



## OXYGEN QUENCHING AND ENERGY TRANSFER IN PYRENE SOLUTIONS

J. C. CONTE

Núcleo de Química-Física Molecular  
Laboratório Calouste Gulbenkian de Espectrometria  
de Massa e Física Molecular (C.E.E.N. do I.A.C.)  
Instituto Superior Técnico  
Lisboa

*Measurements have been made of the fluorescence emission of pyrene solutions in cyclohexene and benzene, both in the absence and in the presence of dissolved oxygen. The results obtained show that the ratio of excimer to monomer intensities from pyrene is independent of the wavelength used for excitation even in the case where solute emission is a result of an energy transfer process from the solvent. The effect of oxygen on the pyrene excimer and monomer intensities has been studied, and it is shown that the rate constant for excimer quenching exceeds that of the monomer.*

FORSTER and KASPER (1) first discovered that when the concentration of pyrene dissolved in an inert solvent was increased, a new, structureless, emission could be detected at longer wavelengths than the usual low concentration emission. The intensity of the new emission increased with increasing concentration of pyrene, while the low concentration emission was quenched according to a Stern-Volmer law (2). This was interpreted as being due to an association between an excited and a ground state pyrene molecule. Similar effects were subsequently detected in other aromatic solutions (3) (4), pure liquids (5) (6) and crystals (7) (8). STEVENS (9) suggested that this association was a general phenomenon and proposed (10) the term excimer for the new emitting species, to distinguish between the dimer which only appears in the excited state and the excited state of a dimer which has a stable ground state. It has been considered evidence that excimers do not have a stable ground state the fact that there is no change in the absorption spectrum of the solutions with increasing concentration (1) and that the rate of excimer formation can be adequately explained by a diffusion-controlled collision process between excited and non-excited molecules (1) (2) (3).

The shape of photofluorescence and scintillation spectra of pyrene solutions in toluene has been reported to be identical for a  $10^{-3}$  mole.  $l^{-1}$  solution (12). However, in a recent work (13) on pyrene solutions in cyclohexane it is reported that the ratio of excimer to monomer intensities is different for u. v. excitation and X-ray excitation. This has been attributed to the formation of quencher molecules under ionizing radiation.

Although for some excimer forming molecules the rate constants for oxygen quenching of monomer and excimer emission have been assumed to be the same (14), there is reference (15) that for a  $10^{-3}$  mole.  $l^{-1}$  solution of pyrene in cyclohexane the rate constant for excimer quenching by oxygen is higher by a factor of about 3 than the corresponding rate for the monomer. It has also been shown (16) that the quenching efficiency of carbon tetrachloride is greater for the pyrene excimer emission than for the monomer emission.

Rate constants for the pyrene monomer-excimer system in various inert solvents (11) and various temperatures (3) have been published, the measurements being made with de-oxygenated solutions. When the solutions have been excited by u. v. radiation the measurements have

been performed under fixed conditions of excitation, and it has been implicitly assumed that the monomer-excimer kinetics was independent of the exciting wavelength. However, with some excimer forming molecules it has been shown (17) (18) that the quantum yield may depend on the exciting wavelength.

In most cases the solvents used to study the monomer-excimer properties of a given molecule have been chosen to be transparent to the exciting radiation, to avoid solvent-solute energy transfer processes. Recent work on these energy transfer processes (19) (20) has shown, however, that when the solvent itself forms excimers energy transfer from both excimer and excited monomer solvent molecules to the solute must be taken into account. In the cases studied so far, the solute concentrations used are such that there is hardly any excimer emission from the solute.

In an attempt to clarify some of the energy transfer processes in excimer forming molecules a series of experiments has been designed. The present paper reports on some of the problems outlined above, namely:

- The use of different wavelengths for excitation;
- The effect of oxygen upon monomer and excimer emission;
- The solvent-solute energy transfer processes when both solvent and solute form excimers.

Pyrene was chosen as solute because of its reasonably high solubility and because with the usual u. v. sources it is possible to consider excitation into different excited states. Cyclohexane was used as inert solvent since data are available on the properties of pyrene solutions in cyclohexane (11), and benzene as an absorbing solvent since there is information about its transfer properties (20), and monomer-excimer rate parameters (21).

## 2 — THEORY

Let us consider a binary system, containing a solvent X (molar concentration  $c_X$ ) and a solute Y (molar concentration  $c_Y$ ). When the solution is excited by u. v. radiation (intensity  $I_0$  photons  $\text{sec}^{-1}$ ) the reactions that can take place are indicated in table I. It is assumed that both solvent and solute form excimers ( $D^*$ ) by interaction of an excited monomer ( $M^*$ ) and a ground state molecule (M), and that solvent-solute energy transfer can occur both from the excited solvent mo-

nomer ( $M_X^*$ ) and excimer ( $D_X^*$ ) to the solute monomer ( $M_Y$ ). This implies that there is no stable ground state for the solute excimer. We shall consider only steady state conditions of excitation.

