using right-angle geometry, with the field of view of the detector near that side of the cell at which the excitation is incident. Under these conditions the distance the fluorescence travels through the sample to the detector is independent of the variation of \( \varepsilon \) with excitation wavelength.

A block diagram of the redesigned instrument is shown in Fig. 2-ia. Both the exciting and analysing components were connected to a light-tight box, which contained only lenses and the cell holder. The optical rail supporting the excitation source could be rotated for either "front-surface" or "right-angle" use.

Excitation was by a Metal XPB 150-watt xenon lamp. (The lamp was powered by a supply that was only partially smoothed; its stability was improved by placing a series of lead accumulators in parallel with it.) Excitation wavelengths were selected by a Bausch & Lomb "high intensity" monochromator in conjunction with a filter. The fluorescence was analysed by a Leiss 9212
CHAPTER 2

EXPERIMENTAL

2.1 THE SPECTROFLUORIMETER

An existing spectrofluorimeter was completely re-built to enable the work described in this thesis to be carried out. The former instrument has been described previously (McDonald 1968) and was adequate for many purposes. However, the difficulties associated with running excitation spectra, and a general lack of flexibility, made reconstruction necessary.

A block diagram of the redesigned instrument is shown in Fig. 2-1a. Both the exciting and analysing components were connected to a light-tight box, which contained only lenses and the cell holder. The optical rail supporting the excitation source could be rotated for either "front-surface" or "right-angle" use.

Excitation was by a Wotan XBO 150-watt xenon lamp. (The lamp was powered by a supply that was only partially smoothed; its stability was improved by placing a series of lead accumulators in parallel with it.) Excitation wavelengths were selected by a Bausch & Lomb "high intensity" monochromator in conjunction with a filter. The fluorescence was analysed by a Zeiss MM12...
Fig. 2-1. A block diagram of the spectrofluorimeter
(a) in the "emission" mode
(b) in the "excitation" mode.

The sections of the instrument used in each mode are shown in heavy outline; those sections not used are shown in faint outline. Lenses are not shown.

L: lamp
M: single monochromator
MM: double monochromator
F: filter
PM: photomultiplier
C: cell holder
B: light-tight box
..... exciting light
... emitted light
double prism monochromator and detected by an EMI 6256B photomultiplier, the outside of which was painted with finely powdered graphite held at the photocathode potential. The output was fed to a Princeton JB/4 phase-sensitive amplifier. Chopping of the light signal was achieved in two ways: by a vibrating reed within the analysing monochromator, or by a rotating chopper in the excitation path.

Fluorescence and excitation spectra were obtained by scanning with the appropriate monochromator. However, the wide bandpass of the excitation monochromator (ca. 2 nm) made it unsatisfactory for obtaining excitation spectra of species with narrow absorption bands. The installation of a Zeiss wavelength drive onto the analysing monochromator made it feasible to use it also as an excitation monochromator. A second light-tight box was placed on the other side of the Zeiss monochromator. Comparison of Figs. 2-la and 2-lb shows the changes that were necessary in order to run excitation spectra. Although it takes time to effect the changeover from "emission" to "excitation" mode, an obvious advantage is that in each case the scanning monochromator (Zeiss) has satisfactory resolution.

2.2 CHEMICALS

Some solvents were available in "spectroquality" grade from B.D.H. and Matheson, Coleman & Bell. These were tested to ensure that they gave no detectable
fluorescence, and then used without further purification. Other solvents were distilled thrice at room temperature, and tested for fluorescence.

Solutes were treated as indicated below.

**anthracene**

**biphenyl**

**1-cyanonaphthalene**

**9-cyanophenanthrene**

**1,4-diazabicyclo[2.2.2]octane**

**diethylaniline**

**dimethylaniline**

**2,5-dimethyl-2,4-hexadiene**

**9-methylanthracene**

**2-methoxynaphthalene**

**naphthalene**

**perylene**

**phenanthrene**

**pyrazine**

Fluorescence, and then used without further purification. Other solvents were distilled thrice at room temperature, and tested for fluorescence.

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**9-methylanthracene**

**2-methoxynaphthalene**

**naphthalene**

**perylene**

**phenanthrene**

**pyrazine**

Fluka puriss., treated with KMnO₄, sublimed and zone-refined.

recryst. from ethanol, recryst. from methylcyclohexane; sublimed under vacuum (collected at 77K)

recryst. from cyclohexane

sublimed twice under vacuum from anhydrous BaO (collected at 77K)

refluxed with acetic anhydride then distilled twice under nitrogen and stored under nitrogen in the dark.

as for diethylaniline

Fluka puriss., used without further purification

recryst. from benzene

recryst. from ethanol, recryst. from cyclohexane

distilled twice from sodium, chromatographed on silica gel, and recryst. twice from ethanol (from Dr. W.H.F. Sasse)

Fluka puriss.; recryst. from benzene

treated with maleic anhydride; sublimed under vacuum

sublimed under vacuum (collected at 77K)
POPOP Fluka puriss. (scintillation grade) used without further purification

pyrene zone-refined

tolan Fluka puriss., zone-refined

triethylamine distilled twice under nitrogen

2.3 TECHNIQUES

Geometry

Parker (1968b) has discussed the factors governing which geometrical arrangement is most suitable in a given case. Because many of the solutions used in this work were strongly absorbing, "front-surface" geometry was used except where stated otherwise.

Deoxygenation

All solutions were deoxygenated by purging with high purity dry nitrogen, presaturated to prevent evaporation of solvent. In common with Berlman (1965), it was found that most of the oxygen was removed very quickly. However, bubbling was continued for ten to fifteen minutes to ensure thorough deoxygenation.

The decay times of solutions of several aromatic hydrocarbons deoxygenated in this way were the same as those deoxygenated by the freeze-thaw-freeze method, as reported by other workers. This is good evidence that purging with nitrogen is a satisfactory technique.
Low-temperature measurements

Studies of frozen solutions were carried out by immersing the samples in liquid nitrogen, contained in a silica Dewar flask. The flask used for front-surface emission measurements was cylindrical; that used for absorption was cylindrical with optically flat discs set into opposite sides. Samples were contained in specially constructed cells, with windows made of Suprasil I silica, 3 mm apart. In addition to the treatment described previously, solvents used at low temperatures were dried over sodium.

When measurements are made photographically, fluctuations in intensity do not affect the quality of the spectra. However, photoelectric detection is subject to such changes during the recording of spectra, and measurements at 77K were complicated by the formation of bubbles of nitrogen on the sides of the Dewar. This was stopped by slowly bubbling a steady stream of helium through the liquid nitrogen.

Pyrazine crystals were grown between two quartz discs; a "hot-bench" melting point apparatus was particularly useful for this purpose, as the temperature of the sample could be varied quickly and easily.

Temperature dependence studies

The solution was contained in a stainless steel vessel with a window of Suprasil I silica. Deoxygenation and constant stirring was achieved by bubbling nitrogen, which had first been passed through a chamber in the metal section of the cell in which it became pre-saturated with solvent at the temperature of the solution.
The solution could be heated or cooled by circulating paraffin oil, methanol or liquid nitrogen "boil-off" through the metal sections of the cell.

**Measurements at room temperature**

Samples studied at room temperature were contained in 10 mm cells made of high quality silica. The face of each cell had an absorbance of <0.005 above 260 nm.

**2.4 CORRECTION OF SPECTRA**

Emission spectra

Fluorescence and phosphorescence spectra obtained in any experiment are functions of the spectral characteristics of the analysing components: monochromator, photomultiplier, and any other optical accessories through which the emission passes before detection. The correction curve applied to spectra obtained from the present instrument is shown in Fig. 2-2a. It results from the greater dispersion of the prism monochromator at shorter wavelengths, and the lower sensitivity of the photocathode (S13) at longer wavelengths. Multiplication of experimental spectra by this function yields spectra in which the ordinate is proportional to quanta of energy per wavenumber (or frequency) interval, as suggested by Chapman et al. (1963). Because correction of most of the emission spectra presented does not alter them drastically, they have not been corrected except where specifically stated. However, where integrated spectra have been
Fig. 2-2a. The correction curve to be applied to emission spectra to make the ordinate proportional to the number of quanta per unit wavenumber interval. The curve was obtained by comparing spectra with those given by Berlman (1965) for benzene, biphenyl, naphthalene, BBD and perylene (after Nott (1971)).

Fig. 2-2b. The fluorescence excitation spectrum of a high-absorbance solution of POPOP in ethanol, used to correct excitation spectra. The portion of the spectrum below 300 nm is identical in shape to the excitation spectrum of a high-absorbance solution of naphthalene in cyclohexane.

---

new lamp

-- -- lamp after 200 h use.
used to obtain quantum yields, spectra of quanta per unit wavenumber interval vs. wavenumber (linear scale) have been used.

Excitation spectra

The large change in intensity with wavelength of excitation sources necessitates correction of excitation spectra.

The excitation spectra of "high absorbance" solutions of pyrene and naphthalene in cyclohexane, and POPOP in ethanol, were found to be identical within experimental error, in the regions where the spectra overlapped. As it is most unlikely that the three compounds exhibit the same variation of fluorescence quantum yield with excitation wavelength, they were assumed to be quantum proportional emitters. Excitation spectra were corrected by comparison with the spectra of one or more of these emitters. Care was taken to record these spectra under exactly the same conditions as the spectra to be corrected. In particular, the same excitation assembly (lamp, monochromator and lenses) and the same cell were used. A typical spectrum is shown in Fig. 2-2b. It was also necessary to take into account the effect of age on the spectral distribution of the lamp; Fig. 2-2b shows the different spectral distributions of a new and an old lamp. Because of this ageing effect, correction spectra were run before and after a batch of excitation spectra.
The use of frozen or glassy solutions for studies of molecular luminescence at low temperatures is time-honoured. An obvious danger when studying systems under these conditions is the possibility of crystallisation of the solute due in some cases to lower solubility at low temperatures, and in other cases to crystallisation of the solvent. The possibility that molecular luminescence in frozen solutions might be complicated by the formation of these aggregates, described as microcrystals, was recognised twenty years ago (Moodie and Reid 1951). However, this possibility has been neglected on some occasions. There are also instances where microcrystal formation has been discounted for the wrong reasons, due partly to the fact that at this stage the criteria for the formation of such aggregates are imperfectly understood.

We have examined a number of systems which have been reported to possess anomalous luminescence characteristics in frozen solution, and have found that in many cases the anomaly is a direct or indirect result of the presence of microcrystals.
Interest in the fluorescence of pyrene in frozen solution started in 1965 when Ferguson obtained a spectrum of pyrene in frozen cyclohexane, containing both monomer- and excimer-like components. The "excimer" emission was observed at concentrations down to $10^{-5}$ mole $^{-1}$, and its intensity increased with concentration. This emission was attributed to the presence in the cyclohexane matrix of pairs of pyrene molecules with orientations suitable for excimer formation. The lifetime of the pyrene monomer was assumed to be sufficiently long to allow excitation energy to migrate until trapped at these sites, even though the fraction of molecules suitably oriented must be very small.

More recently Mataga, Torihashi and Ota (1967) have measured the excitation spectra of "monomer" and "excimer" bands of pyrene fluorescence in frozen cyclohexane solution, and found them to be different. The excitation spectrum of the "excimer" extends to lower energy than that of the "monomer", and is claimed to arise from a transition to a higher electronic state of a pyrene dimer which is forced to exist in the cyclohexane matrix.

In the most recent work on this topic, Loewenthal, Tomkiewicz and Weinreb (1969) have investigated the influence of concentration, solvent, temperature and excitation wavelength on the emission of pyrene in frozen solutions. Their principal results and conclusions are...
Results obtained using frozen solutions of pyrene in methylcyclohexane and toluene differ from those obtained in cyclohexane and benzene. No excimer-type emission is observed from frozen solutions of the first two solvents, and the following observations refer to frozen solutions of pyrene in cyclohexane or benzene.

The emission spectra exhibited an "excimer" band similar to that observed in fluid solutions, even at quite low concentrations ($\sim 10^{-4}$ mole $l^{-1}$ in cyclohexane). The "excimer yield" (the ratio of "excimer" to "monomer" emission, measured by two suitable peak heights) increased with concentration.

The excimer yield increased if the solution was cooled more slowly, or if the solution was annealed. The emission spectrum was sensitive to excitation wavelength.

For a given excitation wavelength, the excimer yield is a maximum near the freezing-point of the solution.

In a more concentrated solution ($5 \times 10^{-3}$ mole $l^{-1}$ in cyclohexane) a new, strong emission band is observed, with maximum at 415 nm.

On first examination it would appear that many of these observations could be explained by the formation of microcrystals, which for pyrene exhibit excimer-type emission (Ferguson 1958). However, Mataga et al. and Loewenthal et al. have examined this possibility and dismissed it, for reasons which are discussed later.
In addition, there are at least two reasons for repeating the previously reported experiments. In one case, the fluorescence spectra were measured using an "in-line" apparatus, with the detection system on the opposite side of the sample cell to the excitation source. This method results in reabsorption of the short-wavelength edge of the fluorescence spectrum. Secondly, many of the results have been discussed in terms of the "excimer yield". This is an unsatisfactory parameter because it relies on peak heights (which do not represent band areas when the band changes shape, as at different temperatures), and because an examination of the "excimer yield" considers a ratio of two effects (on the "monomer" and "excimer" fluorescence intensities) which need to be considered separately.

3.11 Influence of concentration and solvent

Following the reported excimer-type emission from frozen solutions of pyrene in cyclohexane and benzene, and the lack of this type of emission from solutions of the methyl-substituted analogues, experiments were carried out in a number of other solvents: ethanol (90%), pentane, p-xylene (chosen because it is electronically similar to benzene and toluene, and has an intermediate freezing-point), and isopentane - methylcyclohexane 3:1 (chosen because it forms a glass rather than crystals).

At concentrations similar to those used previously ($\sim 10^{-3}$ mole $l^{-1}$) no excimer-type emission was observed from solutions in any of these solvents. However, in-
creasing the concentration of pyrene resulted in excimer emission from solutions of pyrene in a number of solvents, including solvents in which excimer emission was not previously reported. The concentrations of pyrene in various solvents which produced approximately equal intensities of "monomer" and "excimer" emission were: cyclohexane $5 \times 10^{-4}$ mole $L^{-1}$, p-xylene $2 \times 10^{-2}$ mole $L^{-1}$, methylcyclohexane $>10^{-1}$ mole $L^{-1}$.

This result suggests that the solvents differ merely in degree, and not in kind as inferred by Loewenthal et al. Cyclohexane may be an exception as the solid exists in at least two crystalline forms (Leach, Lopez-Delgardo and Grajcar 1966) and it is possible that the annealing processes used previously will cause reversion to the more stable monoclinic crystal form. Such changes in the environment of the solute may well affect its behaviour.

3.12 Excitation spectra of pyrene solutions

The excitation spectrum of a solution of pyrene in cyclohexane at room temperature is shown in Fig. 3-1. The concentration of the solution was $10^{-3}$ mole $L^{-1}$ and to attain "low-absorbance" conditions at this concentration an optical path length of 0.01 mm was used. After normalisation the excitation spectra of monomer and excimer peaks (measured at 383 nm and 470 nm respectively) were identical. To within the limit of resolution of the excitation monochromator, the spectra closely resemble the absorption spectrum of pyrene monomer. This is, in fact, a necessary property of prompt excimer
Fig. 3-1. Fluorescence excitation spectrum of pyrene, $10^{-3}$ mole $l^{-1}$ in cyclohexane, in 0.01 mm cells at room temperature. The spectrum shown represents the excitation spectra of both the monomer and excimer bands, which are identical in shape.
emission, and follows from the definition of an excimer. This observation is included to emphasise that if two species result (directly or indirectly) from the same absorption process, they will have identical excitation spectra. Having noted this, we proceed to study the results obtained in frozen solutions.

The excitation spectra of solutions of pyrene in cyclohexane at 77K are shown in Fig. 3-2. The "monomer" excitation spectrum (solid line) was monitored at 382.5 nm and that of the "excimer" (dashed line) at 470 nm.

The two different excitation spectra indicate the presence of two distinct absorbing species.

The excitation spectrum of the pseudo-excimer peak in $10^{-2}$ mole $\ell^{-1}$ solution is flat below 350 nm to within the accuracy of the correction curve (see section 2.4). In $10^{-3}$ mole $\ell^{-1}$ and $10^{-4}$ mole $\ell^{-1}$ solutions the "troughs" produced in this spectrum become more pronounced, and are associated with peaks in the excitation spectrum of the monomer.

This can be explained on the basis of two competing species in a "high-absorbance" solution, and the amount of fluorescence from each species will be given by eq.

* Excitation spectra were recorded by setting the analysing monochromator at the required wavelength, then recorded again using a slightly different wavelength. Coincidence of the spectra occurred in all cases, indicating that the excitation spectra are not caused by a shift of emission peak with excitation wavelength.
Fig. 3-2. Emission and excitation spectra of frozen solutions of pyrene in cyclohexane at 77K.

(a) Emission spectra
(b) Excitation spectra. The broken line represents the excitation spectrum of the "excimer" band, and the solid line the spectrum of the monomeric species.
This will of course not be the case for the weakly absorbing tail of the absorption spectrum, where absorption of light by one species does not occur to the detriment of the other. Thus the dashed line in the region from 390 nm to about 350 nm is expected to trace out the absorption spectrum of this species.

The spectrum of $10^{-2}$ mole $\lambda^{-1}$ solution indicates a large proportion of the species giving excimer emission, and a small proportion of monomer, such that the fraction of light absorbed by the monomer is very small.

The spectra of $10^{-3}$ mole $\lambda^{-1}$ and $10^{-4}$ mole $\lambda^{-1}$ solutions vividly show that there is competition between two species: there is a predominance of the species giving excimer emission, but wherever the monomer absorbs strongly it does so to the detriment of the other species to an extent dependent on their relative concentrations.

At $10^{-5}$ mole $\lambda^{-1}$ the system is transmitting most of the incident light, and is approaching low-absorbance conditions throughout the whole wavelength range. Thus, if there were two different species present we would expect to see two different excitation spectra, each similar to the absorption spectrum of the corresponding emitting species.

The excitation spectra of $10^{-5}$ mole $\lambda^{-1}$ solutions show that the spectra of the two species are different.

3.13 Discussion

It is assumed that the higher-energy excitation spectrum traces out the absorption spectrum of pyrene
monomer because

. it corresponds to the room-temperature absorption spectrum of pyrene, shifted slightly, and

. it is also observed at low concentrations (and under conditions of low-absorbance) in solvents in which there is no reason to suspect the presence of any other species.

All the observations in the present work, and those of others (Ferguson 1958; Mataga et al. 1967; Loewenthal et al. 1969), can be explained by assigning the lower-energy emission to microcrystals of pyrene which are formed in all solvents above a certain solute concentration. This explains

. The higher proportion of low-energy to high-energy emission in more concentrated solutions (Fig. 3-2a);

. the excitation spectrum of the higher-energy emission in the most concentrated solution: the wavelength of the first excitation band corresponds to the first absorption band of a pyrene crystal at the same temperature. As this absorption band is very weak the mixture is not in the limit of high absorbance at this wavelength, even at the high concentration used, and an excitation band is therefore expected;

. the observation (Loewenthal et al. 1969) that the ratio of intensities of the two emissions reaches a maximum value at the freezing-point of the solution, and is consistent with the effect of annealing the solution. The decrease in this
ratio at temperatures below the freezing-point of the solvent can be attributed to different variations of the fluorescence quantum yields of the two species with temperature, as the ratio of emission intensities depends not only on the proportion of the two species present but also on their relative quantum yields.

In the light of these results much of the previously cited evidence against microcrystals can be discounted. Mataga et al. dismiss the possibility that the "excimer" band is due to microcrystals because its excitation spectrum does not resemble the absorption spectrum of the crystal. However, no reference is made to the concentration of solute; this is important as only a weakly absorbing solution has similar excitation and absorption spectra. In any case, the comparison should be made with a crystal absorption spectrum at 77K, not at room temperature.

Loewenthal et al. likewise dismiss this possibility. They note that pyrene is more soluble in those solvents in which the "excimer yield" is high. However, the solubility at room temperature has no obvious correlation with the solubility in frozen solution.

The intensity of "excimer" emission is not higher for excitation at 376 nm (where the monomer absorbs only weakly) than at lower wavelengths at which it absorbs strongly. However, this neglects the change with wavelength of the extinction coefficient of pyrene crystals, which will also govern the
competition between the two species to absorb light.

The absorption spectrum of a solution from which "excimer" emission was dominant was reported to be purely that of the monomer. In the present work the solutions giving "excimer" emission were hazy, and an absorption spectrum could not be obtained.

Although the existence of microcrystals clarifies many of the previous results obtained with frozen solutions of pyrene, there is one piece of work which it does not explain. Loewenthal, Tomkiewicz and Weinreb (1968) have reported that the excitation spectrum of the highest energy vibronic band of the fluorescence spectrum of pyrene is different to the excitation spectrum of all other bands. This is unlikely to be due to microcrystals, due to the use of a glassy solvent (methylcyclohexane) and a low concentration of solute (5 x 10^{-4} mole l^{-1}).

Attempts to repeat these results gave spectra which were dissimilar in some ways to those reported. One feature was that the difference between the excitation spectra of the different fluorescence bands was strongly dependent on concentration. This observation, together with the fact that it is the excitation spectrum of the highest-energy vibronic band which is different to that of all the other bands, forces one to think in terms of a reabsorption effect, possibly complicated by re-emission. Fig. 1-2 shows the large extent to which reabsorption can modify fluorescence excitation spectra, and re-emission of the absorbed fluorescence will complicate all the
excitation spectra, not only the excitation spectrum of the reabsorbed band.

3.14 Possibility of impurity emission

It is obvious from the emission spectra in Fig. 3-2a that the previously reported peak at 415 nm has not been observed. However, anthracene is a common impurity in pyrene, and it has proved difficult to remove all traces of it even by extensive zone-refining. Thus the spectra of frozen solutions of pyrene deliberately doped with anthracene have been studied. A peak at 415 nm emerged in frozen solutions of pyrene in p-xylene when the pyrene contained 0.01% anthracene, and in solutions of cyclohexane when the anthracene concentration was 0.1% that of the pyrene. The excitation spectrum of this new peak is identical to that of the emission band which we have attributed to crystals. This implies that the anthracene receives excitation not directly by absorption but by energy transfer from pyrene within the crystal. In this way the relative intensity of anthracene emission is much larger than would be expected from the proportion of anthracene to pyrene. This result, common in crystal spectroscopy, reinforces the argument that the results obtained in frozen solutions of pyrene are due to microcrystals.

3.2 NAPHTHALENE

Kawakubo, Okada and Shibata (1966) have reported an excimer-type emission from frozen solutions of
naphthalene in hydrocarbon solvents at 77K. Their observation that "excimer" emission occurs much more readily from hexane than from cyclohexane solutions, together with the results for pyrene, led Loewenthal et al. (1969) to suggest that the formation of excimers in frozen solutions is not a function of the melting-point of the solvent.

As it appears that the low energy emission from pyrene is not due to excimers, it is worthwhile to examine the naphthalene system. Unlike pyrene, the crystal structure of naphthalene is such that no two molecules are in an orientation favourable for excimer formation. The fluorescence spectrum of crystalline naphthalene contains no excimer component at normal pressures, and thus the observation of "excimer" emission cannot in this case be attributed directly to emission from naphthalene crystals, although at the concentrations used precipitation is likely to occur.

