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Low-temperature flash photolysis of 4-amino azobenzene and 4-dimethylamino azobenzene [1]

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Abstract

Using laser flash photolysis, the photoisomerization and *cis–trans* equilibrium relaxation of 4-amino azobenzene and 4-dimethylamino azobenzene was studied. At low temperature, *cis* conformers on photoexcitation produced *trans* conformers along with a fast-decaying intermediate absorbing in 450–490 nm region. These short-lived intermediates were assigned as their zwitterions.

Keywords: Laser flash photolysis; Photoisomerization; 4-Dimethylamino azobenzene; 4-Amino azobenzene

1. Introduction

Azo dyes isomerise readily on photoexcitation. The process of *trans* to *cis* isomerization takes place in two different routes. The $\pi\pi^*$ excitation favours rotational mechanism around azo linkage while the $n\pi^*$ excitation favours the inversion mechanism through one of the azo nitrogen [1,2]. However the dark process of *cis* to *trans* relaxation proceeds via inversion mechanism [3–6]. The azo compounds in which donor–acceptor groups are present, an intermediate zwitterionic species of quinonoid structure appears during *cis* to *trans* relaxation [7–11]. This tautomerization leaves one of the azo nitrogen out of conjugation favouring the inversion mechanism with much lower activation energy. In case of 4-amino azobenzene and 4-dimethylamino azobenzene, the activation energies of interconversion appear to be insensitive to the donor substituent group [1]. Hence it is interesting to know the behaviour of zwitterionic states in these compounds. The low-temperature laser flash photolysis studies have been taken to throw some light on this matter.

2. Experimental

The spectroscopic measurements have been done using Shimadzu spectrophotometer (model MPS-2000). The low-temperature accessories consisting of a glass dewar have been used for low-temperature absorption studies. The same dewar has also been used for laser flash photolysis work at low temperature. The sample temperature has been measured using copper–constantan thermocouple. The flash excitation is made by third harmonic of Nd:YAG laser (355 nm) model DCR-11, Spectra Physics, USA. The monitoring system consists of a 100 W tungsten halogen lamp as source and IP 28 photomultiplier as detector connected to a 100 MHz digital storage oscilloscope from Gould, UK. The details experimental set-up have been described elsewhere [12].

Solutions were used without removing oxygen because the removal of oxygen has no significant effect on the flash excitation spectra and decay kinetics. The 4-amino azobenzene and 4-dimethylamino azobenzene (SIGMA) have been used as obtained without further purification. The ethanol has been purified and dried using standard procedures.

3. Result and discussion

The absorption spectra of 4-amino and 4-dimethylamino azobenzenes in ethanol are shown in Fig. 1. At room temperature, the 4-amino azobenzene absorbs at 380 nm and the dimethyl derivative absorbs at 405 nm. With the lowering of temperature, absorption of both the compounds show red shifting. At −130°C, the absorption band of 4-amino azobenzene shifts to 410 nm (Fig. 1A) and that of the 4-dimethylamino azobenzene shifts to 425 nm with a hump at 450

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[1] Prof. M. Chowdhury on the occasion of his sixtieth birthday

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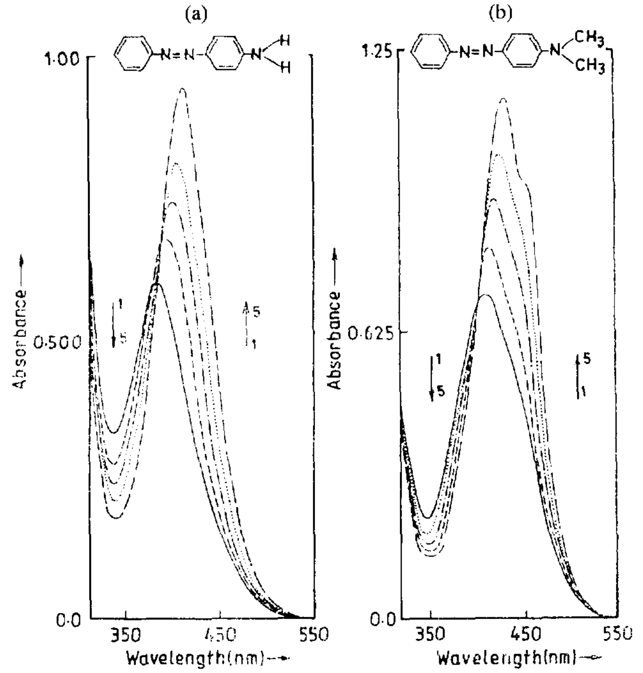

