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A latent photoreaction enhanced upon cyclodextrin encapsulation: Photochemistry of α-alkyl dibenzyl ketones in water

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Abstract

α-Alkyl dibenzyl ketones that are capable of undergoing both Norrish Type I and Type II reactions generally yield products of Norrish Type I reaction in organic solvents. These water insoluble ketones form water-soluble host–guest complexes with β and γ-cyclodextrins. Irradiation of the above β-cyclodextrin complexes in water leads to products of Norrish Type II reaction. This change in behavior between the guest alone in organic solvent and as host–guest complexes in water is consistent with the influence of other ordered media such as micelles and reactants such as benzoin alkyl ethers and alkyl deoxy benzoins.

Keywords: Norrish Type I; Norrish Type II; Cyclodextrin; Conformational control; α-Alkyl dibenzyl ketones

1. Introduction

Interest in the chemistry of cyclodextrins, a family of three well known commercially available cyclic oligosaccharides containing 6–8 glucopyranose units, has grown quite rapidly over the last two decades [1]. Cyclodextrin (CD) is water-soluble and adopt a bucket-like arrangement with a hydrophilic exterior and hydrophobic interior (Fig. 1). In spite of the fact that during the last two decades a number of synthetic organic hosts such as cucurbiturils, calixarenes, cavitands, carcerands and hemicarcerands have become available, cyclodextrins continue to attract the most attention owing to their commercial availability, aqueous solubility, and low cost.

Our interest in confined nanoreaction cavities has focused on using them to control excited state processes. This has led us to explore natural and synthetic micelles [2], dendrimers [3,4], cyclodextrins, cucurbiturils [5,6], calixarenes [7], octa acid [8,9], Pd nanocage [10], organic crystals [11], zeolites [12,13] and polymers [14] as reaction media. Results of these studies, we hope will help us develop a model with predictive power to achieve desired selectivity in excited state processes. Photoreactions we have investigated include photo-Fries and photo-Claisen rearrangements, Type I and Type II reactions of benzoin alkyl ethers, α-alkyl deoxybenzoins and α-alkyl dibenzyl ketones, Type II reactions of phenyl alkyl ketones, singlet oxygen mediated oxidation of olefins, photodimerizations of cinnamic acids, coumarins, acenaphthylenes and stilbazoles and numerous enantio and diastereo selective photoreactions [12,13,15]. Almost a decade ago we had investigated the photochemistry of cyclodextrin complexed α-alkyl dibenzyl ketones in solution and in solid state [16,17]. In solid state the decarbonylated AB product resulting via Norrish type I cleavage was the main product (Scheme 1). In aqueous solution we believed that we obtained mostly (50–75%) the rearrangement product via the Norrish type I cleavage process (Scheme 1). This surprising result prompted us to examine the photobehavior of α-alkyl dibenzyl ketones in various confined media. Of the various media examined only within the octa acid capsule we obtained the rearrangement product in yields above 50% [8]. Based on the fact that the interior of the octa acid capsule is closed while that of cyclodextrin is open the earlier results in cyclodextrin seemed suspect. This prompted us to reexamine the photochemistry of α-alkyl dibenzyl ketones within cyclodextrins. The current results presented in this report and reproduced by several group members suggest that the main product in aqueous solution is not the rearrangement product but dibenzyl ketone formed via the Norrish type II reaction.

