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EMISSION AND INTERSYSTEM CROSSING QUANTUM YIELDS OF ANILINE SOLUTIONS: PHOTOSTATIONARY STATE DIAGRAM

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Summary

We measured the emission quantum yields of aniline in various solvents. For phosphorescence (in ether–isopentane–ethanol at 77 K) a photoionization by a biphotonic process occurred for exciting wavelengths below 290 nm. Using tris(dibenzoylmethano)europium as the acceptor in a triplet–triplet energy transfer the intersystem crossing quantum yields of aniline in liquid solutions at 20 °C were measured. We also calculated the quantum yields of aniline transitions and constructed state diagrams.

1. Introduction

Several techniques have been used to measure intersystem crossing quantum yields — either spectroscopic methods using flash photolysis [1 - 3] and delayed fluorescence [4 - 6] or methods using an energy transfer [7 - 10]. Spectroscopic methods are inefficient for aniline because the aniline triplet state has never been observed with flash photolysis and this molecule has no delayed fluorescence.

When biacetyl is used as the acceptor in the triplet–triplet energy transfer, the biacetyl reacts with aniline and, because it undergoes enolization with ethanol, it can be used only with paraffinic solvents.

We formulated a method using tris(dibenzoylmethano)europium (EuD_3) as the acceptor. The EuD_3 intersystem crossing quantum yields were measured using benzophenone and then diphenylamine as donors [11]. This meant that the aniline intersystem crossing quantum yields could be measured. We also calculated the quantum yields of aniline transitions.

2. Experimental materials

2.1. *Apparatus*

We used a Bearn-type Jobin & Yvon spectrofluorimeter for the emission and intersystem crossing quantum yield measurements. This apparatus is energy corrected [12].

2.2. *Products*

Aniline was purified by distillation under atmospheric pressure and then under a vacuum. Benzophenone, diphenylamine and 9,10-diphenylanthracene were purified by recrystallization.

EuD_3 was prepared by direct reaction of $EuCl_3$ with dibenzoylmethane. The chelate complex was purified by two recrystallizations and dried under a vacuum at 60 °C for 24 h [11].

We used solvents which were free of fluorescence. For the phosphorescence measurements either methylcyclohexane–pentane (MP) or ether–isopentane–ethanol (EPA) mixtures were used as solvents [12].

Concentrated solutions contained 3 g l^{-1} of aniline (optical density greater than 2 in the range 300 - 200 nm). Dilute solutions had optical densities between 0 and 1.5 (thickness, 1 cm).

3. Results

3.1. *Fluorescence Φ_F and phosphorescence Φ_P quantum yields*

The results [12] are summarized in Table 1 (relative error 10%). It can be seen that there is a variation of Φ_F with concentration for the cyclohexane solutions and a variation of Φ_P with exciting wavelength for the EPA solutions. We also measured the fluorescence quantum yields in several solvents of various polarities. The results are summarized in Table 2. Φ_F decreases with increasing dielectric constant for the solvents without hydroxyl groups. Dioxan and water show peculiar results.

3.2. *Intersystem quantum yields Φ_{IC}*

We used a triplet–triplet transfer process with EuD_3 as the acceptor in liquid solutions at 20 °C. This process has been described previously [11]. We obtained Φ_{IC} and τ°_T (triplet lifetime for aniline molecules) values and the results are summarized in Table 3. The concentration of aniline is 10^{-3} M and the relative errors are about 5% for τ°_T and about 10% for Φ_{IC}.

TABLE 1

Aniline concentration	*Solvent*	*Temperature*	λ_{EX} (nm)	$\lambda_{F\,max}$ (nm)	$\lambda_{P\,max}$ (nm)	Φ_F	Φ_P
3 g l^{-1}	Cyclohexane	20 °C	265 - 310	315		0.08	
3 g l^{-1}	Ethanol	20 °C	265 - 300	339		0.10	
3 g l^{-1}	MP	77 K	265 - 290	330	420	0.08	0.074
3 g l^{-1}	EPA	77 K	265 - 290	340	420	0.10	0.76
8×10^{-5} M	Cyclohexane	20 °C	265 - 295	315		0.17	
8×10^{-5} M	Ethanol	20 °C	275 - 295	339		0.10	
8×10^{-5} M	MP	77 K	275 - 300	330	420	0.17	0.65
8×10^{-5} M	EPA	77 K	290	340	420	0.10	0.85
8×10^{-5} M	EPA	77 K	290	340	420	0.10	0.50