If all the exciting light is absorbed by the solute alone and the solution contains no oxygen, reactions 10 to 16 are the only ones to be considered (with  $k_{oY} = I_0$ ). It has been shown (3) that the intensities of monomer and excimer emission are given, respectively, by

$$I_{MY} = I_0 q_{MY} \frac{c_{hY}}{c_Y + c_{hY}} \quad (1)$$

$$I_{DY} = I_0 q_{DY} \frac{c_Y}{c_Y + c_{hY}} \quad (2)$$

with

$$q_{MY} = \frac{k_{fMY}}{k_{fMY} + k_{iMY}} \equiv \frac{k_{fMY}}{k_{MY}} \quad (3)$$

$$q_{DY} = \frac{k_{fDY}}{k_{fDY} + k_{iDY}} \equiv \frac{k_{fDY}}{k_{DY}} \quad (4)$$

$$c_{hY} = \frac{k_{MY} (k_{DY} + k_{MDY})}{k_{DY} k_{DMY}} \quad (5)$$

If under the same conditions of excitation the solutions contain oxygen, reactions 19 and 20 must also be considered. Then the intensities of monomer and excimer emission are (18):

$$I'_{MY} = I_0 q'_{MY} \frac{c'_{hY}}{c_Y + c'_{hY}} \quad (6)$$

$$I'_{DY} = I_0 q'_{DY} \frac{c_Y}{c_Y + c'_{hY}} \quad (7)$$

with

$$q'_{MY} = \frac{q_{MY}}{1 + \chi'_{MY} [O_2]} \quad (8)$$

$$q'_{DY} = \frac{q_{DY}}{1 + \chi'_{DY} [O_2]} \quad (9)$$

$$c'_{hY} = c_{hY} \frac{1 + \chi'_{MY} [O_2]}{1 + \chi'_{DY} [O_2]} (1 + \chi'_{MDY} [O_2]) \quad (10)$$

$$\chi'_{MY} = \frac{k_{MY}}{k_{MY}} \quad (11)$$

$$\chi'_{MY} = \frac{k'_{DY}}{k_{DY}} \quad (12)$$

$$\chi'_{MDY} = \frac{k'_{DY}}{k_{DY} + k_{MDY}} \quad (13)$$

Let us assume now that there is absorption by the solvent with subsequent transfer to the solute, the optical density of the solvent being much greater than that of the solute so that direct solute excitation can be neglected. The intensities of monomer and excimer solute emission can be obtained from the steady state analysis of reactions 1 to 15 (with  $k_{oX} = I_o$ ) for de-oxygenated solutions. It is possible to obtain then

$$I_{XMY} = I_o q_{MY} \frac{c_{hY}}{c_{hY} + c_Y} F_{XY} \quad (14)$$

$$I_{XDY} = I_o q_{DY} \frac{c_Y}{c_{hY} + c_Y} F_{XY} \quad (15)$$

with

$$F_{XY} = \frac{A_Y c_Y}{1 + A_Y c_Y} \quad (16)$$

$$A_Y = \frac{k_{XY}^m (k_{DX} + k_{MDX}) + k_{XY}^d (k_{XY}^m c_Y + k_{DMX} c_X)}{k_{MX} (k_{DX} + k_{MDX} + k_{XY}^d c_Y) + k_{DX} k_{DMX} c_X} \quad (17)$$

If

$$k_{DX} \ll k_{DMX}$$

$$k_{XY}^m c_Y \ll k_{DMX} c_X \quad (18)$$

$$k_{XY}^d c_Y \ll k_{MDX}$$

then

$$A_Y = \frac{k_{XY}^m k_{MDX} + k_{XY}^d k_{DMX} c_X}{k_{MX} k_{MDX} + k_{DX} k_{DMX} c_X} \quad (19)$$

and is independent of  $c_Y$  (19)

