

Isomerisation dynamics of a thiocarbocyanine dye in different electronic states and in different classes of solvents

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Abstract

A study of the isomerisation dynamics of 3,3'-diethylthiocarbocyanine in the excited state in alkanenitriles as well as in the ground state in both alkanenitriles and *n*-alcohols, using ps transient grating spectroscopy and flash photolysis is reported. The intrinsic activation energy for isomerisation has been determined from isoviscosity plots. In the ground state, the activation energy amounts to 12.9 kcal/mol in both nitriles and alcohols, while it is equal to 3.0 kcal/mol in the excited state. The reduced isomerisation rate constant shows a fractional dependence on the solvent viscosity, with a fractional exponent α of 0.20 and 0.38 for the ground state isomerisation in alcohols and nitriles and of 0.65 for the excited state isomerisation. The data have been analysed within the framework of the Kramers theory using different models for friction. The best agreement was obtained with the Grote–Hynes model, which takes into account the frequency dependence of the friction. The solvent dependence of α for the ground state isomerisation is accounted for by a different average value of the infinite frequency shear modulus in alcohols and nitriles. The barrier height dependence of α is explained by a decrease of the barrier's top frequency by going from the ground to the excited state.

1. Introduction

Over the past years, a great theoretical and experimental effort has been devoted to the understanding of the dynamics of cis–trans isomerisation reactions in the condensed phase. The model compounds used for these studies were mainly diphenylpolyenes [1–11], cyanines [12–20] and triphenylmethane dyes [21–28]. In most cases, the rate of isomerisation was measured as a function of the solvent viscosity, which was varied either by pressure or temperature or/and by using a series of solvents with increasing *n*-alkyl chain length. The observed decrease of the rate of isomerisation with increasing viscosity has usually been rationalised with the Kramers model [29], which considers the isomerisation as a Brown-

ian motion in a one-dimensional harmonic potential. According to this model, the friction dependence of the rate of barrier crossing shows three distinct regions. In the low friction region, the rate of reaction increases with increasing friction. In this regime, the molecule reaches the top of the barrier through collision with the solvent. In the intermediate friction region, the rate begins to decrease as friction increases. In the region of higher friction, the Smoluchowski limit, the rate becomes inversely proportional to friction. The intermediate friction region corresponds to the turnover from the energy controlled regime to the Smoluchowski limit. If a hydrodynamic model is assumed, friction is then proportional to viscosity. Most of the isomerisation processes studied in solution are in the intermediate and

high friction regimes. Among the different data of friction dependence of isomerisation, only a few could be fitted to the hydrodynamic Kramers expression [3,5,30]. In most studies [2,4,10,11,15,26], the whole friction range could not be fitted to this expression with a single set of parameters.

Other models were proposed to describe friction. In the Kramers–Hubbard model [31], friction is determined from the rotational diffusion of the isomerising molecule. This procedure proved to be successful to describe the isomerisation dynamics of several diphenyl polyenes in alkanes [32–34]. On the other hand, the isomerisation of DODCI in both the ground and the excited state did not fit to the Kramers–Hubbard model, the rotational diffusion being essentially hydrodynamic [15]. Bowman and Eisenthal [35] showed that experimental translational diffusion coefficients for naphthalene in hydrocarbons were equivalent measures of the friction experienced in the rotational diffusion of 1,1'-binaphthyl and therefore of the friction experienced by the torsional motion leading to radiationless decay of binaphthyl. Similarly, Sun and Saltiel [36] reported that the Kramers equation could give a good fit to the photoisomerisation of *t*-stilbene in alkanes, when the shear viscosity was multiplied by the microfriction factor for translational diffusion, calculated with the semi-empirical formula of Spornol and Wirtz [37]. This procedure was not so satisfactory with the isomerisation of cyanines in *n*-alcohols, although the Kramers fit was clearly improved [38]. Similar improvements were also obtained using the free space model of Dote, Kivelson and Schwartz [38–40]. However, all the isomerisation data could be fitted to an empirical expression proposed by Fleming and co-workers [5,14,15]

$$k_{\text{iso}} \propto \eta_s^{-\alpha}, \quad (1)$$

where k_{iso} is the rate constant of isomerisation, η_s is the shear viscosity and α can vary from 0.1 to 1. The Smoluchowski limit corresponds to an α -value of unity. Large values of α have predominantly been observed in the case of excited state isomerisations with small barrier heights E_0 , as for example *cis*-stilbene in alkanes with $E_0 \approx 0$ kcal/mol and $\alpha = 0.89$ [41]. On the other hand, the smallest α -values have been measured for ground state isomerisations, which have a higher barrier height, as for

example DODCI in alcohols with $E_0 = 13.7$ kcal/mol and $\alpha = 0.26$ [15]. This barrier height dependence of α has been explained as the consequence of the frequency dependence of friction. This effect has been taken into account in an extended Kramers model proposed by Grote and Hynes [42]. For high barrier crossing frequencies, this model predicts a much weaker friction dependence at high viscosities than the hydrodynamic Kramers model. Such high frequencies occur when the barrier's top is sharp, that is for high barriers. In this case, friction due to low frequency motion does not influence the barrier crossing. This explains why the strongest departures from the hydrodynamic Kramers model have been observed for ground state isomerisations. Expressions for the frequency dependent friction have been proposed by Bagchi and Oxtoby [43]. The latter as well as Hochstrasser and co-workers [10] and Waldeck and co-workers [11] have analysed the friction dependence of the photoisomerisation of DODCI, stilbene and stilbene derivatives in terms of the Grote–Hynes theory. Although the friction dependence could be fitted to the Grote–Hynes expression, the barrier frequencies obtained were, in all cases, unrealistically small. This effect was ascribed to the breakdown of the one-dimensional approximation due to the involvement of other modes in the isomerisation. However, apart of the small values of the barrier frequencies, the relative magnitude of the frequencies showed realistic trends when different solute/solvent systems were compared. Waldeck and co-workers have compared the parameters obtained from the fit of the Grote–Hynes expression to the photoisomerisation data of *t*-stilbene and 4,4'-dimethoxystilbene in alkanes and nitriles [11]. They observed realistic trends, such as the increase of the barrier frequency with increasing barrier height. However, the barrier height differences were small and therefore the change of barrier frequency was not very pronounced.

An alternative interpretation of Eq. (1) is provided by the medium enhanced barrier model developed by Saltiel and co-workers [44,45]. In this case, α represents the fraction of the viscous flow activation energy that is experienced by the solute as an additional barrier. The variation of α in the photoisomerisation of substituted stilbenes in *n*-alkanes could be successfully explained with the medium enhanced

barrier model [46], which, however, has not been extended to isomerisations in polar solvents.

