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SPECTROSCOPY AND KINETICS OF THE TWISTED INTERNAL CHARGE-TRANSFER (TICT) EXCITED STATE FORMATION IN p-SUBSTITUTED DIALKYLANILINES[*],[**]

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The proximity of two excited states in substituted dialkylanilines causes vibronic coupling effects in anisotropies but seems not to be related to the TICT state formation. The model of kinetics of the last process adequately describes the temperature behaviour of the double fluorescences. Many kinetic and some thermodynamic data are evaluated.

1. Introduction

Since the first and most general rationalisation by Jabłoński [1] of the multiple luminescences phenomena, and later formulation of the rule of Kasha [2], the term "multiple luminescence" is attached usually only to a given (e. g., singlet or triplet) manifold. Multiple fluorescences observed in some systems are being ascribed either to a chemical relaxation resulting in a different excited species (see, e. g., Birks [3]) or — seldom — to thermal or kinetic violations of the Kasha's rule (hence the term "anti-Kasha fluorescence", AKF [4]).

Lippert, Lüder and Boos [5] discovered that p-cyano-N, N-dimethylaniline (I; synonymous: p-dimethylamino-benzonitrile), and its N, N-diethyl analogue (III), exhibit in medium- or high-polarity fluid solvents two fluorescence bands. From the solvent shifts it was evident that the low-energy fluorescence emitting state was highly polar. Lippert et al. [5] ascribed the dual fluorescence to an inversion of states, ^1L_a and ^1L_b in the Platt's classification [6], whereby the much more polar ^1L_a state was stabilized by a reorientation of

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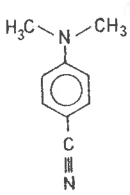
the polar surroundings. According to their assignment, the transitions should be mutually perpendicularly polarized. Observation of the parallelity of both transitions compelled us to assume an internal rotamer structure (II) for the polar excited state [7].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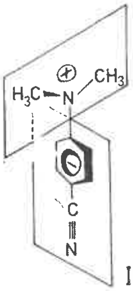
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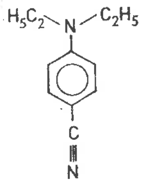
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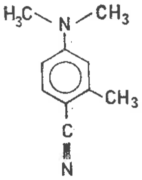
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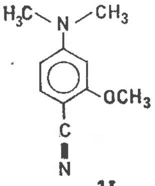
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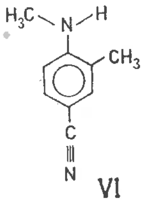
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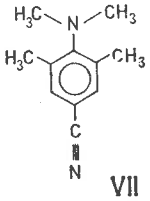
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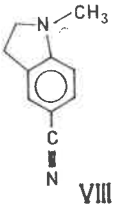
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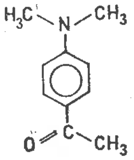
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Nature of this dual fluorescence has recently been subjected to considerable controversies which need not to be referred here; an account is given by Kosower and Dodiuk [8] or by Rotkiewicz et al. [9], the references being quoted therein. The internal rotation hypothesis seems to be proved by the studies of a series of specially synthesized model compounds [9, 10]. Rapidly growing number of compounds exhibit a similar behaviour so that we consider their emitting polar states as a common class of twisted internal charge-transfer states (TICT, [11])[1]. The electronic structure of TICT states being the subject of the parallel paper [12], we try to find here answers to two important questions, which run throughout all the controversy:

(*i*) what is the role of the originally [5] proposed "^1L_a" and "^1L_b" states in the phenomena?
(*ii*) which factors control the kinetics of formation of the TICT excited states?

2. *Experimental*

2.1. Instrumentation

All steady-state luminescence measurements were done by means of the multifunctional modular Jasny spectrofluorimeter equipped with polarisation optics and temperature-controlled cell [13]. Lifetime of (VII) was determined with a laboratory-made pulse sampling taumeter; other cyano compounds could not be excited with the N_2 laser.

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[1] Hereinafter the higher-energy emitting state and fluorescence band will be denoted as *b*, the lower-energy relaxed ones — either as *a* or TICT (equivalently).