Fig. 1. Absorption spectra of (A) 4-amino azobenzene (1.5×10^{-5} M) in ethanol at (1) +25°C (———), (2) −10°C (- - -), (3) −50°C (– · –), (4) −90°C (· · ·) and (5) −130°C (– – –). (B) 4-dimethylamino azobenzene (2.1×10^{-5} M) in ethanol at (1) +25°C (———), (2) −10°C (- - -), (3) −60°C (– · –), (4) −90°C (· · ·) and (5) −130°C (– – –).

nm (Fig. 1B). The absorption bands become more intense at the expense of absorption at 330 nm and 350 nm respectively. The azobenzene derivatives are known to exist in equilibrium of *cis* and *trans* conformeric species. Though this equilibrium distribution is susceptible to the exposure of light, in the present case we did not find any appreciable change of optical densities during absorption studies allowing the light to fall for long time and on just exposure to the monitoring light. Between the two species *trans* and *cis*, the *trans* species are of low energy. The red shift of absorption band with lowering of temperature in both the cases might be related to the shift of equilibrium towards *trans* because *cis* conformer absorbs in the regions of 330–350 nm and 470–490 nm. Although the decrease of absorption is pronounced in the short wavelength region, but in the long wavelength region, it cannot be detected.

It is difficult to estimate the *cis–trans* ratio at different temperature, however attempt has been made in the following way where equilibrium has been expressed as

$$trans \rightleftharpoons cis$$

$$K=\frac{[cis]}{[trans]}=\frac{D_{\rm mx}-D_i}{D_i-D_{\rm mn}}=K_0e^{-H/RT_i} \quad (1)$$

where K is equilibrium constant and D_i's are observed optical densities. The parameters $D_{\rm mx}$ and $D_{\rm mn}$ are maximum and minimum optical densities in case of complete conversion to *trans* or *cis* forms. It has been assumed that $D_{\rm mn}$ is zero at 410 and 425 nm where *trans* form of 4-amino azobenzene and 4-dimethylamino azobenzene absorb strongly. With this approximation, Eq. (1) takes the form

$$\ln[(D_{\rm mx}-D_i)/D_i]=\ln K_0-(H/R)/T_i \quad (2)$$

For an input of $D_{\rm mx}$, the quantities $(D_{\rm mx}-D_i)/D_i$ in Eq. (2), are used to estimate ln K_0 and ($-$H/R). These estimated quantities are used to compute optical densities at different temperatures T_i. The minimum square deviation of computed and observed optical densities has been used to determine the best $D_{\rm mx}$. At 10 different temperatures in the range 25°C to −165°C, 10 different values of optical densities in the range of 0.428 to 1.110 at 410 nm of 1.50×10^{-5} M, 4-amino azobenzene and 0.607 to 1.20 at 425 nm of 2.10×10^{-5} M, 4-dimethylamino azobenzene are used to find the best parametric equations $(1.117-D_i)/D_i=26.82\exp(-855/T_i)$ and $(1.221-D_i)/D_i=9.82\exp(-682/T_i)$ for them, respectively. The neglect of absorption of *cis* form completely might be an overestimation of *trans* form. However these relations will give us an idea of relative change of *trans* form with temperature. The estimated percentage of *trans* form present in the solution used for laser flash have been shown in Table 1.

The laser flash excitation spectra of 4-amino and 4-dimethylamino azobenzenes at room temperature are shown in Fig. 2. The excitation wavelength is 355 nm obtained from the third harmonic of Nd:YAG laser beam. In the case of 4-

Table 1

4-amino azobenzene ($C=1.5\times10^{-5}$ M; $\lambda=380$ nm)			4-dimethylamino azobenzene ($C=2.1\times10^{-5}$ M; $\lambda=405$ nm)		
Temperature (°C)	% *trans*[a]	$k_{\rm eff}$ (s^{-1})	Temperature (°C)	% *trans*[a]	$k_{\rm eff}$ (s^{-1})
−25	54.00	0.527	−25	61.50	0.580
−50	63.30	0.570	−40	65.60	0.590
−70	71.60	0.612	−60	71.50	0.613
−90	80.00	0.643	−80	78.00	0.640
−110	87.60	0.682	−100	84.00	0.678
$E_a=-1.024$ KJ mol^{-1}			$E_a=-0.710$ KJ mol^{-1}		

[a] The method of calculation for percentage of *trans* form has been given in the text.

The expression for $k_{\rm eff}$ used in the table is $-({\rm d}/{\rm d}t)(\Delta D)=k_{\rm eff}(\Delta D)$, $k_{\rm eff}(T_i)=A\exp(-E_a/RT_i)$.

