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Solvent and Viscosity Effect on the Kinetics of the Thermal *cis–trans* Isomerization of 3′-Nitro-4-diethylaminoazobenzene

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ABSTRACT

The thermal cis–trans *isomerization of 3′-nitro-4-diethylaminoazobenzene in various solvents and in poly(ethyleneglycol methylethers) of different molecular weights has been studied kinetically as a function of temperature. The dependence of the experimental data on medium polarity, using both alcohols and aprotic solvents, and on polymer viscosity is discussed and compared with the behaviour of other similar dyes. An inversion mechanism, passing through an* sp-*hybridized linear transition state, appears to be the general path for all 4-diethylaminoazobenzenes. No viscosity effect could be observed. The possibility of using this reaction as a probe of the dynamic behaviour of bulk polymer molecules is discussed.*

1 INTRODUCTION

The kinetics of the *cis–trans* isomerization of azobenzenes has been used by many research groups as a convenient probe of the dynamic behaviour of bulk polymer molecules. Many reasons justify this choice: the easy availability of a large number of azo dyes with different substituents which can interact in many specific ways with the polymer matrix, the extreme sensitivity of the rate of isomerization to small changes in the physical and chemical properties of the medium, the possibility of generating easily the *cis* form directly *in situ* by low-intensity irradiation in the visible region of the spectrum, and the high thermal and photochemical stability of these dyes and their good dyeing properties, which allow the use of small concentrations and, consequently, introduce only small perturbations into the system under investigation.

In a series of previous papers,[1-4] we have studied the kinetics of the geometric isomerization of some 4-diethylaminoazobenzenes in poly(ethylene terephthalate), poly(propylene) and poly(ethylene oxides) in order to obtain a deeper insight into the structure of these polymers and a better understanding of the nature of the glassy state. However, the unambiguous interpretation of the experimental results is difficult owing to the intertwined action of many different physico-chemical factors or to the presence of specific dye–polymer interactions. For this reason we have also carried out studies centered directly on the physico-chemical properties of the dyes themselves.[5-7]

In this paper, an investigation of the behaviour of 3′-nitro-4-diethylaminoazobenzene (**I**) in different solvents and in poly(ethyleneglycol methylethers) (PEGME) of different viscosities is reported. The kinetic and spectroscopic data thus obtained are compared with the results of our previous studies giving further insight into the identification and separation of the various effects governing the behaviour of azo dyes in different environments.

2 EXPERIMENTAL

2.1 Materials

3′-Nitro-4-diethylaminoazobenzene (**I**) and 4′-nitro-4-diethylaminoazobenzene (**II**) were kindly supplied by ACNA S.p.A. and purified by repeated crystallizations from 1-butanol. Spectrograde solvents were always used and, if necessary, purified by standard techniques.[8] Poly(ethyleneglycol methylethers) (PEGME) were purchased from Fluka AG. The average molecular weights declared by the producer were 1000 and 2000 for the two cases examined here.

TABLE 1
Values of Zero-shear Viscosities (η_0) vs Temperature (T) and Activation Energies of Viscous Flow (E_{vis}) of PEGME 1000 and 2000

	η_0 *(Pas)*						E_{vis} *(kcal mol^{-1})*
	45°C	*55°C*	*60°C*	*65°C*	*75°C*	*80°C*	
PEGME 1000	0·049	0·037	0·031	0·026	0·022		6·08 ± 0·48
PEGME 2000			0·119	0·089	0·079	0·064	6·36 ± 1·27

2.2 Measurements

Spectral and kinetic measurements were carried out on 2×10^{-5} M solutions. The absorption spectra were measured on a Beckmann Model DU 7 spectrophotometer, samples being kept in the dark for at least 24 h before any measurement in order to avoid the presence of the *cis* isomer. For the determination of *cis–trans* isomerization rates the samples were exposed for 10 min, in a thermostatted quartz cell, to a 100 W tungsten lamp, a time long enough to reach a photostationary state.[7] After irradiation, the cell was quickly transferred into the cell compartment of the spectrophotometer and the absorbance change at or near the absorption maximum of the *trans* form was followed. Irradiation and thermal return monitoring were performed at the same temperature. When the *cis–trans* isomerization rate was too fast for the procedure described above, the measurements were executed by means of a Nortech model FPX-1 flash photolysis apparatus. In all cases strictly first-order behaviour was observed. A small amount of diethylamine (*c.* 0·5%) was always added to the solutions under investigation in order to avoid adventitious contamination by acid impurities, which were found to affect strongly the thermal reaction rate.