Table I

reaction	rate (sec <sup>-1</sup> )	process
(1) $M_X \longrightarrow M_X^*$	$k_{oX}$	solvent excitation
(2) $M_X^* \longrightarrow M_X + h \nu_{MX}$	$k_{fMX}$	monomer emission (solvent)
(3) $M_X^* \longrightarrow M_X$	$k_{iMX}$	monomer radiationless de-activation (solvent)
(4) $M_X^* + M_X \longrightarrow D_X^*$	$k_{DMX} c_X$	excimer formation (solvent)
(5) $D_X^* \longrightarrow M_X^* + M_X$	$k_{MDX}$	excimer dissociation (solvent)
(6) $D_X^* \longrightarrow M_X + M_X + h \nu_{DX}$	$k_{fDX}$	excimer emission (solvent)
(7) $D_X^* \longrightarrow M_X + M_X$	$k_{iDX}$	excimer radiationless de-activation (solvent)
(8) $M_X^* + M_Y \longrightarrow M_X + M_Y^*$	$k_{XY}^m c_Y$	solvent-solute transfr (from solvent monomer)
(9) $D_X^* + M_Y \longrightarrow M_X + M_X + M_Y^*$	$k_{XY}^d c_Y$	solvent-solute transfer (from solvent excimer)
(10) $M_Y^* \longrightarrow M_Y + h \nu_{MY}$	$k_{fMY}$	monomer emission (solute)
(11) $M_Y^* \longrightarrow M_Y$	$k_{iMY}$	monomer radiationless de-activation (solute)
(12) $M_Y^* + M_Y \longrightarrow D_Y^*$	$k_{DMY} c_Y$	excimer formation (solute)
(13) $D_Y^* \longrightarrow M_Y^* + M_Y$	$k_{MDY}$	excimer dissociation (solute)
(14) $D_Y^* \longrightarrow M_Y + M_Y + h \nu_{MY}$	$k_{fMY}$	excimer emission (solure)
(15) $D_Y^* \longrightarrow M_Y + M_Y$	$k_{iMY}$	excimer radiationless de-activation (solute)
(16) $M_Y \longrightarrow M_Y^*$	$k_{oY}$	solute excitation
(17) $M_X^* + [O_2] \longrightarrow M_X$	$k'_{MX} [O_2]$	monomer oxygen quenching (solvent)
(18) $D_X^* + [O_2] \longrightarrow M_X + M_X$	$k'_{DX} [O_2]$	excimer oxygen quenching (solvent)
(19) $M_Y^* + [O_2] \longrightarrow M_Y$	$k'_{MY}$	monomer oxygen quenching (solute)
(20) $D_Y^* + [O_2] \longrightarrow M_Y + M_Y$	$k'_{DY} [O_2]$	excimer oxygen quenching (solute)

If the solutions contain oxygen, using reactions 1 to 15 and 17 to 20 from table I it is possible to obtain (18)

$$I'_{XMY} = I_o q'_{MY} \frac{c_Y}{c_Y + c'_{hY}} F'_{XY} \quad (20)$$

$$I'_{XDY} = I_o q'_{DY} \frac{c'_{hY}}{c_Y + c'_{hY}} F'_{XY} \quad (21)$$

with

$$F'_{XY} = \frac{A'_Y c_Y}{1 + A'_Y c_Y} \quad (22)$$

$$A'_Y = \frac{k'_{XY}(k_{DX} + k'_{DX}[O_2] + k_{MDX}) + k^d_{XY}(k'_{MX}c_Y + k_{DMX}c_X)}{(k_{MX} + k'_{MX}[O_2])(k_{DX} + k'_{DX}[O_2] + k_{MDX} + k'_{XY}c_Y) + (k_{DX} + k'_{DX}[O_2]) K_{DMX} c_X} \quad (23)$$

In all these expressions,  $I_{MY}$  and  $I_{DY}$  are the total intensities of monomer and excimer solute emissions, respectively. This means that to use the above equations it is necessary to measure the fluorescence emission, and obtain the areas under the spectra, having corrected the spectra for the relative response of the monochromator-photomultiplier system. However, as shown below, it is possible to obtain some information about the occurring processes even if the spectra are not corrected. This has the advantage of avoiding the errors introduced by the calibration curves. For a given wavelength of emission  $\lambda$  the monomer and excimer emission intensities will be given by

$$i_M(\lambda) = K S_M(\lambda) I_M \quad (24)$$

$$i_D(\lambda) = K S_D(\lambda) I_D \quad (25)$$

Where  $S_M(\lambda)$  and  $S_D(\lambda)$  are proportional to the calibration factors (which depend on the wavelength) and  $I_M$  and  $I_D$  are given, for each particular case, by the relationships derived above.

### 3—EXPERIMENTAL

The fluorescence spectra of the different systems were analysed using a 500 mm Bausch and Lomb grating monochromator. An E. M. I. 6256 B quartz window (S 13 response) 13 stage photomultiplier (working

voltage 1800 volt) was used as a detector. The current delivered by the photomultiplier was measured with a galvanometer (Scalamp, type 7901/S). A high intensity Bausch and Lomb monochromator with a mercury arc source (HP-100) was used for excitation. The 2537 Å and 3130 Å mercury lines were used to excite the solutions.

