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Photodissociation in Molecular Crystals

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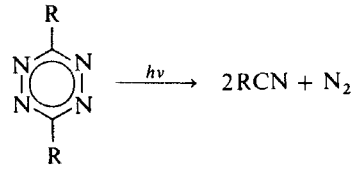
The photodissociation of s-tetrazine (ST) and its dimethyl derivative (DMST) is discussed. The presence of an intermediate in the dissociation process is inferred from the dependence of the photodissociation on exciting light intensity of ST and DMST as guests in molecular crystal hosts. The absorption spectrum of the intermediate is also described. These results illustrate the usefulness of studying photochemical reactions at low temperatures using high-resolution spectroscopic techniques.

In this paper the photodissociation of s-tetrazine (ST) and its dimethyl derivative (DMST) are considered. These molecules are known to dissociate in the following way:[1]



where R = —H(ST), —CH_3(DMST). It has generally been assumed that this reaction is concerted, that is that no intermediates are involved and that both ST and DMST dissociate upon excitation to their lowest excited singlet state (S_1) at about 5800 Å. As a result of the work to be discussed here, we will show that neither of these conclusions is correct and that the photodissociation process is more complicated than it at first seemed to be.[2]

The difference in reactivity between ST and DMST can be seen in Figure 1. Here the absorption spectra of hexane solutions of these two species are shown before and after irradiation into S_1. There is clearly no evidence of any photodissociation of DMST after 20 hours of irradiation, while ST

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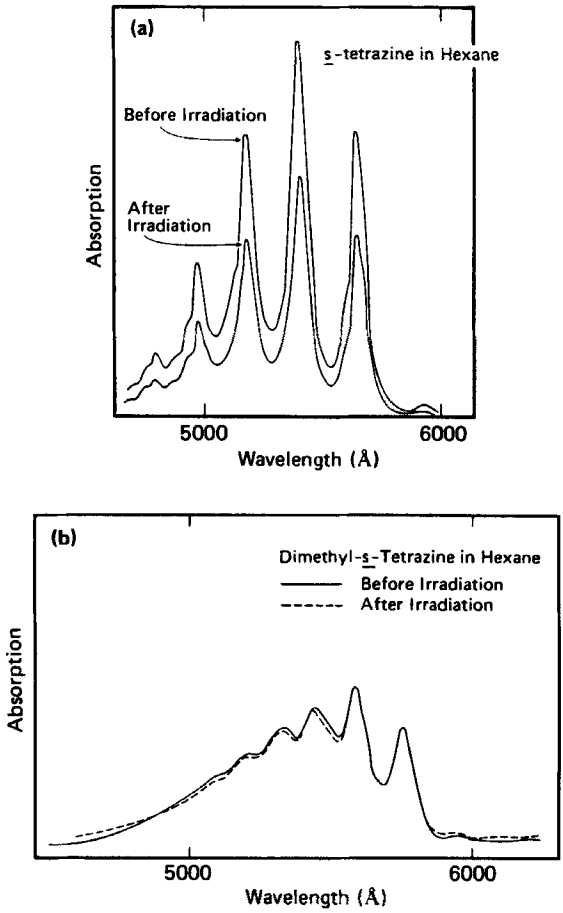

FIGURE 1 The solution photochemistry of the tetrazines. (a) The absorption spectra of ST in hexane before irradiation and after 18 hours of irradiation with a Xe lamp filtered so that $\lambda > 4500$ Å. (b) The absorption spectra of DMST before and after 20 hours of irradiation with the same filtered Xe lamp.

shows about 50% dissociation after 18 hours of irradiation. These studies imply that in hexane solutions the quantum yield of photodissociation for DMST is at least 10 times lower than that for ST. Both ST and DMST dissociate efficiently when excited into their second singlet using 2537 Å radiation from a low pressure Hg lamp.

Photodissociation of ST[3] and DMST[4] has definitely been observed when these molecules are imbedded in molecular crystal hosts at 2 K. This raises the interesting problem of reconciling the room temperature solution results

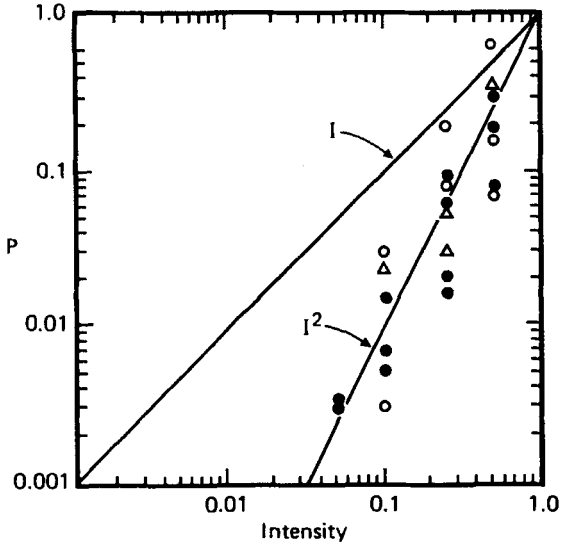

FIGURE 2 The extent of photodissociation P vs. exciting light intensity. P is proportional to the fraction of tetrazine molecules dissociated per unit time and is measured by monitoring the decrease in tetrazine absorption intensity upon irradiation. P is normalized to unity for the maximum light intensity used in each experiment. ○ = DMST in durene at 2 K. Pulsed dye laser excitation into lowest singlet at 5875 Å. △ = DMST in *p*-xylene at 2 K. Pulsed dye laser excitation into lowest singlet at 5882 Å. ● = ST in benzene at 2 K. Pulsed dye laser excitation into lowest singlet at 5802 Å.

that show DMST to be relatively photochemically inert with the low temperature results that indicate that both ST and DMST are photochemically active. To investigate this problem, we have looked at the exciting light intensity dependence of the photochemistry of ST and DMST in various host molecular crystals at temperatures below 10 K. These results are summarized in Figures 2 and 3.

