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Intersystem Crossing of Radical Pair in Solvent Cage. External Heavy Atom Effect on Dual Photoreactions of Phthalazine[1)]

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The effects of the temperature, initial concentration, and chemical quenchers on dual photoreactions of phthalazine were investigated. The results give further supporting evidence for a previously proposed reaction mechanism, i.e., phthalazine in the lowest excited singlet and triplet states affords singlet and triplet radical pairs, respectively, in the initial hydrogen abstraction process from 2-propanol. The singlet radical pair gives a reduction product in a solvent cage, whereas the radicals produced in the triplet state escape from the solvent cage, causing dimerization. On the basis of the reaction mechanism of dual photoreactions, external heavy-atom effects on the radical pairs within a solvent cage have been studied. The results indicate that heavy-atom perturbations bring about an enhancement of the intersystem crossing efficiency from the triplet-state radical pair to the singlet one, including a spin inversion of the radical pair in the solvent cage, rather than $S_1 \rightarrow T_1$ intersystem crossing induced within a single molecule of phthalazine.

The spin multiplicities of a caged radical pair formed during the initial step of photochemical reactions govern the reactivities of the subsequent reactions of the radicals, affecting the product distribution. In general, singlet radical pairs undergo cage reactions efficiently, while triplet ones do so inefficiently.[2)] In the latter case, the triplet radical pairs must undergo a spin inversion to singlet radical pairs prior to cage reactions. Thus, the intersystem crossing of this type concerning radical pairs in a solvent cage competes with the escape of radicals from the cage.[3)] In this connection, the effects of an external magnetic field on caged reactions have been widely investigated.[2,4–6)] However, studies on the internal and external heavy-atom effects on the intersystem crossing process of a radical pair in a solvent cage have scarcely been reported. A 2-propanol solution of phthalazine may serve as a relevant reaction system for studying the above-mentioned effects.[7)]

In a previous paper[7)] we reported that phthalazine (P) simultaneously undergoes dual photoreactions to afford 1,2-dihydrophthalazine (**1**) and 1,1′,2,2′-tetrahydro-1,1′-biphthalazine (**2**) upon ultraviolet light irradiation in a 2-propanol solution. From the observed photochemical behavior and the phosphorescence characteristics under the influence of a quencher, sensitizer, and surfactant, the following reaction mechanism has been proposed. During the initial step of the dual photoreactions, phthalazine (P) abstracts a hydrogen atom from the 2-propanol(RH) used as a solvent to form a radical pair of the 1,2-dihydro-1-phthalazinyl radical (PH·) and the 1-hydroxy-1-methylethyl radical (R·) in a solvent cage. The resulting singlet radical pair ($^1[\mathrm{PH}\cdot+\mathrm{R}\cdot]$), derived from the lowest excited singlet state (S_1) of the substrate, participates in a subsequent hydrogen abstraction to produce **1** in a solvent cage. On the other hand, the same radical, PH·, derived from the lowest triplet state (T_1) of the substrate, escapes from the solvent cage, causing dimerization to afford product **2** (Scheme 1).

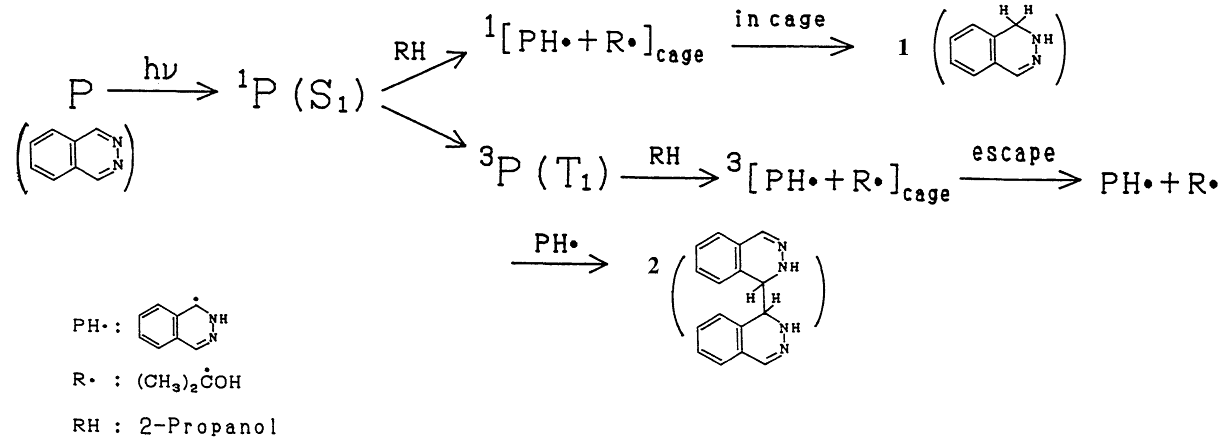
In the current work, studies of the temperature and initial concentration effects on the photochemical reactivities of phthalazine, and chemical quenching in 2-propanol, were carried out in order to obtain further supporting evidence concerning the reaction mechanism. On the basis of the reaction mechanism presented in Scheme 1, the observed external heavy-atom effects on the reactivities and phosphorescence are discussed, and an example of an intersystem crossing process that includes spin inversion from the triplet to the singlet radical pair within a solvent cage is presented.

