

## A LASER FLASH PHOTOLYSIS STUDY OF 4-*N,N*-DIETHYLAMINO-AZOBENZENE IN SOLUTION: INFLUENCE OF EPOXY RESIN COMPONENTS

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(Received January 5, 1984; in revised form February 13, 1984)

### Summary

Laser flash photolysis of 4-*N,N*-diethylaminoazobenzene (DEAB) in propan-2-ol solution at 353 nm results in the conversion of the *trans*-DEAB to *cis*-DEAB. Neither epoxy resin of the bisphenol A type nor hardener of the polyamine type had any effect on this process, indicating that photoisomerization is the only significant event at this excitation wavelength. On excitation of the dye at 265 nm, photoisomerization is much less significant. When the bisphenol-type epoxy resin is excited at this wavelength, a triplet state is produced which is deactivated by oxygen and the azo dye. The potential involvement of all transient species observed in this study in the photofading of epoxy resins containing azo dyes is discussed.

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### 1. Introduction

The photoinduced fading of dyes in polymeric media is an area of study which has received much attention using steady state photolysis techniques [1 - 6]. More recently, flash photolysis studies of these systems have greatly facilitated the understanding of the mechanisms involved in photofading [7 - 9]. In earlier work, this fast reaction technique was used to investigate the photoreductive fading of anthraquinone dyes in epoxy resins based on bisphenol A [7]. This investigation was extended to azo dyes using conventional flash photolysis with a resolution of several hundred microseconds [8]. In that work hydrazyl free radical formation was observed and the yield under a variety of resin-hardener conditions showed a good correlation with

observed rates of photofading. In particular, the polyamine hardeners appeared to play an important role. In the present study, the azo dye 4-*N,N*-diethylaminoazobenzene (DEAB) is the object of a laser flash photolysis study where the time resolution is 15 ns. The aim is to identify any short-lived excited states and free radicals produced in the system and to determine their role in the photofading of the dye in the presence of epoxy resin and polyamine hardener. The light stability of dyes in epoxy resins is important because of their use in museum conservation work [1, 2].

## 2. Experimental details

DEAB was supplied by L. B. Holliday Co. Ltd. The epoxy resin AY105 is a diglycidyl ether of bisphenol A and was supplied by Ciba-Geigy (Plastics and Additives). The hardener XD716 is based on polyoxypropylenetriamine (Ciba-Geigy). Toluene and propan-2-ol were of AnalaR grade. Laser flash photolysis experiments were carried out using a neodymium laser (J. K. Lasers Ltd.) which delivered 15 ns pulses of either 265 or 353 nm radiation (approximately 100 mJ). Transient absorption changes were measured by illuminating the 1 cm path length quartz reaction cell with light from a pulsed xenon lamp. Wavelength selection was achieved with a diffraction grating high irradiance monochromator with 5 nm bandwidth. Kinetics changes in the light signal at preselected wavelengths were detected and amplified using a photomultiplier (RCA 1P28A) prior to collection by a storage oscilloscope.

## 3. Results and discussion

In the series of experiments discussed in this paper, both 265 and 353 nm laser radiation have been used to excite *trans*-DEAB in the presence of an epoxy resin (AY105, a diglycidyl ether of bisphenol A) and an amine hardener (XD716, polyoxypropylenetriamine) using toluene and propan-2-ol as solvents. In propan-2-ol solution, DEAB absorbs light maximally at 400 nm, the band being assigned to a singlet  $\pi, \pi^*$  transition [10]. This absorption was not affected by addition of the hardener XD716 but did undergo some change on addition of the resin AY105. Figure 1 shows that a small amount of resin ( $5 \text{ g l}^{-1}$ ) causes a reduction in absorbance at 400 nm with some concomitant increase in the region 330 - 370 nm. Such effects could not be emulated by addition of either acid (HCl) or base (NaOH) to a solution of the dye alone, showing that the resin is not acting as an acid or a base in the dye-resin system. It would appear therefore that there is some dark interaction between the dye and the resin.

