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Phosphorescence of Lyophilized Complexes between Cyclodextrins and β-Arylpropiophenones★

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Abstract. β-Arylpropiophenones do not phosphoresce in homogeneous solution as a result of excited state quenching by the β-aryl group. In the presence of cyclodextrins the parent substrate, β-phenylpropiophenone, shows readily detectable phosphorescence. The complexes show strong phosphorescence after lyophilization to dryness. The phosphorescence intensity of ring-substituted derivatives is strongly dependent upon molecular size and cavity dimensions, suggesting that the β-arylpropiophenones can be used to probe these properties.

Key words: Cyclodextrins, phosphorescence, β-arylpropiophenones.

1. Introduction

Cyclodextrins (CDs) are cycloamyloses containing 6, 7 or 8 glucose units; these are designated α, β and γ-CD, respectively. The host-guest chemistry of their inclusion complexes with organic compounds has received a great deal of attention over the years [1]. Crystallographic studies have shown that suitable substrates can be incorporated in channel or cage complexes [2]. Spectroscopic studies have demonstrated that hydrophobic effects are of importance in the binding of guest molecules and in stabilizing adducts in aqueous solution [3,4]. It has also been suggested that a considerable part of the enthalpic gains associated with inclusion are due to the displacement of intra-cavity water that can then acquire the normal structure of liquid water [5]. Recently, the inclusion capacity of CDs has been used to enhance the room temperature phosphorescence of aromatic hydrocarbons in aqueous solution [6].

We report here that the phosphorescence emission of β-phenylpropiophenone (β-PP) and some of its derivatives can be readily detected when these ketones form complexes with α, β and γ-CD in aqueous solution or after lyophilization to dryness. This process enhances emission several-fold and we suggest that it could be used to extend the uses of CD complexes as analytical tools.

We also find a dramatic dependence of emission intensity with the size of the guest substrate. The size of β-arylpropiophenones was varied by chemical substitution on the β-phenyl ring (see Chart 1). As in the case of previous studies in zeolite systems [7,8], we find oxygen to be an inefficient quencher. This insensitivity toward oxygen is such that measurements can be performed under air or pure oxygen atmospheres.

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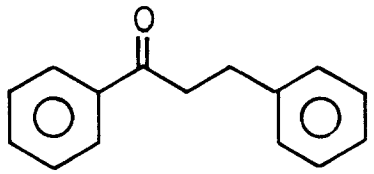

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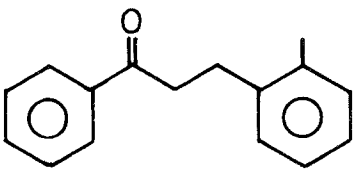

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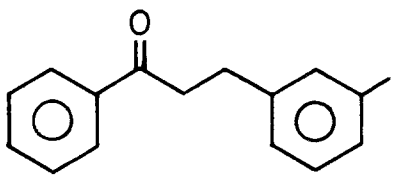

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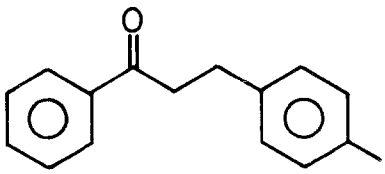

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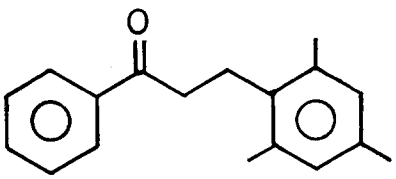

V

2. Experimental

The compounds investigated (**I–V**) have been described previously [9]. α, β and γ-CDs were obtained from Aldrich and used as received. Fisher HPLC-quality water was used throughout these experiments. Sucrose, D-glucose, maltose, fructose and galactose were obtained from Pfanstiehl Laboratories and used without further purification.

