

THERMAL *cis* → *trans* ISOMERIZATION OF 4-HYDROXYAZOBENZENE IN THE VAPOUR PHASE: A FLASH SPECTROSCOPY STUDY

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Summary

The Arrhenius parameters reported in the literature for the thermal *cis* → *trans* isomerization of hydroxyazoic compounds disagree with those of other azobenzenes. This behaviour has been related to the interaction of hydrogen bonds leading to tautomerization to the corresponding phenyl-hydrazone. The kinetic features of the reaction in the vapour phase under almost unperturbed conditions have not been reported so far. The thermal uncatalysed *cis* → *trans* isomerization was investigated in the vapour phase between 85 and 275 °C using the microsecond flash photolysis technique. The results suggest that the straightforward kinetics characterizing the majority of azobenzene isomerizations above 200 °C also apply to 4-hydroxyazobenzene. At these temperatures the isomerization proceeds by inversion with an activation energy of $107 \pm 5 \text{ kJ mol}^{-1}$ and a frequency factor of $10^{13 \pm 0.3} \text{ s}^{-1}$. At lower temperatures ($T < 190 \text{ °C}$) the reaction is complex with obvious heterogeneous catalysis features (wall reaction).

1. Introduction

The gaseous system offers several advantages over the solution system in that reactions can be studied in the absence of perturbing solvent-solute interactions such that a straightforward kinetic analysis is possible. Therefore for reactions exhibiting complex solution kinetics corresponding studies in the vapour phase may provide a suitable method of obtaining valuable mechanistic information. Flash photolysis experiments in the vapour phase have recently been used [1] to show that the highly bipolar 4-dimethyl-amino-4'-nitroazobenzene isomerizes by an inversion mechanism in the solution (as well as in the vapour phase) and not according to a rotation mechanism [2] as was previously believed. Hydroxyazoic compounds constitute another class of azobenzene derivatives for which the kinetic behaviour in the solution phase has been reported to be complex [3 - 7].

Gabor *et al.* [5] have reported that the spontaneous *cis* → *trans* reversion of 4-hydroxyazobenzene is strongly solvent and concentration

dependent, and they have ascribed this behaviour to the interaction of hydrogen-bonded dimers leading to tautomerization to the corresponding phenylhydrazone. According to them the thermal reversion in alcoholic solutions between -70 and -100 °C was roughly a first-order reaction with an activation energy of 35.6 kJ mol^{-1} and a frequency factor of $6.3 \times 10^6 \text{ s}^{-1}$. In the non-polar solvent methylcyclohexane, however, the reaction exhibited a rather unusual and complex temperature dependence with the maximum rate at about -20 °C. Schulte-Frohlinde [7] showed that the same compound in benzene solutions rearranged autocatalytically to the *trans* form following a first-order rate law with an activation energy of 22.4 kJ mol^{-1} and a frequency factor of 5.6 s^{-1} . The Arrhenius parameters reported for this *cis* \rightarrow *trans* conversion of 4-hydroxyazobenzene in the solution phase appear to be very different from those normally describing the uncatalysed isomerization of closely related azobenzenes [8-12]. Therefore the objective of this work was to investigate whether the *cis* \rightarrow *trans* reaction resumes "normal azobenzene behaviour" in the absence of solvent-solute interactions (as in the vapour phase).

2. Experimental details

4-hydroxyazobenzene (EGA-Chemie) was purified by recrystallization from ethanol and vacuum sublimation at 100 °C. Argon (Alfax; purity, 99.998%) was used as received as the buffer gas in the flash photolysis reaction system. An aqueous CatX filter solution of concentration 0.2 g dm^{-3} (see ref. 1) was used to limit the spectral range of the exciting light between 240 and 310 nm. The apparatus utilized and the experimental principles and techniques applied are described in refs. 1 and 12. The computational methods are explained in ref. 1 and will not be repeated in this paper.

