Intersystem Crossing Quantum Yields of Phthalazine and Pyridazine[1]

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The quantum yields of $S_1 \rightarrow T_1$ intersystem crossing have been determined for phthalazine and pyridazine in EPA at 77°K by using the technique of T–T energy transfer. Phthalazine and pyridazine were used as the energy donor, and naphthalene-h_8 and naphthalene-d_8 as energy acceptor. The intersystem crossing quantum yields were found to be 0.49 for phthalazine and 0.24 for pyridazine. These values lead to the conclusion that the weakness or lack of phosphorescence in the compounds is due to an anomalously high rate of the radiationless transition from their phosphorescent triplet state as compared with the rate of the corresponding radiative transition.

The radiative and radiationless processes in nitrogen heterocyclic compounds have been studied extensively.[2–11] Although most of these compounds show strong phosphorescence, *ortho*-diazines such as pyridazine, phthalazine, and 9,10-diazaphenanthrene show either only very weak phosphorescence or none at all. Several attempts have been made to explain this phenomenon. El-Sayed proposed that the rate of $S_1 \rightarrow T_1$ intersystem crossing is low in pyridazine because the $^3(\pi,\pi^*)$ state lies above the lowest $^1(n,\pi^*)$ state and the only path for the intersystem crossing is $^1(n,\pi^*) \rightarrow {}^3(n,\pi^*)$, which should be slower than $^1(n,\pi^*) \rightarrow {}^3(\pi,\pi^*)$ by a factor of 10^3.[6] Cohen and Goodman attributed the lack of phosphorescence in pyridazine to an efficient intersystem crossing process from the phosphorescent triplet state to a low-lying excited singlet state.[7] Hochstrasser and Marzzacco suggested that the lack of phosphorescence is due to the fact that the $T_1 \rightarrow S_0$ radiationless process is much faster than the radiative one.[8] Thus, despite widespread interest the problem remains unsettled, little quantitative information being available concerning the radiationless transition.

We found recently that phthalazine gives no emission in hydrocarbon solvents, but it phosphoresces with a moderate intensity in polar solvents such as EPA.[2,3] It was suggested in addition that phthalazine has a high intersystem crossing quantum yield.[2]

With a view to elucidating the mechanism of excitation-energy relaxation in *ortho*-diazines, we measured quantitatively the intersystem crossing quantum yields of phthalazine and pyridazine in EPA rigid glass solution at 77°K, using the technique of T–T energy transfer.[12] Phthalazine and pyridazine were used as energy donor, and naphthalene-h_8 and naphthalene-d_8 as energy acceptor.

Experimental

Phthalazine (Aldrich Chemical Co.) was recrystallized from diethyl ether and then sublimed under reduced pressure. Pyridazine was purified by vacuum distillation. Naphthalene-h_8 and -d_8 (the latter was obtained from Merck, Sharp & Dohme of Canada) were purified by recrystallization or vacuum sublimation. Diethyl ether was carefully purified after the method described by Kanda and Shimada.[13] Isopentane was passed through a silica-gel column. Spectrograde ethyl alcohol was used without further purification. EPA (5:5:2 parts by volume of diethyl ether, isopentane and ethyl alcohol) was used as solvent. All the sample solutions were degassed by repeated freeze-thaw cycles.

Phosphorescence spectra were measured at 77°K with a Hitachi MPF-2A fluorescence spectrophotometer, equipped with a phosphoroscope.

The phosphorescence spectra were corrected for the spectral sensitivity of the system of monochromator and photomultiplier, using quinine sulfate in 1 N sulfuric acid and β-naphthol in acetic acid-sodium acetate buffer solution as standards.[14] The phosphorescence quantum yield of phthalazine was found to be 0.04 in a previous study,[3] and the quantum yields of naphthalene-h_8 and -d_8 were determined by comparing the corrected phosphorescence spectra of these compounds with the spectrum of phthalazine. In all systems of phthalazine-naphthalene-h_8 and -naphthalene-d_8, and pyridazine-naphthalene-d_8, excitation was carried out at 340 nm, where only the donor molecules show absorption.

Procedures

Intermolecular triplet-triplet excitation energy transfer is known to take place in systems where the energy levels of the lowest excited singlet state S_1^D and lowest triplet state T_1^D of the donor are bracketed by the same two levels of the acceptor, as illustrated in Fig. 1.