2.2. Substances

The compounds (IV–VIII) were synthesized by Kühnle or by Krówczyński as already described [7, 9] or analogously. All compounds were thoroughly identified and purified; the purity was checked by TLC. The compounds were recrystallized freshly before use. The solvents were either Merck "for fluorescence spectroscopy" (CH_2Cl_2 additionally dried, CH_3OH) or purified by chromatography successively through several sorbents, freshly distilled, and checked for spurious fluorescence. Some of the solvents are abbreviated in the text as follows: MTHF (2-methyl-tetrahydrofurane); PrOH (n-propanol); EGDA (ethyleneglycol diacetate).

3. *Spectroscopy*

3.1. Two neighbouring excited states

Two lowest excited singlet states of benzene, ^1L_b and ^1L_a in the FEMO perimeter model [6] (in group theory notation $^1B_{2u}$ and $^1B_{1u}$, respectively), are lowered by substituents; specially large is the influence of two opposite substituents, donor and acceptor, in position para. A plot of the energies of both transitions against the independent structural parameter characterizing the substituents, $f(\sigma)$,[2] (Fig. 1), reveals a crossing of the correla-

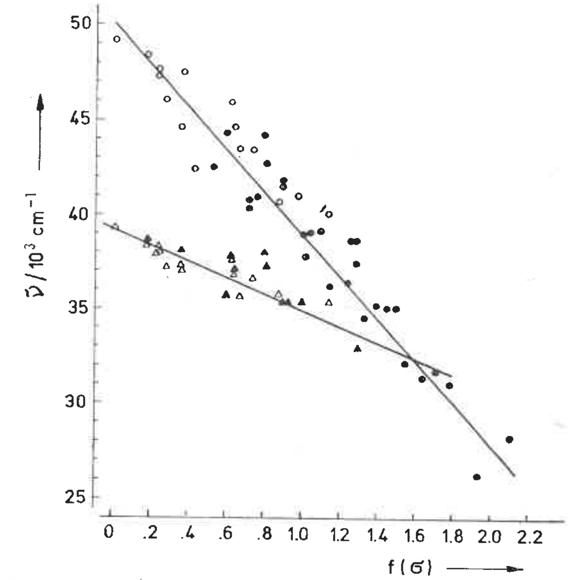

Fig. 1. Plot of the wavenumbers of the absorption maxima of mono- and p-disubstituted benzenes (open and full points, resp.) vs the chosen structural parameter $f(\sigma)$ defined in the footnote[2]. Experimental points taken mostly from Doub and Vandenbelt [17]

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[2] The substituent Hammett constants [14] are those recommended by Jaffé [15]: σ_p^* if available (with exception of $-CN$), otherwise σ_p. For $-N(CH_3)_2$ $\sigma_p = -.97$ (Ref. [15], table 10); as no corresponding value for $-O^-$ was known, this substituent was not included. For $-NH_3^+$ and $-N(CH_3)_3^+$ the value $\sigma = 0$ was arbitrarily assumed because of their negligible effect on the π-electronic levels. $f(\sigma)$ was chosen for monosubstituted benzenes as $f(\sigma) = |\sigma|$. For p-disubstituted, $X-\varphi-Y$, only opposite substituents were selected, $\sigma_X < 0$ and $\sigma_Y \geqslant 0$: $f(\sigma) = \sigma_Y + |\sigma_X|$. The correlations of that type are very rough and have no good explanation [16].

tion lines at $f(\sigma) \approx 1.6$ what corresponds to the compound (I): the two states should be nearly degenerate. This type of reasoning led another day Lippert to choose (I) as the object for his study, and to ascribe the double fluorescence to an inversion of two neighbouring states [5]. This was apparently supported by polarisation measurements.

3.2. Fluorescence anisotropy and the vibronic coupling

In their early paper Lippert et al. [18] noted that the positive polarisation of fluorescence and of its excitation decrease close to the 0–0 transition. As we have already reported at the XIII Europ. Congress on Molec. Spectroscopy in Wrocław, 1977, the typical results of anisotropy measurements, like those in Fig. 2 (VI, VIII), open a new problem. In absorption, the transition (in maximum) is polarized along the molecule axis. The TICT fluorescence is polarized in the same direction, but in rigid glasses no TICT state is formed; the molecule (VIII) is rigidly planar and cannot transform into TICT state at all, while it shows the effect most clearly. Are therefore *two* emitting states in low-temperature glasses? Is the positively polarized fluorescence an AKF from the upper excited state? Or, are inhomogeneities of local environment so large to produce an inversion of states in a fraction of all molecules? The last possibility may be excluded as the effect is observed for several compounds, (I, VI, VIII), in several solvents. Invoking an AKF would require very improbable assumptions; a satisfactory vibronic coupling mechanism (see, e. g., Hochstrasser and Marzacco [20]) may be offered instead (Fig. 3). If two excited states, denoted here as Γ_x and Γ_z, vibronically mix — the 0–0 transition would be nearly pure x-polarized,