In Figure 2, we see that the low temperature photodissociation of both DMST and ST depends quadratically on the exciting light intensity.[2] This we interpret as evidence of a two photon photodissociation process. The first absorbed photon creates an excited intermediate state that subsequently absorbs a second laser photon and dissociates.

In Figure 3, we see the intensity dependence for UV exciting light of ST photodissociation in hexane solution at room temperature and in a benzene crystal at 2 K. The photodissociation is linear at room temperature but quadratic in the low temperature crystal host. These results indicate that the intermediate that absorbs the second photon is not the lowest singlet state (S_1) of the tetrazine molecule. If it were the S_1 state, then the dissociative state reached by two photon absorption could be reached directly by a single

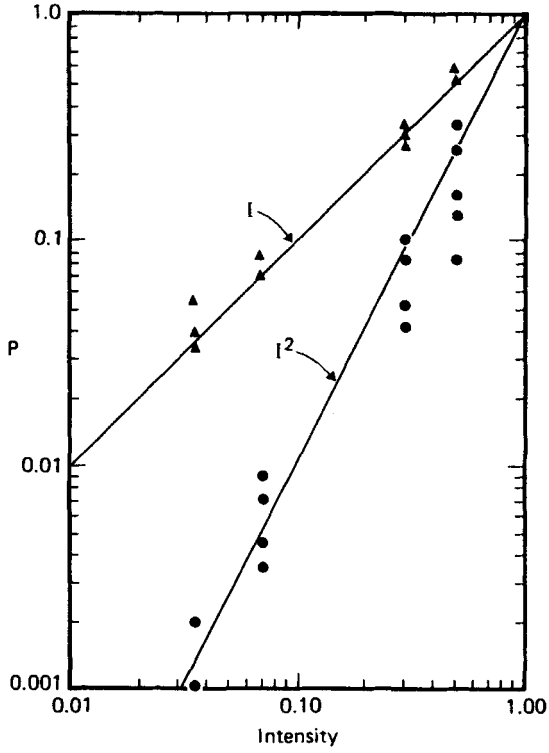

FIGURE 3 The extent of photodissociation P vs. exciting light intensity. ▲ = 10^{-4} M solution of ST in hexane at room temperature using 2537 Å Hg lamp excitation. ● = ST in benzene at 2 K. The pulsed dye laser excitation is at 2901 Å.

photon of twice the S_1 energy. Direct UV excitation of this higher state should then exhibit a linear intensity dependence.

These results led us to the conclusion that the ST and DMST photodissociation at low temperatures involves an intermediate state different from S_1. It is unlikely that this state is the lowest triplet state (T_1). Hochstrasser, *et al.*[1,5] have shown that excitation of the ST singlet state does not result in significant production of the lowest triplet state. It seems more likely that this intermediate is a different chemical species formed from the tetrazines and that the tetrazine photodissociation is thus not a concerted single step process as previously assumed.

To confirm the presence of this hypothesized intermediate, we next looked for transient absorption occurring after excitation of DMST into S_1 with a N_2 pumped pulsed dye laser. In Figure 4, we see the observed transient absorption. The maximum occurs at a wavelength longer than 6100 Å (the

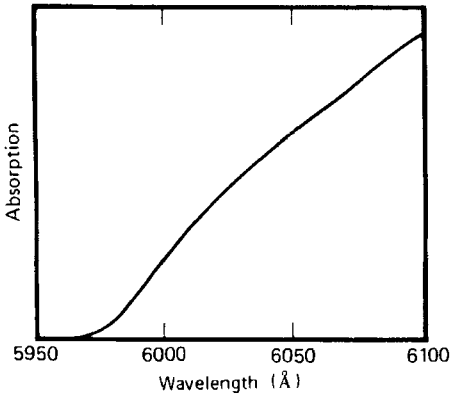

FIGURE 4 The transient absorption observed in a crystal of DMST in durene at 2 K. The DMST is excited at 5875 Å with a 6 nsec pulse. The absorption is recorded in a window that begins 100 nsec. after the pulse and is 10 msec. wide. The figure shows the difference between the transmitted light with and without laser excitation.

limit of the spectral sensitivity of our system). Dellinger, *et al.*[6] have also recently observed transient absorption in this wavelength region upon excitation of various tetrazines to S_2.[7]

The model for the photodissociation of the tetrazines that emerges from this work can be summarized as follows: at low temperatures in crystalline matrices both ST and DMST dissociate in a two-step fashion. In the first step, a photon is absorbed producing the tetrazine S_1 state. This state subsequently decays to an intermediate. The intermediate then absorbs a second photon and dissociates. In solution at room temperature this intermediate for ST is presumably thermally unstable and can dissociate without the assistance of a second photon.

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7. Intermediates have also been observed in the IR spectrum of DMST in an Ar matrix at temperatures below 20 K (J. Pacansky, unpublished result).