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Photophysics of 2-(2′-hydroxyphenyl) benzoxazole in the presence of α-cyclodextrin: Deactivation of ESIPT through back protonation

Santi Kundu, Subhas Chandra Bera & Nitin Chattopadhyay*
Department of Chemistry, Jadavpur University,
Calcutta 700 032, India

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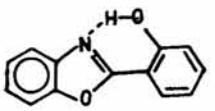
The complex photophysics of 2-(2′-hydroxyphenyl)-benzoxazole (HBO) in the presence of α-cyclodextrin (αCD) has been investigated using steady state as well as time-resolved spectroscopy. The 480 nm emission of HBO in aqueous medium has been found to be suppressed meaningfully in the presence of cyclodextrin. Steady state study as well as decay analyses suggest that the tautomer undergoes back protonation reaction in the excited state through the participation of αCD.

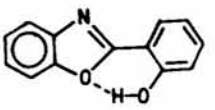
Considerable interest is recently being provoked by 2-(2′-hydroxyphenyl)benzoxazole and related thiazole, indazole and triazole due to their complex photoprocesses including excited state intramolecular proton transfer (ESIPT)[1-14]. Photophysics of these compounds are important because they can serve as ultraviolet stabilisers[14], liquid laser materials[15] and models for keto-enamine tautomerisation occurring in enolamines[3]. Rotamers, tautomers and anions of the compounds have been proposed. Tautomer formed through ESIPT has been proposed from the very large Stokes shifted (≈ 10000 cm^{-1}) emission of the compounds in aprotic as well as protic solvents. That ESIPT is extremely fast has been established from the time-resolved studies[2,3,11]. Involvement of triplet states have also been indicated by Mordzinski *et al*[2,5].

The fluorescence of HBO depends largely on the nature of the solvent. Emission of HBO is observed principally in three regions: (i) around 360 nm, ascribed to the normal or enolic form of the molecule (I); (ii) around 480 nm, attributed to the tautomeric species (III) and (iii) around 440 nm, more prominently found in protic solvents, corresponding to the ground state rotamer II having an absorption near 360 nm.

This note reports a study of the complicated photoprocesses of HBO in aqueous medium in the presence of α-cyclodextrin. The results show that αCD reduces the tautomer fluorescence yield as well as the corresponding lifetime and this has been argued in the light that the keto form of HBO, in its excited singlet state, undergoes back protonation reaction through the involvement of cyclodextrin.



(I)



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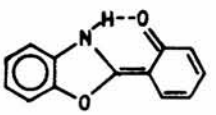

(III)

Experimental

HBO (Aldrich) was purified through chromatography on acidic alumina using 1:1 toluene-hexane as eluent, sublimation and finally recrystallisation from ethanol. Fine needle shaped crystals were obtained. α-Cyclodextrin (Aldrich) was used as received. Triply distilled water was used throughout the experiment. Fresh 2×10^{-6} mol dm^{-3} HBO solution was prepared in water. Only aerated solutions were taken for the experiments.

Absorption and emission spectra were recorded on Shimadzu MPS 2000 spectrophotometer and Perkin-Elmer MPF 44B spectrofluorimeter respectively. The time-resolved experiments using time-correlated single-photon counting (TCSPC) technique[16], was performed using nitrogen flash lamp (Edinburgh Instruments, 199 fluorescence spectrometer) as a source of excitation beam. FWHM of the exciting pulses were 1.2 nanoseconds.

Results and discussion

Absorption study

The absorption spectra of HBO in aqueous solution as a function of αCD are shown in Fig. 1. With increase in cyclodextrin concentration, 360 nm band increases slightly whereas the shorter wavelength band is decreased giving an isosbestic point (at 343 nm). This reflects the interaction of HBO

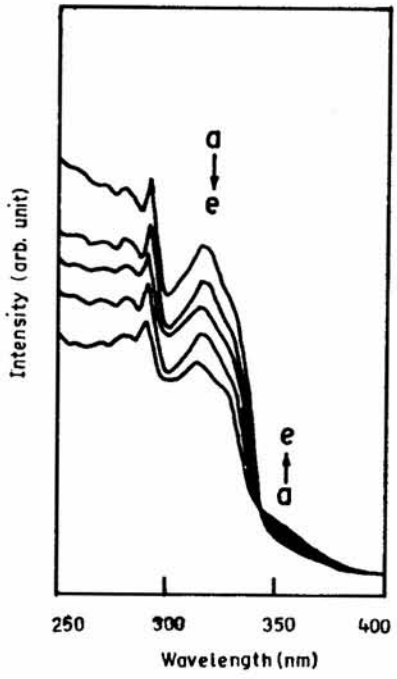

Fig. 1—Absorption spectra of HBO solution as a function of αCD. In solutions αCD concentrations are: (a) 0, (b) 1, (c) 4, (d) 6 and (e) 10 m mol dm^{-3}

