

FLASH PHOTOLYSIS EXPERIMENTS IN THE VAPOUR PHASE AT ELEVATED TEMPERATURES
I: SPECTRA OF AZOBENZENE AND THE KINETICS OF ITS THERMAL *cis-trans* ISOMERIZATION

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Summary

The kinetics of the thermal *cis-trans* isomerization of azobenzene in the vapour phase were studied by the conventional microsecond flash photolysis technique as a function of temperature, concentration and buffer gas pressure. The results collected over the interval 181 - 322 °C indicate that the *cis* → *trans* reaction proceeds according to the inversion mechanism with an activation energy of 118 kJ mol⁻¹. Quantitative UV spectra of the two geometric isomers in the vapour phase are given. The spectrophotometric measurements undertaken revealed a temperature dependence of the *trans* spectrum with changes qualitatively analogous to those induced by light. These effects are discussed in terms of a possible temperature-dependent chemical equilibrium between the two geometric isomers.

1. Introduction

The thermal and photochemical isomerization of azobenzenes has been the subject of many investigations which have contributed to an increased knowledge of the different excited states involved in the photoisomerization [1 - 7] as well as to an understanding of the mechanism by which the thermal isomerization proceeds [8 - 12]. Although azobenzene and stilbene are isostructural and isoelectronic with regard to π and σ electrons the kinetics of the isomerization around these bonds are quite different. Whereas the stilbenes rearrange according to the rotation mechanism with an activation energy of 142 - 155 kJ mol⁻¹ in solution [13] and 180 kJ mol⁻¹ in the gas phase [14], the azobenzenes are readily isomerized with a substantially lower activation energy of 96 kJ mol⁻¹ [9 - 11]. Molecular orbital calculations [15 - 17] predict that the barrier to rotation around the N=N double

bond is higher than that to rotation around the C=C bond, and in the light of this an alternative reaction mechanism equivalent to that of imines and imides [18] has been suggested [8]. In this process one of the lone pair dipoles at either of the nitrogen atoms is assumed to convert into a p orbital in the linear transition state. This mechanism, which is known as inversion, is now widely accepted as essentially the correct description of the thermal isomerization of several azobenzenes and azomethines and explains the low activation energies observed. Ljunggren and Wettermark [19] used a complete neglect of differential overlap (CNDO/2) method to calculate the energy barriers of rotation and inversion at the bridging group of azobenzene and obtained values of 293 kJ mol^{-1} and 137 kJ mol^{-1} respectively. The experimental activation energy of about 96 kJ mol^{-1} in solution therefore clearly favours the inversion mechanism as it is not believed [8] that the barrier to rotation can be reduced to such a large extent by solvent-solute interactions. It has been reported [20], however, that in highly bipolar azobenzenes the thermal isomerization probably proceeds according to the rotation mechanism, despite the low activation energy observed. Most kinetic investigations to date have been confined to the condensed phase in which the molecules are subjected to various degrees of perturbing solvent-solute interactions which sometimes both complicate and prevent a detailed analysis of the results.

The purpose of this work is to investigate the mechanisms by which photochemical and thermal isomerization proceeds under almost unperturbed conditions for the groups of molecules given above. In order to perform these experiments we have designed a variety of furnaces, some of which are described in this paper. The flash photolysis technique was used to investigate the thermal *cis* \rightarrow *trans* reaction from 181 to 322 °C and the corresponding Arrhenius parameters were determined. The absorption spectra of both conformers in the vapour phase are also included. Furthermore, the *trans* spectrum was found to be influenced by the temperature which produced changes qualitatively analogous to those induced by light. These effects are discussed in terms of a possible temperature-dependent *cis-trans* equilibrium.

2. Experimental details

2.1. Materials

Azobenzene (Fluka) was recrystallized several times from ethanolic solutions and was then sublimed into the flash photolysis reaction vessel at reduced pressure (1 mPa). Argon (Alfax, 99.998% purity), oxygen and nitrogen (Aga, S grade), and NaNO_2 and NiSO_4 (Kebo, p.a. grade) were used as received. 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene iodide (CatX) was prepared and used as described by Schwarzenbach and Lutz [21] and Kasha [22].

2.2. Filters

The spectral range of the flash light was limited by aqueous filter solutions (25 °C) containing 0.4 mol dm⁻³ NaNO₂ ($\lambda > 370$ nm) or 2.0 mol dm⁻³ NiSO₄ and 0.2 g dm⁻³ CatX (240 nm < λ < 310 nm) for excitation in the n, π^* or the π,π^* bands of azobenzene respectively.

2.3. Apparatus

The flash photolysis apparatus used in this investigation has been described previously [23, 24]. A comprehensive description of the various furnaces designed and the experimental arrangements and principles applied will be given elsewhere [25, 26]. However, for convenience a summary is given below.