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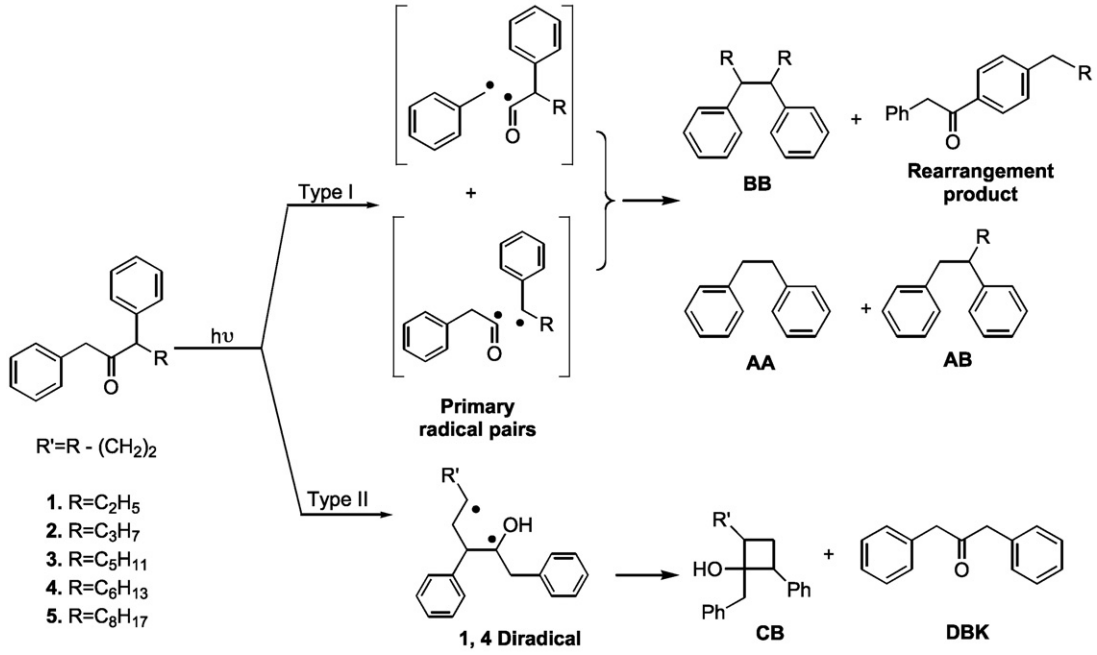


Scheme 1. Possible photoreactions of dibenzylketones **1**–**5**.

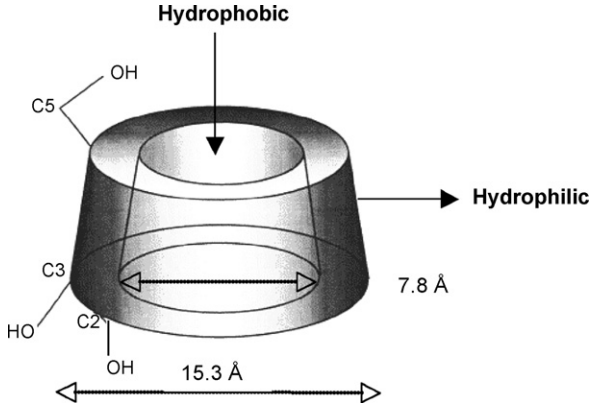


Fig. 1. A cartoon representation of cyclodextrin cavity. The internal and external widths for β-cyclodextrin are noted in the figure. The height of the cavity is presumed to be ∼8 Å.

In addition to the studies by our group numerous other groups have investigated the excited state photochemistry and photophysics of carbonyl compounds included within cyclodextrins [18–24]. In almost all cases a slight modification on the excited state behavior of the guest ketone has been noted. As for as we are aware no general trend has emerged. Results that we currently report on α-alkyl dibenzyl ketones are consistent with that of alkyl benzoin ethers and α-alkyl deoxy benzoins investigated previously. The results presented here demonstrate that cyclodextrins could enforce conformational control and cage effect on reactant molecules and reactive intermediates.

2. Results

Addition of dibenzyl ketones **1**–**5** to saturated aqueous solutions of β- and γ-CD precipitated a white solid suggesting the formation of host–guest complexes. However, upon addition of excess water the complex went into solution. None of these ketones formed complexes with α-CD, most likely because of its smaller cavity size. The procedures adopted for preparation and photolysis of β- and γ-CD inclusion complexes of ketones **1**–**5** are described in the experimental section.

Support for the inclusion of DBK within cyclodextrins in aqueous solutions came from UV–vis absorption spectra of CD complexes. Addition of β-CD to aqueous solutions of ketone **2** resulted in the enhancement of the absorption intensity. The stability constants (K_a) for β- and γ-CD complexes of ketone **2** were estimated to be 2.9×10^4 and $1.6 \times 10^4\ M^{-1}$ from the difference in absorption intensities in the presence and in the absence of CD. A linear Benesi–Hildebrand plot of $1/[A–A_0]$ and 1/[CD] suggested that the cyclodextrin complexes most likely have 1:1 host to guest ratio (Fig. 2) [25].