3. Results and discussion

The linear relation established between $\ln(AT)$ and $1/T$ [12], where A is the absorbance at 313 nm for an optical path length of 9.0 cm, shows that for temperatures between 96 and 134 °C and concentrations in the range $(0.2 - 4.5) \times 10^{-6} \text{ mol dm}^{-3}$ the occurrence of side reactions such as dimerization, tautomerization and adsorption can be excluded. The vapour pressure parameters α and β (defined in ref. 12) were $(13.0 \pm 0.2) \times 10^3 \text{ K}$ and 29.9 ± 0.4 respectively.

3.1. *Trans* spectrum

Figures 1 and 2 show the absorption spectra of *trans*-4-hydroxyazobenzene (*trans*-AB-OH) in the solvents ethanol and cyclohexane at 25 °C and in the vapour phase at 195 °C. Three prominent absorption bands can be distinguished which correspond to the $n-\pi^*$, $\pi-\pi^*$ and $\phi-\phi^*$ electronic

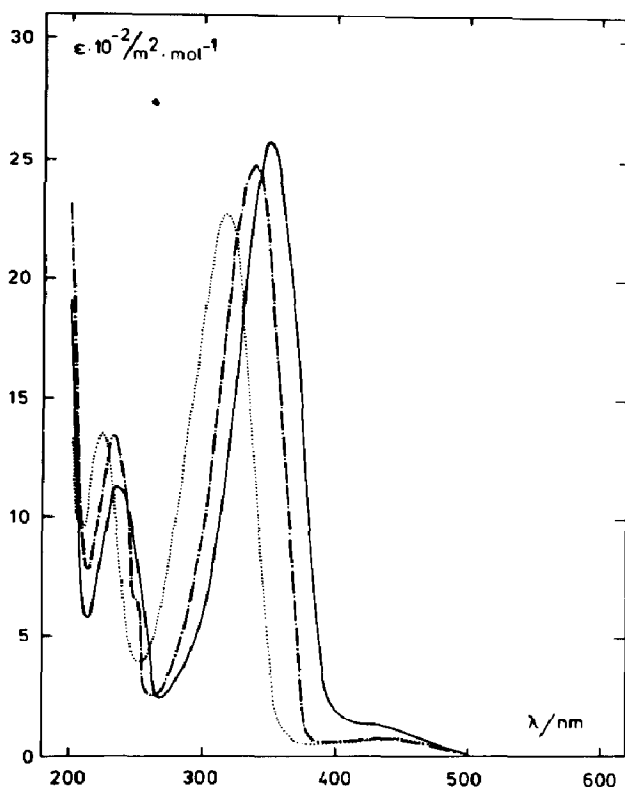


Fig. 1. Absorption spectra of *trans*-4-hydroxyazobenzene in the solvents ethanol (—) and cyclohexane (- · -) at 25 °C and in the vapour phase at 195 °C (.....).

transitions. On going from polar solutions to the gaseous system, the UV band exhibited hypochromic as well as hypsochromic effects (see Fig. 1). The low intensity $n-\pi^*$ transition centred at 433 nm in cyclohexane and the vapour phase could be resolved as individual bands clearly separated from the considerably stronger $\pi-\pi^*$ transition. In ethanol, however, this was not possible and the $n-\pi^*$ band developed only as a shoulder around 430 nm. Whereas the position of the $n-\pi^*$ band in azobenzene was almost unaffected by the OH substitution, the intensity increased by a factor of 2 from 37.5 to 75.0 $\text{m}^2 \text{mol}^{-1}$. We ascribe the latter effect to the increased electron density at the nitrogen atoms and to some mixing between the n and π orbitals (twisted configuration).

