Radiative and Radiationless Processes in Phthalazine[*1]

Hiroaki Baba, Iwao Yamazaki and Takeshi Takemura
Division of Chemistry, Research Institute of Applied Electricity, Hokkaido University, Sapporo

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Although nitrogen heterocyclic compounds generally exhibit strong phosphorescence, *ortho*-diazines such as pyridazine, phthalazine, and 9,10-diazaphenanthrene are known to show either no phosphorescence or very weak phosphorescence. The problem of such puzzling emission properties of the *ortho*-diazines has attracted much attention,[1-4] but remains unsettled. With phthalazine, no emission has been reported, except for a phosphorescence emission in an acidic solution,[5] where the protonation may give rise to an essential change in its emission property. We have recently examined both the radiative and radiationless processes in phthalazine at 77°K. It was found that phthalazine gave no emission in hydrocarbon solvents, but in polar solvents like EPA it did exhibit phosphorescence. In all these cases we were unable to obtain fluorescence from phthalazine.

The phosphorescence spectrum in EPA is shown in Fig. 1, together with the excitation spectrum (corrected). The latter spectrum is seen to be in agreement with the absorption spectrum within experimental errors, indicating that the phosphorescence originates from phthalazine itself. A polarization measurement was made by the photoselection method, with the result that the transition moment of the phosphorescence is parallel to the moment of the 0–0 band of the $^1A \rightarrow {}^1L_b$ absorption; namely, the phosphorescence is polarized along the long axis of the molecule. The lifetime and quantum yield of the phosphorescence were determined to be 0.7 sec and 0.04, respectively.

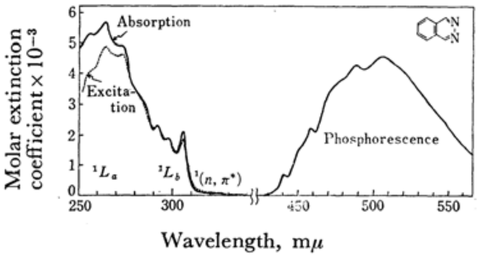

Fig. 1. Phosphorescence, excitation, and absorption spectra of phthalazine in EPA at 77°K.

The radiationless processes in phthalazine were investigated through the phenomenon of the intermolecular T–T energy transfer, with phthalazine as the donor and naphthalene as the acceptor. The solubility of phthalazine in the pure hydrocarbon was so low that a mixture of ether and isopentane (1 : 1) was used as the solvent. In this mixture phthalazine was found to give a phosphorescence emission with a quantum yield of 0.008. The donor(1×10^{-3} M)-acceptor(3.3×10^{-2} M) system was excited at 330 mμ in the region of the $n \rightarrow \pi^*$ absorption of the donor, where the absorption of the acceptor was negligible. An effective energy transfer occurred which led to the sensitized phosphorescence of naphthalene. The overall quantum yield of the acceptor phosphorescence (relative to the donor excitation) amounted to about 0.07. This figure implies that the donor molecule has a considerably high intersystem crossing yield (>0.7), since for naphthalene the ratio of the radiationless triplet-decay rate constant to the radiative constant is known to be large (>10).[1]

These observations lead to the following suggestions. (1) The lack of fluorescence in phthalazine is caused by an efficient intersystem crossing process. (2) The vanishing or low phosphorescence quantum yield of phthalazine results from an anomalously high radiationless rate constant as compared with the radiative rate constant for the $T_1 \rightarrow S_0$ transition. Details of the experiments and further discussions will be presented in a paper to be published later.

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