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Azo–hydrazo tautomerization and cis–trans isomerization of 2-carboxy-2′-hydroxy-4′-methyl azobenzene

Manabendra Sahu, Manju Bikash Saha, Subhash Chandra Bera *

Department of Chemistry, Jadavpur University, Calcutta-700 032, India

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Abstract

2-Carboxy-2′-hydroxy-4′-methyl azobenzene in its trans configuration absorbs at 380 nm in isopropanol. In aqueous medium, it remains as the azo ($\lambda_{max}=355$ nm) and hydrazo ($\lambda_{max}=480$ nm) monoanions in equilibrium. The equilibrium process requires an enthalpy change of 26.8 kJ mol^{-1} in aqueous medium and 15.3 kJ mol^{-1} in an isopropanol–water (1:1) mixture. On photoexcitation, the trans isomer changes to the cis isomer which absorbs in the region 420–430 nm. The back conversion of the cis to trans isomer occurs via an intermediate hydrazo tautomeric monoanion. The rate-determining step of the conversion process depends on the amount of base present or the alkalinity of the system. The conversion of the cis isomer to the hydrazo monoanion and the equilibrium relaxation of the hydrazo monoanion to the trans isomer are competing reactions. In the absence of base, the cis to hydrazo conversion is slower than the equilibrium relaxation of the hydrazo to the trans form, while in the presence of base, it is faster.

Keywords: Tautomerization; cis–trans Isomerization

1. Introduction

In recent years, the cis–trans isomerization of azobenzene derivatives has received much attention. The normal ground state configuration of azobenzene derivatives is trans. On photoexcitation, the trans configuration changes into the cis form, with photoisomerization proceeding via two different routes. The excitation of the $n\pi^*$ state causes the inversion of the molecule through one of the azo nitrogens, whereas $\pi\pi^*$ excitation results in rotation of one half of the molecule against the other [1,2]. The reverse process of cis to trans isomerization can take place on photoexcitation [3] as well as in the dark, i.e. thermally. The cis to trans isomerization has been studied under various conditions, such as in micellar media [4], in the presence of cyclodextrin [5–7], on incorporation in a membrane [8], in polypeptides [9] etc., and reveals the predominance of the inversion mechanism [10–13]. This process requires an activation energy of 96.1 kJ mol^{-1} (23 kcal mol^{-1}) and this value remains constant for different azobenzene derivatives [10,14]. However, lower activation energies are found in highly bipolar azobenzenes [15–19] and *ortho*-hydroxy azobenzene derivatives [20,21]. In the case of highly bipolar azobenzenes, an intermediate tautomeric species due to internal bond rearrangement may be responsible for a lowering of the activation energy. However, in the case of *ortho*-hydroxy azobenzenes, an intermediate azo–hydrazo tautomerization is assumed to be responsible. In both cases, the role of the inversion process is not clear, which has prompted us to investigate the process flash photolytically using an *ortho*-hydroxy derivative.

2. Experimental details

Spectral studies were carried out using Shimadzu spectrophotometers (models UV-VIS-NIR 365 and MPS 2000). For flash photolysis work, an Nd:YAG laser (model DCR 11, Spectraphysics, USA) and a 100 W tungsten halogen lamp with an IP 28 photomultiplier and a 100 MHz digital storage oscilloscope (Gould Inc., UK) were used and have been described elsewhere [22]. Solutions were used without removing oxygen as oxygen has no significant effect on the flash excitation spectra and their kinetics.

The compound was prepared following Ref. [23]. A diazotized solution of anthranilic acid was added dropwise to alkaline *m*-cresol. The orange–yellow dye was

* Corresponding author.

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precipitated on acidification with dilute hydrochloric acid. The compound was recrystallized in distilled alcohol and was purified by silica gel column chromatography using petroleum ether–chloroform as eluent. The IR and UV spectra and melting point of the compound were compared with the reported values.