In all cases we used ketone : CD ratios of 10% wt/wt, which should provide a molar excess of CD in all cases, assuming a 1 : 1 complex stoichiometry. Inclusion complexes of the ketones and CDs were formed by dissolving the CDs in H_2O (such that solutions were 0.01 M in CD) and adding the solid ketone to the aqueous solution which was then agitated with a vortex mixer or by ultrasonics (no differences in behaviour were found using either of these two

mixing methods). Alternatively, the ketone was added to the aqueous solution as a saturated solution in methanol. After stirring, the methanol was removed by bubbling dry nitrogen through the mixture. While these aqueous solutions were being agitated they turned cloudy and a very fine powder deposited as a consequence of the decreased CD solubility following complexation. After agitation the solutions (which are 0.01 M in CD) were studied as such or were lyophilized to dryness (for periods longer than 14 h).

The phosphorescence spectra (uncorrected, front face for solids; 90° for solutions) were recorded on a Perkin-Elmer LS-5 gated fluorescence spectrometer with a 10 μs pulsed excitation lamp. In all cases the excitation wavelength was 313 nm; besides the appropriate setting on the spectrometer we used a 313 nm interference filter in the excitation beam. Typically, the phosphorescence spectra were recorded with a delay time of 50 μs between excitation and detection and with a 30 μs detection gate. The samples were contained in either 10×10 mm^2 (for solutions) or 3×7 mm^2 (for solids) cells made of Suprasil quartz. The atmosphere of the sample can be varied from pure N_2 to pure O_2 or N_2/O_2 mixtures of known composition, without moving the cells, by using a Matheson model 610 gas mixing system.

3. Results and Discussion

3.1. EMISSION FROM KETONE-CYCLODEXTRIN COMPLEXES

β-Phenylpropiophenone (**I**) is photostable in solution, even in solvents that are known to be highly reactive toward carbonyl triplets [9, 10]. This photostability is due to its very short triplet lifetime ($\tau_T \sim 1$ ns) which reflects the efficient deactivation of the carbonyl triplet by intramolecular quenching by the β-phenyl ring [11]. The quenching efficiency is directly related to the ability of the molecule to achieve conformation **Ia** (see Figure 1) in which the β-phenyl ring can deactivate the carbonyl triplet. In systems where the molecule is locked in conformation **Ib** this ketone phosphoresces, and its triplet lifetime is enhanced by several orders of magnitude over the solution value [7, 8]. Under these conditions the kinetic and spectroscopic behaviour of **I** becomes almost identical to that of acetophenone. For example, we have observed this type of behaviour when **I** is included in the channel system (~ 6 Å diameter) of zeolites such as Silicalite where conformation **Ia** cannot be achieved [7, 8].

The appropriate cavity sizes of α, β and γ-CD are ~ 6, 8 and 10 Å, respectively, with cavity depths of ~ 7 Å [1, 2, 4, 12]. We expect that **I** can be accommodated in all these cavities from either the PhCO— or the $PhCH_2$— end of the molecule (see Chart 1). Chemical substitution in the β-phenyl ring, particularly in the *ortho* and *meta* positions is expected [13] to make inclusion less favourable, due to increased molecular diameter, particularly in the case of the smaller cavities (α and β-CD). It should be noted however, that inclusion at the benzoyl end should remain largely unaffected by chemical substitution in the other aromatic ring.

Inclusion of **I** in α or β-CD leads to formation of a fine precipitate (see Section 2). We find that the clear solution obtained after separation of this precipitate shows weak phosphorescence, illustrated in Figure 2A for the complex of **I** with α-CD, prepared from a solution initially 0.01 M in α-CD (see Experimental). This luminescence is that characteristic of aromatic ketones ($\lambda_{max} \sim 420$ nm); this was further confirmed by its excitation spectrum. This emission, which is not observed in any homogeneous solvents, is assigned to complex formation with α-CD. The simplest explanation for the relatively low intensity of this emission is the low solubility of these complexes which causes extensive precipitation.

