

TRIPLET-STATE PROPERTIES OF *N,N*-DIMETHYLANILINE: LASER FLASH PHOTOLYSIS STUDY

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Summary

The laser flash photolysis of *N,N*-dimethylaniline in cyclohexane at 266 nm has been studied. The triplet-triplet absorption spectrum was determined: $\lambda_{\max} = 350$ nm and $\epsilon_{350} = 4800 \pm 500 \text{ M}^{-1} \text{ cm}^{-1}$; $\lambda_{\max} = 460$ nm and $\epsilon_{460} = 4000 \pm 400 \text{ M}^{-1} \text{ cm}^{-1}$. The triplet decays by second-order kinetics with a diffusion-controlled rate constant and a delayed fluorescence was observed at the same time. It was shown that this fluorescence arises from a triplet-triplet annihilation process. In methanol the triplet decays by a first-order process with a rate constant of $1.6 \times 10^6 \text{ s}^{-1}$.

1. Introduction

Photochemical reactions which involve aromatic amines as electron donors either in their excited or their ground states have been widely documented (for example, see ref. 1). These types of reactions are of interest from a practical point of view as they are model systems for solar energy conversion [2] and also because these amines are used as photoreactive materials [3]. Among the most widely used are *N,N*-dialkylanilines, and despite the large number of works on photoelectron transfer and exciplex formation processes, studies of their own primary photoprocesses are scarce.

In the case of *N,N*-dimethylaniline (DMA) the triplet-state properties have been studied by means of laser or conventional flash photolysis in the pure liquid [4] or in liquid paraffin [5]. The triplet-triplet absorption spectrum was reported to have maxima at 340 and 480 nm in the hydrocarbon solvent and a maximum at 465 nm in pure DMA. The lifetimes also differ considerably. $\tau_{1/2} = 250$ ns in pure DMA and $\tau_{1/2} \sim 100$ μs in liquid paraffin. The intersystem crossing quantum yield was estimated to be 0.95 in neat DMA [4] which together with a fluorescence quantum yield of 0.1 in cyclohexane [6] can be taken as an indication that the only singlet-

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state processes in non-polar solvents are fluorescence and intersystem crossing. The intermediates in the nanosecond pulse radiolysis of DMA in cyclohexane have also been studied [4, 7]. The triplet was found to absorb at 460 nm and a second more intense peak at 370 nm was attributed to the cyclohexadienyl radical formed by hydrogen atom addition to DMA [7].

Although all these studies corroborate the triplet absorption around 460 nm, the existence of a second band below 400 nm, which was also observed by Cadogan and Albrecht [8] at low temperatures, does not seem to be clearly established in fluid solutions.

One of the main objectives of the present laser flash photolysis study of DMA was to determine the triplet-state parameters in cyclohexane and to clarify the apparent contradictory reports concerning its absorption spectrum and decay kinetics. Some preliminary results in methanol are also presented.

2. Experimental details

DMA (Aldrich; purity, 99%) was used as received and kept under nitrogen. The solvents were of the highest purity commercially available (spectrophotometric grade) and were used without further purification. The computer-controlled laser flash photolysis system has been described previously [9]. The excitation at 266 nm was produced by a Nd-YAG laser (Quanta Ray) with frequency quadruplication. The laser pulse width was 6 ns. The exciting beam was defocused over the ground face of absorption cells of path length 2 mm in order to eliminate hot spots in the beam. The excitation was at 90° with respect to the analyzing beam. A photodiode was employed in conjunction with a beam splitter to measure the laser intensity. All the solutions were deaerated by purging with oxygen-free nitrogen or argon. The DMA concentrations were $(1 - 2) \times 10^{-4}$ M and the solutions were renewed after two or three laser shots. All measurements were carried out at room temperature.

3. Results and discussion

When DMA is laser-flash irradiated in cyclohexane at 266 nm a transient absorption is observed immediately following the pulse in the region 360 - 600 nm. At the same time a strong luminescence is observed below 350 nm. The decay time of this emission is 1 - 2 μ s and depends on the laser pulse intensity. When the luminescence is extinguished the absorption spectrum shows two peaks at 350 and 460 nm (Fig. 1). We attribute both bands to the triplet-triplet absorption on the following grounds. The observed decays at both wavelengths follow a second-order rate law with the rate constants