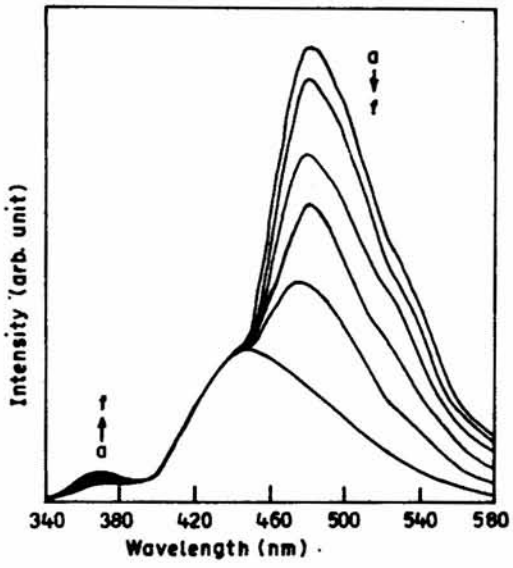

Fig. 2—Fluorescence spectra of HBO solutions as a function of αCD. In solutions αCD concentrations are: (a) 0, (b) 1, (c) 4, (d) 6, (e) 10 and (f) 15 m mol dm^{-3}

molecule with αCD. Existence of the isosbestic point indicates the formation of 1:1 complex between the two. Formation of such 1:1 complex of probes with CDs is now a very common observation[17,18]. Matching of the cavity size of cyclodextrin with the size of the probe moiety as a whole or a part thereof is an important factor for the formation of such stoichiometric adducts. Cavity size of αCD would, perhaps, correspond to the encapsulation of the phenolic part of HBO. αCD has been taken intensionally to avoid the possibility of any deviation from the aforesaid 1:1 stoichiometry[18,19].

Fluorescence study

The fluorescence spectra of aqueous HBO solutions as a function of αCD concentration are presented in Fig. 2. In the absence of CD, the spectra consists of three distinct bands, consistent with the literature, the maxima are at around 360 nm (F_1), 440 nm (F_2) and 480 nm (F_3). The intensity of the bands are in the order $F_3 > F_2 > F_1$. The yields of the bands are in conformity with some other findings for similar other compounds[7,9]. As consistent with the absorption, the excitation spectrum corresponding to 440 nm emission shows a band around 360 nm. The normal Stokes shifted emission (F_1) is ascribed to originate from the excitation of the normal HBO molecule (I) where the proton is attached to the phenolic oxygen[3,9]. The 440 nm emission is taken to originate from the rotamer (II)[3]. The lowest energy emission (F_3) with a large Stokes shift ($\approx 10400\ cm^{-1}$) from the corresponding excitation can be ascribed to the tautomer species formed through ESIPT, in which the proton goes to the nitrogen atom of the heterocyclic ring.

Table 1—Decay analyses of three emissions of HBO as a function of αCD ($\lambda_{excitation} = 316$ nm)

[αCD] m mol dm^{-3}	Lifetimes (nanoseconds) at wavelength		
	360 nm	440 nm	480 nm
0.0	1.5	2.9	6.8
1.0	1.4	3.0	6.3
4.0	1.5	2.8	6.0
6.0	1.3	2.9	5.7
15.0	1.4	3.0	3.0

Figure 2 shows that as αCD concentration in the solution increases F_3 band intensity gradually diminishes. At αCD > 10^{-2} mol dm^{-3}, the 480 nm emission is practically masked by the 440 nm emission. Time resolved study also provide same lifetime values at the two wavelengths reflecting that 480 nm emission is only the tail of the F_2 emission. The gradual decrease in the tautomer emission yield with addition of αCD may be due to two reasons. (i) Ground state trapping of transferable proton within the CD cavity: as clear from the absorption spectra, HBO forms a 1:1 inclusion complex with αCD and