Fig. 3-3a shows the fluorescence spectrum of a frozen solution of chemically purified naphthalene. The experimental conditions are the same as those used by Kawakubo et al. It is apparent from the figure that no excimer emission has been found, although there is a greater proportion of emission at long wavelengths than in a dilute fluid solution or in an ether-pentane-alcohol glass. The spectra of other samples of naphthalene do contain some peaks to longer wavelengths (Figs. 3-3b, c), and these are quite pronounced with a sample that has been only zone-refined (Fig. 3-3c). These peaks are not due to naphthalene phosphorescence.
Fig. 3-3. The fluorescence spectra of $5 \times 10^{-2}$ mole $l^{-1}$ solutions of different samples of naphthalene in hexane at 77K. The spectra at wavelengths below 360 nm are identical for all samples and are probably due to both crystalline and dissolved naphthalene.

- (a) chemically treated and chromatographed naphthalene
- (b) "scintillation grade" naphthalene
- (c) zone-refined naphthalene.
and so it appears that there are one or more impurities in naphthalene that are not removed by zone-refining. The slight amount of emission to longer wavelengths in Fig. 3-3a indicates that even this sample of naphthalene may not be completely free of impurities.

No fluorescence to longer wavelengths (except the true excimer fluorescence at high concentrations) is observed in fluid solutions of the same samples, and the amount of any impurity present is therefore quite small. The longer wavelength emission is attributed to an impurity which co-crystallises with the naphthalene and acts as an energy trap in the same way as the impurity in pyrene in the previous section. The spectra were not exactly reproducible, possibly because the formation of naphthalene crystals incorporating impurity was subject to variation. This may be related to the observation by Bolotnikova and Gurov (1970) of differences in the fluorescence spectra of different parts of a frozen solution containing microcrystals.

The hypothesis of impurity emission from microcrystals explains the greater intensity of long-wavelength fluorescence when the sample is cooled more slowly, and the lack of any such emission in this region from solutions in a frozen ether-pentane-alcohol glass, in which crystals are not formed. It also explains the peaks superimposed on the broad emission obtained by Kawakubo et al., although the source of the sample will obviously be important and it is therefore impossible to repeat the experiment in the absence of this information.

Because the absorption and fluorescence spectra of
crystalline naphthalene overlap that of the dissolved molecule under these conditions, it is not possible to glean any additional information from excitation spectra. However, on the basis of the results presented in Fig. 3-3 the previously reported dual luminescence of naphthalene in frozen solutions is attributed to impurity emission, resulting from microcrystal formation.

3.3 PYRAZINE

The strong phosphorescence of pyrazine was early observed by Goodman and Kasha (1958) in frozen ether-pentane-alcohol, a hydroxylic solvent in which, with the wisdom of hindsight, one might expect the basic pyrazine molecule to be particularly soluble. El-Sayed and Robinson (1961) subsequently observed the same emission in matrix-isolation experiments. These phosphorescence spectra were quite unremarkable. The first indication of an anomaly came from later measurements in frozen cyclohexane and carbon tetrachloride by Shimada (1961) and in cyclohexane by Loustauneau, Nouchi and Rousset (1963). In carbon tetrachloride the phosphorescence is "doubled", in the sense that there appear to be two origins, 290 cm\(^{-1}\) apart, on each of which is developed the same kind of characteristic vibrational structure, with a spacing of 600 cm\(^{-1}\). Loustauneau et al. reported the same kind of doubling in cyclohexane, the spacing between the origins being 350 cm\(^{-1}\) in that case, but Shimada, and subsequently, Moomaw and El-Sayed
Logan (1966) encountered the same kind of inconsistency in the course of measurements in frozen hydrocarbon glasses. These measurements, which also disclosed the weak fluorescence of pyrazine (Logan and Ross 1965), were plagued by the occasional appearance of a second spectral type. The anomalous, and rare, lower-energy spectrum always occurred in both fluorescence and phosphorescence simultaneously. In addition, the lower-energy spectrum was weakly present in the spectrum which was usually obtained. Various parameters (purity, addition of water, temperature, concentration, freezing procedure) were varied in an attempt to discover the cause of the different spectra, but without success.

The inconsistency of the results of this apparently simple experimental measurement is notable.

3.31 Phosphorescence of pyrazine

In an attempt to reproduce the above results, solutions of pyrazine in hydrocarbon glasses were studied. Two phosphorescent systems were observed. However, in contrast to the work of Logan, the most commonly observed spectrum contained only the progression originating at 377 nm (26530 cm⁻¹), similar to Fig. 3-4a. Another spectrum, observed only rarely, contained this progression together with one with origin at 381 nm (26250 cm⁻¹), similar to Fig. 3-4b. There are thus two emissions, both containing vibrational intervals of 600 cm⁻¹. The higher-energy spectrum starts at the
Fig. 3-4. Phosphorescence spectra of a 0.01 mole l\(^{-1}\) solution of pyrazine in a hydrocarbon (isopentane : methylcyclohexane 3:1) glass at 77K, using different wavelengths of excitation.

(a) 320 nm  
(b) 300 nm  
(c) 330 nm
origin of $T_1 + S_0$ absorption, and is thus regarded as normal molecular phosphorescence.

In crystalline solvents, line splittings may result from molecules which lie in a limited number of different environments, but in a glass such site effects merely cause line broadening. The observations therefore point to the existence, in frozen glasses (and because the effects are so similar, in $CCl_4$ and cyclohexane as well) of two different kinds of pyrazine emitter.

If the results were due to the formation of crystals, it might be expected that they would be affected by changing concentration, method of cooling, composition of the glass, or purity. These parameters were varied systematically.

Concentrations used (calculated using the volume of the solution at room temperature) were between $0.05$ mole $l^{-1}$ and $0.0003$ mole $l^{-1}$, below which concentration the solution absorbs only a negligible fraction of the light.

Fast cooling was achieved by dipping the sample cell in a Dewar flask containing liquid nitrogen. To achieve a slow cooling effect the sample cell was held in a stream of very cold nitrogen, and its temperature slowly reduced.

The composition of the glass was changed gradually from 3 parts isopentane : 1 part petroleum ether (60-80) by volume to straight petroleum ether. Similar mixtures of isopentane and methylcyclohexane were also used.
Experiments were carried out using both pyrazine as commercially supplied and pyrazine which had been freshly vacuum-sublimed.

Systematic variation of all the above conditions indicated that no single one of them determined which spectrum was observed. The spectrum containing both progressions was observed infrequently, and its appearance was not obviously connected with any particular parameter.

Insight came with variation of the wavelength of excitation. Previous work had used Hg lines. Fig. 3-4 shows the phosphorescence spectrum of 0.01 mole\(^{-1}\) pyrazine in a frozen isopentane - methylcyclohexane (3:1) glass, excited at 320, 300 and 330 nm. The first and last of these are plainly different spectra, and 300 nm excitation produces the spectrum commonly obtained by Logan in petroleum ether solutions. The higher-energy component of this spectrum thus comes from a species which absorbs at 320 nm, and not at 330 nm, while the lower-energy emission comes from a species which absorbs at 330 nm and not at 320 nm. Both species absorb at 300 nm.

Nevertheless, frozen hydrocarbon glasses of pyrazine still tended to give occasional erratic results, indicating that such solutions are not always identical. The experiments were therefore repeated in cyclohexane. At concentration 10\(^{-3}\) mole\(^{-1}\) in this solvent, excitation with light of all wavelengths within the absorption band of the system yields the spectrum shown in Fig. 3-5a. However, by exciting at a wavelength
Fig. 3-5. Phosphorescence spectra of a $10^{-3}$ mole l$^{-1}$ solution of pyrazine in cyclohexane at 77K, using different wavelengths of excitation
(a) 334 nm
(b) 340 nm
Spectrum (b) is observed against a background of scattered light due to the low absorbance of the system at this wavelength.
which appears to be on the edge of the absorption band of one of the species, Fig. 3-5b is obtained. This spectrum resembles those previously reported (Loustauneau et al. 1963; Shimada 1961). Much more clear-cut results were obtained in CC\textsubscript{4}. Fig. 3-6 shows the spectra of $2 \times 10^{-4}$ mole $^{-1}$ pyrazine in this solvent, again excited at three different wavelengths, with just the same kind of result. The splitting observed by Shimada can now be attributed to a fortuitous choice of exciting wavelength, which excited each of two kinds of absorber.

To explore the nature of the two kinds of absorber/emitter, the measurements in CC\textsubscript{4} were repeated at different concentrations. Decreasing the concentration of pyrazine increased the relative intensity of the higher-energy spectrum, i.e. the spectrum with origin at 377.4 nm. This points to the higher-energy spectrum as originating from molecular pyrazine, and to molecular aggregates as the source of the lower-energy spectrum (origin at 381.4 nm). Aggregates are suggested because the vibrational structure is essentially the same in both cases, and crystals normally absorb and emit at lower energies than isolated molecules.

Further confirmation comes from phosphorescence excitation spectra. Although they have been used to investigate singlet-triplet transitions they can also be used to study singlet-singlet transitions, assuming that the rate constant for intersystem crossing is independent of the initial singlet state to which the molecule is excited.
Fig. 3-6. Phosphorescence spectra of a \(2 \times 10^{-4}\) mole \(^{-1}\) solution of pyrazine in carbon tetrachloride at 77K, using different wavelengths of excitation.

(a) 330 nm
(b) 332 nm
(c) 296 nm
In a dilute hydrocarbon glass the excitation spectrum of the high-energy phosphorescence follows closely the absorption spectrum of the same solution (Fig. 3-7), although the limited resolution of the excitation monochromator has an obvious broadening effect on the spectrum. The peaks in both spectra correspond in wavelength to the absorption spectrum of a pyrazine solution at room temperature.

In respect of the low-energy emission, the same kind of direct comparison cannot be made, since any attempt to measure the absorption of the solutions which show both kinds of emission would disclose a superposition of monomer and aggregate absorption. One may, however, observe a pure sample of aggregate in crystalline pyrazine itself. This absorption follows the excitation spectrum of the low-energy emission when measured under conditions of low-absorbance of the exciting radiation (Fig. 3-8).

These last measurements permit us to think of the proposed molecular aggregates specifically as microcrystals, though they are not visible crystals. Microcrystals large enough to cause light scattering are produced only when the concentration in hydrocarbon glass exceeds 0.05 mole l⁻¹. Most of the measurements described here were performed at substantially lower concentrations.

If the second kind of emission is due to microcrystals in all solvents, then the location of the origin of its phosphorescence should be essentially independent of the solvent, and coincident with the origin of
Fig. 3-7. (a) The absorption spectrum of a $10^{-4}$ mole $1^{-1}$ solution of pyrazine in hydrocarbon glass at 77K.

(b) The excitation spectrum of the high-energy phosphorescence peak (377.4 nm) in the same solution. (Bandwidth of excitation 2 nm).
Fig. 3-8. (a) The absorption spectrum of a pyrazine crystal at 77K.

(b) The excitation spectrum of the low-energy phosphorescence peak (381.4 nm) in a 10^{-4} mole l^{-1} solution of pyrazine in carbon tetrachloride at 77K. A similar spectrum is obtained in hydrocarbon solvents.

There is some evidence that fluorescence in the solid state is less efficient than in solution because of some solutions showing a marked quenching of the fluorescence. This is a well-known effect and is more pronounced with pyrazine. It is possible that the weak fluorescence of pyrazine is not solely due to the overlapping of the two emissions: contributions from peaks to either side come from the other species, which absorbs in those regions where this one does not, and so tend to destroy the structure.
phosphorescence from the pure crystal*. The phosphorescence of macrocrystalline pyrazine at 77K was measured and its origin found to lie at 381.4 ± 0.4 nm, which is in reasonable agreement with the value of 380.9 nm obtained by Moomaw and El-Sayed. This coincides, within experimental error, with the origin of the second kind of phosphorescence in all three solvents (hydrocarbon glasses 381.6 ± 0.4; CCl₄ 381.4 ± 0.4; cyclohexane 381.6 ± 0.4 nm).

3.32 Fluorescence of pyrazine
The weak fluorescence of pyrazine (quantum yield 6 x 10⁻⁴; Cohen and Goodman 1967) could not be detected in these experiments. Logan's observation that the anomalous behaviour of pyrazine was observed simultaneously in fluorescence and phosphorescence is accepted, and it is assumed that the fluorescence of pyrazine is similarly affected by the formation of microcrystals.

3.33 Attempted direct T₁ → S₀ excitation
Because of the hazy nature of some solutions (using solvents which crystallised) it was thought possible that light could be reflected within a sample, giving a longer effective pathlength and thus a larger absorbance

*There is some evidence of a slight difference in the wavelength of emission from microcrystals and macrocrystals. McAlpine (1968) has found a difference of 23 cm⁻¹ in the fluorescence of biphenyl. Such a difference is insignificant in the present context.
than calculated. This suggested the possibility of direct population of the triplet state.

Direct excitation at 377 nm failed to produce any noticeable phosphorescence. This correlates with the experiments on pyrene (section 3.12) in which the onset of high- and low-absorbance conditions indicated that reflection of light does not occur to a large extent within crystals of these solvents.

3.34 Discussion

There is consistent evidence that the higher-energy fluorescence and phosphorescence of pyrazine originates from dissolved isolated molecules. The second, lower-energy luminescence is attributed to microcrystals because the species responsible has an absorption spectrum (observed as an excitation spectrum) which coincides with the absorption of crystalline pyrazine, and, the lower-energy phosphorescence in all solvents has the same origin as the phosphorescence of crystalline pyrazine. The fact that the two luminescences have different excitation spectra shows that energy transfer from dissolved molecules to microcrystals does not occur efficiently in these solutions.

One may well ask why phosphorescence spectra of this kind are not commonplace: there is nothing obviously special about pyrazine as a solute, and the microcrystal spectra were observed in a variety of solutions. Pyrazine is a favourable case for detecting microcrystal phosphorescence as such because the absorption spectra of the crystal and free molecule
are both well resolved and do not overlap (Figs. 3-5a and 3-6a); the same holds for the emission spectra. Further, as far as phosphorescence is concerned, pyrazine is one of the minority of aromatic compounds from which crystal phosphorescence is detectable - a consequence of the short radiative lifetime of the triplet state.

3.4 CONCLUSION

All the mixtures of isolated dissolved molecules and microcrystals which have been studied exhibit distinctive properties. The dual luminescence of pyrene consists of a completely dissimilar emission in addition to that of the isolated molecule, whereas the two luminescences of pyrazine have the same Franck-Condon envelope and are only distinguished by virtue of the shift of the crystalline emission compared with that of molecular pyrazine. The effect of aggregation in frozen solutions of naphthalene is more insidious in that it is only manifest as emission from impurities - the distinct emissions of dissolved and crystalline naphthalene are not visibly separated at low resolution.

The lack of any general consequence of microcrystal formation means that there is no single simple way of testing for this complication.

The study of these three systems has shown that the effect of microcrystal formation on the observed lumini-
escence spectra is governed by many factors: the absorption and emission spectra of the two species, wavelength of excitation, radiative lifetime of the crystalline state, solvent, concentration, rate of cooling, temperature, and the presence of impurities. There may well be other parameters. In some cases the presence of microcrystals is far from obvious, and an examination of the change in the observed luminescence with the above parameters is necessary before their presence can be discounted.

4.11 Emission from photosassociated species

The deactivation of a potentially fluorescent dissolved molecule by collision with a molecule in its ground electronic state is common. In some cases interaction between the two molecules results in electronic energy transfer between them, and the quenching of the fluorescence of one species is accompanied by the reappearance of the energy as emission from the quencher. However, most frequently the energy contained within the weakly bound collision complex is dissipated to the solvent as vibrational energy, and there is a total conversion of luminescent to thermal energy.

The first observation of fluorescence from a photosassociated species was made by Förster and Kasper (1954, 1955) who observed, from solutions of pyrene, the phenomenon that is now known as excimer fluorescence. Similar studies of other aromatic hydrocarbons have shown that excimer fluorescence is quite a general consequence of the self-quenching that such compounds
CHAPTER 4

EXCIPLEXES

4.1 INTRODUCTION

4.11 Emission from photoassociated species

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The discovery of pure excimers was followed by reports of emission from excited-state complexes composed of different molecules possessing the same aromatic core. Fluorescence from these "mixed excimers" or "heteroexcimers" was observed from differently substituted alkylanthracenes (Vember and Cherkasov 1959), from mixtures of pyrene and methylpyrenes (Birks and Christophorou 1962; Selinger 1964), and subsequently from a number of other compounds.

The next basically new system to be investigated was the type of photophysical reaction exemplified by the quenching of the fluorescence of perylene by dimethylaniline, reported by Leonhardt and Weller (1963). Photoassociated complexes were subsequently reported to be formed between aromatic hydrocarbons and aryl amines (Mataga, Ezumi and Takahashi 1965; Mataga, Okada and Yamamoto 1966) and between an aryl amine and a number of aromatic esters (Miwa and Koizumi 1966; Kaneta and Koizumi 1967).

Walker, Bednar and Lumry (1966, 1967) reported the formation of 1:2 exciplexes between indole and n-butanol, and of 1:1 exciplexes between indole and non-associating solvents such as acetonitrile and dioxan. Longworth (1968) has since observed a 1:1 exciplex between 1,2-dimethylindole and isopropanol, but was unable to reproduce the results of Walker et al. concerning 1:2 ex-
ciplexes. The formation of a 1:2 exciplex between 1,4-dicyanobenzene and naphthalene, in very concentrated solutions of the latter, has also been postulated (Beens and Weller 1968a).

Several workers have found that exciplexes are also formed between aliphatic amines and aromatic hydrocarbons (Kuzmin and Guseva 1969; Knibbe, Rehm and Weller 1969; Nakajima 1969). Exciplex emission has also been observed from a mixture of ethoxynaphthalene and dimethyl-m-phthalate (Murata, Kokubun and Koizumi 1970) and from alkynaphthalenes and benzoic acid (Ellis, Hamel and Solomon 1970). A compilation of exciplexes formed by aromatic hydrocarbons has been given by Birks (1970b).

The summary given here is by no means exhaustive, and does not include many systems considered in detail later. Nonetheless, it indicates the range of complexes which are stable only in the excited state, from which fluorescence has been observed.

The formation of exciplexes resembles the excimer case, firstly because the emission from the photo-associated species consists of a broad band considerably to the red of the quenched monomer emission, and secondly because the additivity of the absorption spectra of the components in the mixture implies the existence of a repulsive ground state. The principal justification for thinking of the exciplex as a completely different species is that the stability of the excited complex may be due in extreme cases entirely to charge transfer interaction. The term "exciplex" was first coined by
Walker, Bednar and Lumry in 1966 and it was later proposed by Birks (1967) that it refer to an excited complex between different molecules, which is stable only in the excited state. The difficulty in detecting photoassociated species which do not emit has caused this term to be commonly restricted to emissive complexes. (In keeping with this terminology we shall use the term "exciplex" to describe excited state complexes between different molecules, which are not stable in the ground state. The term "charge transfer complex" will be used to refer to complexes which exist in the ground state.)

The red shift of the exciplex emission band in polar solvents has been shown to be a quite general property of exciplexes and is evidence of their dipolar nature. Such a study is both easy and informative, and it has been applied to many different systems. Typical results are those of Weller (1967), who found that the emission maximum of some arylamine - aromatic hydrocarbon exciplexes shifted by up to 4000 cm\(^{-1}\) in changing the solvent from hexane to acetone. The accompanying decrease in the intensity of the emission has been attributed to the competing process of direct formation of solvated ion pairs from the primarily excited molecule and the quencher. This view has been reinforced by flash photolysis studies in polar solvents which have served to identify the solvated anion of the electron acceptor, the cation of the electron donor and the triplet state of the acceptor - the last allegedly formed by reverse electron transfer within the solvated ion.
pair (Dmitrievskii and Terenin 1963; Koizumi and Yamashita 1968; Knibbe, Rehm and Weller 1968; Okada, Oohari and Mataga 1970; Grellmann, Watkins and Weller 1970). The reverse process, whereby an exciplex is produced from a solvated ion pair, has recently been observed by Weller and Zachariasse (1971).

It has also been reported that the triplet state of the electron acceptor is populated even in non-polar solvents, in which solvated ion pairs are not formed (Goldschmidt, Potashnik and Ottolenghi 1971). Thus one route of deactivation of an exciplex is

\[(\text{A}^-\text{D}^+)_{\text{solv}} \rightarrow \text{3A}^* + \text{D}\]

although the importance of this step is not known.

The contribution of charge transfer interaction to the stability of exciplexes has also been shown by the dependence of the fluorescence maximum on the electrical properties of the constituent molecules. Mataga and Ezumi (1967) observed a variation of the emission energy of dimethylaniline - aromatic hydrocarbon exciplexes with the electron affinity of the aromatic hydrocarbon, and Knibbe, Rehm and Weller (1967) obtained a scattered linear correlation between the energy of the exciplex emission maximum and the reduction potential of the hydrocarbons. Chandross and Ferguson (1967) found that the energy of the emission band of the exciplex formed between 9,10-dicyanoanthracene and a number of aromatic hydrocarbons had an obvious dependence on the oxidation potential of the hydrocarbon. Rehm and Weller (1970a) have recently attempted to classify exciplexes in terms
of the nature of the bond between the two partners, by considering the dependence of the emission energy on the oxidation potential of the electron donor and the reduction potential of the acceptor.

Despite the dissimilarity between the properties of some exciplexes and those of pure excimers, the dependence of the emission energy on the electrical properties of the constituents has a counterpart in excimer emission. Ferguson (1958) suggested that excimer emission from crystalline pyrene occurred from a charge transfer state. It has subsequently been shown that there is a correlation between the maxima of emission from excimers of aromatic hydrocarbons and the function

\[ I - \Delta E(1L_b) - A \]  

(4-1)

where \( I \) is the ionisation potential and \( A \) the electron affinity of the hydrocarbon, and the energy \( \Delta E \) of the singlet state is measured by the \( 1L_b \) band (Slifkin 1963). The significance of this correlation is not clear, as Chandra and Lim (1968) have found a better linear correlation between the energy of the excimer emission and that of the \( 1L_a \) band of the monomer. However, theoretical studies have indicated that configuration interaction between exciton resonance and charge resonance is necessary to account for the observed properties of excimers (Murrell and Tanaka 1964; McGlynn, Armstrong and Azumi 1964).

An excimer can thus be considered to be a special type of exciplex - one in which the donor and acceptor
molecules are the same. This had led to the formulation of the excited state wave function of all such photo-associated complexes as

\[ \Psi = \sum c_{1,i} \psi(D^*A) + \sum c_{2,i} \psi(DA^+) + c_3 \psi(D^-A^+) \]

\[ + c_4 \psi(D^+A^-) \]  

(4-2)

where \( D^*_1 \) and \( A^*_1 \) represent different excited states of the donor (D) and acceptor (A) molecules (Mataga, Okada and Ezumi 1966). This formulation is essentially similar to that used to represent the excimer: the difference lies in the relationship between the coefficients \( c_1, c_2, c_3 \) and \( c_4 \). In the excimer wave function

\[ c_{1,i} = -c_{2,i} \] and \( c_3 = -c_4 \), and the relative importance of the last two terms depends on the electrical properties of the monomeric species. In the extreme case of an exciplex in which there is a large energy difference between the interacting states, and therefore negligible excitation resonance, the wave function is dominated by the last term alone. Intermediate cases are just as easily accommodated within the scheme, and the dipole moment of the complex is given by

\[ \mu = (c_4^2 - c_3^2) \mu_{D+A^-} \]  

(4-3)

where \( \mu_{D+A^-} \) is the dipole moment of the pure charge transfer complex. Mixing of the charge transfer state with other states would then be expected to decrease
and therefore to decrease the dipole moment. This has been found for a series of exciplexes with varying proportions of "pure charge transfer" and "pure excimer" character (Beens and Weller 1968b).

