NONRADIATIVE ENERGY TRANSFER. II - THE INFLUENCE OF THE CONCENTRATION OF THE ENERGY DONOR (*)

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ABSTRACT — The results obtained for fluorescence emission from solutions of pyrene (Py) and 9,10 diphenyl anthracene (DPA) in benzene containing oxygen at atmospheric pressure and excited under steady state conditions with u.v. light were analysed to get information about the quenching effect of oxygen on pyrene excited monomer. The influence of pyrene concentration is discussed.

1 — INTRODUCTION

In part I of this work the results obtained for the transfer rate constants from pyrene (Py) to 9,10 diphenylanthracene (DPA) dissolved in benzene and under conditions of steady state excitation with u.v. radiation were presented. The results refer to deoxygenated (by N_2 bubbling) solutions. However, during the experimental work fluorescence emission from air-equilibrated samples was also obtained which makes possible the study of the effect of oxygen which is known [1] to be a quenching agent for fluorescence, whereby fluorescence intensity is reduced relative to that observed when there is no oxygen present.

When the solutions contain dissolved oxygen, the equations that give the intensities of pyrene excited monomer emission (I'_{MY}), pyrene excimer emission (I'_{DY}) and DPA emission (I'_{Z}) have a simi-

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lar form to those that can be derived for deoxygenated samples in similar conditions [2], namely

$$I'_{MY} = \frac{c'_{hY}}{(1+\sigma'^{m}_{ZY}\, c_Z)\, c'_{hY} + c_Y}\, q'_{MY}\, I_o \tag{1}$$

$$I'_{DY} = \frac{c_Y}{(1+\sigma'^{m}_{ZY}\, c_Z)\, c'_{hY} + c_Y}\, q'_{DY}\, I_o \tag{2}$$

$$I'_{Z} = \frac{\sigma'^{m}_{ZY}\, c_Y\, c'_{hY}}{(1+\sigma'^{m}_{ZY}\, c_Z)\, c'_{hY} + c_Y}\, q'_{Z}\, I_o \tag{3}$$

where the quantum efficiencies q'_{MY} q'_{DY} and q'_Z, the half-value concentration c'_{hY} and the «Stern-Volmer constant» for transfer from the energy donor monomer σ'^{m}_{ZY} in the presence of oxygen are related whith the corresponding quantities for deoxygenated samples through the «Stern-Volmer constants» for oxygen quenching defined as

$$\chi'_{MY} = k'_{MY}\ \tau_{MY} \tag{4}$$

$$\chi'_{DY} = k'_{DY}\ \tau_{DY} \tag{5}$$

$$\chi'_{Z} = k'_{Z}\ \tau_{Z} \tag{6}$$

τ_{MY}, τ_{DY} and τ_Z being the decay constants for Py excited monomer and excimer emission and DPA emission, respectively and k'_{MY}, k'_{DY}, k'_Z the rate constants for oxygen quenching corresponding to the same entities.

As a matter of fact, in terms of the quantities defined in part I

$$q'_{MY} = \frac{q_{MY}}{1+\chi'_{MY}\,[0_2]} \tag{7}$$

$$q'_{DY} = \frac{q_{DY}}{1+\chi'_{DY}\,[0_2]} \tag{8}$$

$$q'_{Z} = \frac{q_{Z}}{1+\chi'_{Z}\,[0_2]} \tag{9}$$

$$\sigma'^{\,m}_{ZY} = \frac{\sigma^{m}_{ZY}}{1+\chi'_{MY}\,[0_2]} \tag{10}$$

$$c'_{hY} = c_{hY}\,\frac{1+\chi'_{MY}\,[0_2]}{1+\chi'_{DY}\,[0_2]}\,(1+\chi'_{MDY}\,[0_2]) \tag{11}$$

with

$$\chi'_{MDY} = \frac{k'_{DY}}{k_{DY}+k_{MDY}} \tag{12}$$

k_{MDY} being the rate parameter for excimer dissociation and k_{DY} the reciprocal of the excimer decay constant.