The solutions were contained in rectangular silica cells (Helma QS) placed near the entrance slit of the analysing monochromator. The system was contained in a specially designed light tight box, and the position of the cell could be varied to choose the best conditions of detection. Care was taken to ensure that the position of the cell was reproducible. All the measurements were made in reflection, to reduce reabsorption effects, and at room temperature. The solutions were de-oxygenated by the passage of nitrogen (type R, Soc. Port. Ar Líquido).

The exciting light intensities were monitored before and after each measurement using a standard solution ( $10^{-2}$  mole.l<sup>-1</sup> P. P. O. in cyclohexane) and all the spectral intensities were thus normalized to the same intensity of excitation.

Pyrene (Koch and Light) was used as solute, cyclohexane (B. D. H. spectrograde) as an inert solvent and benzene (Merck's, p. a.) as an absorbing solvent, the absorption and emission properties being checked with those reported in the literature.

### 4—RESULTS AND DISCUSSION

Measurements were made of the fluorescence emission of pyrene solutions in cyclohexane and in benzene, for various concentrations of pyrene, with and without oxygen present, the solutions being excited by the 2537 Å and 3130 Å mercury lines. Typical fluorescence emissions, uncorrected for the spectral response of the monochromator-photomultiplier system, are depicted in fig. 1 and agree well with published spectra (11). The intensities observed for  $\lambda_1 \approx 394$  nm (the monomer peak where self-absorption effects can be neglected (22)) and for  $\lambda_2 \approx 467$  nm (the excimer peak) were chosen to use in the equations derived before.

#### a) Solutions of pyrene in cyclohexane

Fig. 2 shows the ratio  $i_D(\lambda_2)/i_M(\lambda_1)$  plotted against pyrene concentration  $c_Y$ , for de-oxygenated and air-equilibrated solutions. It is seen that values obtained

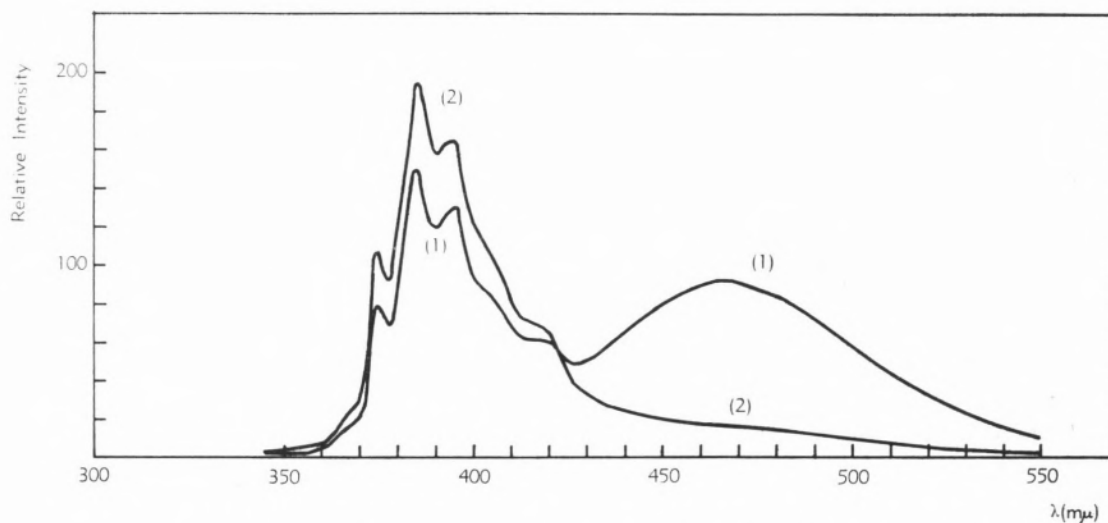


Fig. 1 — Fluorescence emission (uncorrected for the spectral response) of de-oxygenated pyrene solutions in cyclohexane. (1)  $c_Y = 10^{-3}$  mole. $l^{-1}$ . (2)  $c_Y = 10^{-4}$  mole. $l^{-1}$ . Excitation with 3130 Å.

do not depend on the wavelength used for excitation, and that the variation is linear. In fact, from reactions 24, 25, 1 and 2,

$$\frac{i_D(\lambda_2)}{i_M(\lambda_1)} = \frac{S_D(\lambda_2)}{S_M(\lambda_1)} \frac{q_{DY}}{q_{MY}} \frac{1}{c_{hY}} c_Y = K c_Y \quad (26)$$

$$\frac{i'_D(\lambda_2)}{i'_M(\lambda_1)} = \frac{S_D(\lambda_2)}{S_M(\lambda_1)} \frac{q'_{DY}}{q'_{MY}} \frac{1}{c'_{hY}} c_Y = K' c_Y \quad (27)$$

From the slopes of the straight lines, it is possible to obtain  $K/K' = 3.10$ . On the other hand, from equations 25 and 2,

(28)

$$\frac{1}{i_D(\lambda_2)} = \frac{1}{KI_0 S_d(\lambda_2) q_{DY}} + \frac{1}{KI_0 S_d(\lambda_2) q_{DY}} \cdot c_{hY} \frac{1}{c_Y}$$

This linear relationship is also well verified (fig. 2). The ratio between the slope and the ordinate at the origin gives  $c_{hY} \simeq 6.60 \times 10^{-4}$  mole. $l^{-1}$  which agrees well with the published (3) value of  $5 \times 10^{-4}$  mole. $l^{-1}$ .