In this paper, we present a study of the friction dependence of the isomerisation of a cyanine dye, 3,3'-diethylthiacarbocyanine iodide (DTCI), in both the ground and the excited state in nitriles. The most stable form of DTICI in the ground state is the trans form (see Fig. 1). Once excited to the first singlet excited state, DTICI decays rapidly to the cis ground state with a yield of 0.95 [47]. The cis ground state isomerises back to the trans form in the ms timescale. The ground state isomerisation of DTICI has furthermore been measured in *n*-alcohols.

The results will be analysed with the Kramers theory with different models for friction: the hydrodynamic model, the semi-empirical microfriction formulas of Spornol and Wirtz and Wilke and Chang and finally, the Grote–Hynes model of frequency dependent friction.

2. Experimental

2.1. Excited state isomerisation

The excited state isomerisation of DTICI was measured by picosecond transient grating spectroscopy. This technique has been reviewed by several authors [48–50] and will be described only briefly here. The sample is excited by two spatially crossed and time coincident laser pulses producing an interference pattern, which creates a spatially modulated distribution of ground state and excited state populations. Consequently, similar distributions of refractive index and absorbance are generated. The amplitude of these grating-like distributions can be measured by a third, time delayed, laser pulse striking the grating at phase matching angle. If its wavelength corresponds to the absorbance and/or refraction spectrum of one of the populations present in the sample, the probe pulse is

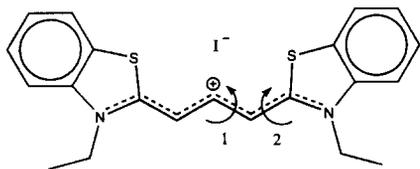


Fig. 1. 3,3'-diethylthiacarbocyanine iodide (DTICI).

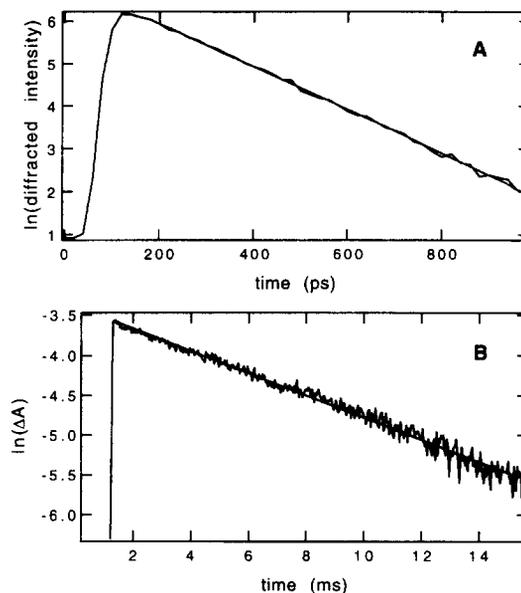


Fig. 2. (a) Logarithmic plot of the time evolution of the diffracted intensity corresponding to the ground state recovery of DTICI in decanenitrile at 293 K and at 532 nm. (b) Logarithmic plot of the ground state recovery kinetics of DTICI trans form in decanenitrile at 293 K obtained by exciting at 532 nm and probing at 570 nm.

partially diffracted. For small diffraction efficiency, as it is normally the case, the diffracted intensity is directly proportional to the square of the photoinduced concentration changes.

In the case of DTICI, the sample was excited with two 532 nm pulses and the grating was read with a third 532 nm pulse. At this wavelength, both the cis and trans forms have almost the same extinction coefficient [51], and therefore the kinetics of the ground state recovery in both cis and trans forms can be obtained by varying the time delay between the pump and probe pulses. Fig. 2a shows the decay of the diffracted intensity measured with DTICI in decanenitrile at 20°C. All the diffracted intensity decays were single exponential. As the diffracted intensity is proportional to the square of the concentration changes, the ground state recovery times, τ_{gsr} , are equal to twice the diffracted intensity decay times. The excited state isomerisation rate constant k_{iso}^* was obtained from the relation $k_{\text{gsr}} = \tau_{\text{gsr}}^{-1} = k_0 + k_{\text{iso}}^*$, where k_0 is the radiative rate constant of DTICI which is equal to $3.22 \times 10^8 \text{ s}^{-1}$ in MeOH [52]. Very close values were obtained from the fluores-

cence quantum yield of DTCI in acetonitrile and in decanenitrile at room temperature and therefore, the same radiative rate constant was used in all solvents. This is a reasonable assumption as k_{gsr} is much larger than k_0 , the smaller value of k_{gsr} being still 10 times larger than $3.22 \times 10^8 \text{ s}^{-1}$. Moreover, the intersystem crossing quantum yield of DTCI has been reported to be ≤ 0.001 [53], therefore the deactivation of the excited state via the triplet state can be neglected.

The picosecond transient grating set up was the same as described in Refs. [54,55] except for the Nd-YAG laser which was an active/passive mode-locked Q-switched laser with a single amplification stage (Continuum model PY61-10). The pulse duration was about 30 ps FWHM, the total pump intensity on the sample was around $100 \mu\text{J}/\text{cm}^2$ and the probe pulse intensity about 10 times smaller. The polarisation of the probe pulse was oriented at 54.7° relative to the polarisation of the pump pulses, in order to avoid contamination of the ground state recovery kinetics by reorientational effects. Each measurement was repeated three times and the average value was used.

2.2. Ground state isomerisation

The $S_1 \leftarrow S_0$ absorption maximum of the trans form is at 560 nm, while that of the metastable cis form is at 545 nm [51]. The ground state isomerisation rate was determined from the kinetics of the trans form recovery at 570 nm after excitation at 532 nm. Fig. 2b shows the ground state recovery of the trans form of DTCI in decanenitrile at 20°C . These measurements were carried out with a conventional laser flash photolysis system equipped with a Q-switched Nd:YAG laser (JK Laser model 2000). The data acquisition was made on a digital storage 100 MHz oscilloscope (Gould 4074), interfaced with a personal computer. Each measurement was repeated three times and the average value was used.