The present procedures for determining intersystem crossing quantum yields are based on the phenomenon of T–T energy transfer in rigid-glass solution. The following assumptions have been made: (1) The solute molecules are uniformly distributed in rigid-

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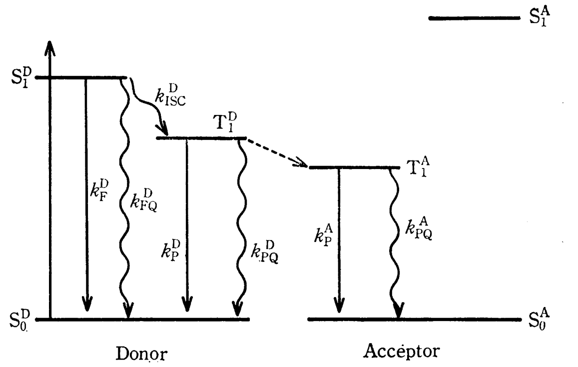

Fig. 1. Energy level scheme for triplet-triplet energy transfer experiment. The symbols k attached to the arrows are the rate constants of the corresponding processes. Solid straight-line arrows represent radiative processes corresponding to absorption or emission of light. Wiggly and dashed lines denote non-radiative and energy transfer processes, respectively.

glass solution. (2) All the unimolecular rate constants defined for the donor and acceptor (Fig. 1) are not affected by the presence of their respective partners, acceptor and donor. (3) The energy transfer from donor to acceptor occurs only through the path $T_1{}^D \rightarrow T_1{}^A$. These assumptions are generally recognized to be valid under the usual conditions.

In this study, two procedures A and B were employed according to two different cases; one where the emission can be observed from both donor and acceptor (Case A), and the other where the donor emission cannot be observed (Case B).

Procedure A. This is applicable only to Case A. A quantity called the quantum yield of sensitized phosphorescence γ_{SP} is available. The quantity was defined by Ermolaev[12] as

$$\gamma_{sp} = \frac{\Phi_{sp}^A}{\Phi_{PO}^D - \Phi_P^D} \tag{1}$$

where Φ_{SP}^A is the quantum yield of the sensitized phosphorescence of the acceptor, and Φ_{PO}^D and Φ_P^D are the quantum yields of the phosphorescence of the donor in the absence and in the presence of the acceptor, respectively. γ_{SP} can be obtained directly from the experiment. Equation (1) can be rewritten as[12]

$$\gamma_{sp} = \frac{\Phi_{ISC}^D}{\Phi_{PO}^D} \cdot \theta_P^A \tag{2}$$

with

$$\theta_P^A = \frac{\Phi_P^A}{\Phi_{ISC}^A} = \frac{k_P^A}{k_P^A + k_{PQ}^A} \tag{3}$$

where Φ_{ISC}^D and Φ_{ISC}^A are the intersystem crossing quantum yields of the donor and acceptor, respectively; Φ_{ISC}^D, for example, is given by

$$\Phi_{ISC}^D = k_{ISC}^D / (k_F^D + k_{FQ}^D + k_{ISC}^D)$$

Φ_P^A is the quantum yield of the phosphorescence of the acceptor, and θ_P^A represents the fraction of triplet molecules which phosphoresce.

Thus, if γ_{SP}, Φ_{PO}^D, and θ_P^A are known, Φ_{ISC}^D can be calculated from Eq. (2).

Procedure B. This is applicable to Cases A and B. If T–T energy transfer is assumed to be caused by the exchange mechanism, Φ_{SP}^A can be written in the form[12]

$$\Phi_{sp}^A = \Phi_{ISC}^D [1 - \exp(-VNC)] \theta_P^A \tag{4}$$

where V is the volume of the sphere of action of quenching, N the Avogadro number, and C the concentration of acceptor. It should be noted that $\exp(-VNC)$ represents the probability that there is no acceptor molecule in the volume V about an excited donor molecule, so that $\Phi_P^D / \Phi_{PO}^D = \exp(-VNC)$.

Differentiation of Φ_{SP}^A with respect to C leads to the form $d\Phi_{SP}^A / dC = \Phi_{ISC}^D \theta_P^A VN \exp(-VNC)$. Thus, we obtain

$$\ln(d\Phi_{sp}^A / dC) = \ln(\Phi_{ISC}^D \theta_P^A VN) - VNC \tag{5}$$

If Φ_{SP}^A as a function of C and θ_P^A are known, Φ_{ISC}^D and V can be obtained from a linear plot of $\ln(d\Phi_{SP}^A / dC)$ *vs.* C.

