Decay times of 4-(dimethylamino)benzonitrile in acetonitrile and conclusions on entropy of activation

Klaas A. Zachariasse a,*, Sergey I. Druzhinin a,*, Peter Mayer b, Sergey A. Kovalenkov c,*, Tamara Senyushkina a

a Max-Planck-Institut für biophysikalische Chemie, Spektroskopie und Photochemische Kinetik, 37070 Göttingen, Germany
b Department Chemie und Biochemie, Ludwig-Maximilians-Universität, Bataanstrasse 5-13, Haus F, 81377 München, Germany
c Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor Strasse 2, 12489 Berlin, Germany

1. Introduction

In a recent Letter [1], Rettig and coworkers presented decay times of five electron donor (D)/acceptor (A) molecules in acetonitrile (MeCN) undergoing a reaction from the locally excited (LE) state to the intramolecular charge transfer (ICT) state. These decay times were determined at 20 °C by fluorescence upconversion, at a wavelength (350 nm) where only LE fluorescence occurs and also at a second wavelength (500 nm) at which predominantly ICT emission is detected [2]. For two of the D/A molecules, the decay time \( \tau \) was measured at more than one temperature: at \(-15, 20 \) and \( 36 \) °C for 4-(dimethylamino)benzonitrile (DMABN) and at \(-15, -7, 22 \) and \( 38 \) °C for 4-(dimethylamino)benzoic acid ethyl ester (DMABE). This was done at an intermediate wavelength (430 nm), where more LE emission is present under the major broad ICT fluorescence band than at 500 nm [2]. The quality of fit for the upconversion traces cannot be ascertained, as residuals are not shown. From these data, Arrhenius activation energies, pre-exponential factors and entropy effects were obtained. These results are critically discussed in the present Letter. The significance of the planarized A/D molecule 1-tert-butyl-6-cyano-1,2,3,4-tetrahydroquinoline (NTC6) as a model for a planar intramolecular charge transfer (ICT) state and the influence of pretwist and size of the amino group is also discussed. For DMABE excited state absorption spectra show a decay of the locally excited (LE) and a rise of the ICT state of 1.0 ps, posing the question whether the lowest excited singlet state is of Lb or La character.

2. Experimental

The synthesis and purification of aldehyde-free DMABN was described before [2]. DMABE (Aldrich) was recrystallized from petroleum. The solvents were chromatographed over Al2O3. The details of the time-correlated single photon counting (SPC) and transient absorption measurements were reported previously [2].

3. Results and discussion

3.1. Picosecond decay times of DMABN in MeCN

For the three temperatures at which the fluorescence decay time \( \tau \) is determined for DMABN in MeCN, an Arrhenius plot is presented in Fig. 1 (red points): 1/\( \tau \) \( \sim \) \( k_0 \) \( \exp(-E_a/RT) \). These data show a substantial scatter, as reflected in the exceptionally large uncertainty reported for the activation energy \( E_a \) of the LE \( \rightarrow \) ICT reaction rate constant \( k_a \) (Scheme 1): 1.4 ± 1.9 kJ/mol [1]. An equally large scatter was found for DMABE: 2.0 ± 2.3 kJ/mol [1].

In looking at these results, it should be noted that only the shortest decay time \( \tau_2 \) of the double exponential LE and ICT fluorescence decays (Eqs. (1)–(4)) is taken into account in Ref. [1]. Although fluorescence decays generally are double exponential when two kinetically communicating excited states (LE and ICT) are involved (Scheme 1), this approximation is acceptable for DMABN in MeCN at 25 °C. This can be seen from the following data that have been reported for this system [2]: \( \tau_2 = 4.1 \) ps and \( \tau_1 = 3800 \) ps, with an amplitude ratio \( A = A_{12}/A_{11} \) of 393 (516 after correction for photoproducts), see Eqs. (1)–(4)