Pulsed laser excitation of the dye alone at 353 nm produced the end-of-pulse difference absorption spectrum shown in Fig. 2. This shows a good resemblance to the ground state absorption spectrum which has its longest

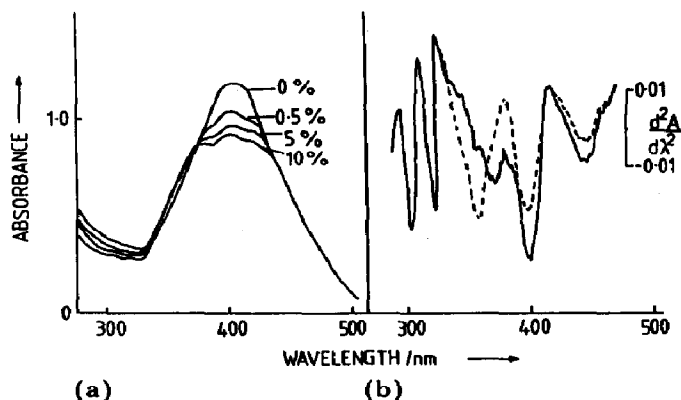


Fig. 1. (a) UV-visible absorption spectrum (zero order) of a DEAB-propan-2-ol solution containing 0%, 0.5%, 5.0% and 10% AY105 resin component; (b) second-order derivative spectrum of a DEAB-propan-2-ol solution with no AY105 resin component (—) and with  $5 \text{ g l}^{-1}$  AY105 resin component (---).

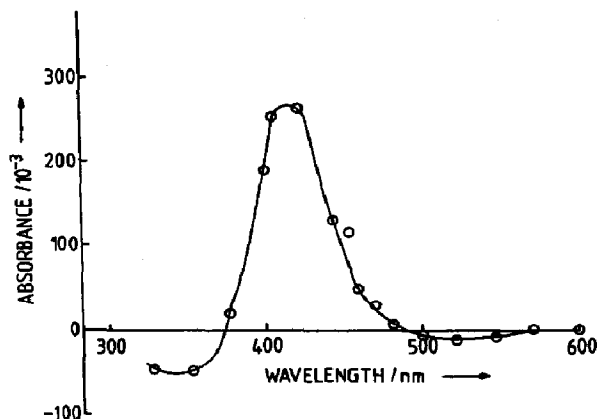


Fig. 2. End-of-pulse transient absorption spectrum for DEAB in nitrogen-saturated toluene solution (laser excitation wavelength, 353 nm).

wavelength absorption maximum at 410 nm. The figure also shows some bleaching of the dye in the region of 350 and 500 nm. It is known that *trans* azo dyes undergo photoisomerization to the *cis* form [10]. For the first  $\pi, \pi^*$  transition, the *cis* isomer is expected to absorb maximally at a slightly different wavelength (by about 5 nm) with a greatly enhanced extinction coefficient (a factor of 3 was found for azobenzene) [11, 12]. It thus seems likely that the transient spectrum shown in Fig. 2 can be assigned to the *cis* isomer of DEAB. In support of this, a repeat of this experiment, but this time in aerated solution, produced no difference in either spectrum or lifetime of the species, making an assignment to the dye triplet state unlikely. There was no appreciable loss of transient up to 100  $\mu\text{s}$  after the laser flash. Similar results were also obtained using toluene as solvent.

Addition of either epoxy resin (AY105) or polyamine hardener (XD716) had very little effect on the transient absorption spectra or transient lifetimes in either aerated or deaerated propan-2-ol or toluene

solution. A minor effect observed on addition of the epoxy resin was a 15% increase in the end-of-pulse transient spectrum compared with a similar experiment where no resin was present. This, however, can be attributed to changes in the absorbance of the solutions at the excitation wavelength as described earlier.