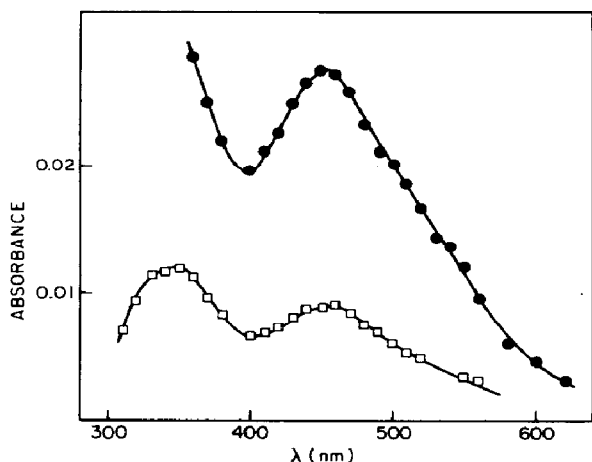


Fig. 1. Triplet-triplet absorption spectra of 10^{-4} M DMA in cyclohexane excited at 266 nm: —●—, 100 ns after the laser pulse; —□—, 6 μ s after the laser pulse.

$$\frac{k_2}{\epsilon_{460}} = (1.8 \pm 0.2) \times 10^6 \text{ s}^{-1} \text{ cm at 460 nm}$$

$$\frac{k_2}{\epsilon_{350}} = (1.4 \pm 0.15) \times 10^6 \text{ s}^{-1} \text{ cm at 350 nm}$$

Taking into account the differences in absorbance at the two wavelengths (Fig. 1), there is good agreement between the two rate constants. Cadogan and Albrecht [8] have also observed two bands in the triplet absorption spectrum of DMA in 3-methylpentane at 77 K at 340 and 460 nm, the 340 nm band being also the more intense but not exactly with the same relative intensity found in the present work. Nevertheless, considering the different experimental conditions the agreement with our results supports the hypothesis that the only absorbing species in the transient absorption spectrum is the triplet. Moreover, the quenching effect of piperylene was studied at both wavelengths and it was found that both absorptions were quenched with a diffusion-controlled rate constant.

From the initial slope of the plot of the triplet yield at 460 nm *versus* the laser intensity, the product $\phi^T \epsilon^T$ was determined, where ϕ^T is the intersystem crossing quantum yield and ϵ^T is the triplet extinction coefficient at 450 nm. Naphthalene in cyclohexane was used as an actinometer. Solutions with matched absorbances of DMA and actinometer were employed. The triplet yield of naphthalene was monitored at 414 nm with a spectral bandwidth of less than 1 nm. A triplet quantum yield and extinction coefficient of 0.75 and $24\,500 \text{ M}^{-1} \text{ cm}^{-1}$ respectively were used for naphthalene [10]. In this way a value of 3500 ± 400 was obtained for $\phi^T \epsilon^T$. From $\phi_F = 0.11$ in cyclohexane [6], and assuming $\phi_F + \phi_T = 1$ as found for many aromatic molecules, one obtains $\phi_T = 0.89$. Also, Land *et al.* [4] reported a value of 0.95 for ϕ_T in pure DMA, so a value of 0.9 for ϕ_T in cyclohexane seems very

reasonable. With this value and the relative absorbances at 5 μs after the flash (Fig. 1) the extinction coefficients $\epsilon_{460} = 4000 \pm 400$ and $\epsilon_{350} = 4800 \pm 500 \text{ M}^{-1} \text{ cm}^{-1}$ are obtained. With these extinction coefficients the second-order rate constant for the triplet decay becomes $(7 \pm 1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ which corresponds to a diffusion-controlled rate process in cyclohexane, as commonly found for triplet-triplet annihilation [11].

In Fig. 2 the time profile of the luminescence observed at 320 nm can be seen in the absence and the presence of $2 \times 10^{-4} \text{ M}$ piperylene. In the time scale of the experiment the point at the maximum intensity corresponds to 500 ns after the laser flash. By this time the prompt fluorescence of DMA ($\tau = 2.4 \text{ ns}$ [6]) has been completely extinguished. Since the decay is very much faster and the intensity decreases in the presence of the triplet quencher, the luminescence can be ascribed to a delayed P-type fluorescence arising in the triplet-triplet annihilation process. This is corroborated in Fig. 3 which shows the emission spectrum. This coincides with the fluorescence emission spectrum of DMA in cyclohexane [6]. Also apparent in Fig. 3 is a linear relationship between the delayed emission intensity and the square of the triplet absorption. This is typical of what can be expected for a delayed fluorescence arising from triplet-triplet annihilation [12].