\[
\begin{align*}
\tau_{\text{LE}} &= A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \\
\tau_{\text{ICT}} &= A_3 \exp(-t/\tau_1) + A_4 \exp(-t/\tau_2) \\
A &= A_{12}/A_{11} \\
A_{21} &= -A_{22}
\end{align*}
\]
In the approach of Ref. [1], one then obtains the following approximate, but for DMABN/MeCN adequate, expressions

\[ i_f(\text{LE}) = A_{11} + A_{12} \exp(-t/\tau_2) \]  
\[ i_f(\text{ICT}) = A_{01} + A_{02} \exp(-t/\tau_2) \]  

For the normalized LE decay (Eq. (5)), \( A_{11} + A_{12} = 1 \), equivalent to \( A_0 + A_1 = 1 \) in Table 1 of Ref. [1]. This expression does not hold, however, in the case of the ICT decay at 500 nm in this table, as then (Eq. (6)) \( A_0 + A_1 = 0 \), see Eq. (4). It also does not hold strictly for the decay at 430 nm (sum of ICT and LE fluorescence, Eqs. (5) and (6)), see Fig. 2.

In Scheme 1, \( k_a \) and \( k_d \) are the rate constants of the forward and backward ICT reaction, \( \tau_0(\text{LE}) \) and \( \tau_s(\text{ICT}) \) are the fluorescence lifetimes, whereas \( k_f(\text{LE}) \) and \( k_f(\text{ICT}) \) are the radiative rate constants.

Decay times \( \tau_2 \) for DMABN in MeCN published in Ref. [2] are also plotted in Fig. 1. From the global analysis of 14 fluorescence decays obtained from picosecond single photon counting (SPC) experiments (black data points) together with the fluorescence spectra, over a temperature range from 75 to -45 °C, an activation energy \( E_a \) of 5.0 ± 0.25 kJ/mol and a preexponential factor \( k_o = 1.83 \times 10^{12} \text{s}^{-1} \) have been calculated (Ref. [2]). From Fig. 1 (including the green ESA data point): \( E_a = 4.6 ± 0.2 \text{ kJ/mol and } k_o = 1.6 ± 0.1 \times 10^{12} \text{s}^{-1} \). The value for \( E_a \) is clearly considerably larger and less uncertain than that (1.4 ± 1.9 kJ/mol) of Ref. [1]. The authors of Ref. [1] claim that this large difference in the \( \tau_2 \) values is caused by the fact that their data are more reliable in view of an presumed better time resolution of their equipment. They report for our SPC equipment a 19 ps apparatus response function, implying that this is too large for an accurate determination of the decay times of DMABN in MeCN, between 7.8 and 3.0 ps, our data from Ref. [2]. In fact, the time resolution in our SPC experiments is after deconvolution better than 3 ps [2], which means that our decay times in Ref. [2] are not affected by insufficient time resolution. This conclusion is fully supported by the \( \tau \) of 4.07 ps (green data point in Fig. 2) determined from femtosecond excited state absorption (ESA) measurements of DMABN in MeCN at 22 °C, having a time resolution better than 100 fs [2]. We therefore conclude that the scatter in the decay times of Ref. [1] and also their small number and narrow temperature range prevent a meaningful determination of the activation energy of the LE → ICT reaction of DMABN in MeCN. This also means that reliable information on the preexponential factor \( k_o \) of this reaction and \( a \) fortiori on its entropy of activation \( \Delta S^\circ \) cannot be obtained from the data presented in Ref. [1], neither for DMABN nor for DMABE.