In order to perform the flash photolysis experiments in the vapour phase a furnace capable of accepting 50 cm cells has been built (Fig. 1). It is T-shaped and is composed of four heating elements, each of which consists of a silica tube bifilarly wound with resistance wire. Separate power units were used for the upper three heating tubes and for the lower vertical heating tube which enabled the temperature to be varied independently in the two parts of the furnace. With this experimental arrangement the Arrhenius parameters could be determined under conditions of almost constant concentration. The flash experiments were always performed on unsaturated vapours which were produced by ensuring that the temperature of the upper parts was

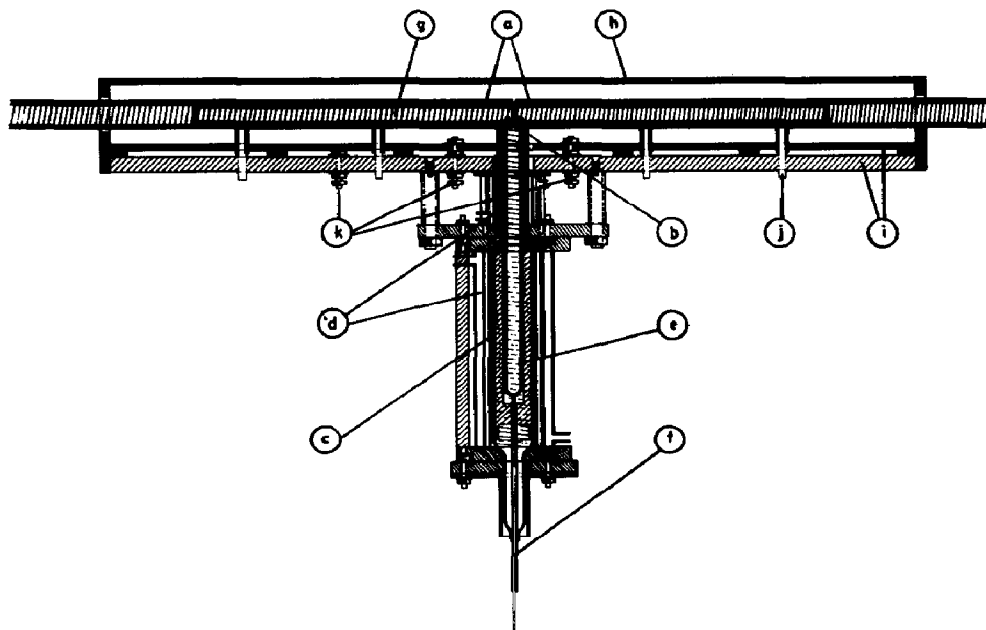


Fig. 1. Diagram of the furnace used in the flash photolysis experiments: a, horizontal heating tubes; b, upper vertical heating tube; c, lower vertical heating tube; d, water jackets; e, aluminium tube; f, iron-constantan thermocouple; g, T-shaped reaction vessel; h, asbestos cover; i, double-layer asbestos-Bakelite bottom plate; j, tapered asbestos pins; k, electrical connections.

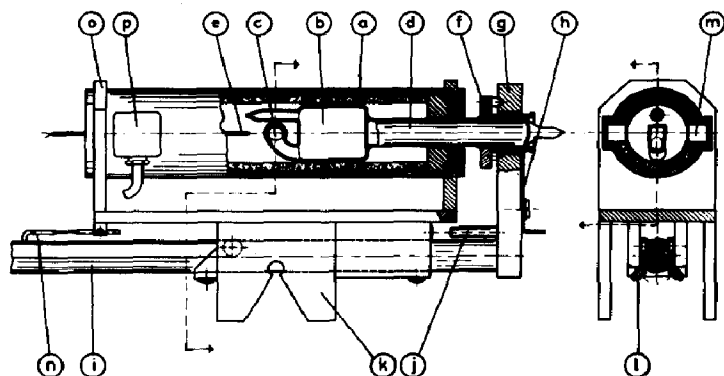


Fig. 2. Diagram of the furnace used in the determination of quantitative vapour phase absorption spectra: a, ceramic tube 80 mm in diameter and 300 mm long; b, silica vessel; c, spectrophotometer cell; d, evacuated silica tube; e, iron-constantan thermocouple; f, aluminium plate attached to tube d; g, aluminium plate; h, spring clamping f and g together; i, centreless ground steel shaft 25 mm in diameter; j, stop for reference position (air); k, base supports; l, ball bearings; m, Suprasil windows (spacing, 6 mm); n, stop for measuring position; o, aluminium framework; p, electrical connections.

higher than that of the finger tip. Two silica vessels placed between the flash lamps and the horizontal heating tubes served as containers for the thermostatted (25°C) filter solution. Depending on the temperature required, the vapour phase spectra were measured either in a detached furnace (Fig. 2) utilizing a single-beam spectrophotometric arrangement or using a Zeiss recording spectrophotometer (DMR 10) provided with heating facilities.

3. Results

3.1. Vapour pressure

The vapour pressure of *trans*-azobenzene (*t*-AB) was evaluated from absorption measurements (301 nm) by applying the relation

$$\ln AT = -\frac{\alpha}{T} + \beta + \ln\left(\frac{\epsilon l}{R}\right) \quad (1)$$

where the constants α and β are defined by

$$\ln P = -\alpha/T + \beta \quad (2)$$

and the other symbols have their usual significance. Figure 3 shows the plot of $\ln AT$ versus $1/T$ and Table 1 gives the parameters α and β .

