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EXCIMER PHOSPHORESCENCE OF NAPHTHALENE IN FLUID SOLUTION

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The phosphorescence spectrum of naphthalene has been measured in fluid isooctane solution in the temperature range of 80 to -100°C. The spectrum is essentially different from that obtained in rigid solution at 77K, and is ascribable to phosphorescence from the triplet excimer of naphthalene. An analysis of the experimental results suggests that the radiative rate constant for the triplet decay is enhanced as a result of the formation of the triplet excimer.

Tsai and Robinson$^{1)}$ and Langelaar et al.$^{2)}$ reported phosphorescence spectra of naphthalene in fluid solution, which are more or less similar to the usual phosphorescence spectrum obtained in a rigid-glass solution at 77K. However, the spectrum reported by the former authors was not well resolved, and that by the latter was obtained in a relatively viscous solution.

The excimer phosphorescence or the triplet excimer has been studied by several workers for aromatic compounds under various conditions.$^{2-7)}$ Existence of the triplet excimer is relatively well established for some substituted benzenes.$^{4,5)}$ Langelaar et al.$^{2)}$ indirectly obtained excimer phosphorescence spectra for naphthalene and phenanthrene by subtracting the phosphorescence spectrum at about 140K (just below the melting point of the solvent, 95 % ethanol) from the spectra at higher temperatures, but the emission assigned to the triplet excimer of phenanthrene turned out to originate from an impurity.$^{5)}$ Briegleb et al.$^{3)}$ also reported excimer phosphorescence for naphthalene and phenanthrene in glassy n-propylether solutions at temperatures near 100K; however, the excimer phosphorescence was observed when the hydrocarbon molecules formed charge-transfer complexes with electron acceptors.

Thus, whether or not unsubstituted aromatic hydrocarbons give excimer phosphorescence still remains open to question. In these hydrocarbons the small charge resonance interaction is supposed to be unfavorable for the formation of a triplet excimer.$^{4,5)}$ We have recently observed phosphorescence of naphthalene in non-viscous fluid solution with the aid of a sensitive spectrophotometer. Through careful measurements we found that the phosphorescence spectrum of naphthalene in isooctane solution is distinctly different from the spectrum in rigid solution and is ascribable to the triplet excimer of naphthalene.

Experimental

Emission spectra were measured with a high-resolution, high-sensitivity spectrophotometer8) constructed recently in our laboratory by using the photon-counting method. Phosphorescence lifetimes were measured with a spectrophosphorimeter8) which was specially designed for measuring emission decay curves and lifetimes ranging from 10^{-2} to 10^{-4} sec by means of the photon-counting method. Naphthalene was carefully purified by vacuum sublimation, zone refining, and by chromatography using activated silica gel. Solutions of naphthalene in isooctane and in glycerol were fully degassed by repeated freeze-thaw cycles (7 or 8 times). Special care was taken to eliminate any impurity emission.

Results

Phosphorescence spectra of naphthalene are measured in isooctane solution (10^{-4} – 10^{-6} M) at various temperatures of 80 – -100°C and at 77K. The representative phosphorescence spectra are shown in Fig. 1. The structured phosphorescence spectrum (1) at 77K with the origin at 470 nm is almost identical with the spectrum of the naphthalene monomer obtained in an EPA rigid-glass solution at the same temperature, and will hereafter be referred to as an M type spectrum. The spectrum (2) at 166K, i. e., at the melting point of isooctane used as the solvent, can be assumed to consist of the M type spectrum and a broad spectrum (a D type spectrum) located at longer wavelengths. Since both the solid and liquid phases of isooctane coexist at 166K, we can assign the M and D type spectra respectively to the solute in solid and liquid phases of the solvent. On raising the temperature the M type spectrum vanishes. As the temperature is raised further and hence the solvent viscosity is lowered, the D type spectrum converges towards the spectrum (3) with a maximum at 510 nm; the spectrum (3) represents the phosphorescence in isooctane at room temperature (~25°C), where the viscosity of the solution is very low. For each of the spectra (1) – (3) in Fig. 1, the corrected phosphorescence excitation spectrum agrees with the corresponding absorption spectrum. The phosphorescence of the isooctane solution of a given concentration of naphthalene at room temperature was found to follow a single exponential decay with essentially the same decay constant over the wavelength range 470 – 580 nm. Table 1 lists the quantum yield Φ_p and the lifetime τ_p, obtained as the reciprocal of the decay constant mentioned above, as a function of the solute concentration. These data indicate that the quantum yield increases and the lifetime decreases with increasing concentration.

