

FORMATION AND DISSOCIATION OF EXCITED DIMERS

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Concentration quenching of fluorescence is of general occurrence in the vapour state as well as in solution. Although its special features depend on the particular case it can be explained, in principle, by the prevalence of non-radiative deactivation processes in dimer aggregates of the fluorescing single molecules. This results from a lower rate constant for radiative deactivation^{1, 2}, and probably also from a higher rate constant for competing non-radiative processes in the lowest excited singlet state of a dimer in its most probable geometrical arrangement. In many cases, the ground state concentration of dimers is high enough to allow them to absorb the exciting light directly³, or to act as sinks in an energy transfer process from primarily excited monomers⁴. In other cases with practically no association in the ground state, transient dimers may be created in the excited state by a diffusional approach of excited and unexcited monomers.

There are, however, exceptions to the general phenomenon of concentration quenching. One of these is represented by acridine orange⁵ where with the disappearance of the original fluorescence, a second, weaker component appears at higher concentrations. From the absorption spectra, appreciable ground state aggregation must be concluded, obviously without complete suppression of radiative deactivation.

Quite a different behaviour has been found in the case of pyrene^{6, 7}, where a high concentration fluorescence component appears without any corresponding ground state association. The fluorescence spectra of heptane solutions of this compound at different concentrations are depicted in *Figure 1*. Apparently, the well structured fluorescence in the u.v. and violet (which, by the way, shows the usual mirror symmetry to the absorption spectrum) is replaced at higher concentration by a structureless emission in the blue. Further investigations have revealed that:

- (i) there is no change in the absorption spectrum within the corresponding concentration range;
- (ii) the decrease of the u.v. component as well as the increase of the blue one with increasing concentration follow Stern-Volmer-type functions with the same half value concentrations in all solvents;
- (iii) these half-value concentrations increase with solvent viscosity.

It has been concluded from this, that the blue component is emitted by excited dimers. These are created as transients, from pairs of excited and unexcited monomers in a diffusion controlled process.

At elevated temperatures the excited dimers may dissociate again⁸.

This is indicated by the temperature dependence of each fluorescence component at intermediate concentrations, which is depicted in *Figure 2* for pyrene in liquid paraffin. Above room temperature the dimer fluorescence increases at the expense of the monomer, which is obviously due to a more

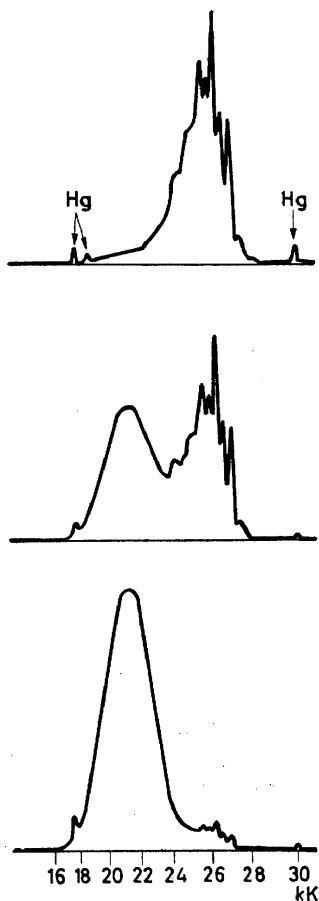


Figure 1. Fluorescence of pyrene in heptane, 10^{-4} , 10^{-3} and 10^{-2} M (from top to bottom), oxygen-free

rapid dimer formation. In the region around 100° , however, both components reverse their behaviour. This increase in the fluorescence of the monomer together with a decrease in that of the dimer, can only be interpreted as a thermal dissociation of the excited dimer with the formation of an excited monomer again. In addition to these processes, the temperature dependence of each component is modified by thermal quenching which, however, does not invalidate our conclusion.

