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Delayed Thermal Excimer Fluorescence of Acriflavine in a Stretched PVA Sheet

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A long-lived emission of acriflavine absorbed into a polyvinylalcohol sheet has been investigated. At higher concentrations, a new, previously-unobserved emission band has been observed. It has been shown that the newly-observed band can be interpreted by a mechanism in which the thermal excitation of the triplet state to the excimer state takes place, followed by an emission. The term "delayed thermal excimer fluorescence" has been given to specify the emission of this type.

It has been known that dyes in general tend to associate or aggregate at higher concentrations. Aggregation affects both absorption and emission properties, but in somewhat different manners: in absorption spectra, aggregation is associated with the appearence of a new band in a shorter wavelength region than normal monomer absorption,[1-3] while in fluorescence spectra it is associated with the shift of the fluorescence band to longer wavelengths.[1,4] Such spectral behavior may be interpreted in terms of the formation of a dimer which exists both in the ground state and in the excited state.

A long-lived emission due to another type of dimeric species, known as excimer, has been observed anew for acriflavine absorbed into a PVA sheet. This emission is different from the usual excimer fluorescence in that it has a long life and a different origin. The preliminary results have already been reported[5]; the present paper will present the details of the further investigation.

Experimental

Acriflavine. Acriflavine was purified by recrystallization from hydrochloric acid five times. Further purification did not cause any change in the absorption or emission spectra.

PVA Sheet. The aqueous solution of polyvinylalcohol (PVA) with the polymerization degree of about 1500 was poured onto a flat glass plate and kept still for several days. The PVA sheet thus obtained is about 0.15 mm thick, and has an absorption below 340 mμ and a faint short-lived fluorescence around 400 mμ. The PVA sheet was immersed into an aqueous solution of acriflavine of a known concentration at room temperature for 12 hr, and then stretched*[2] to about three times at room temperature while it was moist.

In this paper, the "concentration" of the sample is conveniently referred to the concentration of the solution into which the PVA sheet was immersed. This may be somewhat different from the real concentration in the PVA sheet; however, such real concentrations are of no significance: we need only the relative concentration in this experiment.

Apparatus. Acriflavine absorbed into the PVA sheet was irradiated by either a xenon short-arc lamp or a high-pressure mercury lamp. The long-lived emission separated by a Becquerel-type phosphoroscope was detected either photographically with a Shimadzu Quartz spectrograph QF-60 on Neopan SSS film or photoelectrically with a Narumi RM-23 grating spectrometer on an EMI 5100 photomultiplier tube. The sample was kept at a constant temperature within ±1°C during the measurements.

Results and Discussion

Concentration Changes. Figure 1 shows the long-lived emission spectrum of acriflavine in a PVA sheet at 20°C and at various concentrations. When the concentration is low, the long-lived emission consists of two bands. The band around 590 mμ is the phosphorescence, an emission from the lowest triplet state to the ground state. The emission band around 485 mμ is due to the mechanism in which there is thermal excitation from the lowest triplet state to the first excited singlet state, followed by an emission to the ground state. This type of emission band has been known for a long time and has been given a variety of names. Föerster[6] called it "high temperature fluorescence", and Lewis, Lipkin, Magel[7] called

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*[2] In this experiment we took the trouble to prepare this stretched PVA sheet because we are going to measure the dichroism of an emission in a future work.

6) T. Förster, "Fluoreszenz Organisher Verbindungen," Vandenhoec und Ruprecht, Götingen (1951).

7) G. N. Lewis, D. Lipkin and T. T. Magel, *J. Am. Chem. Soc.*, **63**, 3005 (1941).