From equations 26, 27, 8, 9 and 10

$$\frac{K}{K'} = 1 + \chi'_{MDY} [O_2] \quad (29)$$

Using  $[O_2] = 2.1 \times 10^{-3}$  mole  $l^{-1}$  (23),  $k_{DY} = 1.55 \times 10^7$  sec $^{-1}$ ,  $k_{MDY} = 0.65 \times 10^7$  sec $^{-1}$  (11) we obtain  $\chi'_{MDY} = 10^3$  mole $^{-1}$ .l and  $k'_{DY} \simeq 2.2 \times 10^{10}$  mole $^{-1}$  l sec $^{-1}$  from equation (13).

Fig. 4 shows the variation of  $i_D(\lambda_2)/i'_D(\lambda_2)$  and  $i_M(\lambda_1)/i'_M(\lambda_1)$  with pyrene concentration. There is good agreement with the reported value of 7 for  $i_M/i'_M$  corresponding to  $c_Y = 10^{-3}$  mole. $l^{-1}$ . The values obtained with either 2537 Å and 3130 Å were similar and the curve is drawn through the average values.

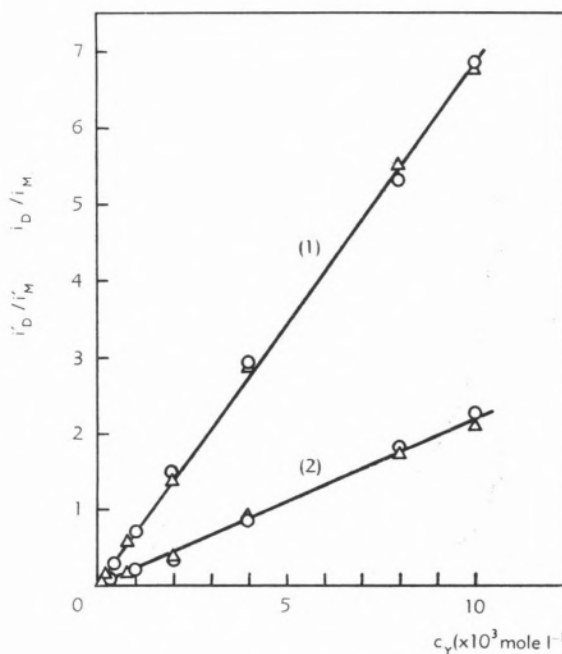


Fig. 2 — Ratio between excimer and monomer intensities for pyrene solutions in cyclohexane. (1): deoxygenated solutions; (2): air-equilibrated solutions; O: 3130 Å excitation; Δ: 2537 Å excitation.

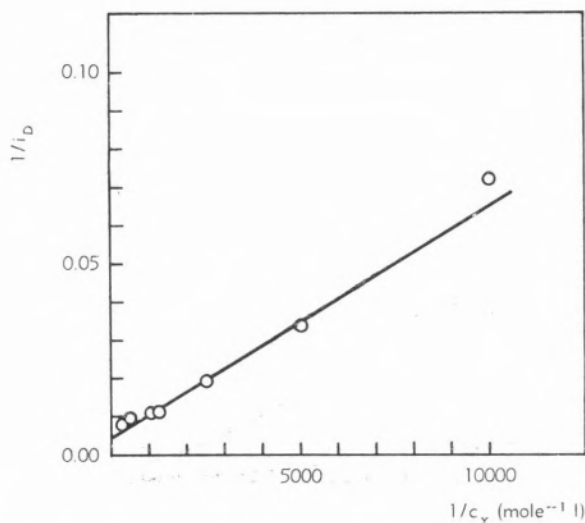


Fig. 3 — Variation of  $1/i_D$  with  $1/c_Y$  for pyrene solutions in cyclohexane. De-oxygenated solutions; 3130 Å excitation.