2.3. Samples

DTCI was obtained from Ilford. The alcohols were of the highest commercially available purity and were used as such. Acetonitrile, propionitrile and butyronitrile were of spectroscopic grade and used

without further purification. The other nitriles were washed twice with half volume of concentrated HCl, then with saturated aqueous NaHCO_3 , dried with MgSO_4 and distilled [56]. For the transient grating measurements, the concentration of DTCI was about $2 \times 10^{-5} \text{ M}$, corresponding to an absorbance at 532 nm of 0.15 on 1 mm, the cell thickness. For the flash photolysis experiments, the thickness of the cell was 1 cm and the absorbance at 532 nm of unity. The temperature of the sample was stable within $\pm 0.25^\circ$. The viscosities have been taken from Ref. [57] for the *n*-alcohols, from Ref. [58] for acetonitrile and from Ref. [11] for the other nitriles.

3. Results

The ground state and excited state isomerisation rate constants have been measured between 10 and 80°C in a series of alkanenitriles (acetonitrile to decanenitrile, except heptanenitrile) and in a series of *n*-alcohols (methanol to octanol, except hexanol and heptanol, ground state isomerisation only). The rate constants of isomerisation in the ground state at various temperatures are listed in Tables 1 and 2 and the rate constants of ground state recovery (equivalent to excited state decay rates) are listed in Table 3. In the excited state, the isomerisation takes place in some tens of picoseconds depending on temperature and viscosity, while the ground state isomerisation is much slower, on the ms timescale. The temperature dependence of the rate constant of isomerisation can be expressed by an Arrhenius type equation

$$k_{\text{iso}}(T) = F(\zeta) \exp(-E_0/k_{\text{B}}T), \quad (2)$$

where $F(\zeta)$ is the reduced isomerisation rate constant depending on the friction, ζ , E_0 is the intrinsic activation energy for the isomerisation and k_{B} is the Boltzmann constant. The activation energy, E_0 , can be determined by measuring the isomerisation rate at constant viscosity but at different temperatures. Such isoviscosity plots are shown in Fig. 3 for both ground and excited state isomerisations. It can be seen that the slopes of the isoviscosity plots are, within experimental error, viscosity independent. This result contrasts with that observed by Åkesson et al. for the excited state isomerisation of a very similar cyanine,

3,3'-diethyltetramethylindocarbocyanine, in alcohols [17]. In this case, the isoviscosity plots were linear, but curved and becoming flatter for the lower alcohols. Zeglinski and Waldeck have observed a similar effect for the isomerisation of 4,4'-dimethoxystilbene in alcohols [59]. However, the isoviscosity plots were linear but their slope decreased with increasing viscosity. On the other hand, the slope of the isoviscosity plots in alkanenitriles was independent of viscosity, as observed here. This effect was ascribed to the slow dielectric relaxation times of alcohols, slowing down the dynamics of solute/solvent interactions and causing a variation of the barrier height within the time-scale of the isomerisation. In the present case, this dynamic solvent effect is not observed for the ground state isomerisation in alcohols.

Table 1
Temperature dependence of the ground state isomerisation rate constant of DTCI in *n*-alcohols (limits of error on $k_{\text{iso}} \pm 2\%$)

Solvent	<i>T</i> (K)	k_{iso} (s^{-1})
methanol	322	1720
	313	930
	303	452
	293	220
ethanol	341	4850
	333	2650
	324	1475
	313	710
	303.5	370
propanol	328	1980
	319.5	970
	312	587
	303	337
	301	306
butanol	292.5	154
	337	3180
	322	1100
	312	578
	303	301
pentanol	297	198
	343	4720
	330	2190
	321	1110
	310	575
octanol	303	347
	339	3520
	327	1300
	315	680
	309.5	358
	303	263
	294	125

Table 2
Temperature dependence of the ground state isomerisation rate constant of DTCI in alkanenitriles (limits of error on $k_{\text{iso}} \pm 2\%$)

Solvent	<i>T</i> (K)	k_{iso} (s^{-1})
acetonitrile	313	1190
	303	548
	283	127
propionitrile	332	3590
	323	1920
	313.5	950
	303	500
butyronitrile	293	244
	333	3580
	323	1680
	313	915
	304	460
pentanenitrile	303	435
	323	1730
	303	427
	283	108
hexanenitrile	273	51
	323	1515
	313	812
	303	368
octanenitrile	291	163
	338	3225
	323	1250
	303	316
nonanenitrile	300	253
	334	2230
	323	1060
	311	474
	303	275
decanenitrile	294	157
	348	5190
	333	2095
	323	1030
	307	333
	303	254
	293	133

This is certainly due to the very slow isomerisation rate, of the order of ms, compared to the average dielectric relaxation rate of alcohols, of the order of a few hundreds of ps. The excited state isomerisation of DTCI in alcohols has not been studied here, due precisely to the impossibility of extracting the intrinsic activation energy from isoviscosity plots.

From these isoviscosity plots, the activation energy for the isomerisation of DTCI in the ground state amounts to 12.9 ± 0.7 kcal/mol in both nitriles and alcohols, while the activation energy for the

excited state isomerisation amounts to 3.0 ± 0.2 kcal/mol in nitriles (see Table 4). This latter value is of the same order of magnitude as that observed for the excited state isomerisation of trans-stilbene in

Table 3
Temperature dependence of the rate constant of DTCI ground state recovery in alkanenitriles (limits of error on $k_{\text{gsr}} \pm 3\%$)

Solvent	T (K)	k_{gsr} (ns^{-1})
acetonitrile	333	18.0
	319.5	13.9
	308	10.9
propionitrile	294	7.7
	341	17.2
	329	13.5
	317.5	10.4
butyronitrile	305.5	8.4
	294	5.8
	354	17.8
	341	14.0
	329.5	11.6
pentanenitrile	318	9.0
	307	7.1
	295	5.4
	352	14.8
	340.5	12.0
	329	9.75
hexanenitrile	318	7.8
	307	6.1
	295	5.0
	352	12.9
	341	10.6
	329.5	8.7
octanenitrile	318	6.7
	307	5.25
	294	4.0
	353	10.5
	342	8.55
	331	6.5
nonanenitrile	319	5.25
	307.5	3.95
	295	3.1
	353	9.6
	342	7.5
	330	6.0
decanenitrile	319	4.3
	307.5	3.6
	295.5	2.7
	355	9.3
	343	7.4
	331	5.65
	319	4.35
	307	3.4
	295.5	2.5