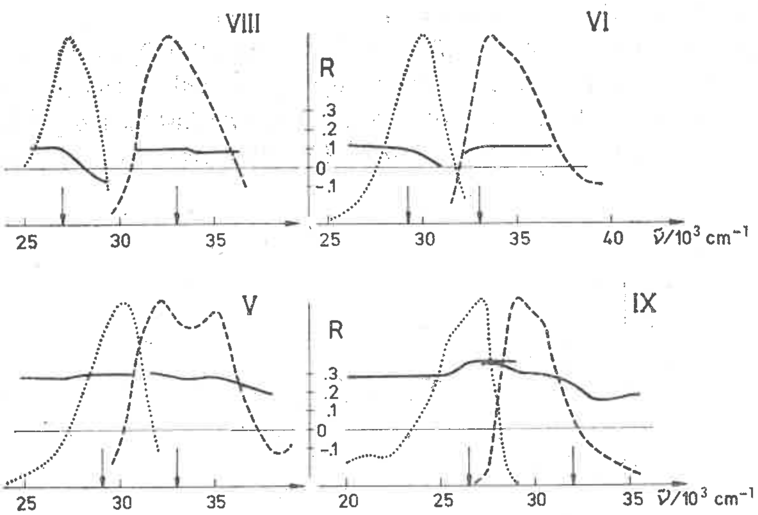

Fig. 2. Anisotropies (as defined by Jabłoński [19]) of fluorescence and of the fluorescence excitation (solid curves) as well as the corresponding fluorescence (dotted curves) and low-temperature absorption (dashed curves) spectra in low-temperature glasses: (V, VI and VIII) in MTHF, (IX) in n-propanol. The absorbancies and the corrected quantum spectra of fluorescence are normalized on an arbitrary scale. Arrows indicate the excitation or emission wavenumbers

whereas the 0–1 and lower odd transitions would be mostly z-polarized, provided the transition to Γ_z is much more allowed than that to Γ_x (as in the molecules considered).

The molecules which show a vibronic drop at 0–0 transition on their fluorescence anisotropy curves — exhibit low anisotropies throughout the fluorescence and excitation band as a result of mixed polarisation (Fig. 2, VI, VIII); those with no 0–0 effect — have much higher anisotropies. Similar conclusions may be drawn from the data of Lippert et al. [18,21].

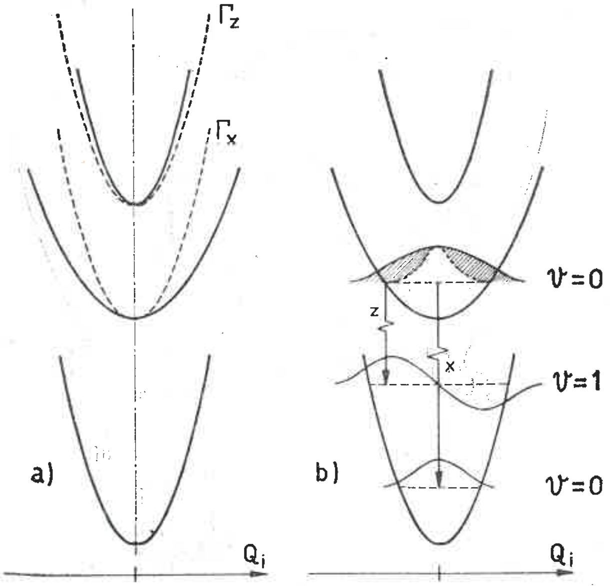

Fig. 3. (a) Two close-lying zero order states, Γ_x and Γ_z (dotted curves) are vibronically mixed by the i-th nontotally symmetric vibration, which results in the vibronic states (solid curves). (b) Mixed polarisation of the vibronic transition in fluorescence depends on the displacement along the i-th mode; the contribution of the z vector is symbolized by the shadowed part of the vibrational wavefunction, $v = 0$, of the lower vibronic state

There seems, however, to be no generic relation between the proximity of Γ_x and Γ_z and the ability of the molecule to form a TICT state (Fig. 2).

