

The Dynamics of Excited State Structural Relaxation of 4-Dimethylaminobenzonitrile (DMABN) and Related Compounds

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The excited state structural relaxation of 4-dimethylaminobenzenes with various *para*-acceptor substituents having double-band emission, local excited (LE) and charge transfer (CT), has been investigated. Fluorescence measurements at different temperatures and in different solvents have confirmed the existence of viscosity-dependent, temperature, and polarity-activated relaxation. The kinetics analysis has shown that the radiative deactivation rate constants of the individual LE and CT states differ by 7–112-fold. The dipole moment changes at the excitation for CT states are significantly larger than those for LE states. The spectral-kinetics behavior of compounds studied agrees with the models $A \rightarrow A^* \rightarrow B^*$ or $A \rightarrow A^* \leftrightarrow B^*$, where A^* is the local excited planar and B^* is the relaxed twisted state of the molecule. The rate constants of the twisted state formation have been calculated in the temperature range 293–77 K. The activation energies of forward process for compounds studied have been estimated.

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1. INTRODUCTION

At the present time, the behavior of 4-(dimethylamino)benzonitrile (DMABN) and DMABN-related compounds at the excitation has been studied extensively. Most of the researchers share the judgement about the dominating contribution of twisted intramolecular charge transfer (TICT) deactivation mechanism for them. The full charge separation in excited DMABN is confirmed by the transient absorption spectra, which match the absorption spectra of acceptor radical anion [1]. The down shift of a vibrational frequency for Ph-N stretch of DMABN to a typical single-bond frequency indicates lowering the bond order in CT state with decoupled amino and benzonitrile fragments [2]. The similarity of spectral position of DMABN and protonated dimethylaniline (DMA-H⁺) indicates some pyramidal character of amine in CT state [3]. All DMABN-related rigid molecules show no CT fluorescence band and ICT also does not occur in crystalline DMABN [4]. On the other hand, the pretwisted samples show the enhanced CT band [5]. There are also evidences of strong viscosity [6] and polarity [7] influence on the rate of the excited state ICT reaction. It is interesting to investigate the effect of *para*-acceptor substituent on the excited state structural relaxation (ESSR). The molecules with a weaker acceptor should possess the reduced

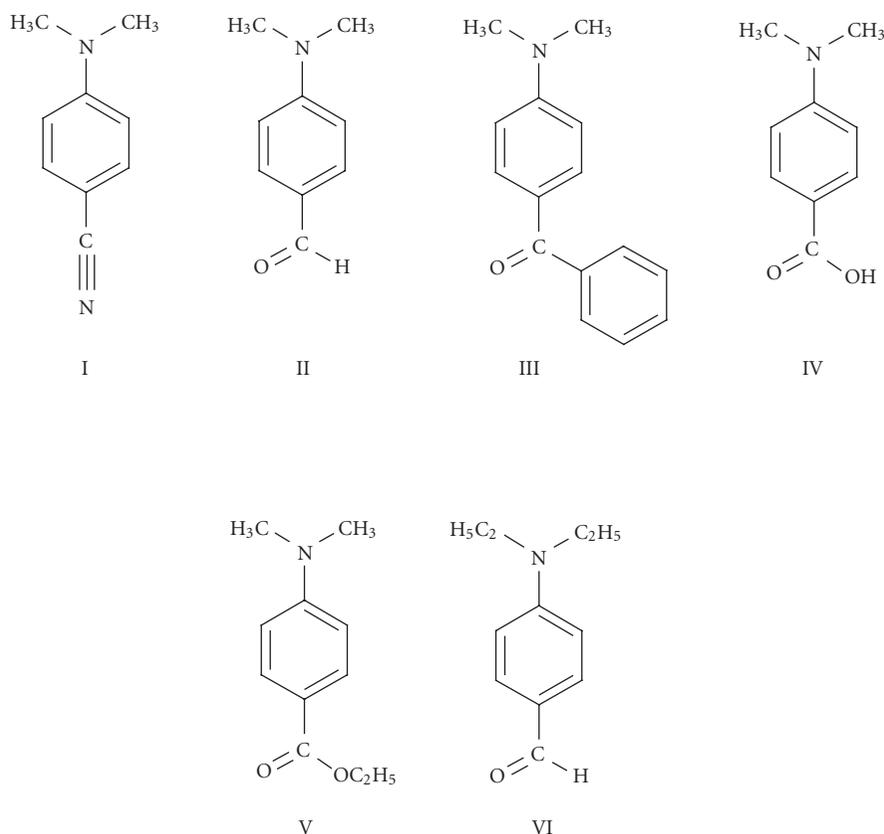
CT fluorescence band. The solvent viscosity and medium polarity were chosen as the main factors controlling the system conditions.