3. Results and discussion

Fig. 1 shows the absorption spectra of 2-carboxy-2'-hydroxy-4'-methyl azobenzene in isopropanol and benzene media. In both solvents, a strong band appears at 380 nm (log $\epsilon = 4.66$ in benzene, log $\epsilon = 4.32$ in isopropanol), which shifts to 480 nm (log $\epsilon = 4.435$) in isopropanol and 460 nm (log $\epsilon = 4.64$) in benzene on addition of triethylamine. The 480 nm band also appears on addition of water to isopropanol medium. It has been reported that *ortho*-hydroxy azobenzenes and *ortho*-hydroxy azonaphthalenes tautomerize to a hydrazo form absorbing in the 480 nm region [20]. The 380 nm band is blue shifted in aqueous medium and appears at 355 nm. This large blue shift cannot be accounted for by the solvent polarity or hydrogen bonding capability of the solvent because the absorption band remains unshifted at 380 nm in benzene (dielectric constant, 2.27), acetonitrile (dielectric constant, 37.5) and isopropanol (dielectric constant, 18.3). Monoanion formation ($CH_3C_6H_3(OH)-N=N-C_6H_4COO^-$) is probably the cause of this shift, and is supported by the pK_a values of 3.61 and 8.5 determined spectrophotometrically and by pH titration [24], although pH titration indicates only one pK_a value of 8.5 whereas spectrophotometric measurements in different buffer solutions show pK_a values at 3.61 and 8.5. The isosbestic point in acetate buffer solution (low pH) appears at 470 nm and in ammonium buffer solution (high pH) at 490 nm. The equilibrium is shifted to the azo monoanion in aqueous medium and to the hydrazo monoanion in a water–isopropanol mixture. The hydrazo form in non-aqueous medium can only be produced in the presence of triethylamine. Even in benzene, the hydrazo tautomer is formed in the presence of triethylamine. This indicates that the removal of the carboxylic proton is essential for azo–hydrazo tautomerization. The effect of temperature on the azo–hydrazo equilibrium shows an enthalpy change of 26.8 kJ mol^{-1} (6.4 kcal mol^{-1}) in aqueous medium (Fig. 2) and 15.3 kJ mol^{-1} (3.67 kcal

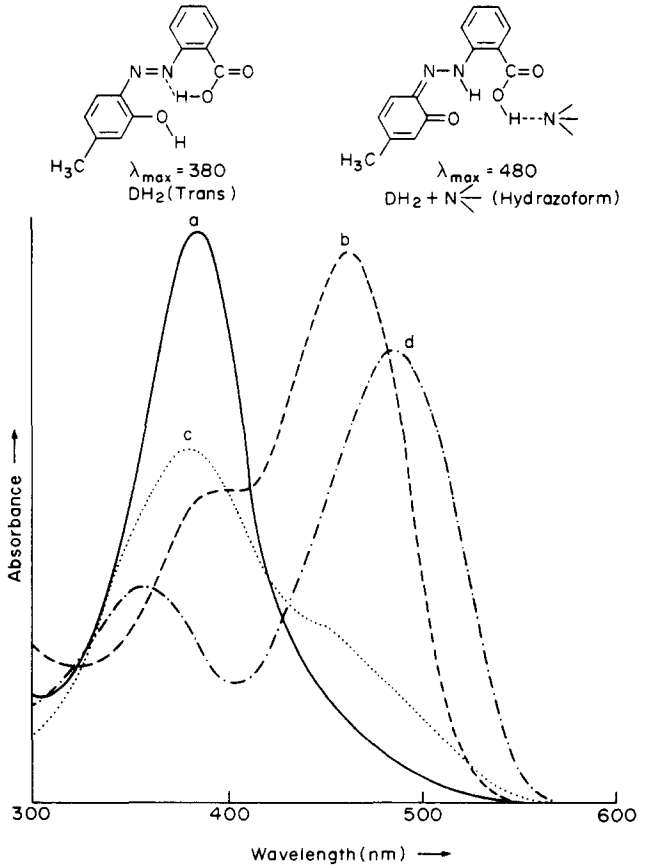

Fig. 1. Absorption spectra of 2-carboxy-2'-hydroxy-4'-methyl azobenzene: (a) 1.5×10^{-5} M in benzene; (b) as (a) but in the presence of 2.0×10^{-4} M triethylamine; (c) 2.0×10^{-5} M in isopropanol; (d) as (c) but in the presence of 2.5×10^{-5} M triethylamine.

