Journal of Photochemistry, 2 (1973/74) 305–408

Short Communication

Stereochemical effects in the fluorescence quenching of alkylphenols and the dependence of excimer fluorescence on the excitation wavelength

A. HARRIMAN and B. W. ROCKETT
Department of Physical Sciences, The Polytechnic, Wolverhampton WV1 1LY (Gt. Britain)
(Received August 13, 1973; in revised form October 18, 1973)

The molecular fluorescence of phenol and alkylphenols is concentration and solvent dependent[1] but excimer formation has not been reported previously. The self-quenching observed for concentrated solutions need not necessarily be explained in terms of excimer formation. Alternative explanations for this effect involve hydrogen-bonding between: (i) two ground state phenol molecules, *i.e.* simple dimerization; and (ii) a ground state phenol and a phenol molecule excited into the lowest singlet state. The lowest singlet state of phenol is more acidic than the ground state[2,3] so the involvement of this excited state in hydrogen bonding could be considerable.

Experimental

Fluorescence spectra were recorded with a Perkin-Elmer Fluorescence Spectrophotometer MPF 2A. Cyclohexane solutions of substituted phenol (0.01 *M*) were purged with oxygen-free nitrogen for 5 min prior to recording the spectra. Quantum yields of fluorescence were determined relative to benzene and toluene standards according to the procedures recommended by Berlman[4]. Electronic absorption spectra were recorded with a Pye Unicam SP800 spectrophotometer.

Results and Discussion

The fluorescence quantum yields (Φ_{MF}) for cyclohexane solutions (0.01 *M*) of phenol and alkylphenols were determined (Table 1). Alkyl substitution at the *o*- and *m*-positions was ineffective in concentration quenching and the two positions appear to be almost equivalent (lines 1–3). However, alkyl substitution at the *p*-position resulted in greatly enhanced concentration quenching (lines 4–6). Electron density calculations[5] have confirmed that the *p*-position occupies a unique environment in the phenol excited singlet states. This is contrary to the ground state molecule where the *o*- and *p*-positions are the important resonance sites[6]. By a comparison of the results in Table 1 it was clear that the size of the substituent was also an important criterion in the quenching mechanism. The efficiency of fluorescence quenching decreased in the order of substituents: 4-Me$>$4-Bu^t $\sim$ 4-nonyl $>$

TABLE 1

FLUORESCENCE PROPERTIES OF ALKYLPHENOLS IN CYCLOHEXANE SOLUTION (0.01 *M*)

Line	Compound	Φ_{MF}[b]	λ_{max} MF (nm)
1	Phenol	0.0042	296
2	*o*-Cresol	0.0051	305
3	*m*-Cresol	0.0048	304
4	*p*-Cresol	0.0022	310
5	*p*-t-Butylphenol	0.0027	310
6	*p*-1,1-Di(methyl)heptylphenol[a]	0.0027	303
7	2,6-Di-t-butyl-4-methylphenol	0.0070	308

[a] Nonylphenol.
[b] Error limits ± 0.0002.

2,6-$(Bu^t)_2$-4-Me. The ineffective fluorescence quenching shown by 2,6-Di-t-butyl-4-methylphenol was due to steric crowding around the hydroxy group. These observations suggested that the mechanism for concentration quenching of the phenol molecular fluorescence involved the hydroxyl group, the stereochemistry of the molecule and the position of substitution.

In order to assess the importance of excimer formation in the quenching mechanism we have studied the fluorescence spectra of alkylphenols at higher concentration (0.11 *M*). With the same excitation wavelength (280 nm) as was used for the more dilute solutions, a new band was observed in the fluorescence spectra of the *p*-substituted phenols. This new emission was characterized by a broad, structureless band at longer wavelength than the molecular fluorescence (Table 2). The fluorescence spectra of diluted (0.01 *M*) and concentrated (0.11 *M*) cyclohexane solutions of *p*-cresol are shown in Fig. 1(a). This new emission was detected only for the *p*-substituted alkylphenols (Table 2), an observation which emphasizes the importance in the fluorescence quenching mechanism of an electron-donating group situated at the *p*-position. Fluorescence excitation spectra indicated that the species responsible for this new emission had an absorption spectrum identical with

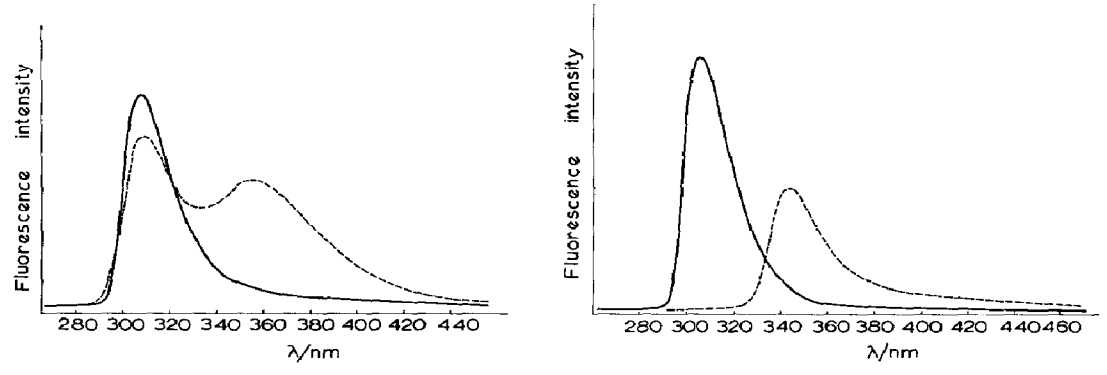

Fig. 1. Fluorescence spectrum of (a) *p*-cresol using 280 nm excitation —— 0.01 *M*, – – – 0.11 *M* cyclohexane solution; (b) *m*-cresol (0.11 *M*) —— 280 nm excitation, – – – 300 nm excitation.

