The Luminescence of the Heteropolar Excimer in the Cyclohexane Matrix

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It has been established now that many aromatic hydrocarbons, such as pyrene, perylene, anthracene, chrysene, phenanthrene, and triphenylene, form stable complexes with such aromatic amines as *N*, *N*-dimethylaniline (DMA), *N*, *N*-dimethyltoluidines (DMT's), and *N*, *N*-dimethylnaphthylamines (DMNA's) only in the excited state.[1] The most important contribution to the intermolecular forces in these complexes seems to be charge transfer from the amine to the excited aromatic hydrocarbon.

Because the complexes are formed only in the excited state, it may be convenient to call the complex the "heteropolar excimer" in contrast to a "homopolar excimer" such as the pyrene excimer, in order to distinguish it from the ordinary CT complex which exists in the ground state as well as in the excited state.

In order to study the electronic processes in the heteropolar excimer at low temperatures, we have measured the fluorescence emission and excitation spectra, and also the fluorescence rise and decay curves. From the results of these measurements, we have confirmed that the heteropolar excimer can be produced easily in the rigid cyclohexane matrix at low temperatures. For example, in the pyrene (10^{-5} mol./l.)-DMA(10^{-2} mol./l.) system, only the long-wavelength and structureless fluorescence band, which seems to be ascribed to the heteropolar excimer, can be observed from 300°K to 77°K. However, when the temperature is lowered, the fluorescence band maximum shifts to red at first, and then makes a blue shift to approximately the same position as it has at 300°K, as one can see in the following:

T (°K)	300	273	240	230—210	190—100
λ_{max}(mμ)	440	450	465	480	440

The relative fluorescence yield and the fluorescence decay time change in a similar way; i. e., they both have minima at ca. 220°K. These facts seem to indicate that some state of the heteropolar excimer which differs from that in the solution at room temperature may be forced to arise in the cyclohexane matrix. However, when the DMA concentration is small (10^{-4} mol./l.), the fluorescence of the complex can be observed only at the wavelength region of 440—450 mμ. Therefore, one of the possible mechanisms for the appearance of the longer-wavelength fluorescence might be the formation of a more highly aggregated state than the 1 : 1 complex. In the above-described systems, no time delay of the heteropolar excimer fluorescence from the exciting light pulse (with a half-value-width of ca. 10 ns) was detected, in contrast to the fact that we have observed a time delay of ca. 100 ns in a liquid paraffin solution at room temperature. This fact may suggest that the stable complex is already formed in the ground state. However, the shape of the fluorescence excitation spectra at various temperatures is practically the same as that of the solution at room temperature, where the complex is not formed in the ground state. Accordingly, although the charge transfer interaction in the ground state is very weak, there may be donor-acceptor pairs with such a small distance between them that they can form the heteropolar excimer immediately after excitation.

When aniline, naphthylamines, *N*-methylaniline, and *N*, *N*-dimethylbenzylamine are used as electron donors in a solution at room temperature, contrary to the case where DMA, DMT's, and DMNA's are used as electron donors, we cannot observe any heteropolar excimer fluorescence, but only a quenching of the aromatic hydrocarbon fluorescence. Although the mechanism of this quenching is not very clear at the present stage of the investigation, it seems quite plausible that a charge transfer interaction in the encounter complex, followed by some very efficient, radiationless transition, plays an important role in these cases. Accordingly, if we can stabilize the complex in a rigid matrix at low temperature in order to decrease the probability of the radiationless transition, it might be possible to observe the heteropolar excimer fluorescence even in these cases.

Actually, we have observed the fluorescence spectra of heteropolar excimers of pyrene complexed with *N*, *N*-dimethylbenzylamine, aniline, and *N*-methylaniline at ca. 450—470 mμ in the cyclohexane matrix at low temperatures. However, in the case of these complexes, the fluorescence yield is much smaller than in the case of complexes of pyrene with DMA and DMT's. That is, even at low temperatures in the rigid matrix, the radiationless process is quite predominant in the former complexes compared with that in the latter ones.

More detailed studies, including studies of other heteropolar excimers, will be published in the near future.

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[1] N. Mataga, K. Ezumi and T. Okada, *Mol. Phys.*, **10**, 201 (1966); N. Mataga, T. Okada and K. Ezumi, ibid., **10**, 203 (1966); International Conf. on Luminescence, Budapest, 1966; N. Mataga and K. Ezumi, This Bulletin, to be published.