We find that much higher luminescence intensities can be observed if the samples are lyophilized and the luminescence measured using the solid samples. Figure 2B shows the

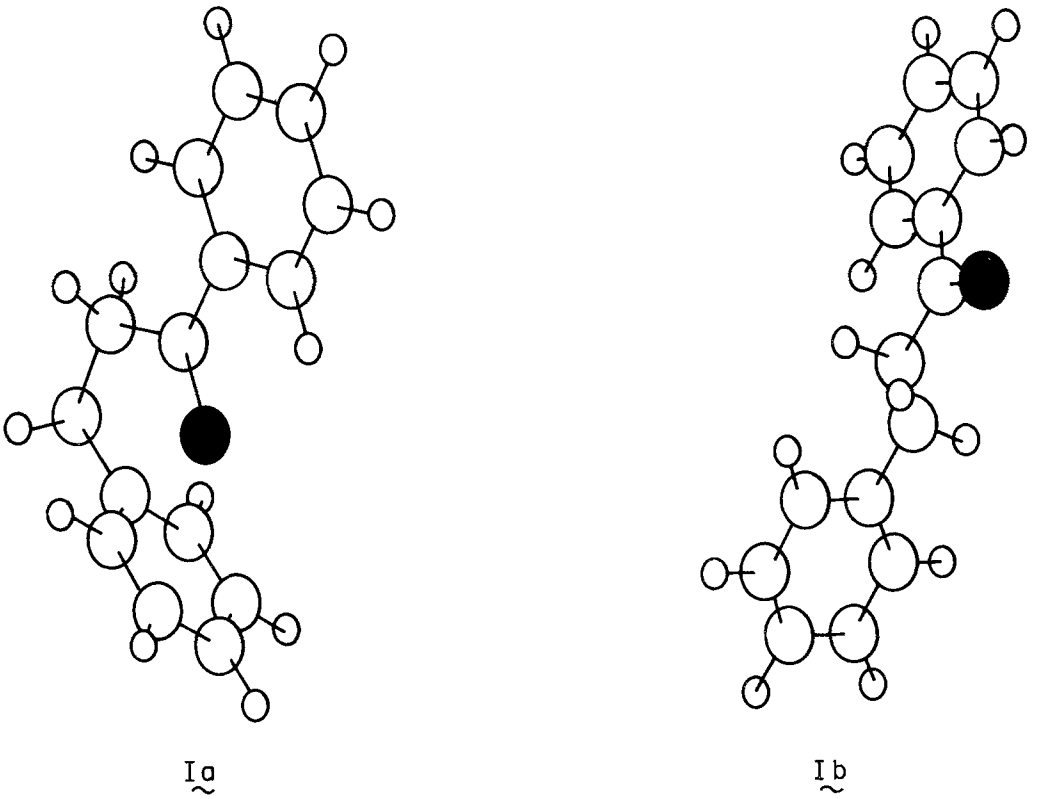

Fig. 1. Different conformations of β-phenylpropiophenone, **I**.

emission spectrum obtained from the solid recovered after lyophilization of the sample used for spectrum 2A. The vertical size of Figure 2B has been reduced by a factor of ~5 compared to 2A.

The same lyophilization procedure was used for samples of **I–V** in the three CDs. The corresponding luminescence intensities have been summarized in Table I. For α and β-CD the relative emission of included β-arylpropiophenones decreases as the molecular cross section of the β-aryl ring increases. It is rather interesting that **II** shows more luminescence than **IV** in the case of α and β-CD. This is perhaps an indication that partial protection of the aryl ring is sufficient to lead to some luminescence. That is, partial entry of the ring into the CD cavity may be enough to prevent considerably the quenching process. Since the cavities of at least α and β CDs can accommodate only one phenyl ring, and we observe a dependence of the phosphorescence intensity with the molecular diameter of the β-aryl ring, it can be proposed that its immobilization (through inclusion) is the determining factor for phosphorescence. In fact, the benzoyl end of the molecules could be accommodated in any of the CD cavities, but in such a situation the C=O group can be accessed by the β-aryl ring and thus, triplet deactivation is not prevented, whereas when the β-aryl group is included it cannot access the C=O group and thus phosphorescence is observed. As a result it is the diameter of the β-aryl ring that determines the phosphorescence intensity.

