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FORMATION AND REACTIONS OF THE TRIPLET STATE OF *SYM*-TRIAZINE IN SOLUTION STUDIED BY LASER SPECTROSCOPY

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The laser photolysis of *sym*-triazine optically excited at 265 nm was studied in acetonitrile, cyclohexane and isopropyl alcohol. The T-T absorption spectrum was observed with maxima at 245 and 303 nm and shoulders at ≈ 345 and ≈ 450 nm. It decays with a rate $k = (1.1 \pm 0.1) \times 10^6 \text{ s}^{-1}$ in acetonitrile solution. The triplet is assigned as (n, π^*) in character based on the efficient quenching by H-atom donors, e.g., cyclohexane and isopropyl alcohol ($k_q \approx (1 - 2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). The formation of the azyl radical and the corresponding solvent radicals from these reactions have been observed and identified.

We have recently reported the triplet-triplet absorption spectra, lifetimes, quantum yields and chemistry of the $^3(n, \pi^*)$ and $^3(\pi, \pi^*)$ states of various diazines in polar and non-polar solvents at room temperature. These included pyrazine [1] and pyrimidine, quinoxaline and phthalazine [2]. Efficient quenching of the $^3(n, \pi^*)$ states of pyrazine and pyrimidine by H-atom donors (e.g., isopropyl alcohol, cyclohexane) was observed with the formation of azyl radicals and the corresponding radical from the H-atom donor. The $^3(\pi, \pi^*)$ states of quinoxaline and phthalazine were quenched about 3 orders of magnitude more slowly by H-atom donors. These molecules were optically excited at 265 nm using a frequency quadrupled neodymium laser with single pulses of ≈ 15 ns duration. Below are presented the results obtained in the course of a similar study with *sym*-triazine.

The electronic spectra, (n, π^*) and (π, π^*) transitions and the energies of the excited singlet state, and triplet state of *sym*-triazine have been studied [3-8]. Efficient intersystem crossing to the triplet state was considered to take place and the lowest-lying state was shown to be $^3(n, \pi^*)$. Other physico-chemical properties of the triplet state of *sym*-triazine in solution do not appear to have been examined.

Details of the laser photolysis experimental apparatus used have been given elsewhere [9]. Optical

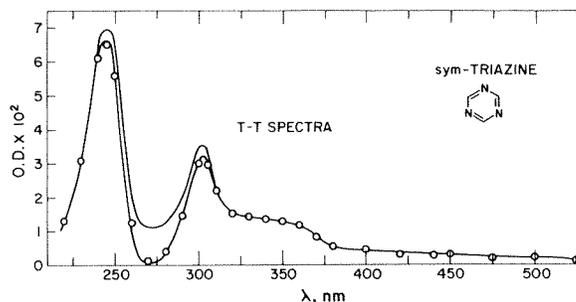


Fig. 1. Triplet-triplet absorption spectrum of *sym*-triazine (1.0 mM) in acetonitrile (1 atm argon). O.D. read at 20 ns, \circ , after the laser pulse. Full line corrected for ground state depletion of triazine based on complete quenching of the triplet state by isopropyl alcohol, and taking $\epsilon_{315} = 1.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ for the extinction coefficient of the triazine radical (see text).

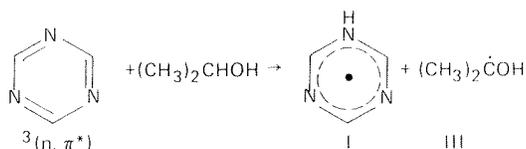
excitation at 265 nm of triazine (1.0 mM, Aldrich Chemicals) in dry spectrograde acetonitrile gave rise to a short-lived transient absorption, see fig. 1, with maxima at 245 and 303 nm and shoulders at ≈ 345 and ≈ 450 nm. This transient species decayed by a first-order process with $k = (1.1 \pm 0.1) \times 10^6 \text{ s}^{-1}$, and is assigned to the triplet-triplet absorption of $^3(n, \pi^*)$ *sym*-triazine (see more below).

Due to the instability of triazine in water, it was not possible to determine the complete T-T spectrum

based on $[O_2] = 2.3 \times 10^{-3}$ M in air-saturated neat cyclohexane.

The spectrum of the peroxy radical I is not known, but it is expected [11,12] to absorb at $\approx 250 \pm 10$ nm and have an extinction coefficient similar to that of $C_6H_{11}O_2^{\cdot}$.

Similar results were obtained on laser photolysis in neat isopropyl alcohol, fig. 2b. The $(CH_3)_2\dot{C}OH$ radical produced



(3)

has a relatively low extinction coefficient and a maximum at $\lambda < 220$ nm [12]. Therefore the maximum observed at $\lambda \approx 230$ nm is due mainly to the second absorption band of radical I. In the presence of oxygen, the $(CH_3)_2C(OH)O_2^{\cdot}$ radical is known [12] to have a maximum at ≈ 250 nm.

Based on the results obtained in neat cyclohexane and an $\epsilon_{315} = 1.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ for radical I, an $\epsilon_{245} \approx 6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ was derived for the T-T absorption of *sym*-triazine in acetonitrile (fig. 1).

The quantum yield for formation of radical I was determined based on anthracene as an actinometer — taking $\phi_{ISC} = 0.75$ for anthracene in cyclohexane solvent, and $\epsilon_{428} = 6.47 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for the T-T absorption. From this comparison a ϕ of 0.6 ± 0.1 and 0.4 ± 0.1 was derived for *sym*-triazine in neat cyclohexane and isopropyl alcohol, respectively. This yield should correspond to ϕ_{ISC} of *sym*-triazine. The lack of agreement between the values in the two solvents could be due to either (a) solvent dependence on ϕ_{ISC} , with the formation of different yields of ${}^3(n, \pi^*)$ state, and/or (b) to preferential quenching of the ${}^1(n, \pi^*)$ singlet excited state by cyclohexane. A difference in the ϵ values in the two solvents should also

be considered. The lifetime of the ${}^1(n, \pi^*)$ state of triazine is not known precisely, but is considered to be ≤ 1 ns.

In conclusion, these results show that the triplet states of aromatic nitrogen heterocyclic compounds (and probably the singlet excited states) can be efficiently quenched by H-atom donors (and probably by electron donors [2]) provided the transition is (n, π^*) in character. Quenching of (π, π^*) states by H-atom donors also takes place but at a much lower rate, and hence the decay of these excited singlet and triplet states cannot compete effectively on a kinetic basis. It is of interest to point out that substituted *sym*-triazines are used as pesticides [13], and the effect of light on them is of some importance.

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