From equations 24, 1, 6, 8 and 10 and for  $c_Y = c_{hY}$

$$\frac{[i_M(\lambda_1)]}{[i'_M(\lambda_1)]} c_Y = c_{hY} = \frac{1}{2} \frac{(1 + \chi'_{DY}[O_2]) + (1 + \chi'_{MY}[O_2])(1 + \chi'_{MDY}[O_2])}{(1 + \chi'_{MDY}[O_2])} \quad (30)$$

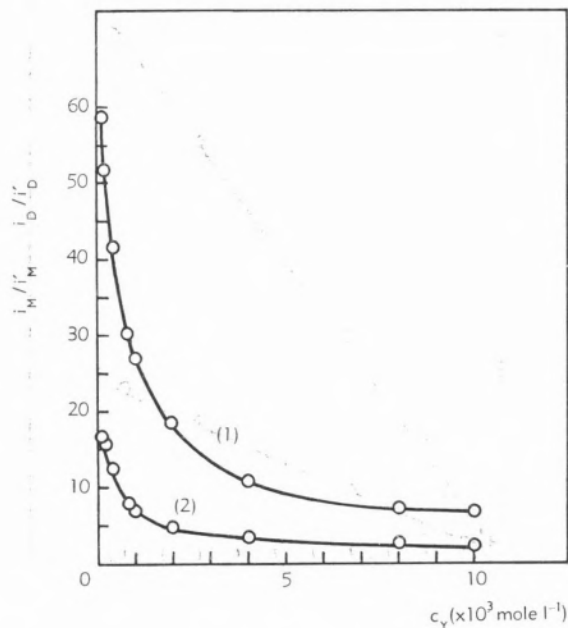


Fig. 4 — The effect of oxygen on excimer and monomer intensities for pyrene solutions in cyclohexane. (1):  $i_D/i'_D$ ; (2):  $i_M/i'_M$ .

Using the value  $c_{hY} \approx 6.6 \times 10^{-4}$  mole.l<sup>-1</sup> we obtain from the curve in fig. 4 the value  $i_M(\lambda_1)/i'_M(\lambda_1) = 9$ . Then, using equations 30, 12 and 11, the values for  $[O_2]$ ,  $k_{DMY}$ ,  $k'_{DY}$ ,  $k_{DY}$  above and the value  $k_{MY} = 2.3 \times 10^6$  sec<sup>-1</sup> (11) we obtain  $\chi'_{MY} = 7480$  mole<sup>-1</sup>. l and  $k'_{MY} = 1.72 \times 10^{10}$  mole<sup>-1</sup>. l. sec<sup>-1</sup>. As with quenching by tetrachloride (16) the rate constant for excimer quenching is greater than that of the monomer. The values of  $k'_{MY}$  and  $k'_{DY}$  are of the same order of magnitude as the value  $3.1 \times 10^{10}$  mole<sup>-1</sup>. l. sec<sup>-1</sup> for oxygen quenching of anthracene in benzene solutions (24).

#### b) Solutions of pyrene in benzene:

Fig. 5 shows the variation of  $1/i_D$  ( $\lambda_2$ ) with  $c_Y$ . Using the same arguments as before, it is possible to obtain

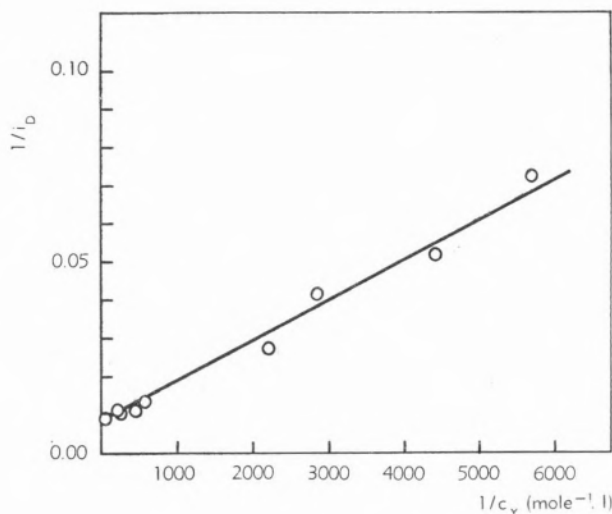


Fig. 5 — Variation of  $1/i_D$  with  $1/c_Y$  for pyrene solutions in benzene. De-oxygenated solutions; 3130 Å excitation.

the value  $c_{hY} \approx 11.0 \times 10^{-4}$  mole. l<sup>-1</sup>. Fig. 6 gives the ratios  $i_D(\lambda_2)/i_M(\lambda_1)$  versus  $c_Y$ , for de-oxygenated and air equilibrated solutions. Here again, straight lines are obtained and, within the experimental error (which is estimated to be about 5 %, taking into account the fluctuations in the source intensity), the values so obtained are the same for excitation with 2537 Å (where there is transfer from benzene) and with 3130 Å (for which only pyrene absorbs). The importance of this fact will be discussed later. From the straight lines it is possible to obtain  $K/K' = 2.81$  and so, from



equation 29, we obtain  $\chi'_{MDY} \approx 1130 \text{ mole}^{-1} \cdot \text{sec}^{-1}$ , taking into account that for benzene  $[O_2] = 1.6 \times 10^{-3} \text{ mole} \cdot \text{l}^{-1}$  (23). There is no information in the literature about the monomer-excimer rate parameters of pyrene in benzene solutions. However, assuming that the values are similar to those in cyclohexane solutions, it is seen that  $k'_{DY}$  is greater for pyrene solutions in benzene than in cyclohexane solutions, which agrees with the fact that the viscosity of cyclohexane is slightly greater than that of benzene, the rate constants for oxygen quenching being viscosity dependent (24).