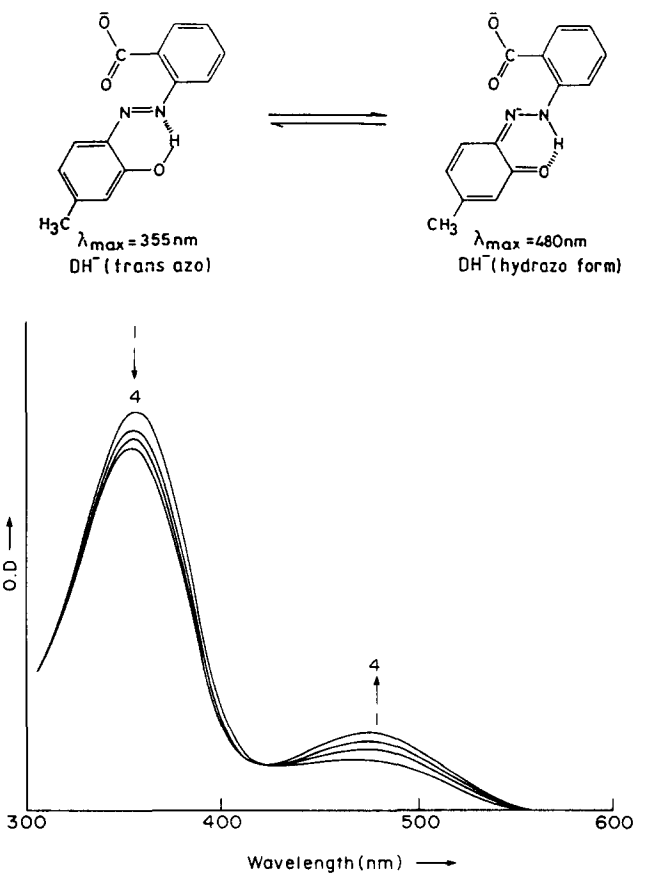

Fig. 2. Temperature effect on the equilibrium of the trans azo and hydrazo monoanions of 2-carboxy-2'-hydroxy-4'-methyl azobenzene in aqueous medium: (1) 40 °C; (2) 50 °C; (3) 60 °C; (4) 70 °C.

mol^{-1}) in a water–isopropanol (1:1) mixture. It seems reasonable that the production of the hydrazo tautomer is facilitated only when acid dissociation occurs or the carboxylic proton is bound by an external base. In the process of tautomerization, the nitrogen involved in hydrogen attachment remains intramolecularly hydrogen bonded with the stronger carboxylic group and is not available for accepting hydrogen from the hydroxyl group unless the carboxyl proton is removed or bound by an external base such as triethylamine.

On flash excitation by a 355 nm laser beam in isopropanol medium, the compound shows bleaching in the visible and near-UV regions. As the removal of oxygen from the solution does not change significantly the nature of bleaching and its decay, we used solutions for flash experiments without removing oxygen. In the near-UV and visible region, the magnitudes of bleaching at the different wavelengths are not proportional to the absorbance at these wavelengths. We have calculated the expected bleaching magnitude relative to the observed bleaching magnitude at the bleaching maximum (360 nm) and plotted the difference in Fig. 3. From this plot, a flash excited transient species absorbing at 420–430 nm is detected. This is the region in which *cis*-azobenzenes are found to absorb. The low absorbance of the cis conformers may be accounted for by the large distortion from molecular planarity. In the cis conformation, the plane of one benzene ring is at an angle of 56° to the plane of the azo group of the other benzene ring [20]. This will cause a distortion in π conjugation and hence a decrease in molar absorbance. The bleaching decay follows first-order kinetics (Flg. 3). This process requires an activation energy of 28.0 kJ mol^{-1} (6.7 kcal mol^{-1}). The cis to trans conformational change usually requires an activation energy of 96 kJ mol^{-1} (23 kcal mol^{-1}) [14]. However, a lower activation energy of the order of 50–58 kJ mol^{-1} (12–14 kcal mol^{-1}) has been reported for *ortho*-hydroxy derivatives [21,23]. The lower activation energy of *ortho*-hydroxy azobenzenes and azonaphthalenes has been explained by assuming the formation of intermediate hydrazo tautomers.