On excitation of DEAB in deaerated propan-2-ol solutions at 265 nm, the end-of-pulse transient spectrum shown in Fig. 3 was produced. The spectrum is characterized by a large bleaching in the 380 - 480 nm region and shows little evidence for *trans-cis* isomerization. In addition, there is some absorption in the regions 360 and 510 nm. At all wavelengths, there was little if any change in signal intensity up to 10  $\mu$ s after the pulse. At shorter time resolutions, *i.e.* within the laser pulse itself, a rapid depletion-emission could also be observed (Fig. 4). Separation of this signal from the signals at longer times after the laser pulse produced a depletion-emission spectrum in the range 360 - 440 nm. The dramatic effect of change in excitation wavelength from 353 to 265 nm must clearly be associated with the change in excitation energy to a second excited  $\pi, \pi^*$  state. In general, azo compounds show a marked reluctance to exhibit fluorescence and (particularly) phosphorescence [10]. However, DEAB was found to fluoresce ( $\lambda_{exc} = 270$  nm;  $\lambda_{em} = 320$  nm), although this may be attributed to an impurity emission. This does not appear to account for the rapid depletion-emission followed by some recovery which occurs during the laser pulse (Fig. 4) since the spectral characteristics are different. It may be therefore, since photoisomerization of diarylazo compounds should proceed readily after both  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  excitation (although the quantum efficiency is generally somewhat less for the latter) [10], that the recovery of transient absorption observed in Fig. 4 can be attributed to the photoisomerization process. This would imply that although photoisomerization of DEAB is a very fast process, *i.e.* still occurring within the laser pulse, it is nevertheless a slower process than that which leads to the original rapid depletion observed in Fig. 4. This interpretation of Fig. 4 would thus indicate that the end-of-pulse

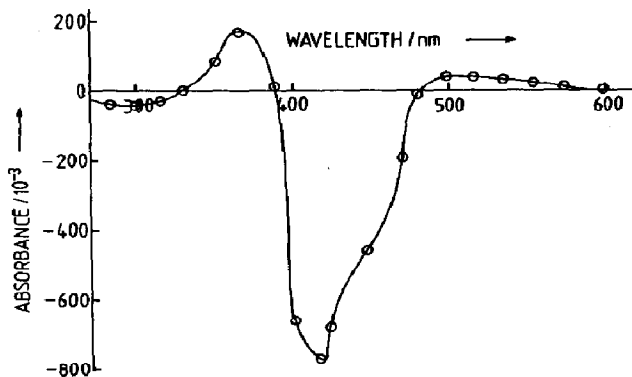


Fig. 3. End-of-pulse transient absorption spectrum for DEAB in nitrogen-saturated propan-2-ol solution (laser excitation wavelength, 265 nm).

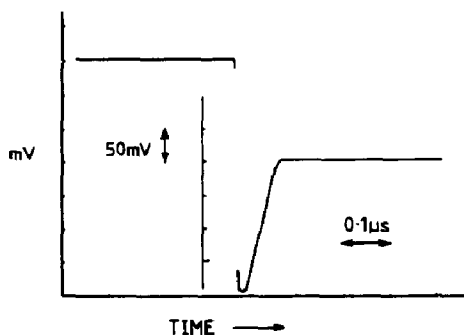


Fig. 4. Oscilloscope trace of emission from DEAB at 410 nm in nitrogen-saturated propan-2-ol solution ( $t_{1/2} \approx 20$  ns).

