Entropic effects in excited state CT reactions

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ABSTRACT

The kinetics of the dual fluorescence of several derivatives of dimethylaminobenzonitrile (DMABN) has been compared using fs-fluorescence upconversion experiments. Variation of the size and twist angle of the donor (dialkylamino group) suggest a large amplitude solvent-viscosity controlled diffusional twisting motion towards larger twist angles as the rate limiting step.

Large rate differences were observed for an ester group as acceptor. Temperature dependent studies indicate that these differences are not connected with different activation barriers but with changes in the Arrhenius preexponential factor. It is argued that conical intersections along the reaction path can bring about these entropy changes.

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1. Introduction

Dialkylanilines with acceptor substituents, among them dimethylaminobenzonitrile (DMABN), show an unusual fluorescence behaviour with two bands [1]. This arises from an adiabatic photoreaction forming an excited state with strong charge transfer character. The most important models for this adiabatic photoreaction are an in-plane geometrical rearrangement [2,3] or a twisting of the molecule [4,5], forming a so-called Twisted Intramolecular Charge Transfer (TICT) state (for a recent review on this subject see [6]). The latter model corresponds to a large amplitude rearrangement which should strongly depend on viscosity, former does not involve large amplitude changes and therefore the reactions kinetics should be little dependent on solvent viscosity. Recent theoretical advances in the understanding of DMABN favour a large amplitude twisting model [7–9]. Robb et al. [7] insinuate in the title of their publication, that the reaction coordinate does not include the twist. The content of the Letter, however clearly states that the twist is the major coordinate, but the transition from the LE to the CT state through a conical intersection seam can occur at many angles including rather planar geometries. This view is entirely consistent with the classical CT formation model with twist as the main reaction coordinate and a conical intersection at non-perpendicular twist angles as reviewed in Ref. [4].

Experimentally, a 'planar' model compound of DMABN, rigidized using a six-membered ring linkage, shows a clear CT emission band. In a recent theoretical paper [8] excited state optimizations suggest that the geometries of both the ground state and the LE fluorescent state are significantly twisted by 30–40° and that the molecule is flexible enough to relax into a more strongly twisted conformation (60–70°) in its relaxed excited CT state. This highly twisted geometry can be viewed responsible for the observed CT fluorescence band. If the bridging is more tightly, by a five-membered ring, no CT band is observed, and it can be assumed that the highly twisted geometry is not any more available for this more rigid compound [10].

The twisting model is also supported by using CASSCF optimizations in the excited state and shows that the dipole moment of the CT state reaches a maximum for perpendicular geometries [9]. These calculations, moreover, identify a second coordinate active in reaching the conical intersection to the CT state: this is the Quinoid–Antiquinoid transition (the benzene aromatization coordinate) involving bond length changes within the benzene ring.

From the experimental side, early investigations revealed a strong viscosity dependence. For low temperature studies, the dependence is, however, somewhat weaker than that of the viscosity itself [11,6]. If viscosity is increased by high pressure, the kinetics can either be slowed down [12], or even enhanced [3]. The reason is that not only the viscosity plays a role in this reaction but also the solvent polarity because the precursor state is considerably less polar than the product state. Usually solvent polarity increases at low temperature due to the density increase, and at the same time viscosity increases, and these competing effects can cancel each other or outweigh each other to either side.

Kinetic measurements with sub-ps time resolution have been possible recently, among them transient absorption [13], infrared [14,15], Raman [16] and mass spectral analysis [17]. Especially the kinetics in acetonitrile at room temperature are well characterized being situated around 4 ps [13,14]. The low temperature viscosity-dependent behaviour was not studied with this high time resolution.