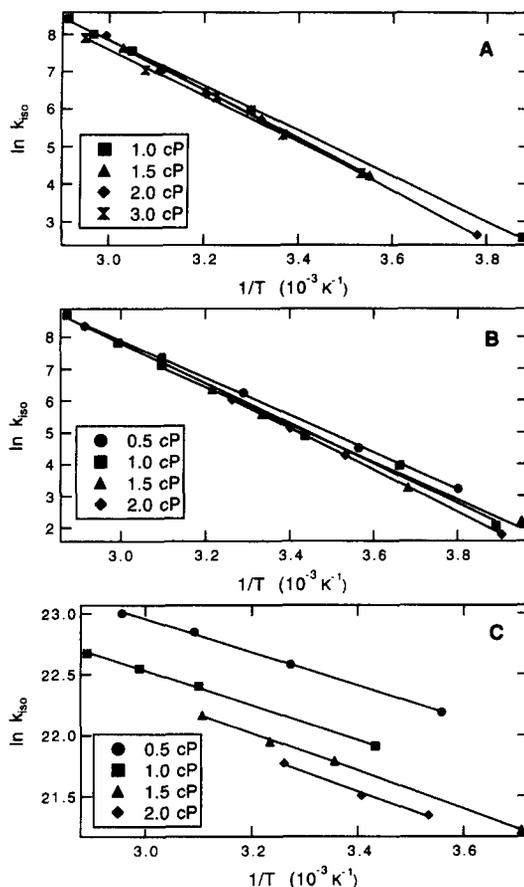


Fig. 3. Isoviscosity plots for (a) DTCI ground state in *n*-alcohols, (b) DTCI ground state in alkanenitriles and (c) DTCI excited state in alkanenitriles.

alkanes (3.5 kcal/mol) and in nitriles (2.6 kcal/mol) [11] and of DODCI in alcohols (2.7 kcal/mol) [60]. The ground state activation energy of DTCI is also close to that of DODCI in alcohols (13.7 kcal/mol) [60]. Moreover, it is the same in both classes of

Table 4

Activation energy, E_0 , obtained from the isoviscosity plots and fractional exponent, α , and intercept, C , obtained from the linear fit of $\ln F(\zeta)$ versus $\ln(\eta_s)$, for the isomerisation of DTCI in the ground state (GS) and the excited state (ES)

State/solvent	E_0 (kcal/mol)	α	C
GS/alcohols	12.9 ± 0.7	0.20 ± 0.02	27.40 ± 0.05
GS/nitriles	12.9 ± 0.7	0.38 ± 0.015	27.32 ± 0.05
ES/nitriles	3.0 ± 0.2	0.65 ± 0.015	26.57 ± 0.05

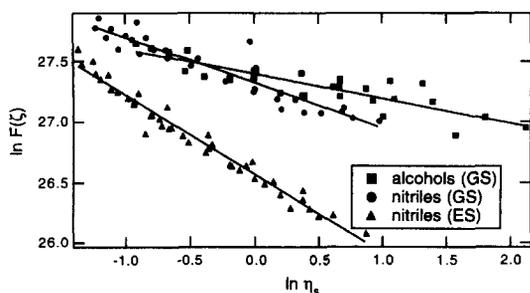


Fig. 4. Logarithmic plots of the reduced isomerisation rate constants of DTCl, $F(\zeta)$, versus viscosity, η_s .

solvents, in agreement with the results of Ponterini and Mimicchioli, who measured a very small variation of the activation energy for the ground state

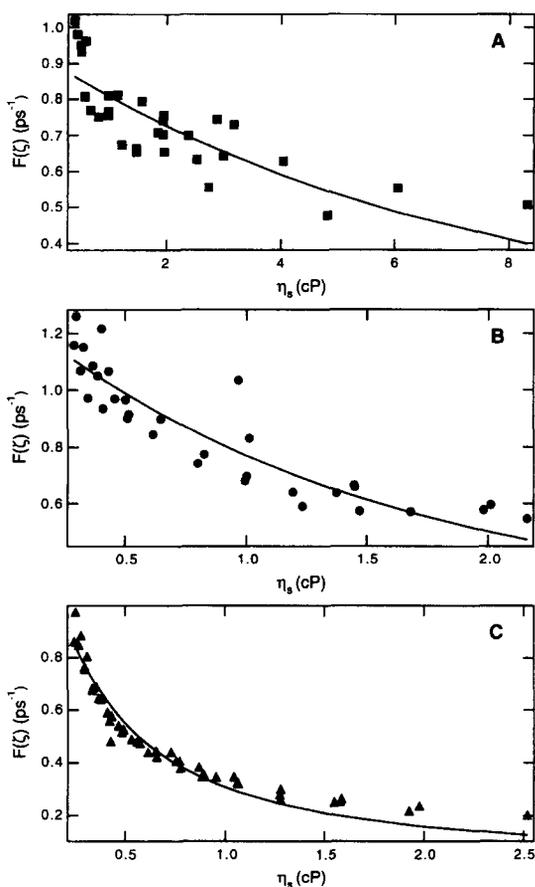


Fig. 5. Best fit of the hydrodynamic Kramers expression, Eq. (4), to the reduced isomerisation rate constants of (a) DTCl ground state in *n*-alcohols, (b) DTCl ground state in alkanenitriles and (c) DTCl excited state in alkanenitriles.

isomerisation of DTCl in methanol, dichloromethane and chlorobenzene [61].

The reduced isomerisation rate constant, $F(\zeta)$, was extracted using Eq. (2) with these activation energies. Fig. 4 shows logarithmic plots of $F(\zeta)$ versus viscosity for the isomerisation of DTCl. The value of the fractional exponent α (see Eq. (1)) can be obtained from the slope of these plots and is listed in Table 4 together with the corresponding activation energy. The striking feature of these data is the large variation of α , from 0.20 in alcohols to 0.38 in nitriles, for the same barrier height. For the ground state isomerisation of DODCl in alcohols, Velsko et al. have also measured a small α -value of 0.26, for an activation energy of 13.7 kcal/mol [15]. In previous reports of the isomerisation dynamics in different classes of solvents, the solvent dependence of α could not be separated and distinguished from the variation of α due to solvent induced changes of the barrier height, in contrast with the present study.

In the next section, the results will be analysed in term of the Kramers theory with different models for friction.

4. Discussion

4.1. Hydrodynamic Kramers model

According to the Kramers model, the reduced isomerisation rate constant is given by

$$F(\zeta) = \frac{\omega_0}{4\pi\omega_b I} \left\{ \left[1 + (2\omega_b I/\zeta)^2 \right]^{1/2} - 1 \right\}, \quad (3)$$

where ω_0 is the frequency of motion in the reactant well, ω_b the frequency of the potential barrier and I the moment of inertia of the moving moiety.