4. Temperature effects and kinetics

4.1. Formal kinetics

After having tried several kinetic models we suggest the scheme shown in Fig. 4, most generally: the reversible reaction kinetics, with only three thermally activated elementary processes:

(i) reaction $b^* \to a^*$: $\vec{k}(T) = \vec{k}^\infty \exp(-E_1/k_B T)$
(ii) reaction $b^* \leftarrow a^*$: $\overleftarrow{k}(T) = \overleftarrow{k}^\infty \exp(-E_2/k_B T)$
(iii) radiative transition in TICT fluorescence:

$$k_{af}(T) = k_{af}^0 + k_{af}^1 \exp(-\varepsilon/k_B T) \quad \text{where} \quad \varepsilon = hc\tilde{\nu}_1.$$

Then, in the stationary state treatment, we obtain for the quantum yields, η:

(*iv*)
$$\eta_b = \frac{k_{bf}[k_a^0 + k_{af}^1(T) + \overleftarrow{k}(T)]}{[k_a^0 + k_{af}^1(T)]\,[k_b^0 + \overrightarrow{k}(T)] + k_b^0\overleftarrow{k}(T)},$$

(*v*)
$$\eta_a = \frac{k_{af}(T)\overrightarrow{k}(T)}{[k_a^0 + k_{af}^1(T)]\,[k_b^0 + \overrightarrow{k}(T)] + k_b^0\overleftarrow{k}(T)},$$

(*vi*)
$$\frac{\eta_a}{\eta_b} = \frac{k_{af}(T)\overrightarrow{k}(T)}{k_{bf}[k_a^0 + k_{af}^1(T) + \overleftarrow{k}(T)]}.$$

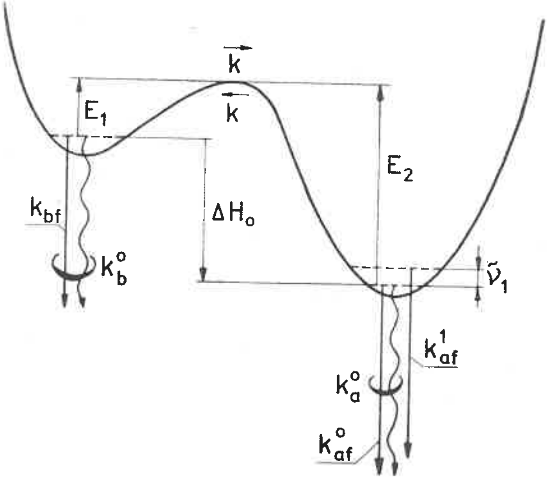

Fig. 4. Kinetic model: cross-section of the excited-state potential energy hypersurface along the reaction coordinate of the process: $b^* \rightleftarrows a^*$. k — rate constants of elementary steps (s^{-1})

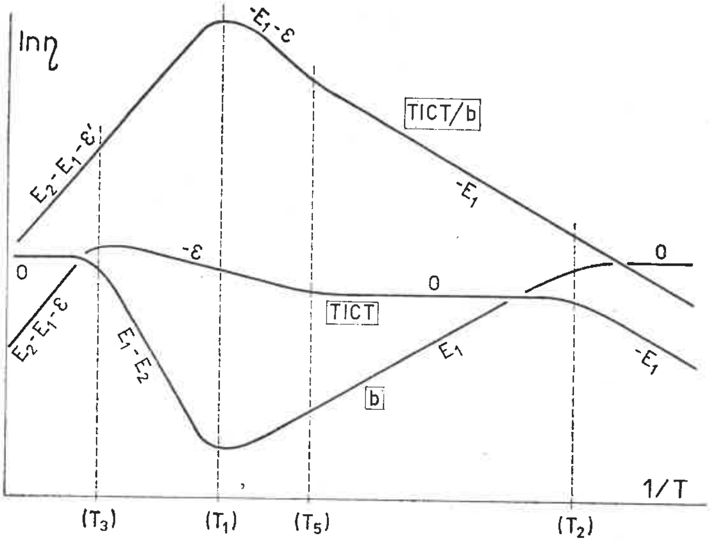

Fig. 5. General scheme of the curves $\ln \eta = f(1/T)$ for η_a, η_b, and η_a/η_b (a being denoted as TICT), in a temperature range with following characteristic temperatures: $T_3 > T_1 > T_5 > T_2$. Explanation of the symbols: in the text, Section 4.1. The curves are shifted arbitrarily along the $\ln \eta$ scale