The focus of the present work is on the quantitative characterization of the dynamics of excited state intramolecular structural relaxation of DMABN and its related compounds with *para*-acceptor substituents.

2. EXPERIMENTAL SECTION

4-(dimethylamino)benzonitrile (I), 4-(dimethylamino)benzaldehyde (II), 4-(dimethylamino)benzophenone (III), 4-(dimethylamino)benzoic acid (IV), ethyl 4-dimethylamino-benzoate (V), and 4-(diethylamino)benzaldehyde (VI) were used as received. Heptane, toluene, ethyl acetate, dichloromethane, 1,2-dichloroethane, chloroform, 2-propanol, *n*-butanol, acetone, butyronitrile, ethanol, acetonitrile, water, and polymethylmethacrylate were of spectroscopic grade quality. Ethanol was dehydrated by the distillation with CaH₂. Ethyl acetate was purified by the distillation with K₂CO₃. Polymethylmethacrylate (PMMA) was obtained by the photoinduced polymerization of methylmethacrylate (100% conversion) and used as received.

The absorption and fluorescence spectra were recorded on a UV-3100 spectrophotometer and an Elyumin-2M



SCHEME 1

spectrofluorimeter. The fluorescence kinetics was recorded with a nanosecond SP-70 spectrometer. The measurements of ϕ_f , the registration of the absorption and the fluorescence spectra, and the fluorescence kinetics at different temperatures were carried out as described earlier [9]. The calculations of the hydrodynamic radii were performed by the molecular modeling system HyperChem 7.0. The viscosity of butyronitrile at different temperatures was calculated using van Velzen equation [10].

3. RESULTS AND DISCUSSION

The double-band emission of I, II, IV–VI observed predominantly in the polar solvents and their spectral-luminescent behavior at various temperatures make these relative compounds perspective for the investigation of the intramolecular photorelaxation process. Since I–V have the identical donor and the different acceptors, it is reasonable to compare the variations in the areas under longwavelength (S_{CT}) and shortwavelength (S_{LE}) bands at the temperature decrease with the corresponding values of the first ionization potential (IP) of the acceptors. The use of the ionization potential instead of the electron affinity (EA) for the acceptor strength estimation is explained by the fact that IP values for the corresponding hydrogenated acceptors were measured by many and widely known methods [8]. It is not the case for EA values. As to the EA values obtained from the calculations of

corresponding heats of formation for neutral molecule and anion, they are rather approximate and may not be used here.

The room-temperature fluorescence spectra of I, IV, V in ethanol and I, II, IV–VI in butyronitrile involve two well separated short- and longwavelength bands. The fluorescence Stokes shifts of longwavelength (CT) bands are anomalously large (Table 1). The fluorescence spectrum of III includes a single wide longwavelength band. For the compounds II and VI in ethanol, we observe only single shortwavelength band with small fluorescence Stokes shift. The absence of CT band in these spectra may be caused by a nonemissive character of their relaxed state that is confirmed by a very small value of ϕ_f .