2 — EXPERIMENTAL RESULTS AND ANALYSIS

For solutions not containing DPA ($c_Z = 0$)

$$\frac{1}{I'_{MY}} = a'_{M} + b'_{M}\,c_{Y} \tag{13}$$

$$\frac{c_{Y}}{I'_{DY}} = a'_{D} + b'_{D}\,c_{Y} \tag{14}$$

$$\frac{I'_{DY}}{I'_{MY}} = b'_{DM}\,c_{Y} \tag{15}$$

with

$$a'_{M} = \frac{1}{q'_{MY}\,I_o} \qquad b'_{M} = \frac{1}{c'_{hY}\,q'_{MY}\,I_o} \tag{16}$$

$$a'_{D} = \frac{c'_{hY}}{q'_{DY}\,I_o} \qquad b'_{D} = \frac{1}{q'_{DY}\,I_o} \tag{17}$$

$$b'_{DM} = \frac{1}{c'_{hY}}\;\frac{a'_{M}}{b'_{D}} \tag{18}$$

Then

$$c'_{hY} = \frac{a'_M}{b'_M} = \frac{a'_D}{b'_D} = \frac{a'_M}{b'_D\, b'_{DM}} \tag{19}$$

The linear relationships (13) (14) and (15) are well verified, as it can be seen from figures 1, 2 and 3 and it is possible to obtain $c'_{hY} = 11 \times 10^{-3}$ mole l^{-1}, $a'_M = 23.63$, $b'_D = 12.63$, while from the corresponding straight lines for deoxygenated samples one gets $c_{hY} = 7 \times 10^{-4}$ mole 1^{-1}, $a_M = 1.40$, $b_D = 4.23$. Now from equations (7), (8), (9), (16), (17), and (18)

$$\chi'_{MY}\,[0_2] = \frac{I_o\, q_{MY}}{I_o\, q'_{MY}} - 1 = 15.9 \tag{20}$$

$$\chi'_{DY}\,[0_2] = \frac{I_o\, q_{DY}}{I_o\, q'_{DY}} - 1 = 1.99 \tag{21}$$

If we take the values [3] $k_{MDY} = 3.7 \times 10^6$ s^{-1}, $k_{DY} = 2.1 \times 10^7$ s^{-1} we further obtain

$$\chi'_{MDY}\,[0_2] = \frac{\chi'_{DY}\,[0_2]}{1 + k_{MDY}/k_{DY}} = 1.70 \tag{22}$$

With these values and the value $c_{hY} = 7 \times 10^{-4}$ mole. 1^{-1}, using [11] it is possible to evaluate $c'_{hY} = 10.7 \times 10^{-3}$ mole. 1^{-1}, in agreement with the value obtained experimentally.

Since the measurements were made at constant temperature, concentration of oxygen, may be assumed to be constant and equal to 1.6×10^{-3} mole. 1^{-1} [4]. This implies then that the quenching constant k'_{MY} does not depend on pyrene concentration in contrast to what happens with the rate transfer constant k^m_{YX} as it was shown in part I of this work. This being true, it is seen from (10) that σ'^m_{ZY} must vary with pyrene concentration, and be proportional to σ^m_{ZY}.

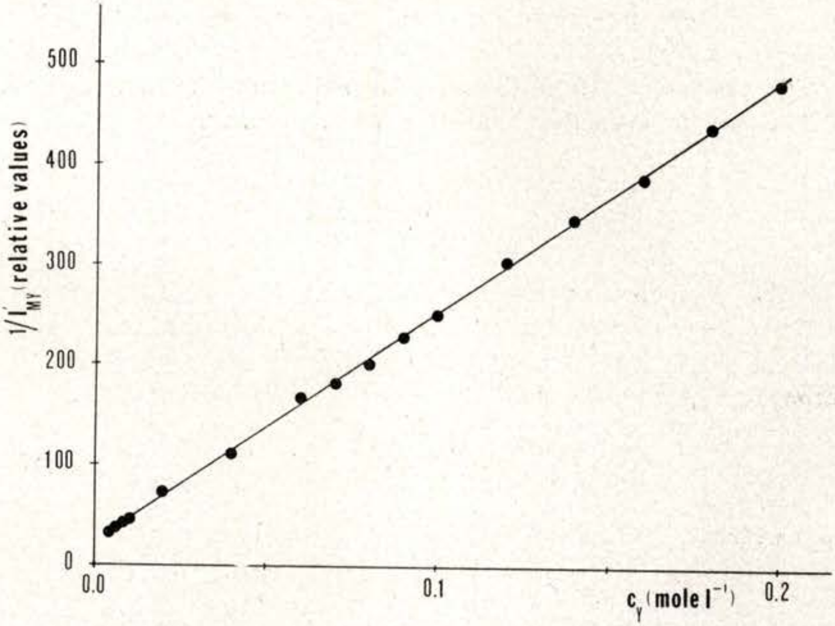

Fig. 1 — Reciprocal of Pyrene monomer fluorescence intensity as a function of Pyrene concentration for air equilibrated pyrene solutions in benzene not containing DPA.