4.12 Fluorescence quenching and charge transfer

Exciplexes represent obvious, well-documented examples of the contribution of charge transfer in some cases of fluorescence quenching. Nonetheless exciplex emission has only been observed from a limited variety of systems. It is reasonable to expect that the contribution of charge transfer interactions to collisional fluorescence quenching is not limited to those cases in which an exciplex can be characterised by its emissive properties.

In fact the observation of emissive exciplexes was preceded by a number of reports that fluorescence quenching either proceeded by complete transfer of an electron or else was dependent on the ability of the molecules involved to donate or accept charge. Weiss and Fischgold (1936) were probably the first to document the quenching of fluorescence by electron transfer. They suggested that fluorescence quenching in solution by iron(II) or halide ions could be represented by

\[ F^* + Fe^{2+} \rightarrow F^- + Fe^{3+} \]

and

\[ F^* + X^- \rightarrow F^- + X . \]
The occurrence of these reactions in the excited state was attributed to the increased electron affinity of the excited fluor, compared with that of the ground-state molecule. In later work Weiss (1938, 1939) explained in similar terms the quenching of the fluorescence of uranium salts, and of some dyes.

These and other experiments led Förster (1951) to suggest that electron transfer may be a general method of fluorescence quenching, although somewhat later Orgel (1954) offered the opinion that "charge transfer is not necessarily the ... most usual mechanism of fluorescence quenching in solution".

Subsequent proposals that fluorescence quenching proceeds via a charge transfer mechanism have relied on the dependence of the rate constant of observed fluorescence quenching on the electrical properties of the molecules involved.

In 1958 Melhuish and Metcalf found that the substitution of electron-attracting groups onto alkyl and aryl halides enhanced their ability to quench the fluorescence of anthracene. Using dipole moments to estimate the electron-attracting power of the substituents they obtained an obvious though qualitative correlation, and concluded that during the quenching process electrons move towards the quencher.

Majumdar and Basu (1960) have explained in terms of charge transfer the different fluorescence quantum yields of polynuclear aromatic hydrocarbons dissolved in a series of substituted benzenes. They found that for all the compounds chosen, the quantum yield de-
creased as the solvent was changed from benzene → toluene → xylene → mesitylene (in decreasing order of ionisation potentials). The results could not be explained in terms of the different dispersing effects of the solvents, nor by absorption of light by the solvents. There was no significant change in the absorption spectra of the solutes, and they concluded that slight quenching via a charge transfer mechanism was involved. However, it must be pointed out just how weak this quenching is: a complete change of solvent (typically of concentration ~10 mole l⁻¹) is required to show a change in the quantum yield of about 50%. This concentration is about four orders of magnitude higher than that normally required for fluorescence quenching of these molecules, and the charge transfer interaction may well be so small that other factors will be more important.

In experiments on the quenching of the fluorescence of acridine by amines, Weller (1961) found that the lower the ionisation potential of an amine the better quencher it is. Leonhardt and Weller (1961, 1962) found a similar effect in the quenching of perylene by amines. In both cases the quenching was much more efficient in polar than in non-polar solvents. Further evidence that a charge transfer mechanism is responsible for the quenching of acridine was obtained by Komiyama, Miwa and Koizumi (1966). They found that the quenching of acridine orange by electron acceptors increased with the "acceptor power" of the quencher, and the effect of these electron acceptors on the neutral molecule was more
severe than on the cationic form. The quenching by a typical electron donor showed the opposite tendency.

Similar results were obtained for the quenching of the fluorescence of zinc phthalocyanine by aryl nitro compounds (McCartin 1963). The shape of the emission spectrum of the phthalocyanine did not change; however, its intensity decreased by an amount greater than could be accounted for by formation of the ground state charge transfer complex with the quencher. The quenching rate constant in acetone correlates with the electron affinity of the aryl nitro compounds.

Recent interest in the contribution of charge transfer to fluorescence quenching has doubtless been stimulated by the work on exciplexes. The extent of quenching of pyrene and anthracene by a series of electron-accepting quenchers which do not cause exciplex formation has been found to be closely related to the electron affinities of the quenching molecules (Nakajima and Akamatu 1968). Schulte-Frohlinde and Pfefferkorn (1968) studied the quenching by some halides and amines of the fluorescence of a number of substituted naphthalenes, and found that the fluorescence of those molecules commonly classified as electron donors was quenched much more effectively by electron acceptors (e.g. CCl₄) than by other electron donors. They deduced that fluorescence quenching in these systems involves a charge transfer interaction, although they made the point that, in cyclohexane anyway, total charge transfer is energetically impossible. Flash photolysis studies showed the same trends for the quenching of triplet states (Ander,
Blume, Heinrich and Schulte-Frohlinde 1968).

A subsequent examination of the quenching of pyrene fluorescence by aliphatic halides has shown that the quenching rate constant depends on the reduction potentials of the halides as well as the spin-orbit coupling parameters (Thomaz and Stevens 1969). Similarly the quenching of anthracene by halide and other ions in solution has been found to depend on the redox potential of the quenching ion (Beer, Davis and Hodgson 1970).

Several years ago it was found that the fluorescence of some aromatic hydrocarbons is quenched by a number of conjugated dienes (Stephenson, Whitten and Hammond 1967). The possibility of photochemical reaction was excluded, and the photophysical interaction was described in terms of catalysis by the quencher of non-radiative decay of the aromatic hydrocarbons (Stephenson and Hammond 1968). Recent work has indicated that this interaction is due to charge transfer. Solomon, Steel and Weller (1969) have shown that the observed quenching rate constant has an obvious dependence on the sum of the singlet excitation energy and reduction potential of the aromatic hydrocarbons. By a similar analysis the quenching of naphthalene, 2,3-diazabicyclo[2.2.2]oct-2-ene and an oxadiazole by alkenes and dienes has been found to depend on the vertical ionisation potential of the quencher (Evans 1971; Evans, Wake and Sifain 1971).

Taylor (1971) has recently observed a new emission concomitant with the fluorescence quenching of 1-cyano- naphthalene by several alkenes and dienes. His comprehensive study of this emission has shown it to be exciplex fluorescence, confirming that in these cases the
quench complex has considerable charge transfer character. Of even more intrinsic interest is the quenching of excited aromatic singlet states by molecular oxygen. Although the effect is well documented, the nature of the quenching process is still not well understood, though the existence of a short-lived charge transfer complex has been invoked to explain the quenching of pyrene (Berlman et al. 1969). However, some good evidence in favour of a charge transfer state has recently been presented (Brewer 1971). The rate constants of fluorescence quenching of alkyl- and fluorobenzenes in the vapour state show an obvious correlation with the ionisation potential of the substituted benzenes, implying charge transfer interaction within the collision complex. As it is known that the quenching of aromatic singlet states by oxygen leads in general to triplets, these results imply that intersystem crossing in the hydrocarbon takes place within an excited charge transfer complex. This agrees with the observation that triplet states result directly from the dissociation of some exciplexes. It is also in accord with the production of a greater proportion of triplet states from exciplexes in cyclohexane than in highly polar solvents, where other deactivating pathways exist (Potashnik, Goldschmidt and Ottolenghi 1971).

4.13 Exciplexes and charge transfer complexes

Any discussion of exciplexes involves a comparison with ground state charge transfer complexes, because (among other reasons) much of the theory developed for
ground state complexes has been adapted and applied to their excited state counterparts. The reason why these two fields of study remain separate lies in the restriction of the methods available to study them.

Although spectroscopic studies normally rely on both absorption and emission data, where both are available, this has not been the case for exciplexes nor for ground state charge transfer complexes. Exciplexes are by definition dissociated in the ground state (and in fact the evidence that this is so is implied from absorption spectra) so they have to be studied by emission alone. On the other hand, the behaviour of charge transfer complexes in solution has been generally studied by absorption alone because of the small number of such complexes which emit under these conditions.

However, recent work points the way toward some unification, and is worth presenting for that reason alone.

It is accepted that exciplexes are formed more readily than ground state charge transfer complexes because of the higher electron affinity and lower ionisation potential of molecules in excited states. One might therefore expect charge transfer complexes to be formed by molecules similar to those forming exciplexes, but with lower ionisation potentials. This is observed with aromatic hydrocarbons and alkylated amines. Aromatic hydrocarbons and N,N-dimethylaniline form exciplexes readily; substitution of another dimethylated amine group onto the benzene ring to form N,N,N,N-tetramethylphenylenediamine results in a molecule
which forms strong ground state charge transfer complexes with aromatic hydrocarbons. That this represents a continuum of behaviour is shown by some recent work (Ishida and Tsubomura 1971) in which the absorption spectra of mixtures of amines and aromatic hydrocarbons adsorbed on silica gel show distinct absorption bands considerably red-shifted from the absorption of the parent molecule. As several workers, including the author, have searched in vain for such bands in solutions containing similar molecules, one can only conclude that the adsorption process perturbs the molecules sufficiently and provides suitable surface sites at which weak complex formation can take place.

Similar results have been obtained with oxygen and aromatic compounds adsorbed on silica gel (Ishida, Takahashi, Sato and Tsubomura 1970). However, in these systems weak charge transfer complexes have also been proposed to explain absorption bands in solution (Evans 1953; Tsubomura and Mulliken 1960). If such complexes are formed between oxygen and some aromatic compounds in the ground state, then there is good reason for believing that quenching of the excited states of similar molecules (but from which no charge transfer absorption is observed) may be due to charge transfer interaction.

Likewise, the suggestion by McCartin (1963) that the quenching of zinc phthalocyanine proceeds by charge transfer is rendered more plausible by the fact that this compound also forms ground state charge transfer complexes with compounds which quench its fluorescence.

Just as studies of exciplexes are restricted to
their emissive properties, so comparable studies of ground state charge transfer complexes have relied on absorption data. Although a number of charge transfer complexes emit in the crystalline state (see for example Czekalla, Briegleb and Herre 1959), until 1967 only one such complex was known to fluoresce in solution: the complex formed between tetrachlorophthalic anhydride and hexamethylbenzene (Czekalla and Meyer 1961). In the last few years fluorescence has been reported from several charge transfer complexes in solution: between naphthalene (or hexamethylbenzene) and pyromellitic dianhydride (Short and Parker 1967), between N-phenylcarbazole and tetrachlorophthalic anhydride, between hexamethylbenzene and tetrachlorophthalic anhydride (Prochorow and Siegoczynski 1969) and between toluene and 1,2,4,5-tetracyanobenzene (Mataga and Murata 1969; Egawa, Nakashima, Mataga and Yamanaka 1971). It has also been reported that the lower homologues of compounds of the type \( p-O\_2NC\_6H\_4 \left( CH\_2 \right)_nNHAr \) show broad absorption and emission bands (Mutai 1970). Studies of the fluorescence spectra of these compounds not only clarify the properties of charge transfer complexes in the excited state, but also enable more meaningful comparison of ground state charge transfer complexes with exciplexes.

Fluorescence from all these complexes has been obtained following excitation into the charge transfer absorption band. It would be interesting to see whether emission can be obtained in any cases following excitation of either of the separate molecules, and if so, whether the emission was the same in all ways as that obtained
by direct excitation of the ground state complex. If this were possible, the continuum of behaviour between the two types of complexes would be demonstrated. Even in the absence of this knowledge, it is perhaps reasonable to foreshadow the discovery of some ground state interaction between some pairs of molecules which are known to form exciplexes.

\[
\frac{k_q}{k_d} = 1 + \frac{k_a}{1 + k_d} \left( \frac{1}{[Q]} \right)
\]

\[
= 1 + \frac{1}{k_0}[Q]
\]

where \( \frac{1}{\tau_0} = \frac{1}{k_a} + \frac{1}{k_q} \) is the lifetime of the exciplex in the absence of dissociation. The Stern-Volmer constant* of fluorescence quenching. \( \tau_0 \) is the concentration of quencher which halves the intensity of fluorescence from \( F^* \), and causes the fluorescence intensity of the associated species to reach half its maximum value.

---

*The parameter \( \tau_0 \) is also used as a measure of the extent of fluorescence quenching.
4.2 TREATMENT OF RESULTS

4.21 Transformation of fluorescence by exciplex formation

The transformation of fluorescence caused by exciplex formation obeys Stern-Volmer kinetics, which is expected in the case of competition between a bimolecular quenching process and unimolecular deactivation processes. In the absence of static quenching the fluorescence quantum yield of the species F in the reaction

\[
\begin{align*}
F^* + Q & \xrightarrow{k_a[Q]} \text{exciplex} \\
& \xrightarrow{k_q} F^* + h\nu \\
& \xrightarrow{k_e} F + Q \\
& \xrightarrow{k_d} F + h\nu'
\end{align*}
\]

is given by

\[
\frac{\phi_0}{\phi} = 1 + \frac{k_a}{1 + k_d \tau_0[Q]}
\]

\[
= 1 + K[Q]
\]

(4-5)

where \(\tau_0' = 1/k_q + k_q'\) is the lifetime of the exciplex in the absence of dissociation. The Stern-Volmer constant*

*The parameter \(c_h\) is also used as a measure of the extent of fluorescence quenching. \(c_h (= 1/K)\) is the concentration of quencher which halves the intensity of fluorescence from \(F^*\), and causes the fluorescence intensity of the associated species to reach half its maximum value.
(K) depends not only on the rate constant of association \( k_a \) and the decay time of \( F^* \) in the absence of quencher, but also on the relative magnitudes of the rate constants of deactivation and dissociation of the exciplex. When the reverse reaction can be neglected eq. (4-5) reduces to

\[
\frac{\phi_0}{\phi} = 1 + k_a \tau_0 [Q] \quad (4-6)
\]

and the quenching takes place at the diffusion-controlled rate. Agreement between \( k_a \) and the rate constant calculated for diffusion has shown that exciplex formation is diffusion-controlled (Knibbe and Weller 1967). There has been much investigation of the rate at which solute molecules diffuse in a solvent. A summary of the present state-of-the-art has recently been given by Birks (1970d). For the purposes of this work it has been found adequate to use

\[
k_a = \frac{8RT}{2000n_{\text{vis}}} \quad (4-7)
\]

derived assuming Stokes' law with "slip", as the solute molecules are comparable in size with those of the solvent.

As the system described by eq. (4-4) is comprised of two emissive species, the ratio of their emission intensities:

\[
\frac{I'}{I} = \frac{k'_{e}}{k_{e}} \cdot \frac{k_{a} [Q]}{k_{d} + k_{e} + k'_{e}} = \frac{\phi'}{k_{e}} \cdot \frac{k_{a} [Q]}{1 + k_{d} \tau_0} \quad (4-8)
\]
may be used to give similar information to the Stern-Volmer equation. In practice it is more difficult to extract an absolute value of $k_a$ from this equation, as the results naturally depend on the emissive properties of both species. More important, its derivation assumes a certain mechanism for the quenching of the initially excited species and the formation of the exciplex. This contrasts with the Stern-Volmer equation, which is concerned simply with the mechanism of the initial quenching, and is only dependent on subsequent reactions in that they affect the term $k_d T_0$ in eq. (4-5).

A method which may prove suitable for studying systems of this type has been used by Hirayama and Lipsky (1969) to examine excimer formation. It differs from the above in that it is not based on kinetic arguments, but merely considers two interconvertible species (for example, A and B) which may become excited by the absorption of a photon by the system as a whole. Let $p_A$ be the probability that A loses the photon by any process except by conversion to B, and $p_B$ be the probability that B loses the photon by any process other than by conversion to A. The intensities of emission per photon absorbed are then given by

$$I_A = p_A \cdot \phi_A$$

$$I_B = p_B \cdot \phi_B$$

where $\phi_A$ and $\phi_B$ are the intrinsic emission quantum yields of A and B respectively; that is, the probability of emission from one species in the absence of conversion to the other. The certainty that the ex-
citation will eventually be lost from the system is given by the sum of the probabilities \( p_A \) and \( p_B \), so that
\[ p_A + p_B = 1, \]
giving
\[
\frac{I_A}{\phi_A} + \frac{I_B}{\phi_B} = 1 \tag{4-9}
\]
Thus a plot of \( I_A \) against \( I_B \) will be a straight line with intercepts \( \phi_A \) and \( \phi_B \) if these quantities are independent of other variable parameters.

The assumption made in the derivation is that the two species are interconvertible. It is insensitive to the details of the kinetics, and in particular does not depend on which species is responsible for absorption of the incident photon.

Although so far applied only to a study of excimer formation, this method holds promise for exciplex studies. The different electron affinities and ionisation potentials of exciplex partners means that association is possible in the ground-state; such association, even if very weak, will result in absorption of excitation by some "exciplex" configurations. This treatment, unlike others, allows calculation of the intrinsic quantum yields irrespective of the proportion of excitation originally absorbed by either configuration. It also allows easy recognition of a variation in the intrinsic quantum yield of either species with quencher concentration.

The Lipsky method has one main limitation compared with the Stern-Volmer treatment, which is a direct result of its insensitivity to the kinetics of association.
It does not yield a value of $k_a$ in the absence of assumptions essentially similar to those made in the other treatments. In addition, in common with a plot of $I'/I$ versus the concentration of quencher, it has an inherent limitation resulting from the use of both monomer and exciplex data.

Although it does not assume any particular mechanism for interconversion of the two species it does assume that there are no other interconvertible species present, and in so doing specifies the mechanism to some extent. Results derived from systems which do not obey this criterion may be misleading. On the other hand, two advantages that are immediately obvious are that the treatment incorporates the possibility of an indeterminate proportion of exciplex emission resulting from static quenching, and the ability to analyse the data without knowing the concentration of quencher.

The relative benefits of the different plots are discussed with reference to the transformations of the fluorescence of pyrene and anthracene caused by the addition of diethylaniline. Figs. 4-1 and 4-2 show the results for pyrene. The plots are as expected for quenching in accordance with eqs. (4-9), (4-5) and (4-8) respectively. However, the quenching of anthracene fluorescence, requiring a larger concentration of diethylaniline due to its much shorter lifetime, shows obvious deviations from linearity (Figs. 4-3 and 4-4). The deviation of Fig. 4-3 is attributed to the decrease of $I'$ with the polarity of the solvent: the addition of diethylaniline beyond about 0.02 mole $l^{-1}$ causes suffic-
Fig. 4-1. A plot of the absolute intensity of emission from the pyrene-diethylaniline exciplex against that from monomeric pyrene in cyclohexane, for different concentrations of diethylaniline.

Fig. 4-2. The transformation in the fluorescence of pyrene in cyclohexane caused by the addition of diethylaniline.
Fig. 4-2. The transformation in the fluorescence of pyrene in cyclohexane caused by the addition of diethylaniline.
Fig. 4-3. A plot of the absolute intensity of emission from the anthracene-diethylaniline exciplex against that from monomeric anthracene in cyclohexane, for different concentrations of diethylaniline.
Fig. 4-4. The transformation in the fluorescence of anthracene in cyclohexane caused by the addition of diethylaniline.
ient change to affect the plot. The Stern-Volmer analysis (Fig. 4-4a) also shows a deviation. This is attributed to the fact that in cyclohexane at room temperature the quenching of anthracene by diethylaniline is not quite irreversible: the dissociation of the exciplex occurs to a small but noticeable extent. The increase in polarity of the solvent caused by adding diethylaniline provides an additional pathway of deactivation of the exciplex, reducing its dissociation and therefore increasing the observed extent of quenching*. The plot of \( I'/I \) against the concentration of diethylaniline (Fig. 4-4b) shows a combination of the two effects - the greater extent of net quenching, and the lower fluorescence quantum yield of the exciplex, as the polarity of the solution is increased by the addition of diethylaniline. These two effects oppose each other: by reference to eq. (4-8) the decrease in \( t_0' \) is partly offset by the decrease in \( \phi' \). Thus the near-linearity of Fig. 4-4b is deceptive.

In short, these results show that the relative advantages of the different treatments depend on which property of the system one is seeking to identify. A Stern-Volmer analysis confirms the existence of a bi-molecular quenching process, and under certain conditions can be used to test whether the quenching is diffusion-controlled. A study of the variation of \( I'/I \) with concentration reveals essentially the same information, although the deceptive near-linearity of Fig. 4-4b is

*It is unlikely that this deviation is due to static quenching as it is not observed with pyrene.
sufficient warning against using any such method of analysis in isolation. The method of Hirayama and Lipsky differs from the Stern-Volmer treatment in that it measures not only the quenching of the initially excited species but the buildup in that of the associated species. The existence of linear plots implies that the intrinsic fluorescence quantum yields of the two inter-convertible species are independent of the concentration of the other. It is useful as it enables analysis of a system in the absence of knowledge of which species is responsible for the absorption of excitation, or the concentrations of quencher used.

4.22 Thermodynamics of exciplex formation: the use of limiting conditions

Under certain conditions the temperature dependence of the emission intensities can be used to determine thermodynamic parameters of exciplex formation. The treatment used is that derived by Döller and Förster (1962) for excimer formation. It assumes that as the emissive rate constant $k_e$ is related to the strength of the absorption transition it is generally independent of temperature. Although there is no absorption corresponding to $k'_e$, this rate constant is also assumed to be temperature independent. The rate constants of radiationless deactivation ($k_q$ and $k'_q$) do vary with temperature, but the variation is much less than that of $k_a$ and $k_d$.

Other rate constants are assumed to have an exponential dependence on temperature:

$$k_i = N_i \exp \left( -\frac{E_i^*}{RT} \right) \quad (4-10)$$
Substitution into eqs. (4-5) and (4-8) yields the expressions:

\[
\left( \frac{I_0/I - 1}{[Q]} \right)^{-1} = \frac{k_e + k_q}{N_a} \exp \frac{E_a^f}{RT} + \frac{k_e + k_q}{N_a} \cdot \frac{N_d}{N_a} \exp \frac{E_a^f - E_d^f}{RT}
\]

(4-11)

\[
\left( \frac{I'/I}{[Q]} \right)^{-1} = \frac{k_e}{k_e'} \cdot \frac{k_e + k_q}{N_a} \exp \frac{E_a^f}{RT} + \frac{k_e}{k_e'} \cdot \frac{N_d}{N_a} \exp \frac{E_a^f - E_d^f}{RT}
\]

(4-12)

A full treatment using equations of this type has been made in a few cases (Selinger 1966). However, it has now become common to simplify them using limiting conditions.

For this purpose it is necessary to define two sets of experimental conditions, which are distinguished by the relative magnitude of the dissociative and deactivating rate constants of the exciplex.

\( \beta \) conditions prevail when the dissociation of the exciplex can be neglected, i.e. \( k_d \ll \Sigma k' \) (where \( \Sigma k' = k_e' + k_q' + \ldots \), and includes the rate constants of all processes apart from dissociation which deactivate the exciplex). It is only under these conditions that the simplified Stern-Volmer equation (4-6) often given, applies. Under these conditions it can be shown that the temperature dependence of \( I'/I \) (and of \( I_0/I \)) gives the activation energy for the quenching of the fluorescence of the initially excited species. In the absence of any appreciable activation required for reaction with a proximate quencher, the measured activation energy is a
measure of the temperature-dependence of the viscosity of the solution.

α conditions are defined by the requirement $k_d >> \Sigma k'$. That is, the photostationary state is an equilibrium which is not perturbed by deactivation of the excited species: the intensities of emission of fluorescence from F* and the exciplex merely act as indicators of the concentrations of each, and play a negligible part in disturbing their steady-state concentrations.

As the intrinsic lifetime ($\tau'_0$) of an exciplex decreases with solvent polarity, a corresponding decrease would be expected in the importance of the dissociation step. In particular, for an exciplex which is weakly bound and for which, therefore, the dissociation is significant in non-polar solvents at room temperature, transition to solvents of higher polarity should cause an increase in the extent of quenching.