The temperature course of $\ln \eta_i$ may exhibit several inflection points connected with the characteristic temperatures $T_1, T_2, \ldots T_7$, defined as follows:

$$\overleftarrow{k}(T_1) = k_a^0 \qquad k_{af}^1 \exp(-\varepsilon/k_B T_4) = k_a^0$$

$$\vec{k}(T_2) = k_b^0 \qquad k_{af}^1 \exp(-\varepsilon/k_B T_5) = k_{af}^0$$

$$k_b^0 \overleftarrow{k}(T_3) = k_a^0 \vec{k}(T_3) \qquad k_{af}^1 \exp(-\varepsilon/k_B T_6) = \overleftarrow{k}(T_6)$$

$$\text{and} \quad k_b^0 \overleftarrow{k}(T_7) = \vec{k}(T_7) k_{af}^1 \exp(-\varepsilon/k_B T_7).$$

Practically, only one or two of the characteristic temperatures are accessible to experiment in a given system. For practical use the scheme of Fig. 5 seems most useful.

4.2. Observed temperature effects

The temperature course of the curves $\ln \eta$ vs T^{-1} was measured for several compounds, in several solvents, in the accessible temperature ranges. The results are collected in Fig. 6. All data fit this or that part of the general diagram (Fig. 5), supporting qualitatively the correctness of assumptions. In several cases an establishment of equilibrium is implied by the high-temperature range (Fig. 6: IV in CH_2Cl_2, V in MTHF and in CH_2Cl_2, probably IX in CH_3CN). In strongly polar solvents (IV) and (V) behave as in the irreversible kinetics, $b^* \rightarrow$ TICT.

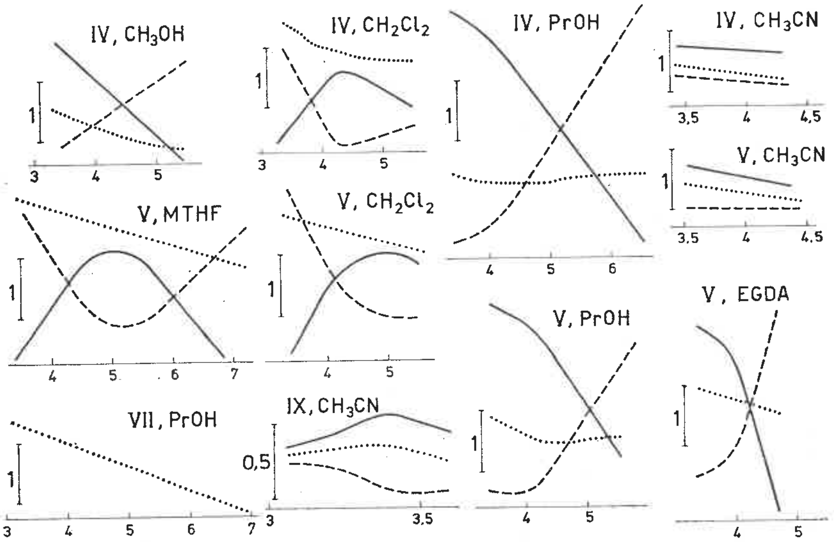

Fig. 6. Observed temperature effects on the fluorescence quantum yields, η : $\ln \eta_{TICT}$ (dotted curves), $\ln \eta_b$ (dashed curves), and $\ln (\eta_{TICT}/\eta_b)$ (solid curves) against T^{-1} (in $10^{-3}K^{-1}$). The compounds and solvents are indicated in the diagrams. The curves are shifted arbitrarily along the $\ln \eta$ scale. The relative $\ln \eta$ scale is indicated

TABLE I

The measured or evaluated kinetic and thermodynamic data for TICT state formation. All energies in (cm^{-1}), absolute rate constants in (s^{-1}). Quantum yields η measured at 293 K. Error limits indicate only the scatter of results from several measurements or evaluation methods