The difference in absorbance of the flash excited species in aqueous–isopropanol (1:1) medium are shown in Fig. 4. In aqueous and aqueous–isopropanol media, the decay pattern of the transient species is totally different from that observed in isopropanol. The bleaching decay kinetics at 360 nm show an initial fast decay, followed by a slow decay and, correspondingly, at 480 nm, an initial bleaching growth is followed by a slow

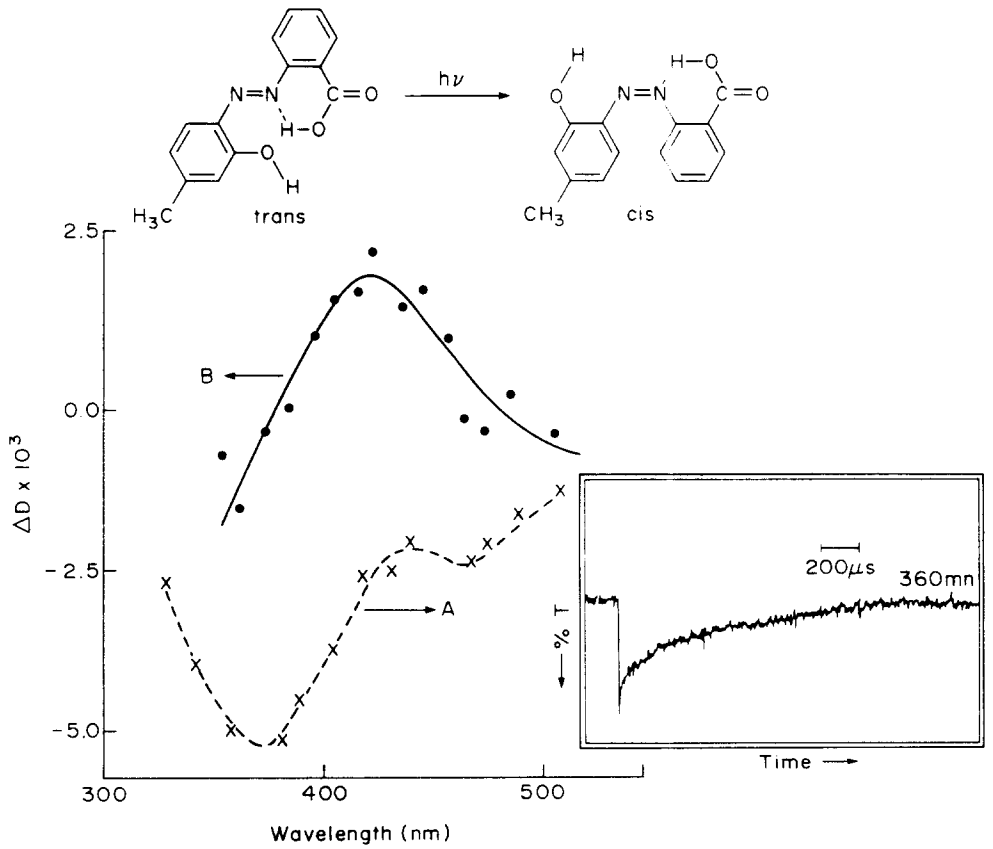

Fig. 3. Flash excitation ($\lambda_{excitation}$ = 355 nm) spectrum of 10^{-5} M 2-carboxy-2'-hydroxy-4'-methyl azobenzene: (A) isopropanol at 5 ms ($\Delta D \times 1.5$); (B) plot of ($\Delta D_{observed} - \Delta D_{expected}$) × 3. The expected ΔD was estimated with respect to the absorbance at 360 nm. Inset: oscillogram showing the bleaching decay in isopropanol (10^{-5} M) at 360 nm.