Photolysis of dibenzyl ketones with abstractable γ-hydrogens (**1**–**5**) in benzene yielded products resulting from Norrish type I and type II reactions as shown in Scheme 1. Recombination products AA, **AB** and BB (formed in a statistical ratio of 1:2:1) resulting from Norrish type I reaction were major (80–95%) and products, dibenzyl ketone and cyclobutanol, through γ- hydrogen abstraction process minor (5–20%). The solution products were analyzed by GC and characterized with the help of GC-MS and ^{1}H NMR spectral data. Photolysis of β-CD inclusion complexes of ketones **1**–**5** in solid state exclusively yielded AB. Irradiation of β-CD complexes of ketones **1**–**5** as homogeneous aqueous solutions resulted in product distributions that are remarkably different from those obtained upon irradiation of the ketones alone in organic solvents and those obtained during irradiation of the solid inclusion complexes. Results obtained upon photolysis of ketones **1**–**5** in solution and within β- and γ-CD are summarized in Table 1. The most important results during irradiations of cyclodextrin complexes in water are the following: (a) Type II products that were minor during irradia-

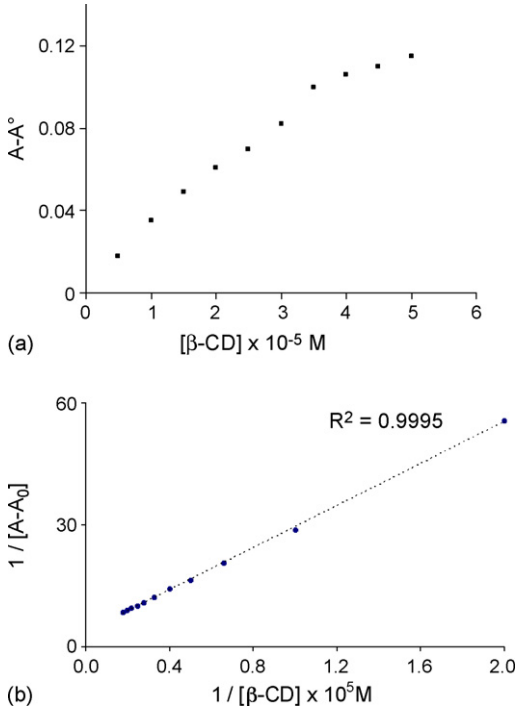


Fig. 2. (a) Binding isotherm for the complexation of α-propyl dibenzyl ketone with β-CD based on UV–vis absorption studies and (b) Benesi–Hildebrand linear plot for the complexation of α-propyl dibenzyl ketone with β-CD.

tion of the guest alone in organic solvents became predominant upon photolysis of β-CD inclusion complexes of ketones **1**–**5** in aqueous solution, (b) Percentage of type II products increased with increase in the length of alkyl chain (ethyl to octyl). (c) Yield of cyclization product (cyclobutanol) via type II process were generally small. (d) Remarkable cage effect was observed in the formation of coupling products AB, BB and AA arising *via* Norrish type I reaction. (e) None of the ketones yielded the rearrangement product upon photolysis within β-CD that is clearly different from our previous observation [16,17]. (f) Photolysis of γ-CD complexes of ketones **1**–**5** in aqueous solution yielded AB as the major product, (g) There were differences in products distribution between β-CD and γ-CD complexes. Within γ-CD only small amounts of the Norrish type II products were obtained while within β-CD the Norrish type II product, dibenzyl ketone was obtained as the major product.

3. Discussion

The linear Benesi–Hilderbrand plot obtained from UV–visible absorption studies of **2** is consistent with 1:1 stoichiometry for β- and γ-CD inclusion complexes. Based on the relatively large K_a value for ketone **2** with β-CD ($2.9 \times 10^4 M^{-1}$) we believe that (β-CD is likely to form strong complexes with ketones **2**–**5** as well. Consistent with the larger size of γ-CD, the K_a value obtained for **2** with γ-CD is slightly lower ($1.6 \times 10^4\ M^{-1}$) than that for the corresponding β-CD inclusion complexes.

At this stage we do not have any spectral data that would help us suggest structures for the host–guest complexes. Unfortunately, the cyclodextrin complexes are not soluble enough in water to record good ^{1}H NMR spectra. We recognize that one could consider several possible structures for the DBK-CD complexes. Based on the linear Benesi-Hilderbrand plot [25] we have not considered 2:1 complex as a possibility. At this stage our suggestion is based only on the product distribution in water. The two most likely structures consistent with product distribution are shown in Fig. 3. In order to make sure that these suggested structures are reasonable we computed the dimensions of the eclipsed conformation of DBK using the MM3 program [26]. As per the computation it has a length of ∼8 Å and a width of ∼5 Å and these are smaller than the internal diameter of β-CD. Thus, we believe that the proposed structures in Fig. 3 are reasonable and the conformation is ideally suited to undergo the Norrish type II reaction.