3.2. Identification of transient species

Temperatures higher than 150 °C ($A \approx 0.35$ at 313 nm and $l = 1.0$ cm) are required to attain sufficient vaporization for the appropriate spectrophotometric measurements to be made in the vapour phase. At these temperatures, however, the transient species (*cis* form) is highly unstable and relaxes within 1 s ($\tau_{1/2} \approx 150$ ms) to the corresponding *trans* form. Therefore, before entering into a discussion of the kinetic results, the equivalence of the transient species and the *cis* isomer of AB-OH must be established. The following observations provide evidence for this equivalence: the vapour

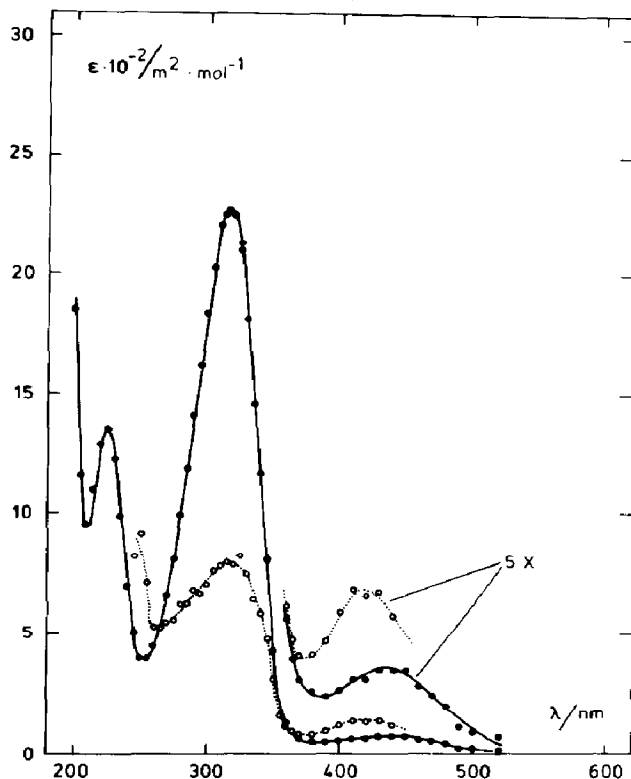


Fig. 2. Vapour phase absorption spectra of the *trans* and *cis* isomers of 4-hydroxyazobenzene: —, *trans* isomer at 195 °C; ·····, *cis* isomer at 205 °C.

phase difference spectrum (Fig. 3, full circles) recorded by the flash photolysis technique ($T = 205\text{ °C}$, $\tau_{1/2} \approx 37\text{ ms}$) is obviously related to that obtained in cyclohexane on irradiating to photostationary state conditions (Fig. 3, full curve); the transient spectrum (Fig. 4) evaluated from the difference spectrum induced by flash photolysis for an assumed *cis* concentration of $4.0 \times 10^{-8}\text{ mol dm}^{-3}$ (see ref. 12) is qualitatively very similar to the solution spectrum of *cis*-AB-OH [5]. A difference spectrum illustrating the irreversible changes produced when the temperature is increased from 195 to 240 °C is also included in Fig. 3 (dotted curve). However, this spectrum reflects decomposition.

3.3. *Cis-trans* reaction

The spontaneous reversion of *cis*-AB-OH to the corresponding *trans* form followed first-order kinetics at temperatures between 87 and 275 °C and wavelengths between 240 and 530 nm. At temperatures above 225 °C a slight irreversibility entered into the relaxation process indicating decomposition. Particular attention has been focused on this decomposition reaction and its possible influence on the *cis* \rightarrow *trans* isomerization. The experimental conditions, such as the vapour concentration, the flash energy and the dimensions of the reaction vessel, were changed but in all cases the