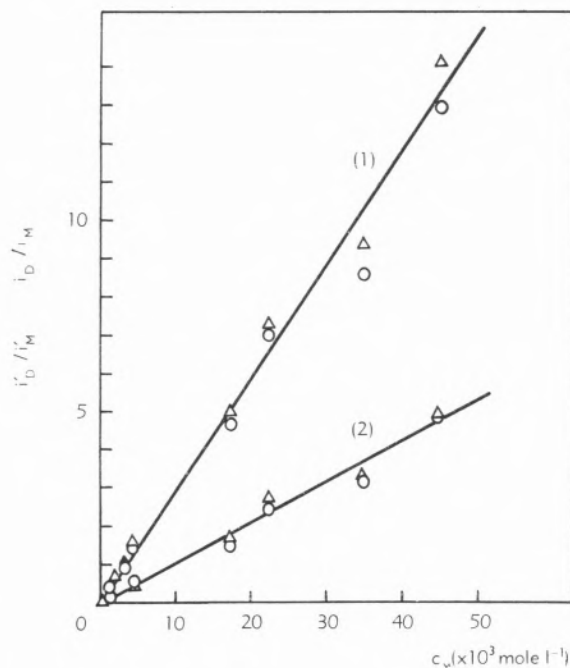


Fig. 6 — Ratio between excimer and monomer intensities for pyrene solutions in benzene. (1) deoxygenated solutions; (2): air-equilibrated solutions:  $\circ$ : 3130 Å excitation;  $\Delta$ : 2537 Å excitation.

The variations of  $i_D(\lambda_2)/i'_D(\lambda_2)$  and  $i_M(\lambda_1)/i'_M(\lambda_1)$  with  $c_Y$  were found to be similar to those obtained with cyclohexane. However different values were obtained for excitation with 2537 Å and 3130 Å (fig. 7).

This is apparent from equations 14, 15, 20 and 21, since the ratio between excimer (and monomer) intensities with and without oxygen present include the ratio of transfer efficiencies  $F_{XY}$ , and  $F'_{XY}$ , when there is solvent-solute transfer. For excitation with 2537 Å benzene absorbs and subsequently transfers energy to pyrene.

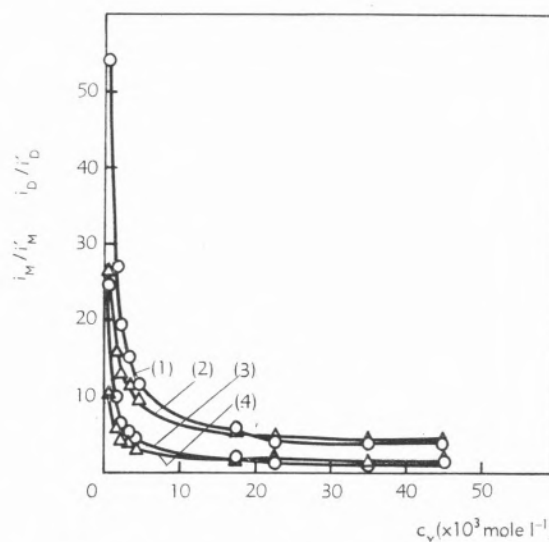


Fig. 7 — The effect of oxygen on excimer and monomer intensities for pyrene solutions in benzene. (1):  $i_D/i'_D$ , 2537 Å excitation; (2):  $i_D/i'_D$ , 3130 Å excitation; (3):  $i_M/i'_M$ , 2537 Å excitation; (4)  $i_M/i'_M$ : 3130 Å excitation.