spectrum shown in Fig. 3 is a composite spectrum consisting of difference absorption spectra attributable to at least two species, one being the *cis* isomer of DEAB. Assignment of a structure to the other species must in this case be uncertain. However, there is very little evidence for the production of a triplet state of DEAB on excitation since a repeat of the experiment depicted in Fig. 3, but in aerated solutions, showed that the bulk of the transient spectrum was unaffected either in intensity or in lifetime. The small negative absorption at 300 nm, however, was replaced with a small positive absorption at the same wavelength. Other candidates are species arising from photocyclization and photoreduction processes [10]. Direct photoreduction of azobenzenes is still a controversial subject since their  $\pi, \pi^*$  triplet states have been predicted to have weak hydrogen abstraction ability [13]. Furthermore, there is little experimental evidence for a process in which an azobenzene excited state abstracts hydrogen atoms from, for example, propan-2-ol. If such a process does indeed occur, its quantum yield can be expected to be low (less than  $10^{-2}$ ) by comparison with the results of other studies [14]. This contrasts sharply with the ease of indirect photoreduction of azobenzenes brought about by, for example,  $\cdot\text{COOH}$  free radicals [15]. Other processes worthy of consideration in deaerated solution are those of photocyclization and production of diazenyl radicals. Photocyclization occurs readily for protonated or complexed azobenzenes where  $n, \pi^*$  states are effectively removed from the system [16]. Diazenyl radicals are produced on photolysis of mixed aliphatic-aromatic azo systems whereupon the nitrogen-alkane bond is cleaved [17]: diarylazo compounds show no tendency to take part in such a process [10]. A further possibility for the rapid depletion process shown in Fig. 4 is the production of an arylazophenyl free radical. This would necessitate photolytic cleavage of the C- $\text{N}(\text{Et})_2$  bond ( $\text{Et} \equiv$  ethyl), which appears to be unlikely and for the moment remains speculative.

On laser excitation at 265 nm of deaerated AY105 resin solutions, very broad characterless transient absorption spectra are observed in the region 300 - 600 nm (Fig. 5) most of which decay away within  $1 \mu\text{s}$  after the laser pulse. The absorption in the narrower region of 300 - 320 nm is longer lived

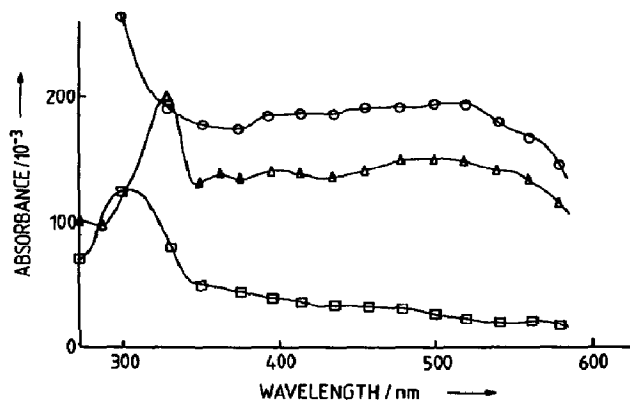


Fig. 5. Transient absorption spectrum for AY105 resin component in nitrogen-saturated propan-2-ol solution 0.2  $\mu$ s ( $\circ$ ), 0.3  $\mu$ s ( $\Delta$ ) and 3  $\mu$ s ( $\square$ ) after the pulse (laser excitation wavelength, 265 nm).

( $t_{1/2} = 3 \mu$ s). UV irradiation of bisphenol-based resins such as AY105 is expected to result in random chain scission to produce, amongst other species, phenoxy radicals ( $\sim \phi-O\cdot$ ). For simpler phenolic substrates, there is evidence that the triplet state is the precursor to phenoxy radical production [18 - 20]. In the case of tyrosine, the triplet-triplet absorption is very broad and ill defined in the region 300 - 700 nm [19] thus matching the spectrum of the species observed immediately after the laser flash in Fig. 5. Further support for the assignment of this absorption to the triplet state of phenol-based units in the resin comes from the similarity of the lifetimes of, for example, the tyrosine triplet state (a few microseconds) and the lifetime of the state producing the 300 - 700 nm band found in this work (Fig. 5). By comparison with earlier work [18], it is likely that this triplet state requires further excitation (*i.e.* a biphotonic process) to produce the phenoxy free radical. Only in alkaline solutions of simple phenols is a monophotonic process likely because of the greater ease of ionization of phenolates. In the case of the bisphenol-based resins which have no phenolic  $-OH$  groups, such a process must be viewed as being improbable. It would appear therefore that at steady state natural light intensities phenoxy radical production from this process is not likely. In the present laser flash photolysis study, however, where the intensity of light is very high, a biphotonic process is more likely. However, this would require the absorption of a 265 nm photon by the triplet state whereas in previous studies with conventional flash photolysis (10  $\mu$ s flash duration) a very much broader excitation from the flash-lamp was available [18]. Since a triplet state from the resin is seen clearly in the present experiments, it would appear that little, if any, has been excited further to produce a phenoxy-type radical. Consistent with this is the absence of any characteristic absorption due to phenoxy radicals ( $\lambda_{max} = 390 - 430$  nm) in Fig. 5. The band observed at 300 - 320 nm in Fig. 5 is therefore assigned to other free radicals produced by direct excitation of the resin, probably aromatic and carbon centred in nature.

