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EXCITED STATE DEPROTONATION REACTIONS OF AROMATIC AMINES: A DIFFUSION-CONTROLLED PROCESS

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Summary

The excited state proton transfer reactions of carbazole (CAZL), indole (IND) and diphenylamine (DPA) were studied using a picosecond time-resolved technique. The forward rate constant for deprotonation shows a slight temperature dependence. The activation energy for the process was determined by taking various bases in both aqueous and non-aqueous media. It is of the order of the diffusional barrier in the solution phase. Hence it is concluded that the process is diffusion controlled. The values of the diffusion-controlled rate constants are discussed.

1. Introduction

The question of whether or not an activation barrier exists in excited state proton transfer reactions is now a subject of intense research [1 - 15]. The contribution to the free energy of activation in an elementary proton transfer reaction

$$AH + B \longrightarrow A + BH$$

may come from two more or less independent processes: (1) the translational and rotational diffusion of reactants and the readjustment of solvent molecules to a configuration which is suitable for proton transfer and (2) the stretching followed by breaking of the AH bond and the formation of another bond BH. The question of whether the latter process of the excited state reaction requires energy has been addressed by several workers through intramolecular studies in rigid or nearly rigid systems; the answers obtained

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are specific to the system chosen. A few instances may be cited. The proton transfer of 7-azaindole has been shown to be very fast, occurring within picoseconds, and cannot be stopped by a lowering of temperature even down to 4 K [13]. Waluk *et al.* [1] correlated the small activation energy to the torsional motion of the molecule. From the lack of temperature dependence of k^H/k^D and the strong temperature dependence of the proton transfer rate of 3-hydroxyflavone (3HF), Strandjord and Barbara [6] concluded that intramolecular proton transfer in excited 3HF follows a complex mechanism. Strandjord and Barbara [6] through isotopic substitution on 3HF and Shizuka *et al.* [14] through studies on 6-(2-hydroxy-5-methylphenyl)-*s*-triazines found a negligible potential barrier. Werner [15] while studying 2-(2-hydroxy-5-methylphenyl)benzotriazole was unable to come to any conclusion about the existence or non-existence of a potential barrier, although he detected a considerable isotope effect on the lifetime and fluorescence quantum yield of the deprotonated species.

A more commonly encountered situation, however, is the intermolecular case. In an intermolecular case both steps (1) and (2) might contribute significantly to the activation energy and it is necessary to discover the relative importance of the steps. With this in mind, we determined the overall activation energies for the excited state deprotonation processes of carbazole (CAZL), indole (IND) and diphenylamine (DPA) (all these compounds possess similar reaction centres but differ in stereorigidity) and compared them with the activation barrier for the hydrodynamic process involved in step (1). In spite of the fact that the N—H bond is covalent and the excited state acidity is weak (*e.g.* $pK^* = 7.6$ for CAZL [4]), our results indicate that the contribution of step (2) is insignificant and the dominant contribution comes from step (1). We varied the base B and the solvent to determine their effect on the diffusion-controlled rate constants.

2. Experimental details

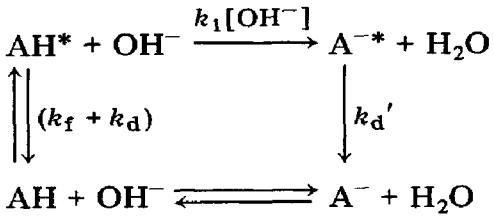
Carbazole was purified as described previously [3]. Indole and diphenylamine (both Aldrich) were recrystallized from 90% ethanol, vacuum sublimed and then recrystallized once again. The purity of the compounds was checked from their melting points and spectroscopic data. Ammonia, ethylamine, diethylamine and triethylamine were all of analytical grade and were used without further processing. Acetonitrile (gold label, Aldrich) was used as solvent when required. Owing to the extremely low solubility, only saturated solutions of the compounds (concentrations $\lesssim 10^{-5}$ M) were used in the experiments.

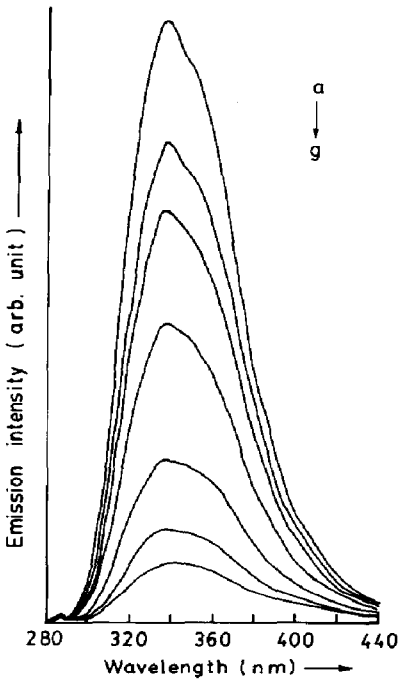
The details of the instruments and methods used are the same as in ref. 3, except that the data from the multichannel analyser were transferred to a Wipro microcomputer (IBM compatible) and were deconvoluted using software developed by ourselves. The reliability of the analysed data was confirmed each time by inspection of reduced χ^2, plots of weighted residuals and autocorrelation functions of the residuals.