As the temperature decreases from 293 to 77 K, the emission spectra of I, IV, and V demonstrate the continuous shortwavelength shift of CT band and the large increase of the total ϕ_f in ethanol (Figure 1). The analogous spectra of II and VI in butyronitrile demonstrate the similar behavior. The LE band position changes insignificantly. The emission spectra of III in ethanol show the continuous shortwavelength shift and the large increase of ϕ_f (Figure 2). Figure 3 illustrates the changes of S_{CT}/S_{LE} ratio with temperature for I, II, IV–VI. In all five cases, the increase of the medium viscosity with a temperature decrease inhibits the CT band formation. When the temperature falls down to 77 K, the CT band contributions approach practically to zero. The largest IP value of nitrile acceptor for I is reflected by the largest

TABLE 1: Absorption, fluorescence, and phosphorescence band maxima ($\lambda_a^{\max}, \lambda_f^{\max}, \lambda_{ph}^{\max}$), fluorescence and phosphorescence quantum yields (φ_f, φ_{ph}), dipole moment changes ($\Delta\mu = \mu_e - \mu_g$), activation energies (E_a, E_d), rate constants of forward and backward reactions (k_1, k_{-1}) of compounds I–VI in ethanol and ionization potentials (IPs) [8].

Code	λ_a^{\max} , nm (293 K)	λ_f^{\max} , nm (293 K)		λ_{ph}^{\max} nm (77 K)	φ_f		φ_{ph} , (77 K)	$\Delta\mu, D$		E_a, E_d kJ/mole	$k_1^{(a)} k_{-1}$, s ⁻¹	IP ^(c) , eV
		LE	CT		(293 K)	(77 K)		LE	CT			
I	292	328	472	403, 423	0.01	0.22	0.24	2.2 ± 1.8	15.8 ± 1.7	8.8 ± 0.5	(1.9 ± 0.5) · 10 ¹¹	13.60
II ^(b)	335	357	540	457	0.06	0.10	0.15	4.6 ± 1.8	14.7 ± 1.7	7.5 ± 0.9	(3.6 ± 0.1) · 10 ¹⁰	10.88
III	354	—	483	490	< 0.001	0.24	0.05	—	13.6 ± 1.1	11.4 ± 0.1	—	9.50
IV	306	338	427	417	0.02	0.10	0.05	5.3 ± 1.1	14.0 ± 1.6	9.2 ± 0.6 11.8 ± 0.3	(1.1 ± 0.5) · 10 ¹¹ (2.0 ± 0.6) · 10 ⁹	11.33
V	310	321	513	418	< 0.01	0.10	0.06	8.9 ± 1.0	22.6 ± 0.3	3.5 ± 0.5 9.7 ± 0.3	(2.3 ± 0.5) · 10 ¹¹ (1.5 ± 0.5) · 10 ⁹	10.61
VI ^(b)	339	368	540	456	< 0.01	0.03	0.11	7.7 ± 1.0	14.2 ± 3.0	11.0 ± 0.9	(2.9 ± 0.9) · 10 ¹⁰	10.88

^(a)For I at 273, for IV at 294, for V at 273.5, and for VI at 254 K.

^(b)For II and VI in PrCN.

^(c)The values indicated for hydrogenated derivatives of acceptor groups.

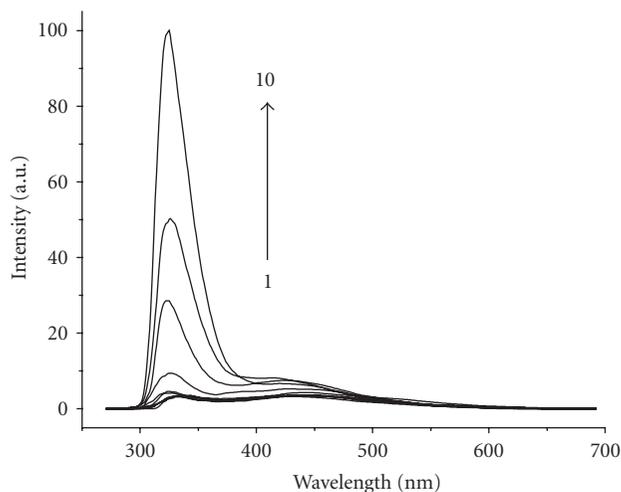


FIGURE 1: The fluorescence spectra of IV in ethanol at different temperatures: 1(294), 2(273), 3(252), 4(231), 5(214), 6(203), 7(174), 8(152), 9(135), and 10(115 K). $\lambda_{exc} = 288$ nm.