Within the context of transition state theory (TST) [3], the rate constant \( 1/\tau_2 = k_o \) for the LE → ICT reaction can be written in terms of the entropy and enthalpy of activation \( \Delta S^\circ \) and \( \Delta H^\circ \), Eq. (7). A

\[ \log k_o^0 = \log k_o - \frac{\Delta H^\circ}{R} \frac{1}{T} - \frac{\Delta S^\circ}{R} \]

Table 1

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>( \tau_2 ) (ps)</th>
<th>( k_o^a ) ( (10^{11} \text{s}^{-1}) )</th>
<th>( E_a ) (kJ/mol)</th>
<th>( k_o^b ) ( (10^{12} \text{s}^{-1}) )</th>
<th>( \Delta H^\circ ) (kJ/mol)</th>
<th>( \Delta S^\circ ) (JK⁻¹mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMABN (Ref. [1])</td>
<td>20</td>
<td>3.7</td>
<td>2.7</td>
<td>1.4 ± 1.9</td>
<td>0.49 ± 0.15</td>
<td>-12.2 ± 0.8</td>
</tr>
<tr>
<td>DMABE (Ref. [1])</td>
<td>20</td>
<td>0.92</td>
<td>10.9</td>
<td>2.0 ± 2.3</td>
<td>2.4 ± 0.3</td>
<td>-0.15 ± 0.44</td>
</tr>
<tr>
<td>DMABN (Ref. [2])</td>
<td>25</td>
<td>4.10</td>
<td>2.4</td>
<td>5.0 ± 0.25</td>
<td>1.83 ± 0.02</td>
<td>2.3 ± 0.2</td>
</tr>
<tr>
<td>DMABN (Ref. [2])</td>
<td>20</td>
<td>4.28</td>
<td>2.3</td>
<td>5.0 ± 0.25</td>
<td>1.83 ± 0.02</td>
<td>2.3 ± 0.2</td>
</tr>
<tr>
<td>DMABN (Ref. [2])</td>
<td>-45</td>
<td>7.35</td>
<td>1.3</td>
<td>5.0 ± 0.25</td>
<td>1.83 ± 0.02</td>
<td>2.3 ± 0.2</td>
</tr>
</tbody>
</table>

\( a \) k = 1/\( \tau_2 \) (Scheme 1).

\( b \) Effective parameters from the plots of our combined SPC and ESA data in Figs. 1 and 3.
plot of ln(h/kTτ2) vs. 1000/T is presented in Fig. 3. It appears that now the upconversion data (red points) result in a positive slope, meaning that the enthalpy of activation is negative: −1.2 ± 0.8 kJ/mol and ΔS° = −30 ± 3 JK−1 mol−1. For our SPC and ESA data, the value for ΔH° is positive (2.3 ± 0.2 kJ/mol and ΔS° = −19.7 ± 0.7 JK−1 mol−1), but smaller than that for E a (4.6 ± 0.2 kJ/mol), a natural consequence of the temperature dependence of the preexponential factor in the TST treatment (Table 1).

\[
1/\tau_2 \sim k_b kT \exp(\Delta S^°/R) \exp(-\Delta H^°/RT)
\]

(7)

3.2. NTC6, a planar ICT model compound for DMABN

NTC6 (Chart 1) undergoes a fast ICT reaction, with a reaction time (decay time τ2) of 2.1 ps in n-hexane at 25 °C and 1 ps in MeCN at 22 °C [4,5]. The activation energy E a is very low, 1 kJ/mol in di(n-buty) ether [4]. In the ICT state of NTC6 obtained from calculations, the conjugation in the phenyl ring is destroyed, brought about by the pyramidal configuration of the atom C4 to which the amino nitrogen N7 is attached [6,7]. A similarly distorted pyramidal ICT structure has been calculated for DMABN [8,9]. For such a substantial structural distortion, a small activation barrier as revealed by the fast ICT reaction of NTC6 would be surprising. In the calculations on NTC6, an activation energy for the ICT reaction pathway has not been reported [6,7].