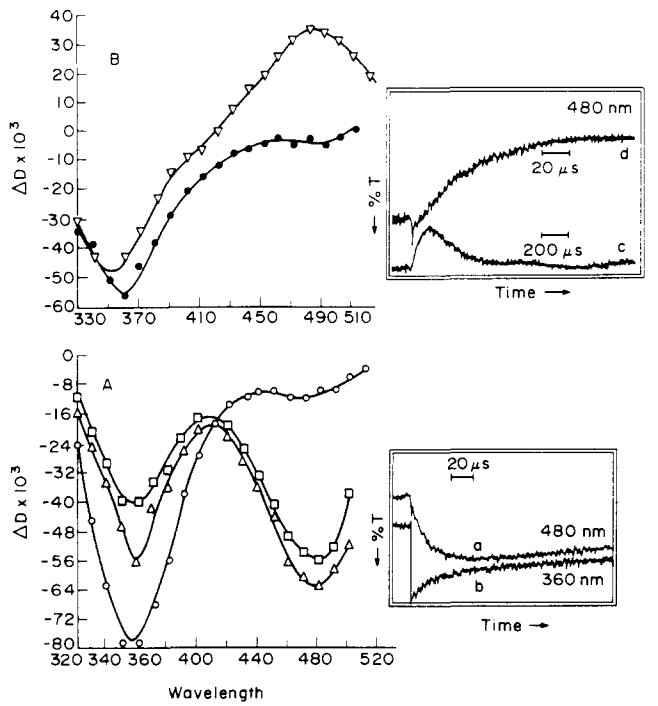

Fig. 4. (A) Flash excited, time-resolved spectra of 2.0×10^{-5} M 2-carboxy-2′-hydroxy-4′-methyl azobenzene in an isopropanol–water (1:1) mixture, 0 μs (○), 60 μs (△) and 160 μs (□) after the flash. (B) In the presence of 1.5×10^{-4} M triethylamine, 0 μs (●) and 300 μs (▽) after the flash. Inset: oscillogram traces of flash excited 2-carboxy-2′-hydroxy-4′-methyl azobenzene excited at 355 nm in: (a) isopropanol and water (1:1) at 480 nm; (b) isopropanol and water (1:1) at 360 nm; (c), (d) in the presence of 10^{-4} M triethylamine in isopropanol–water (1:1) at 480 nm, 200 μs and 20 μs (%T amplified) after the flash.

decay (Fig. 4). The initial growth of bleaching at 480 nm shows that, on flash excitation, the conversion of some trans to cis isomer probably creates a non-equilibrium situation between the trans isomer and the hydrazo tautomer and the equilibrium is relaxed before the cis isomer is transformed into the hydrazo tautomer. From temperature variation, in aqueous medium, the activation energy of the ground state recovery process is 40.1 kJ mol^{-1} (9.6 kcal mol^{-1}). From the decay kinetics, it is found that the rate-determining slow step is the conversion of the cis form to the hydrazo tautomer. Thus the activation energy of 40.1 kJ mol^{-1} (9.6 kcal mol^{-1}) is associated with this conversion process, which is close to the values reported in Ref. [21].

A large amount of hydrazo monoanion ($\lambda_{max}=480$ nm) is present in the isopropanol–water (1:1) mixture. It gives a transient absorption at 440 nm on flash excitation by a 532 nm laser beam (second harmonic). The decay of the transient follows first-order kinetics and shows no other intermediate steps.

A different transient behaviour and decay kinetics are observed in the presence of triethylamine in an isopropanol–water (1:1) mixture or in alkaline aqueous buffer solutions. Instead of bleaching at all wavelengths extending from the near-UV to the visible region, an initial growth of transient absorption is observed at 480 nm followed by a slow decay. At 360 nm, a single decay is noted which corresponds to the slow decay of the 480 nm transient absorption (Fig. 4). The transient absorption occurs at 480 nm with bleaching at 360 nm. The transient absorption intensity at 480 nm reaches a maximum at pH 8.5 and then decreases with increasing pH of the buffer solution (Table 1). This is because, above pH 8.5, a dianion is produced, and with increasing pH, excitation of the dianion becomes prominent. The bleaching and absorption of the transients correspond to the conversion of the trans isomer (absorbing at 355 nm in aqueous medium and 380 nm in an isopropanol–water (1:1) mixture) to the hydrazo tautomer (absorbing at 480 nm). The 480 nm species or tautomeric hydrazo monoanions increase with increasing pH or on addition of triethylamine to an isopropanol–water (1:1) mixture. From the monoanion, the formation of the hydrazo tautomer is favoured because the azo nitrogen is not hydrogen bonded by the carboxyl group but bonded by the hydroxyl group (Fig. 2). Both the growth and decay kinetics of the transients increase with increasing pH of the buffer solutions or concentration of base (Table 1). In the absence of base or at low pH, the conversion of the cis isomer to the hydrazo tautomer is slow and equilibrium relaxation between the hydrazo tautomer and the trans isomer is fast. In the presence of base or at high pH, both processes become faster, but the conversion of the cis isomer to the hydrazo tautomer is more rapid than equilibrium relaxation. Thus, in the presence of base, the growth of bleaching is replaced by the growth of absorption at 480 nm due to rapid change of the cis isomer to the hydrazo monoanion.

