THE FLUORESCENCE AND PHOSPHORESCENCE SPECTRA OF DIMETHYLPHENOL AT 77 K

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Summary

The fluorescence and phosphorescence spectra of the dimethylphenols were studied at 77 K. Changes in the pK_a values in the excited singlet (S_1) and triplet (T_1) states for 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dimethylphenol in ethanol and ethanol–NaOH solutions were estimated by means of the Förster cycle.

We found that the acidity of the hydroxyl group in the first excited singlet is greater than that in the ground state. This is also true for the first triplet state, although the acidity of the first triplet state of 2,6-dimethylphenol is an exception, owing to the influence of the methyl groups on the hydroxyl group.

1. Introduction

The object of this work was to study the emission properties of dimethylphenols at 77 K and to estimate the change in the pK_a values for the acid–base equilibrium ($AOH \rightleftharpoons AO^- + H^+$) in the first excited singlet and triplet states derived from the fluorescence and phosphorescence spectra by means of the Förster method [1].

Hence we investigated the emission spectra of dimethylphenols in both the acid form (AOH) and the basic form (AO^-) in the solid phase at 77 K. The solvents were ethanol and ethanol–NaOH mixtures respectively.

The absorption spectra in these solvents were recorded to identify the molecular species dominant in each medium, by comparing them with the corresponding spectra in aqueous solution [2]. We found that for each compound AOH is present in ethanol whilst AO^- is the dominant species in ethanol–NaOH.

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2. Experimental details

2.1. Materials

The dimethylphenols were supplied by Fluka Chemicals and Biochemicals, as purum grade reagents, except for the 2,4- and 2,6-dimethylphenol isomers which were supplied in practical grade form. 2,4-Dimethylphenol, being a liquid, was purified by two fractional distillations until a constant boiling point of 210.0 °C was observed. The other isomers were purified by standard fractional sublimation until no further changes in their melting points were observed.

The acid species of these molecules were dissolved in ethanol (Uvasol grade from Merck) while the basic species were dissolved in ethanol—NaOH (0.5 M) (analytical grade from Merck).

The solute concentration was 10^{-4} M in each case.

2.2. Apparatus

Corrected fluorescence and phosphorescence spectra were recorded using a Perkin—Elmer LS-5 spectrofluorometer equipped with a phosphorescence accessory.

The spectra at 77 K were recorded in transparent matrices produced by freezing the system to liquid nitrogen temperature.

3. Results and discussion

3.1. Fluorescence spectra

We recorded the fluorescence spectra in the liquid phase at 25 °C and in the solid phase at 77 K to study their response to phase rigidity and low temperatures.

The fluorescence spectra of the two species of 2,5-dimethylphenol at 298 and 77 K are shown in Fig. 1. The behaviour of the other isomers is quite similar, and consequently their spectra are omitted.

It should be noted that the resolution of the fluorescence spectra of the rigid phase is not any better than that at 25 °C. The fluorescence maxima for the molecules studied are summarized in Table 1.

The fluorescence bands for both AO⁻ and AOH are blue shifted at 77 K with respect to their position at room temperature, although the shift is larger for AO⁻.

3.2. Phosphorescence spectra

The phosphorescence spectra of all the dimethylphenols at 77 K are similar. Because of the low resolution of the spectra the location of the 0–0 band cannot be clearly established.