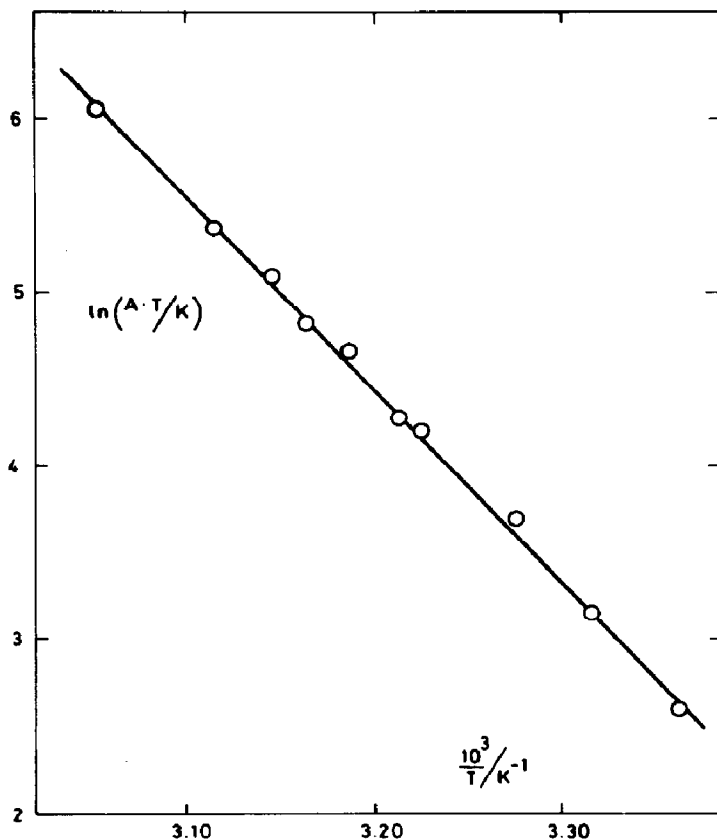


Fig. 3. The absorbance of azobenzene vapour at 301 nm as a function of the temperature plotted according to eqn. (1).

TABLE 1

Vapour pressure data for *trans*-azobenzene

Reference	α (K^{-1})	β	Temperature interval ($^{\circ}C$)
[27]	11288 ± 15	30.73 ± 0.05	0 - 42
This work	11053 ± 400^a	31.79 ± 1.34^a	24 - 55

^a Accurate to the 95% confidence interval.

3.2. Spectrum of *trans*-azobenzene

The *t*-AB absorption spectrum (Fig. 4) exhibits three bands centred around 440 nm ($37.5 \text{ m}^2 \text{ mol}^{-1}$), 301 nm ($2130 \text{ m}^2 \text{ mol}^{-1}$) and 220 nm ($1430 \text{ m}^2 \text{ mol}^{-1}$) corresponding to the n, π^* , π, π^* and ϕ, ϕ^* electronic transitions respectively. Vibrational structures were observed at $220 \pm 16 \text{ cm}^{-1}$ and $1350 \pm 50 \text{ cm}^{-1}$ in the π, π^* band whereas the low intensity n, π^* band was structureless (Fig. 5).

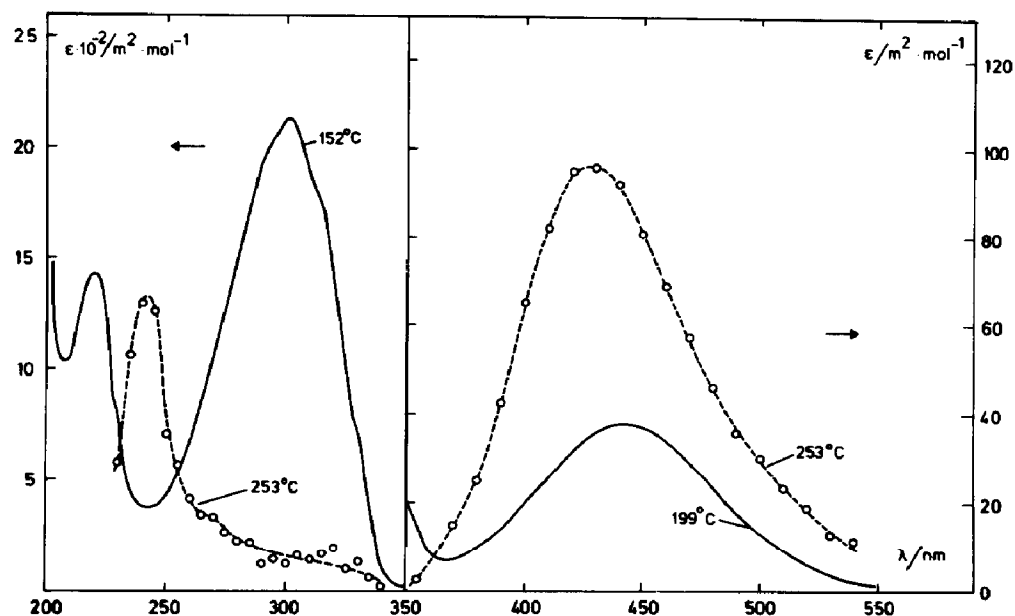


Fig. 4. Vapour phase absorption spectra of *t*-AB and *c*-AB. The n, π^* band of *t*-AB was measured at 199 °C, and the π, π^* and ϕ, ϕ^* bands were measured at 152 °C. The *c*-AB spectrum was calculated from the difference spectrum in Fig. 6 ($\Delta C = 2.0 \times 10^{-6} \text{ mol dm}^{-3}$) and refers to 253 °C.