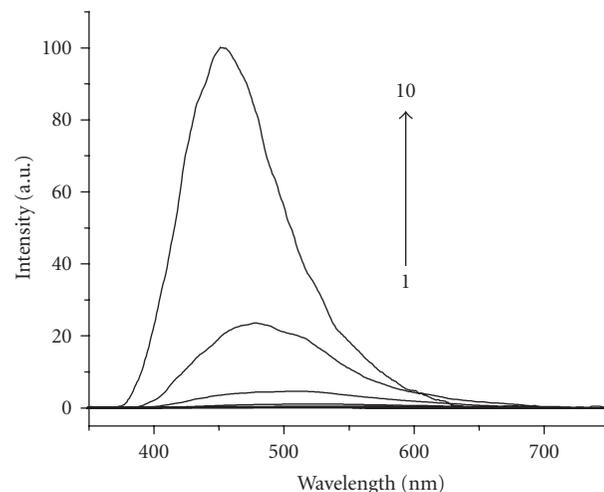


FIGURE 2: The fluorescence spectra of III in ethanol at different temperatures: 1(296), 2(273), 3(253), 4(232), 5(214), 6(192), 7(175), 8(152), 9(131), and 10(114 K). $\lambda_{exc} = 354$ nm.

S_{CT}/S_{LE} ratio in a wide temperature range. The dependences $S_{CT}/S_{LE}(T)$ for II and V with the same acceptors and different donors are similar. It is predictable because the IP values for $(CH_3)_2NH$ and $(C_2H_5)_2NH$ are very close (8.24 and 8.35 eV) [8].

All these observations point out the presence of the viscosity-dependent relaxation process in excited I–VI. The gradual disappearance of the longwavelength bands and the rise of the shortwavelength ones indicate the probable parent-daughter relationship between LE and CT states of the excited molecules. The important contribution of the

medium viscosity to the inhibition of the process is also supported by the behavior of the fluorescence spectra of the samples in PMMA at 293 K. At these conditions, only LE bands are present, while CT bands completely disappear. The fluorescence spectra positions of I, II, IV–VI in PMMA and heptane are close. The spectral position of III fluorescence in PMMA is blue shifted by 66 nm with respect to heptane. A peculiarity of the compounds studied is the appearance of the phosphorescence observed at 77 K for I–VI in ethanol and butyronitrile glass matrix (Table 1).

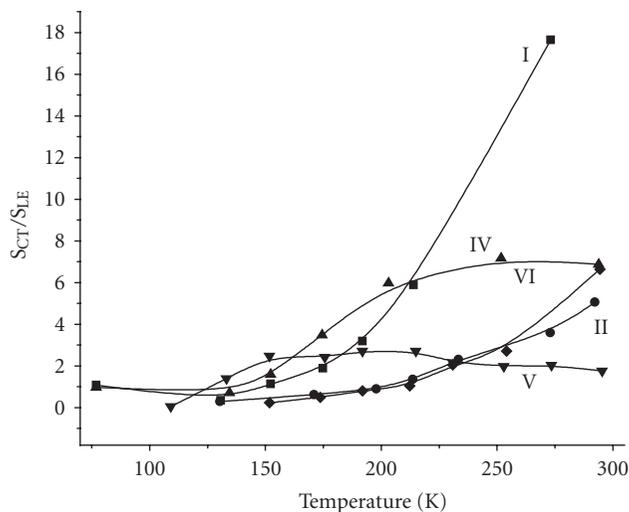


FIGURE 3: The ratios of the areas under the longwavelength (CT) and the shortwavelength (LE) fluorescence bands of the compounds I, IV, V in ethanol and II and VI in butyronitrile at various temperatures in the range 293–100 K.