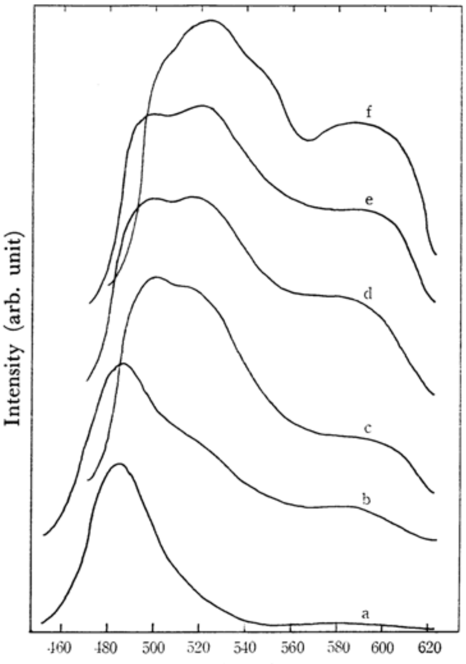

Fig. 1. Microphotometer tracings of long-lived emission of acriflavine in stretched PVA sheets at 20°C and at various concentrations (mol/*l*). The ordinate is approximately normalized.
a: 10^{-5}; b: 5×10^{-5}; c: 5×10^{-4};
d: 7.5×10^{-4}; e: 10^{-3}; f: 2.5×10^{-3}

it "α-phosphorescence", while Parker and Hatchard[8] called it "E-type delayed fluorescence"; on the other hand, Windsor[9] named it "slow fluorescence". We have chosen the name "delayed thermal fluorescence" because the process is fluorescent in nature, but it is accompanied by a delay induced by thermal excitation.[10]

As the concentration increases, two effects are observed. The first effect is the apparent, slight shift of the peak of the delayed thermal fluorescence. This effect is trivial. It may be attributed to self-absorption. The second, more important effect is the appearance of a new emission band around 525 mμ. The presence of this band has not been reported so far; an effort will be made below, to investigate the nature of this emission.

The above concentration change first suggests the possibility that the newly-observed band might be due either to a dimer or to an excimer. The absorption spectra of these samples were, therefore, recorded by a Hitachi EPU-2 spectrophotometer; they are shown in Fig. 2. As may be seen in Fig. 2 the variation in concentration does not bring about any change in the absorption spectral distribution. Consequently, it may be concluded that the newly-observed band is not due to a dimer which is stable in the ground state. An alternative explanation is that the newly-observed band might be due to an excimer; because of its long lifetime, emission of this type has been called "delayed excimer fluorescence."

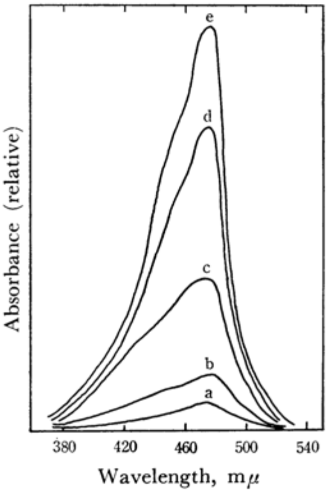

Fig. 2. Absorption spectra of acriflavine in stretched PVA sheets at 20°C and at various concentrations (mol/*l*).
a: 10^{-5}; b: 5×10^{-5}; c: 5×10^{-4};
d: 7.5×10^{-4}; e: 10^{-3}

Effect of the Intensity of the Exciting Light. Delayed excimer fluorescence has previously been observed for a limited number of polyacenes in liquid solutions[11-13] and in solid solutions[14,15].

In all the cases investigated, the delay of the emission has been ascribed to triplet-triplet annihilation; namely, two molecules in the triplet state interact to produce an excimer. In this case, it has been predicted theoretically and verified experimentally[16] that the intensity of the delayed emission varies proportionally to the square of the phosphorescence intensity as the intensity of the exciting light varies. However, as Fig. 3

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[8] C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.*, **57**, 1894 (1961).

