BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (3), 745—746 (1974)

Flash-Spectroscopic Study of Phthalazine1)

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(Received July 19, 1973)

Synopsis. The phthalazine triplet and the hydrogen-abstracted radical were obtained in ethanol *etc.* at room temperature, suggesting that the T_1 is of $n\pi^*$ type, whereas only the T–T absorption spectrum was obtained in acidic ethanol as reported in EPA glass at 77 K.

The lowest triplet states of hetero-cyclic aromatic compounds containing nitrogen are known to be mostly of the $\pi\pi^*$ type.2) Azobenzenes containing more than two nitrogen atoms, however, have been concluded to have the lowest excited triplet states of the $n\pi^*$ type from several spectroscopic studies on T←S transitions in gas phase as well as on phosphorescence in rigid glasses.3)

Hetero-polycyclic aromatic compounds containing nitrogen have also received much attention in connection with the assignment of the lowest excited singlet and triplet states.2) Phosphorescence and triplet-triplet (T–T) absorption studies2,4–8) of some hetero-polycyclic compounds in EPA glasses at 77 K have indicated that their lowest triplet states are of the $\pi\pi^*$ type at least in the 77 K EPA glasses. Phthalazine is one of typical examples in which a large interaction between two adjacent nitrogen atoms might cause the $^3n\pi^*$ state to be the lowest triplet. Recently, Baba *et al.*7) have concluded from phosphorescence and phosphorescence-polarization studies that the phosphorescent state of phthalazine should be of $^3B_2(\pi\pi^*)$ in EPA glass at 77 K. The $^3n\pi^*$ and $^3\pi\pi^*$ states of phthalazine are thought to be so close that the order of these two energy levels might be dependent on solvent and temperature. It is still unknown which state $^3n\pi^*$ or $^3\pi\pi^*$ is the lowest in solution at room temperature.

Since no flash photolysis studies have been reported for phthalazine in solution at room temperature, we have attempted to carry out flash photolysis experiments with a variety of solutions of phthalazine, with particular emphasis on studying the solvent effects of transient species.

Experimental

Flash experiments at room temperature were carried out with degassed solutions containing 10^{-4}—10^{-5} M phthalazine in ethanol, ether, *n*-hexane, benzene and acidic ethanol, 20 cm quartz cells being used. Low-temperature flash experiments were performed at 77 K in rigid glasses of a mixture of ether, isopentane and alcohol (EPA, 5: 5: 2) and a mixture of methylcyclohexane and isopentane (MP, 1: 1) with a 1 cm quartz cell immersed in liquid nitrogen. The flash spectroscopic apparatus used here was the same as that described previously.9) Phthalazine was purchased from Aldrich Chemical Co. and purified by vacuum sublimation. Ethanol, ether, isopentane, *n*-hexane and benzene were purified by usual methods.10)

Results and Discussion

The transient absorption spectra obtained by the flash photolysis of phthalazine (10^{-4}—10^{-5} M) in ethanol, ether, *n*-hexane and benzene at room temperature are shown by curves a—d in Fig. 1 and that obtained for an acidic ethanol solution of 1×10^{-2} M phthalazine by curve e. The transient absorptions were observed only under degassed condition immediately after flash, a considerable amount of photoproducts being finally obtained. Each transient spectrum shown in Fig. 1 was obtained by subtracting the spectrum measured a few minutes after flash from that immediately after flash. The shorter wavelength parts of the spectra shown by broken lines are suffered from the absorption of the phthalazine molecule in the ground state. Thus, the absorption intensity in this region is somewhat smaller than the true value.

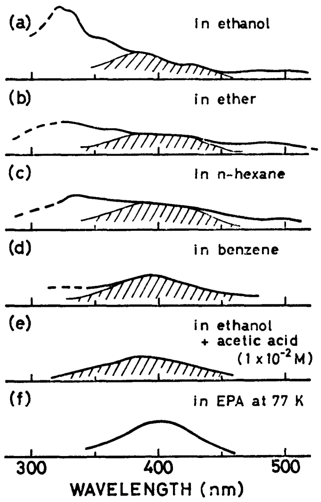

Fig. 1. Transient absorption spectra obtained for photoirradiated phthalazine. Curves a–e were obtained at room temperature under degassed condition with 20 cm quartz cells. Shaded portions indicate the absorption bands due to T-T transition. Concentrations of phthalazine: (a) 3×10^{-5}M; (b, c) 5×10^{-5}M; (d, e) 1×10^{-4}M. Curve f was obtained in EPA glass at 77 K, with a 1 cm quartz cell.