Apparent viscosities were obtained by a Haake–Couette viscometer in the shear rate ($\dot{\gamma}$) range 2·72–147 s^{-1}. Zero shear viscosities (η_0) of the two polymers at different temperatures are collected in Table 1. Plots of $\ln \eta_0$ vs T^{-1} resulted in good correlations, giving activation energies of 6·08 kcal mol^{-1} and 6·36 kcal mol^{-1} for PEGME 1000 and PEGME 2000, respectively.

3 RESULTS

The transition energies (E_{max}) of 3′-nitro-4-diethylaminoazobenzene (**I**) and 4′-nitro-4-diethylaminoazobenzene (**II**) in different solvents, together with the values of Kamlet–Taft π^* solvent polarity parameter[9] are shown in

TABLE 2

Transition Energies (E_{max}) of the Visible Absorption Band of 3′-Nitro-4-diethylaminoazobenzene I and 4′-Nitro-4-diethylaminoazobenzene (II) in Various Solvents

Solvent	π^{*}[a]	E_{max}	
		I	II
n-Heptane	−0·081	—	63·13[b]
Cyclohexane	0·000	66·73	—
Tetrachloromethane	0·294	65·97	61·37[b]
1-Butanol	0·503	—	59·09[b]
Ethanol	0·540	64·08	58·97[b]
Tetrahydrofurane	0·576	63·97	—
Diglyme	—	63·77	—
Methanol	0·586	—	58·73[b]
Acetone	0·683	63·60	58·49[b]
Acetonitrile	0·713	63·44	58·37[b]
Dimethylformamide	0·875	61·97	57·00
Ethyleneglycol	0·932	61·20	—
Dimethylsulfoxide	1·000	61·11	56·20[b]

[a] Kamlet–Taft solvent polarity parameter.[9]
[b] From Ref. 6.

TABLE 3

First-order Rate Constants (*k*) at 25°C and Activation Enthalpies ($\Delta H^{\neq}$) and Entropies ($\Delta S^{\neq}$) of the Thermal *cis–trans* Isomerization of 3′-Nitro-4-diethylaminoazobenzene (I) and 4′-Nitro-4-diethylaminoazobenzene (II)

Solvent	I			II		
	10^4k (s^{-1})	$\Delta H^{\neq}$ (*kcal* mol^{-1})	$\Delta S^{\neq}$ (*cal* $°C^{-1}$ mol^{-1})	k (s^{-1})	$\Delta H^{\neq}$ (*kcal* mol^{-1})	$\Delta S^{\neq}$ (*cal* $°C^{-1}$) mol^{-1})
n-Heptane	—	—	—	0·007 1[a]	17·3 ± 0·2[a]	−11·8 ± 0·5[a]
Cyclohexane	0·99	18·8 ± 1·0	−13·9 ± 3·2	—	—	—
Tetrachloromethane	1·27	16·4 ± 1·7	−21·8 ± 5·5	0·006 6[a]	—	—
1-Butanol	—	—	—	16·7[a]	9·0 ± 0·1[a]	−23·0 ± 0·4[a]
Ethanol	139·2	5·7 ± 0·4	−47·8 ± 1·2	38·7[a]	9·5 ± 0·9[a]	−20 ± 3[a]
Tetrahydrofurane	2·61	18·4 ± 1·6	−14·2 ± 5·1	—	—	—
Diglyme	1·50	18·2 ± 0·4	−15·2 ± 1·3	—	—	—
Methanol	—	—	—	90·0	9·7 ± 0·2	−17·0 ± 0·7
Acetone	3·02	19·2 ± 2·1	−10·2 ± 6·6	17·6[a]	9·8 ± 0·1[a]	−19·6 ± 0·2[a]
Acetonitrile	3·07	26·2 ± 3·1	−13·3 ± 9·9	58·0	9·7 ± 0·4	−18·2 ± 0·6
Dimethylformamide	6·89	18·0 ± 0·4	−12·8 ± 1·1	138	8·8 ± 0·1	−19·3 ± 0·1
Ethyleneglycol	396 3	14·4 ± 0·6	−12·1 ± 2·1	—	—	—
Dimethylsulfoxide	13·91	17·6 ± 0·6	−12·6 ± 1·9	452	8·8 ± 0·3	−17·50 ± 0·9

[a] From Ref. 10.