Not only DMABN with a cyano acceptor shows dual fluorescence and an adiabatic photoreaction but likewise derivatives with

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weaker (such as amide [18]) or stronger acceptors (such as ester and carbonyl [19–21]), and it can be asked how their kinetics is affected by this change. It is known from these previous studies that compounds with a stronger acceptor show significantly increased reaction rate constants as compared to the reference compound DMABN. DMABN has therefore a kinetic hindrance slowing down the reaction with respect to the derivatives with a stronger acceptor, which can either be due to an increased activation energy or to a decreased preexponential factor in the Arrhenius kinetic description. Even though the reaction may be a large amplitude twisting rearrangement which is diffusively controlled and hindered by solvent viscosity, it has the possibility to be much faster than in the case of DMABN, for essentially the same size of the rotors. Also aniline derivatives with donors different from dimethylamino, such as pyrrolidino or piperidino compounds, can yield interesting mechanistic and kinetic information [22–25].

In this work, we report sub-ps fluorescence up-conversion results on a number of DMABN derivatives which differ in both acceptor and donor substituents and investigate the low temperature behaviour in acetonitrile depending on both viscosity and polarity.

2. Experimental

The compounds investigated are listed in Scheme 1, together with their abbreviations. All measurements were performed in acetonitrile (ACN), which was of the highest commercially available purity and was used as received.

The fluorescence up-conversion set-up used for the measurements was basically the same as that described earlier [26]. Excitation was performed at 267 nm using the frequency-tripled output of a Kerr lens mode-locked Ti:sapphire laser (Tsunami, Spectra-Physics) operating at 82 MHz. The pump intensity on the sample was around 10^{13} photons cm^{-2} pulse^{-1}. The polarisation of the pump pulses was at magic angle relative to that of the 800 nm gate pulses. In order to separate the up-converted signal around 250 nm from the background locally excited (LE) fluorescence, a specially designed interference filter with a narrow transmission window (Create-Shoji Ltd., Japan) was placed at the entrance of the monochromator. The full width at half maximum of the instrument response function was around 420 fs.

For room temperature measurements, the sample solutions were placed in a rotating cell with 1 mm pathlength. For measurements at different temperatures, the solutions were flowed

through a 1 mm thick cell. The concentration of the different compounds was adjusted to have an absorbance of about 0.1 at 267 nm over 1 mm. All solutions were purged with argon before use. The sample temperature was simultaneously measured at both the entrance and the exit of the cell and the average value was taken for the temperature in the cell. The uncertainty on the temperature can be estimated to be around ±0.5 °C which is sufficient for the temperature range covered, especially in view of the same results measured for different pairs of compounds.

The fluorescence dynamics of the various compounds at room temperature in ACN was measured at wavelengths coinciding with the LE and charge-transfer (CT) fluorescence bands observed in the steady state spectrum. The so-obtained time profiles were intensity normalized and analyzed globally by iterative reconvolution of the instrument response function using the trial function given in the following equation:

$$I(t) = A_0 + A_1 \exp(-t/\tau) \tag{1}$$

where A_0 accounts for the fluorescence signal intensity that remains constant within the time window of the measurements. The relative error on the lifetime is about ±10%.

3. Results

Fig. 1 displays an overview of absorption and fluorescence spectra for PYRBN and PYRBE as a representative example. Both compounds possess similar dual fluorescence with maxima very close to each other ([6] and references therein).

Fig. 2 shows fluorescence time profiles recorded with DMABN and DMABE at two wavelengths, and the best-fit parameters, namely the lifetime, τ, and the relative amplitude A_1, are listed in Table 1. At 350 nm, which is slightly on the blue side of the LE emission maximum, the fluorescence time profiles decay exponentially to a value close to zero. The lifetime measured for DMABN at room temperature (3.7 ± 0.4 ps) is fully consistent with results of other fs studies (essentially 4.0 ps) reported in the literature [13,14]. The observation that the use of 290, 276 or 266 nm excitation did not result in different lifetime values for DMABN supports the view that vibrational cooling due to the excess energy present for our short wavelength excitation (267 nm) is not of importance for the kinetics measured in our study.