Experimental

Materials. Phthalazine (Aldrich Chem. Co.) was purified by recrystallization from a mixture of benzene and hexane. 1,2-Dibromoethane and bromoform were purified by repeated fractional crystallizations. 2-Allylphenol and cinnamyl alcohol (Wako Pure Chemical Ind.) were used as received.

Measurements. The phosphorescence spectra were taken with a Shimadzu RF-500 spectrofluorimeter equipped with a cylindrical rotating sector at 77 K. The triplet lifetimes were determined with a previously described method in a mixture of ethanol and methanol (1:1 v/v) at 77 K.[8)]

Light Source and Irradiation. A 450 W high-pressure mercury lamp (Ushio UM-452) and a set of filters comprising a solution (1% K_2CO_3 aqueous solution containing 10^{-2} mol dm^{-3} K_2CrO_4) and a Corning glass filter (CS-7-54) were used for 313-nm light irradiation. A 70 W low-pressure mercury lamp (Ushio UL1-7SQ) and a solution filter ($NiSO_4$ 500 g dm^{-3}) were



Scheme 1.

used for 254-nm light irradiation. 2-Propanol solutions of phthalazine in a 5×10^{-2} dm^3 quartz cylindrical reaction cell were flushed with nitrogen passed through a pyrogallol solution and a silica-gel column both before and during irradiation. The temperatures of the reaction system were controlled by passing temperature-controlled water into a reaction cell with a jacket.

Actinometry and Analysis of Photoproducts. Actinometry was performed by using a potassium trioxalatoferrate(III) solution.[9] The amounts of the photoproducts were spectrophotometrically determined by the same manner described previously.[7]

Results and Discussion

Temperature and Concentration Dependence of the Dual Photoreactions. In addition to the results reported earlier, the effects of the temperature and initial substrate concentrations on the formations of products **1** and **2** have been examined in order to obtain a further confirmation of the mechanism of the dual photoreactions.

In Fig. 1, the concentrations of the produced **1** and **2** are plotted against the irradiation times for reactions at various temperatures. It can be seen from this figure that product **2** is formed in higher yields at higher temperatures, while the yield of **1** is not affected by the temperature.[10] In addition, the dependence of the reactivity on the initial substrate concentrations can be seen from Table 1. The quantum yield for the formation of **1** is not altered with a change in the concentration of phthalazine, while that for **2** increases with increasing concentration.

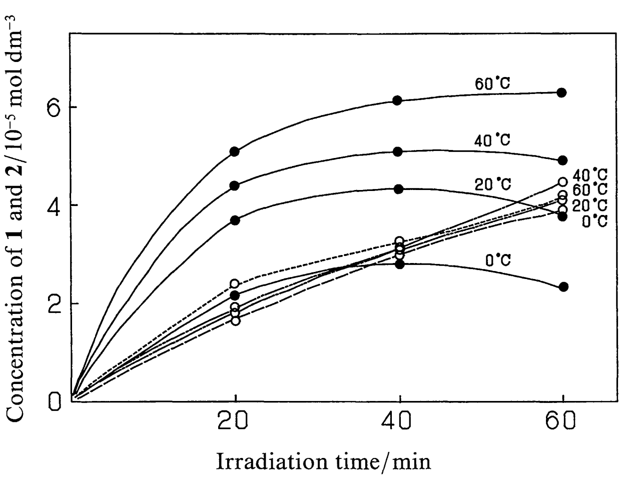


Fig. 1. Temperature dependence of the formations of **1** (○) and **2** (●). [Phthalazine]=4×10^{-4} mol dm^{-3}, Solvent: 2-Propanol, Excitation wavelength: 253.7 nm.