TABLE 4
Rate Constants (k) vs Temperature (T) and Activation Parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$) of the Thermal *cis–trans* Isomerization of 3'-Nitro-4-Diethylaminoazobenzene (I) in PEGME 1000 and 2000

	10^2k (s^{-1})						$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal °C^{-1} mol^{-1})
	45°C	55°C	60°C	65°C	75°C	80°C		
PEGME 1000	0·29	0·68	0·81	1·58	3·30	4·77	17·4 ± 0·9	−15·5 ± 2·6
PEGME 2000			1·14	1·87	3·40	5·64	17·1 ± 1·5	−16·2 ± 4·3

Table 2. Table 3 gives the first-order rate constants (k) of the thermal *cis–trans* isomerization of (I) and (II) at 25·0°C, as well as the corresponding activation enthalpies ($\Delta H^{\neq}$) and entropies ($\Delta S^{\neq}$). The latter values were obtained by applying the Eyring equation to the experimental data in the temperature range 15–50°C. The errors are quoted as standard deviations from linear regression analysis. The isomerization rate constants of **I**, measured at different temperatures in PEGME 1000 and 2000, are collated in Table 4, together with the values of the relevant activation parameters.

4 DISCUSSION

As observed in the case of other 4-diethylaminoazobenzenes, the energies of the visible absorption maxima of **I** undergo a marked bathochromic shift in polar solvents, indicating the CT nature of the electronic transition.[6] A good linear correlation is found when plotting $(E_{\max})_{\mathrm{I}}$ as a function of the polarity parameter in aprotic solvents. The following empirical equation is obtained:

$$(E_{\max})_{\mathrm{I}} = 67{\cdot}22 - 5{\cdot}73\pi^* \qquad r = 0{\cdot}983 \tag{1}$$

No significant change is detected if alcoholic solvents are also taken into account, the corresponding equation then being:

$$(E_{\max})_{\mathrm{I}} = 67{\cdot}29 - 5{\cdot}98\pi^* \qquad r = 0{\cdot}981 \tag{2}$$

The π^* polarity scale[9] was derived from solvent effects on p–π^* and π–π^* electronic spectral transitions of a variety of nitro aromatic compounds chosen so that π^* should represent only dipole–dipole or dipole-induced dipole interactions. Therefore, in this case, the solvatochromism appears to be determined predominantly by polar interactions, whilst hydrogen bonding does not seem to play an important role. This behaviour is parallel to that of 4'-nitro-4-diethylaminoazobenzene (**II**), for which

$$(E_{\max})_{\mathrm{II}} = 62{\cdot}89 - 6{\cdot}56\pi^* \qquad r = 0{\cdot}995 \tag{3}$$

in aprotic solvents and

$$(E_{\mathrm{max}})_{\mathrm{II}} = 62{\cdot}73 - 6{\cdot}54\pi^{*} \qquad r = 0{\cdot}991 \tag{4}$$

if alcohols are also included.[6]

The stronger electron-withdrawing effect of the nitro group in position 4′ rather than 3′ is reflected in the fact that the values of the intercepts of the straight lines representing eqns (3) and (4) and referring to **II** are *c.* 5 kcal mol^{-1} lower than those of **I**. On the other hand, the small differences in the slopes of the solvatochromic plots of the two dyes chosen here show the substantial identity of the physical forces involved in the stabilization of both excited and ground states of **I** and **II** by the solvent.

A useful consequence of these results is that E_{max} for both dyes may be used as an indicator of the solvent polarity, and is as appropriate as π^{*}.

It is well known that the thermal *cis–trans* isomerization reaction of azobenzenes accelerates on increasing the polarity of the medium. In particular, 4-diethylaminoazobenzenes substituted by 4′-electron-withdrawing substituents, e.g. dye **II**, show dramatic enhancement of the corresponding rate constants, from $6{\cdot}1 \times 10^{-3}\,\mathrm{s}^{-1}$ in *n*-hexane to $517\,\mathrm{s}^{-1}$ in dimethylsulfoxide at 25°C.[7] Here again a good correlation with π^{*} is found in aprotic solvents. Therefore, it is not surprising that, using the values in Tables 2 and 3, least squares linear analysis results in satisfactory correlations, giving the following equation for **II**:

$$\ln k_{\mathrm{II}} = 109{\cdot}2 - 1{\cdot}82(E_{\mathrm{max}})_{\mathrm{II}} \qquad r = 0{\cdot}965 \tag{5}$$

and, analogously, for **I**

$$\ln k_{\mathrm{I}} = 20{\cdot}38 - 0{\cdot}45(E_{\mathrm{max}})_{\mathrm{I}} \qquad r = 0{\cdot}936 \tag{6}$$

