A Delayed Excimer Fluorescence of Acriflavine Stretched PVA Sheet

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A delayed excimer fluorescence of (the excimer fluorescence of long-lived) acriflavine has been observed. Acriflavine, absorbed into a stretched polyvinylalcohol (PVA) sheet, was irradiated by a high-pressure xenon lamp; the long-lived emission was then observed by means of a Shimadzu spectrograph. At a dilute concentration, the long-lived emission is composed of α-phosphorescence and β-phosphorescence.[1] At a high concentration, a new, previously-unobserved band arises about 1400 cm^{-1} to the red of the α-phosphorescence; this band increases in intensity as the concentration increases. (See Fig. 1.) The absorption spectra of these samples as recorded by a Hitachi EPU-2 absorption spectrometer exhibit no change in spectral distribution. On this ground, the newly-observed long-lived emission may be ascribed to an excimer species.

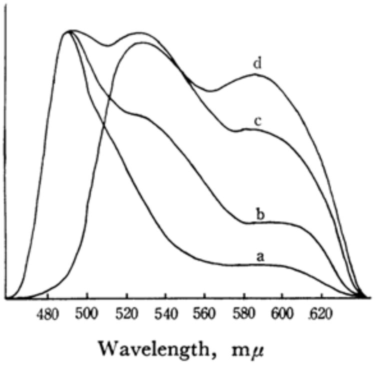
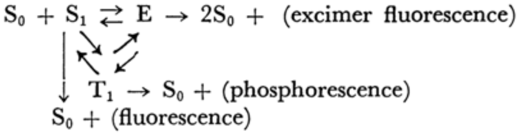


Fig. 1. Microphotometer tracings of the long-lived emission of acriflavine in streched PVA sheets. Samples were prepared by immersing PVA sheets in solutions of acriflavine at concentrations of: a: 5×10^{-5}; b: 9×10^{-5}; c: 4.6×10^{-3}; 10^{-2} mol./l. The ordinates are approximately normalized.

A long-lived excimer fluorescence has previously been observed for a limited number of polyacenes in liquid solutions[2,3] and in solid solutions.[4] In all the cases investigated, the delay of the emission has been ascribed to triplet-triplet annihilation. In the present case, however, the delayed excimer fluorescence is interpreted to be the excimer α-phosphorescence, consisting of thermal excitation from the triplet state to the excimer state followed by emission. The mechanism can be represented by the following reaction scheme:



where S_0 and S_1 are, respectively, the ground state and the first-excited singlet state, and where T_1 is the lowest triplet state. The parentheses indicate that there are both radiative and radiationless transitions. No distinction is made between the triplet state of the monomer and that of the excimer, since the exciton band width of the triplet state may very well be equated with zero. According to this reaction scheme, the Arrhenius plots of ϕ_f/ϕ_p and ϕ_e/ϕ_p should yield the activation energies for the $T_1\rightarrow S_1$ and $T_1\rightarrow E$ processes, respectively, where ϕ_f, ϕ_p, and ϕ_e are the quantum yields of the monomer α-phosphorescence, the β-phosphorescence, and the delayed excimer fluorescence, respectively. The experiments were performed between $-20°C$ and $-44°C$; the activation energies obtained were 10 and 4.5 kcal./mol. for the $T_1\rightarrow S_1$ and $T_1\rightarrow E$ processes, respectively. These values are in agreement with the energy differences of the corresponding peaks of emission spectra. These kinetic treatments substantiate the above identification of the newly-observed band is being the excimer α-phosphorescence.

The fact that the spectrum of dimeric species is observed in a stretched PVA sheet is another point of interest. This will facilitate the polarization measurements of dimeric species, which has not hitherto been attempted.

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[2] C. A. Parker and C. G. Hatchard, *Proc. Roy. Soc.*, **A269**, 574 (1962).

[1] The terminology is those of G. N. Lewis, D. Lipkin and T. T. Magel, *J. Am. Chem. Soc.*, **63**, 3005 (1941).

[3] C. Tanaka, J. Tanaka, E. Hutton and B. Stevens, *Nature*, **198**, 1192 (1963).

[4] T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **39**, 3533 (1963); F. Smith and S. P. McClynn, ibid., **42**, 4308 (1965).