The relative intensities with γ-CD show a more complex trend. While emission decreases in going from guests **I** to **II** to **III**, the relative intensity increases for compounds **IV** and **V**.

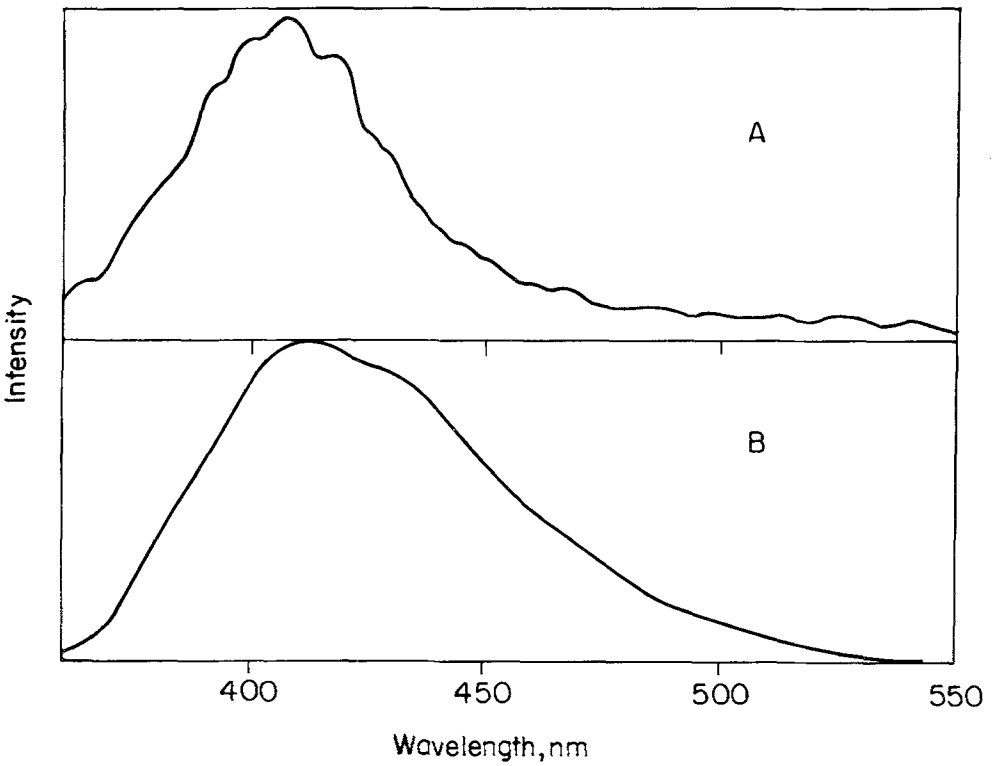

Fig. 2. Room temperature phosphorescence emission spectrum of β-phenylpropiophenone (**I**) complexed with α-CD: (A) In aqueous solution, and (B) as a solid after lyophilization to dryness.

Table I. Relative emission intensity[a] of the samples studied

Compound	λ_{max}^{em} (nm)	Cyclodextrin		
		α	β	γ
I	420	6	9.5	6.6
II	422	0.9	4	2.0
III	425	0	1	2.1
IV	425	0	0	10.6
V	430	0	0	9.4

[a] Measured as the intensity at λ_{max}^{em}.

We believe that the emission observed in these experiments is due to the aromatic ketones which are locked in such a conformation that intermolecular quenching cannot occur. Control experiments demonstrate that the ketones are included in the cavities of the cyclodextrin. The ketones studied do not show emission in aqueous solution or in the solid state; furthermore, mixtures of solid CDs and **I** (which are ground in a mortar but not dissolved or dispersed in water and lyophilized) do not show phosphorescence emission. Thus, emission from ketones **I**–**V** is observed when the CD and the ketone are allowed to interact closely in

solution. The conclusion is that complexes of the general characteristics of the well known CD complexes are formed, and as a consequence conformation **Ia** is prevented to a sufficient extent as to lead to readily detectable phosphorescence.