Equations (5) and (6) refer only to aprotic solvents. If alcoholic solvents are also considered, strong deviations from linearity are observed, especially in the case of **I**. The kinetic data are reproduced graphically in Fig. 1 as $\ln k$ vs $(E_{\mathrm{max}})_{\mathrm{I}}$ plots. On the basis of the kinetic behaviour of **II**, Schanze *et al.*[10] suggested that the degree of charge-transfer in the transition state and in the Franck–Condon *trans* excited state are comparable. This fact appeared to be in favour of a rotational mechanism, where the original π-bond of the azo group is broken heterolytically, rather than an inversion path consisting in the in-plane shift of one of the azo nitrogens through an *sp*-hybridized linear transition state. However, the slope of eqn (6), which refers to **I**, is much smaller than that of eqn (5), although the correlation is still satisfactory. Therefore, the transition state of **I** seems to be much less polar than the excited state of the *trans* isomer. This could be attributed to the non-planar structure of the transition state, but it is difficult to explain why this effect should not be operative in the case of **II**. The presence of a nitro group in the

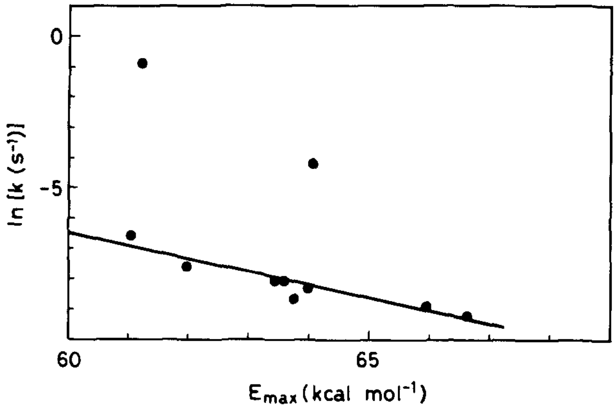
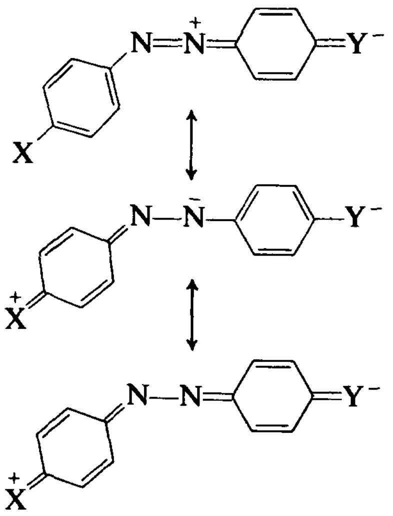


Fig. 1. Natural logarithm of the thermal *cis–trans* isomerization kinetic constants (*k*) as a function of transition energies of the visible absorption maxima (E_{max}) of **I**. The straight line is obtained by applying least squares analysis only to aprotic solvents (see eqn (6)); the data deviating strongly from linearity refer to alcoholic solvents.

4'-position, instead of the 3'-position, does not seem to be able to increase so dramatically the dipole moment of the strongly dipolar rotational transition state, which, in both cases, can be envisaged as consisting of two oppositely charged moieties connected by a single N–N bond. In fact, the lack of planarity of the rotational transition state should minimize mesomeric effects.



On the contrary, an inversion mechanism can justify such a difference. In the transition state, if a 4'-electron-withdrawing substituent is present, coplanar resonance structure such as those reproduced in the scheme above may be hypothesized, and these are not possible when the nitro group is in the 3'-position.[3,11-14]

As stated above, hydrogen bonding has no effect on the solvatochromism of the *trans* form of both dyes, whilst the rate constants of the thermal geometrical isomerization measured in alcohols deviate markedly from the simple behaviour observed in aprotic solvents, described by eqns (5) and (6). In particular, the effect on **I** is stronger than on **II**. If we compare the kinetic data for ethanol and acetone, which are characterized by similar polarities (as shown by $E_{\max}$ and π^* values), in the case of **I** $k_{\mathrm{EtOH}}/k_{\mathrm{Acetone}} = 41{\cdot}8$, while the same ratio is 2·2 for **II**.

This observation further confirms that the analogy between the Franck–Condon state of the *trans* form and the transition state of the isomerization reaction cannot be easily assumed. Apart from geometry differences, the process going from the *cis* to the *trans* species occurs under conditions of quasi-equilibrium with the solvent and with at least partial retention of specific interactions, in contrast with the electronic excitation. As a consequence, in alcohols, the transition state may be stabilized by a large system of hydrogen bonds, not too dissimilar from that of the starting *cis* species. As suggested by Schanze *et al.*,[10] hydrogen bonding to the nitro group enhances its electron-withdrawing ability, making polarity effects stronger, but the simultaneous weakening of the interaction of the diethylamino group with the alcoholic solvents acts as a compensating effect, particularly in the case of the strongly dipolar dye **II**. An experimental quantitative indication of such an effect is given by the values of the activation enthalpies and entropies. In alcohols, $\Delta H_{\mathrm{I}}^{\neq}$ is always lower than in aprotic solvents of comparable polarity, while in the case of **II**, the accelerating effect is almost equally distributed between enthalpic and entropic factors.