Fig. 4-5 shows the increase in the Stern-Volmer quenching constant with the dielectric constant of the solvent, for the diethylaniline - perylene exciplex*. In toluene the quenching constant is quite low; although the system is not quite under α conditions (it can be calculated that $k_d/\Sigma k' \sim 10$) the dissociation of the exciplex is quite significant. This is shown vividly by transition to polar solvents: in propyl acetate $k_d \% \Sigma k'$ while in methanol true β conditions are attained and $k_d << \Sigma k'$.

*As the effect of viscosity varies with the relative magnitude of $k_d$ and $\Sigma k'$, solvents of the same viscosity have been used.
Fig. 4-5. The variation in the Stern-Volmer quenching constant with solvent dielectric constant for the quenching of perylene by diethylaniline. The dotted lines enclose the values of K calculated for irreversible quenching on the basis of the reported decay time of perylene: 4.9 ns (Birks and Dyson 1963), 5.02 ns (Ware and Baldwin 1965), 5.2 ns (Ware 1962) and 6.9 ns (Berliner 1965) in benzene, and 6.2 ns in methanol (Ware 1962). It is assumed that the decay time in ethyl acetate is not very different.
Although complete analyses of thermodynamic data are possible, the simplified method normally used requires that the limiting (a) condition \( k_d \gg k' \) holds.

(However, it is worth noting that two additional restrictions proposed by Birks (1970c): \( k_d \gg k_e + k_q \) and \( k_a[Q] \gg k'_e + k'_q \), are not necessary requirements.)

a conditions are favoured by:

- a complex having a low stability, resulting in a high value of \( k_d \);
- a solvent of low viscosity;
- a high temperature, although the relative magnitudes of \( k_d \) and \( k'_q \) determine the efficiency with which increasing temperature brings about a conditions.

It is possible to test in several ways whether a system is obeying a conditions:

- A decrease in solvent viscosity (increasing \( k_a \) and \( k_d \) in proportion) will not be accompanied by an increase in the amount of quenching of \( F^* \) or an increase in the fluorescence intensity of the exciplex, as \( k_d \) is already much larger than the other deactivating processes of the exciplex.

This can be represented as the dominance of the term \( k_d^{-1} \) in the denominator of eq. (4-5) leading to

\[
\frac{I_0}{I} = 1 + \frac{k_a}{k_d^{-1} 0} \tau_0[Q]
\]

and a similar modification to eq. (4-8). \( k_a \) and \( k_d \) both have the same dependence on viscosity and
hence the invariance of quenching to viscosity if the system is under \( \alpha \) conditions.

The ratio of intensities of excimer to monomer emission \( (I'/I) \) is insensitive to the addition of a small amount of a species (e.g. oxygen) which quenches the fluorescence of the exciplex (the "oxygen test" of Cohen and Selinger (1969)). Although such a quencher would also most likely quench the fluorescence of F* this is immaterial, as the ratio \( I'/I \) does not depend on the quantum yield of the initially excited species. The addition of another radiationless deactivation process will affect the intensities of monomer and exciplex emission, but will not affect their ratio if, in this case, \( k_d >> k_e' + k_q' + k_0' [O_2] \).

Under irreversible conditions, the fluorescence of an associated species exhibits a build-up prior to its normal decay. The extent of this "delay" is a function of the radiative lifetimes of both excited species, the concentration of quencher and the magnitudes of the associative and dissociative rate constants. On the other hand, \( \alpha \) conditions imply that the formation of the exciplex is much faster than its rate of deactivation. Thus the amount of delay under \( \alpha \) conditions is only a small fraction of the exciplex lifetime, and is not observed on the time-scale over which the exciplex lifetime is normally measured.

\( \alpha \) conditions imply a "coupling" between the initially excited species and the exciplex; thus the decay times of both species should be the same.
4.23 Determination of thermodynamic data

Application of eqs. (4-11) and (4-12) to systems under a conditions yields the simplified equations:

\[ \frac{I_0}{I} = 1 + \frac{k_e'}{k_e + k_q'} N_a \frac{N_a}{N_d} \exp \left( \frac{-\Delta H^*}{RT} \right) \]

(4-13)

in the determination of \( \Delta H^* \), \( \Delta S^* \) and \( \Delta G^* \) of a number of complexes in non-polar solvents. Enthalpy values range from 15 to 30 kJ mol\(^{-1}\) for the 1,2-benzenanthracene - diethylaniline complex to 24 to 47 kJ mol\(^{-1}\) for the much more planar complexes.

\[ \frac{I'}{I} = \frac{k_e' N_a}{k_e N_d} \exp \left( \frac{-\Delta H^*}{RT} \right) \]

(4-14)

where \( \Delta H^* = E_d^\ddagger - E_a^\ddagger \).

In practice, the latter equation is more convenient to apply as it is not affected by changes in excitation intensity; a plot of \( \ln \frac{I'}{I} \) versus \( 1/T \) yields a straight line of gradient \( -\Delta H^* \) and intercept

\[ \ln [Q] \frac{k_e'}{k_e} N_a , \frac{N_a}{N_d} \]

The equilibrium constant for the association is given by

\[ K^* = \frac{[FQ^*]}{[F^*][Q]} = \frac{I'/k_e'}{(I/k_e')[Q]} \]

from which comparison with eq. (4-8) yields \( K^* = \frac{k_a}{k_d} \).

The entropy change for the association is given by

\[ \Delta S^* = R \frac{d}{dT} \left( T \ln K^* \right) = R \frac{d}{dT} \left( T \ln \frac{N_a}{N_d} - \frac{\Delta H^*}{R} \right) = R \ln \frac{N_a}{N_d} \]

leading to the relationship
\[ \ln \left( \frac{T'}{T} \right) = \ln [Q] + \ln \left( \frac{k'_e}{k_e} \right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \]  (4-15)

Evaluation of \( k_e \) and \( k'_e \) enables calculation of \( \Delta H^*, \Delta S^* \) and therefore \( \Delta G^* \).\(^\dagger\)

Knibbe, Rehm and Weller (1969) have used this method in the determination of \( \Delta H^*, \Delta S^* \) and \( \Delta G^* \) of a number of exciplexes in non-polar solvents. Enthalpy values range from -43 kJ mole\(^{-1}\) for the anthracene - diethyl-aniline exciplex to -11 kJ mole\(^{-1}\) for the much more weakly bound exciplex formed between 1,2-benzanthracene and triethylamine. The entropy of formation of all the exciplexes studied, \(-76 \pm 4 \text{ J deg}^{-1} \text{ mole}^{-1}\), is similar to that found for excimer formation (Döller and Förster 1962; Stevens and Ban 1964), indicating a fairly ordered configuration.

The change in the enthalpy of formation of exciplexes with solvent polarity has also been the subject of study. Murata, Kokubun and Koizumi (1970) have reported that for the exciplex formed between 2-ethoxynaphthalene and

\(^\dagger\) A variation of this method has been proposed by Stevens and Ban (1964), who have observed that the spectra of many monomer-excimer systems over a range of temperatures exhibit an isoo emissive point. The observation of such a point effectively reduces the number of independent variables in eq. (4-15), which enables calculation of \( k_e \) and \( k'_e \) without reference to decay time and quantum yield measurements. The existence of an iso- emissive point requires that both \( \phi \) and \( \phi' \) be invariant with temperature, restricting the application of the method to such systems.
dimethyl-m-phthalate the enthalpy of formation becomes more negative in solvents of higher polarity. This is in accord with the concept of the stabilisation of the exciplex by interaction with a polar solvent, leading to a smaller $h_{\text{max}}^v$ and similarly to a more negative enthalpy of formation than in a non-polar solvent. However, the opposite behaviour has been observed with the pyrene - dimethylaniline exciplex (Okada, Matsui, Oohari, Matsumoto and Mataga 1968). This has been explained in terms of the different effect of solvent polarity on intermolecular distance within an exciplex, affecting its enthalpy of formation (Murata et al. 1970). Both these results rest on the assumption that $\Delta H^*$ can be calculated from the linear high-temperature region in a plot of $\ln (I'/I)$ against $1/T$. However, it does not seem to be appreciated that a linear plot of positive slope is not evidence per se that a system is in the $a$ region. It has been pointed out that linearity may also occur if $k_d$ and $k_q'$ are both much larger than $k_e'$ (Cohen and Selinger 1969).

The effect of solvent polarity on the enthalpy of formation of exciplexes is of some interest, as it can serve to confirm the currently accepted theory of exciplex stabilisation (examined in more detail in section 4.6) or to prove it wrong. In an attempt to clarify this effect, the temperature dependence of the formation of the pyrene - diethylaniline exciplex has been studied. The upper curve in Fig. 4-6 shows the results obtained in o-xylene, which are very similar to those obtained in methylcyclohexane. The addition of oxygen
Fig 4-6. The temperature dependence of the ratio of the intensity of exciplex ($I'$) to pyrene ($I$) emission, for the exciplex formed between pyrene and diethylaniline in different solvents.
in the high-temperature region produces no change in 
$I'/I$, so the system is under $a$ conditions. Therefore 
the value of $\Delta H^*$ obtained from the slope of the straight 
line in the high-temperature region ($-39 \text{ kJ mole}^{-1}$) is 
valid.

It is known that in more polar solvents the reaction

$$\text{exciplex} \xrightarrow{k_i'} A^-_{\text{solv}} + D^+_{\text{solv}}$$

(4-16)

becomes dominant over other deactivation processes, 
leading to no exciplex emission in solvents of high 
dielectric constant. Even in solvents of relatively 
low dielectric constant the term $k_i'$ increases the rate 
of the deactivating processes ($k_e' + k_q' + k_i'$) over the 
rate ($k_e' + k_i'$) in non-polar solvents of $\epsilon \approx 2$. This 
large change of $k_i'$ with polarity might well affect the 
equilibrium between the species, so that a system which 
is under $a$ conditions ($k_d > k_e' + k_q'$) in methylcyclo- 
hexane at a certain temperature might not be under $a$ 
conditions (now $k_d > k_e' + k_q' + k_i'$) in a more polar 
solvent at the same temperature.

Fig. 4-6 shows that for the pyrene - diethylaniline 
exciplex the transition from high- to low-temperature 
behaviour occurs at $25^\circ$ in o-xylene and $60^\circ$ in ethyl 
acetate. In diethyl ether no transition was observed 
to within $8^\circ$ of its boiling-point.

The ethyl acetate curve shows that even by extend- 
ing measurements to the boiling-point of the solution it 
is not possible to obtain with accuracy the slope of the 
line in the high-temperature region. Further, the
addition of a small concentration of oxygen to this solution near its boiling-point causes a large change in the ratio I'/I, showing that the system is not under α conditions. That is, in spite of the linear plot at high temperature, ΔH* cannot be obtained.

In non-polar solvents the relative magnitudes of the rates of dissociation and deactivation are such that, at high temperatures, ΔH* of the pyrene-diethyl-aniline exciplex can be obtained. However in more polar solvents the sum of the rate constants of deactivation increases markedly, so that α conditions are impossible to attain. Any values of ΔH* obtained in these solvents will be considerably in error. They will be a function not only of the true enthalpy of formation of the exciplex but also of the temperature dependence of the viscosity and the polarity of the solvent. As k_d ≫ k' for the pyrene-dimethylaniline exciplex in all polar solvents, the decrease in ΔH* with solvent polarity could well be caused by the increase in k' in more polar solvents.

The pyrene-dimethylaniline exciplex is not quite as strongly bound as the one studied, and is thus slightly more favourable for ΔH* studies. However the oxygen test shows quite clearly that it is not under α conditions even in solvents of only moderate polarity. Thus the values of ΔH* in polar solvents quoted by Okada et al. (1968) are not acceptable as the heats of formation of the exciplex.

As the attainment of α conditions is achieved by a
complex of low stability, and a solvent of low polarity, the exciplex formed between anthracene and triethylamine has been studied.

Table 4-1. The application of the "oxygen test" to the anthracene - triethylamine exciplex in ether at 25°C.

<table>
<thead>
<tr>
<th></th>
<th>deoxygenated solution</th>
<th>oxygen added</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity of anthracene emission (I) (arbitrary units)</td>
<td>93.5</td>
<td>76.5</td>
</tr>
<tr>
<td>Intensity of exciplex emission (I') (arbitrary units)</td>
<td>6.5</td>
<td>3.0</td>
</tr>
<tr>
<td>I'/I</td>
<td>0.070</td>
<td>0.039</td>
</tr>
</tbody>
</table>

Table 4-1 shows that the addition of a small amount of oxygen to an ether solution causes unequal changes in I' and I, and therefore this system is not in the α region at room temperature. Despite the use of a weakly bound exciplex (ΔH* in toluene = -17 kJ mole⁻¹; Knibbe, Rehm and Weller 1968) and a solvent which is not very polar (ε = 4.3), α conditions are not achieved quite close to the boiling point of the solvent.

This examination shows that only in non-polar solvents, within a carefully defined region of viscosity and temperature, is the photostationary state an equilibrium unperturbed by deactivation processes. Thus, in polar solvents, accurate thermodynamic data can only be obtained from a complete analysis of the temperature dependence of I' and I.
4.24 Alternative treatment

The derivation of thermodynamic relationships enabling calculation of $\Delta H^\ast$, $\Delta G^\ast$ and $\Delta S^\ast$ is based directly on eq. (4-4), which defines the mechanism by which exciplexes are assumed to be formed. The physical significance of the calculated values of the thermodynamic parameters will depend on how accurately this equation represents the true mechanism. In this context it is worthwhile to consider a mechanism which has been proposed for ion pair formation in polar solvents. The scheme is essentially similar to that proposed by North (1966) for treating diffusion-controlled reactions in general, and considers a reaction to be composed of consecutive transport and chemical processes:

$$F^* + Q \xrightarrow{k_{\text{diff}}} F^*|Q \xrightarrow{k_{\text{ct}}} F^+|Q^- \xrightarrow{k'_{\text{ct}}}$$

(4-17)

where $k_{\text{ct}}$ and $k'_{\text{ct}}$ are the rate constants for the charge transfer processes, $F^*|Q$ represents a proximite pair, and $F^+|Q^-$ an ion pair. Using this scheme, Rehm and Weller (1969, 1970b) have obtained a relationship giving the observed rate constant for bimolecular quenching as:

$$k_{\text{quenching}} = \frac{k_{\text{diff}}}{1 + \frac{k_{\text{diff}}}{k_{\text{ct}}} + \frac{k'_{\text{diff}}}{k'_{\text{ct}}}} \cdot \frac{1}{K_{\text{ct}}}$$

where $K_{\text{ct}} = \frac{k_{\text{ct}}}{k_{-\text{ct}}} = \exp(-\frac{\Delta G_{\text{ct}}}{RT})$. 

If the assumption is true that the energy difference between the protonated form $Q^+$ and the unprotonated $Q$ is zero, and that the protonation equilibrium is achieved only if $Q^\dagger$ is assumed to be a monotonous function of $Q_{\text{ct}}$. Given the form of the rate equation, the values of the rate constants, the use of the scheme described by the use of the scheme described by Rehm and Weller (1969, 1970b) has been obtained.
Substitution of \( k_i = N_i \exp \left(- \frac{\Delta G^\ddagger_{ct}}{RT} \right) \) together with the assumption that all electron transfer processes occur by the same general outer-sphere type mechanism*, yields the equation:

\[
k_{\text{quenching}} = \frac{k_{\text{diff}}}{1 + \frac{k_{\text{diff}}}{k_{ct}'} \left( \exp \frac{\Delta G^\ddagger_{ct}}{RT} + \exp \frac{-\Delta G^\ddagger_{ct}}{RT} \right)}
\]

(4-18)

Rehm and Weller have applied this equation to a large number of donor-acceptor systems in acetonitrile, a solvent in which ion pair formation is the predominant result of fluorescence quenching, and have concluded that the results could be fitted only if \( \Delta G^\ddagger_{ct} \) is assumed to be a monotonic function of \( \Delta G^\ddagger_{ct} \). Given the form of this function, eq. (4-18) allows the calculation of the free energy of electron transfer without the use of temperature studies.

However, this method of analysis is of additional intrinsic interest since, although it is derived for ion pair formation, it provides a possible alternative treatment of exciplex formation to that given on the basis of eq. (4-4). If the formation of an exciplex were similarly treated as consecutive processes of

*If this assumption is true the frequency factor \( N \) for the processes \( k_{ct}' \), \( k_{-ct} \) and \( k_{ct}' \) is the same: the further assumption that \( \Delta G^\ddagger \) for the process \( k_{ct}' \) (the final electron transfer) is negligible means that the frequency factor equals \( k_{ct}' \), and yields the result.
diffusion and chemical interaction, the reaction could be written:

\[
\begin{align*}
F^* + Q \xrightarrow{k_{\text{diff}}} F^*Q \xrightarrow{k_{\text{ct}}} k' \xrightarrow{k_{\text{e}}} Q,
\end{align*}
\]

Under a conditions, it can be derived that

\[
\frac{I'}{I} = \left[Q\right] \cdot \frac{k'_{e}}{k_{e}} \cdot \frac{k_{\text{diff}}}{k_{\text{ct}}} \cdot \frac{k_{\text{ct}}}{k_{\text{e}}},
\]

which can be compared with the limiting form \((k_{d} >> k'_{e} + k'_{q})\) of eq. (4-8):

\[
\frac{I'}{I} = \left[Q\right] \cdot \frac{k'_{e}}{k_{e}} \cdot \frac{k_{a}}{k_{d}}.
\]

The result that under a conditions \(k_{a}\) and \(k_{d}\) are given in terms of a product of the two appropriate rate constants (of formation and dissociation of the exciplex) is not surprising. It follows that temperature studies which when applied to reaction (4-4) gave a value of \(E_{a}^{*} - E_{d}^{*} (= \Delta H^{*})\), will give for reaction (4-19) a value which can be equated to \((E_{\text{diff}}^{*} + E_{\text{ct}}^{*}) - (E_{-\text{diff}}^{*} + E_{-\text{ct}}^{*})\). These relationships hold even if there are two distinct activated processes which will occur if the proximate pair is stabilised relative to the separated molecules. Such a stabilisation will
affect both the net forward and reverse rates and (a common result in reaction kinetics) leave the equilibrium constant unchanged.

This is of interest because the Arrhenius equation (4-10) is, for obvious reasons, only a true expression of a rate constant if only one major activated process is involved; however the validity of thermodynamic data obtained (under equilibrium conditions) on the assumption of only one activated process is not eroded if there is more than one such process taking place consecutively.

Equation (4-19) can be combined with the relation derived by Knibbe, Rehm and Weller (1968):

$$\Delta G_{ct} = E_k(ox)D - E_k(red)A - \Delta E_{0,0} - \frac{e^2}{\varepsilon a}$$

to give a dependence of $k_{\text{quenching}}$ on the electrical properties of the molecules. This justifies the conclusions reached by the many workers (section 4.12) who inferred the formation of a charge transfer state from quenching data.
4.3 EXCIPEX FORMATION IN NON-POLAR SOLVENTS

The quenching of the fluorescence of a large number of excited aromatic hydrocarbons (electron acceptors) by tertiary amines proceeds according to

$$A^* + D \leftrightarrow \text{exciplex} \quad (4-21)$$

Knibbe and Weller (1967) have also shown that in a few cases the fluorescence of excited donors is quenched by acceptors according to the alternative mechanism

$$D^* + A \leftrightarrow \text{exciplex} \quad (4-22)$$

which has been found to operate for diethylaniline - naphthalene, diethylaniline - biphenyl and naphthalene - benzonitrile.

There is no apparent reason why a given electron donor-acceptor pair should not form an exciplex according to both reactions (4-21) and (4-22). However the test of such a hypothesis is not easy in practice, as it requires the selective excitation of each species in the presence of a suitable concentration of the other. Such selective excitation is easiest when one species absorbs to longer wavelengths than the other, and all results so far reported have been of this type. Excitation of the species absorbing at shorter wavelengths is difficult as its absorption is totally overlapped by that of the other component.

An examination of a large number of donor-acceptor
pairs shows that, in fact, very few of them are available for study according to both mechanisms above, without making calculations involving the absorption spectra of both species. The decay time of the initially excited species dictates the concentration of quencher necessary to produce a suitable amount of exciplex. This concentration in turn determines the concentration of initially excited species necessary in order that it absorbs all but a negligible proportion of the light. The magnitude of this concentration commonly results in one of a number of complications:

- excimer formation (e.g. 1-cyanonaphthalene was found to exhibit excimer emission at concentrations above 0.002 mole $^{-1}$)
- in the case of a dipolar molecule the required concentration may significantly alter the polarity of the solution (e.g. diethylaniline)
- the required concentration of quenched species may exceed its solubility.

Four donor-acceptor pairs have been found suitable for study, in that selective excitation of each species is possible: diethylaniline - naphthalene, diethylaniline - biphenyl, naphthalene - 1-cyanonaphthalene and diethylaniline - phenanthrene.

4.31 Selective excitation

The fluorescence spectra of diethylaniline in the presence of different concentrations of naphthalene is shown in Fig. 4-7a. The fluorescence of naphthalene with different concentrations of diethylaniline is shown
**Fig. 4-7a.** Fluorescence spectra of diethylaniline (0.09 mole 1\(^{-1}\) in cyclohexane) alone (a), and with added naphthalene:

- (b) 0.0066 mole 1\(^{-1}\)
- (c) 0.030 mole 1\(^{-1}\)
- (d) 0.060 mole 1\(^{-1}\)
- (e) 0.094 mole 1\(^{-1}\)

(Excitation at 315 nm)

**Fig. 4-7b.** Fluorescence spectra of naphthalene (0.17 mole 1\(^{-1}\) in cyclohexane) alone (a), and with added diethylaniline:

- (b) 0.00031 mole 1\(^{-1}\)
- (c) 0.00125 mole 1\(^{-1}\)

(Excitation at 285 nm)
Fig. 4-7c. Fluorescence spectra of diethylaniline (0.01 mole l\(^{-1}\) in cyclohexane) alone (a), and with added biphenyl:

(b) 0.015 mole l\(^{-1}\)
(c) 0.031 mole l\(^{-1}\)
(d) 0.130 mole l\(^{-1}\)

(Excitation at 303 nm)

Fig. 4-7d. Fluorescence spectra of biphenyl (0.14 mole l\(^{-1}\) in cyclohexane) alone (a), and with added diethylaniline:

(b) 0.005 mole l\(^{-1}\)
(c) 0.010 mole l\(^{-1}\)

(Excitation at 240 nm)
Fig. 4-7e. Fluorescence spectra of naphthalene (0.055 mole l⁻¹ in cyclohexane) alone (a), and with added 1-cyanonaphthalene:

(b) 0.0003 mole l⁻¹
(c) 0.005 mole l⁻¹
(Excitation at 255 nm)

Fig. 4-7f. Fluorescence spectra of 1-cyanonaphthalene (0.0017 mole l⁻¹ in cyclohexane to prevent excimer formation) alone (a), and with added naphthalene:

(b) 0.002 mole l⁻¹
(c) 0.007 mole l⁻¹
(d) 0.025 mole l⁻¹
(Excitation at 321 nm)
in Fig. 4-7b. Fluorescence spectra of the other two donor-acceptor pairs are shown in Fig. 4-7c to f. In each case the fluorescence of the primarily excited species is quenched in accordance with the Stern-Volmer relation, and an analysis of the simultaneous increase in exciplex emission shows linear plots of $I'$ against $I$, and of $I'/I$ against concentration of quencher. This observation is in marked contrast to the case of energy transfer, in which the existence of efficient quenching of one species by another implies the absence of the reverse process.

The fluorescence of phenanthrene is not noticeably affected by the addition of up to 0.01 mole $l^{-1}$ diethyl-aniline. (This is 100 times the concentration of diethylaniline required to noticeably affect the fluorescence of naphthalene; the decay times differ by only a factor of two.) Phenanthrene quenches the fluorescence of diethylaniline, resulting in energy transfer; the Stern-Volmer constant ($K = 58 l$ mole$^{-1}$) gives an observed quenching rate constant of $1.7 \times 10^{10}$ $l$ mole$^{-1}$ s$^{-1}$, but no emission characteristic of an exciplex is observed, in contrast to a previous report (Rehm and Weller 1970a).