These transfer efficiencies can also be obtained. From equations 1, 2, 6, 7, 14, 15, 20, 21, 24 and 25

$$\frac{i_{XMY}(\lambda_1)}{i_{MY}(\lambda_1)} = \frac{i_{XDY}(\lambda_2)}{i_{DY}(\lambda_2)} = F_{XY} \quad (31)$$

$$\frac{i'_{XMY}(\lambda_1)}{i'_{MY}(\lambda_1)} = \frac{i'_{XDY}(\lambda_2)}{i'_{DY}(\lambda_2)} = F'_{XY} \quad (32)$$

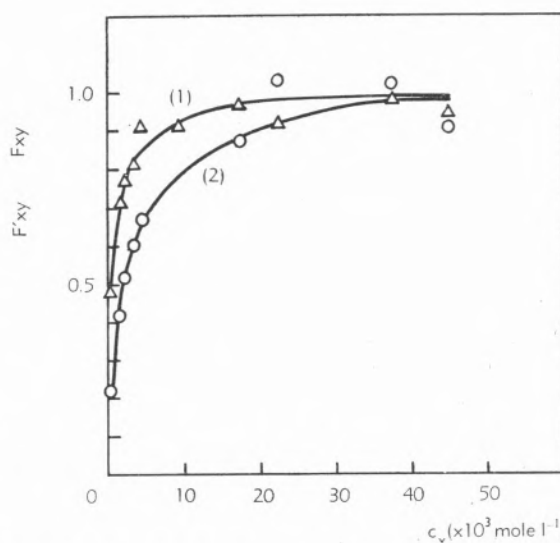


Fig. 8 — Variation of transfer efficiencies from benzene to pyrene. (1)  $F_{XY}$  (in the absence of oxygen); (2)  $F_{XY}$  (with oxygen present).

Fig. 8 shows the variation of  $F_{XY}$  and  $F'_{XY}$  with  $c_Y$ . These values represent the average values of  $F_{XY}$  and  $F'_{XY}$  obtained from both excimer and monomer relative intensities. The energy transfer efficiencies were normalized to unity for the highest concentration of pyrene. Measurements were made on solutions with concentrations up to 0,45 M and from the inspection of spectra it was possible to see that no emission from benzene could be detected. The values of  $F_{XY}$  and  $F'_{XY}$  were then taken to be unity.

## 5—CONCLUSIONS

The fact that within the experimental error the ratio between excimer and monomer intensities for pyrene solutions in cyclohexane is the same for excitation with 2537 Å and 3130 Å (corresponding to excitation of pyrene into different excited states) shows that if, as reported (13), this ratio is different when using ionizing radiation to excite the solutions, the reason for this fact must be connected with effects of high energy excitation. There is identity between the spectra obtained under different conditions of ultraviolet excitation.

There is a marked difference between the excimer and monomer oxygen quenching constants although no difference was detected, within the experimental error, when using different exciting wavelengths. This seems to indicate that the effect is not due to a static quenching (16). The fact that  $k'_{DY} > k'_{MY}$  is probably related with a greater efficiency of singlet-triplet intersystem crossing for the excimer. Some preliminary results already obtained with mixtures of benzene and cyclohexane indicate that also for benzene the excimer oxygen quenching rate constant exceeds that of the monomer.

For solutions of pyrene in benzene the ratio  $i_D/i_M$  is the same when there is transfer from benzene (2537 Å excitation) and when there is direct excitation of pyrene (3130 Å excitation). This represents an additional proof that pyrene excimers do not have a stable ground

state since an increase in excimer population should be expected as a result of direct transfer from the solvent if dimers were formed prior to excitation of pyrene monomer. It suggests also that no photodimers (25) are formed since no increase in transfer efficiency with time was detected.

From the values of  $F_{XY}$  and  $F'_{XY}$  in fig. 8 it is possible to obtain the quantities  $A_Y$  and  $A'_Y$  defined by 17 and 23. It was found that  $A_Y$  and  $A'_Y$  do vary with concentration. This indicates that unless radiative transfer (26) or some solute absorption (27) occur the approximations 18 cannot be used in this case. This contrasts with some cases of energy transfer studied so far (19) (20) and offers a means of assessing the role of excimers in the process of energy transfer. Work is in progress at this laboratory along these lines.

## 6—ACKNOWLEDGEMENTS:

I wish to thank Mr. V. PEREIRA who helped in the measurements and the assistance of the Núcleo de Estudos e Construção de Aparelhagem Científica (C. E. E. N.) for workshop facilities. A grant from N. A. T. O. (Research Grant nº 242) for the purchase of equipment is gratefully acknowledged.

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## RESUMO

Estuda-se o espectro de emissão de soluções de pireno em ciclo-hexano, para soluções contendo oxigénio dissolvido e para soluções sem oxigénio. Os resultados obtidos mostram que a razão entre as intensidades do excímero e monómero no pireno são independentes do comprimento de onda da radiação ultravioleta usada para excitação, mesmo nos casos em que há transferência de energia do solvente para o soluto. Estuda-se o efeito do oxigénio como agente de extinção da fluorescência excimérica e monomérica no pireno. Mostra-se que a constante de extinção para o excímero do pireno é maior do que a constante de extinção para o monómero.