Assuming hydrodynamic friction, Eq. (3) can be expressed as

$$F(\zeta) = \frac{A}{B\eta_s} \left\{ \left[1 + (B/\eta_s)^2 \right]^{1/2} - 1 \right\}, \quad (4)$$

with $A = \omega_0/2\pi$ and $B = 2I\omega_b/C\pi r d^2$, where $C = 4$ for slip boundary condition and $C = 6$ for stick boundary condition, r is the radius of the moving moiety and d its radius of gyration.

Fig. 5 shows the fit of Eq. (4) to the reduced isomerisation rate constants of DTCl. As already

Table 5

Reactant well frequency, ω_0 , and barrier frequency, ω_b , obtained from the fit of the Kramers expression, Eq. (4), with η_s (hydrodynamic friction) and η_μ (microviscosity) to the reduced isomerisation rate constants, $F(\zeta)$, of DTCl

State/solvent	Friction	ω_0 (cm ⁻¹)	ω_b (cm ⁻¹)
GS/alcohols	η_s	30	5.1×10^4
	η_μ	32	2.5×10^4
GS/nitriles	η_s	44	9500
	η_μ	51	3500
ES/nitriles	η_s	49	2480
	η_μ	155	432

observed by many authors, the hydrodynamic Kramers expression cannot fit the observed rate constants with a single set of parameters A and B . The frequencies ω_0 and ω_b obtained from the best fit with $r = 3.5$ Å, $d = 2.65$ Å and $I = 3.8 \times 10^{-44}$ kg m² and $C = 6$ are listed in Table 5. Although the values of ω_0 are physically reasonable, the frequencies ω_b are unrealistically large, especially for the ground state isomerisation. The failure of the hydrodynamic Kramers model could already be expected from the strong departure from unity of α (see Table 4).

4.2. Spornol–Wirtz and Wilke–Chang microfriction formula

Sun and Saltiel have obtained good Kramers fit of the photoisomerisation of *t*-stilbene in *n*-alkanes by substituting in Eq. (4) the shear viscosity by the microviscosity experienced by a molecule of toluene accomplishing a translational motion. The translational microviscosity was determined from the semi-empirical formula of Spornol and Wirtz relating experimental diffusion coefficient, D_{exp} , to the Stokes–Einstein diffusion coefficient, D_{SE}

$$D_{\text{exp}} = D_{\text{SE}}/f, \quad (5)$$

$$f = (0.16 + 0.4r/r_L)(0.9 + 0.4T_{\text{rL}} - 0.25T_r), \quad (6)$$

where f is the microfriction factor for translation, r and r_L are solute and solvent molecular radii, respectively, and T_r and T_{rL} are reduced solute and solvent temperatures

$$T_{\text{rL}} = \frac{T - T_{\text{mp}}}{T_{\text{bp}} - T_{\text{mp}}}, \quad (7)$$

where T_{mp} and T_{bp} are the melting and boiling points of the solute and solvent. The microviscosity, defined as $\eta_\mu = f\eta_s$, can be substituted to η_s in the Kramers expression (Eq. (4)).

For DTCl, f was calculated for the diffusion of a molecule of 2-methyl-3-ethyl-benzothiazole using Eq. (6) for alkanenitriles. Schuh and Fischer showed that this equation does not give good f -values for alcohols [62]. For these solvents, these authors recommended the formula of Wilke and Chang [63]:

$$f = \frac{k_B V^{0.6}}{6\pi \times 7.4 \times 10^{-10} r (\kappa_L M_L)^{1/2}}. \quad (8)$$

This equation has been designed for cgs units; V is the molar volume of the solute, M_L the solvent molecular weight and κ_L is a solvent specific association parameter, which is 1.9 for methanol and 1.5 for ethanol. For the other alcohols, this parameter can be calculated as follows

$$\kappa_L = (\Delta H_{\text{v,L}}/\Delta H_{\text{v,H}})^{0.6}, \quad (9)$$

where $\Delta H_{\text{v,L}}$ is the enthalpy of vaporisation of the alcohol and $\Delta H_{\text{v,H}}$ the enthalpy of vaporisation of its homologue, where a methyl group replaces the hydroxyl group.

Fig. 6 shows the best fit of Eq. (4) with η_μ to the reduced isomerisation rate constants. A slight improvement on the hydrodynamic Kramers model can be observed. However, the predicted isomerisation rate constants in the high friction region are still substantially slower than observed. The frequencies ω_0 and ω_b obtained from the A and B fitting parameters are listed in Table 5. As for the hydrodynamic Kramers model, the ω_0 frequencies are physically reasonable. The barrier frequencies, ω_b , are smaller than those obtained from the hydrodynamic Kramers fit, but are still too large, although the frequency for the excited state isomerisation, $\omega_b = 432$ cm⁻¹, might be not too far from reality.

This slight improvement is confirmed by the values of α obtained from the slope of the logarithmic plot of $F(\zeta)$ versus η_μ (not shown). By going from η_s to η_μ , α increases from 0.20 to 0.25 for the ground state isomerisation in alcohols, from 0.38 to 0.51 for the ground state isomerisation in nitriles and from 0.65 to 0.85 for the excited state isomerisation.

The use of isoviscosity plots for the determination of the intrinsic activation energy has been questioned

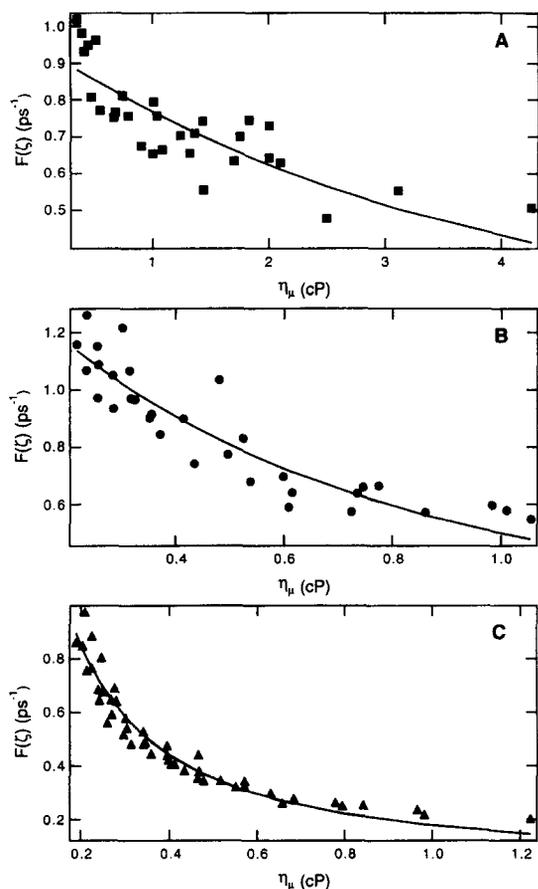


Fig. 6. Best fit of the Kramers expression, Eq. (4), using the microviscosity, η_μ , obtained from the Spornol and Wirtz formula to the reduced isomerisation rate constants of (a) DTCl ground state in *n*-alcohols, (b) DTCl ground state in alkanenitriles and (c) DTCl excited state in alkanenitriles.