3. Results and discussion

The variation in steady state luminescence of IND and DPA with pH (using NaOH) is shown in Figs. 1 and 2 and the same for CAZL can be found in ref. 3. CAZL exhibits luminescence of its anion [16], but the corresponding species of IND and DPA do not fluoresce. Throughout the range of concentration of the bases the absorption and excitation spectra of the probes (CAZL, IND and DPA) remain unchanged, negating the possibility of the formation of any association complex between the reaction partners in the ground state.

The kinetic scheme for the proton transfer of carbazole has been discussed in detail elsewhere [3]. Owing to the non-luminescent nature of the anions (*i.e.* short lifetime of the anions and consequent absence of back transfer) the schemes become somewhat simpler for indole and diphenylamine





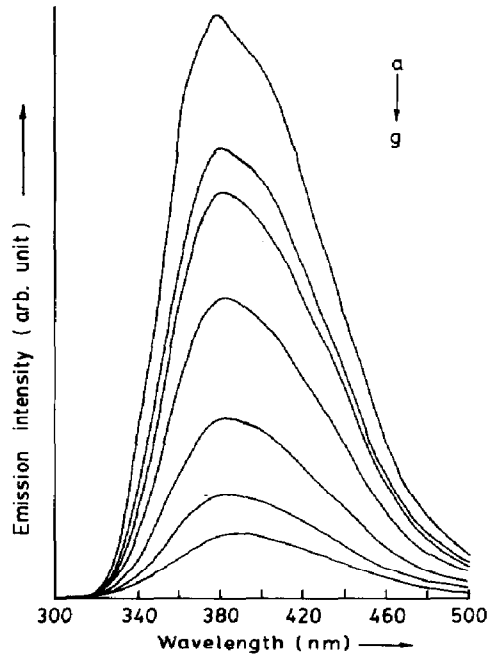


Fig. 1. Steady state fluorescence spectra of indole at different pH values: (a) 7.0; (b) 11.4; (c) 11.7; (d) 12.0; (e) 12.4; (f) 12.7; (g) 12.9.

Fig. 2. Steady state fluorescence spectra of diphenylamine at different pH values: (a) 7.0; (b) 11.4; (c) 11.7; (d) 12.0; (e) 12.4; (f) 12.7; (g) 12.9.

where AH and A^- represent neutral IND or DPA and the corresponding anions; k_f, k_d, k_d' and k_1 are the rate constants for fluorescence, non-radiative deactivations and the pseudo-first-order deprotonation reaction. The asterisk denotes species in the excited state. Neglecting back transfer from A^{-*} we obtain the differential equations

$$-\frac{d[AH^*]}{dt} = (k_f + k_d + k_1[OH^-])[AH^*] \quad (1)$$

and

$$-\frac{d[A^{-*}]}{dt} = k_d'[A^{-*}] \quad (2)$$

Using the boundary condition $[AH^*] = [AH^*]_0$ at $t = 0$, we have

$$[AH^*]_t = [AH^*]_0 \exp\{-(k_f + k_d + k_1[OH^-])t\} \quad (3)$$

It is obvious from eqn. (3) that the neutral form should decay monoexponentially. One set of decays for indole at a fixed OH^- concentration at different temperatures is shown in Fig. 3. The slope of the λ_1 ($= \tau_1^{-1}$) *vs.* $[OH^-]$ plot gives k_1. By obtaining k_1 values at different temperatures it is easy to determine the activation energies for the forward reactions by an Arrhenius plot of $\ln k_1$ *vs.* $1/T$. Figure 4 shows these plots. Experimental results are summarized in Tables 1 and 2. The values of the rate constants at 26 °C agree well with those obtained from the steady state Stern–Volmer plots. For other temperatures the steady state experiments were not performed.