Phosphorescence spectra in glycerol are shown in Fig. 2. For a naphthalene concentration of 10^{-4} M, the spectrum in glycerol at 2°C or 23°C, where the solvent viscosity is relatively high (cf. η = 10 poise at 25°C), is on the whole similar to the M type spectrum in EPA at 77K. The peak at 470 nm diminishes as the temperature increases and the spectrum becomes similar to the D type spectrum in isooctane at room temperature. For a solute concentration of 10^{-3} M, even at a relatively low temperature of 15°C, the phosphorescence spectrum in glycerol was found to resemble the D type spectrum in isooctane.

Table 1. The quantum yield and lifetime of the phosphorescence of naphthalene in isooctane at room temperature

Concentration $[^1M] \times 10^4$ (M)	Quantum yield $\Phi_p \times 10^4$	Lifetime $\tau_p \times 10^3$ (sec)
0.02	1.2	3.6
0.11	3.3	3.0
0.25	3.6	3.5
0.90	8.6	2.3
1.45	8.3	1.8

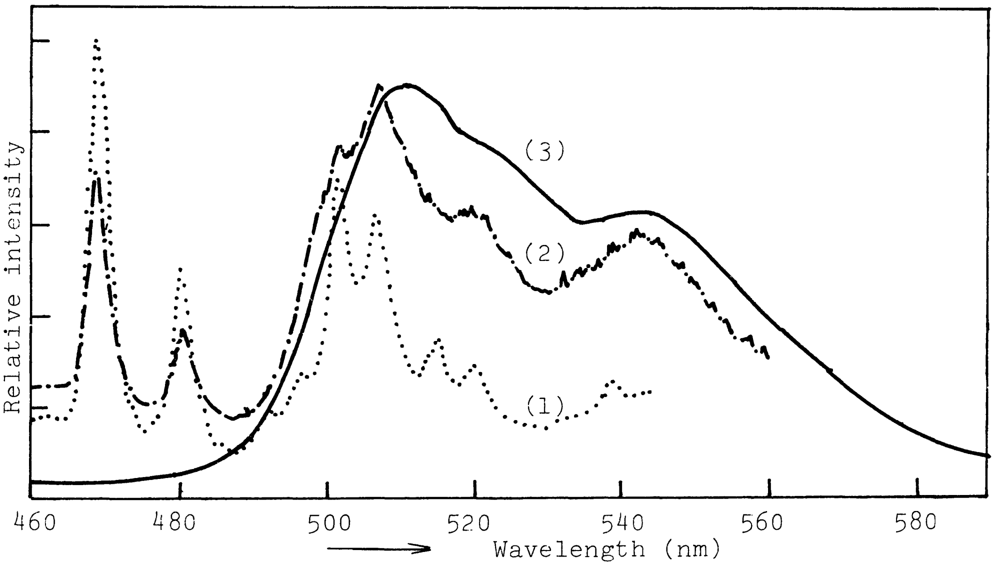


Fig. 1. Phosphorescence spectra for 1.5 × 10^{-4} M naphthalene solution in isooctane at different temperatures. (1) 77K; (2) 166K; (3) room temperature.