Results and Discussion

In order to determine the intersystem crossing quantum yield of phthalazine and pyridazine, we used these diazines as energy donor, and naphthalene-h_8

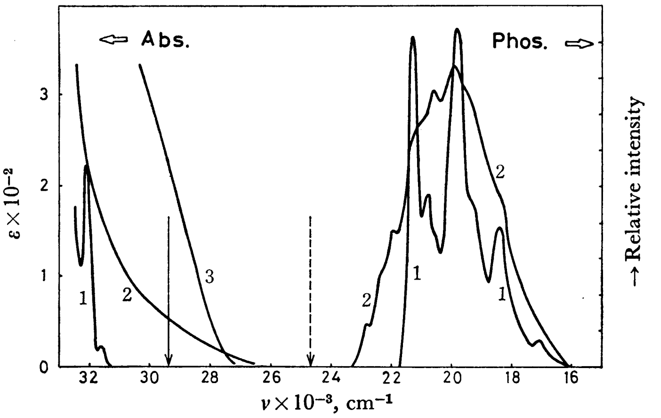

Fig. 2. Absorption and phosphorescence spectra of phthalazine and naphthalene-h_8, and absorption spectrum of pyridazine in EPA at 77°K. The phosphorescence spectra are uncorrected for the spectral sensitivity. 1, 2 and 3 represent naphthalne-h_8, phthalazine and pyridazine, respectively.

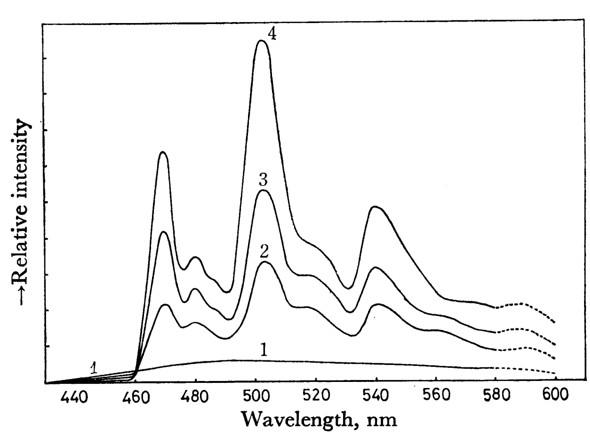

Fig. 3. Changes in the phosphorescence spectrum of phthalazine-naphthalene-d_8 system in EPA at 77°K caused by increase of the concentration of naphthalene-d_8. The concentrations of naphthalene-d_8: 1, 0; 2, 2.5×10^{-2}; 3, 5×10^{-2}; 4, 1×10^{-1} mol/l. The intensity of the phosphorescence spectra represents the relative quanta per unit wavelength interval.

Table 1. Intersystem crossing quantum yields of phthalazine and pyridazine

Donor	Acceptor	Procedure	Φ^{D}_{ISC}
Phthalazine	Naphthalene-h_8	A	0.45 ± 0.05
Phthalazine	Naphthalene-d_8	A	0.50 ± 0.05
Phthalazine	Naphthalene-h_8	B	0.51 ± 0.05
Phthalazine	Naphthalene-d_8	B	0.48 ± 0.05
Pyridazine	Naphthalene-d_8	B	0.24 ± 0.05

and naphthalene-d_8 as energy acceptor. The absorption and phosphorescence spectra of phthalazine and naphthalene-h_8, and the absorption spectrum of pyridazine are shown in Fig. 2. The excitation frequency adopted throughout the T–T energy transfer experiments is indicated by a solid arrow, and the estimated position of electronic origin in the T_1 state of pyridazine by a dashed arrow. All the donor-acceptor combinations chosen satisfy the optimum conditions for the experiment of intermolecular T–T energy transfer.

Intersystem Crossing Quantum Yield of Phthalazine. The changes in the phosphorescence spectrum of phthalazine-naphthalene-d_8 system in EPA at 77°K caused by the increase in amount of naphthalene-d_8 are shown in Fig. 3. In the absence of phthalazine, no phosphorescence was observed from naphthalene-d_8 upon excitation at the frequency mentioned above. The spectral changes are therefore regarded as due solely to T–T energy transfer.