The difficulties described above in the interpretation of the kinetic data in alcohols and in the discrimination of the various active factors could also be partly due to simultaneous occurrence of acid catalysis. While in aprotic solvents, addition of small amounts of diethylamine works satisfactorily in eliminating residual acid traces, this procedure cannot ensure with certainty comparable hydrogen ion activities in alcohols, which are characterized by different autoprotolytic equilibrium constants, and this does not guarantee completely that different mechanistic paths are not adopted by the system. Although control experiments with different concentrations of diethylamine have been carried out and no rate change has been found above a certain limit concentration of diethylamine, such an investigation requires a more systematic approach and is now in progress.

At this present stage, therefore, the results reported here for dye **I** support preferentially an inversion mechanism, not different from that ascertained in the case of 4'-donor-4-diethylaminoazobenzenes.[7,11–14] The differences shown by **II** with respect to **I** do not appear to be of a fundamental nature, but can be satisfactorily explained in terms of the electronic mesomeric effects active on the inversion planar transition state.

In conclusion, as also suggested by Nishimura *et al.*[11–14] in studies in which substituent, solvent and pressure effects were examined, the isomerization inversion scheme is likely to be general for all 4-diethylaminoazobenzenes, independent of the substituents and the solvents.

In the last few years, the dependence of thermal isomerization rates around double bonds on the medium viscosity has been the object of many theoretical studies,[15–18] but progress in this field is hampered by the lack of sufficient adequate experimental data and by the aforementioned problems connected with the separation of the various factors affecting isomerization reactions. In a recent paper, we reported an investigation on the thermal *cis–trans* isomerization rate of **I** in a series of poly(ethylene oxides) characterized by different molecular weights.[3] k_I was found to decrease markedly on increasing polymer viscosity until a limiting value was reached for polymer molecular weights greater than the critical value ($\bar{M}$). Unfortunately, the polymer chosen for that study also showed a regular variation in the free hydroxyl group concentration and in polarity, as measured by E_{max} values. Even if the prevailing role of viscosity in determining the isomerization rate could be proven, it was not possible to reach a clear-cut discrimination between the various factors cited above. We therefore examined the kinetic behaviour of **I** in PEGME 1000 and 2000, which are characterized by markedly different viscosities, but do not introduce complications connected with large polarity changes and free hydroxyl group presence.

In Table 4 the kinetic data, referring to **I**, obtained in PEGME 1000 and 2000 at different temperatures are reported. As usual, small amounts of diethylamine were added in order to neutralize acidic impurities. The data in Table 4 clearly show that large changes in viscosity do not significantly modify the isomerization rate of **I**, even if, in this case, we are well below $\bar{M}$. Moreover, the order of magnitude of the kinetic constants and activation enthalpies and entropies appear well in line with the corresponding values observed in diglyme. Such a behaviour is in striking contrast to that found in poly(ethylene oxides). A simple explanation of this fact cannot be given easily, but could be related to the presence of specific interactions between the dye and OH groups, as revealed by our experiments in alcoholic solvents. As a consequence of the more intimate connection with the polymer, in poly(ethylene oxides) the microenvironment of the dye molecules, as well as the effective free volume available for the isomerization reaction, could be quite different from that indicated, by macroscopic parameters, such as viscosity. On the contrary, in PEGME a more uniform dye distribution leads to a behaviour conforming to that observed in solvents of comparable structure and polarity.

5 CONCLUSION

The thermal *cis–trans* isomerization reaction of 3′-nitro-4-diethylaminoazobenzene has been studied in various solvents and in PEGME of different molecular weights. The dependence of the kinetic results on the solvent polarity and comparison with the behaviour of 4′-nitro-4-diethylaminoazobenzene lead to the conclusion that the general mechanism of the thermal isomerization of azo dyes passes through an *sp*-hybridized linear transition state (inversion mechanism). Large changes in viscosity do not appear to modify markedly the kinetic parameters in contrast with previous observations in the case of poly(ethylene oxides). These results show that the use of this reaction as a probe of the dynamic behaviour of the bulk polymer molecules requires further attention and the availability of a large amount of experimental data in order to discriminate the actions of the many different physico-chemical parameters deriving from the characteristics of the dye and the polymer matrix and from their interactions.

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