It is then to be expected that the ICT ESA spectrum of NTC6 with a distorted phenyl ring would be different from that of the benzonitrile radical anion, in which all C atoms of the phenyl ring are conjugated, as deduced from its ESR spectrum [10]. This is not the case, however, as the transient spectrum of the ICT state of NTC6 resembles that of the benzonitrile anion [5], similar to what has been observed in the case of DMABN [2,11–13]. It should be noted in this connection that benzonitrile and derivatives with various para-substituents have similar radical anion absorption spectra [14,15], indicating that structural information such as on the dimethylamino twist angle θ cannot be deduced from the ESA spectra. When a possibility to reach a strongly twisted ICT structure by phenyl ring distortion would exist for NTC6, it likewise would be expected for its N-methyl (NMC6), N-ethyl (NEC6) and N-isopropyl (NIC6) derivatives, for which molecules, in fact, an ICT reaction does not occur [4].

3.3. Amino twist angles in the S0 ground state (pretwist)

According to Ref. [1], deduced from photoelectron spectra [16], the dimethylamino group of DMABN is twisted over an angle θ of about 30° relative to the plane of the benzonitrile moiety, whereas 4-[(N-pyrrolo)benzonitrile (P5C, Chart 2) is close to planar. This is surprising, as in Ref. [16] a twist angle of around 0° is reported for both molecules (Table 2). Also from an X-ray structure analysis of DMABN [17,18] and PSC a small twist angle θ close to 0° is found (Table 2).

The decadic molar absorption coefficients εmax of the lowest-energy band in the absorption spectrum of DMABN and PSC in n-hexane and MeCN (Table 2) likewise lead to the conclusion that their amino group is not twisted. This comes from the condition that εmax is proportional to cos² θ [19]. A planar structure for DMABN in the ground state is also found by several computations [6,9,20]. The discussion in Ref. [1] of the difference in ICT reaction time between the effectively planar molecules DMABN and PSC based on assumed differences in their twist angle θ is therefore not relevant.

Data from X-ray crystal analysis (cit. files in Supplementary material) for 4-[(diethylamino)benzonitrile (DEABN), 4-(N-piperidino)benzonitrile (P6C) and 3,5-dimethyl-4-[(diethylamino)benzonitrile (MMD) are also included in Table 2, together with εmax values, for comparison with the θ (PE) results from photoelectron spectra, also serving as a further illustration of the relationship between the twist angle θ and εmax. Care must be taken in defining the amino twist angle θ and the pyramidal angle ϕ for molecules with pyramidal amino groups, see footnotes a and b of Table 2 and Chart 2. Note that for P6C and MMD (Table 2) the angles θ and ϕ both contribute to the electronic decoupling of the amino group from the benzonitrile moiety in aminobenzoanitriles, an increase of both angles leading to a decrease of εmax.

The influence of a ‘pretwist’ of the amino group of 4-aminobenzoanitriles in the S0 ground state on the efficiency of the LE → ICT reaction is questionable anyway, as the molecular structure of the S0(LE) state (twist angle, amino pyramidality, bond lengths) and not that of the ground state S0 is significant for the ICT reaction. In addition, twist angles up to around 30° will be of little photophysical consequence as compared to a planar structure, because of the fact that the electronic coupling between the amino and benzonitrile moieties is governed by cos² θ [19].
3.4. Size of amino substituents and ICT reaction rate

In Ref. [1], it is stated that the larger rotational volume of the pyrrolidino group of P5C as compared with that of the dimethylamino group in DMABN contributes to a slower ICT reaction (longer decay time $\tau_2$) of the former molecule. To single out the influence of macroscopic solvent viscosity on the ICT reaction of a D/A molecule such as DMABN is a complicated issue due to the difficulty to change the viscosity by employing a series of solvents, without simultaneously changing other solvent properties such as polarity (dielectric constant $\varepsilon$) and polarizability (refractive index $n$). This is caused by the sensitivity of the ICT reaction on the magnitude of the energy gap $\Delta E(S_1, S_2)$, which gap is affected by $\varepsilon$ and $n$ [21–23]. This is even the case when the variation in viscosity is brought about by way of exerting hydrostatic pressure. In such a case measurements as a function of pressure have to be combined with those carried out at different temperatures. From such a combined experimental approach with DMABN in diethyl ether (DEE) at 20 °C it was found that by increasing the pressure from 1 to 4500 bar, as an example, the solvent viscosity increased from 0.23 to 1.8 CP, whereas the polarity increased from 4.3 to 6.3. By this increase in pressure, the ICT/LE fluorescence quantum yield ratio $\Phi$(ICT)/$\Phi$(LE) became larger, from 0.32 to 0.95, making clear that the effect of pressure on solvent viscosity has a smaller impact on the ICT kinetics than that on polarity [23,24].