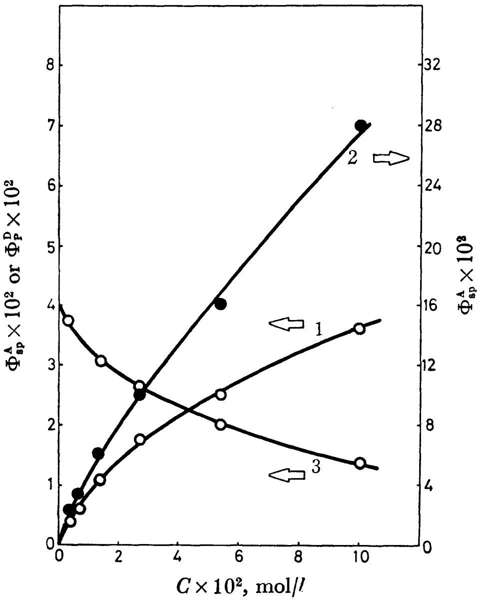

Fig. 4. Quantum yields of the sensitized phosphorescence Φ^{A}_{sp} of the acceptor, naphthalene-h_8 (1) or naphthalene-d_8 (2), as a function of the acceptor concentration C, and phosphorescence quantum yield Φ^{D}_{p} of the donor, phthalazine (3) as a function of C with naphthalene-d_8 as acceptor.

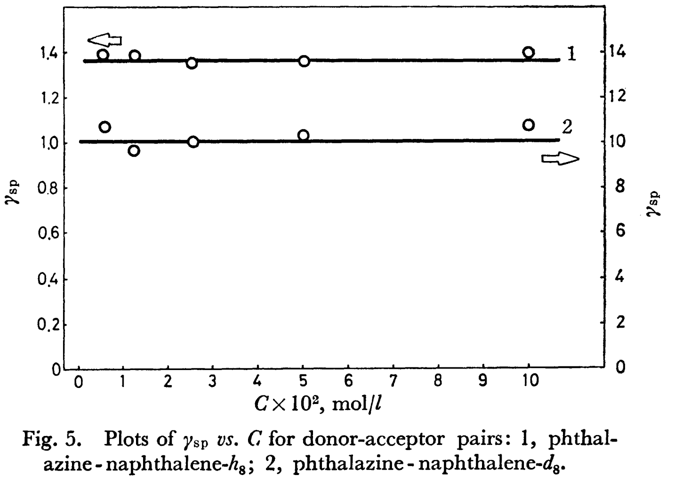

Fig. 5. Plots of γ_{sp} *vs.* C for donor-acceptor pairs: 1, phthalazine-naphthalene-h_8; 2, phthalazine-naphthalene-d_8.

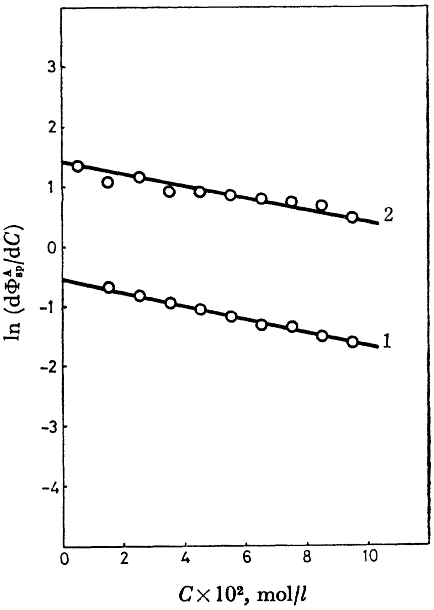

Fig. 6. Plots of ln(dΦ^{A}_{sp}/dC) vs. C for donor-acceptor pairs: 1, phthalazine-naphthalene-h_8; 2, phthalazine-naphthalene-d_8.

The sensitized phosphorescence quantum yield Φ^{A}_{sp} of the acceptor, naphthalene-h_8 or naphthalene-d_8, as a function of C is shown in Fig. 4. A plot of the donor phosphorescence quantum yield *vs.* C with naphthalene-

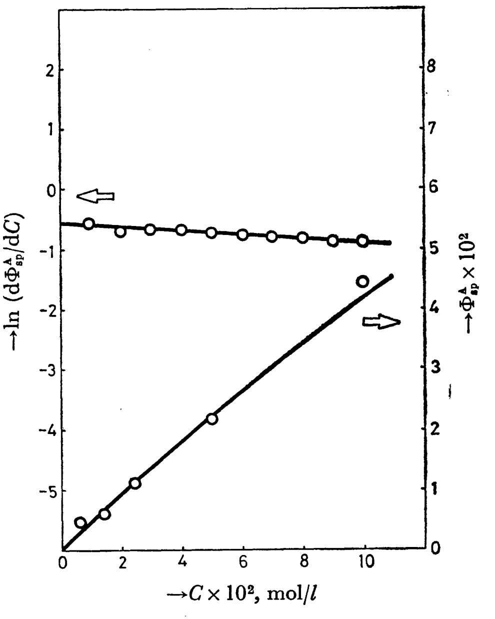

Fig. 7. Plots of Φ^{A}_{sp} and ln(dΦ^{A}_{sp}/dC) *vs.* C for pyridazine-naphthalne-d_8 system.