The fluorescence spectra of the other three pairs show that either species may be excited to produce an exciplex. The small difference in spectral characteristics of the exciplex emission, which appears to depend on which species is primarily excited, probably arises from a change in the polarity of the medium, as very different concentrations of solute are used to ensure
Fig. 4-8. Data for a solution containing 0.098 mole 1⁻¹ diethylaniline and 0.0042 mole 1⁻¹ naphthalene in methylcyclohexane:

(a) the predicted excitation spectrum of the naphthalene-diethylaniline exciplex, if only excited diethylaniline formed the exciplex

(b) the fraction of light absorbed by naphthalene (this corresponds to the predicted exciplex excitation spectrum if only excited naphthalene formed exciplex)

(c) the experimental excitation spectrum (corrected) of the naphthalene-diethylaniline exciplex at 50°C.
separate excitation of each species.

The same result is obtained in a different way in Fig. 4-8, which shows the fluorescence excitation spectrum of a mixture of a typical donor-acceptor pair, diethylaniline and naphthalene. Under high-absorbance conditions the excitation spectrum of each species, in the absence of the other, is a horizontal straight line. Figs. 4-8a and 4-8b show the proportion of light absorbed by diethylaniline and by naphthalene, respectively, calculated from absorption spectra. If excitation of only one of these species resulted in exciplex formation, the excitation spectrum of the exciplex fluorescence would follow curve (a) or (b). Curve 4-8c shows that, in fact, absorption of light by both species results in exciplex emission. The relatively long decay time of naphthalene results in efficient formation of exciplex, so that at those wavelengths at which the naphthalene absorbs a fraction of the light, the intensity of exciplex emission is markedly increased.

Table 4-2 shows that in all three cases the extent of fluorescence quenching, given by $K$, is largely determined by the decay time ($\tau_0$) of the initially excited species in the absence of quencher. The variation in the values of $k_a/1 + k_d\tau_0$ (= $K/\tau_0$) in the last column result from the different extents of reversibility of the quenching reactions. Comparison with the calculated value of $k_a$ ($16 \times 10^9$ l mole$^{-1}$ s$^{-1}$ in cyclohexane) shows that in some cases the reverse reaction can be neglected in this solvent at room temperature.

In Table 4-3 the data are analysed in terms of the
Table 4-2. Details of fluorescence quenching leading to exciplex formation. An asterisk denotes the initially excited species.

<table>
<thead>
<tr>
<th>Exciplex</th>
<th>( \tau_0 ) (ns)</th>
<th>( K \times 10^{-9} ) (l mole(^{-1}))</th>
<th>(l mole(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylaniline* naphthalene</td>
<td>2.8</td>
<td>36</td>
<td>13.0</td>
</tr>
<tr>
<td>Diethylaniline* naphthalene</td>
<td>119</td>
<td>1370</td>
<td>11.5</td>
</tr>
<tr>
<td>Diethylaniline* biphenyl</td>
<td>2.8</td>
<td>13</td>
<td>4.6</td>
</tr>
<tr>
<td>Diethylaniline* biphenyl*</td>
<td>16</td>
<td>263</td>
<td>16.4</td>
</tr>
<tr>
<td>Naphthalene* 1-cyanonaphthalene</td>
<td>119</td>
<td>810</td>
<td>6.8</td>
</tr>
<tr>
<td>Naphthalene 1-cyanonaphthalene*</td>
<td>17</td>
<td>76</td>
<td>4.5</td>
</tr>
</tbody>
</table>

(a) from Knight and Selinger (1971)  
(b) from Berlman (1965)

Quenching of the primarily excited species and the simultaneous increase in the fluorescence intensity of the exciplex, rather than in terms of the change in the first parameter alone. Eq. (4-8) can alternatively be expressed as

\[
\frac{k_a}{1 + k_d \tau_0} = \frac{I'}{I} \cdot \frac{1}{[Q]} \cdot \frac{1}{\varphi''} \cdot k_e
\]  

(4-23)

where \( \varphi'' \), the intrinsic quantum yield of the exciplex, is obtained by extrapolation of the exciplex intensity...
Table 4-3. Data enabling calculation of $k_a/1 + k_d'\tau_0$ according to eq. (4-23).

<table>
<thead>
<tr>
<th>Compound 1</th>
<th>$k_a/1$</th>
<th>$k_d'\tau_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylaniline*</td>
<td>5.7</td>
<td>0.21</td>
</tr>
<tr>
<td>Naphthalene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethylaniline</td>
<td>0.24</td>
<td>12.0</td>
</tr>
<tr>
<td>Naphthalene*</td>
<td>0.24</td>
<td>6.9</td>
</tr>
<tr>
<td>Diethylaniline</td>
<td>0.13</td>
<td>5.8</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>1.2</td>
<td>16.5</td>
</tr>
<tr>
<td>Biphenyl*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>1-cyanonaphthalene</td>
<td>2.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

$k_e$ was calculated from $k_e = \phi_0/\tau_0$. Values of $\tau_0$ were taken from Table 4-2. Values of $\phi_0$ were obtained by comparison with quinine sulphate in 1N $H_2SO_4$ ($\phi = 0.55$): naphthalene 0.23, diethylaniline 0.16, biphenyl 0.18, 1-cyanonaphthalene 0.34.

to infinite quencher concentration.

The good agreement between values of $k_a/1 + k_d'\tau_0$ obtained from analysis of both the initial quenching and the exciplex emission intensity (the last column in Tables 4-2 and 4-3) is good evidence that each exciplex is formed directly from the initially excited species. The possibility that energy transfer to the lower-energy species is followed by collision and exciplex formation as a separate, consecutive process,
can thus be discounted.

4.32 Nature of the exciplex equilibrium

The observation that the three exciplexes studied may be produced following excitation of either the electron donor or acceptor leads to the question of whether exciplex formation and dissociation is more properly represented by:

\[ D + A^* \rightarrow \text{exciplex} \rightarrow D^* + A \]  \hspace{1cm} (4-24)

Two methods have been devised to test this hypothesis; they rest on an examination of (i) fluorescence spectra, and (ii) fluorescence excitation spectra, of judiciously chosen mixtures of the two species.

(i) Fluorescence spectra

If the quenching of one species by another is described by the "double equilibrium" (4-24), addition of quencher Q (which may be either D or A) would not only cause a decrease in the fluorescence quantum yield of the primarily excited species F* but would also result in the formation of Q*. The fluorescence of this species might then be observed in addition to the fluorescence of F* and exciplex. This test suffers from the disadvantages that the fluorescence of Q* would not be observed if either its spectrum were similar to the fluorescence spectrum of F* (unless the latter can be
completely quenched), or the concentration of F (determined by the necessity to excite it alone) quenches the fluorescence of the Q* that is formed.

(ii) Excitation spectra

It has been shown earlier that the "high-absorbance" excitation spectrum of a species in a mixture obeys the equation

$$F_i(\lambda) = \frac{\varepsilon_i(\lambda)c_i}{\sum_i \varepsilon_i(\lambda)c_i}$$

Any deviation of the observed excitation spectrum \( F_i(\lambda) \) from this equation is evidence that excitation energy is not emitted by the species which absorbed it.

This method allows study of the interaction of a donor-acceptor pair of molecules with similar fluorescence spectra. It has an advantage over method (i) in that it can be used in conditions under which the fluorescence of only one species can be observed.

**Diethylaniline - naphthalene**

It is not possible to tell using fluorescence spectra whether excitation of diethylaniline results in emission from naphthalene, because the concentration of diethylaniline necessary would completely quench any naphthalene fluorescence. Likewise, if excitation of naphthalene resulted in emission from diethylaniline it would not be observed as it is in the same spectral
region as that of naphthalene, it is structureless and its quantum yield under these conditions is much less than that of naphthalene.

A study of excitation spectra is more fruitful. Fig. 4-9a shows the excitation spectrum at high absorbance of diethylaniline in a mixture of naphthalene, and Fig. 4-9b shows the calculated excitation spectrum. The concentrations have been chosen so that the fraction of excitation absorbed by naphthalene undergoes a large variation with excitation wavelength, and so that all naphthalene fluorescence is quenched. Comparison of (a) and (b) indicates the amount of "excitation loss" from diethylaniline to be expected because of the competitive absorption by naphthalene. The excitation spectrum (a) obtained at room temperature differs noticeably from the predicted curve (b) in that there is less loss of excitation by diethylaniline than predicted by eq. (2-7). There is an even smaller loss of excitation at higher temperatures (curve (c)). Thus some of the excitation originally absorbed by naphthalene is transferred to diethylaniline, by a process which is more efficient at higher temperatures.

Fig. 4-10 shows that between room temperature and 60° the system goes from the "turnover point" where the probabilities of deactivation and dissociation of the exciplex are of the same order of magnitude, to the high temperature linear region where deactivation is relatively improbable. The excitation loss is thus attributed to processes (α) and (β) in:
Fig. 4-9. Corrected excitation spectra of the fluorescence of diethylaniline from a solution containing 0.048 mole l\(^{-1}\) diethylaniline and 0.0066 mole l\(^{-1}\) naphthalene in methylcyclohexane.

(a) observed at room temperature
(b) calculated from absorption spectra
(c) observed at 60°.
Fig. 4-10. Temperature dependence of the ratio of intensity of exciplex to diethylaniline emission, for the naphthalene-diethylaniline exciplex in methylcyclohexane. Conditions were chosen so that only the diethylaniline absorbed the incident radiation.
naphthalene* + diethylaniline
\[ \xrightarrow{\alpha} \text{exciplex} \xrightarrow{\beta} \]
\[ \xrightarrow{-\alpha} \]

diethylaniline* naphthalene

The existence of process \((-\beta)\) is shown by the formation of exciplex from excited diethylaniline. It is not possible to confirm the existence of process \((-\alpha)\) by doing the reverse experiment, i.e. by testing whether excitation originally on diethylaniline can appear on naphthalene. To do this it would be necessary to study the excitation spectrum of naphthalene in a mixture containing sufficient naphthalene to quench any diethylaniline fluorescence produced. In order that the diethylaniline absorb a significant proportion of the excitation at some wavelength its concentration would be so high that it would quench the naphthalene fluorescence.

Although there is no way of confirming the existence of process \((-\alpha)\), there is no obvious reason why it should not occur.

**Naphthalene - 1-cyanonaphthalene**

In this case the large degree of similarity between the spectra of the two species precludes their separation. Thus it is necessary to examine an appropriate excitation spectrum to see whether excitation on 1-cyanonaphthalene can, after exciplex formation and dissociation, appear on naphthalene. A high concentration of naphthalene ensures complete quenching of the fluorescence of 1-cyanonaphthalene, so that fluorescence observed at a wavelength within the naphthalene emission
is solely that of naphthalene. The concentration of 1-cyanonaphthalene is chosen so that it does not have a large quenching effect on naphthalene, and so that within the range of excitation the proportion of light absorbed by it undergoes a large variation.

Fig. 4-11 shows the fluorescence excitation spectrum of naphthalene in a mixture of naphthalene and 1-cyanonaphthalene. Curve (b), obtained at low temperature, shows the result which is expected on the basis of competitive absorption alone: the intensity of fluorescence of naphthalene is proportional to the fraction of light it absorbs.

At the higher temperature (curve (a)) the loss of excitation is much less. This shows that energy originally absorbed by 1-cyanonaphthalene is transferred to naphthalene by a mechanism which is dormant at temperatures where the dissociation of exciplex is negligible. Temperature studies show that at the higher temperature (60°) the rate constant of dissociation of the exciplex ($k_d$) is large compared with that of the other deactivating processes ($k_e' + k_q'$); at low temperatures the reverse is true and the deactivation processes dominate over the dissociation.

The smaller loss of excitation energy at higher temperatures is entirely consistent with the dominance of the dissociation of exciplex at these temperatures, if it is formed according to the scheme

\[
\text{naphthalene}^* + \overset{\gamma}{\underset{\delta}{\text{exciplex}}} \overset{\delta}{\underset{\gamma}{\text{naphthalene}}} + \overset{\gamma}{\underset{\delta}{\text{1-cyanonaphthalene}}} \]
Fig. 4-11. Corrected excitation spectra of the naphthalene fluorescence from a solution containing 0.195 mole l⁻¹ naphthalene and 0.00274 mole l⁻¹ 1-cyanonaphthalene in methylcyclohexane.

(a) at 60°
(b) at -15°

Curve (b) is identical to the curve predicted on the basis of no energy transfer.
The reversibility of the right-hand step above (i.e. the existence of process $\delta$) cannot be demonstrated by either of the methods devised. Thus, some uncertainty remains, although as in the previous case there is no reason why this process should not occur.

**Diethylaniline - biphenyl**

The extent to which excitation originally on diethylaniline appears on biphenyl is deduced from the fluorescence spectrum of a mixture of the two species. The concentration of diethylaniline is chosen so that it would not quench any excited biphenyl formed, and the biphenyl is present in sufficient concentration to form a large amount of exciplex.

No biphenyl fluorescence is observed following excitation of diethylaniline at temperatures up to 75°. This is not surprising, as the difference in the spectroscopic energy levels of the two molecules is about 3000 cm$^{-1}$.

The low value of $k_a/1 + k_d$' in Table 4-2 indicates that the reaction of diethylaniline* with biphenyl is reversible. In addition, the dependence of exciplex formation on temperature shows that at least one of the formation processes is reversible, and the lack of dissociation of exciplex to give excited biphenyl means that dissociation takes place to give excited diethylaniline. The formation of the diethylaniline - biphenyl exciplex is represented by
The double equilibria between naphthalene and diethylaniline, and between naphthalene and 1-cyano­naphthalene, have been proposed as a natural extension of the two separate equilibria:

\[ \text{D}^* + \text{A} \rightleftharpoons \text{exciplex} \]

and

\[ \text{D} + \text{A}^* \rightleftharpoons \text{exciplex} \]

However, the differences in the excitation spectra only prove that excitation transfer occurs. The participation of an exciplex as an intermediate in the process has been inferred rather than observed, although the temperature dependence of the process compels us to think in terms of transfer occurring through a collision complex of some sort. Confirmation that this complex is the exciplex is obtained by observing the effect on such energy transfer of a solvent which quenches the exciplex fluorescence. Fig. 4-12 shows the predicted and observed excitation spectra of diethylaniline in a mixture with naphthalene; the conditions are essentially the same as those used in Fig. 4-9 except that the solvent is methanol. The spectra are identical within the
Fig. 4-12. Corrected excitation spectra of the fluorescence of diethylaniline from a solution containing 0.0492 mole 1⁻¹ diethylaniline and 0.00781 mole 1⁻¹ naphthalene in methanol:

(a) calculated from absorption spectra
(b) observed at room temperature
error of the experiment, indicating that no energy transfer takes place in this solvent. Methanol completely quenches the exciplex fluorescence because of the dominance of ion pair formation over the radiative process; similarly ion pair formation would be expected to dominate over dissociation and therefore result in no energy transfer. Irrespective of how it is formed, the exciplex acts as a "sink" for excitation energy in this solvent.

The prevention of energy transfer by transition to a polar solvent is compelling evidence that in this case energy transfer occurs only via the formation and subsequent dissociation of an exciplex.

4.34 Discussion

On the basis of the results presented there is no doubt that a given exciplex may be formed following excitation of either the electron donor or the acceptor. The agreement between quenching constants obtained from the concentration dependence of both $I_0/I$ and $I'/I$ indicates that the initially excited species is a partner in the collision complex which undergoes charge transfer to form an exciplex*. Thus, the possibility can be discounted that long-range energy transfer to the lower-energy species is a necessary forerunner to exciplex formation. It is possible that energy transfer within a collision complex may immediately precede charge trans-

*Time resolved studies of exciplex buildup and decay, subsequently carried out in this laboratory, have confirmed this result (Knight and Selinger 1971).
fer, as suggested by Förster (1971), but there is no way of deciding this question.

The difference between the observed excitation spectra and those calculated from absorption spectra is, if a true effect, evidence of excitation migration. As different absorption and excitation spectra of a single compound have previously been attributed to instrumental artifacts, this possibility is briefly examined. The resolution of the excitation monochromator (2 nm) is much worse than that of the spectrophotometer used to obtain the absorption spectra. However, the coincidence of the predicted and observed spectra of the naphthalene - 1-cyanonaphthalene system at low temperatures means that the discrepancy at higher temperatures is not due to this difference in resolution. (The spectra of diethylaniline, naphthalene and 1-cyanonaphthalene do not change markedly with temperature.) For the same reason the discrepancy cannot be attributed to reabsorption followed by fluorescence from the other species in the mixture. In addition, the fluorescence quantum yields of all compounds used were found to be independent of excitation wavelength. It is concluded that the difference between the calculated and observed excitation spectra, and the change of the latter with temperature, are due to changes in the kinetic scheme. The absence of any energy transfer in a solvent which efficiently deactivates the exciplex is proof that the transfer takes place through formation and dissociation of such a species.

The existence of a "double equilibrium" in exciplex
formation may well be a general phenomenon where the spectroscopic energy levels of the electron donor and acceptor are not far apart. Some of the uncertainty regarding the existence of process (δ) above can be removed by considering the energy levels of the two species. The absorption and fluorescence of naphthalene in cyclohexane both have their origins at 32200 cm$^{-1}$; that of 1-cyanonaphthalene has not been positively identified but inspection of the absorption and emission spectra shows that it is not greater than 31200 cm$^{-1}$. Thus on energy grounds, process (δ) is more likely than (−γ) and so it is likely that energy transfer in both directions occurs via exciplex formation.

The endothermic energy transfer observed in processes (γ) and (δ) is well within reach of typical thermal energies. At room temperature kT ≈ 200 cm$^{-1}$. Classically an energy deficit of 2nkT in antistokes fluorescence (an analogous consideration) may be covered thermally, if the excited-state lifetime is long enough to establish thermal equilibrium with the environment (Dushinskii 1937). At room temperature not all the n (= 3N - 6) degrees of freedom are expected to be active, but the "hot band" observed at 31200 cm$^{-1}$ in the absorption spectrum of naphthalene indicates that such an energy deficit is within thermal reach.

Such a comparison cannot be made as easily in the case of the diethylaniline - naphthalene exciplex because of the lack of structure in the absorption and emission spectra of the former. Estimation of the energy of the 0,0 transition as the mid-point between
the absorption and emission peaks indicates that naphthalene lies about 1000 cm\(^{-1}\) to higher energy than diethylaniline. Fig. 4-13 shows the magnitude of the antistokes shift exhibited by diethylaniline: excitation at about 330 nm is effective in exciting fluorescence, which extends to about 315 nm — an antistokes shift of 1500 cm\(^{-1}\). (In addition, measurements of the vibrational heat capacity of aniline vapour have shown that at 200\(^{\circ}\) four or five vibrational modes are active (LaPaglia 1964).) Thus in this case also, it is reasonable to expect excitation transfer in both directions.

One result of the double reversibility is that thermodynamic data derived for such systems reflects the change with temperature in the concentrations of all three excited species in equilibrium. For this reason the enthalpy and entropy of formation of such exciplexes cannot be measured in the usual way.

In the case of a donor-acceptor pair whose spectroscopic energy levels are far apart, dissociation of the exciplex to give the excited higher-energy species would not be expected. This is confirmed by the behaviour of the diethylaniline - biphenyl system, in which excitation of biphenyl results in the establishment of an equilibrium between diethylaniline and exciplex.
It has been suggested that, in general, fluorescence quenching proceeds via an electron transfer mechanism within the collision complex. This theory has gained some strength with recent reports (section 4.12) that the constants of fluorescence quenching depend on the electrical properties of the molecules involved.

The group of molecules forming collision complexes are known to be stabilised by intramolecular electron transfer and can be observed directly by virtue of their emission radiates in the process. Since we have noted that compounds having similar emission potentials and electron affinities the proportions of the extreme ionic forms contributing to the stability of the collision complex are expected to be small and approximately equal. By analogy with the eximer case, the polarity of the solvent is expected to have no effect.

---

**Fig. 4-13.** Fluorescence spectrum of diethylaniline in cyclohexane at room temperature.

(The "excitation band" shows the maximum contribution that scattered exciting light could have made to the observed spectrum).
4.4 ENERGY TRANSFER AND CHARGE TRANSFER

It has been suggested that, in general, fluorescence quenching proceeds via an electron transfer mechanism within the collision complex. This theory has gained some strength with recent reports (section 4.12) that rate constants of fluorescence quenching depend on the electrical properties of the molecules involved.

The group of molecules forming exciplexes represent a most favourable case for study in that exciplexes are known to be stabilised by charge transfer, and can be observed directly by virtue of their emission. We have noted that some exciplexes act also as intermediates in the process of energy transfer (e.g. naphthalene - diethylaniline), and the transfer process does not occur in polar solvents. From this it is reasonable to expect that the use of solvents of different polarity might yield information about the nature of collision complexes formed upon fluorescence quenching.

4.41 Energy transfer between electrically similar molecules

Transfer of energy from phenanthrene to anthracene occurs by a diffusion-limited process (Stevens and Dubois 1966). As the compounds have similar ionisation potentials and electron affinities the proportions of the extreme ionic forms contributing to the stability of the collision complex are expected to be small and approximately equal. By analogy with the excimer case, the polarity of the solvent is expected to have no effect
on the complex.

In Fig. 4-14 the fluorescence spectrum of a mixture of phenanthrene and 9-methylantracene in cyclohexane is compared with that of phenanthrene in the absence of 9-methylantracene. Table 4-4 shows the variation which occurs on transition to methanol.

Table 4-4. Effect of solvent on the quenching of phenanthrene by 9-methylantracene.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$K_a$</th>
<th>$k_a$ (quenching) $b$</th>
<th>$k_a$ (viscosity) $c$</th>
<th>$\frac{I_{9MA}}{I_P}$ $d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\times 10^{-9}$</td>
<td>$\times 10^{-9}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclohexane</td>
<td>849</td>
<td>14.2</td>
<td>11.3</td>
<td>1305</td>
</tr>
<tr>
<td>methanol</td>
<td>1050</td>
<td>17.5</td>
<td>16.3</td>
<td>1675</td>
</tr>
<tr>
<td>methanol/cyclohexane</td>
<td>1.24</td>
<td>1.24</td>
<td>1.44</td>
<td>1.28</td>
</tr>
</tbody>
</table>

(a) from the Stern-Volmer equation (4-5)
(b) from eq. (4-6) assuming the decay time of phenanthrene in the absence of quencher to be 59.5 ns in both solvents (Birks and Georghiou 1968)
(c) from eq. (4-7)
(d) presented for a hypothetical quencher concentration of 1 mole $\cdot$ l$^{-1}$; i.e. the values tabulated are the average values of $\frac{I_{9MA}}{I_P}$ for a number of values of $[Q]$.

$I_{9MA} =$ intensity of fluorescence from 9-methylantracene; $I_P =$ intensity of fluorescence from phenanthrene.

The difference in the observed quenching constant $K$ (in the second column of the Table) is attributed to the difference in viscosities between cyclohexane and methanol. Assuming the decay time of phenanthrene to be insensitive to solvent, values of $k_a$ (quenching) are in good agreement
Fig. 4-14. (a) The fluorescence spectrum of phenanthrene, 0.05 mole 1\(^{-1}\) in cyclohexane.

(b) The fluorescence spectrum of the above solution, to which 0.00273 mole 1\(^{-1}\) 9-methylantracene has been added.
with those calculated from viscosities. The change in the values of $I_{9MA}/I_F$ parallels the increase by a factor of 1.24 in the initial quenching constant (columns 3 and 5). In this case the energy transfer process is independent of solvent polarity: the collision complex is subject to no additional deactivating process in the more polar solvent.