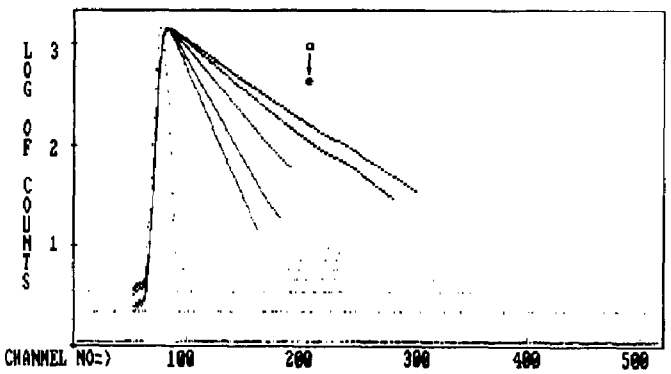


Fig. 3. Decay profiles of indole at different temperatures in 0.0025 N NaOH solution: (a) 6 °C; (b) 16 °C; (c) 26 °C; (d) 38 °C; (e) 46 °C (1 channel = 0.086 ns).

The values of k_1 ($\approx 10^9$ M^{-1} s^{-1}) for all the deprotonation reactions studied indicate that diffusion does play a role in the process. The activation energies determined lie within the range 3 - 4 kcal mol^{-1} in aqueous medium; when acetonitrile is taken as the solvent an activation energy of approximately 1 kcal mol^{-1} is obtained. The error limits are given in Table 2 taking all relevant sources. The values closely resemble those for intramolecular proton transfer reactions reported by Mordzinski and Grabowska [2] and

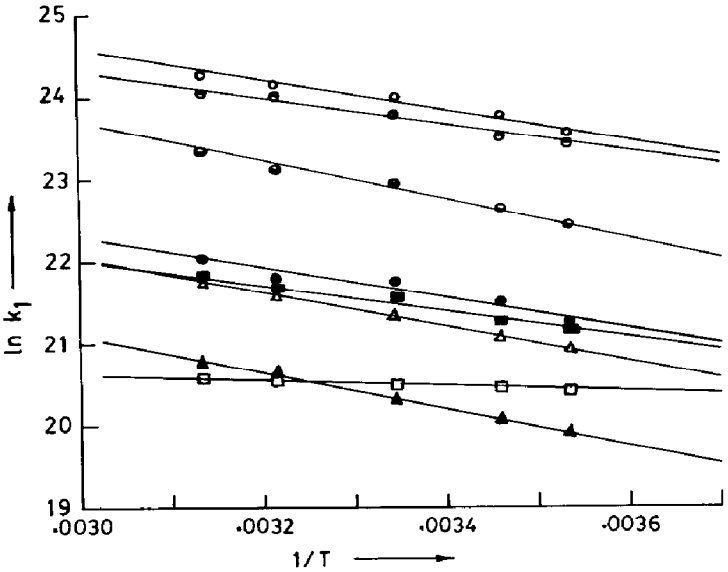


Fig. 4. Plots of ln k_1 *vs.* $1/T$ for different experimental sets: —○—, IND–NaOH; —◐—, DPA–NaOH; —⊖—, CAZL–NaOH; —▲—, CAZL–NH_3; —■—, CAZL–$EtNH_2$; —●—, CAZL–Et_2NH; —△—, CAZL–Et_3N (all in aqueous solutions); —□—, CAZL–Et_3N (in acetonitrile solution).

TABLE 1

Rate constants for different deprotonation reactions at various temperatures

Compound	*Base*	*Medium*	*Rate constant* (10^9 M^{-1} s^{-1})				
			6 °C	*16 °C*	*26 °C*	*38 °C*	*46 °C*
IND	NaOH	H_2O	17.60	21.61	26.38	31.12	35.01
DPA	NaOH	H_2O	15.31	16.73	21.50	26.69	28.51
CAZL	NaOH	H_2O	5.54	6.84	9.03	11.81	14.42
	NH_3[a]	H_2O	0.40	0.47	0.59	0.83	0.93
	$EtNH_2$[a]	H_2O	1.44	1.56	1.94	2.36	2.55
	Et_2NH[a]	H_2O	1.56	1.85	2.52	2.62	3.35
	Et_3N[a]	H_2O	1.10	1.19	1.62	2.03	2.40
		CH_3CN	0.74	0.77	0.80	0.84	0.86

[a]Contributions from the dissociated forms in aqueous solutions were taken into consideration in the evaluation of rate constants.