TABLE 2

EXCIMER FLUORESCENCE PROPERTIES FOR ALKYLPHENOLS IN CYCLOHEXANE SOLUTION (0.11 *M*)

Line	Compound	$\lambda_{excit.}$ (nm)	λ_{EF} (nm)	Φ_{EF}[b]
1	Phenol	300	—	0.0
2	*o*-Cresol	300	362	0.0037
3	*m*-Cresol	300	347	0.0027
4	*p*-Cresol	280	357	0.0003
		300	357	0.0141
5	*p*-t-Butylphenol	280	353	0.0001
		300	353	0.0092
		310	361	0.0044
		320	367	0.0025
6	*p*-1,1-Di(methyl)heptylphenol[a]	280	351	0.0001
		300	351	0.0088
		320	353	0.0073
		340	367, 428	0.0034
		360	440	0.0028
		380	445	0.0031
7	2,6-Di-t-butyl-4-methylphenol	300	—	0.0

[a] Nonylphenol.
[b] Error limits for $\Phi_{EF} \pm 10\%$.

the alkylphenol. On the basis of the fluorescence excitation spectra and the shape and position of the emission band in the fluorescence spectrum, this new emission was identified as excimer fluorescence. The higher excimer fluorescence efficiency (Φ_{EF}) shown by *p*-cresol compared to the other *p*-substituted phenols suggested that some degree of steric hindrance was involved with the tertiary carbon substituents.

Excimers must fulfil specific geometry requirements not normally associated with monomeric excited states[7] in order to obtain sufficient orbital overlap to stabilize the species. This is illustrated by the excimer fluorescence observed for 1,3- but not for 1,2- or 1,1-diphenylpropanes[8]. The importance of a chain length of three carbon atoms separating the interacting groups has also been demonstrated for other intramolecular excimers[9,10]. These observations concerning excimer geometry suggested that the phenols also utilized a bridge three atoms in length, with the hydroxyl groups providing the three atoms by hydrogen-bonding (Fig. 2). The greater acidic character shown by *p*-substituted phenol excited singlet states would enhance hydrogen-bonding for these compounds, and this may explain the lack of excimer fluorescence for *o*- and *m*-cresols.

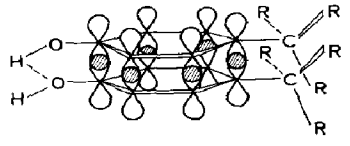

Fig. 2. Excimer formed for *p*-substituted alkylphenols.

Both *p*-nonylphenol and *p*-t-butylphenol exhibited an excimer fluorescence maximum that varied with excitation wavelength (Table 2, lines 5 and 6). The bulky *p*-substituents in these alkylphenols were in close proximity in the excimer state; this impeded rotation and suggested the formation of rotational conformers (Fig. 2). Each conformer would have a different environment and a series of excimer energy levels could be formed, each energy level pertaining to a specific rotational conformer[11]. Hence, irradiation at a particular wavelength would allow excitation to the conformer of that energy. *p*-Nonylphenol showed more fluorescence maxima than *p*-t-butylphenol indicating an increased number of rotational conformers imposed upon the excimer by the nonyl side-chain.

The excitation wavelength dependence studies (Table 2) show that excimer fluorescence was observed for excitation at longer wavelengths than usually associated with phenol absorption transitions indicating that ground state association occurred. This was evident in the absorption spectrum of the substituted phenols as a small tail towards longer wavelength. Excitation at this wavelength (300 nm) resulted in a new, broad, structureless band in the fluorescence spectra of *o*- and *m*-cresols, suggesting that excimer formation also occurred for these compounds. The fluorescence spectra for *m*-cresol at both 280 nm and 300 nm excitation are given in Fig. 1(b). Quantum yields (Φ_{EF}) of excimer fluorescence are given for all the substituted phenols in Table 2 and again the *p*-substituted phenols showed greater reactivity than *o*- or *m*-cresol. Ground state association may occur through simple hydrogen bonding. Absorption of electronic energy must result in the phenol dimer adopting a suitable configuration for excimer formation such that the excimer arising from absorption by a ground state dimer is identical with the excimer formed by association between a phenol molecule in the lowest excited singlet state and a ground state phenol molecule. This suggested that the species responsible for quenching the phenol molecular fluorescence was an unassociated phenol molecule and not a ground state dimer.

We thank the Science Research Council for a CAPS studentship (A.H.).

1 R. S. Becker, *Theory and Interpretation of Fluorescence and Phosphorescence*, Wiley–Interscience, New York, 1969, p. 147.
2 C. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968, p. 340.
3 E. Wehry and L. Rogers, *Spectrochim. Acta*, 21 (1965) 1976.
4 I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, London and New York, 1971, p. 24.
5 E. Yeargers, *Photochem. Photobiol.*, 13 (1971) 165.
6 J. D. Roberts and M. S. Caserio, *Basic Principles of Organic Chemistry*, W. A. Benjamin, New York, 1964, p. 905.
7 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley–Interscience, New York, 1970, p. 321.
8 F. Hirayama, *J. Chem. Phys.*, 42 (1965) 3163.
9 D. R. G. Brimage and R. S. Davidson, *Chem. Commun.*, (1971) 1385.
10 E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, 9 (1971) 397.
11 A. N. Fletcher, *J. Phys. Chem.*, 72 (1968) 2742.