This is the result that is intuitively expected for such a system - it is useful in that it shows the agreement between quenching and sensitisation data to be expected under conditions of simple energy transfer.

4.42 Energy transfer between electrically dissimilar molecules

It is reasonable to expect that a complex formed between 9-methylanthracene and 9-cyanophenanthrene would be stabilised to some extent by charge transfer due to the electron-withdrawing effect of the -CN group. Fig. 4-15a shows the quenched fluorescence of initially excited 9-cyanophenanthrene together with the fluorescence of 9-methylanthracene produced by energy transfer, and a new band attributed to the exciplex formed between them.

Use of methanol instead of benzene as a solvent causes a small change in the extent of initial quenching but a much larger change in the intensity of emission from the subsequently formed species, the exciplex and excited 9-methylanthracene (Fig. 4-15b and Table 4-5). By contrast to the previous system, sensitisation of the fluorescence of the energy acceptor is extremely depend-
Fig. 4-15. Fluorescence spectrum of a solution containing 0.050 mole l⁻¹ 9-cyanophenanthrene and 0.020 mole l⁻¹ 9-methylandanthracene, in (a) benzene (b) methanol drawn using the same intensity scales. The dotted lines show the contribution of exciplex emission to each observed spectrum. (Excitation at 292 nm, to excite 9-cyanophenanthrene)
Table 4-5. Effect of solvent on the quenching of 9-cyanophenanthrene by 9-methylanthracene.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$K_{\text{mole}^{-1}}$</th>
<th>Intensities of emission (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>exciplex</td>
</tr>
<tr>
<td>benzene</td>
<td>539</td>
<td>20</td>
</tr>
<tr>
<td>methanol</td>
<td>460</td>
<td>6</td>
</tr>
<tr>
<td>methanol benzene</td>
<td>0.85</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Effect of solvent polarity. In this system energy transfer presumably takes place via the exciplex.

4.43 Fluorescence quenching leading to no new emission

Tertiary amines and aromatic hydrocarbons form exciplexes so commonly that any exception is notable. The addition of diethylaniline to solutions of phenanthrene and azulene causes no exciplex emission, and these systems have therefore been examined to see whether any of their properties resemble those of systems from which exciplex emission is observed. Fig. 4-16 shows the fluorescence spectrum of a mixture of phenanthrene and diethylaniline in cyclohexane. As only diethylaniline is excited the phenanthrene fluorescence results from energy transfer; the calculated quenching rate constant agrees with that for a diffusion-controlled reaction. Transition to the more polar solvent methanol leaves the quenching rate constant essentially unchanged, but no phenanthrene fluorescence can be detected.

Confirmation that this effect is due to an additional
Fig. 4-16. Fluorescence spectrum of a solution containing 0.030 mole l\(^{-1}\) diethylaniline and 0.0094 mole l\(^{-1}\) phenanthrene in cyclohexane. The dotted lines show the contribution of each species to the observed spectrum.
deactivating process acting on the collision complex is obtained by considering the reverse reaction, the quenching of phenanthrene by diethylaniline. In cyclohexane, diethylaniline has no observable quenching effect on phenanthrene; this is expected as energy transfer from phenanthrene to diethylaniline is highly unfavourable. However, quenching is observed in methanol (Table 4-6).

Table 4-6. The quenching of the fluorescence of phenanthrene by diethylaniline.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>K (l mole(^{-1}))</th>
<th>K/τ(_0) x 10(^{-9}) (l mole(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>&lt;0.2</td>
<td>&lt;0.003</td>
</tr>
<tr>
<td>methanol</td>
<td>58.3</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Both these results can be explained by charge transfer stabilisation of the collision complex, leading to its destruction in a polar solvent.

Similar results have been obtained with azulene, another aromatic hydrocarbon which does not form exciplexes with tertiary amines. The fluorescence of diethylaniline in cyclohexane is quenched by azulene, sensitising the fluorescence of the latter. In methanol, fluorescence quenching still occurs but no azulene fluorescence is produced.

In both cases energy is transferred from the higher- to the lower-energy species by some mechanism which is dormant in methanol, a solvent which is sufficiently polar to quench exciplexes formed between
molecules similar to those studied here. Quenching of the fluorescence of the lower- by the higher-energy moiety also occurs, leading not to unfavourable energy transfer but to the formation of a complex which is de-activated much more easily in a polar solvent.

Similarly it has proved possible to study other systems which are suspected of forming charge transfer collision complexes. The quenching of the fluorescence of aromatic hydrocarbons by dienes is thought to proceed by such a mechanism, but this has not really been proven. Data obtained from the quenching of the fluorescence of three such aromatic hydrocarbons by 2,5-dimethyl-2,4-hexadiene is shown in Table 4-7. The greater extent of

Table 4-7. Quenching of the fluorescence of aromatic hydrocarbons by 2,5-dimethyl-2,4-hexadiene.

<table>
<thead>
<tr>
<th>Quenched species</th>
<th>$\tau_0$ (ns)</th>
<th>$K/\tau_0 \times 10^{-9}$ (\text{l mole}^{-1} \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>methanol</td>
<td></td>
</tr>
<tr>
<td>naphthalene</td>
<td>110\textsuperscript{a}</td>
<td>3.3</td>
</tr>
<tr>
<td>anthracene</td>
<td>4.2\textsuperscript{b}</td>
<td>0.83</td>
</tr>
<tr>
<td>perylene</td>
<td>5.4\textsuperscript{b}</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

(a) from Mataga, Tomura and Nishimura (1965)  
(b) average of published values

fluorescence quenching in methanol than in benzene is attributed to the formation of a complex which is destroyed more easily in a more polar solvent. The increase in quenching of naphthalene is not large, bearing in mind that although the macroscopic viscosities of benzene and methanol are the same, their microscopic vis-
cosities could differ slightly. However, the quenching of anthracene is much enhanced in methanol. Similarly, perylene is not noticeably quenched in benzene; in methanol the amount of quenching is still small but is easily measurable. Even in methanol the quenching occurs at significantly below the diffusion-controlled rate, indicating that even in this solvent complexes of this type will dissociate rather than become deactivated.

4.44 Discussion

The systems chosen, spanning the range from electrically similar molecules to those which are very dissimilar, give some insight into the mechanism of collisional fluorescence quenching and concomitant energy transfer. It is assumed that the only difference in the effect of solvents of similar viscosities but different polarities is to enable solvation of ions and hence to facilitate the dissociation of a collision complex in which some degree of charge transfer has occurred. (Where the intrinsic fluorescence quantum yield of the energy acceptor changes with solvent polarity this has been taken into account.)

The evidence is that a dissimilarity between the electrical properties of an energy donor and acceptor causes transfer of energy to occur via an excited collision complex containing some charge transfer character. That is, the process of energy transfer is connected with electron transfer in such complexes. The observation that the substitution of the -CN group onto phenanthrene causes suppression of all energy transfer
to 9-methylandanthracene in a polar solvent (compared with energy transfer from phenanthrene itself, which is unaffected) means that in such a solvent, formation of an exciplex occurs much more readily than energy transfer purely by resonance interaction. This gives some idea of the ease of electron transfer between two such species, at least in a polar solvent.

This current work follows a period of interest in the mechanism of a large number of quenching processes which do not lead to any new emission. The quenching has been attributed to charge transfer processes for reasons that rest on the perturbation of a given system to produce an emissive complex, and the correlation of quenching efficiencies with ionisation potentials and electron affinities. The present results add two more methods to this list. Both rely on the additional deactivation by a polar solvent of a transient complex with charge transfer character. It is convenient to illustrate both methods by reference to the reaction scheme (4-26), where H is a species whose spectroscopic energy is higher than that of the (lower-energy) species L:

\[
H^* + L \xrightarrow{\alpha} \text{collision complex} \xrightarrow{\gamma} H + L^* \quad (4-26)
\]

The first method relies on the decrease in the sensitisation of the fluorescence of the energy acceptor L due to the decrease in the concentration of
the complex, resulting from an efficient additional pathway of deactivation (β). Energy transfer is thus represented by the consecutive processes α and γ. The agreement between calculated rate constants of quenching of \( H^* \) and sensitisation of \( L^* \) for a number of systems in non-polar solvents has shown that process β can be neglected: under these conditions the intervention of the complex is irrelevant to the kinetic treatment of the observed properties of the system.

In some cases the fluorescence of \( L^* \) is quenched by a species with a higher electronic energy level; in these cases energy transfer is discounted. Such observations lead to the second proposed method. In the absence of any process β in the above scheme, the only way in which \( L^* \) can be quenched is by endothermic energy transfer via \(-γ\) and \(-α\), which will be impossible if the energy levels of the two species are sufficiently far apart. Thus the fluorescence of 9-methylanthracene is not affected by the addition of phenanthrene.

The importance of process β is that it provides an alternative way in which \( L^* \) can lose energy and thus be quenched. By analogy with eq. (4-5) the rate constant of quenching of \( L^* \) is given by

\[
\frac{k_{-\gamma}}{1 + \frac{k_{\gamma}}{k_{\beta}}}.
\]

On this basis the quenching of anthracene by 2,5-dimethyl-2,4-hexadiene in benzene is attributed to the formation of a loosely-bound complex: the small quenching rate constant indicates the extent to which the equilibrium \( \frac{\gamma}{\gamma} \) is perturbed. In cases such as this, where the observed quenching takes place at much less than the diffusion-controlled rate, an increase in the rate
constant of deactivation of the complex will result in increased quenching. The detection of charge transfer stabilisation in a complex relies on the fact that in a polar solvent the dissociation of such a complex into ions is greatly facilitated. Thus, if a solvent of similar viscosity but higher polarity results in greater quenching, the collision complex is alleged to possess some charge transfer stabilisation. This method differs from the former in that it relies on the change of quenching in the direction of unfavourable energy transfer, rather than in the change in the extent of sensitisation of fluorescence produced by exothermic energy transfer.

These methods offer some advantages over those used previously, in that they rely neither on the emission of the complex of interest, nor on any correlation of the electrical properties of the molecules concerned. It may fairly be said that the characterisation of an exciplex formed between 1-cyanonaphthalene and a diene (Taylor 1971) does not show that all hydrocarbon-diene quenching reactions are due to charge transfer. The change in the nature of the phenanthrene - 9-methylanthracene complex effected by substitution of a -CN group on the former is evidence that such substitutions may be responsible for the "charge transfer" behaviour that is observed.

A disadvantage of the "sensitisation" method proposed is that it is only applicable when the higher energy species can be electronically excited without the risk of photochemical reaction, which makes it of little
use for some compounds of current interest. The second method proposed does not suffer this disadvantage, as it is only necessary to be able to excite the lower energy moiety and observe its fluorescence. Although less direct in theory, this latter method thus has the advantage of wider possible application.

\[
\begin{align*}
F^+ & + Q \rightarrow \text{exciplex} \\
\end{align*}
\]

where the only change engendered by a polar solvent is to cause the process \( k_f \) to become significant. If this were the only change, transition to a solvent of higher polarity would result in the same changes in the intensity of emission from the exciplex and in its decay time. For the diethylaniline - anthracene exciplex, Knibbe et al. have found that a change in dielectric constant from 2 to 12 causes the exciplex intensity to decrease by a factor of 19; in the same polarity range the decay time decreases by a factor of only 3.5. In similar studies on the dimethylaniline - pyrene exciplex Mataga et al. have reported changes by factors of 44 and 2.4 respectively.
4.5 MECHANISM OF EXCIPLEX FORMATION IN POLAR SOLVENTS

The mechanism by which exciplexes are formed and destroyed in polar solvents differs from that in non-polar solvents in that an excited electron donor-acceptor pair may form a non-fluorescent solvated ion pair. This provides an additional alternative pathway for deactivation of an exciplex. However, from two independent reports (Knibbe, Röllig, Schäfer and Weller 1967; Mataga, Okada and Yamamoto 1967) it is apparent that the reaction scheme cannot be represented simply by:

\[
\begin{array}{c}
F^* + Q \\
\xrightarrow{k_q} \text{exciplex} \\
\xrightarrow{k_e} F + h\nu \\
\end{array}
\]

where the only change engendered by a polar solvent is to cause the process \( k'_1 \) to become significant. If this were the only change, transition to a solvent of higher polarity would result in the same changes in the intensity of emission from the exciplex and in its decay time. For the diethylaniline - anthracene exciplex, Knibbe et al. have found that a change in dielectric constant from 2 to 12 causes the exciplex intensity to decrease by a factor of 35; in the same polarity range the decay time decreases by a factor of only 3.5. In similar studies on the dimethylaniline - pyrene exciplex Mataga et al. have reported changes by factors of 44 and 2.8 respectively.
Before investigating the reason for this change it is prudent to clarify the effect of dialkylanilines on the fluorescence of the exciplexes produced, as previous investigations have commonly used these compounds. All amines are ubiquitous quenchers of fluorescence, and it has been known for some time that the addition of amines in excess of that necessary for exciplex formation actually causes a decrease in the intensity of exciplex emission. Chandross and Thomas (1971b) have reported that the emission from the intramolecular exciplex formed by a suitably tailored molecule (N,N-dimethyl-3-(1-naphthyl)propylamine) is altered by the addition of various amines. They interpret the change in the spectrum in terms of the quenching of the exciplex and the formation of a 2:1 amine - hydrocarbon complex which emits at longer wavelengths with a lower quantum yield.

Because amines are quite polar, an alternative possible explanation is that this is merely a manifestation of the well-known effect of solvent polarity on exciplex emission, whereby the solvent stabilises the exciplex and also provides an alternative pathway to deactivation. This results in quenching and a shift of the emission to longer wavelengths. In the absence of further data this question begins to resemble the controversy over the existence or otherwise of stoichiometric complexes between ground state charge transfer complexes and solvent molecules, which was current in the 1940's.

In this case, the question can be resolved by eliminating the influence of added amine on the dielectric
constant of the solution. In cyclohexane the addition of amine beyond about 0.15 mole $^{-1}$ actually causes a decrease in the intensity of exciplex emission: the quenching effect of the amine on the exciplex is more significant than the greater amount of quenching of the initially excited species. However, when the experiment is repeated in a system kept at the same dielectric constant throughout the addition of amine, the effect is no longer evident* (Fig. 4-17).

Leaving aside the semantics of whether one should consider the effect of polar solvents to be due to formation of a definable complex, it is clear from this result that the effect on the exciplex of diethylaniline is due to the same cause as that of ethyl acetate. In the absence of any evidence that this latter compound is prone to complex formation, there is no reason to consider the effect of diethylaniline (and, by inference, amines in general) to be due to anything other than the altered polarity of the solution.

In order to pursue the more basic question of the mechanism by which polar solvents alter the emissive properties of exciplexes, the behaviour of a typical exciplex has been investigated as a function of both polarity and viscosity.

* Although the dielectric constant of diethylaniline has not been measured, it will be less than that of aniline ($\varepsilon = 6.8$). The use of ethyl acetate ($\varepsilon = 6$) ensures that addition of diethylaniline does not cause much change in $\varepsilon$. 
Fig. 4-17. Intensity of emission from the anthracene-diethylaniline exciplex as a function of the concentration of diethylaniline.
Table 4-8. The effect of solvent polarity on the quenching of the fluorescence of anthracene by diethylaniline.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ε</th>
<th>n_{vis} (cp)</th>
<th>k_α (quenching) x 10^{-9} (s^{-1} mole^{-1})</th>
<th>k_α (viscosity) x 10^{-10} (s^{-1} mole^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>2</td>
<td>0.89</td>
<td>9.5</td>
<td>0.84</td>
</tr>
<tr>
<td>benzyl benzoate</td>
<td>4</td>
<td>10.3</td>
<td>3.7</td>
<td>4.1</td>
</tr>
<tr>
<td>ethyl propionate</td>
<td>5</td>
<td>0.54</td>
<td>12.9</td>
<td>0.72</td>
</tr>
<tr>
<td>isobutyl acetate</td>
<td>5</td>
<td>0.68</td>
<td>10.2</td>
<td>0.71</td>
</tr>
<tr>
<td>phenyl acetate</td>
<td>5.2</td>
<td>2.65</td>
<td>3.0</td>
<td>0.81</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>6</td>
<td>0.455</td>
<td>22.7</td>
<td>1.06</td>
</tr>
<tr>
<td>isobutanol</td>
<td>17</td>
<td>4.1</td>
<td>7.0</td>
<td>3.0</td>
</tr>
<tr>
<td>isopropanol</td>
<td>18.3</td>
<td>3.2</td>
<td>9.8</td>
<td>3.3</td>
</tr>
<tr>
<td>acetone</td>
<td>20.7</td>
<td>0.326</td>
<td>25.1</td>
<td>0.84</td>
</tr>
<tr>
<td>methanol</td>
<td>33</td>
<td>0.60</td>
<td>15.6</td>
<td>0.96</td>
</tr>
</tbody>
</table>

(a) determined using a Ubbelohde viscometer; values not marked were taken from the CRC Handbook of Chemistry and Physics.

(b) from eq. (4-6), assuming negligible dissociation. The decay time of anthracene was taken to be 4.9 ns in all solvents. Birks (1970e) has found its decay time to be relatively independent of solvent.

(c) from eq. (4-7).
4.51 Viscosity and polarity effects

The effect of polarity on the quenching of anthracene by diethylaniline is summarised in Table 4-8. For a series of solvents of moderate to low viscosity, and of varying dielectric constant (ε = 2 to 33) the ratio \( k_a(\text{quenching})/k_a(\text{viscosity}) \) has the value 0.9 ± 0.2. (The much higher ratio in viscous solvents is attributed to the failure at high viscosities of the Stokes-Einstein relationship which leads to eq. (4-7).)

Thus, the difference between the change in \( I' \) and τ' with solvent polarity cannot be attributed to a different rate of quenching of the initially excited species.

As less quenching will take place in solvents of higher viscosity, a lower exciplex:monomer ratio would be expected and therefore a lower value of \( I'/I \). Table 4-9 shows that although \( I'/I \) varies with viscosity for a series of solvents of similar ε, the variation is less than would be expected if the viscosity influenced only the rate of formation of the exciplex. If this were the case, eq. (4-8) predicts that \( \frac{I'/I}{k_a} \) would be constant with viscosity; the last column of the Table shows that this parameter exhibits a gradual increase.

4.52 Discussion

The lack of any dependence of the quenching of the initially excited species on solvent polarity requires the formation of a quench complex, not the emissive exciplex, as the primary result of fluorescence quenching. The decay time and intensity measurements reported
Table 4-9. Variation of $I'/I$ with solvent viscosity for the anthracene-diethylaniline exciplex.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\eta_{\text{vis}}$ (cp)</th>
<th>$k_a$ (viscosity) $\times 10^{-9}$</th>
<th>$I'/I$</th>
<th>$I'/I/k_a$ $\times 10^9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyl acetate</td>
<td>0.455</td>
<td>21.5</td>
<td>11.2</td>
<td>0.63</td>
</tr>
<tr>
<td>ethyl propionate</td>
<td>0.54</td>
<td>18.1</td>
<td>12.9</td>
<td>0.75</td>
</tr>
<tr>
<td>isobutyl acetate</td>
<td>0.68</td>
<td>14.4</td>
<td>12.3</td>
<td>1.08</td>
</tr>
<tr>
<td>phenyl acetate</td>
<td>2.65</td>
<td>3.7</td>
<td>4.2</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Values of $I'/I$ are presented for a hypothetical diethylaniline concentration of 1 mole $^{-1}$.

Previously are accommodated by assuming that in a polar solvent this quench complex may be deactivated directly:

\[
\begin{align*}
F^* + Q & \xrightarrow{k_a} (FQ)^* \xrightarrow{k_d} \text{exciplex} \\
F & \xrightarrow{k_q} F^* + h\nu \\
F & \xrightarrow{k_i} F + h\nu
\end{align*}
\]

The nature of the quench complex $(FQ)^*$ is hard to specify. The molecules are close enough for exchange interaction to occur between them, but they do not comprise the emissive exciplex. It seems most likely that the difference lies in the arrangement of solvent around them. This would at first resemble that between the two species before collision. Interaction of the quench complex with
the solvent and subsequent reorientation then leads
either to a solvent-stabilised exciplex or to solvated
ion pairs.

Some recent work offers justification for thinking
of the quench complex as a separate entity. When the
charge transfer complex formed between toluene and
1,2,4,5-tetracyanobenzene is excited at low temperatures,
a delay is observed prior to emission from the excited
complex (Egawa, Nakashima, Mataga and Yamanaka 1971).
As the molecules are necessarily in contact during the
act of absorption, the delay has been attributed to
reorientation of solvent molecules around the excited
complex: this is analogous to the relaxation of solvent
around the quench complex, allowing the formation of a
solvent-stabilised exciplex. This mechanism also
accounts for the results in Table 4-9, in which the
variation in $I'/I$ is less than expected. The rate
constants $k_i$ and $k_i'$ are for dissociation reactions,
which have previously been shown to have the same
viscosity dependence as association reactions (Seidel
and Selinger 1965). Thus, at higher viscosities the
dissociation of the quench complex into ions is reduced,
allowing more exciplex to be formed (albeit from less
quench complex) and the dissociation of the exciplex
itself into ions is also reduced. The net effect of
increasing viscosity is to reduce the production and
destruction of the quench complex and fluorescing exci-
plex so that the intensity of exciplex fluorescence is
relatively insensitive to viscosity. A more detailed
manipulation of the kinetics (Appendix A2) shows that
this is true, and this accounts for the good polarity correlations found in the previous work by Knibbe et al. (1967) despite the neglect of the variation in viscosities. This explanation differs from that of Mataga et al. (1967) in that the radiative rate constant $k'_e$ is assumed constant. Their suggestion that $k'_e$ changes (by a factor of 15 from hexane to pyridine) is contrary to the assumptions usually made when considering photoassociated species. However, the stability of an exciplex is very dependent on the nature of the solvent. It is possible that its structure will be changed sufficiently by a polar solvent that the radiative rate constant would be affected. Some estimation of the likely variation in $k'_e$ with solvent polarity can be obtained by considering the oscillator strength of absorption by charge transfer complexes which exist in the ground state. Because emission from an exciplex takes place from a relaxed state in which charge transfer has occurred, a valid comparison can only be made with a complex which exists in an ionised form in the ground state, and in which the act of absorption results in annihilation of the charge on both species. The fact that the extinction coefficient of such complexes is not strongly dependent on polarity leads us to reject the explanation offered by Mataga et al.

The mechanism proposed for exciplex formation allows one to think in terms of a continuum of behaviour of photoassociated species which are stabilised by charge transfer interaction. One extreme of behaviour is exhibited by the quenching of perylene by dienes, which
occurs only in polar solvents (Section 4.43). Anthra­
cene is somewhat more affected by dienes in that quenching
takes place to some extent in a non-polar solvent, but
again the quenching is more pronounced in solvents of
higher polarity. There is a continuum of behaviour from
this extreme to the cases where a new emission allows the
identification of an "exciplex". The energies of the
different species are represented by Fig. 4-18. In a
non-polar solvent the ions are unstable with respect to
the exciplex. The lack of quenching of perylene by
dienes in non-polar solvents can then be interpreted by
supposing the exciplex to possess a higher energy than
that of the isolated molecules. A polar solvent stabil­
ises the exciplex and the solvated ions, thereby making
pathways available for deactivation of the quench
complex $F^*|Q$. The slight quenching of anthracene and
naphthalene by dienes in non-polar solvents is then
attributed to formation of an exciplex in which radiation­
less pathways compete favourably with emission.