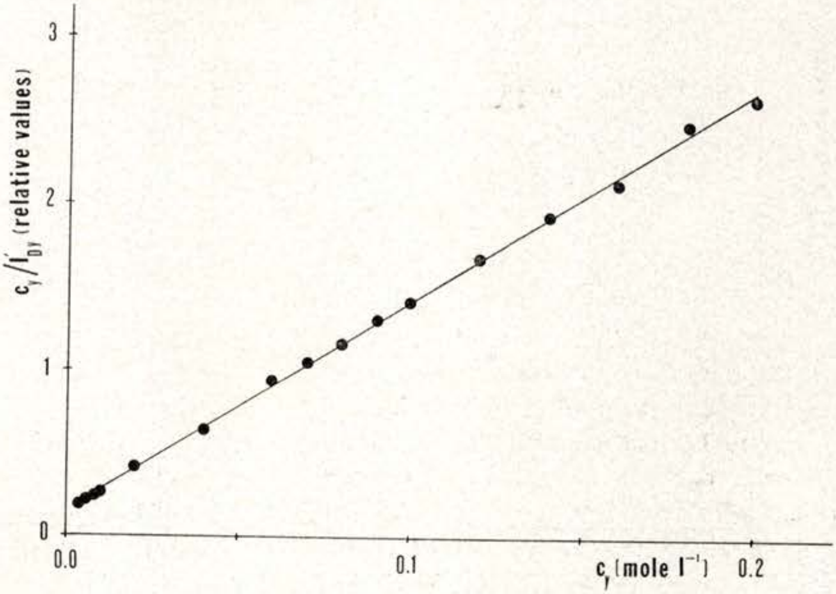

Fig. 2 — The ratio between Pyrene concentration and excimer fluorescence intensity as a function of Pyrene concentration for air equilibrated pyrene solutions in benzene not containing DPA.

To evaluate σ'^{m}_{ZY} from the experimental results the same process as that used to evaluate σ^{m}_{ZY} must be used. From (**2**)

$$\frac{1}{I'_{DY}} = A'_{D} + B'_{D}\, c_{Z} \tag{23}$$

with

$$A'_{D} = \frac{1}{I_o\, q'_{DY}} \left(\frac{c'_{hY}}{c_{Y}} + 1 \right) \tag{24}$$

$$B'_{D} = \frac{1}{I_o\, q'_{DY}} \, \frac{c'_{hY}}{c_{Y}} \, \sigma'^{m}_{ZY} \tag{25}$$

from which

$$\sigma'^{m}_{ZY} = \frac{B'_{D}}{A'_{D}} \left(1 + \frac{c_{Y}}{c'_{hY}} \right) \tag{26}$$

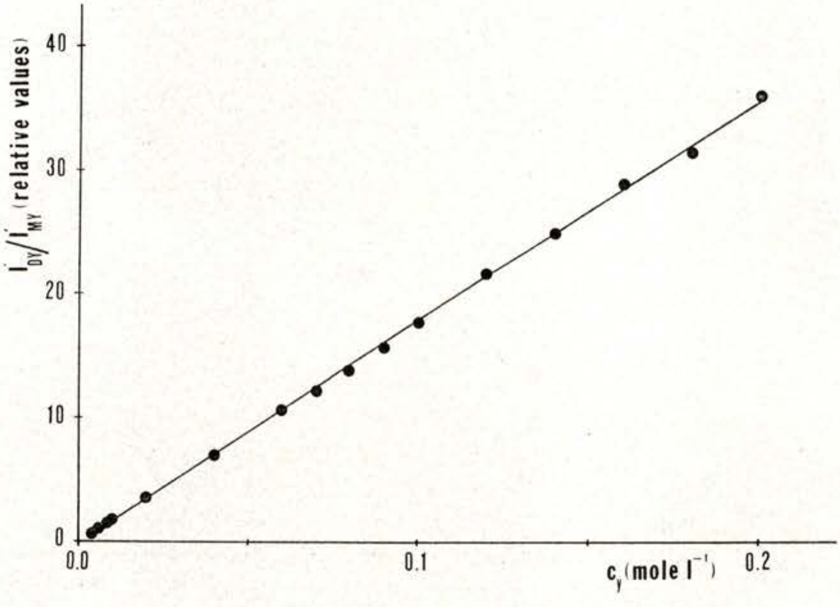

Fig. 3 — The ratio between the fluorescence intensities of Pyrene excimer and monomer as a function of Pyrene concentration for air equilibrated pyrene solutions in benzene not containing DPA.