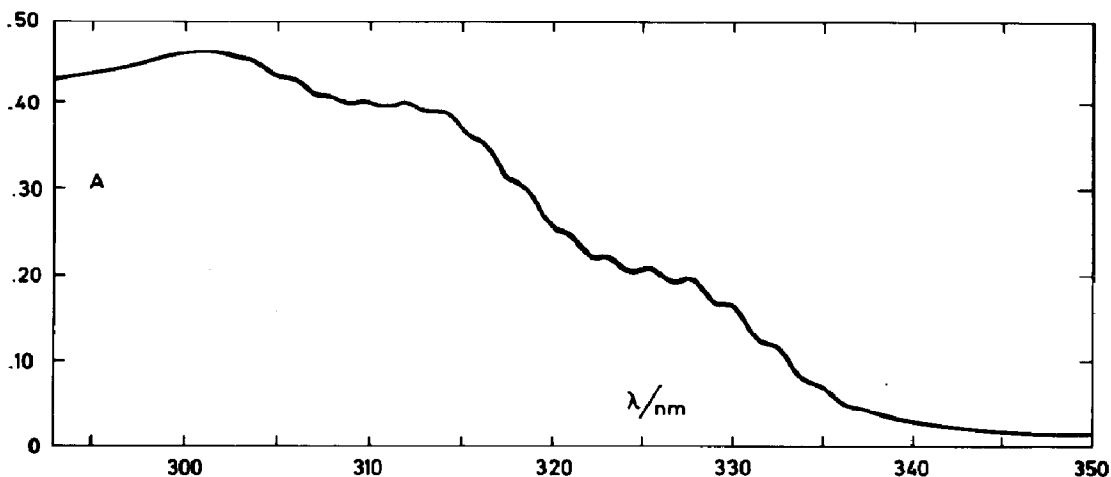


Fig. 5. The π, π^* absorption band of *t*-AB recorded using the Zeiss DMR 10 spectrophotometer at maximum sensitivity and resolving power (0.01 absorbance units nm^{-1} ; $\Delta\lambda < 0.05 \text{ nm}$) showing the progression of the 1350 and 220 cm^{-1} vibrational modes.

3.3. *Cis-trans* reaction

Excitation of the *t*-AB vapour with a short pulse of light in either the n, π^* or the π, π^* band caused transient changes in the absorption spectrum (Fig. 6). Identical *t*-AB spectra were obtained for the original vapour and for a vapour which had been subjected to several flashes, suggesting com-

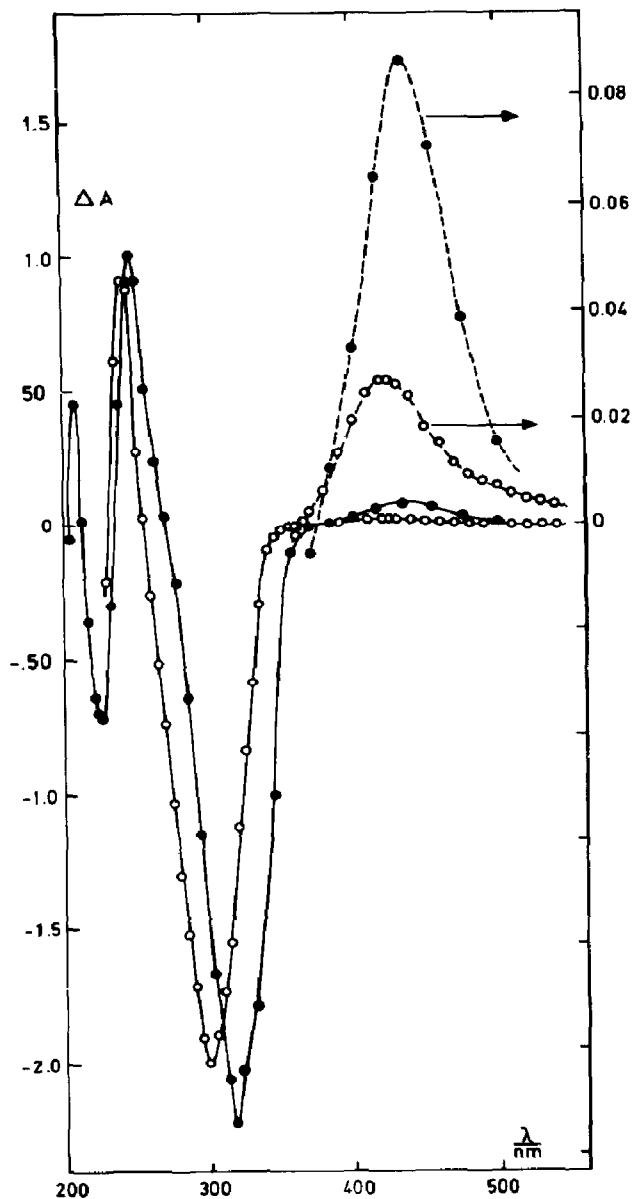


Fig. 6. Difference spectrum of azobenzene in the vapour phase at 253 °C (○) and in hexane at 25 °C (●). The latter spectrum was simulated (*cf.* text).

plete reversibility of the photochemical and thermal reactions. Regardless of the excitation conditions (Table 2), the reaction always followed a first-order rate law with identical rate constants in the interval 230 - 530 nm. The rate constant was unaffected by changes in the total pressure from 13 to 130 kPa (argon, nitrogen, air) or by changes in the concentration over a 2000-fold range from 0.5×10^{-7} to 1.0×10^{-4} mol dm⁻³. However, a significant decrease in the photochemical production of the transient species was caused by the presence of oxygen at a pressure of 100 kPa (Table 3).

TABLE 2

Rate constants of the *cis-trans* isomerization reaction for different excitation conditions

Temperature (°C)	Excitation band	No. of flashes	Rate constant (s ⁻¹)
181	n,π*	25	2.29 ± 0.03 ^a
	π,π*	21	2.29 ± 0.06 ^a
204.5	n,π*	30	9.41 ± 0.10 ^a
	π,π*	23	9.34 ± 0.18 ^a

^a Accurate to the 95% confidence interval.