In nonpolar heptane, the fluorescence spectra of I, II, IV, V represent only the shortwavelength band (VI shows no emission here). In more polar media (for IV and V even in toluene), we observe also an appearance of the longwavelength bands, their contributions increase with an increase of the solvent polarity. The compound III in either solvent shows wide single band having the pronounced solvatochromism. Thus it is obvious that the CT band formation is also strongly polarity-dependent. The pronounced donor-acceptor character of the compounds makes possible to use the solvatochromic determination of the dipole moment changes at the excitation by Lippert's equation [11]. Figure 4 shows the corresponding slopes of a dependence $\tilde{\nu}_{a-f}$ versus $\Delta f(\epsilon, n)$ for short- and longwavelength bands. The longwavelength bands are characterized by a larger charge transfer degree, that is, the relaxed CT state is more polar. The calculated parameters $\Delta\mu^{\text{CT}}$ and $\Delta\mu^{\text{LE}}$ do not correlate with IP values of the corresponding acceptors. It is not surprising since the acceptor dimensions vary. The values λ_f^{max} , φ_f , $\Delta\mu$ for the fluorescence band of III correspond to the similar data for the CT bands of I, II, IV–VI. The continuous shortwavelength fluorescence shift of III with the temperature decrease also corresponds to the behavior of these compounds. It allows us to consider the room-temperature emission of III as originated mainly from CT state.

For the compounds showing single-band fluorescence with anomalously large Stokes shift, we proposed the procedure indicating the change of their fluorescent state at the excitation [9]. The indicator of such change is the pronounced subsequent variation of the averaged \bar{k}_f in a wide temperature range. Indeed, for III in ethanol, $\bar{k}_f(293 \text{ K}) = 2.1 \cdot 10^4 \text{ s}^{-1}$ and $\bar{k}_f(77 \text{ K}) = 3.9 \cdot 10^7 \text{ s}^{-1}$. As for the compounds showing

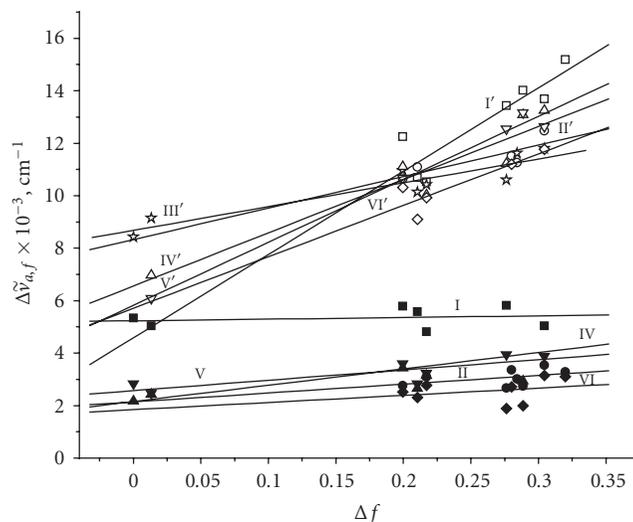


FIGURE 4: The dependence of the fluorescence Stokes' shift for LE and CT bands of the compounds I–VI on the solvent polarity parameter Δf at 293 K: I, I' (\square); II, II' (\circ); III' (\star); IV, IV' (\triangle); V, V' (∇); VI, VI' (\diamond). The filled symbols stands for LE and the hollow symbols stands for corresponding CT bands.

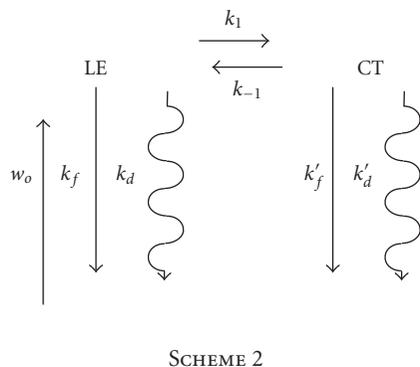
double-band emission, we could not register this dependence properly. In this case, it is enough to compare k_f of individual bands, obtained by the following approximations: $k'_f \approx \varphi_f^{\text{CT}}/\tau_f^{\text{CT}}$, $k_f \approx \varphi_f^{\text{LE}}/\tau_f^{\text{LE}}$. To receive more precise τ_f data, the corresponding kinetics was measured at CT and LE band maxima at 293 and 77 K, respectively. The results for k'_f and k_f are I/EtOH, $2.6 \cdot 10^6 \text{ s}^{-1}$ and $8.4 \cdot 10^7 \text{ s}^{-1}$; II/PrCN, $2.3 \cdot 10^6$ and $3.5 \cdot 10^7 \text{ s}^{-1}$; IV/EtOH, $4.0 \cdot 10^6 \text{ s}^{-1}$ and $2.9 \cdot 10^7 \text{ s}^{-1}$; V/EtOH, $2.5 \cdot 10^5 \text{ s}^{-1}$ and $2.8 \cdot 10^7 \text{ s}^{-1}$; VI/PrCN, $3.4 \cdot 10^6 \text{ s}^{-1}$ and $4.1 \cdot 10^7 \text{ s}^{-1}$. The observable strong change of k_f agrees with TICT model, postulating that CT band presents the orthogonally twisted daughter of parent LE band. Otherwise, according to [12], such observations only cannot support the validity of the TICT or PICT model, since the difference between radiative rate constants reflects just a larger ICT state dipole moment.