The phosphorescence emission of all the ketone : CD systems studied followed a non-exponential decay law. Thus, no simple kinetic analysis could be performed. However, the first observable lifetime measured following a 10 μs excitation pulse and a 20 μs delay was ~ 0.05 ms for all systems. The close similarity of the lifetimes suggests that the ketones are all residing in very similar environments with comparable immobilization. This is somewhat surprising given the different diameters of the CD cavities, especially comparing α with γ.

In previous studies of phosphorescence emission in Silicalite we found longer 'lifetimes' for the same ketones indicating greater immobilization in the case of Silicalite [7, 8].

Nonexponential decay laws for the luminescence of guest molecules in inclusion adducts or surface adsorbed species are generally explained as due to the heterogeneity of the systems [14], i.e., multiple inclusion sites, surface defects, etc. In the case of the present measurements, heterogeneity in terms of cavity is not expected. In principle the cavities of all CD molecules of a given type are the same. The nonexponential decay law could be due to different positions of the ketones inside the CD cavities (such as inclusion at one end, the other or both). The relatively short 'lifetimes' suggest that some kind of motion (responsible for deactivation) must occur.

The emission observed in the present experiments showed a remarkable lack of sensitivity to added molecular oxygen. In all cases practically no difference was observed when the atmosphere in the sample cell was changed from pure N_2 and pure O_2. Previous studies have also shown lack of oxygen sensitivity of the emission of molecules included in CD cavities [6, 15, 16]. In the solid state CDs adopt crystalline structures in which the axial holes formed by the cyclic molecules are blocked on each end by nonaxial alignment of adjacent dextrin molecules [12]. This type of arrangement practically ensures that there is no exchange of O_2—N_2 molecules between the inside and outside of the cavity. In the case of the emission in aqueous solution we observed partial quenching by molecular oxygen such that the emission of **I** in β-CD under 1 atm of O_2 was 90% of the emission under 1 atm of N_2.

3.2. EMISSION OF I CO-CRYSTALLIZED WITH CARBOHYDRATES

Finally, we would like to comment on some attempted control experiments. When we prepared lyophilized samples of **I** with several carbohydrates following the same procedures used for CDs we found emission in all cases. The relative intensities are listed in Table II along with those of appropriate blanks.

As in the case of CD samples, we found the emission to be insensitive to oxygen and the decay to be nonexponential. Since **I** needs to be locked in conformation **Ib** for phosphorescence emission and no emission is observed from pure **I** in the solid state★ we propose that when **I** and the carbohydrates listed in Table II crystallize from solution, a crystal is formed in which molecules of **I** are forced to pack with the β-phenyl ring as in conformation **Ib**. At the same time the carbohydrate molecules isolate the ketone molecules in such a way that the intermolecular distances do not allow quenching.

The lack of quenching by added oxygen to a polycrystalline system such as **I** : carbohydrate mixtures is more puzzling and probably suggests a very close association between **I** and the carbohydrate molecules.

★ Presumably due to intermolecular quenching.

Table II. Relative intensities[a] of phosphorescence emission of **I** and carbohydrates

Carbohydrate	Relative intensity[b]	
	Lyophilized sample	(Blank)[c]
Sucrose	28	(0.25)
Galactose	23	(0.8)
Maltose	27	(0.8)
D-Glucose	19	(0.02)
D-Fructose	22	(0.06)

[a] See footnote a of Table I.
[b] Monitored at 420 nm.
[c] Blank experiments: samples are mixtures of **I** with the carbohydrates (10% wt/wt) thoroughly milled before measurement.

These preliminary experiments using simple carbohydrates in the solid state suggest the possibility of co-crystallization as a tool for room temperature phosphorescence enhancement. Undoubtedly, structural studies are necessary to understand the nature of these carbohydrate : ketone solids.

Acknowledgement

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