Despite the description given to various entities
in Fig. 4-18, it is necessary to retain a flexible model.
In general it may be more accurate to think in terms of
definable regions of the reaction co-ordinate rather than
in terms of species whose existence as separate entities
cannot be proven. For instance, it may be more correct
to think not of deactivation of the quench complex but
of deactivation of some unspecified precursor to exciplex
formation. In the lack of evidence, any endeavour to
define the species more fully reduces to a semantic
argument.
As an alternative way of describing the system, one may consider that the deactivation of the quench complex in a polar solvent changes the steady-state concentration of the exciplex. Thus, although the radiative rate constant of the exciplex remains constant, the rate of emission (rate constant × concentration) decreases. The results can then be interpreted in terms of the sensitivity of the exciplex emission intensity to the initial concentration of the solvent produced in a specific solvent, compared with the independence of the intensity with such variation.

The existence of the "exciplex" as a separate entity means that the quenching in polar solvents needs to be considered differently than in non-polar solvents. In particular, the treatment of data obtained from such systems still be linear. On the basis of the reaction scheme (4-29) the slope is calculated as

\[ \text{Fig. 4-18. Schematic representation of the energies of the quench complex, exciplex and solvated ions} \]

- non-polar solvents
- polar solvents

Stack-Volmer plots will not be affected by polarity as long as the dissociation of the quench complex
As an alternative way of describing the system, one may consider that the deactivation of the collision complex in a polar solvent changes the steady-state concentration of the exciplex. Thus, although the radiative rate constant of the exciplex remains constant, the rate of emission (rate constant x concentration) decreases. The results can then be explained in terms of the sensitivity of the exciplex emission intensity to the different initial concentrations of exciplex produced in different solvents, compared with the independence of the decay time to such variation.

The existence of the "quench complex" as a separate entity means that exciplex formation in polar solvents needs to be considered differently to similar systems in non-polar solvents. In particular, it affects the treatment of data obtained from such systems.

Plots of I'/I versus quencher concentration will still be linear. On the basis of the reaction scheme (4-28) the slope is calculated as

\[
\frac{k'}{k_e} \cdot \frac{k}{k_d + k' + k'_b} \cdot \frac{k_b}{k'_e + k' + k'_i}
\]

which contrasts with that obtained in non-polar solvents:

\[
\frac{k'}{k_e} \cdot \frac{k}{k_d + k'_e + k'_q}
\]

(from 4-8).

Stern-Volmer plots will not be affected by polarity as long as the dissociation of the quench complex...
is negligible. Quenching leading to very weakly bound complexes will be affected, and this is the basis for the identification of charge transfer interaction proposed in the previous section. Information gained from a plot of $I'$ against $I$ (section 4.21) rests on the assumption that there are only two interconvertible excited species. Thus, the non-linearity of Fig. 4-3 can be attributed not only to the change with solvent polarity of the fluorescence quantum yield of the exciplex but to the existence of a third excited species through which energy may be lost from the system.

Determination of thermodynamic data will also be affected. The temperature dependence of $I'/I$ will reflect the variation with temperature of $k_d$ and $k'_i$ in addition to the rate constants important in non-polar solvents. Without knowledge of this temperature dependence, the determination of such data by a full analysis (in the absence of limiting conditions) will not yield useful information.

4.53 Calculation of rate constants

Notwithstanding the comments on the validity of differentiating between the quench complex and the exciplex, it is worthwhile to calculate rate constants on the basis of the mechanism proposed above.

The calculation is simplified slightly by assuming that in solvents of reasonable polarity, $k_d$ can be neglected. $k_e$ and $k_d$ are calculated in the normal way from the fluorescence quantum yield and the decay time
of the primarily excited species in the absence of quencher. Measurement of the intrinsic exciplex quantum yield \( \phi' = \lim_{[Q] \to \infty} I' \) and its decay time in non-polar solvents similarly allows calculation of \( k'_e \) and \( k'_q \). \( k_a \) is obtained from the Stern-Volmer equation.

The assumption of a steady-state in all three excited species in reaction (4-28) leads to the expressions

\[
[F^*] = \frac{I_{\text{abs}}}{k_e + k_q + k_a[Q]}
\]

\[
[(FQ)^*] = \frac{k_a[Q][F^*]}{k_i + k_b}
\]

\[
[\text{exciplex}] = \frac{k_b[(FQ)^*]}{k_i + k'_e + k'_q}
\]

from which

\[
I' = k'_e[\text{exciplex}]
\]

and

\[
\frac{I'}{I_{\text{abs}}} = \frac{k'_e}{k_i + k'_e + k'_q} \cdot \frac{k_b}{k_i + k_b} \cdot \frac{k_a[Q]}{k_e + k_q + k_a[Q]}
\]

Measurement of \( \tau' \) in polar solvents allows calculation of \( k'_i \), and then measurement of \( I' \) for a given quencher concentration enables the ratio \( k'_i/k_b \) to be obtained. The rate constants are defined by reaction (4-28), except \( k_i \) and \( k'_i \). These two rate constants are defined as polarity-dependent nonradiative rate constants, and in
defining them in this way $k'_q$ is necessarily independent of polarity. Although it is very likely that polarity-dependent nonradiative pathways will lead to solvated ions it is possible that there are other products, as yet unidentified, formed by this mechanism.

Table 4-10 shows the results for one of the systems studied.

Table 4-10. Data for the 2-methoxynaphthalene - 1-cyanonaphthalene exciplex in cyclohexane and methanol.

<table>
<thead>
<tr>
<th></th>
<th>cyclohexane</th>
<th>methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi$</td>
<td>0.42</td>
<td>0.38</td>
</tr>
<tr>
<td>$\tau$, ns</td>
<td>19.0</td>
<td>17.0</td>
</tr>
<tr>
<td>$k_e \times 10^{-7}$</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>$k_q \times 10^{-7}$</td>
<td>3.0</td>
<td>3.7</td>
</tr>
<tr>
<td>$k_a \times 10^{-7}$</td>
<td>1120</td>
<td>1180</td>
</tr>
</tbody>
</table>

(a) from Nott (1972)
4.6 CHARACTERISATION OF EXCIPLEXES

Proof that exciplex formation is essentially a charge transfer process has rested mainly on two types of observation. Firstly, the energy of the emission band shifts substantially with solvent polarity, no matter whether the polarity is measured according to a theoretical or empirical model. Secondly, the energy of the emission band depends on the electrical properties of the constituent molecules. Both measurements have enabled comparisons to be made between different exciplexes. In this section the basis of these comparisons is examined, and an additional criterion is suggested for comparing the extent of charge transfer in exciplexes.

4.61 Stabilisation by solvent

Interaction with a polar solvent is responsible for the stability of any charged or polar species. This is reflected in the solvent sensitivity of the absorption spectra of charge transfer complexes which possess ionic ground states, the emission spectra of complexes with ionic excited states, and similarly the emission of exciplexes. This sensitivity has led to attempts to find a parameter which allows quantitative measurement of the ability of a solvent to stabilise a charged solute species.

Much work has been done on the effect of solvent on charge transfer complexes, and Lippert (1957) has derived a relationship between the wavenumbers of the absorption and emission bands of a charge transfer complex:
\[ \nu_{\text{absorption}} - \nu_{\text{emission}} = \frac{2(\nu_{\text{excited}} - \nu_{\text{ground}})^2}{\hbar c a^3} \cdot (f - f') \]  

(4-30)

where \( f = \frac{\varepsilon - 1}{2\varepsilon + 1} \) and \( f' = \frac{n^2 - 1}{2n^2 + 1} \).

This has been applied to the complex formed between hexamethylbenzene and tetrachlorophthalic anhydride (Czekalla and Meyer 1961), although its use has been restricted by the small number of charge transfer complexes that fluoresce in fluid solution.

In addition to this theoretical treatment, prolonged interest in the effect of solvent on chemical reactions has led to the development of several empirical measures of solvent polarity. Although the term "polarity" lacks an exact definition, it can be regarded as the effect of all the intermolecular interactions of which the solvent is capable. One measure of polarity (the "Y-value") relies on the ionising power of the solvent. It is given in terms of the rate constant of solvolysis of t-butyl chloride:

\[ Y = \log \left( \frac{k_{\text{BuCl}}}{k_0} \right) \]

where \( k_0 \) is the rate constant for solvolysis by a reference solvent (Grunwald and Winstein 1948; Winstein, Grunwald and Jones 1951).

A parameter which is applicable to a wider range of solvents has been proposed by Kosower (1958a), using the fact that the Franck-Condon state produced by
annihilation of an ion pair is unstable to an extent that depends on the energy of interaction of the solvent with the ground state. Naturally an ion pair must be chosen rather than a species which is non-polar in the ground state: the absorption spectrum of the latter is not particularly sensitive to solvent polarity, because of the restriction on relaxation of the solvent cage during the transition*. The charge transfer band of 1-substituted pyridinium iodides has been found to be particularly sensitive to solvent, and the Z-value is thus defined as the transition energy (kcal mole\(^{-1}\)) of the 1-ethyl-4-carbamethoxy pyridinium iodide complex (Kosower 1958a). Z-values defined in this way correlate reasonably well with the shift in the charge transfer absorption bands of a variety of compounds, although in all except very similar molecules there is some scatter (Kosower 1958b).

Other parameters have been used: S-values (Brownstein 1960), \[\text{E}_\text{T}\]-values (Berson, Hamlet and Mueller 1962), \[\text{ET}\]-values (Dimroth, Reichardt, Siepman and Bohlmann 1963) and X-values (Gielen and Nasielski 1963). These are similar in concept to the Y- and Z-values but are more useful under certain conditions.

* As charge transfer complexes which are non-polar in the ground state become, by definition, polar in the excited state, the emission spectra of such species would be expected to be solvent sensitive if the radiative lifetime were long enough to permit relaxation of the solvent cage. This has been observed (Czekalla and Meyer 1961; Davis 1969).
The energies of the emission maxima of exciplexes show an obvious dependence on the dielectric constant of the solvent (Mataga, Okada and Yamamoto 1966). Lippert's relationship (eq. 4-30) which applies to charge transfer complexes, has been modified to enable it to be applied to exciplexes (Beens, Knibbe and Weller 1967):

\[ \frac{1}{v_{\text{max}}} = \frac{1}{v_0} - \frac{2\mu^2}{\hbar c a^3} (f - \frac{1}{2}f') \]  

(4-31)

Studies of the effect of solvent on the emission maxima of exciplexes have used this equation. Although such plots exhibit some scatter due to specific solvent-solute interactions, they enable the dipole moment (\(\mu\)) to be estimated for an assumed value of the radius (a) of the cavity containing the exciplex. Assuming \(a = 5 \, \text{Å}\) for the anthracene-diethylaniline exciplex, its dipole moment has been estimated to be \(>10\, \text{D}\) (Beens, Knibbe and Weller 1967). The emission bands of a variety of exciplexes have been found to obey eq. (4-31) (Kuzmin and Guseva 1969; Taylor 1971).

The energy of the emission maximum of some exciplexes has also been found to have a linear dependence on the empirical solvent-polarity parameter \(E_T\) (Davis 1969).

4.62 Ionisation potentials and electron affinities

The Franck-Condon vertical frequency of a charge transfer absorption band has been given by Briegleb (1961) and by Mulliken and Person (1962) as
where $I_D^V$ and $A_A^V$ are the vertical ionisation potential of the electron donor and electron affinity of the acceptor, $G_0$ is the sum of the attraction and repulsion terms between the two species at their equilibrium configuration in the ground state and $G_1$ the same quantity for the excited state complex. The resonance energies of interaction between the two states, $X_0$ and $X_1$, are not independent of $I_D$ and $A_A$, and so for closely related weak complexes of a series of donors with a given acceptor the absorption frequency can be expressed by

$$h\nu'_{\text{max}} \approx I_D^V - A_A^V + G_1 - G_0 + X_1 - X_0$$

(4-32)

where $C_1$ embodies a correction to the adiabatic value of $I_D^V$, and includes the terms $A_A^V$, $G_1$ and $G_0$. This equation fits the frequencies of a number of charge transfer bands quite well (Hastings, Franklin, Schiller and Matsen 1953).

For complexes in which the donor has a sufficiently high ionisation potential the last term can be neglected, and a linear dependence of the energy of the charge transfer band on $I_D$ is expected. This linear relationship has been found in a large number of complexes (Briegleb and Czekalla 1959, 1960) and appears to be the cause of the common belief that the linearity of a plot of $h\nu'_{\text{max}}$ against $I_D$ has a theoretical basis. It is merely fortuitous that compounds commonly used in such studies fulfill the simpler relation; e.g. for complexes
formed by iodine, the predicted curve becomes obviously non-linear below $I_D \approx 7.5$ e.v.

The energy required to transfer an electron from a species $X$ to $Y$ is given by $I_X - A_Y$. For a given pair of molecules the process requiring the least energy will take place, and the direction of electron transfer is thus given by

$$I_D - A_A < I_A - A_D$$

i.e.

$$(I + A)_D < (I + A)_A$$

The same criterion is expected for electron transfer between two species, one of which is in the excited state. The lower ionisation potential and higher electron affinity of a molecule in an excited state, compared with the same quantities in the ground state, results in a correspondingly large number of exciplexes. As the ionisation potential and electron affinity of a species in the excited state is given by

$$I^* = I - \Delta E_{0,0}$$

$$A^* = A + \Delta E_{0,0}$$

the direction of electron transfer as given by $I + A$, is independent of which species is excited, as

$$I + A = I^* + A^*$$

A Born-Haber cycle may be constructed (Fig. 4-19) to give the energy ($E'$) of the solvated exciplex relative
Fig. 4-19. Born-Haber cycle for exciplex formation.
to that of the separated solvated constituent molecules:

$$E' = I_D - A_A - C - U - W_{\text{solv}}$$

where C is the coulombic energy change in bringing the ions together, U is the resonance stabilisation energy and $W_{\text{solv}}$ the difference in solvation energies of the exciplex and the separated molecules. From Fig. 4-20 the emission maximum is then given by

$$h\nu'_{\text{max}} = E' - E_{\text{rep}}$$

and thus

$$h\nu'_{\text{max}} = I_D - A_A - C - U - W_{\text{solv}} - E_{\text{rep}} \quad (4-33)$$

This equation is the basis for the expected linear relationship between $h\nu'_{\text{max}}$ and $I_D - A_A$ for a series of donors and acceptors. However, such an expectation assumes that the other terms are independent of $I_D$ and $A_A$: the validity of this assumption is considered shortly.

Because of the difficulty in determining electron affinities (and to some extent ionisation potentials) it has become common to use polarographic reduction and oxidation potentials instead. The relationship between them is given closely by

$$E_{\frac{1}{2}}(\text{red}) = A_A - \Delta G^-_{\text{solv}} + E_{\text{ref}} \quad (4-34)$$

$$E_{\frac{1}{2}}(\text{ox}) = I_D + \Delta G^+_{\text{solv}} + E_{\text{ref}} \quad (4-35)$$
4.6 Estimation of charge transfer character

Fig. 4-20. Potential diagram for exciplex formation.

It is of interest to see how both these parameters, which function as indicators of solvent polarity, are affected in a series of exciplexes.
where $E_{\text{ref}}$ is the e.m.f. of the reference and $\Delta G^+_\text{solv}$, $\Delta G^-\text{solv}$ the free energies of solvation of the ions. The use of redox potentials enables the study of a larger number of compounds, although the use of such data has limitations which will be discussed later.

In studies on exciplexes formed between 9,10-dicyanoanthracene, Chandross and Ferguson (1967) showed that an obvious relationship existed between $h\nu'_{\text{max}}$ and $E_{1/2}(\text{ox})$ of a number of aromatic hydrocarbons, although they did not attempt to quantify it. Knibbe, Rehm and Weller (1967) found a reasonably good linear correlation between $h\nu'_{\text{max}}$ and $E_{1/2}(\text{red})$ for exciplex formation by diethylaniline and a series of aromatic hydrocarbons, although the slope is somewhat different from unity. Subsequently, Rehm and Weller (1970a) reported a linear dependence of $h\nu'_{\text{max}}$ on $E_{1/2}(\text{ox}) - E_{1/2}(\text{red})$ for a series of aromatic hydrocarbons although a number of compounds do not fit the dependence.

**4.63 Estimation of charge transfer character**

Just as the polarity of the solvent affects the energy of exciplex emission by stabilisation, so the ratio $I'/I$ depends on polarity for reasons discussed in section 4.5. It is of interest to see how both these parameters, which function as indicators of solvent polarity, are affected in a series of exciplexes.

The polarity dependence of the energy of the emission maximum, and of $I'/I$, has been measured for three species which intuitively straddle the exciplex – heteroexcimer barrier: the anthracene – diethylaniline exciplex owes...
its stability almost totally to charge transfer, the naphthalene - 1-cyanonaphthalene exciplex will be stabilised partly by resonance interaction, and the exciplex formed between 2-methoxynaphthalene and 1-cyano-­
naphthalene would be expected to be between the two because of the opposite effects on the naphthalene nucleus of the cyano- and methoxy- groups.

In solvents of similar viscosity the quantity I'/I, which depends on the ease of formation of the solvated ions (i.e. k₁ and k₁') gives a good qualitative estimate of the extent to which charge has been transferred. Table 4-11 shows the results obtained in ethyl propionate and in methanol, both compared to cyclohexane. Transition from a true exciplex (anthracene - diethylaniline) to a heteroexcimer causes a systematic increase in the relative values of I'/I without, in this case, a corresponding systematic shift in the peak maxima. This effect is observed in both of the solvents tabulated, and is therefore not due to specific interaction.

4.64 Discussion

As exciplexes range from highly polar species to "heteroexcimers" which have little charge transfer stabilisation, it is desirable to have some measure of the "charge transfer character" of the species. For complexes, this is not an easy property to estimate. Dipole moments, which measure the extent of charge transfer over a distance, have been calculated. However, their calculation, from the variation in emission energy as a function of (f - 1/2f'), involves an assumption as to
Table 4-11. Estimations of charge transfer character of exciplexes in different solvents.

<table>
<thead>
<tr>
<th>Exciplex</th>
<th>cyclohexane</th>
<th>ethyl propionate</th>
<th>methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>I'/I relative to cyclohexane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>anthracene</td>
<td>1</td>
<td>0.31</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>diethylaniline</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-methoxynaphthalene</td>
<td>1</td>
<td>0.75</td>
<td>0.21</td>
</tr>
<tr>
<td>1-cyanonaphthalene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>naphthalene</td>
<td>1</td>
<td>0.88</td>
<td>0.67</td>
</tr>
<tr>
<td>1-cyanonaphthalene</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Shift in position of exciplex maximum relative to cyclohexane (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Exciplex</th>
<th>cyclohexane</th>
<th>ethyl propionate</th>
<th>methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>anthracene</td>
<td>0</td>
<td>1360</td>
<td>-</td>
</tr>
<tr>
<td>diethylaniline</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-methoxynaphthalene</td>
<td>0</td>
<td>310</td>
<td>1390</td>
</tr>
<tr>
<td>1-cyanonaphthalene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>naphthalene</td>
<td>0</td>
<td>710</td>
<td>1660</td>
</tr>
<tr>
<td>1-cyanonaphthalene</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The I'/I values have been corrected to take into account the variation with solvent of the intrinsic fluorescence quantum yield of the primarily excited species.
the size of the solvent cavity containing the exciplex.

The variation of emission maximum with \((I_D - A_A)\) has also been invoked to show the charge transfer character of exciplexes. However, treatment of the results according to the equation

\[
    h\nu'_{\text{max}} = I_D - A_A - C - U - W_{\text{solv}} - E_{\text{rep}}
\]

involves the assumption, as stated before, that \(C, U, W_{\text{solv}}\) and \(E_{\text{rep}}\) are independent of \(I_D\) and \(A_A\). There is currently no evidence that this is so. It is reasonable to expect that both \(W_{\text{solv}}\) and \(C\) could depend on the size of the exciplex and therefore on the size of the components. As the values of \(A\) and \(I\) of aromatic hydrocarbons may depend on their size (for example, \(A\) increases and \(I\) decreases with the number of rings fused together in a line) any such dependence of \(W_{\text{solv}}\) and \(C\) on size will give a bias to plots of \(h\nu'_{\text{max}}\) against \((I_D - A_A)\). Such an effect would be expected to be more obvious in polar solvents due to the greater interaction with the dipolar complex. Fig. 4-21 shows plots of \(h\nu'_{\text{max}}\) versus \(A_A\) for exciplexes formed between diethylaniline and a number of aromatic hydrocarbons. Two differences are notable in the plots. There is a greater scatter of points when diethylaniline rather than hexane is used as solvent, and the slopes of the lines are different and both somewhat less than 1 (Table 4-12). Both these effects can be explained satisfactorily by the dependence of \(W_{\text{solv}}\) and \(C\) on the size of the complex. The greater scatter in the polar solvent diethylaniline is most likely due to the
Fig. 4-21. The variation in the energy of the emission maximum \( (h \nu'_{\text{max}}) \) of exciplexes formed between diethylaniline and a series of aromatic hydrocarbons with electron affinity \( A_A \).

The data was extracted from the published work of Briegleb (1964) and Knibbe (1969).

In addition, it is only by virtue of this technique that it is possible to determine the position of the repulsive state of the two neutral components, if the repulsive state of the two neutral components, as determined from the absorption frequencies of ground state charge transfer complexes, as given by Briegleb (1964).
Table 4-12. Characteristics of exciplexes formed between diethylaniline and aromatic hydrocarbons.

<table>
<thead>
<tr>
<th>Plot of $h v'_\text{max}$ versus:</th>
<th>solvent</th>
<th>gradient</th>
<th>standard dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron affinity</td>
<td>hexane</td>
<td>-0.84</td>
<td>0.036</td>
</tr>
<tr>
<td></td>
<td>diethylaniline</td>
<td>-0.66</td>
<td>0.046</td>
</tr>
<tr>
<td>Reduction potential</td>
<td>hexane</td>
<td>-0.96</td>
<td>0.036</td>
</tr>
<tr>
<td></td>
<td>diethylaniline</td>
<td>-0.73</td>
<td>0.032</td>
</tr>
</tbody>
</table>

Data taken from Fig. 4-21

larger magnitude of specific solute-solvent interactions. The lower slope in diethylaniline seems to indicate that $W_{\text{solv}}$, the energy term most sensitive to changes in solvent polarity, is in some way dependent on $A_A$—possibly for the reason given above. Both these effects are minimised by using a non-polar solvent, but even then the slope of the graph is notably different from unity*.

In addition, it is only by virtue of the addition of the term $E_{\text{rep}}$ into eq. (4-33) that the energy of the maximum of the emission band has any theoretical significance. Therefore, the use of $h v'_{\text{max}}$ is only justified if the repulsive state of the two neutral components,

*It is appreciated that if the values of the electron affinities were to take account of the uncertainty of their values when determined by different methods, the scatter due to this uncertainty would dominate both graphs. In Fig. 4-21 all values of $A_A$ have been determined from the absorption frequencies of ground state charge transfer complexes, as given by Briegleb (1964).
with the same nuclear configuration as in the exciplex, has the same energy for all species considered. \( E_{\text{rep}} \) can be calculated according to

\[
\Delta E_{0,0} = \Delta H^* + h\nu'_{\text{max}} + E_{\text{rep}} \tag{4-36}
\]

which is obtained from Fig. 4-20. For exciplexes formed between diethylaniline and some aromatic hydrocarbons it has been found to vary by over 0.1 e.v. If this variation is dependent in some way on \( A_A \), it would have the effect of biasing the slope; if not, it is likely to be the cause of some of the scatter in Fig. 4-21a.

Another limitation inherent in eq. (4-33) is the difficulty in obtaining reliable values of ionisation potentials and electron affinities. Compilations of these parameters (Gutmann and Lyons 1967; Blaunstein and Christophorou 1971) give some idea of the lack of precision with which they are known. The necessity to use ionisation potentials and electron affinities has been avoided by the use of redox potentials instead. These are related to the former terms by eqs. (4-34) and (4-35) given earlier.