by Saltiel and co-workers who obtained better results in *n*-alkanes by using isomicroviscosity plots [36]. Such microviscosity plots were produced for the ground state isomerisation in alkanenitriles. However, in contrast to the isoviscosity plots, the slopes of the isomicroviscosity plots decreased systematically with increasing microviscosity, going from 13.1 kcal/mol at $\eta_\mu = 0.25$ cP to 11.5 kcal/mol at $\eta_\mu = 0.6$ cP. Moreover, the average intrinsic activation energy was close to that obtained from isoviscosity plots, indicating that the value of E_0 used to calculate the reduced isomerisation rate constants is reasonable.

4.3. Grote–Hynes model

The failure of the last two models to reproduce the friction dependence of the isomerisation of DTCl, especially in the ground state, might be due to the occurrence of non-Markovian effects such as the correlation of the random forces exerted by the solvent on the isomerising molecule on the time scale of the barrier crossing. These effects have been taken into account in an extended Kramers model proposed by Grote and Hynes [42]. Within this model, the reduced isomerisation rate constant, $F(\zeta)$, is given by

$$F(\zeta) = \frac{\omega_0 \lambda_r}{2\pi\omega_b}, \quad (10)$$

where the reactive frequency, λ_r , is given by the following self-consistent equation

$$\lambda_r = \frac{\omega_b^2}{\lambda_r + \hat{\zeta}(\lambda_r)/I}, \quad (11)$$

$\hat{\zeta}(\lambda_r)$ is the value of the Laplace transform $\hat{\zeta}(s)$ of the time dependent friction at $s = \lambda_r$. Explicit expressions for the calculation of the frequency dependent friction have been proposed by Bagchi and Oxtoby [43]. The isomerisation is modelled as the rotational motion of a sphere of hydrodynamic radius, r , around a fixed axis. The total friction experienced by this sphere, whose centre is at a distance d from the rotation axis, is the sum of two contributions

$$\zeta = d^2\zeta_{tr} + \zeta_r, \quad (12)$$

where ζ_{tr} and ζ_r are the translational and rotational frictions, respectively. The frequency dependent translational friction is given by

$$\hat{\zeta}_{tr}(s) = \frac{4\pi}{3} \eta_s(s) dX^2 (2(X+1)P + (1+Y)Q), \quad (13)$$

with

$$X = \left(\frac{s\rho}{\eta_s(s)} \right)^{1/2} d, \quad Y = s \left(C_s^2 + \frac{s\eta_l(s)}{\rho} \right)^{-1/2} d, \\ P = \frac{3}{\Delta} (3 + 3Y + Y^2),$$

$$Q = \frac{3}{\Delta} \left(3 + 3X + X^2 + \frac{X^2(1+X)}{2 + \beta/\eta_s(s)} \right),$$

$$\Delta = 2X^2(3 + 3Y + Y^2) + Y^2(3 + 3X + X^2) + \frac{3X^2(1+X)(2 + 2Y + Y^2)}{2 + \beta/\eta_s(s)},$$

where $\eta_s(s)$ is the frequency dependent shear viscosity, $\eta_l(s)$ is the frequency dependent longitudinal viscosity, ρ is the solvent density, C_s is the velocity of sound in the solvent and β is the slip parameter, zero for pure slip and infinity for stick boundary condition. The longitudinal viscosity can be determined from the shear viscosity and the bulk viscosity, $\eta_v(s)$

$$\eta_l(s) = \frac{4}{3}\eta_s(s) + \eta_v(s). \quad (14)$$

In the pure slip boundary condition, there is no friction for the rotational motion of a sphere. This boundary condition has been assumed by Hochstrasser and co-workers for the isomerisation of *t*-stilbene in *n*-alkanes [10] as well as by Waldeck and co-workers for the isomerisation of *t*-stilbene and 4,4'-dimethoxystilbene in alkylnitriles [11]. This assumption is reasonable because these molecules are non-polar. Indeed, the rotational diffusion of non-polar molecules in non-polar solvents or aprotic polar solvents follows slip hydrodynamics [64]. However, stick boundary condition seems to be more appropriate for the isomerisation of DTCl, a charged molecule, in alcohols and nitriles. The rotational diffusion of polar or charged molecules in polar solvents follows essentially stick hydrodynamics [54]. For the stick boundary limit, the frequency dependent friction for the rotational motion is given by

$$\hat{\zeta}_r(s) = \frac{1 + X + \frac{1}{3}X^2}{1 + X} 8\pi\eta_s(s)d^3. \quad (15)$$

For the frequency dependent viscosities, $\eta_s(s)$, the following simple Maxwell forms have been assumed:

$$\eta_s(s) = \eta_s^0 / (1 + s\tau_s), \quad \eta_v(s) = \eta_v^0 / (1 + s\tau_v), \quad (16)$$

where η_s^0 and η_v^0 are the zero frequency shear and bulk viscosities. The viscoelastic relaxation times τ_s and τ_v have been modelled with the relations:

$$\tau_s = \eta_s^0 / G_\infty, \quad \tau_v = \eta_v^0 / K_r, \quad (17)$$

where G_∞ is the infinite frequency shear modulus and K_r the relaxation part of the bulk modulus.

Eq. (10) has been fitted to the experimental data for the isomerisation of the ground and excited state of DTCl in both classes of solvents. An important problem in using this model is the difficulty to find most of the above mentioned physical constants for alcohols and nitriles. For this reason, several approximations have been made:

– the frequency dependent longitudinal viscosity has been taken as $\eta_v(s) = 6\eta_s(s)$ [11];

– average values were used for several solvent parameters, namely the density, $\rho = 0.80 \text{ g/cm}^3$ and $\rho = 0.81 \text{ g/cm}^3$ for alkylnitriles and alcohols [57] and the velocity of sound, $C_s = 1200 \text{ m/s}$ in both classes of solvents [65].