The value of A_1 is positive for observation at 350 nm corresponding to a fast decay of the LE state and amounts to 0.91 for

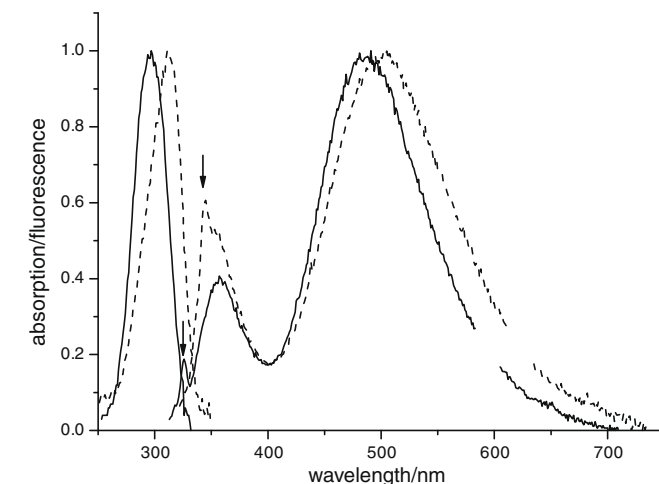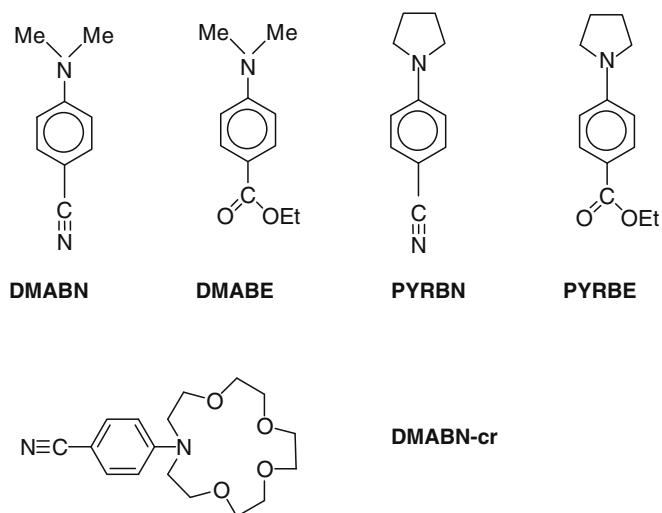**Scheme 1.** Formula of the investigated compounds.

Fig. 1. Normalized absorption and corrected fluorescence spectra of PYRBN and PYRBE (dashed) in acetonitrile at room temperature ($c \cong 10^{-5}$ mol/l). The arrows indicate the Raman peaks of the solvent. The second order Rayleigh peaks were omitted.

Fig. 2. Time profiles of the fluorescence intensity of DMABN in ACN recorded at different wavelengths.
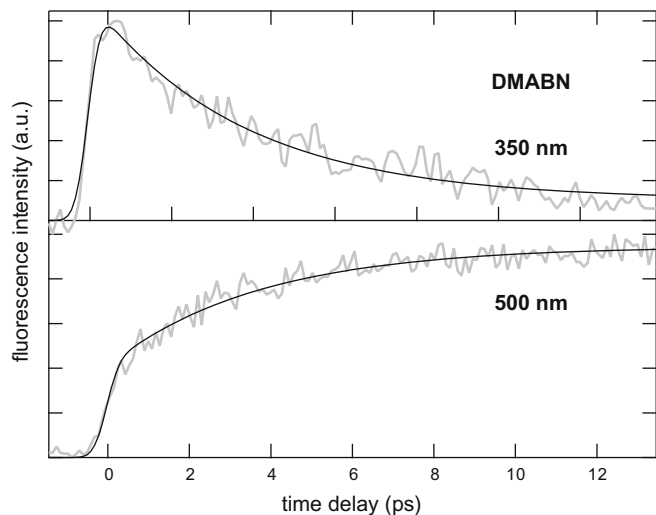