TABLE 3

The effect of oxygen on *cis*-azobenzene production ΔA and the isomerization rate constant k

Buffer gas	No. of flashes	$\Delta A_{25 \text{ ms}}$	k (s ⁻¹)
Ar (66 kPa)	5	-0.032	9.55 ± 0.20 ^a
Air (100 kPa)	5	-0.032	9.34 ± 0.24 ^a
O ₂ (100 kPa)	6	-0.013	10.8 ± 0.3 ^a

Temperature, 204.5 °C; wavelength, 301 nm.

^a Accurate to the 95% confidence interval.

TABLE 4

Activation parameters for the thermal *cis* → *trans* reaction of azobenzene

	Melt [28]	Heptane solution [10]	Vapour phase
E_a (kJ mol ⁻¹)	103.4	95.4	117.7 ± 1.4 ^a
log A^b	12.21	12.88	13.96 ± 0.15 ^a
ΔS^\ddagger (J mol ⁻¹ K ⁻¹) ^c	-19.5, -21.3	-40.8, -42.6	14.0, 12.2
ΔH^\ddagger (kJ mol ⁻¹) ^c	100.9, 100.3	92.9, 92.3	115.2, 114.6
ΔG^\ddagger (kJ mol ⁻¹) ^c	106.7, 108.3	105.1, 108.2	109.0, 107.5

^a Accurate to the 95% confidence interval.

^b A in reciprocal seconds.

^c Data obtained at 25 and 100 °C.

The Arrhenius plot in Fig. 7 is linear from 181 to 322 °C giving an activation energy of 117.7 kJ mol⁻¹ (Table 4). Below 175 °C an upward deviation from the linear relationship was observed (not included in Fig. 7).

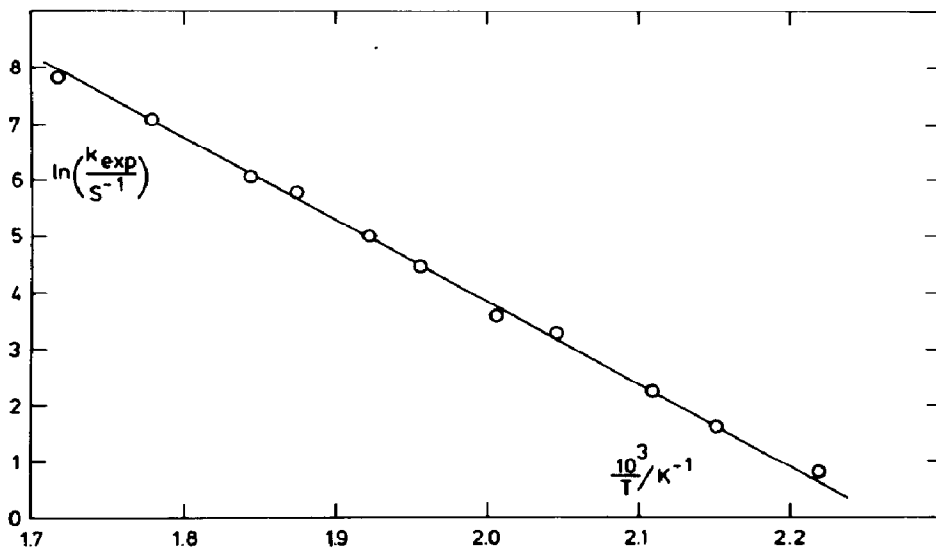


Fig. 7. Arrhenius plot of the *cis-trans* isomerization reaction of azobenzene in the vapour phase from 181 to 322 °C.

3.4. Difference spectra

Figure 6 shows the light-induced difference spectrum measured 0.75 ms after the onset of the light flash with excitation in the n,π^* band (vapour temperature, 253 °C; $\tau_{1/2} = 3.7$ ms). A 3.0 cm cell was required for wavelengths shorter than 325 nm; otherwise the 50.0 cm cell was used. A simulated difference spectrum of AB in hexane [29, 30] calculated for a *cis-trans* conversion equivalent to that in the flash experiment ($\Delta C = 2 \times 10^{-6}$ mol dm $^{-3}$) is included for comparison. Figure 8 shows the vapour phase spectra of *t*-AB at different temperatures. As can be seen the increase in temperature reduces the absorption in the central part of the π,π^* band (12%) with a concomitant increase in the wings. Under equivalent conditions the n,π^* band exhibits a hypsochromic effect (6%). The positions of the bands were essentially unaffected by the temperature.

3.5. Evaluation of the transient spectrum

The absorption spectrum of the light-induced transient species x was calculated from the relation

$$\epsilon_x(\lambda) = \frac{\Delta A(\lambda)}{C_x l} + \epsilon_t(\lambda) \quad (3)$$

where ϵ_x and ϵ_t are the absorption coefficients of the transient species and *t*-AB, C_x is the concentration of the transient at a specified time τ after the onset of the light flash, $\Delta A(\lambda) = A_\tau(\lambda) - A_0(\lambda)$ is the change in absorption and l is the cell length.