No first-order component could be detected in the decay of the triplet under the present experimental conditions. Even at the lowest triplet con-

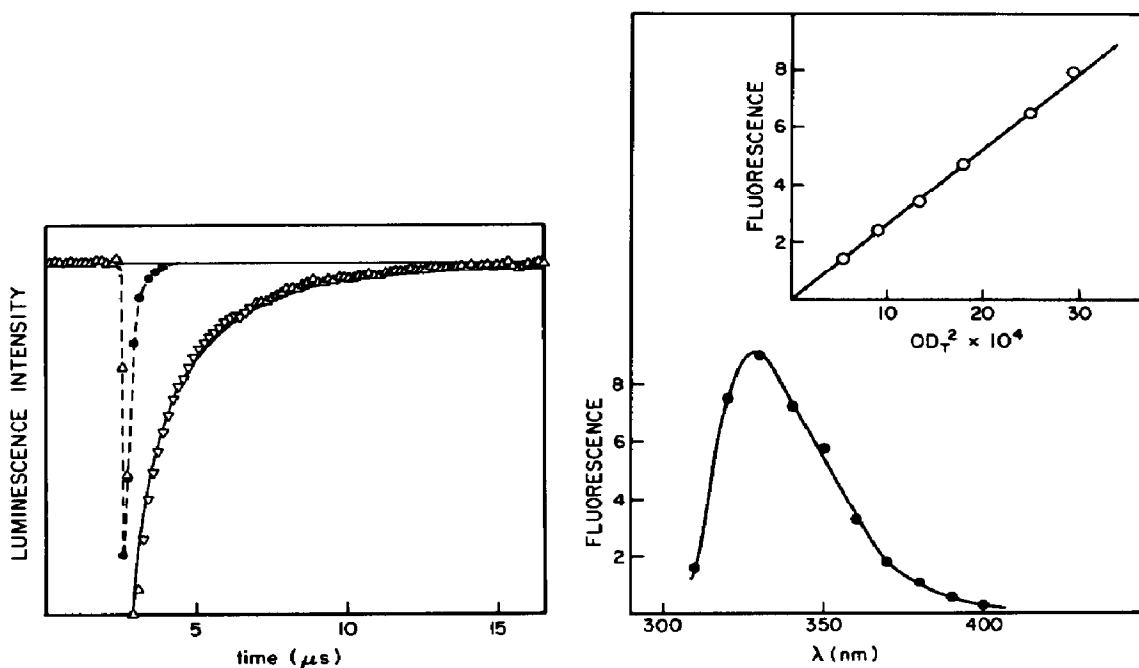


Fig. 2. Delayed fluorescence at 320 nm of 10^{-4} M DMA in cyclohexane after excitation at 266 nm in the absence ($-\triangle-$) and in the presence ($-\bullet-$) of $2 \times 10^{-4} \text{ M}$ piperylene.

Fig. 3. Delayed fluorescence emission spectrum. Inset: delayed emission intensity at 320 nm (arbitrary units) vs. the square of the triplet absorbance at 460 nm using consecutive laser pulses of equal energy.

centration the decay was pure second order. Under these conditions an upper limit for a possible first-order decay rate constant can be estimated as 10^4 s^{-1} . This is in contrast with a first-order constant of $2.7 \times 10^6 \text{ s}^{-1}$ observed by Land *et al.* [4] in pure DMA. In order to check if this faster decay is due to self-quenching or a more general solvent effect, we carried out laser flash experiments on DMA in methanol. A transient absorption was observed with $\lambda_{\text{max}} = 460 \text{ nm}$. During the first microseconds this absorption decays by first-order kinetics with a rate constant of $1.6 \times 10^6 \text{ s}^{-1}$. The intermediate is quenched by piperylene with a rate constant of $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. After the initial decay a long-lived absorption remains with a spectrum typical of the DMA radical cation [7]. The difference spectrum obtained by subtracting the absorbance at $5 \mu\text{s}$ after the flash from that after 200 ns is very similar to the triplet spectrum in cyclohexane. It can be concluded that in methanol the triplet decays by a fast first-order process. This fast decay is very unlikely to be due to impurity quenching, since in the same solvent other species with similar triplet energy levels decay much more slowly [13].

In addition, some experiments were carried out with 0.5 M DMA in methanol irradiated at 337.1 nm with a nitrogen laser. Under these conditions the initial absorption at 460 nm has a higher contribution from the radical cation, so the triplet decay was monitored in the region 520 - 540 nm, in which the absorption is mostly due to the triplet. Again the decay was first order with a rate constant of $3 \times 10^6 \text{ s}^{-1}$. This is a factor of 2 higher than the value for dilute solutions and the difference may be due to some self-quenching or impurities in the DMA.

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