The flash photolysis of phthalazine in the EPA glass at 77 K gave rise to a transient spectrum shown by curve f in Fig. 1. In an MP glass at 77 K, the transient absorption was too weak to obtain a well-defined spectrum. The lifetime of the transient 390 nm band in the EPA glass was found to be roughly consistent with

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the available phosphorescence lifetime of phthalazine (0.4 s).[7] Furthermore, the transient spectrum (curve f in Fig. 1) is in good agreement with the T–T absorption spectrum recently obtained by Alvarez and Hadley[11] in a rigid matrix of *n*-butanol and isopentane at 77 K and by Yamazaki and Baba[12] with a laser flash technique in EPA at 77 K. Therefore, there may be no doubt that the 77 K spectrum obtained here is due to the T–T transition of phthalazine.

As seen from Fig. 1, the transient spectra obtained in benzene and acidic ethanol solutions (spectra d and e) seem to differ considerably from those in ethanol, ether and *n*-hexane (spectra a—c), and are similar to the T–T spectrum of phthalazine (curve f). Thus, spectra d and e may be mainly due to the phthalazine triplet. As revealed from its shape, spectrum d may have a minor contribution of another transient species.

The transient spectra obtained with the ethanol, ether and *n*-hexane solutions at room temperature (curves a—c in Fig. 1) indicate the existence at least two sorts of transient species. The absorption intensities in the range 380 to 450 nm are independent of the solvents used, whereas those in the two ranges 300—380 and 450—520 nm considerably depend on the solvents. According to the time-resolved spectrophotographs obtained in the present study, the 380—450 nm bands decay much faster than the 300—380 nm and 450—520 nm bands: The 380—450 nm bands were detected only within several μs, whereas the 300—380 and 450—520 nm bands were observed until about 100 μs. Therefore, we may conclude that there exists another transient species in ethanol, ether and *n*-hexane, in addition to the triplet phthalazine.

The order of the yield of the transient species with the bands at 300—380 nm and 450—520 nm is:

$$n\text{-hexane} < \text{ether} < \text{ethanol}$$

This order seems to be correlated with the hydrogen-donating ability of the solvents. By adding acetic acid (1×10^{-2} M) to the ethanol solution, the ability of hydrogen abstraction of phthalazine is expected to be reduced significantly, since the nature of its lowest triplet excited state is changed by protonation from the $n\pi^*$ type to the $\pi\pi^*$ one. (It should be mentioned that the absorption spectrum of the ground state phthalazine in an acidic ethanol solution containing more than 10^{-3} M acetic acid shows no absorption corresponding to the $n\pi^*$ band of the ethanol solution of phthalazine appearing at about 330 nm, although this fact gives no direct information as to the triplet-state energy levels.) The $n\pi^*$ state of phthalazine is considered to have a greater ability of hydrogen abstraction than the $\pi\pi^*$ state, as is well known with carbonyl compounds.[13,14]

The experimental facts presented here concerning the second transient species may be explained by considering that this species is ascribed to the 2-hydrophthalazyl radical. It is interesting to note that the transient bands appearing at 330 and 480 nm resemble those of the naphthalene anion radical showing absorption maxima at 370 and 450 nm.[15] This fact strongly supports the assignment of the second species to the 2-hydrophthalazyl radical, which is isoelectronic to the naphthalene anion in π-electron structure. Judging from the short lifetimes (a few μs) of the T–T bands observed in ethanol, ether, *n*-hexane and benzene at room temperature, we may conclude that the lowest triplet states of phthalazine are of the $n\pi^*$ type but the lowest $\pi\pi^*$ and $n\pi^*$ triplet states are close to each other and mix to a considerable extent.

The present authors wish to express their sincere thanks to Professor H. Baba and Dr. I. Yamazaki for their helpful discussions.

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