Table 1. Quantum Yield for the Formation of **1** (Φ_1) and **2** (Φ_2) at Room Temperature

[Phthalazine]/mol dm^{-3}	Φ_1	Φ_2	Φ_2/Φ_1
4×10^{-4}	0.010	0.041	4.1
5×10^{-3}	0.0095	0.069	7.2

These observed effects of the initial concentrations and temperature can be considered to give further supporting evidence for the reaction mechanism proposed earlier. That is, because the formation of **1** occurs in a solvent cage, which includes 1,2-dihydro-1-phthalazinyl radical (PH·) and alcohol radical (R·) produced in the initial hydrogen abstraction reaction, the yield of **1** may be influenced inefficiently by both the concentration and temperature. Moreover, from the temperature dependence, it is demonstrated that the efficiency of the escape process of the radicals from the solvent cage of the present system is not subjected to the effect of temperature in the range 0 to 60 °C.

On the contrary, the formation of **2** is susceptible to concentration and temperature effects, since it takes place in a bulk solution through encounters of 1,2-dihydro-1-phthalazinyl radicals escaping from the solvent cage.

Quenching for the Formation of 2 by Olefins. The in-cage (S$_1$) and out-of-cage (T$_1$) reaction mechanisms for

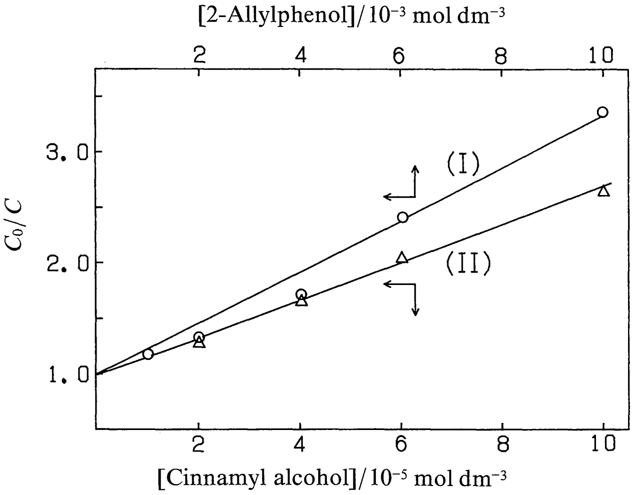


Fig. 2. Quenching for the formation of **2** by 2-allylphenol (I) and cinnamyl alcohol (II). [Phthalazine]=2×10^{-3} mol dm^{-3}, Solvent: 2-Propanol, Excitation wavelength: 313 nm. C_0 and C are the concentrations of **2** formed without and with the quenchers, respectively.

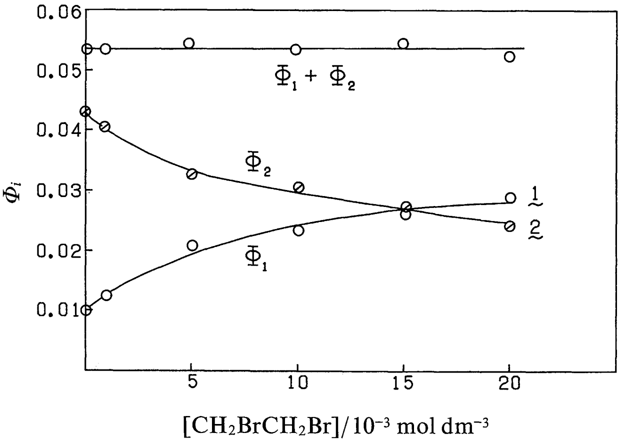


Fig. 3. External heavy-atom effect on the quantum yields by 1,2-dibromoethane. [Phthalazine]=4×10^{-4} mol dm^{-3}, Solvent: 2-Propanol, Excitation wavelength: 313 nm Φ_1: **1**, Φ_2: **2**.