The photorelaxation of I, III, IV, V in ethanol and II and VI in butyronitrile can be represented by the processes shown in Scheme 2.

At the approximation of the steady-state conditions, the following equation holds:

$$\frac{\varphi_{\text{CT}}}{\varphi_{\text{LE}}} = \frac{k'_f[\text{CT}]}{k_f[\text{LE}]} = \frac{k'_f k_1}{k_f(k_d + k'_d)}, \quad (1)$$

where [LE] and [CT] are the photo steady-state concentrations of LE and CT states; k_1 and k_{-1} are the rate constants of forward and back reactions; $k_f(k_d)$ and $k'_f(k'_d)$ are the radiative (nonradiative) rate constants of LE and CT states. The temperature dependence of k_1 and k_{-1} can be described by $k_1 = k_1^0 \exp(-E_a/RT)$ and $k_{-1} = k_{-1}^0 \exp(-E_d/RT)$. With this



substitution, (1) takes the known form [13]

$$\begin{aligned} \frac{\varphi_{\text{CT}}}{\varphi_{\text{LE}}} &= \frac{k'_f k_1^0 \exp(-E_a/RT)}{k_f k_{-1}^0 \exp(-E_d/RT) + k_f (k'_f + k'_d)} \\ &= \frac{A \exp(-E_a/RT)}{B \exp(-E_d/RT) + C} \end{aligned} \quad (2)$$

In order to proceed, we suppose that the parameters A , B , and C are temperature independent. The experimental data fitting for I in ethanol and II and VI in butyronitrile to (2) showed that $B, E_d \rightarrow 0$, that is, the backward photoreaction can be neglected (3):

$$\frac{\varphi_{\text{CT}}}{\varphi_{\text{LE}}} = \frac{k'_f \tau_0'}{k_f} k_1^0 \exp\left(-\frac{E_a}{RT}\right). \quad (3)$$

On the other hand, the best fit for IV and V in ethanol shows the presence of the forward and backward reactions with the corresponding activation energies. For the determination of k_1^0, k_{-1}^0, E_a , and E_d , we used the above-mentioned parameters estimation: $k'_f \approx \varphi_f^{\text{CT}}/\tau_f^{\text{CT}}$, $k_f \approx \varphi_f^{\text{LE}}/\tau_f^{\text{LE}}$, and $\tau_0' \approx \tau_f^{\text{CT}}$ at 293 K.

We suppose that the observed wide fluorescence spectrum of III in ethanol represents a superposition of closely arranged LE and CT bands. Because of this, it is possible to get just overestimated activation energy value from the steady-state fluorescence data. It may be calculated from the slope of a plot $\ln(1/\varphi_f - 1)$ versus $1/T$ according to (4) [14]:

$$\ln\left(\frac{1}{\varphi_f} - 1\right) = \ln\left(\frac{A}{k_f}\right) - \frac{E_a}{RT}, \quad (4)$$

where A denotes the preexponential term of the Arrhenius equation. The assumptions used to derive this formula are the following: $k_1(T) \gg k_d, k_1(T) \gg k_{-1}(T)$. The results are shown in Table 1.