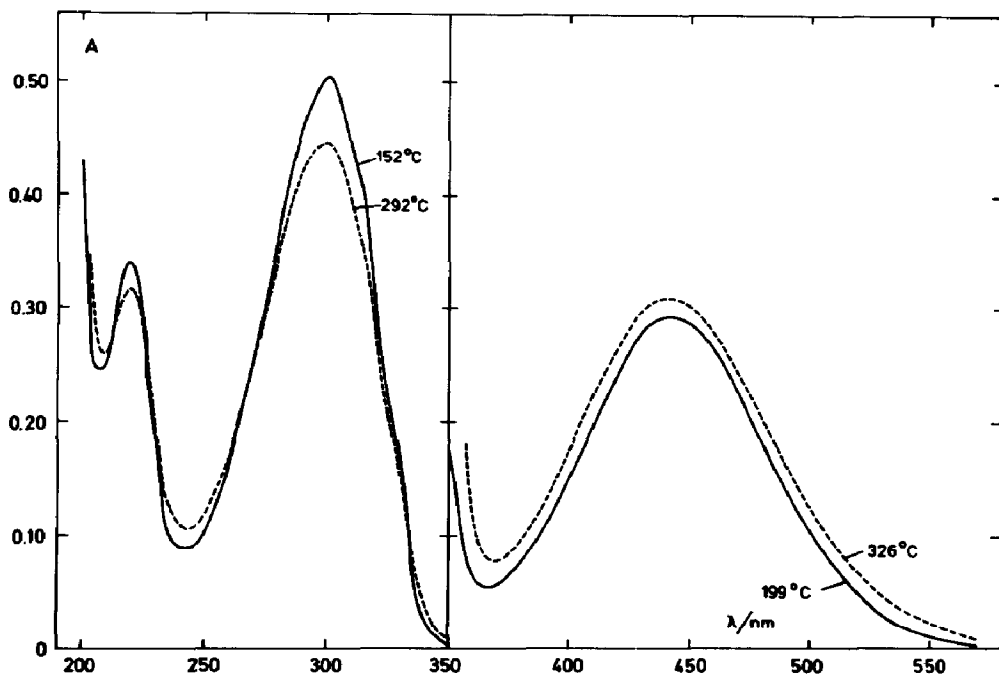


Fig. 8. The influence of temperature on the *t*-AB spectrum in the vapour phase.

The concentration C_x was calculated in a semiquantitative way by relating the light-induced changes in the photobleached region ($\Delta A < 0$; 260 - 360 nm) solely to the reduction in the *t*-AB concentration, *i.e.*

$$C_x = \frac{\Delta A(\lambda)}{I\{\epsilon_x(\lambda) - \epsilon_t(\lambda)\}} \geq -\frac{\Delta A(\lambda)}{I\epsilon_t(\lambda)} = C_x^*(\lambda) \quad (4)$$

The maximum value of $C_x^*(\lambda)$ then sets a lower limit on C_x ($C_x \geq C_x^*(\lambda)$). Figure 9 shows three examples of transient absorption spectra obtained for different selected values of C_x ($C_{x,\min}^*(330 \text{ nm}) = 1.64 \times 10^{-6} \text{ mol dm}^{-3}$).

4. Discussion

4.1. Vapour pressure

The vapour pressure data of *t*-AB determined from the absorption measurements are in satisfactory agreement with those obtained by Schulze *et al.* [27] (see Table 1) employing the effusion technique. A minor discrepancy exists between the β values (see eqn. (2)) but this falls within the error limits of the present method.

4.2. Spectrum of *trans*-azobenzene

The spectrum of *t*-AB in the vapour phase shows no qualitative difference from those obtained in various polar and non-polar solvents, except for

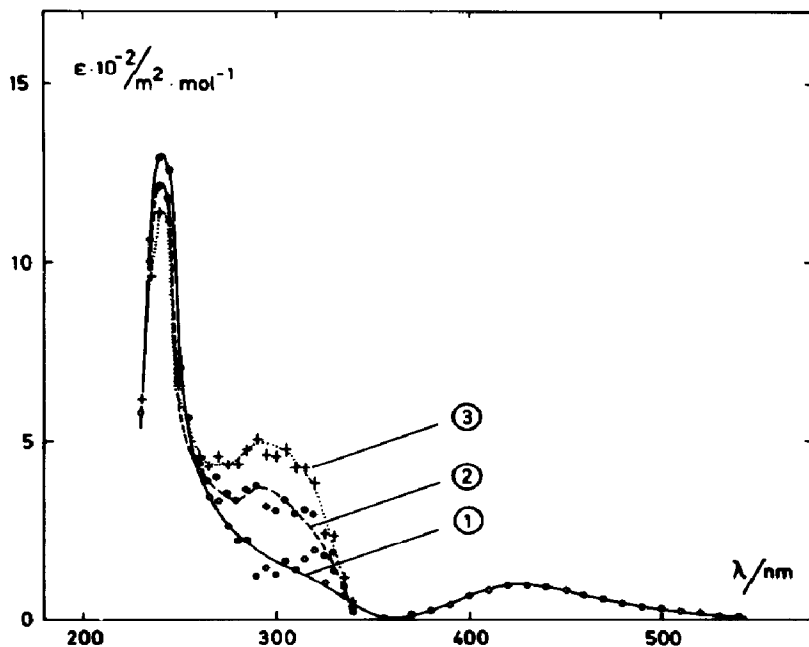


Fig. 9. Transient spectra (*cis* isomer) calculated from the flash-induced difference spectrum with various transient concentrations C_x : curve 1, $2.0 \times 10^{-6} \text{ mol dm}^{-3}$; curve 2, $2.2 \times 10^{-6} \text{ mol dm}^{-3}$; curve 3, $2.4 \times 10^{-6} \text{ mol dm}^{-3}$.

a small hypsochromic shift. Furthermore, a quantitative analysis of the spectrum confirms that the intensity of the π, π^* band is almost unaffected by the change from solution to the vapour phase. It has been pointed out that the *t*-AB molecule in solution has a planar configuration [31] equivalent to that in the solid state [32]. This conclusion was based mainly on the relationship between the spectrum in solution and the spectrum of *t*-AB in a KCl disc. We question the reliability of such an analysis as the application of similar reasoning to the spectra in the vapour phase and in solution would lead to a twisted configuration [33] of *t*-AB in solution.