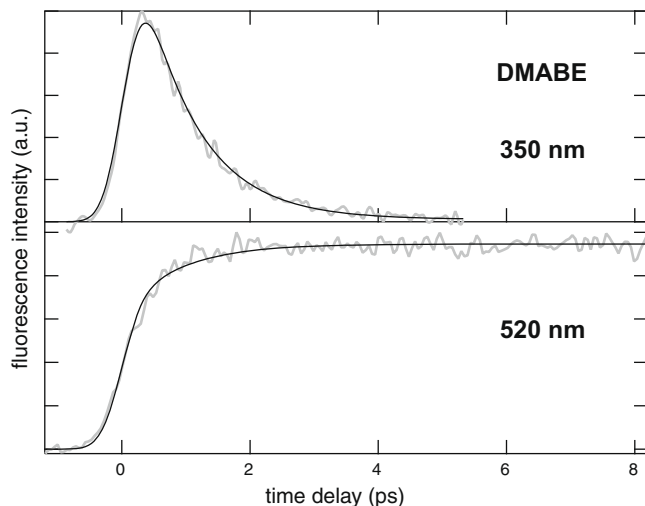**Fig. 3.** Time profiles of the fluorescence intensity of DMABE in ACN recorded at different wavelengths.

DMABN and to essentially 1 for DMABE (see Table 1). The amplitude of the residual signal at long times, accounted for by A_0 in Eq. (1), remains constant within the time window of the experiment. A_0 can be interpreted as a fluorescence decay with a very long time constant, in the nsec region. This is compatible with the expected behaviour of a biphasic fluorescence decay for excited state equilibrium reactions [27]. On the other hand, we cannot exclude some formation of a short wavelength emitting photoproduct produced by photolysis [13] which would also show up as a very long-lived essentially constant decay component in ps experiments. As A_0 is a time-independent contribution, it can be excluded in our experiments, that the measured ps kinetics are affected by possible photoproduct formation. Qualitatively similar time profiles were measured with the other compounds in this spectral region (Fig. 3).

The fluorescence dynamics at 430 nm, i.e. on the blue side of the CT emission maximum, is similar to that measured at 350 nm, except that the amplitude of the decaying component is markedly smaller as illustrated in Table 1. This increased background or ns-component indicates that at this intermediate wavelength, some contribution of the longlived CT band is also present.

At 500–520 nm, i.e. on the red side of the CT emission maximum, the amplitude A_1 is negative, i.e. the time profiles exhibit a rise with the time constant τ. Additionally to this ps component, a prompt rise with an amplitude $1 - A_1$ is also present.

The prompt rising component most probably originates from a contribution of the LE fluorescence. This is somehow unexpected by considering the stationary spectra, which show that at this wavelength, the stationary intensity is almost entirely due to the CT band. It should however be reminded that the stationary intensity is proportional to $k_{rad} \cdot \tau$, where k_{rad} is the radiative rate con-

stant and τ the fluorescence lifetime, while the intensity of the up-converted signal is proportional to k_{rad} only, provided the time resolution is sufficiently high. In the case of DMABN, the radiative rate constant of the LE emission is known to be about seven times larger for LE, $k_{rad} = 4.8 \times 10^7 \text{ s}^{-1}$, than for CT emission, $k_{rad} = 0.7 \times 10^7 \text{ s}^{-1}$ [28]. Moreover, according to the fluorescence spectrum of DMABN in hexane, the intensity in the red edge of the LE emission band falls much less abruptly than in the blue edge, and thus LE emission in acetonitrile can be expected to extend with a small tail up to 500 nm. For DMABE, the difference in k_{rad} is even larger, $k_{rad}(CT) = 0.7 \times 10^7 \text{ s}^{-1}$, $k_{rad}(LE) = 22 \times 10^7 \text{ s}^{-1}$ [28], in agreement with a large prompt rise measured at 520 nm. These two factors, namely larger k_{rad} and long red tail of LE band, can explain why LE fluorescence shows up in the time-resolved measurements even at wavelengths where the stationary intensity is dominated by the CT emission.

For exactly the same reasons, a contribution of the CT fluorescence at 350 nm, as the origin of the residual signal intensity accounted for by A_0 is very improbable.

The fluorescence dynamics of DMABN and DMABE at 430 nm was also measured at different temperatures between −15 and 38 °C. As shown in Table 2, only a weak decrease of τ with increasing temperature was observed with both compounds. The values of τ are somewhat different from those obtained from the global analysis at room temperature. It should be noted that the absolute error on the τ values in Table 2 is larger than those in Table 1 because they were obtained from the analysis of a single time profile. The error on τ can be estimated to be at most ±10%. An Arrhenius plot of these data, taking this uncertainty into account, indicates an

Table 1
Best-fit parameters obtained from the global analysis of the fluorescence time profiles at 20 °C using Eq. (1).