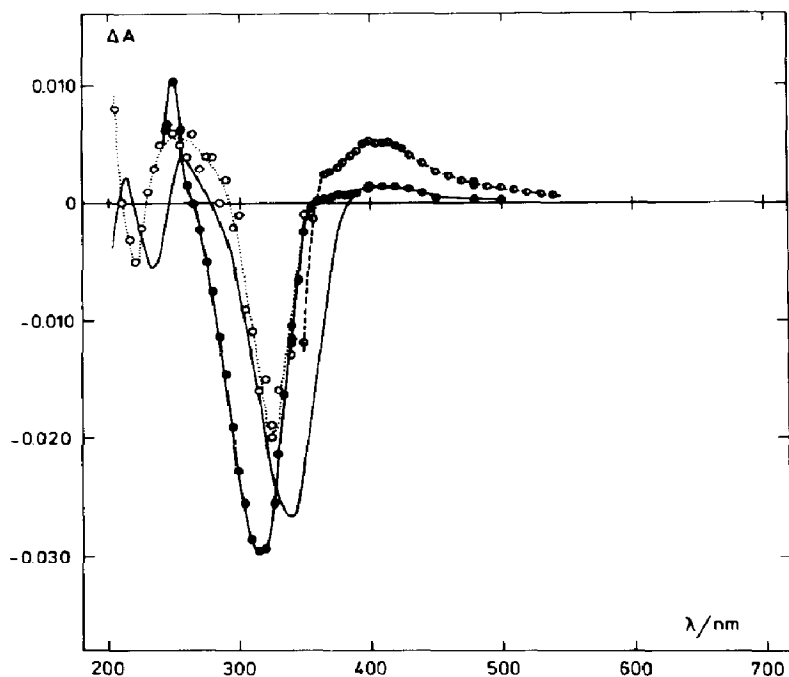


Fig. 3. Difference spectra of 4-hydroxyazobenzene in the vapour phase induced either by light (●, flash photolysis (205 °C, $\tau_{1/2} \approx 37$ ms) with the spectrum recorded 100 ms after the onset of the flash; ○, as for the previous experiment but with a higher concentration of *trans*-4-hydroxyazobenzene; —, irradiated with light from a xenon lamp (450 W) filtered through an NaNO_2 solution ($\lambda > 370$ nm)) or thermally (....., difference between spectra measured at 195 and 240 °C).

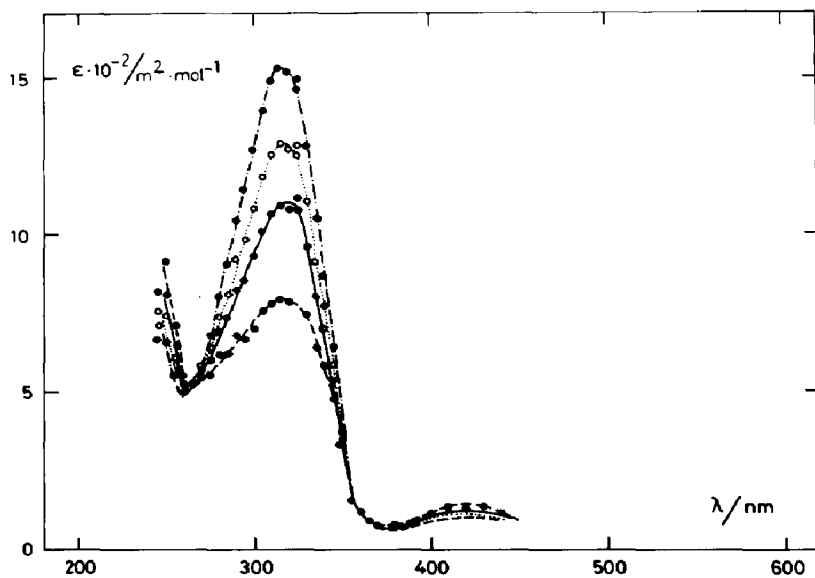


Fig. 4. The *cis* spectrum of 4-hydroxyazobenzene in the vapour phase at 205 °C evaluated for various degrees of *trans* → *cis* conversion in the flash experiment ($C_c^* = 2.62 \times 10^{-8}$ mol dm^{-3}): ---, 4.0×10^{-8} mol dm^{-3} ; —, 5.0×10^{-8} mol dm^{-3} ;, 6.0×10^{-8} mol dm^{-3} ; - · -, 8.0×10^{-8} mol dm^{-3} . The semiquantitative method applied has been described elsewhere [12].