In the presence of oxygen ( $10^{-3}$  mol dm $^{-3}$ ), the triplet state absorption described above was rapidly quenched (within 1  $\mu$ s) as expected. Similarly, concentrations of azo dye in the region of  $10^{-4}$  mol dm $^{-3}$  effectively quenched all the resin triplet state absorption within a few microseconds again producing little or no detectable absorption in the region 320 - 700 nm at the end of the "quenching" reaction.

#### 4. Conclusions

The effect of laser flash excitation of DEAB in either propan-2-ol or toluene solutions depends strongly on the wavelength of the laser radiation used. At 353 nm, it appears that *trans*  $\rightarrow$  *cis* photoisomerization would be the only significant event in solutions of DEAB itself or in solutions of DEAB containing epoxy resin or polyamine hardener. With 265 nm radiation, there is some indication that both photoisomerization and another process, possibly photolytic cleavage of the C-NEt $_2$  bond, occur. Photoisomerization appears to be somewhat slower than the other process, perhaps indicating that isomerization may take place from a longer-lived state (presumably a triplet state).

On laser flash excitation of the bisphenol-based epoxy resin at 265 nm, evidence has been given for triplet state formation from the bisphenol unit. Both dye and oxygen were found to quench it. There was no evidence for phenoxy free radical production. As with 353 nm excitation, the polyamine hardener appeared to play no role in the photolysis of the mixed systems.

A surprising feature of the present study was the absence of hydrazyl free radical formation. Hydrazyl free radicals are easily formed on reduction of azo dyes and have characteristic absorption spectra [15]. This presumably indicates that none of the reactive intermediates produced on photolysis of DEAB-resin-hardener systems has any significant reducing power. It would appear therefore that photofading processes in the DEAB-epoxy resin systems may be related to (i) photoisomerization, (ii) the fate of the triplet state derived from the bisphenol unit and (iii) possible cleavage of the C-NEt $_2$  bond producing arylazophenyl radicals. Although oxygen has a pronounced effect on the lifetime of the triplet state of the resin, oxygen was found to have no effect on the steady state fading of this azo dye-epoxy resin system [8]. This could indicate that neither the triplet state of the resin nor singlet oxygen is involved in the photofading process. Even if singlet oxygen is produced, it is likely to be physically quenched by the polyamine hardener. It is also unlikely that O $_2^{\cdot-}$  is involved in photofading since there is no evidence for concomitant phenoxy radical (or cation radical) formation. Finally, comparison of the results of this laser flash photolysis study with the previous conventional flash photolysis study produces some distinct differences, *i.e.* in the earlier study (i) the polyamine hardener was found to play a role in photofading and (ii) there was some evidence of hydrazyl radical production. It may be that both these differ-

ences can be related to excitation of the solvent, toluene, in the previous multiwavelength flash excitation study.

### Acknowledgment

One of us (J.P.B.) thanks the Science and Engineering Research Council for a research studentship.

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