For the fitting procedure, the adjustable parameters were ω_0 and ω_b . The fit was repeated with different values of the shear modulus, G_∞ . In a first stage, the best value for G_∞ in nitriles was obtained by searching the value resulting in good fits for both ground and excited state isomerisation data. The best G_∞ for the whole friction range was found to be equal to $5.0 \times 10^8 \text{ Pa}$. This value lies between that used by Rothenberger et al. for *n*-alkanes ($G_\infty = 7 \times 10^7 \text{ Pa}$) [10] and that used by Sivakumar et al. for both *n*-alkanes and *n*-alkyl nitriles ($G_\infty = 10^9 \text{ Pa}$) [11]. The frequencies ω_0 and ω_b , obtained from the fit, are listed in Table 6. In a second stage, the fit of Eq. (10) to the rate constants for the ground state isomerisation in alcohols was carried out with various values of G_∞ until ω_0 and ω_b frequencies similar to those found with the ground state isomerisation in nitriles were obtained. The best fit over the whole friction range was found with $G_\infty = 2.5 \times 10^8$

Table 6

Reactant well frequency, ω_0 , barrier frequency, ω_b , and infinite frequency shear modulus, G_∞ , obtained from the fit of Eq. (10) to the reduced isomerisation rate constants, $F(\zeta)$, of DTCl (for the ground state isomerisation in nitriles, several values of the barrier height have been tested)

State/solvent	ω_0 (cm^{-1})	ω_b (cm^{-1})	G_∞ (10^8 Pa)	E_0 (kcal/mol)
GS/alcohols	59	29	2.5	12.9
GS/nitriles	69	37	5.0	12.9
	260	12	5.0	13.4
	1700	3	5.0	14.7
ES/nitriles	265	2.6	5.0	3.0

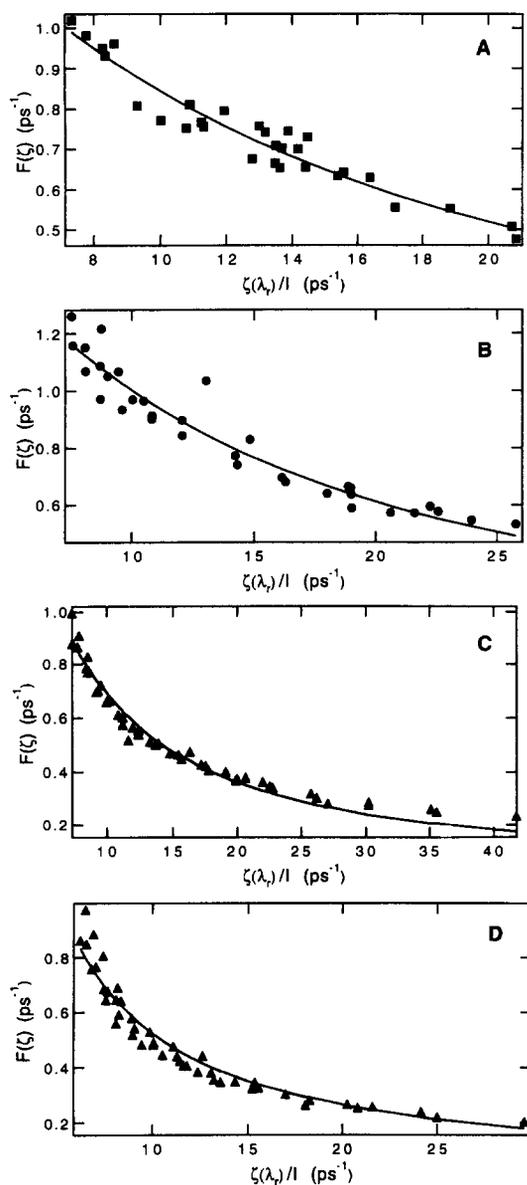


Fig. 7. Best fit of the Grote-Hynes model, Eq. (10), to the reduced isomerisation rate constants of (a) DTCl ground state in *n*-alcohols, (b) DTCl ground state in alkanenitriles and (c) DTCl excited state in alkanenitriles, (d) DTCl excited state in alkanenitriles using microviscosity instead of shear viscosity in Eqs. (13)–(15).

Pa. The parameters of the best fits are listed in Table 6 and the corresponding fits illustrated in Fig. 7. From this figure, it can be seen that the quality of the fits is much better than those depicted in Figs. 5 and

6, the main discrepancy being at high reduced friction for the excited state isomerisation in nitriles. A better agreement in this friction range can be obtained by using a slightly lower value for G_{∞} of 4×10^8 Pa. In that case, however, the fit in the low friction region is very poor. The occurrence of such an effect is reasonable if one considers that G_{∞} is different for each solvent and for each temperature. The use of a single average value of G_{∞} in the calculation of the frequency dependent friction is not too bad an approximation as long as the friction and especially the frequency range is not too large. This seems to be the case for the ground state isomerisation, where the variation of the rate constant over the all friction range is smaller than a factor two. As a consequence, the value of the reduced frequency dependent friction varies from 7 to 25 ps^{-1} . In the case of the excited state, the rate constant of isomerisation changes by a factor 3.7. This leads to a larger range of reduced frequency dependent friction, from 7 to 42 ps^{-1} . This explains why the use of a single value for G_{∞} does not result in a very good fit with experimental data. A slightly better fit over the whole friction range for the excited state isomerisation in nitriles can, however, be obtained by substituting the shear viscosity in Eqs. (13)–(15) by microviscosity as defined in Section 4.2 (see Fig. 7d). However, the frequencies obtained from the fit are almost unchanged ($\omega_0 = 260 \text{ cm}^{-1}$, $\omega_b = 3.5 \text{ cm}^{-1}$). For the two other data sets, this modification does not bring any significant change either in the magnitude of the frequencies nor in the quality of the fits.

The different average values of G_{∞} in nitriles and alcohols are probably at the origin of the large variation of α , from 0.20 in alcohols to 0.38 in nitriles, for the same barrier height. One of the major differences between alcohols and nitriles is certainly the dielectric relaxation times, which are substantially longer for alcohols than for nitriles of the same viscosity. For example, the Debye relaxation time of ethanol at room temperature ($\eta_s = 1.07 \text{ cP}$) is equal to 139 ps [66], while that of pentanenitrile at the same temperature ($\eta_s = 1.01 \text{ cP}$) amounts to 18.2 ps [67]. Consequently, the solvent motion spectrum must be located at lower frequencies for alcohols than for nitriles. As friction due to low frequency motion does not influence the barrier crossing, which is at high frequency, one can therefore expect a weaker

friction dependence at high viscosities in alcohols than in nitriles. This could explain qualitatively why the effect of frequency dependent friction is more pronounced in alcohols than in nitriles.