The phosphorescence spectra of the acid and basic forms of 2,3-dimethylphenol are shown in Fig. 2. The spectra of the other dimethylphenols are very similar. In each molecule the phosphorescence of the basic
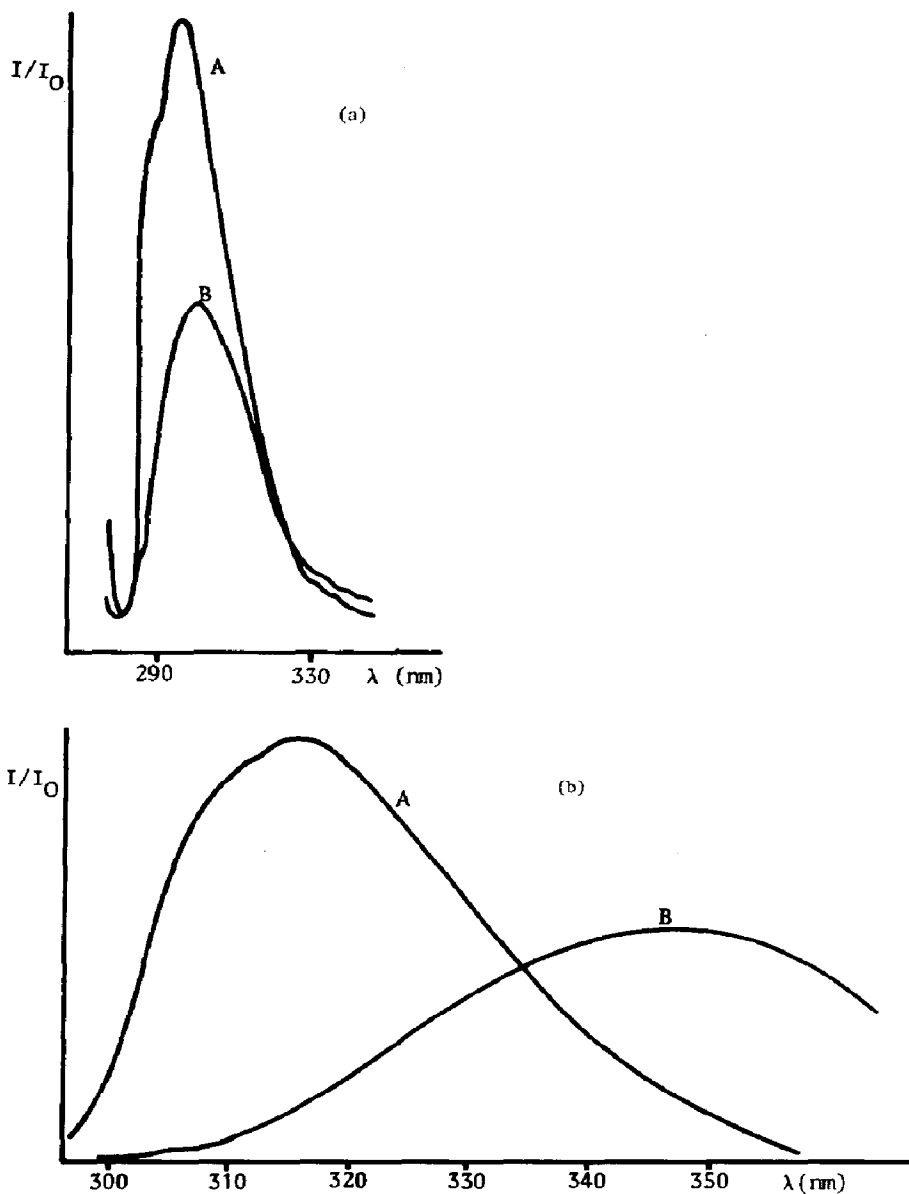
Fig. 1. Fluorescence spectra of 2,5-dimethylphenol at 77 K (curve A) and 298 K (curve B): (a) acid form (AOH), λ_{ex} = 270 nm; (b) basic form (AO$^-$), λ_{ex} = 280 nm.

species occurs at a lower frequency than that of the acid species, except for 2,6-dimethylphenol. A summary of the wavelengths of these maxima is given in Table 2.

When we tried to record the phosphorescence emission using methyl-cyclohexane and other hydrocarbon glasses no phosphorescence was found for these compounds. This behaviour is in accord with similar findings reported for α- and β-naphthol and phenol [3 - 5].