isomerization rate was unaffected. Furthermore no correlation was found between the number of flashes to which the vapour was subjected and the *cis* → *trans* conversion rate. Figure 5 shows the temperature dependence of the rate constant between 87 and 275 °C (Arrhenius plot). The upward curvature obtained for temperatures below 190 °C ($\tau_{1/2} \approx 70$ ms) can be related to heterogeneous catalysis (wall reaction). Similar non-linear behaviour of the Arrhenius plot was also found in the azobenzene system [12]. Straightforward calculations showed that in the azobenzene system curvature occurs when the diffusion time required to transport molecules from the centre of the cell to the wall of the reaction vessel (diameter, 10 mm) was of the same magnitude as the half-life $\tau_{1/2}$ of the *cis* → *trans* reaction, *i.e.* 50 ms. An activation energy of 107 ± 5 kJ mol⁻¹ and a frequency factor of $10^{13.0 \pm 0.3}$ s⁻¹ (the limits correspond to the 95% confidence intervals) were calculated from the linear relation established in the Arrhenius plot from 195 to 275 °C (owing to the large number of experimental points used in these calculations the *t* factor is roughly 2). These parameters agree with those reported for other azobenzenes [1, 8 - 12]. From this we conclude that the reaction studied in the vapour phase corresponds to the thermal uncatalysed *cis* → *trans* isomerization of 4-hydroxyazobenzene and that the isomerization, by analogy with several other closely related azobenzenes [1, 8 - 12], proceeds by inversion. Talaty and Fargo [10] found in their experimental study of the kinetic features of substituted azobenzenes in the solution phase that all *para* substitution led to an acceleration in the *cis* → *trans* rate. This relation also holds for AB-OH in the vapour phase.

In addition to the *cis* → *trans* reaction, AB-OH may undergo other reactions in the solution phase. These are the formation of dimers and

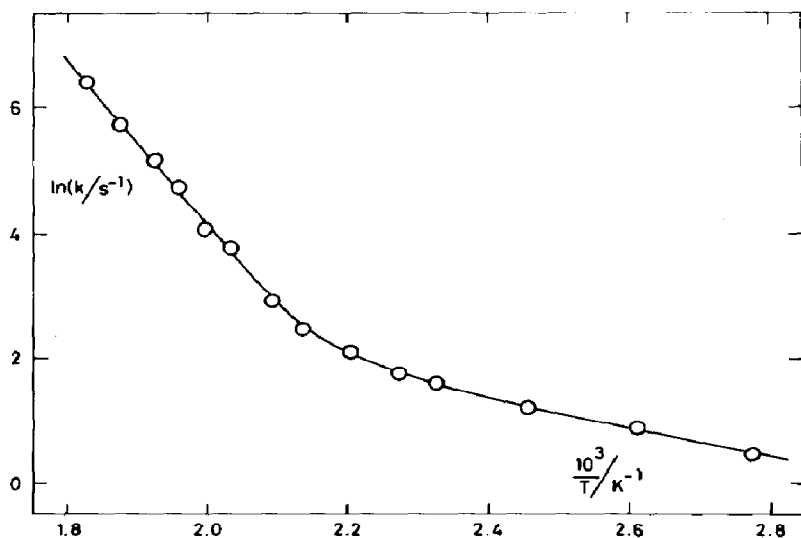


Fig. 5. Temperature dependence of the first-order rate constant plotted according to the logarithmic form of the Arrhenius equation.

tautomerization to form the corresponding phenylhydrazone. The question of whether similar reactions can be expected in the present vapour phase system then arises. It appears that dimerization energies for gas phase hydrogen-bonded dimers varies considerably from 22 kJ mol⁻¹ for H₂O dimers [13] to as high as 56 kJ mol⁻¹ for heterodimers of the type H₂O-HF [14]. However, the experimental conditions under which the flash photolysis experiments were performed ($T > 190$ °C, $C < 10^{-6}$ mol dm⁻³) suggest that these additional reactions are not likely to occur. Furthermore no spectroscopic indications of these species exist in the gaseous system.

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