Turning now to the frequencies, it appears that the reactant well frequency is substantially larger for the excited state than for the ground state isomerisation. However, it must be noted that the uncertainty on the ground state reactant frequency is very large. Indeed, an increase of the activation energy of 0.5 kcal/mol, from 12.9 to 13.4 kcal/mol (about 4% change, within the limits of error, see Table 4), for the ground state isomerisation leads to two times larger reduced isomerisation rate constants! Consequently the potential well barrier increases to 260 cm^{-1} and the barrier frequency decreases to 12 cm^{-1} (see Table 6). For this reason, the absolute magnitude of the reactant well frequency for the ground state listed in Table 6 must be considered with caution.

On the other hand, the barrier frequency difference between the two states is clearly more pronounced than for the reactant well frequency. Even by varying slightly the activation energy, ω_b remains larger for the ground than for the excited state. The activation barrier for the ground state isomerisation has to be changed from 12.9 to 14.7 kcal/mol (about 15% change, outside the limits of error, see Table 4), in order to obtain the same barrier frequency in the two states. In that case the reduced isomerisation rate constant become very large and the reactant well frequency becomes unrealistic. Consequently, it is safe to affirm that the barrier frequency is at least 4 times larger in the ground than in the excited state. This observation is in full agreement with the larger barrier height in the ground state than in the excited state. This also confirms the weak trend observed by Waldeck and co-workers with the excited state isomerisation of *t*-stilbene and dimethoxystilbene in alkanes and nitriles [11]. However, in their case the barrier height dependence of the barrier frequency was obtained by comparing *t*-stilbene to dimethoxystilbene isomerisation dynamics. Nevertheless, changes of ω_b could also be due to a difference in molecular properties.

The reactant well frequency for excited isomerisation is of the same order of magnitude as those obtained with dimethoxystilbene (396 cm^{-1} in alkanes and 130 cm^{-1} in nitriles) [11] and with *t*-stil-

bene (360 cm^{-1} [10] and 300 cm^{-1} in alkanes and 90 cm^{-1} in nitriles [11]). The magnitude of ω_0 for the ground state isomerisation of DTCl is slightly smaller but, as mentioned above, this could be due to the uncertainty in the barrier height, ω_0 being equal to 260 cm^{-1} with $E_0 = 13.4\text{ kcal/mol}$.

The order of magnitude of barrier top frequencies is also similar to those obtained by Waldeck and co-workers [11] and Hochstrasser and co-workers [10], i.e. of the order of 10 cm^{-1} . As already mentioned by these authors, these frequencies are too low. The structure of DTCl (see Fig. 1) shows that isomerisation could take place around two different bonds. In the above analysis, it was assumed that isomerisation takes place around the bond located in the middle of the polymethine chain (1 in Fig. 1). The analysis was repeated assuming that the isomerisation is taking place around a bond located between the polymethine chain and a benzothiazolyl-group (2 in Fig. 1). In this case there is no translational motion during isomerisation and therefore the total friction is equal to the rotational friction only, i.e. Eq. (10) simplifies to $\zeta = \zeta_r$. With slip boundary conditions, there would be no friction for this process and the reduced isomerisation rate constants would be independent of viscosity. With stick boundary conditions, ω_0 and ω_b frequencies are even slightly smaller than those listed in Table 6, although their relative magnitudes are very similar.

The origin of these low barrier top frequencies could be due to approximations made in the Grote-Hynes theory and/or in the calculations of the frequency dependent friction. Another possible explanation is the concerted participation of several bonds to the isomerisation processes. Indeed, the Grote-Hynes model described here considers only a single reactive degree of freedom and in the above discussion we have considered the single-bond isomerisation around two different bonds. However, the actual isomerisation of DTCl could be due to the concerted motion around both bonds. Such a motion treated with a one-dimensional model could result in apparently too low frequencies.

5. Summary and conclusion

We have reported on the isomerisation dynamics of DTCl in the ground state in alcohols and in

nitriles as well as in the excited state in nitriles. The isomerisation rate constants span from the ps time scale in the excited state to the ms time scale in the ground state. One interesting feature of the ground state isomerisation is the intrinsic activation energy, which is the same in both classes of solvents. However, the dynamics are substantially different, as shown by the α -values of 0.20 and 0.38 in alcohols and in nitriles, respectively.

None of the three sets of data could be fitted to the hydrodynamic Kramers model, the measured isomerisation rate constants in the high friction domain being always larger than predicted. Some improvement could be obtained, especially for the excited isomerisation, by multiplying the shear viscosity in the Kramers expression by a microviscosity factor, estimated from the semi-empirical formulas of Spernol and Wirtz and of Wilke and Chang for the calculation of translational diffusion constants in alkanenitriles and in *n*-alcohols, respectively.

The data were then analysed within the framework of the Grote–Hynes theory [42] using the expressions of Bagchi and Oxtoby to describe the frequency dependent friction [43]. The solvent effect can be explained by different values of the infinite frequency shear modulus, G_∞ , for alcohols and nitriles. The G_∞ values obtained from the analysis are in qualitative agreement with the relative magnitude of the average Debye relaxation time of nitriles and alcohols. In previous reports on isomerisation with different molecules, a change in the type of solvent was always accompanied by a variation of the activation energy [5, 11], contrarily to the present case. For this reason a variation of α was ascribed to the change of the activation energy only, but not to a different value of G_∞ . In the present study, the effect of barrier height on the isomerisation dynamics was investigated by comparing the isomerisation dynamics of DTCl in both the ground and the excited states in nitriles, where the activation energies are 12.9 and 3.0 kcal/mol, respectively. The value of α changed from 0.38 in the ground state to 0.65 in the excited state. This behaviour is in accordance with the Grote–Hynes theory, which predicts a more pronounced frequency dependence of friction (i.e. a smaller α) for isomerisation with large barrier height. Indeed, the analysis of the data with the Grote–Hynes expression gave a clearly larger barrier fre-

quency for the ground state than for the excited state isomerisation.

Apart from the absolute magnitude of the barrier top frequencies, which seemed to be too small, the effect of barrier height as well as the effect of the solvent on the isomerisation dynamics of DTCl are in good qualitative agreement with the predictions of the Grote–Hynes theory.

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