The vibrational structures observed in the π, π^* band at 1350 and 220 cm^{-1} are due to the N=N central bond stretching and N=N-Ph bending modes [34 - 36]. These progressions have been observed previously by Imanshi and Tachi [37] and Kanda [38] using conventional spectrographic methods.

The n, π^* transition of *t*-AB is of low intensity with an oscillator strength of only 0.0071 at 199 °C which, however, increased to 0.0077 at 326 °C. This behaviour, which has been postulated theoretically by Albrecht [39] and applies only to forbidden or low intensity transitions, is due to increased vibronic coupling in the electronic transition at progressively higher temperatures.

4.3. Spectrum of *cis*-azobenzene

The vapour phase spectrum of *cis*-azobenzene (*c*-AB), which is identified below as the transient species in flash photolysis experiments, shows no

structure in any of the pronounced absorption bands centred around 425 nm (n, π^*) and 240 nm (ϕ, ϕ^*). The weakly developed shoulder at 265 nm (Fig. 4) is probably due to the diminished π, π^* transition and the reduction in intensity is probably caused by the increased twisting of the phenyl rings in the vapour phase.

4.4. *Cis-trans* reaction

As the *c*-AB molecule cannot be isolated in the vapour phase, identification of the transient species as the *cis* isomer of AB has to be carried out on a comparative basis by referring to the kinetic results obtained in solution. Some of the features explicitly distinguishing the transient species as the *cis* isomer can be summarized as follows.

(1) The light-induced difference spectrum shows isosbestic points which are not affected by the concentration of AB or the concentration of the transient species.

(2) The reaction is first order and reversible with the rate constant independent of the *t*-AB concentration.

(3) There are no qualitative dissimilarities between the light-induced difference spectrum in the vapour phase and that of a simulated *cis-trans* conversion in hexane (Fig. 6).

(4) The Arrhenius parameters for the observed reaction are of the expected order of magnitude ($10^{13} - 10^{14} \text{ s}^{-1}$) when compared with the corresponding *cis-trans* reaction of *t*-AB in solution.

The strong upward curvature observed in the Arrhenius plot for temperatures below 175 °C is probably due to heterogeneous catalysis at the acidic SiO₂ wall of the reaction vessel. At this temperature (175 °C) the average translational diffusion time [40] from the centre of the cell (diameter, 10 mm) to the wall is of the same magnitude (about 0.45 s) or less than the half-life of the reaction ($\tau_{1/2} < 0.50 \text{ s}$).

As indicated above and experimentally documented in a number of investigations [41 - 44] vapour phase isomerizations are often subjected to surface effects and side reactions leading to apparent decreases in activation energies and frequency factors. These difficulties were avoided in the azobenzene system by simply raising the temperature.

Although thermal *cis-trans* isomerization is well established for the aromatic diazenes (e.g. azobenzenes) it is not a common reaction in their aliphatic counterparts [45, 46]. Comparison with other vapour phase isomerizations around the N=N bond is impeded by the lack of experimental data (flash photolysis experiments in the vapour phase have now been performed on several *N*-benzylideneanilines, stilbenes and azobenzenes [47]).

4.5. Arrhenius parameters

The Arrhenius parameters describing the *cis-trans* reaction in the vapour phase are higher than those in the condensed phase (Table 4), as is the case in the analogous stilbene system [13, 14]. The activation energy predicted by the CNDO/2 method [19] is 137 kJ mol⁻¹ for the inversion mech-

anism, whereas that for rotation around the N=N bond is 293 kJ mol^{-1} . In the light of this the value of 118 kJ mol^{-1} obtained in the vapour phase clearly favours the inversion mechanism. Therefore it can be concluded that equivalent mechanisms operate in the solid, condensed and gaseous phases (see Section 4.6). Moreover the high frequency factor of 10^{14} s^{-1} effectively rules out the intervention of triplet states in the thermal isomerization reaction.

4.6. Activation parameters

The experimental entropy ΔS^\ddagger , enthalpy ΔH^\ddagger and Gibbs free energy ΔG^\ddagger of activation (Table 4) were calculated according to the relations

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad (5)$$

$$\Delta H^\ddagger = E_a - RT \quad (6)$$

$$\Delta S^\ddagger = R \left\{ \ln \left(\frac{A h}{k T} \right) - 1 \right\} \quad (7)$$

The isokinetic plot in Fig. 10 shows that regardless of the environmental conditions, *i.e.* solution, melt or vapour, a linear relationship exists between ΔS^\ddagger and ΔH^\ddagger with an isokinetic temperature of 360 K. This behaviour also suggests that identical mechanisms operate in the different phases. The linear transition state of the inversion mechanism is of lower polarity than that of the *cis* species ($\mu = 3$ debyes) [48]. (One of the lone pair dipoles of the transition state disappears and is converted into a p orbital.) Consequently, a