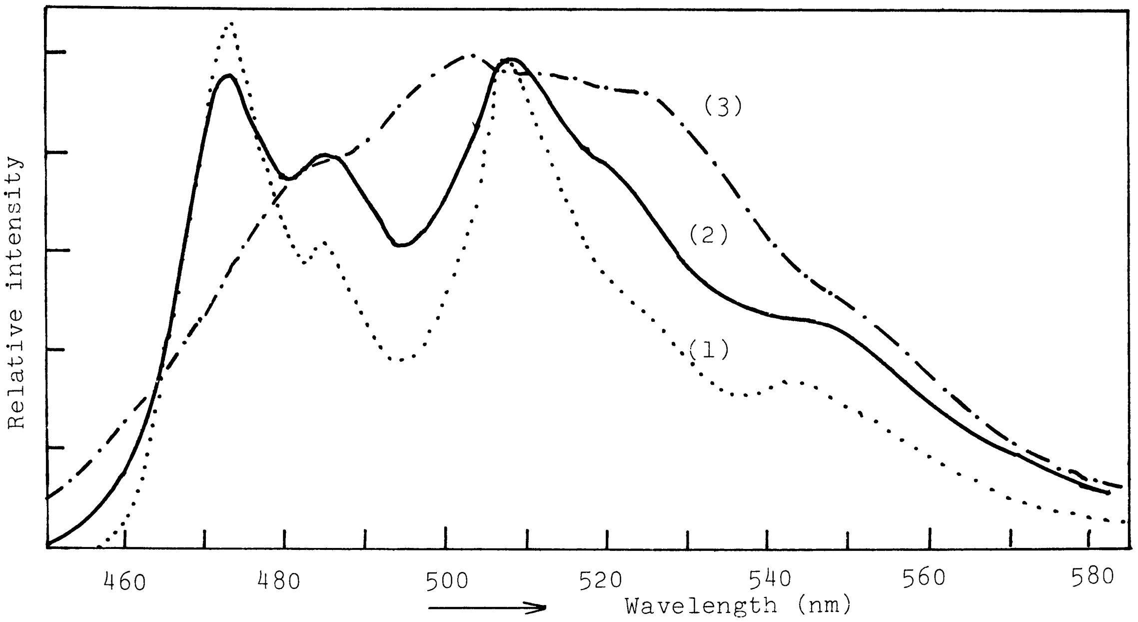
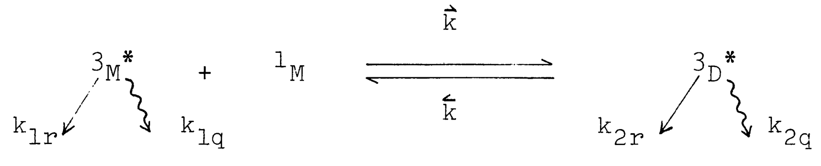


Fig. 2. Phosphorescence spectra for 1.0 × 10^{-4} M naphthalene solution in glycerol at different temperatures. (1) 2°C; (2) 23°C; (3) 80°C.

Discussion

The broad D type emission spectrum in fluid solution shown in Fig. 1 may be attributed to (a) an impurity emission, (b) the monomer phosphorescence, or (c) the excimer phosphorescence. The phosphorescence excitation spectrum is in complete agreement with the absorption spectrum, and on exciting in the wavelengh region 320 – 500 nm no emission can be detected even with the highest sensitivity of the spectrophotometer. Furthermore, the observed phosphorescence lifetime τ_p depends on the naphthalene concentration. The possibility of (a) may, therefore, be excluded. The possibility of (b) is also rejected, because significant changes take place in Φ_p and τ_p with increasing $[^1M]$. Moreover, if the phosphorescence spectrum in question were due solely to the monomer phosphorescence, a combination of $\Phi_p \simeq 10^{-3}$ and $\tau_p \simeq 10^{-3}$ sec (see Table 1) would lead to a radiative rate constant of ~1 sec^{-1}, which is too large to be assigned to the radiative constant for the naphthalene phosphorescence (~0.02 sec^{-1}).[5]

To examine the possibility of (c), we consider the following reaction scheme:



$$^3M^* + {}^1M \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftharpoons}} {}^3D^* \qquad (1)$$

$$^3M^* \xrightarrow{k_{1r}},\ {}^3M^* \xrightarrow{k_{1q}};\qquad {}^3D^* \xrightarrow{k_{2r}},\ {}^3D^* \xrightarrow{k_{2q}}$$

where ^1M, $^3M^*$, and $^3D^*$ stand for the ground singlet monomer, excited triplet monomer, and excited triplet dimer (triplet excimer), respectively; k_{1r}, k_{1q}, k_{2r}, and k_{2q} are the radiative (r) and nonradiative (q) decay constants for the triplet monomer and triplet excimer, respectively. The rise of the phosphorescence emission was too rapid to follow with the time resolution employed in the measurement of the emission decay. On this basis, we can assume that a dynamic equilibrium is attained in the reaction of the triplet excimer formation (1), as is often the case with the singlet excimer formation.5) The lifetime τ_p common to $^3M^*$ and $^3D^*$ is then given by

$$1/\tau_p = (k_1 + k_2K[^1M])/(1 + K[^1M]) \qquad (2)$$

where $k_1 = k_{1r} + k_{1q}$, $k_2 = k_{2r} + k_{2q}$, and K is the dynamic equilibrium constant, i. e. $K = \vec{k}/\overleftarrow{k}$. Also, the quantum yield of the excimer phosphorescence, Φ_D, is given by