	τ (ps)	A_1 (350 nm)[a]	A_1 (430 nm)[a]	A_1 (500 nm)[a]
DMABN	3.7	0.91	0.70	−0.56
DMABE	0.92	0.998	0.94	−0.32
PYRBN	11.0	0.77	0.61	−0.78
PYRBE	2.63	0.97	0.69	−0.38
DMABN-c	6.06	0.89	0.39	−0.78

[a] For $A_1 > 0$, $A_0 = 1 - A_1$; for $A_1 < 0$, $A_0 = 1$.

Table 2
Best-fit parameters obtained from the analysis of the time-profiles of DMABN and DMABEE at 430 nm at different temperatures.

T (°C)	τ (ps)	A_1
DMABN		
−15	3.67	0.72
20	3.56	0.73
36	3.27	0.65
DMABE		
−15	1.08	0.90
−7	1.05	0.91
22	0.98	0.84
38	0.91	0.79

activation energy of 1.4 ± 1.9 and 2.0 ± 2.3 kJ/mol for DMABN and DMABE, respectively. This is very small as compared to the activation energy of viscosity for acetonitrile ($E_\eta \cong 7.5$ kJ/mol [29]).

The activation energy determined here for DMABN in acetonitrile is considerably smaller than that reported previously (5.0 kJ/mol [13]). The latter value was obtained with a single photon counting equipment and a 19 ps apparatus response function. In [13], the decay times increase by only 1.6 ps for the temperature interval used by us as compared to an increase of 0.4 ps in our measurements. In view of the better time resolution of our equipment we consider our measurements to be more reliable.

Additionally, an increase of A_1 (corresponding to a decrease of the residual contribution A_0) is observed with decreasing temperature (Table 2), indicating a decreasing contribution of the CT fluorescence to the signal at 430 nm. This effect can be explained by the thermochromic shift of the CT band, because both the dielectric constant and the refractive index increase with lowering temperature. Therefore, as the temperature decreases, the CT band shifts to longer wavelengths and thus its relative intensity at 430 nm lowers.

4. Discussion

4.1. Comparison of derivatives with variation of the donor group at room temperature suggest a large amplitude twisting motion

The fluorescence time traces can be globally analyzed at short and long wavelengths within the dual fluorescence spectral shape (Table 1). This indicates that the decay time of the precursor at 350 nm and the rise time of the product (at 520 nm) are equal which corresponds to a simple precursor–successor kinetic relationship as previously found in most cases [6].

Similar as previous results with much lower time resolution and conducted at low temperature [30], the esters are always significantly faster than the corresponding nitriles. The present measurement is the first one to compare these values under 'standard conditions', i.e. in the polar solvent acetonitrile at room temperature, where most of the previous sub-ps measurements were done [13,14]. For both pairs of compounds, DMABN/DMABE and PYRBN/PYRBE, the ratio of the rate constants amounts to about 4 in favour of the ester. The slower rate for the nitrile is therefore not linked to the shape and size of the donor substituent.

If we compare the pyrrolidino to the dimethylamino compounds, we note that the reaction kinetics for the former are slower by a factor of about 3 for both ester and nitrile pair. At low temperature in the less polar solvent n-butyl chloride, this factor even amounts to 7 [23]. The slower rate constant for the pyrrolidino pair of compounds as compared to the dimethylamino pair can be understood on the basis of the more planar ground state twist angle and the larger rotational volume of the pyrrolidino group [23].