TABLE 2

Solvent	*Dielectric constant*	*Absorption*		*Fluorescence*			*Energy of 0–0 band* (cm^{-1})
		λ_{max} (nm)	ϵ	λ_{max} (nm)	$\bar{\nu}_{max}$ (cm^{-1})	Φ_F	
Cyclohexane	2.023	287.5	1 760	315	31 746	0.17	32 937
Diethyl ether	4.335	289	1 920	331	30 211	0.13	32 255
Benzene	2.284	289	1 800	327	30 581	0.14	–
Dioxan	2.209	290	2 260	339	29 498	0.13	31 992
Tetrahydrofuran	7.39	290.5	1 840	335	29 850	0.12	31 923
Butanol	17.8	286	1 480	340	29 411	0.11	32 062
Propanol	20.1	285.5	1 440	340	29 411	0.10	32 062
Ethanol	24.3	284	1 480	340	29 411	0.10	32 062
Methanol	33.62	282	1 430	340	29 411	0.09	32 132
Water	80.37	280	1 300	342	29 239	0.12	–

TABLE 3

Solvent	Φ_{IC}	τ°_{T} (s)
Cyclohexane	0.75	8.1×10^{-7}
Ethanol	0.90	8.3×10^{-7}

4. Discussion

4.1. Fluorescence and phosphorescence quantum yields

For cyclohexane solutions Φ_F varies from 0.17 (dilute solutions) to 0.08 (concentrated solutions). It is apparent that aniline molecules in the singlet state are autodeactivated and that this deactivation increases with aniline concentration. For pure aniline the fluorescence intensity is almost zero [13].

The variation of Φ_P with exciting wavelength has been studied previously [14]. For exciting wavelengths below 290 nm a photoionization process occurs (biphotonic process) with the formation of a delayed phosphorescence.

The results for the variation of Φ_F with the polarity of the solvents without hydroxyl groups are in agreement with those of Kochemirovskii [15] and Blais and Gauthier [13]. For the solvents containing hydroxyl groups it has been shown [16 - 20] that a bond is formed between the solvent and the substituted aromatic hydrocarbon. In the case of aniline this bond is between the hydrogen of the solvent and the non-bonding electrons of the nitrogen; a 1:1 complex is formed (see Fig. 1). Consequently increasing the solvent polarity leads to a partial blocking of the nitrogen lone pair, to an enhancement of the n → π transition and to a low Φ_F value. This is in good agreement with previous results [13].

In the case of dioxan Forbes [21] and Meallier [20] have shown the formation of an aniline–dioxan bond (see Fig. 2) which enhances the electron transfer from the nitrogen to the ring, thus explaining the strong red shift of the absorption spectra and the high Φ_F value.

4.2. Quantum yields and state diagrams

For a low concentration of aniline in a deaerated solution and for $\lambda_{EX} > 290$ nm (no radical formation) we propose the following reaction scheme:

$S_0 + h\nu \longrightarrow S_1$	light absorption	I
$S_1 \rightsquigarrow S_0$	internal conversion	$k_d\ (S_1)$
$S_1 \rightsquigarrow T_1$	intersystem crossing	$k_{IC}\ (S_1)$
$T_1 \rightsquigarrow S_0$	intersystem crossing	$k_D\ (T_1)$
$T_1 \longrightarrow S_0 + h\nu'$	phosphorescence	$k_P\ (T_1)$
$T_1 \longrightarrow S_0 + h\nu''$	fluorescence	$k_F\ (S_1)$

If τ is the measured lifetime and $\tau°$ is the radiative lifetime, then Φ_F and Φ_P are the fluorescence and phosphorescence quantum yields respectively.

$$k°_F = 1/\tau°_F = \Phi_F/\tau_F$$

$$k°_P = \frac{1}{\tau°_P} = \frac{1}{\tau_P}\ \frac{\Phi_P}{1 - \Phi_F}$$

$$k°_D = k°_P\ \frac{1 - (\Phi_P + \Phi_F)}{\Phi_P}$$

$$k_{IC} = \frac{\Phi_P}{\Phi_F}\frac{k°_F}{k°_P}\ (k°_D + k°_P)$$

For liquid solutions (at 20 °C)

$$k_{IC} = \Phi_{IC}/\tau_F$$

and

$$k°_T = 1/\tau°_T$$

In Table 4 are summarized the fluorescence and phosphorescence quantum yields, the lifetimes of the excited states and the various radiative and non-radiative constants for aniline.

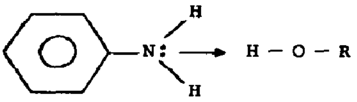

Fig. 1. The 1:1 complex formed between a solvent containing a hydroxyl group and aniline.