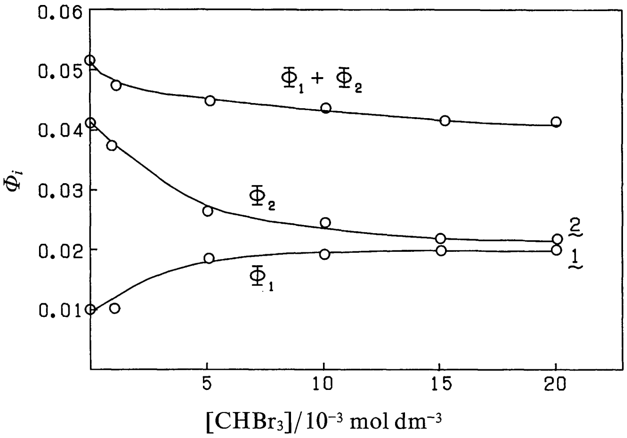
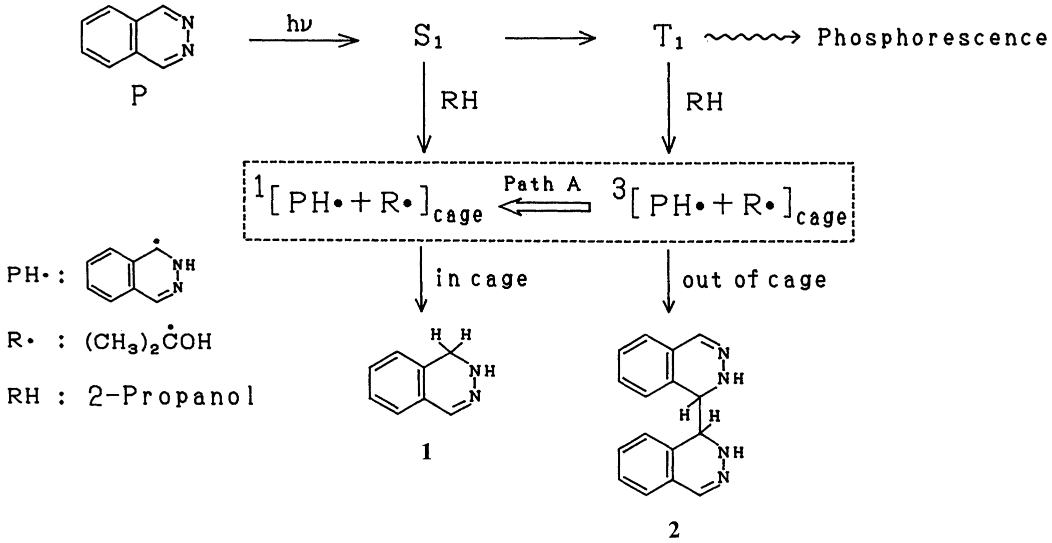


Fig. 4. External heavy-atom effect on the quantum yields by bromoform. [Phthalazine]=4×10^{-4} mol dm^{-3}, Solvent: 2-Propanol, Excitation wavelength: 313 nm Φ_1: **1**, Φ_2: **2**.

the respective **1** and **2** formations can also be demonstrated by the chemical quenching using olefinic compounds such as 2-allylphenol and cinnamyl alcohol. These compounds quench the formation of **2**, but not the formation of **1**. Stern-Volmer quenching plots are presented in Fig. 2. Since the lowest triplet energies of the above-mentioned compounds are not available, they have been estimated from their phosphorescence spectra as being 289 kJ mol^{-1} (69.2 kcal mol^{-1}) and 303 kJ mol^{-1} (72.4 kcal mol^{-1}) for 2-allylphenol and cinnamyl alcohol, respectively. These values are larger than the lowest triplet energy values of phthalazine (256 kJ mol^{-1}, 61.2 kcal mol^{-1});[11] thus, the observed quenching can not be regarded as being to a triplet–triplet energy transfer from phthalazine to the quenchers. In fact, the intensity of the phthalazine phosphorescence is not affected by these quenchers. Accordingly, the results can be explained as a sort of chemical quenching of the 1,2-dihydro-1-phthalazinyl radical by the olefinic compounds in a bulk solution. The absence of quenching for the formation of **1** is attributed to an in-cage reaction of this radical.