An in-plane relaxation as the main rate determining factor (model a) [2,3] would not be expected to account for the rate difference of a factor 3–7 for the comparison of dimethylamino- to pyrrolidino compounds, nor for the factor 4 observed for the two ester/nitrile pairs. A second possible explanation (model b) is the larger rotor size of a twisting pyrrolidino versus a dimethylamino group. The observed rate changes, however, are much larger than would be expected on the basis of the rotational volume change alone which increases only moderately from the dimethylamino to the pyrrolidino group [23]. A more important factor is probably conformational control by the ground state twist angle (model c) The analysis of photoelectron spectra of different DMABN derivatives [23] indicates that PYRBN is close to planar, whereas DMABN is twisted by about 30° due to some sterical hindrance. The increased rate constant for the dimethylamino compounds can then

be interpreted as a 'pretwist' within the model of TICT formation [6] because the starting twist angle is closer to the final one for the dimethylamino compounds, and in a diffusive Debye–Stokes–Einstein model [31], this will lead to faster CT formation times.

Both models b and c are consistent with an intramolecular twisting and support the TICT mechanism. An in-plane structural relaxation model is not supported by these results.

A similar argument can be used for explaining the rate constant for DMABN-cr, where the cyclic 'crown' moiety is even much larger than the pyrrolidino one, but nevertheless, the reaction rate is nearly two times faster than for PYRBN. In this case, the ground state conformational control is even more important, because the crown moiety is twisted to such an extend in the ground state that CT formation is even observed in a nonpolar alkane solvent [32].

These differences in kinetics and their dependences on structure point to a large amplitude motion as part of the reaction coordinate. An in-plane structural rearrangement through bond lengths changes is not expected to depend on the size of the donor substituent and is not supported by our results.

All traces can be described by a single exponential model within experimental error. A similar observation has been made for DMABN by other groups and different methods with better precision. This fact will be important for the discussion below.

4.2. Variable temperature results suggest a near barrierless reaction

The temperature dependence of the reaction rates (inverse of τ), can be interpreted by the Arrhenius equation,

$$1/\tau = A \exp(E_{obs}/RT) \tag{2}$$

where RT is the molar thermal energy, E_{obs} the experimentally observed activation energy, and A is the so-called Arrhenius prefactor.

The temperature change of $1/\tau$ is unexpectedly small with a factor of only 1.1–1.2 in the temperature range considered, leading to an experimentally observed activation energy E_a of only 1.4 ± 1.9 and 2.0 ± 2.3 kJ/mol for DMABN and DMABE, respectively. This is close to or even smaller than the thermal energy in this temperature range (2.5 kJ/mol at room temperature). This is also much smaller than the activation energy E_η of viscosity which amounts to ca. 7.5 kJ/mol for acetonitrile [29]. The latter would lead to a change of the rate by a factor of 1.5 at the lowest temperature, which would clearly have been seen within experimental error here. Previous studies similarly observed a temperature dependence much below that of solvent viscosity [11,33,34].

If the reaction were dominated only by viscosity, we would expect that the activation energies for the reaction and for solvent viscosity should be equal. As this is not the case, a further influence must be important reducing this temperature dependence.

Hicks et al. [33] suggested this to be the solvent polarity which increases at low temperature and reduces activation energies if the precursor state is less polar than the product state. In their low temperature study with a time resolution of 8 ps and butyronitrile as the least viscous solvent, they used the following model assumption: for a given solvent viscosity, the polarity influence of the solvent manifests itself only through a change of the activation energy. The preexponential factor is constant. This is a reasonable assumption as long as only one compound (DMABN) is investigated, without comparing compounds of similar structure but with strongly differing rate constants.

If this model is applied to DMABN, the rates in various neat nitriles at the same temperature can be corrected for the different solvent polarity such that the pure viscosity influence appears. The conclusion of their study was that there is no viscosity influence.

Applying the Hicks–Eisenthal model [33] to the comparison of our results for DMABN/DMABE, we meet an inconsistency: the

finding that the temperature dependences of the rates for DMABN and DMABE are essentially equal signifies that the assumed activation barriers must be equal, which is also consistent with the fact that the solvent polarity is identical in both cases. But in spite of the same barrier, DMABE shows a considerably faster rate which in the Hicks–Eisenthal model must be connected with a reduced activation energy as compared to DMABN. This discrepancy can be solved if the Hicks–Eisenthal model is generalized by assuming that not only barrier changes can take place: in addition to these, a more general treatment also has to take into account the changes of the preexponential factor, and if the latter are the decisive changes for the comparison of DMABN/DMABE, the discrepancy is solved.