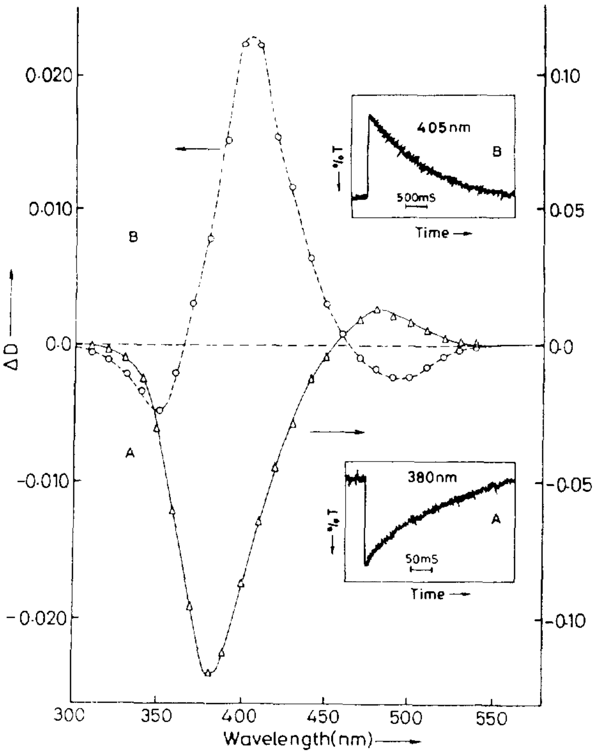

Fig. 2. Flash excitation (λ_{exc} = 355 nm) spectrum of (A) 4-amino azobenzene (1.5×10^{-5} M), (B) 4-dimethylamino azobenzene (2.1×10^{-5} M) in ethanol at 25°C. Inset: oscillograms (A) 4-amino azobenzene at 380 nm, (B) 4-dimethylamino azobenzene at 405 nm.

dimethylamino azobenzene, flash excitation spectra show the bleaching at 350 and 490 nm and absorption increment at 405 nm. The bleaching maxima at 350 nm and 490 nm correspond well with the absorption of *cis* conformer [1] and the increased absorption at 405 nm indicates that photoexcitation generates more *trans* species from *cis* conformers. In contrast, the flash excitation spectra of 4-amino azobenzene show bleaching at 380 nm and increased absorption at 480 nm. This is due to the fact that absorption spectra of 4-amino derivative as a whole is blue-shifted compared to that of the dimethyl derivative and the excitation beam of 355 nm excite *trans* form to generate more *cis* isomers.

With the lowering of temperature, absorption of both the compounds shift towards red (Fig. 1), hence the laser flash of 355 nm will be absorbed more by *cis* conformers than that by the *trans* conformer. The flash excitation spectra at −130°C of the 4-amino azobenzene in ethanol are shown in Fig. 3. The initial spectra within 10 μs show bleaching maxima at 490 nm, and absorption at 410 nm with a hump in the region of 440–480 nm. The time-resolved spectra show that the absorption at 410 nm grows at the expense of absorption in the 440–480 nm region. The initial bleaching maxima at 490 nm shifts to 480 nm with time. The shifting of bleaching maxima from 490 to 480 nm occurs due to fast decay of intermediate absorption appearing as hump in the 440–480 nm region. The 4-dimethylamino azobenzene shows the similar spectral behaviour on flash excitation at −130°C. In Fig. 4, the time resolved flash excitation spectra show the initial bleaching at 350 and 500 nm, and absorption at 425 with a hump extending from 450–490 nm. The decay of this absorption hump corresponds well with the growth of absorption at 425 nm. The fast decay of the absorption in the region of 450 to 490 nm causes the shifting of bleaching maxima from 500 to 490 nm.