If we take the values of I'_{DY} obtained for the same solutions as those used for the evaluation of the different values of σ^{m}_{ZY} and indicated in Tabel I of Part I of this work it is possible to get the values of σ'^{m}_{ZY}. These values are indicated in Table I.

TABLE I

c_Y (mole. l^{-1})	σ^{m}_{ZY} (l mole.$^{-1}$)
0.200	697.7
0.180	635.4
0.160	631.2
0.140	503.0
0.120	564.6
0.100	447.4
0.090	516.2
0.080	498.6
0.070	484.7
0.060	435.2
0.040	428.4
0.020	323.5
0.010	304.9
0.008	290.4
0.006	285.4
0.004	237.9

Although σ'^{m}_{ZY} varies with pyrene concentration as σ^{m}_{ZY} does, the fact is that the two quantities are not proportional. If now we consider equation (10) to be valid, this fact implies that k'_{MY} must vary with c_Y. In fact, using (10) we can obtain the curve in figure 4 which, in contrast with the conclusion reached before, would prove that the quenching effect of oxygen upon pyrene excited monomer would depend on an energy migration process among pyrene molecules, in a similar way as the nonradiative energy process discussed in Part I.

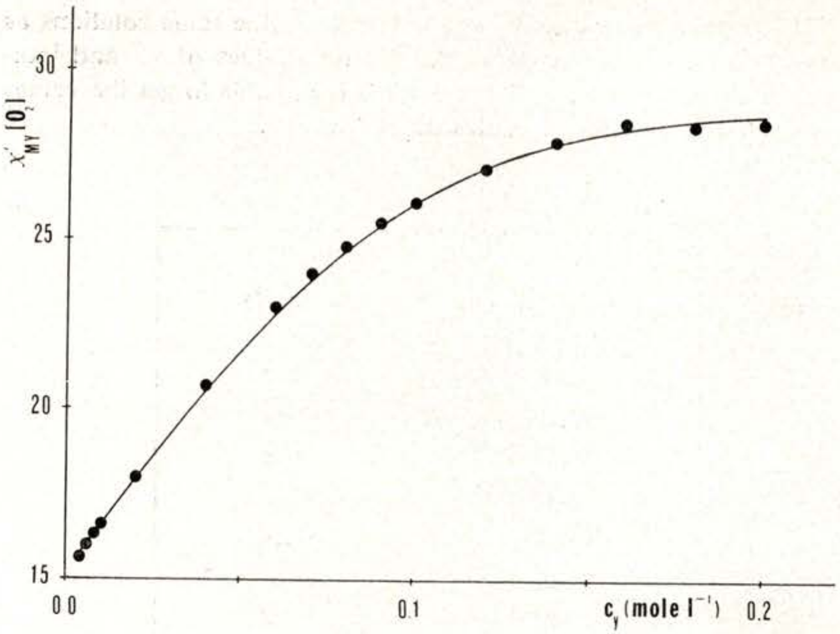

Fig. 4 — The Stern Volmer rate constant for oxygen quenching of Pyrene monomer times oxygen concentration as a function of Pyrene concentration.

3 — CONCLUSIONS

The possible analogy between quenching processes and non radiative energy processes in binary systems has already been stressed in a number of publications [5]. On this basis, it would be expected that if before it reaches an acceptor molecule the energy migrates among energy donor molecules the same would happen before a quenching process would take place.

However the problem as it is presented here lies deeper. It has to do with the consistency of the model. On one hand the results favour a model which does not give evidence for a variation of k'_{MY} with c_Y. But this same fact can be used to reach the conclusion that this variation must exist.

It is known [6] that oxygen quenching may be a complex process. But this alone does not explain the discrepancies reported here. As pointed out in Part I, no correction for any radiative energy transfer (which would affect the Y → Z transfer but not the oxygen quenching effect) was made so far. Also, the results were analysed assuming that the transfer to DPA only takes place from the excited pyrene monomer. If this is reasonable for energetic reasons, it is a fact that an equilibrium does exist between pyrene monomer and excimer involving energies above and below the first excited singlet state of DPA. However, the assumption of a negligible transfer from the excimer is supported by the good linear correlations of the variations of $1/I_{DY}$ and $1/I'_{DY}$ with c_Z.

Furthermore, the fact that oxygen is present introduces another feature in the process. The quenching effect competes with the transfer for the dissipation of energy from the excited pyrene monomer, and it is known [7] that in this case the overall process is the sum of the individual effects. What is not known is what happens when these individual processes depend on migration and/or diffusion for which case difficulties in the mathematical analysis have already been stressed [8].

All these problems must be clarified. They are under study at this Laboratory and the results will be reported later.

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