Regarding the observed activation energy E_{obs} as compared to that of viscosity E_η, we can set up the following model: if the gas phase intrinsic activation energy E_{int} (i.e. the energy barrier without solvent influence) would be unchanged by solvent polarity and the viscosity influence would be absent, an experimental activation energy $E_{obs} = E_{int}$ would be observed. Now we introduce the solvent polarity influence: if E_{int} is reduced at low temperature by the polarity influence, E_{obs} will be reduced, and we can put $E_{obs} = E_{int} - E_\varepsilon$ where E_ε represents the temperature influence on the rate constant (which can be expressed as a formal activation energy induced by the increasing polarity at low temperatures). E_ε counteracts E_{int} by stabilizing the product at low temperature and reducing the effective barrier according to the Bell–Evans–Polanyi principle [35]. We additionally consider the viscosity influence which will slow down the rates a low temperature, represented by a further term proportional to E_η, the activation energy of solvent viscosity. This will add to E_{obs} and increase it. In a general treatment, we can vary the viscosity control by a factor α between 0 and 1 leading to the following equation:

$$E_{obs} = E_{int} - E_\varepsilon + \alpha E_\eta \tag{3}$$

The factor α of solvent viscosity control can be judged by the response of E_{obs} to a change of E_η for different solvents, if the other two contributions are assumed to remain unaffected. It was found in all cases that changes in E_{obs} are fully correlated with changes in E_η [11,36] and that E_{obs} is smaller than E_η by a factor around 0.6–0.7 [11,33], and this factor is roughly independent of the compound investigated [23,24]. A correlation of E_{obs} with E_η would not be expected if α is very small. If we put $\alpha = 1$, on the other hand, we can interpret our data within the normal diffusional model where large amplitude motions are fully controlled by viscosity. In this case, the observed activation energy E_{obs} will be reduced to approximately 2/3 of E_η due to the contribution of $E_{int} - E_\varepsilon$ which must be negative.

This latter interpretation of full diffusional control is supported by the conclusions drawn at room temperature from the comparison of the compounds with different sizes of the dialkylamino group. The interpretation of the measured activation energy E_{obs} therefore has to take into account the effect of solvent viscosity, i.e. E_η, and for the case observed here, where $E_{obs} < E_\eta$, E_{obs} cannot be interpreted as being a true energy barrier for the intramolecular photoreaction [13], but rather as a diffusively induced temperature effect on the rate.

This generalized model allows to interpret our result that $E_{obs} \leqslant E_\eta$ in two possible ways:

(i) The different rate constants for DMABN and DMABE are due to different sizes of E_{int} significantly larger than the thermal energy kT.

As a consequence, E_ε must be larger than E_{int} in order to result in the observed relation $E_{obs} \leqslant E_\eta$. On the other hand, the observation

that the temperature dependence for both compounds in acetonitrile is identical, is incompatible with different sizeable values of E_{int} for these two compounds: if E_{obs} is similar for both compounds then also E_{int} should be essentially the same for both DMABN and DMABE, because the contributions αE_η and E_ε which both depend on the solvent only, are not expected to differ. This model of a control by E_{int} leads to internal inconsistencies.

(ii) These difficulties are resolved if $E_{int} \cong 0$ and the preexponential factor A controls the difference in rate constant for the two compounds:

In this case, E_{int} is smaller than the thermal energy as well as the other contributions E_ε and αE_η (i.e. an essentially barrierless reaction). Then we can account for the observed nearly identical activation energy E_{obs} for many different compounds and also for the comparison of DMABN with DMABE because the external influences $E_\varepsilon + \alpha E_\eta$ are not expected to depend on the solute.

For case (ii), $E_{int} \cong 0$, we have an additional constraint: both DMABN and DMABE show the same E_{obs} mainly due to solvent influences alone, yet their rate is about four times different, and this difference must therefore be due to the preexponential factor A as outlined above.