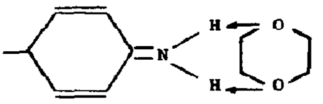

Fig. 2. The complex formed between dioxan and aniline.

TABLE 4

	Φ_F	τ_F (ns)	Φ_P	τ_P (s)	Φ_{IC}	τ°_T (ms)	k°_F (s^{-1})	k°_P (s^{-1})	k°_D (s^{-1})	k°_{IC} (s^{-1})	*Figure*
Aniline solution in MP (77 K)	0.17	3.9[a]	0.65	4.2	–	–	4.3×10^7	0.18	5.1×10^{-2}	–	Fig. 3; $a + b + c + d = 18\%$
Aniline solution in cyclohexane (20 °C)	0.17	3.9[a]	–	–	0.75	0.81	4.3×10^7	–	–	1.9×10^8	Fig. 3; $a + c = 8\%$
Aniline solution in EPA (77 K)	0.10	2.7[b]	0.85	5.4	–	–	3.7×10^7	0.17	1.0×10^{-2}	–	Fig. 4; $a + b + c + d = 5\%$
Aniline solution in ethanol (20 °C)	0.10	2.7[b]	–	–	0.90	0.83	3.7×10^7	–	–	3.3×10^8	Fig. 4; $a + c = 0\%$

[a] Taken from ref. 22.
[b] Taken from ref. 23.

5. Conclusions

Using EuD_3 we measured the intersystem crossing quantum yields Φ_{IC} and the triplet lifetimes τ°_{F} at 20 °C for aniline. These results allow photostationary state diagrams to be constructed (Figs. 3 and 4).

In liquid solutions (at 20 °C) $\Phi_F + \Phi_P = 100\%$ for polar solvents and the radical quantum yield is very small. This result agrees with radical quantum yield measurements carried out in our laboratory using flash photolysis (0.8%).