The dependence of the relaxation constants on the temperature shown in Figure 5 follows the common tendency: an intermission of the reaction in highly viscous glassy media at 77 K and the progressive rise of k_1 as the temperature

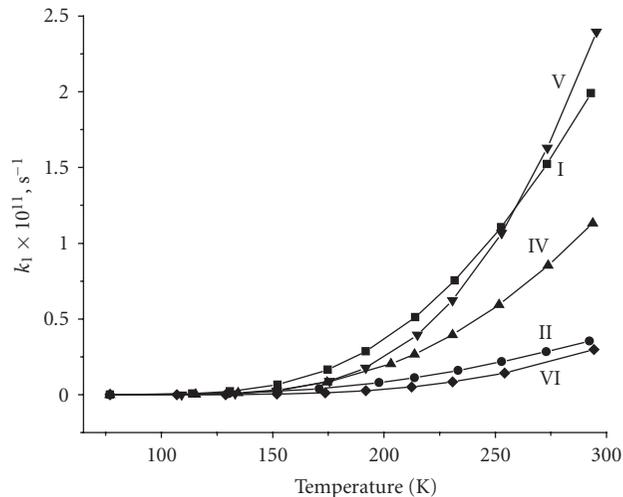


FIGURE 5: The rate constants of the forward photoreaction for the compounds I, IV, V in ethanol and II and VI in butyronitrile at different temperatures in the range 293–100 K.

increases. In the range ~ 133 – 173 K, the obtained k_1 and k_{-1} values are of the order of the analogous photorelaxation rate constants of 1-ethyl-3-(5-phenyloxazol-2-yl)pyridinium 4-methyl-1-benzenesulfonate [9], *N*-(2-anthryl)-2,4,6-trimethyl-pyridinium perchlorate, and 10-(1-anthryl)-1,2,3,4,5,6,7,8-octahydro-acridinium perchlorate [14] in ethanol. The obtained k_1 values for I in toluene [15] ($\epsilon = 2.38$) and ethyl ether [16] ($\epsilon = 4.34$) at 293 K are $1.8 \cdot 10^{10} \text{ s}^{-1}$ and $2.3 \cdot 10^{10} \text{ s}^{-1}$, respectively. The obtained k_1 value for I in ethanol at 293 K is $(1.9 \pm 0.5) \cdot 10^{11} \text{ s}^{-1}$. Indeed, the higher ethanol polarity ($\epsilon = 24.55$) should favor faster reaction. In the previous studies, the variations of k_1 for photoisomerization of I in nitriles were attributed chiefly to polarity barrier [7]. To our opinion, the strong viscosity influence on the relaxation was not noticed by the reason that the experiments were conducted in the narrow temperature range, where η simply does not increase to a significant value.

The reaction from LE to CT state has been observed for 4-(di-isopropylamino)benzonitrile (DIABN) even in nonpolar *n*-hexane at 25°C ($k_1 = 3.4 \cdot 10^{11} \text{ s}^{-1}$ [17]). Indeed, IP value for (*i*-Pr)₂NH is equal to 7.6–7.73 eV [8], that is, di-isopropylamine has more stronger donor character than dimethyl- or diethylamine. The ICT stabilization enthalpies ($-\Delta H = E_a - E_d$) for IV and VI are very small, $-2.6, -6.2 \text{ kJ/mol}$, and they are less than the activation energy of the viscous flow in ethanol.

4. CONCLUSIONS

The compounds studied (I–VI) undergo the excited state structural relaxation. This relaxation depends on the medium viscosity and on the solvent polarity. The photorelaxation of IV and VI in ethanol is reversible and the reaction of I in ethanol and II and VI in butyronitrile was found to be irreversible. The short- and the longwavelength bands in

fluorescence spectra of I, II, IV–VI reflect parent-daughter relationship between LE and CT states. The CT band apparently belongs to the orthogonally twisted conformer. The rate constants of the forward processes in ethanol and butyronitrile are rather high. The activation energies of the forward process for compounds studied are small. It points out that this process is presumably viscosity-dependent one.

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