4.3. Reactions with conical intersections may lead to entropic control

In order to qualitatively understand the rate ratio of 4 induced by the preexponential factor A in both pairs of compounds DMABN/DMABE and PYRBN/PYRBE, we can refer to the theory of the activated complex for unimolecular reactions [37]. In this theory, the preexponential factor can be expressed as being a function of the activation entropy $\Delta S^{\#}$:

$$A = B \exp(\Delta S^{\#}/R)$$

where $B \cong 10^{12}$ or 10^{13} s^{-1}.

For unimolecular reactions with a tight transition state, $\Delta S^{\#}$ is negative and $A < B$. In order to account for the observed rate difference, the reduction of the Arrhenius prefactor A by the exponential term containing $\Delta S^{\#}$ must be larger for DMABN than for DMABE, hence for DMABN, the activation entropy must be more negative. $\Delta S^{\#}$ can be described by the reduction of phase space necessary for the molecule to reach the transition state. In DMABN, this reduction is larger consistent with a tighter transition state.

$\Delta S^{\#}$ can be described by the fraction of thermal energy of the molecule which is necessary to be concentrated along the reaction coordinate within the activated complex [37]. An alternative description is the probability or ease of reaching the activated complex. Applied to the results for our compounds, the more negative activation entropy signifies that the reaction is less probable for DMABN than for DMABE, all other factors being equal.

One major difference for the adiabatic photoreaction of the two compounds is that a conical intersection (COI) between S_1 and S_2 occurs for DMABN. This can be concluded from fs time-resolved mass spectroscopy [17,38] or from high-level quantum chemical treatments [7,39]. A further indication that both compounds behave differently is given by fluorescence polarization experiments [20,40]. In the case of DMABN, the degree of polarization of the LE and CT bands is different, indicating that the transition moment for the LE state is perpendicular to the long axis but parallel to it for the CT state, consistent with the ^1L_b nature of the LE emission of DMABN [20]. DMABE behaves differently: both bands are long-axis polarized, consistent with an ^1L_a-type emitting LE state [5,6,20,40]. The different nature of the emitting LE state in DMABN and DMABE has also been verified by the size of the radiative rate constant which is ca. 4 times larger for DMABE consistent with the more

allowed character of the ^1L_a state [20]. Since precursor (LE) and product state (CT) are of different symmetry in DMABN, a conical intersection can occur. If they are of similar symmetry as in DMA-BE, the COI does not occur.

The presence of a COI for DMABN restricts the possibility for distribution of the remaining vibrational energy in the transition state because more internal coordinates are required to possess a well defined value as compared to the case without COI. Hence, the probability to reach transition state conditions is smaller for DMABN with a COI than for DMABE without it, and $\Delta S^{\#}$ must be more negative for DMABN and the A factor will be reduced. A reduction of A by a factor of 4, as indicated by our results, corresponds to a $\Delta S^{\#}$ value for DMABN which is more negative by $R\ln 4 \cong 11.5\,\mathrm{J\,mol^{-1}\,K^{-1}}$ as compared to DMABE.

5. Summary

The results of our fs-kinetic studies of various derivatives of DMABN can be explained within a model where a large amplitude motion with diffusional kinetics being controlled by solvent viscosity is the rate limiting step of a complex reaction path involving additionally electron transfer and a conical intersection between S_1 and S_2. Comparison of model compounds with different rotor sizes and ground state twist angles suggests that this motion corresponds to twisting of the dialkylanilino group in the direction of larger twist angles.

But even for identical rotor sizes and ground state twist angles, large rate differences can be found if the acceptor substituent is varied e.g. from a nitrile to an ester group. This can be called an electronic effect. Temperature dependent studies suggest that these rate differences are not connected to differences in the size of the activation barriers but rather to changes in the Arrhenius preexponential factor connected with the activation entropy. These changes may be due to the different involvement of a conical intersection along the reaction path for the compounds compared: to go through a conical intersection involves a geometry along the conical intersection seam which is restricted as compared to the much larger phase space available in normal transition state reactions.

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