Use of redox potentials to estimate \( I \) and \( A \) demands that within a group of compounds of interest, the solvation free energies of the ions remain constant. As highly polar solvents are used to make these measurements the solvation energies are large, and even relatively small differences may turn out to be significant. The assumption of a constant solvation energy is only valid for a closely related group of compounds; for a series
of aromatic hydrocarbons substituted by alkyl or aryl groups, a plot of I against \( E_{\frac{1}{2}}^{(ox)} \) has a scatter of ca. 0.1 e.v. (Pysh and Yang 1963). Electrically dissimilar substituents can cause a significant change in the solvation energy. It has been estimated that the difference between aromatic hydrocarbons and nitriles is 0.3 e.v. (Batley 1971). It has also been suggested that if an excess of electron density resides primarily on a substituent group, the solvation energy may be dominated by localised solvation terms (Hinchcliffe and Ali 1966).

Table 4-12 shows that the assumption of a constant \( \Delta G_{\text{solv}} \) term in eq. (4-34) is not legitimate: the slopes of plots of \( h\nu'_{\text{max}} \) against reduction potential (in hexane and diethylaniline) are different to the slopes of \( h\nu'_{\text{max}} \) against electron affinity.

In view of the uncertainties outlined above, it is difficult to estimate the value of correlations obtained according to the equations relating \( h\nu'_{\text{max}} \) to \( I_D \) and \( A_A \) (or to \( E_{\frac{1}{2}}^{(ox)}D \) and \( E_{\frac{1}{2}}^{(red)}A \)). It has been found that ground state charge transfer complexes lend themselves to a number of correlations in addition to those mentioned previously. For example, \( h\nu'_{\text{max}} \) of complexes formed between chloranil and aromatic hydrocarbons exhibits a better correlation with the energy of the \( T_1 + S_0 \) transition in the hydrocarbon than with its ionisation potential (Peticolas 1957), and there is some correlation (although not good) between the \( S_1 + S_0 \) energy of aromatic hydrocarbons and \( h\nu'_{\text{max}} \) of the complexes they form with iodine (McConnell, Ham and Platt 1953). Observations like this indicate that empirical
correlations are easily made with ground state charge transfer complexes, and the same may be true of exciplexes.

The lack of a slope of unity in plots of $h\nu_\text{max}$ of exciplexes against $E_\text{H}^\\text{ox}(D) - E_\text{H}^\\text{red}(A')$ and the different slopes in different solvents, are both not predicted by the theory which has been used to treat them. Thus the correlations that are observed are at this stage empirical. Although the large dependence of $h\nu_\text{max}$ on the electrical properties of the constituent molecules is doubtless a result of charge transfer interaction, it is doubtful whether such correlations in themselves give sufficient information to allow different exciplexes to be compared.

It is in this context that the current results are considered. The change in $I'/I$ from a non-polar to a polar solvent is a measure of the ease with which both the "quench complex" and the exciplex form solvated ions. This depends on the degree to which charge has been transferred, and also on the solvation free energies of the ions. (It has been shown in section 4.51 that the ratio $I'/I$ is only moderately sensitive to solvent viscosity.) The change in $I'/I$ cannot be used to give an accurate quantitative measure of the "charge transfer character" of exciplexes, as it results from a combination of effects. However, it has the advantage that it can be used to compare exciplexes in the absence of data on the electrical properties of the constituents. The results in Table 4-11 emphasise that the different measures of charge transfer character do
not measure the same properties: the variation of the exciplex emission frequency with solvent depends on the dipole moment of the exciplex, while it has been suggested that the dependence of $h\nu_{\text{max}}$ on $E_{\frac{1}{2}}(\text{ox})D - E_{\frac{1}{2}}(\text{red})A$ gives information about the nature of the bond between the two components. The variation of the intensity of exciplex emission (measured by $I'/I$) is a function of how easily both the "quench complex" and the solvent-stabilised exciplex form an ion pair, and as such it is a measure of the degree to which charge has been transferred in the exciplex. In situations where this is important, the variation in $I'/I$ may well be a useful measure of "charge transfer character".

All other methods have been transcribed from well established work on ground state charge transfer complexes. Here we have a method specifically relevant to exciplexes (which cannot in fact be used for ground state complexes).

It may be worthwhile to consider the problem in reverse; that is, to use a given exciplex as a microscopic probe of solvent polarity. The $Z$-values of Kosower are derived from spectral shift data, and as such do not rank solvents according to their ability to solvate ions. Winstein's $Y$-values do this, as they rely on the rate constant of an $S_N1$ solvolysis, although they are necessarily restricted to highly polar solvents. The parameter $I'/I$ is closer to these $Y$-values in nature than any other empirical parameter. It should be useful
for measuring the solvating power of solvents of medium to low polarity, except for those solvents which are general quenchers of fluorescence.
CHAPTER 5

PHOTOPHYSICS AND PHOTOCHEMISTRY

Photochemical reactions proceed from excited states, and in all except unimolecular reactions, are preceded by photoassociation. Studies of photoassociation are limited, in general, by the lack of emission from complexes which undergo photochemistry. For this reason photochemical reactions which proceed via exciplexes or related compounds should be amenable to study by both photophysical and photochemical methods.

An example of photochemistry occurring via excimer formation has been known for some time. The concentration quenching of the fluorescence of anthracene results in photodimer formation rather than excimer emission (Cherkasov and Vember 1959). Bulky substituents in the 9 or 10 positions prevent the transformation, and excimer emission is observed, showing that in the unsubstituted case an excimer is formed but emission is not observed because of competition from the photochemical transformation. It is also likely that excimers act as precursors to the photodimerisation of naphthacene and pentacene (Birks, Appleyard and Pope 1963), 2-methoxynaphthalene
Mention has been made in the literature of the effect of exciplex formation on photochemical reactions. However, discussion has been restricted mainly to those cases in which exciplex formation results in a lower yield of photoproduct due simply to an additional deactivating process on the initially excited species (see for example, Brimage and Davidson 1971; Rao and Ramakrishnan 1971). The participation of an exciplex as a precursor to photochemical reaction is much more difficult to confirm. The method proposed in section 4.4 provides a way of identifying charge transfer stabilisation within a photoassociated species, and has been applied to a photochemical reaction.

5.1 THE TOLAN - NAPHTHALENE PHOTOADDITION

The photoaddition of tolan to naphthalene and related compounds has been comprehensively studied by photochemical methods. In an attempt to characterise the metastable photoassociated complex, the quenching of naphthalene fluorescence by tolan has been studied in different solvents.

Table 5-1 shows that in cyclohexane the quenching proceeds at considerably less than the diffusion-controlled rate. As energy transfer is energetically unfavourable, the quenching results from deactivation.
Table 5-1. The quenching of naphthalene fluorescence by tolal in cyclohexane and ethanol.

<table>
<thead>
<tr>
<th></th>
<th>cyclohexane</th>
<th>ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_a \times 10^{-9}$ from viscosity (l mole$^{-1}$ s$^{-1}$)</td>
<td>11.3</td>
<td>6.1</td>
</tr>
<tr>
<td>$\frac{k_a}{1 + k_d/\Sigma k'} \times 10^{-9}$ a from quenching (l mole$^{-1}$ s$^{-1}$)</td>
<td>0.6</td>
<td>2.3</td>
</tr>
</tbody>
</table>

(a) $\Sigma k'$ is the sum of the rate constants of deactivation of the photoassociated species.

of the photoassociated species, presumably by formation of the adduct. Nevertheless, the reverse reaction still occurs. In ethanol, the extent of reversibility of the reaction is markedly less. By analogy with the behaviour of exciplexes, this is attributed to the deactivation of the charge transfer stabilised complex by the formation of solvated ion pairs. When this is coupled with the observation that less photoadduct is produced in polar solvents (Sasse, Collin, Roberts and Sugowdz 1971), the mechanism of the reaction may be understood a little more clearly. Quenching of excited naphthalene by tolal leads to a complex which is stabilised by charge transfer; this complex then loses its energy by bond rearrangement (leading to photoadduct) rather than by emission. A polar solvent causes a decrease in the yield of adduct, by offering
an alternative mode of deactivation of the complex. For the same reason a polar solvent decreases the amount of dissociation of the complex, thereby increasing the observed extent of quenching of the initially excited species.

5.2 EFFECT OF CARBON DIOXIDE

The use of carbon dioxide in photophysical experiments has been restricted, in the past, to its use as a thermalising gas in vapour phase measurements. It is not known to form complexes with any electronically excited molecules, and there is no evidence from vapour phase experiments that would lead us to expect any effect on electronically excited states in solution. However, Sasse (1971) has recently found that saturation of a solution of tolan and naphthalene with CO$_2$ results in a lower yield of photoadduct.

5.2.1 Photophysical measurements

Because of this anomalous photochemistry, the effect of CO$_2$ on the fluorescence of a number of aromatic compounds in solution has been investigated. The saturation with CO$_2$ of previously deoxygenated solutions of many compounds has been found to have no effect on the shape or intensity of their fluorescence. Compounds which are unaffected include benzene and derivatives (cyano-, 1,4-dicyano-, methoxy-, 1,3-dimethoxy- and phenol), naphthalene and derivatives
(1-cyano-, 2-methoxy-), perylene, indole, POPOP, rhodamine-B and a number of amines (aniline, diphenylamine, triphenylamine, N,N-dimethylnaphthylamine). The fluorescence of some typical exciplexes was similarly unaffected.

However, carbon dioxide exerts a definite quenching effect on the intensity of fluorescence of diethylaniline, dimethylaniline and 1,4-diazabicyclo[2.2.2]octane. In all cases there is no change in the shape of the fluorescence spectrum, and no new bands are observed to longer wavelengths in the absorption spectra of concentrated solutions saturated with CO₂. No new emission has been found at temperatures down to -50°C, despite the effect of temperature on fluorescence quantum yield and on the solubility and therefore the concentration of CO₂. The selective nature of the quenching effect means that it is not due to impurity oxygen in the CO₂.

The first step in an investigation of fluorescence quenching is to see whether the systems obey Stern-Volmer kinetics. Without a specially constructed cell it is not possible to add metered amounts of CO₂ to a given sample. However, an indication of the extent of quenching has been obtained in different solvents, in which the solubility of CO₂ is known. The results for diethylaniline are shown in Table 5-2.

In all solvents studied, the quenching occurs at much less than the diffusion-controlled rate. This might be attributed to a large difference between the calculated and true rate constants of diffusion for
Table 5-2. Quenching of diethylaniline by carbon dioxide in various solvents.

<table>
<thead>
<tr>
<th>Solubility of CO₂ (^a) (converted to mole (-1))</th>
<th>cyclo-hexane</th>
<th>benzene</th>
<th>methanol</th>
<th>methyl acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_a) (viscosity) (^b) (10^{-9} (\text{mole}^{-1} \text{s}^{-1}))</td>
<td>11.3</td>
<td>15.4</td>
<td>16.3</td>
<td>26.3</td>
</tr>
<tr>
<td>(k_a) (quenching) ((\text{mole}^{-1} \text{s}^{-1})) (1 + k_d T_0) (x 10^{-9})</td>
<td>0.57</td>
<td>1.07</td>
<td>0.75</td>
<td>0.46</td>
</tr>
<tr>
<td>((k_a) (quenching) (1 + k_d T_0)) (^{-1})</td>
<td>0.050</td>
<td>0.069</td>
<td>0.046</td>
<td>0.017</td>
</tr>
</tbody>
</table>

(a) from Seidell (1958)
(b) from eq. (4-7)

such a small molecule. However, by analogy with oxygen one would expect a greater amount of quenching compared with that calculated from viscosity, rather than the reverse. The discrepancy is most likely to be caused by the formation of a very weak quench complex, which is responsible for the loss of a small proportion of energy from the system.

This is confirmed by the temperature dependence of the quenching reaction. If the rate constant of diffusion is given by eq. (4-7) then the Stern-Volmer equation may be expressed as:
which takes into account the variation of $k_a$ with temperature. Table 5-3 shows the dependence of the quenching on temperature. If $k_d$ were insignificant compared with the rate constants of deactivation of the quench complex then the parameter on the left hand side of the above equation would be expected to vary little with temperature. The bottom row of Table 5-3 shows the variation that occurs. This is attributed to the temperature dependence of $k_d$ and $k'_q$, and is evidence that $k_d$ is significant. If the system is in the $a$ region ($k_d \gg k'_e + k'_q$), the enthalpy of formation of the complex may be estimated from the variation of $(\Phi_0/\Phi - 1)/[CO_2]$ with temperature as tabulated. As the variation is not large compared with the accuracy of the experiment (due particularly to the small extent of quenching) any estimate of $\Delta H^*$ will only be approximate. The value of $-1.7 \text{ kJ mole}^{-1}$ which is obtained shows that the enthalpy of formation is about an order of magnitude weaker than that of typical excimers and exciplexes.

Dimethylaniline gives very similar results to those above. The fluorescence of 1,4-diazabicyclo-[2.2.2]octane is quenched much more strongly, doubtless as a result of its much longer lifetime, which is estimated by oxygen quenching to be 80 to 90 ns in cyclohexane.
Table 5-3. Quenching of diethylamine fluorescence by carbon dioxide in toluene at different temperatures.

<table>
<thead>
<tr>
<th></th>
<th>0°C</th>
<th>30°C</th>
<th>43°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi / \phi_0$</td>
<td>1.36</td>
<td>1.22</td>
<td>1.18</td>
</tr>
<tr>
<td>$\eta_{vis}$ (cp) $^a$</td>
<td>0.772</td>
<td>0.526</td>
<td>0.45</td>
</tr>
<tr>
<td>Solubility of $CO_2$ $^b$ (mole l$^{-1}$)</td>
<td>0.136</td>
<td>0.088</td>
<td>0.075</td>
</tr>
<tr>
<td>$(\phi / \phi_0 - 1) / [CO_2]$</td>
<td>2.63</td>
<td>2.50</td>
<td>2.40</td>
</tr>
<tr>
<td>$(\phi / \phi_0 - 1) \frac{\eta_{vis}}{T} / [CO_2]$</td>
<td>0.0074</td>
<td>0.0043</td>
<td>0.0034</td>
</tr>
</tbody>
</table>

(a) from CRC Handbook of Chemistry and Physics
(b) using $d \ln \alpha = \frac{\Delta H}{RT^2}$, where $\alpha$ is the absorption coefficient of a gas in a liquid, to interpolate between tabulated values.

5.22 Discussion

The most notable aspect of fluorescence quenching by carbon dioxide is its selectivity: only three compounds (two of them very similar) have been found to be affected. With this limited number of positive results it is difficult to attempt a description of the complex resulting from the quenching, although it is notable that unstable photochemical products are formed between tertiary amines and $CO_2$ (Sasse 1972). The most probable description may be in terms of a charge transfer stabilised complex. The electrical properties of the molecules make it certain that if charge transfer takes place the
CO₂ acts as an electron acceptor. Its electron affinity (ca. 3.8 e.v.; Buchel'nikova 1958) is several e.v. higher than those of the aromatic hydrocarbons which commonly form exciplexes with diethylaniline and dimethylaniline. This indicates that exciplex formation is quite possible. However, transfer of charge remains unfavourable without the addition of large coulombic and solvation terms, and as in the case of exciplexes these will be most important in determining the stability of the complex.

If the complex were stabilised by charge transfer the quenching would be expected to be greater in solvents of higher polarity (section 4.43). Table 5-2 shows that the extent of quenching in methanol is similar to that in cyclohexane and less than that in benzene, while the quenching in methyl acetate is much weaker than in either of the hydrocarbon solvents.

The significance of these results is dubious: they rely completely on tabulated values of the solubility of carbon dioxide, and on the applicability of eq. (4-7) to such a small molecule.

The study of the quenching effect of carbon dioxide has posed many questions. As it quenches the fluorescence of some excited species, the results of Sasse might be interpreted in terms of the quenching of some intermediate, although the nature of the complex formed bears further investigation.

Further work should start with a Stern-Volmer analysis of the quenching. This requires the applic-
ation of a variable, measurable pressure of CO$_2$ to a fluorescent solution. A cell is presently under construction to enable this to be done. The effect of polar solvents on the quenching may then be studied in detail, as well as the quenching of differently substituted tertiary arylamines. Such an investigation should reveal whether or not the quench complex is stabilised by charge transfer, and thereby indicate other species likely to be similarly affected.
Al. The fluorescence spectrum of perylene

The effect of reabsorption on the fluorescence excitation spectrum of perylene (section 1.43) is a direct result of the reabsorption of the short-wavelength edge of its fluorescence spectrum. Fig. 1-2, which shows the effect of such reabsorption on the excitation spectrum, was obtained using solutions normally considered sufficiently dilute to circumvent this problem. The fluorescence spectrum is likely to suffer similarly from reabsorption, and for this reason the variation of the fluorescence spectrum with concentration has been studied (Fig. A-2). It is necessary to descend to the concentration of 5 × 10⁻⁵ mol before a further decrease in concentration results in no detectable change in the shape of the spectrum, and it is therefore assumed that Fig. A-2e represents the true fluorescence spectrum of perylene. Assuming that at this concentration, fluorescence is produced and reabsorbed evenly throughout the front 4 cm of the cell (the portion viewed by the detector), the amount of reabsorption of the highest-energy fluorescence band (442 nm) may be estimated. At this wavelength λ = 2.5 × 10⁴ giving an absorbance of (2.5 × 10⁴) × (8 × 10⁻⁷) × 0.7 = 0.0825; this corresponds to a transmittance of 99.4% and thus an error of about 1%. In general, however, it is not possible to estimate the error in a spectrum without knowing the optics of the detection system.

Berman (1965), in his widely used handbook, has recorded a fluorescence spectrum which resembles Fig. A-1c, for a 3 × 10⁻⁴ mol L⁻¹ solution of perylene in
The fluorescence spectrum of perylene

The effect of reabsorption on the fluorescence excitation spectrum of perylene (section 1.43) is a direct result of the reabsorption of the short-wavelength edge of its fluorescence spectrum. Fig. 1-2, which shows the effect of such reabsorption on the excitation spectrum, was obtained using solutions normally considered sufficiently dilute to circumvent this problem. The fluorescence spectrum is likely to suffer similarly from reabsorption, and for this reason the variation of the fluorescence spectrum with concentration has been studied (Fig. A-1). It is necessary to descend to the concentration of $5 \times 10^{-7}$ mole $l^{-1}$ before a further decrease in concentration results in no detectable change in the shape of the spectrum, and it is therefore assumed that Fig. A-1e represents the true fluorescence spectrum of perylene. Assuming that at this concentration, fluorescence is produced and reabsorbed evenly throughout the front 4 mm of the cell (the portion viewed by the detector), the amount of reabsorption of the highest-energy fluorescence band (442 nm) may be estimated. At this wavelength $\varepsilon = 2.5 \times 10^{4}$, giving an absorbance of $(2.5 \times 10^{4}) \times (5 \times 10^{-7}) \times 0.2 = 0.0025$; this corresponds to a transmittance of 99.4% and thus an error of about $\frac{1}{4}$%. In general, however, it is not possible to estimate the error in a spectrum without knowing the optics of the detection system.

Berlman (1965), in his widely used handbook, has recorded a fluorescence spectrum which resembles Fig. A-1c, for a $3 \times 10^{-4}$ mole $l^{-1}$ solution of perylene in
Fig. A-1. Corrected fluorescence spectra of perylene in cyclohexane, excited at 408 nm.

(a) $1.5 \times 10^{-4}$ mole $l^{-1}$, using "in-line" geometry
(b) $1.5 \times 10^{-4}$ mole $l^{-1}$
(c) $4.6 \times 10^{-5}$ mole $l^{-1}$ using "front-surface" geometry
(d) $1.5 \times 10^{-5}$ mole $l^{-1}$
(e) $5.0 \times 10^{-7}$ mole $l^{-1}$
cyclohexane. Integration of this spectrum gives a quantum yield of 0.94. Melhuish (1961) used similar and higher concentrations in three different solvents, and obtained quantum yields between 0.79 and 0.84. The Figure indicates the amount of reabsorption that takes place at these concentrations, and thus we would expect the true fluorescence quantum yield of perylene to be higher than calculated by either Berlman or Melhuish.

The fluorescence spectrum of perylene has also been reported by Birks and Dyson (1963) in a study of the mirror-image relationship between the fluorescence and absorption spectra of some aromatic molecules. The reported spectrum is similar to Fig. A-1d. The true fluorescence spectrum of perylene actually resembles the mirror-image of the absorption spectrum more closely than the spectrum used by Birks and Dyson.
A2. Kinetics of exciplex formation in polar solvents

Expressions for $I'/I$ and $I'$ are derived for the reaction scheme given in section 4.5:

\[
\begin{align*}
F^* + Q & \xrightarrow{k_a} (FQ)^* \xrightarrow{k_b} \text{exciplex} \\
& \xrightarrow{k_i} \text{exciplex} + Q_{\text{solv}} \\
& \xrightarrow{k_i'} \text{exciplex} + Q_{\text{solv}} \\
& \xrightarrow{k_q} F + Q \\
& \xrightarrow{k_e} F + Q + h\nu'
\end{align*}
\]

Assuming a steady state in all three species $F^*$, $(FQ)^*$ and exciplex,

\[
\begin{align*}
\frac{d[F^*]}{dt} &= 0 = I_{abs} - (k_e + k_q + k_a [Q])[F^*] + k_d [FQ^*] \\
I' &= k_e [\text{exciplex}] \\
I' &= k_d [FQ^*] + k_i [F^*] + k_b [FQ^*] \\
\frac{d[(FQ)^*]}{dt} &= 0 = k_a [Q][F^*] - (k_d + k_i + k_b) [FQ^*] \\
\text{from which } [F^*] &= \frac{(k_d + k_i + k_b) [FQ^*]}{k_a [Q]} \\
\frac{d[\text{exciplex}]}{dt} &= 0 = k_b [FQ^*] - (k_i' + k_e' + k_q') [\text{exciplex}] \\
\text{from which } [\text{exciplex}] &= \frac{k_b [FQ^*]}{k_i' + k_e' + k_q'} \\
\text{Then } I' &= k_e [\text{exciplex}] \\
I &= k_e [F^*] \\
\text{so } \frac{I'}{I} &= \frac{k_e'}{k_e} \cdot \frac{k_b}{k_i' + k_e' + k_q'} \cdot \frac{k_a [Q]}{k_d + k_i + k_b}
\end{align*}
\]
If \( k_i \) and \( k'_i \) are both dependent on viscosity in the same way as \( k_a \), we can write

\[
k_i = k_0 k_a \quad \text{and} \quad k'_i = k'_0 k_a,
\]

from which

\[
\frac{I'}{I} = \frac{k'_e}{k_e} \cdot \frac{k_b}{k_0 k_a + k'_e + k'_q} \cdot \frac{k_a[Q]}{k_0 k_a + k_b}
\]

as \( k_d \) can be neglected in polar solvents. This results in a much weaker dependence of \( I'/I \) on \( k_a \) for solvents of the same polarity.

A similar result is obtained for \( I' \):

\[
I' = k'_e[\text{exciplex}]
\]

\[
= I_{\text{abs}} \cdot \frac{k'_e}{k'_e + k'_q + k'} \cdot \frac{k_b}{k'_i + k_b} \cdot \frac{k_a[Q]}{k_e + k'_q + k_a[Q]}
\]

from eqs. (A2-1), (A2-2) and (A2-3).

If \( k_i = k'_0 k_a \) and \( k'_i = k'_0 k_a \), substitution into the above equation would make \( I' \) less sensitive to viscosity.
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