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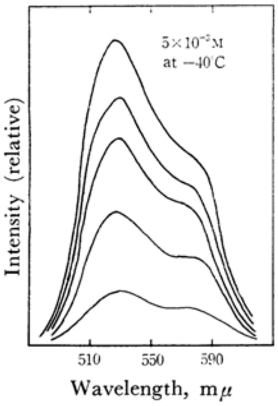

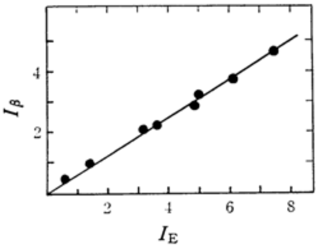

Fig. 3. Variation of the intensity of the long-lived emission upon varing the intensity of the exciting light.

shows, the intensity of the long-lived emission around 525 mμ varies to the first power, and not to the second power, of the intensity of the exciting light. It may consequently, be concluded that the delayed excimer fluorescence observed anew in this experiment is not due to triplet triplet annihilation. A mechanism similar to that of delayed thermal fluorescence supplies a good interpretation for the above results. The long-lived excimer fluorescence due to this mechanism may then be called "delayed thermal excimer fluorescence."

Kinetics. Assuming that the newly-observed band is delayed thermal excimer fluorescence, as has been suggested above, the following reaction scheme may be constructed:

$S_0 + h\nu \rightarrow S_1$		absorption
$S_1 \rightarrow S_0 + h\nu_M$	k_{fM}	monomer fluorescence
$S_1 \rightarrow S_0$	k_{iM}	quenching of monomer fluorescence
$S_1 \rightarrow T_1$	k_{TM}	intersystem crossing
$S_1 + S_0 \rightarrow E$	k_{EM}	excimer formation
$E \rightarrow S_1 + S_0$	k_{ME}	excimer dissociation
$E \rightarrow 2S_0 + h\nu_E$	k_{fE}	excimer fluorescence
$E \rightarrow 2S_0$	k_{iE}	quenching of excimer fluorescence
$E \rightarrow E_T(T_1+S_0)$	k_{E_TE}	intersystem crossing
$E_T \rightarrow E$	k_{EE_T}	thermal excitation
$T_1 \rightarrow S_1$	k_{MT}	thermal excitation
$T_1 \rightarrow S_0 + h\nu_P$	k_{pT}	phosphorescence
$T_1 \rightarrow S_0$	k_{iT}	quenching of phosphorescence,

where S_0 and S_1 indicate, respectively, the ground and the first excited singlet state; T_1 the lowest triplet state; E and E_T, the excimer state and the triplet state of the excimer respectively, and c the concentration of the ground state molecules. The various k's are rate constants associated with the specified reaction. No distinction is made between the energy of the triplet state of the monomer and that of the excimer since the exciton band width of the triplet state is quite small and may very well be equated with zero.

Let the quantum yields of the delayed thermal fluorescence, the delayed thermal excimer fluorescence, and the phosphorescence be designated as ϕ_M, ϕ_E, and ϕ_T, respectively. Then one easily obtains, considering the above kinetics, the following formulas:

$$\left.\begin{aligned} \frac{\phi_M}{\phi_T} &= \frac{k_{fM}}{k_{pT}} \cdot \frac{k_{MT}}{k_{fM} + k_{iM} + k_{TM} + k_{EM}c} \\ \frac{\phi_E}{\phi_T} &= \frac{k_{fE}}{k_{pT}} \cdot \frac{ck_{EE_T}}{k_{E_TE} + k_{fE} + k_{iE} + k_{ME}} \end{aligned}\right\} \quad (1)$$

Of these, the temperature-dependent parameters are k_{MT}, k_{EE_T}, k_{EM}, and k_{ME}. At relatively low temperatures, it may well be assumed that:

$$\left.\begin{aligned} k_{EM}c &\ll k_{fM} + k_{iM} + k_{TM} \\ k_{ME} &\ll k_{fE} + k_{iM} + k_{E_TE} \end{aligned}\right\} \quad (2)$$