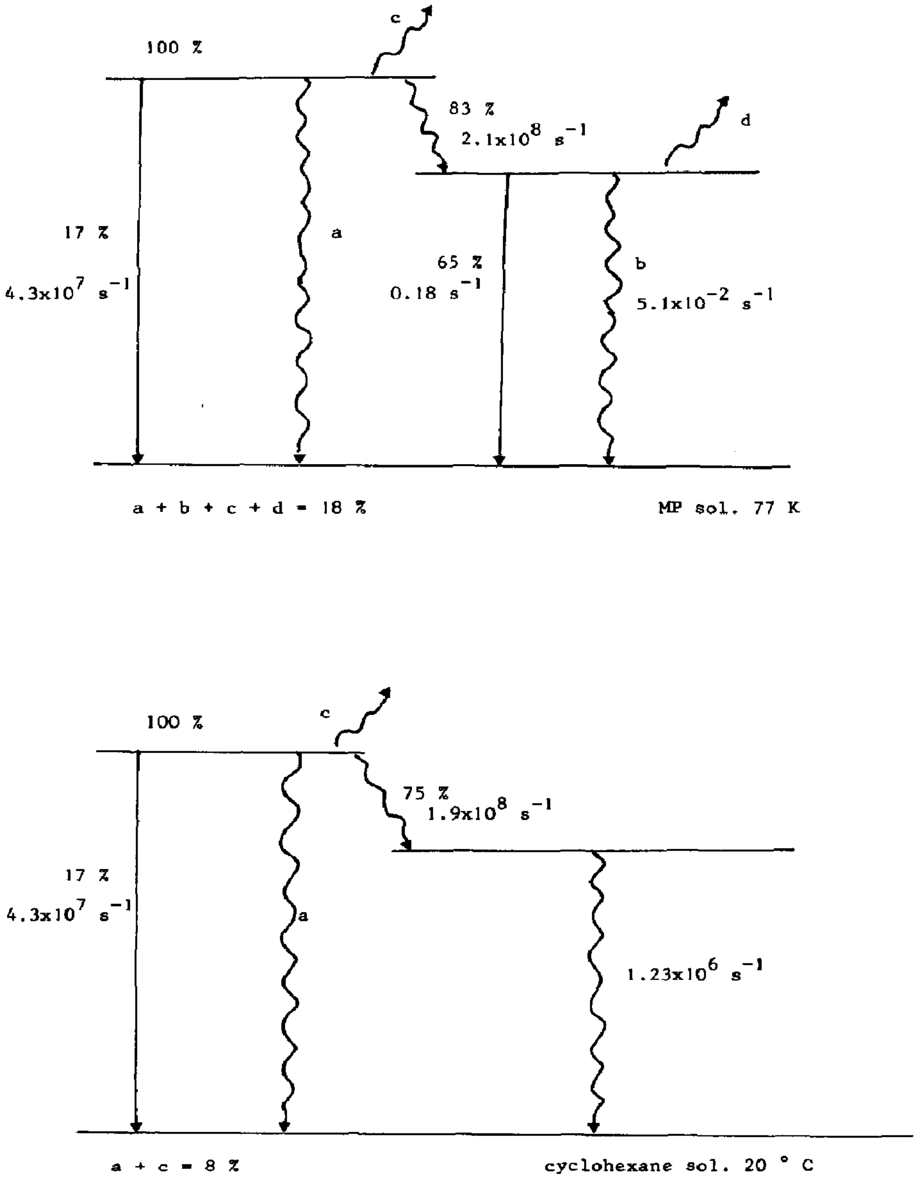

Fig. 3. State diagrams for aniline–MP (77 K) and aniline–cyclohexane (20 °C).

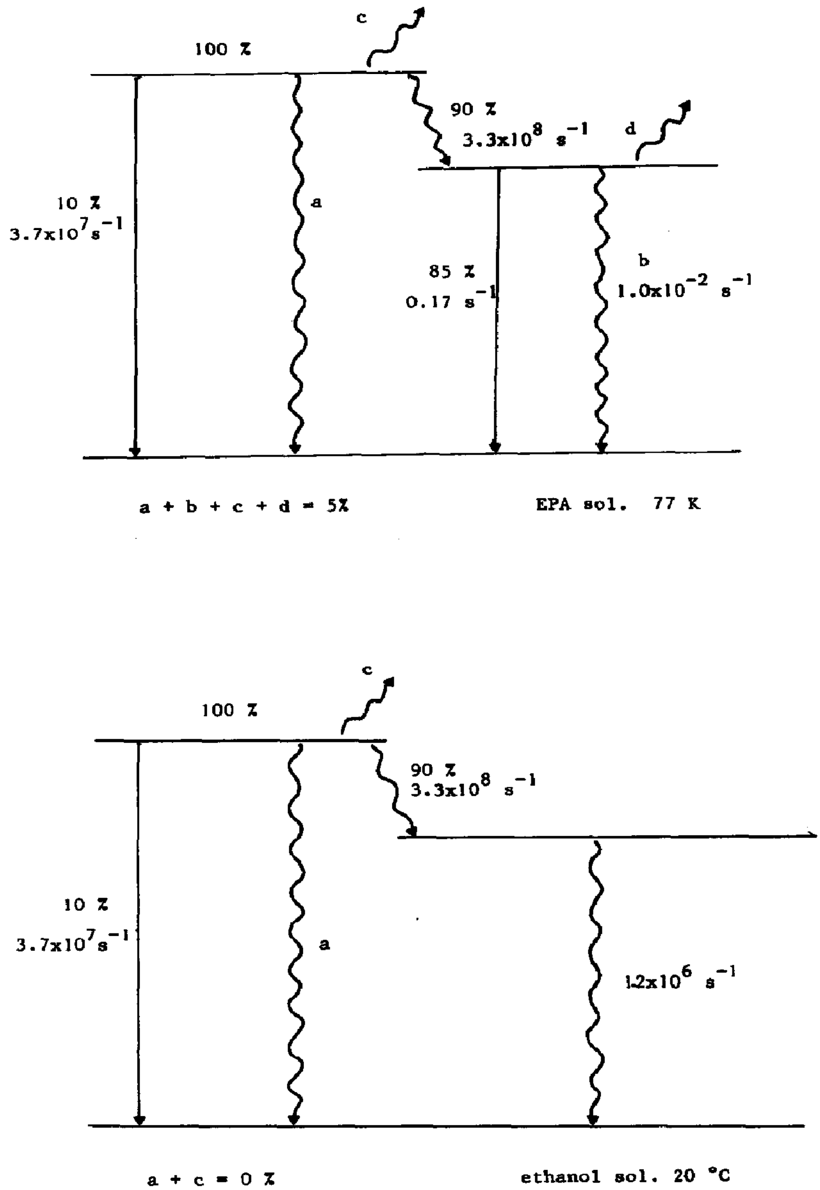

Fig. 4. State diagrams for aniline–EPA (77 K) and aniline–ethanol (20 ° C).

For aniline–cyclohexane solutions $\Phi_F + \Phi_P = 92\%$. In our laboratory a radical quantum yield of 1.3% has been found using flash photolysis. However, a labile compound which absorbs between 350 and 450 nm with a lifetime of several hours has been detected using flash photolysis. Because of this long lifetime the compound is probably not a radical and it may be an important intermediate in the aniline photo-oxidation.

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