Barbara and coworkers [6, 7]. However, nothing can be inferred from this since our results are related to intermolecular processes while theirs are related to intramolecular processes. Since in a liquid phase diffusion must have some activation barrier due to the fluidity of the medium, these barriers were estimated from the literature values of viscosities of the solvents at different temperatures [17]. The values obtained are 4.1 and 1.25 kcal mol^{-1} in aqueous and acetonitrile media respectively; this clearly indicates

TABLE 2

Activation energies for different deprotonation reactions

Compound	*Base*	*Activation energy* (kcal mol^{-1})	
		Aqueous medium	*Acetonitrile medium*
IND	NaOH	3.0 ± 0.2	
DPA	NaOH	3.1 ± 0.2	
CAZL	NaOH	4.2 ± 0.2	
	NH_3	4.0 ± 0.2	
	$EtNH_2$	2.9 ± 0.2	
	Et_2NH	3.5 ± 0.2	
	Et_3N	3.8 ± 0.2	0.9 ± 0.2
Diffusional barrier		4.1	1.2

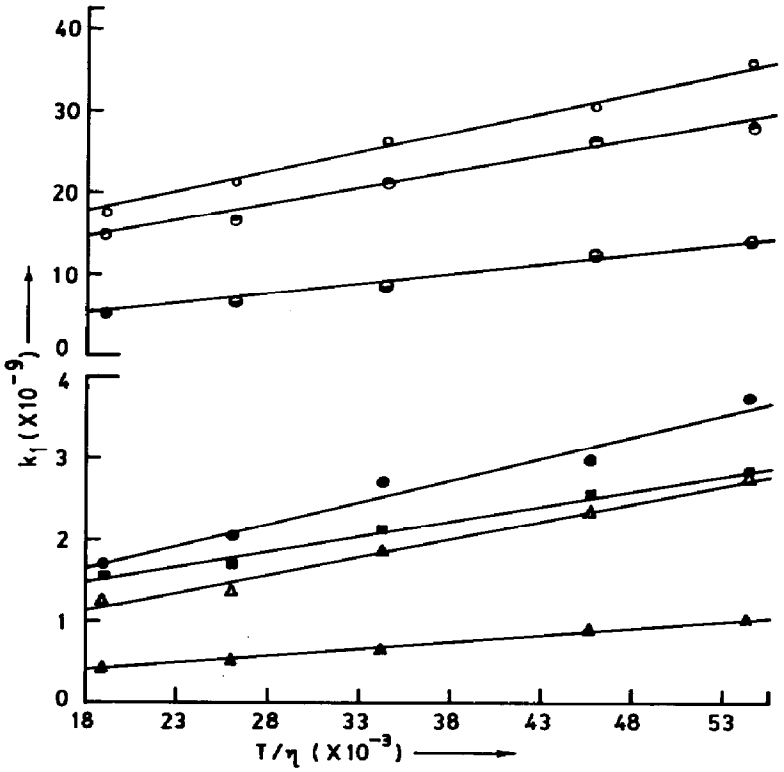


Fig. 5. Plots of k_1 *vs.* T/η for different experimental sets: —○—, IND–NaOH; —⊖—, DPA–NaOH; —⊖—, CAZL–NaOH; —▲—, CAZL–NH_3; —■—, CAZL–$EtNH_2$; —●—, CAZL–Et_2NH; —△—, CAZL–Et_3N (all in aqueous solutions).

that the energy barrier for the process is simply the barrier experienced by the medium to flow. That the process is diffusion controlled was further established from the linearity of the plots of k_1 *vs.* T/η (Fig. 5) for aqueous solutions [18]. Our excited state result is consistent with the theory of

Vorotintsev *et al.* [19] for intermolecular ground state proton transfer reactions in polar media.

Certain trends can be seen in the diffusion-controlled rate constants listed in Table 1. Firstly, the deprotonation rate is much higher for OH^- than for amines. Similar observations have been made for ground state deprotonation rates [18]. This is presumably a result of the much higher mobility of OH^- due to the Grotthus type of migration [20, 21]. Secondly, the deprotonation rate constant with OH^- is lower for CAZL in comparison with IND or DPA. This is probably indicative of some steric requirement for the approach of OH^- to the $>$NH group of planar CAZL where the reaction centre is flanked by two rigid phenyl groups. Thirdly, rate constants for the various bases follow their order of pK values. Again, this trend is similar to the observations on ground state proton transfer reactions where it is found that when pK(acceptor) — pK(donor) (*i.e.* ΔpK) is close to zero, the rate constant is slightly lower than the maximum diffusion-controlled rate [18]. In the present case we estimate that the pK^* value of CAZL is 7.6; ΔpK is lowest for NH_3 and its rate constant is lowest. We should be able to test this point better by using triethanolamine as a base [4]. The fact that the rate of the diffusion-controlled process is not dependent on the size of the base is not surprising since although an increase in size [22] slows down the diffusion rate it increases the collision probability proportionally. Lastly, the rate constant for the Et_3N–CAZL reaction is lower in acetonitrile than in water. The deprotonation of carbazole by neutral amine leads to ionic products which are less stable in acetonitrile ($\epsilon = 39$) than in water ($\epsilon = 78$). This leads to a lowering of the ΔpK values of the two bases (carbazole)$^{-*}$ and Et_3N resulting in a slight reduction in the diffusion-controlled rate constant.

Acknowledgments

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