TABLE 1

Wavelengths of the fluorescence maxima

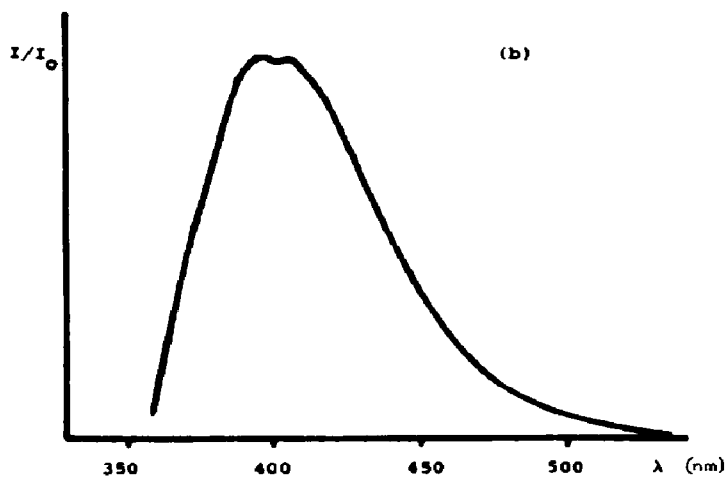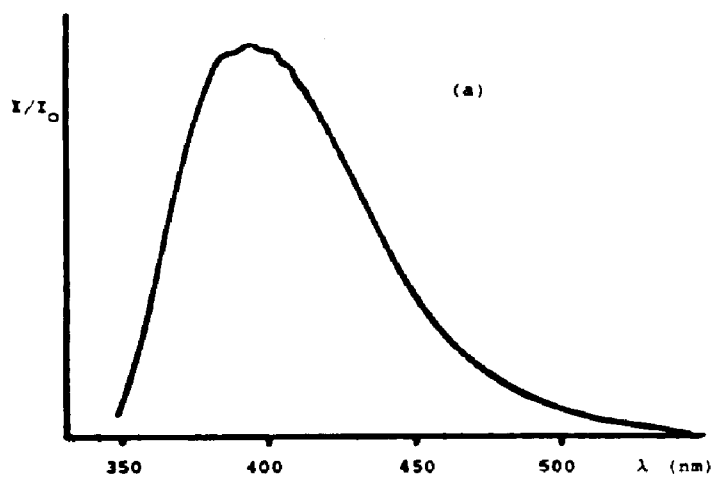|	$(\lambda_{em})_{max}$ (nm) at 298 K		$(\lambda_{em})_{max}$ (nm) at 77 K	
	AOH	AO⁻	AOH	AO⁻
2,3-Dimethylphenol	299	344	297	312
2,4-Dimethylphenol	310	353	307	322
2,5-Dimethylphenol	304	347	301	317
2,6-Dimethylphenol	298	345	298	313
3,4-Dimethylphenol	306	350	303	319
3,5-Dimethylphenol	300	345	299	313

Fig. 2. Phosphorescence spectra of 2,3-dimethylphenol at 77 K: (a) acid form (AOH), λ_{ex} = 270 nm; (b) basic form (AO⁻), λ_{ex} = 290 nm.

TABLE 2

Phosphorescence maxima at 77 K

	λ_{em} (nm)	
	AOH	*AO⁻*
2,3-Dimethylphenol	393	397
2,4-Dimethylphenol	388	395
2,5-Dimethylphenol	392	395
2,6-Dimethylphenol	419	390
3,4-Dimethylphenol	390	401
3,5-Dimethylphenol	387	395

This feature is commonly interpreted as arising from a non-radiative intersystem crossing process which competes with the phosphorescence.

The energy differences between the first excited states are shown in Table 3. The values given were derived from the maxima of the fluorescence and phosphorescence spectra at 77 K.