FORMATION AND DISSOCIATION OF EXCITED DIMERS

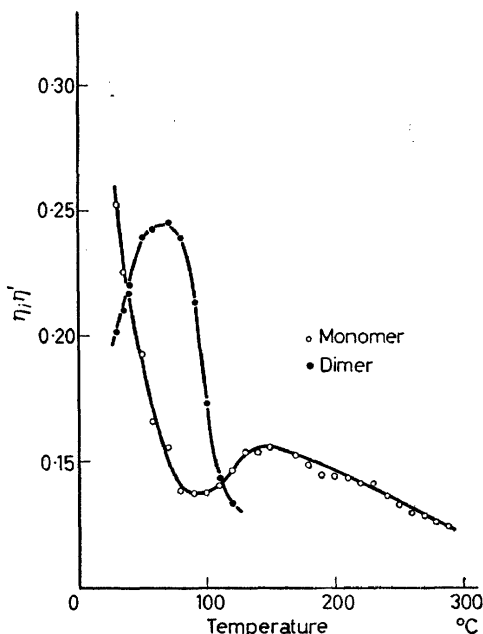
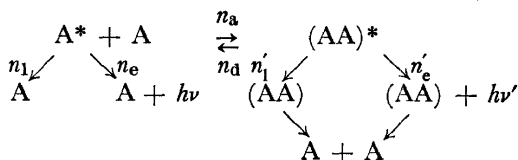


Figure 2. Monomer and dimer quantum yields of pyrene in liquid paraffin
(from T. Förster. *Pure Appl. Chem.* 4, 129, 1962)

The following reaction scheme has been used for the numerical evaluation of our results:



Here A^* and $(AA)^*$ represent the monomer and the dimer in their lowest excited singlet states and n_a etc. are the respective rate constants. Our mechanism leads to a Stern-Volmer concentration dependence where the half-value concentration as well as the maximum quantum yields of both components can be expressed by the rate constants at the temperature in question. With the assumption of temperature independent rates n_e and n'_e for the radiative processes and of an Arrhenius dependence for the others, our measurements at different concentrations and temperatures in the aliphatic solvents nonane⁹, hexadecane⁹ and liquid paraffin¹⁰ could be represented fairly well by the detailed formulae derived for this mechanism. It was found that the activation energies for nonradiative degradation of the dimer 4.2, 4.5 and 4.4 kcal/mole (in these solvents) are higher than those of the monomer (1.5, 1.6 and 1.8 kcal/mole). The apparent activation energies increase with solvent viscosity (3.4, 3.7 and 6.5 kcal/mole for formation,

13.1, 13.8 and 17.5 kcal/mole for dissociation of the dimer) but their differences are approximately constant, yielding an average of $\Delta H = 10.3$ kcal/mole for the heat of dissociation of the dimer in aliphatic solvents.

From our measurements, together with those of fluorescence decay times¹¹, the rate factors of the different processes have also been calculated but will not be given here. It is relevant to mention that values of about $\Delta S_0 = 20$ cal/deg have been obtained for the standard entropy of dissociation. This is in agreement with the strong binding in the excited dimer which must be concluded already from the corresponding energy value.

It may also be mentioned that pure liquid pyrene shows only the blue fluorescence component at temperatures close to the melting point (150°). But at higher temperatures the appearance of the u.v. component indicates that dissociation also occurs under these conditions.

High concentration components have also been observed in the fluorescence spectra of some pyrene derivatives such as 4-methyl-, 3-cyano- and 3-bromopyrene in organic solvents and pyrene-sulphonates in aqueous solution¹². With most of these, however, the effects are less pronounced insofar as the dimer components are weaker or the half-value concentrations higher than that of the parent hydrocarbon.

Until recently, no similar observations had been made for other aromatic hydrocarbons. Certainly, the formation of fluorescent dimers depends on several stringent conditions. The monomer lifetime must be long enough to allow an encounter with an unexcited monomer at an attainable concentration. Non-radiative deactivation processes must not be too fast in the dimer. Finally, dissociation of the excited dimer must not take place.

Non-radiative deactivation and dissociation will be slower at lower temperatures. We therefore tried some other aromatic hydrocarbons under these conditions. *Figure 3* shows some fluorescence spectra of naphthalene in

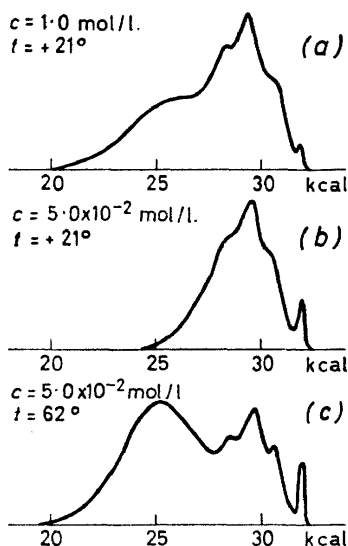


Figure 3. Fluorescence of naphthalene in toluene, oxygen-free (from E. Döller and T. Förster, by courtesy of *Z. physik. Chem. N.F.* **31**, 275, 1962)