The interconversion mechanism under three different conditions, i.e. in non-ionizing medium (isopropanol), in ionizing medium (aqueous medium or isopropanol–water (1:1) mixture) and in basic medium, can be represented as

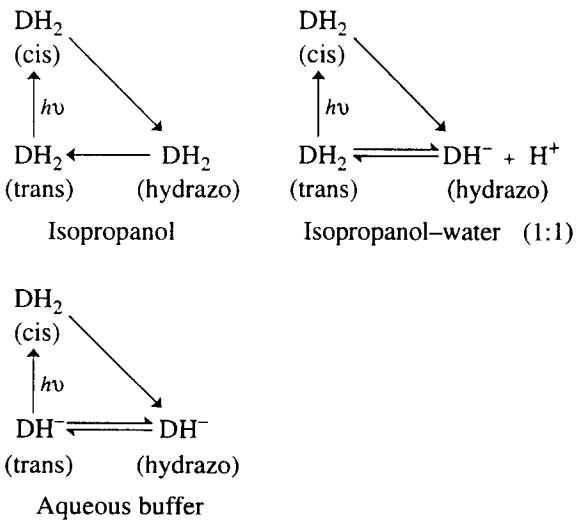

Table 1
Growth and decay rate constants of 1.5×10^{-5} M 2-carboxy-2′-hydroxy-4′-methyl azobenzene on excitation at 355 nm (monitoring wavelength, 480 nm) in aqueous buffer solution (A) and in the presence of triethylamine (TEA) in an isopropanol–water (1:1) mixture (B)

(A)

pH (buffer)	k_{growth} at 480 nm (s^{-1}) ($\times10^{-4}$)	k_{decay} at 480 nm (s^{-1}) ($\times10^{-3}$)	ΔD_{max} at 480 nm ($\times10^{3}$)
7.28	1.45	0.65	7.11
8.04	1.5	0.782	9.88
8.23	2.0	1.75	12.10
8.5	4.6	6.77	14.35
8.75	5.6	8.95	13.80
9.50	26.2	51.11	8.22

(B)

TEA (M) ($\times10^{3}$)	k_{growth} at 480 nm (s^{-1}) ($\times10^{-3}$)	k_{decay} at 480 nm (s^{-1}) ($\times10^{-2}$)	ΔD_{max} at 480 nm ($\times10^{3}$)
0.7	1.02	1.15	42.75
1.4	2.0	1.50	42.75
2.1	2.5	2.08	44.25
2.8	4.0	2.37	45.75
3.5	4.33	3.44	47.27
4.9	5.09	4.16	47.25
7.7	6.30	5.16	42.75

The linear dependence of the growth and decay rates of the transients confirms that the conversion of the cis isomer to the hydrazo tautomer depends on the availability of the dissociated monoanion, i.e. azo nitrogen free from hydrogen bonding (Table 1). In aqueous buffer solution at pH > 9.5, where ground state absorption shows appreciable dianion concentration, on flash excitation, a transient absorption appears in the 340–350 nm region. The decay of the transients follows first-order kinetics.

4. Conclusions

The cis to trans isomerization of *ortho*-hydroxy azobenzene derivatives proceeds through an azo–hydrazo tautomerization process. This process facilitates the inversion mechanism in azobenzene. For 2-carboxy-2′-hydroxy-4′-methyl azobenzene, the inversion mechanism appears to proceed through the nitrogen centre adjacent to the carboxyl group.

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