3.3. Basicity of the first singlet and triplet excited states

The change in the pK_a values of the first excited states with respect to the ground state was estimated by applying the Förster equation

$$\Delta pK_a = \frac{0.625}{T} \Delta\bar{\nu}_{0-0}$$

$$\Delta pK_a = pK_a(T_1 \text{ or } S_1) - pK_a(S_0)$$

where T is the absolute temperature and $\Delta\bar{\nu}_{0-0}$ (cm⁻¹) is the difference between the 0—0 frequencies of the phosphorescence or fluorescence spectra of the basic and the acid species in the acid—base equilibrium considered.

Owing to difficulty in locating the 0—0 transition accurately in the phosphorescence and fluorescence spectra of the molecules studied, we used the phosphorescence or fluorescence maxima to estimate the $\Delta\bar{\nu}_{0-0}$ values. In the cases where the spectra were structured, we used the maxima corresponding to the most energetic emission.

The pK_a values for excitation to the first singlet and triplet states are listed in Table 4.

It can be seen that the acidity of these molecules is greater in the first excited singlet state (S_1) than in the ground state (S_0). This behaviour is similar to that observed for other phenolic systems [6, 7].

Conversely, the acidity of the first excited triplet state (T_1) is very similar to that of the ground state, in agreement with the behaviour most commonly reported in the literature [8 - 10], except for the case of 2,6-dimethylphenol for which a high $pK_a(T_1)$ is found. This anomaly can be explained in terms of steric hindrance, since the presence of two methyl

TABLE 3

Energy differences between the lowest electronic states

	$\Delta E(S_0-S_1)$ (kJ mol^{-1})		$\Delta E(S_0-T_1)$ (kJ mol^{-1})		$\Delta E(S_1-T_1)$ (kJ mol^{-1})	
	AOH	AO$^-$	AOH	AO$^-$	AOH	AO$^-$
2,3-Dimethylphenol	402.9	383.5	304.1	301.4	98.8	82.1
2,4-Dimethylphenol	389.7	371.6	308.4	302.9	81.3	68.7
2,5-Dimethylphenol	397.5	377.4	305.2	302.9	92.3	74.5
2,6-Dimethylphenol	401.5	382.3	285.5	306.8	116.0	75.5
3,4-Dimethylphenol	394.9	375.1	306.4	298.0	88.5	77.1
3,5-Dimethylphenol	400.2	382.3	309.2	302.9	91.0	79.4

TABLE 4

Excited state pK_a values estimated from the emission data at 77 K

	pK_a(S$_0$)[a]	pK_a(S$_1$)	pK_a(T$_1$)
2,3-Dimethylphenol	10.42	7.02	9.95
2,4-Dimethylphenol	10.54	7.35	9.58
2,5-Dimethylphenol	10.43	6.91	10.02
2,6-Dimethylphenol	10.45	7.07	14.17
3,4-Dimethylphenol	10.29	6.82	8.82
3,5-Dimethylphenol	10.07	6.93	8.98

[a]See ref. 2.

groups in the ortho position with respect to the hydroxyl group influences considerably the steric environment of this group.

The exceptional behaviour for this compound can be related to the data reported by Perrin and Issartel [11] which indicate that it has a constant dipole moment over a wide range of temperatures. Also, Codoñer et al. [12] found that the apparent equilibrium constant for the complex pyridine–2,6-dimethylphenol in benzene solution at 25 °C is lower than the values for the other dimethylphenols. Thus the solvation energies for the S$_0$ and T$_1$ states will differ, contradicting one of the assumptions on which the Förster method of evaluating pK_a differences is based.

The data summarized in Table 4 suggest that the effect of the relative position of the substituent groups is larger in the first excited singlet state than in the first excited triplet state. Futhermore, since the degree of basicity is not the same in the two states, it can be assumed that they are influenced differently by the position of the substituents.

However, the emission observed in each case corresponds to the species which is dominant in the ground state. This fact together with the increase in the acidity in the first excited state allows us to conclude that the acid–base equilibrium between the dimethylphenols and the solvating molecules in the rigid phase is not established during the lifetime of the excited state.

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