d_8 as acceptor is also shown. Almost the same plot was obtained when naphthalene-h_8 was used as acceptor.

The sensitized phosphorescence quantum yields γ_{SP}, defined in Eq. (1), were calculated from the above data. Figure 5 shows plots of the resulting γ_{SP} values against the concentration of acceptor, C. As expected, γ_{SP} is independent of C, indicating the validity of the present treatment of the T–T energy transfer.

In EPA at 77°K, the phosphorescence quantum yield of phthalazine (Φ^D_{PO}) is known to be 0.04.[3] We found the phosphorescence quantum yields of naphthalene-h_8 and -d_8 to be 0.03 and 0.20, respectively. It has been reported that the intersystem crossing quantum yield is 0.25 for both naphthalene-h_8 and -d_8.[15] By using these values and the γ_{SP} values shown in Fig. 5, we determined the intersystem crossing quantum yield of phthalazine, Φ^D_{ISC}, in EPA at 77°K. The results are shown in Table 1.

On the other hand, $\ln(d\Phi^A_{SP}/dC)$ was plotted against C (Fig. 6). Analysis of the resulting straight lines by Eq. (5) also gives Φ^D_{ISC} (Table 1). The radius R of the sphere of action, defined by $V=(4\pi/3)R^3$, is found to be 15.8 Å.

From Table 1 we see that the Φ^D_{ISC} values for phthalazine obtained by Procedures A and B and with the use of naphthalene-h_8 and -d_8 agree within the limit of experimental error; the average value of Φ^D_{ISD} is 0.49. Also, the value of R, 15.8 Å, is seen to be reasonable in reference to the R values reported in the literature[12] for analogous donor-acceptor pairs involved in T–T energy transfer in rigid-glass solution, indicating that the excitation transfer occurs by the exchange mechanism.[12]

Intersystem Crossing Quantum Yield of Pyridazine. Although the lowest triplet state T_1 of pyridazine is not known, it should be of (n,π^*) type by the analogy of other monocyclic diazines. Then, the 0-0 band of the phosphorescence spectrum, if it appears at all, would be situated at about 400 nm (*cf.* Fig. 2).[7] Thus, with pyridazine as an energy donor, naphthalene can be chosen as an acceptor, as in the case of phthalazine. Because of the lack of phosphorescence, only Procedure B can be used for pyridazine.

The relation of Φ^A_{SP} to C for pyridazine-naphthalene-d_8 system is shown in Fig. 7, together with the relation of $\ln(d\Phi^A_{SP}/dC)$ to C. From these data and Eq. (5), $\Phi^D_{ISC}=0.24\pm0.05$ and $R=10$ Å are obtained immediately. This Φ^D_{ISC} value for pyridazine in EPA at 77°K is essentially the same as that reported by Cohen and Goodman,[7] although their value (0.2) was obtained from a photochemical measurement in fluid solution at room temperature. In addition, the R value mentioned above agrees with values in other analogous donor-acceptor systems.[12]

Thus, all the results obtained show that the excitation energy transfer from pyridazine to naphthalene-d_8 occurring under our experimental conditions is attributable to the exchange mechanism as in the case of phthalazine-naphthalene system.

Deactivation Path of Excitation Energy in Phthalazine and Pyridazine. The experimental results (Table 1) indicate that a fairly efficient intersystem crossing occurs between $S_1{}^D$ and $T_1{}^D$ to populate the $T_1{}^D$ state in both phthalazine and pyridazine. The quantum yields of intersystem crossing in these *ortho*-diazines do not differ essentially from those of other diazines such as pyrazine, pyrimidine and quinoxaline. We are thus led to the conclusion that the deactivation of the excited *ortho*-diazine molecules occurs to a good extent *via* their phosphorescent triplet state, and that the weakness or lack of phosphorescence in the *ortho*-diazines is due to an anomalously fast rate of the radiationless transition from the triplet state.

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