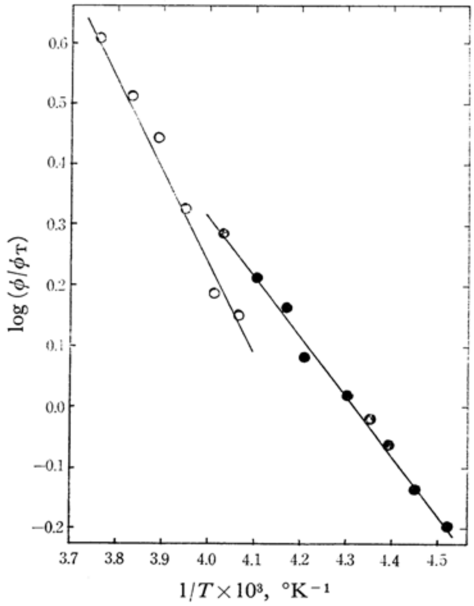

Fig. 4. The Arrhenius plots of ϕ_M/ϕ_T and ϕ_E/ϕ_T.

The following equations are then obtained:

$$\left.\begin{array}{l}\phi_{\mathrm{M}}/\phi_{\mathrm{T}} = K_1 \exp(-W_{\mathrm{MT}}/\boldsymbol{k}T) \\ \phi_{\mathrm{E}}/\phi_{\mathrm{T}} = K_2 \exp(-W_{\mathrm{EE_T}}/\boldsymbol{k}T)\end{array}\right\} \quad (3)$$

where $\boldsymbol{k}$ is the Boltzmann constant, and where W_{MT} and $W_{\mathrm{EE_T}}$ are, respectively, the activation energies for k_{MT} and $k_{\mathrm{EE_T}}$. K_1 and K_2 are new temperature-independent constants. The Arrhenius plots of $\phi_{\mathrm{M}}/\phi_{\mathrm{T}}$ and $\phi_{\mathrm{E}}/\phi_{\mathrm{T}}$ are obtained between −20°C and −44°C; they are shown in Fig. 4. The activation energies obtained from Fig. 4 are:

$$W_{\mathrm{MT}} = 10\ \mathrm{kcal/mol}$$

$$W_{\mathrm{EE_T}} = 4.5\ \mathrm{kcal/mol.}$$

These values should be associated with the energy gaps between the triplet state and the first excited singlet state, and between the triplet state and the excimer state. The peak-to-peak separation between the delayed thermal fluorescence and the phosphorescence, and between the delayed thermal excimer fluorescence and the phosphorescence are, respectively, 9.7 kcal/mol and 4.7 kcal/mol. These values are in good agreement with the activation energies obtained above. Such experimental findings are also consistent with the above kinetic treatments.

Lifetimes. The kinetic treatments of the decay pattern of the delayed thermal fluorescence, the delayed thermal excimer fluorescence, and the phosphorescence demonstrate that the decays of these three emissions may always be expressed as the single exponential decay of the identical lifetime, as long as a Becquerel-type phosphoroscope is used in the lifetime measurements.

The lifetimes measured at 20°C are 0.6 sec for all three of the emission bands. This result, again, is in consistent with the kinetics treated above.

All the treatments described so far seem to substantiate the idea that the newly-observed long-lived emission band is the delayed thermal excimer fluorescence; namely, it is due to the mechanism in which excimer fluorescence is followed by the thermal excitation of the triplet state to the excimer state.

Future Problem

There remain a number of questions, some of which we shall now summarize:

(i) In this paper, the concentration changes are not treated quantitatively in terms of the kinetics. This is due to the defficulty in determining the exact concentration in the PVA sheet.

(ii) It is not easy to conceive of the diffusion or collision processes in the solid state. Therefore, the mechanism by which the excimer is formed in the PVA sheet must be investigated further from other points of view.

(iii) The energy difference between the peak of the delayed thermal fluorescence and the delayed thermal excimer fluorescence observed in this experiment is 1400 $\mathrm{cm^{-1}}$. This value is significantly smaller than the separations of 6000 $\mathrm{cm^{-1}}$ observed in the majority of polyacenes,[16] but it is of the same magnitude as the energy difference observed for anthracene.[17,18] Why the energy separations should be small in the cases of anthracene and acriflavine remains an unsolved question.

These questions, among others, will be the subjects of further investigations, and will be treated in future publications.

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