FORMATION AND DISSOCIATION OF EXCITED DIMERS

toluene solution¹³. At room temperature, a long wavelength component is seen to be present, but it appears merely as a shoulder in the long wavelength tail of the monomer emission even at the highest possible concentration. It appears, however, quite distinctly at lower temperatures, even in less concentrated solutions. From our more detailed studies in that range we are able to conclude that naphthalene behaves in complete analogy to pyrene with the only exception that dissociation of the excited dimer occurs at much lower temperatures. Similar observations have been made for some derivatives of naphthalene¹⁴. Pure 1-methylnaphthalene and 1,6-dimethylnaphthalene, which are liquids at room temperature, show nearly exclusively the dimer fluorescence component. Below room temperature such a component has also been found for 1,2-benzanthracene⁹ but none for phenanthrene.

It would seem, from these results, that the ability for fluorescent dimer formation depends in a very critical way on the separation of the different singlet states in the monomer. In all these hydrocarbons the lowest excited singlet states are 1L_b -states. The long lifetimes of these states allow excited dimer formation at reasonable monomer concentrations. But there must be further requirements for the stability of the excited dimer. It is our opinion⁸ that this stability results mainly from the resonance force between excited and unexcited molecules of the same kind. This resonance force is proportional to the f -value of the transition between ground- and excited state which for 1L_b -states is very low (~ 0.002). Strong resonance forces should, however, result from a higher 1L_a -state with its large f -value if its separation from the lower 1L_b -state is only small. This situation is nearly optimal for pyrene ($\Delta\tilde{\nu} = 3100 \text{ cm}^{-1}$, $f = 0.39$), less for naphthalene ($\Delta\tilde{\nu} = 2600 \text{ cm}^{-1}$, $f = 0.18$) and quite unfavourable for phenanthrene ($\Delta\tilde{\nu} = 5100 \text{ cm}^{-1}$, $f = 0.18$).

For reasonable fluorescence yield the singlet excited dimer molecule must also be fairly stable to non-radiative degradation which, according to present opinions, occurs mainly by intercombination *via* triplet states. The relative position of singlet and triplet states in the monomer and its alteration under dimer formation may, therefore, be important too. It is possible that the small separation between these states in typical dye molecules contributes to the usual non-fluorescence of their stable dimers.

Excited dimer formation has also been reported for 2,5-diphenyloxazole¹⁵. The very short monomer lifetime (2.6×10^{-9} sec in xylene solution) necessitates high concentrations for this, so that even in 0.5 molar solution the dimer emission appears only in the tail of the monomer one. Its lifetime has been measured at 14×10^{-9} sec which reflects the partial forbidden nature of this transition in comparison to the corresponding one of the monomer. It has been concluded¹⁶ from a detailed study of the decay process, that in addition to excited dimer formation the collective excitation of closely lying, but otherwise independent, monomers (so called solute domains) plays some rôle.

Crystalline pyrene emits a broad fluorescence which is similar to that of concentrated solutions. This seems to occur generally in crystals where the molecules are stacked in parallel pairs¹⁷. Nevertheless, these do not interact strongly in their lattice positions because the absorption spectrum (at least

in its long wavelength part) is quite similar to that of the single molecule. Probably, some readjustment of local geometry takes place here following excitation, allowing the formation of excited dimers similar to that in solution. It must be mentioned, however, that no strict parallelism exists between fluorescence in the crystalline state and that in concentrated solution. Although concentrated naphthalene solutions exhibit dimer fluorescence, the fluorescence of crystalline naphthalene does not show similar features.

Recently, Hochstrasser¹⁸ has reported mixed dimer emission from pyrene crystals containing up to 10^{-2} parts of perylene. From the position of this emission, which is intermediate between those of the pure crystals, he has concluded that a charge transfer state (perylene⁺-pyrene⁻) instead of a resonance state might be responsible for that emission. It might be difficult, however, to accept this interpretation for dimers of identical molecules.

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