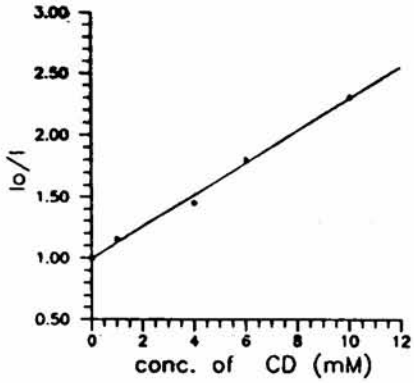

Fig. 3—Plot of I_0/I for the tautomer emission against αCD concentration

because of the cyclodextrin encapsulation; the −OH proton may not be accessible to the nitrogen atom of the heterocycle. (ii) Non-radiative decay of the excited tautomer: species with oxygen atom doubly bonded to a phenyl ring (as is the keto form of HBO) are known to abstract hydrogen from suitable donors in the photoexcited states. In the presence of a cyclodextrin, which is known to be a good hydrogen donor[18,20,21], the tautomer, in its excited singlet state, undergoes a back protonation reaction to produce the enolic species. This non-radioactive channel is expected to diminish the fluorescence yield of the keto form (480 nm emission) as well as the corresponding excited state lifetime (Table 1). The observation matches exactly with the expectation. A gradual increase in the enol fluorescence (360 nm band) with the addition of αCD, further substantiates the formation of enol from the keto form. We have also followed the steady state quenching of the tautomer fluorescence and noticed that it obeyed the Stern-Volmer equation very well yielding a straight line when I_0/I was plotted against αCD concentration (Fig. 3). The values of the Stern-Volmer constant and the quenching rate constant came out to be 0.13 dm^3mol^{-1} and 1.9×10^7 $dm^3\ mol^{-1}s^{-1}$ respectively. The above discussion, in association with the decay analyses, led us to conclude that the back prototropic reaction occurs in the excited singlet state.

Time-resolved study

Time-resolved analyses of the fluorescence decays indicate that all three emissions are single exponential in nature. Table 1 summarises the lifetime data for HBO emissions in different αCD concentrations. In the absence of αCD, the lifetimes come out to be 1.5ns, 2.9ns and 6.8ns for F_1, F_2 and F_3 respectively. The F_1 lifetime value matches with the reported value (1.6 ns

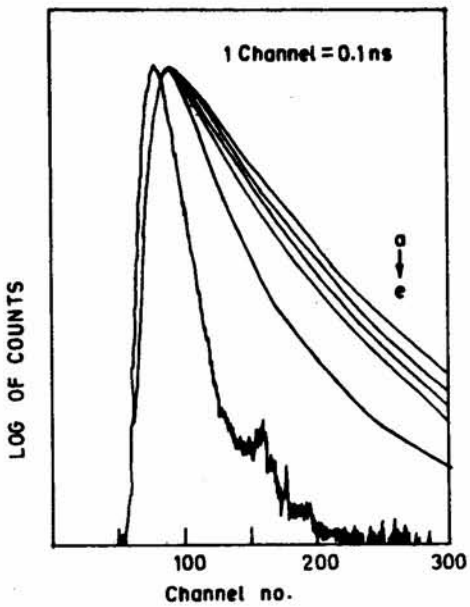

Fig. 4—Decay profiles of the 480 nm emission as a function of αCD. The different concentrations of αCD are: (a) 0, (b) 1, (c) 4, (d) 6 and (e) 15 m mol dm^{-3}

for MBO[5] and 1.5 ns for HPBI[9]). The τ value obtained by us for F_3 emission, though a bit higher, is of the order to those reported in literature for similar compounds in some other solvents, viz., 4. 1 ns for HBT in aqueous ethanol[7] or 4 ns for HPBI in ethanol[9]. The decays of the first two emissions are practically indifferent to cyclodextrin concentration (Table 1). This constancy in τ values reflects that both F_1 and F_2 come from the direct excitation of the ground state rotamers I and II and αCD has hardly any effect on the excited photophysics of these rotamers. Decay of the 480 nm emission is, however, found to be sensitive to αCD concentration. The tautomer lifetime goes on decreasing with the addition of cyclodextrin (Fig. 4). At αCD concentration $> 10^{-2}$ mol dm^{-3} τ values for 480 nm and 440 nm emissions are equal indicating that the tautomer emission is masked by the other band. Had ground state CD-encapsulation of the phenolic proton, responsible for ESIPT, been the only factor then with an increase in αCD concentration, one would expect, not a decrease in the tautomer lifetime but a decrease in the tautomer fluorescence intensity. The decrease in tautomer lifetime with increasing αCD reveals that CD influences the decay channels of the excited singlet species. The above discussion proposes that the tautomer, in its excited singlet state, undergoes back protonation reaction through the participation of αCD and due to the inclusion of a non-radiative channel in the presence of αCD, the 480 nm fluorescence decays faster.

Thus α-cyclodextrin influences the photophysics of HBO not only by providing steric rigidity towards the fluorophore but also through back protonation reaction.

Acknowledgement

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