External Heavy Atom Effect. It has been found that the dual photoreactions of phthalazine are affected by added bromine-containing compounds, such as 1,2-dibromoethane and bromoform.[12] The quantum yields for the formations of **1** (Φ_1), **2** (Φ_2), and **1**+**2** ($\Phi_1+\Phi_2$) are plotted as a function of the concentrations of these bromo compounds in Figs. 3 and 4. The addition of bromo compounds brings about an increase in the yield of **1**, together with a decrease in the yield of **2**. This indicates that the efficiency of an intersystem crossing which is associated with the photoreactions is altered through an enhancement of the spin–orbit coupling. Moreover, it has been found that the emission intensity of phthalazine phosphorescence (with a maximum at 482 nm and a lifetime (τ=0.51 s) of the phosphorescent lowest triplet state at 77 K in a 1:1 mixture of ethanol and methanol) is not influenced by the addition of 2×10^{-2} mol dm^{-3} of the bromine compounds (1,2-dibromoethane: 0.49 s, bromoform: 0.56 s).

From the following considerations, the present observations can not be explained in terms of external heavy-atom effects on the $S_1\rightarrow T_1$ and the $T_1\rightarrow S_0$ intersystem crossing processes occurring in a single molecule of phthalazine. First, if the $S_1\rightarrow T_1$ intersystem crossing in an excited phthalazine molecule could be affected by heavy-atom perturbations, the addition of bromine compounds might lead to an increase in the yield of **2**, together with an enhancement of the phosphorescence intensity. This is clearly not the case for the present system. Second, the possible heavy-atom enhanced $T_1\rightarrow S_0$ intersystem crossing decay process of



Scheme 2.

triplet phthalazine can not be responsible for the observed variation in the photoreactivity. That is, although the observed change in Φ_2 may reflect the $T_1 \rightarrow S_0$ mechanism, the observed increase in Φ_1 can not be interpreted from this mechanism, which predicts no change for a reaction occurring prior to the $T_1 \rightarrow S_0$ intersystem crossing. Third, the constancy of the phosphorescence intensity and the lifetime indicates the absence of a heavy-atom induced variation in the efficiencies of the formation and decay of the T_1 species of the phthalazine molecule.

Consequently, we have reached the following conclusion on the basis of a spin-correlated reaction mechanism in which **1** is formed from a singlet radical pair within a solvent cage as well as the findings, described above. In the present photoreaction systems including bromine compounds, the observed change in the reactivity and phosphorescence characteristics of phthalazine can be reasonably ascribed to the enhancement of an intersystem crossing process, involving a radical pair within a solvent cage formed during the initial step of the dual photoreactions; no events occurred in a single phthalazine molecule. The spin inversion from the triplet state ($^3[\mathrm{PH}\cdot + \mathrm{R}\cdot]$) of the radical pair to the singlet one ($^1[\mathrm{PH}\cdot + \mathrm{R}\cdot]$) in a solvent cage is induced under the influence of a heavy-atom spin–orbit interaction. The proposed reaction pathways are illustrated according to Scheme 2. In this scheme Path A is the proposed spin inversion (intersystem crossing) of the radical pair within the solvent cage; it competes with the escape of radicals and a back reaction to the starting materials, phthalazine (P) and 2-propanol (RH). A similar spin inversion has been revealed in several photoreactions by studies on photoreactions under an external magnetic field.[1,3-5] In this case, however, the inversion of the spin state is dominated by electron-molecular hyperfine interactions. Few descriptions are available concerning the spin inversion resulting from a spin-orbit coupling in a radical pair. Turro et al.[4] reported that the bromine-substituted dibenzyl ketone showed an internal heavy-atom effect on intersystem crossing in its radical pair. Recently, Tanimoto et al.[13] have reported that the photolysis of 2-naphthylphenyldiazomethane involves a spin inversion in a radical pair within a solvent cage under an external magnetic field. Accordingly, the results presented here are examples of photochemical reactions in which heavy-atom perturbed intersystem crossing between the singlet and triplet states of the radical pair in the solvent cage plays an important role in the product distribution and reactivity. It, therefore, seems that in some cases the selective formation of a desired product from dual photochemical reactions involving different spin-correlated radical pairs may be attained by using a heavy-atom containing compound.

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