$$\Phi_D = (k_{2r}K[^1M]\Phi_T\tau_p)/(1 + K[^1M]) \qquad (3)$$

where Φ_T is the quantum yield of the triplet formation from the excited singlet. If we consider that the observed lifetime τ_p corresponds to τ_p defined by Eq. (2), and that the observed phosphorescence emission originates mainly from the triplet excimer, i. e. $\Phi_p \approx \Phi_D$, then we can readily explain the experimental results in Table 1. Thus, plots of $1/\tau_p$ and Φ_p/τ_p versus $[^1M]$ give straight lines, as is expected from Eqs. (2) and (3) under a reasonable assumption that $1 \gg K[^1M]$ (see below). The former plot leads to $k_1 = 3 \times 10^2$ sec^{-1} and $k_2K = 2 \times 10^6$ sec^{-1}M^{-1}, and the latter to $k_{2r}K = 4 \times 10^3$ sec^{-1}M^{-1}. Since the energy separation between the monomer and excimer phosphorescence maxima is about 1700 cm^{-1}, a maximum value of K is estimated to be 10^2M^{-1}.

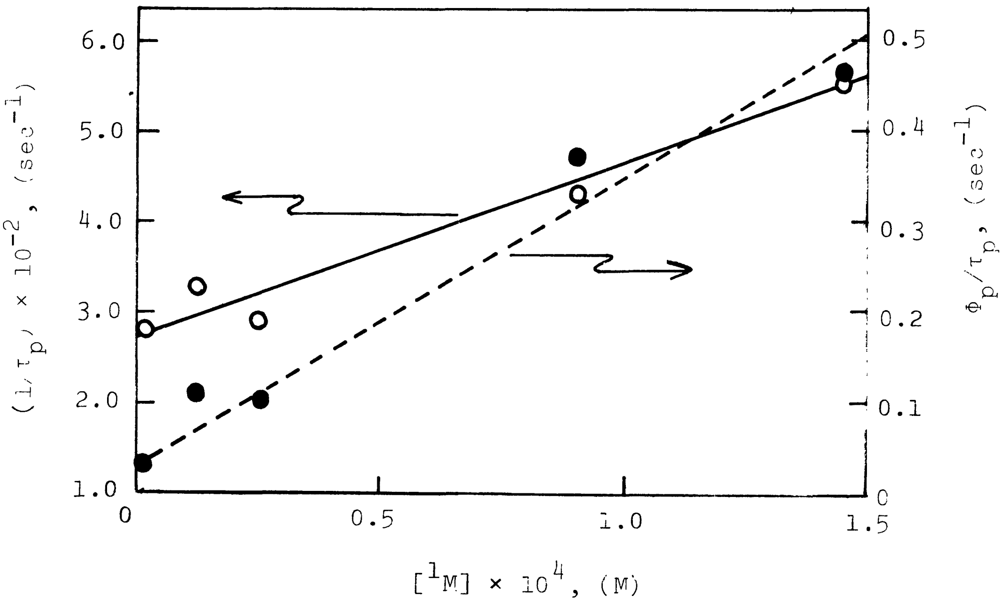


Fig. 3. Plots of $1/\tau_p$ and Φ_p/τ_p vs. $[^1M]$ for naphthalene in isooctane at room temperature.

The value of k_{2r} then amounts to at least 5 × 10 sec^{-1}. These considerations lead to the most likely conclusion that the D type phosphorescence spectrum is due to the triplet excimer.

It should be noted here that the radiative decay constant k_{2r} is very large compared with k_{1r}. In a planar molecule, the spin-orbit interaction between π, π^* states is vanishingly small. When an excimer is formed, however, the spin-orbit matrix element between singlet and triplet π, π^* states may have a non-zero value. Since the oscillator strength of the transition from the ground state to the coupling singlet may be generally large, the probability of the transition from the excimer triplet to the ground singlet state would be of comparable magnitude to the transition probability between an n, π^* triplet and the ground singlet.$^{9)}$ Thus, if k_{2r} becomes far greater than k_{1r}, phosphorescence from the triplet excimer is expected to be observed even when $K[^1M]$ is much smaller than unity.

In viscous glycerol solutions, the assumption for a dynamic equilibrium will not hold. An inspection of Fig. 2 suggests that the spectra include contributions of the phosphorescence from both the monomer and the excimer, and that the weight of the excimer emission is reduced with increase in viscosity of glycerol. An increase in the solute concentration, however, may offset the increase in the solvent viscosity.

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