Compound:	IV				V					VII
solvent	CH_2Cl_2	PrOH	CH_3OH	CH_3CN	MTHF	CH_2Cl_2	EGDA	PrOH	CH_3CN	PrOH
η_a	0.013	....	0.0077	0.026	0.024	....	....	0.025	0.036 *	0.019
η_b	0.0035	....	4.3×10^{-4}	$\sim5\times10^{-4}$	0.025	....	....	0.004	0.0053	....
$\tilde{\nu}_1$	~200	0	200 ± 35	185	180 ± 35	185 ± 30	210	0	250	250
E_1	190	1000 ± 40	470 ± 30	0	715 ± 30	~700	2300	1210 ± 40	0	....
T_1/K	258	$\geqslant293$	>293	>293	198	204	~290	~273	>293	....
ΔH_0	-2250	....	....	....	-1275	~-1240	....	....	....	....
k_{af}^0	$\leqslant0.003k_a^0$	....	$\leqslant5\times10^6$	$\leqslant5\times10^6$	$\leqslant0.006k_a^0$	....	....	$0.02k_a^0$	....	$<1.4\times10^6$
k_{af}^1	$0.03k_a^0$	....	2.6×10^7	1.5×10^7	$0.06k_a^0$	....	....	....	$0.12k_a^0$	1.7×10^7
k_a^0	$1\times10^{-6}\overleftarrow{k}^{\infty}$	....	1.2×10^9	2.3×10^8	$5\times10^{-7}\overleftarrow{k}^{\infty}$	$8\times10^{-7}\overleftarrow{k}^{\infty}$	....	....	....	2.7×10^8
k_{bf}	....	....	6.5×10^6	$\sim5\times10^7$	$8\times10^{-6}\overrightarrow{k}^{\infty}$	....	....	$3\times10^{-6}\overrightarrow{k}^{\infty}$	$5\times10^{-3}\overrightarrow{k}^{\infty}$	....
$\overrightarrow{k}^{\infty}$	....	....	1.6×10^{11}	9.2×10^{10}	....	....	....	....	....	....

Effect of temperature on the fluorescence of (VI) and (VIII) — which in these solvents emit only the fluorescence b — is not included under consideration.

4.3. Evaluation of the quantitative data

(i) Application of the equations of Section 4.1 to the data illustrated by Fig. 6 results in evaluation of the energies involved: E_1, E_2, ΔH_0, $\tilde{\nu}_1$.

(ii) Measured absolute values of quantum yields, η_i, allow us to calculate the relative rates, i. e., the ratios of some rate constants.

(iii) In the cases where absolute lifetimes were determined, either directly, (VII), or from the analysis of the strong quenching kinetics — as for (IV) in CH_3CN [22] or in CH_3OH (Rotkiewicz and Grellmann, to be published) — the absolute rate constants could be found. The results are collected in the Table.

4.4. Discussion of the kinetics

The process of the formation of a TICT state consists of the geometry change of the molecule (against the viscosity of the medium), of the solvent reorientation (dependent on the solvent relaxation time, related to viscosity), and of the electron transfer step. The overall rate is controlled by the slowest step. We compared the E_1 values with the known activation energies for viscous flow (560 cm^{-1} for CH_2Cl_2, 1320 cm^{-1} for PrOH, 575 cm^{-1} for CH_3CN, 887 cm^{-1} for CH_3OH). The TICT formation kinetics of (V) in PrOH, CH_2Cl_2, and probably in MTHF (in tetrahydrofurane the viscosity $E_a = 630$ cm^{-1}; in MTHF it should not be much different), as well as of (IV) in PrOH, seem to be viscosity controlled. In the cases of (IV) in CH_2Cl_2 and in CH_3OH, most probably the rate-determining step is the solvent reorientation. Most fascinating are the results concerning (IV), (V) and (IX) in acetonitrile, the reorientation autocorrelation time of which is only 1 ps [23]. Here the results, $E_1 = 0$, suggest that we are already in the activation entropy controlled kinetic range.

The formation of TICT states belongs to the most rapid reactions studied. The present data indicate that the process may be reversible, preferentially in medium-polarity solvents; this makes possible to apply the thermodynamic concepts. The rate constants of individual elementary steps (see Table) support the model shown in Fig. 4, in particular for the radiative processes in TICT state ($\tilde{\nu}_1 \approx 200$ cm^{-1}).

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