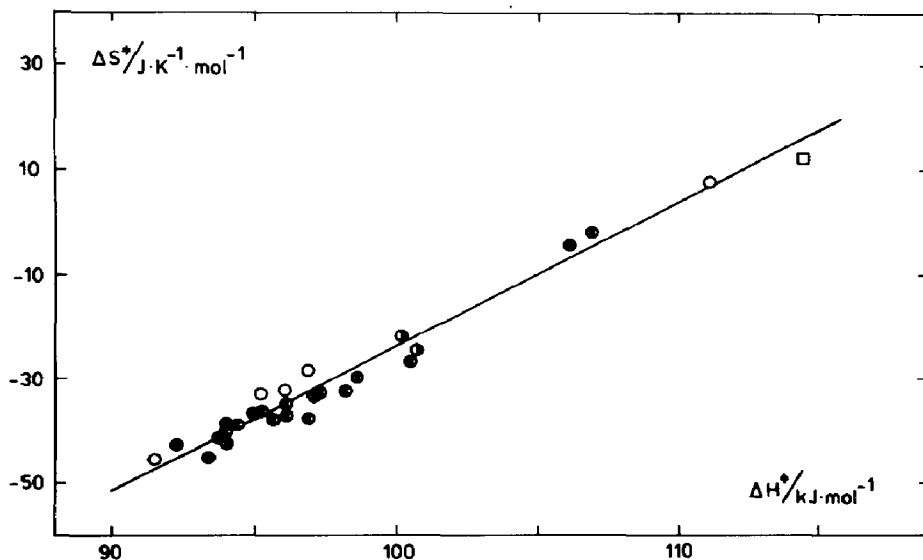


Fig. 10. Isokinetic plot at 100°C showing ΔS^\ddagger vs. ΔH^\ddagger for the *cis-trans* isomerization reaction of azobenzene in various solvents and phases: \odot , ref. 28; \circ , ref. 11; \bullet , ref. 9; \ominus , ref. 10; \square , this experiment (vapour phase).

substantial number of solvent-solute interactions are lost in solution by the structural rearrangement from the *cis* configuration to the transition state. In the light of this the negative activation entropies observed in the various solvents are expected. In the vapour phase, however, where these interactions are absent the positive ΔS^\ddagger value reflects a transition state of greater rotational freedom than that of the *cis* state (Table 4).

The Gibbs free energy of activation ΔG^\ddagger in the vapour phase is 109 kJ mol^{-1} at 25°C , and this value falls in the interval $106 - 109 \text{ kJ mol}^{-1}$ that determines ΔG^\ddagger for a large number of solvents [9 - 11, 28].

4.7. Quenching experiments

No information has been obtained regarding the mechanism of the photoisomerization process, *i.e.* no transient absorptions other than those associated with the *cis-trans* reaction could be detected using the microsecond photolysis technique.

Royanette and coworkers [6, 7] showed by the irradiation of azobenzene in cyclohexane to photostationary state (PSS) conditions that a dissolved oxygen concentration of 1 mmol dm^{-3} did not have any effect on the PSS composition. However, the *cis*-AB production decreased by roughly 60% in the (vapour) flash experiments when an oxygen concentration of 40 mmol dm^{-3} was admitted to the system (Table 3). With air in the system ($C_{\text{O}_2} = 8 \text{ mmol dm}^{-3}$) the *cis* production returned to a value identical with that of the degassed system. Ground state molecular oxygen is known to be an efficient quencher of excited singlet and triplet states of organic molecules, and with few exceptions (*e.g.* $^1(n\pi^*)$) [49] the rate constant of the quenching reaction is $10^{11} \text{ mol dm}^{-3} \text{ s}^{-1}$ in the vapour phase. Consequently, an oxygen concentration of 40 mmol dm^{-3} leads to specific quenching rates of about $4 \times 10^9 \text{ s}^{-1}$, which suggests that the conversion rates between the various excited states involved in the photoisomerization should be of the same magnitude in order to compete efficiently with the quenching reaction. Straightforward calculations applied to a simplified model in which steady state conditions were established for the singlet and triplet states during the flash predicted a triplet lifetime of less than 0.6 ns assuming a singlet lifetime of 25 ps [50] and quenching rate constants of $10^{11} \text{ mol dm}^{-3} \text{ s}^{-1}$. The presence of molecular oxygen also had an accelerating effect on the thermal isomerization rate of 15%.

4.8. Thermal experiments

The thermally induced changes shown in Fig. 8 proved to be somewhat elusive and were qualitatively similar to those of a *cis-trans* conversion (Fig. 6). When the observed spectral changes are related to a temperature-dependent *cis-trans* equilibrium, application of eqns. (3) and (4) gives a *cis* spectrum with the absorption bands centred around 235 nm ($1530 \text{ m}^2 \text{ mol}^{-1}$), 270 nm ($1050 \text{ m}^2 \text{ mol}^{-1}$) and 440 nm ($100 \text{ m}^2 \text{ mol}^{-1}$). However, a quantitative analysis based on simultaneous measurements at 301 nm (π, π^*) and 440 nm (n, π^*) leads to different equilibrium constants, *i.e.* 0.136 and 0.025,

a discrepancy which is increased by contributions from trivial thermal effects. As it is difficult to discriminate between these two effects further analysis is not possible.

The energy separation between the two isomers has been determined to be 47 kJ mol^{-1} [28, 51, 52], and if this value is retained in the vapour phase it is evident that the spectral changes induced in the limited temperature range $181 - 322^\circ\text{C}$ must be negligible.

Acknowledgment

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