For the relative small ICT reaction efficiency of P5C in MeCN the following different explanation can be found in the literature. The increase of the ICT rate constant $k_b$ with increasing size of the cyclic amino group in the series 4-(N-azetidino)benzonitrile (P4C), P5C, P6C in MeCN, although the volume of the cyclic amino group becomes larger, has been attributed to the lowering of the amino nitrogen inversion barrier for the LE → ICT reaction when going from P4C to P6C [25].

3.5. ESA spectra of DMABE in MeCN. $S_1(L_b)$ and $S_2(L_a)$ states

It is reported in Ref. [1] that the LE and ICT fluorescence bands of DMABE are both long-axis polarized. From this information, the question whether the lowest excited singlet state $S_1$(LE) is of $^1L_a$ or $^1L_b$ nature can, however, not easily be decided with certainty, as the $S_1$ and $S_2$ states in the absorption spectrum are in close proximity. Experimentally, it is very difficult to interpret the polarization direction when $S_2$(1L_a) is just below $S_1$(1L_b), due to vibronic coupling between these states, apart from the intrinsic difficulty to measure the $S_1$ absorption band separately under these conditions. Ironically, perhaps, the TICT model was introduced because of the finding that LE and ICT fluorescence of DMABN in glycerine both had a long-axis polarization [11,26], thereby not taking the vibronic coupling between these close-lying states into account.

From ESA spectra of DMABE in MeCN at 22 °C (Fig. 4a) it appears that the band with a maximum at 375 nm decays with 1.0 ps (Fig. 4b) [27], a time similar to the fluorescence decay of 0.98 ps reported in Ref. [1]. The band integral around the ICT absorption maximum at 465 nm shows a growing-in with the same time of 1.0 ps. This means that the 375 nm ESA band can be attributed to the initially excited $S_1$(LE) state, the precursor in the ICT reaction. Whether this LE state is of $L_b$ or $L_a$ parentage cannot easily be decided. For DMABN in n-hexane, the energy gap $\Delta E(S_1, S_2)$ before the $S_1$(Lb)/$S_2$(La) energy order-
activation energies $E_a$ and $E_d$ with an exceptionally large uncertainty are obtained. From these data, conclusions on the entropy effects can obviously not be made. The same is the case for DMABE.

The argument derived from computations that the ICT state of NTC6 has a nonplanar structure with a pyramidal C atom to which the amino nitrogen is attached, appears to be unlikely, as the ESA ICT spectrum resembles that of the benzonitrile radical anion with a fully conjugated phenyl ring. Because of the fact that both DMABN and P5C are planar in the S0 ground state, a discussion of the difference in the ICT reaction rate constant of these molecules in MeCN based on a presumed pretwist of DMABN is not relevant. The slower ICT reaction of P5C has previously been attributed to a larger nitrogen inversion barrier. Femtosecond ESA spectra of DMABE in MeCN show a decay of the LE state and a growing-in of the ICT state, both with a time of 1.0 ps. The assumption made in Ref. [1] that the lowest excited singlet state of DMABE is of La character is questioned.

Acknowledgement

Many thanks are due to Prof. N.P. Ernsting (Humboldt University Berlin) for the use of the femtosecond absorption equipment in the investigations reported here.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2009.10.094.

References