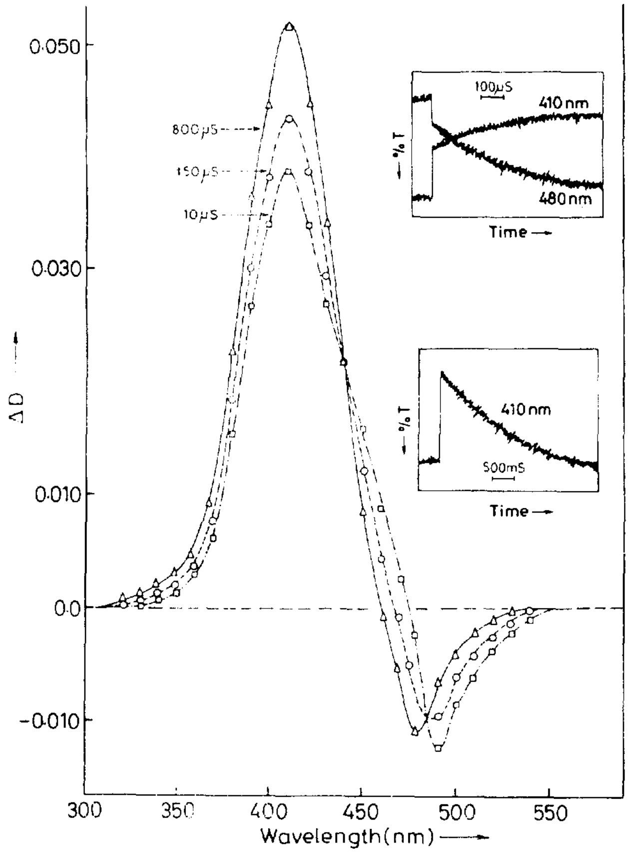

Fig. 3. Flash-excited spectra at −130°C 4-amino azobenzene (1.5×10^{-5} M) in ethanol glass at 10 μs (□), 150 μs (○) and 800 μs (△). Inset: oscillograms monitored at 410 nm and 480 nm.

The flash excitation spectra of both the compounds indicate that photoexcited *cis* conformers produce two species, one of which is *trans* conformer and another is a fast decaying intermediate with time changes to the long lived *trans* conformer. The zwitterionic species produced from azobenzene derivatives containing donor–acceptor couple show absorption in the region of 450–490 nm [8,10,11] and the hydrazo tautomer also absorbs in this region [12–14]. The fast-decaying intermediate absorbing in the region of 450–490 nm produced from either 4-amino or 4-dimethylamino azobenzene might be assigned as their zwitterionic forms.

The presence of only donor group of amino or dimethylamino might not be enough to stabilise the zwitterionic state to intervene the activation process of the *cis–trans* conversion. In azobenzene derivatives containing donor–acceptor couple, the activation energy is found to be much lower and zwitterionic species are present in equilibrium with other conformers.

The decay kinetics are found to be of first order. On flash excitation, the normal *cis–trans* equilibrium is disturbed and

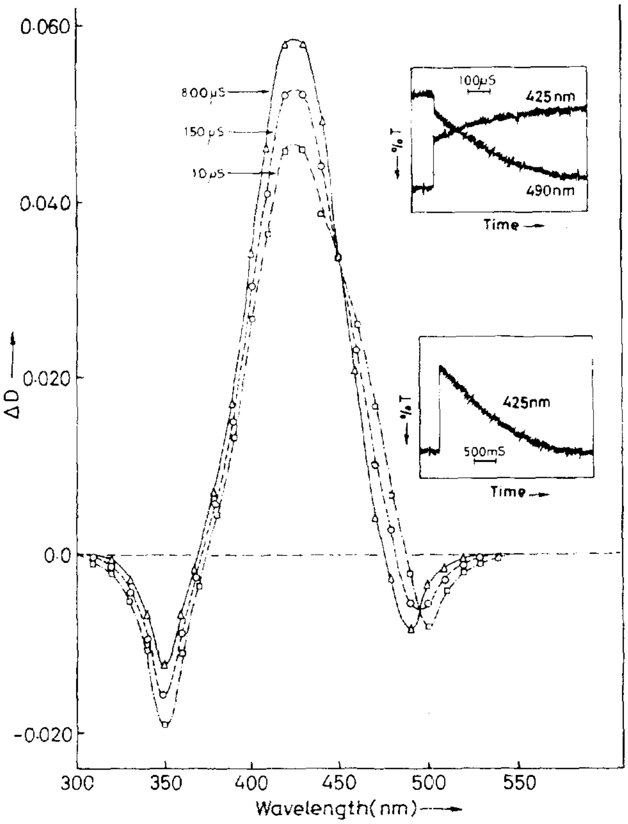

Fig. 4. Flash excited spectra at −130°C. 4-dimethylamino azobenzene (2.1×10^{-5} M) in ethanol glass at 10 μs (□), 150 μs (○) and 800 μs (△). Inset: oscillograms monitored at 425 nm and 490 nm.

the relaxation process is expected to follow first order kinetics. The effective rate constants of equilibrium restoration are listed in Table 1. The rate constants appear to increase slowly with the lowering of temperature. The negative activation energy (Table 1) indicate that relaxation process occurs in multiple steps where at least one of them is exergonic equilibrium step.

4. Conclusion

The activation energies of *cis–trans* interconversion of 4-amino and 4-dimethylamino azobenzenes are not different from the other azobenzene derivatives without donor group. Azobenzenes containing donor–acceptor couple show much lower activation energy due to participation of their zwitterions in activation process. In the present case, photoexcitation produces zwitterions, but their energy is not low enough to intervene the activation process.

Acknowledgements

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