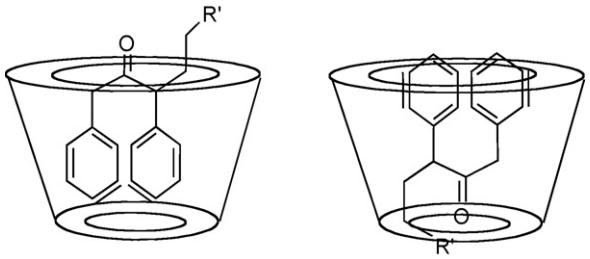


Fig. 3. The two possible structures considered in this study favor the Norrish Type II reaction.

Support for the proposed structures come from literature reports on similar systems. Turro, Eaton and their groups have established through photophysical studies that 1,3-dinaphthyl propane systems are accommodated within β-CD in an eclipsed conformation [27,28]. These molecules are slightly larger in size than ketones **1**–**5** being investigated here. Turro and his co-workers have reported that 1-α-naphthyl-3-(dimethylamino) propane that is similar in size to the ketones **1**–**5** arranges itself within a β-CD in a conformation favorable for exciplex formation [29]. Similar observations have been made with [*n*-(4-bromonaphthoyl)alkyl] trimethylammonium bromide within β-CD [30]. In addition to these several reports by the groups of Nocera [31] and Hamai [32–34] have shown that a single β-CD cavity can accommodate two different molecules such pyrene, acenaphthylene, naphthalene and long chain alcohols. The sizes of the molecules included in the above reports are nearly the same as the ones investigated in this study. Literature precedence as well as molecular dimensions of the ketones and the cavity suggest that the proposed structures in Fig. 3 are likely to be valid. Most importantly the host–guest structures presented in Fig. 3 nicely rationalizes the observed product distribution.

The exclusive formation of coupling product AB during the solid-state irradiation of ketones **1**–**5** is a result of the remarkable cage effect provided by β-CD. Absence of products due to γ-hydrogen abstraction in the solid state suggests that either the structure of the host–guest complex in solution and solid state are not the same or in the solid state the alkyl chains of the ketones are frozen in a conformation that is not favorable for γ-hydrogen abstraction. Unlike in benzene and water, the reaction

Table 1
Product distribution upon photolysis of α-alkyl dibenzyl ketones **1–5** in solution and within β and γ-cyclodextrin

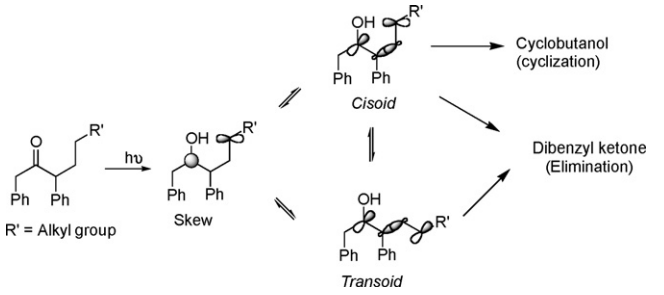
Substrate	Medium	Product distribution (%)[a]					Cage effect[b]	Type I/Type II
		Type I			Type II			
		AA	AB	BB	CB	DBK		
1	Hexane[c]	20	47	27	2	–	0.00	47
	H_2O[c,d]	21	48	26	Trace	5	0.01	19
	β-CD (solid)[e]	–	>99	–	–	–	0.99	–
	β-CD (aqueous)[f]	2	57	–	–	41	0.96	1.4
	γ-CD (solid)[e]	–	>99	–	–	–	0.99	–
	γ-CD (aqueous)[f]	–	>99	–	–	–	0.99	–
2	Hexane[c,d]	21	41	20	12	6	0.00	4.5
	H_2O[c,d]	20	39	21	11	9	0.00	4
	β-CD (solid)[e]	–	>99	–	–	–	0.99	–
	β-CD (aqueous)[f]	4	27	–	13	56	0.87	0.4
	γ-CD (solid)[e]	–	>99	–	–	–	0.99	–
	γ-CD (aqueous)[f]	3	90	–	–	7	0.97	13.3
3	Hexane[c]	14	42	25	12	7	0.03	4.3
	H_2O[c,d]	11	38	28	17	6	0.00	3.3
	β-CD (solid)[e]	–	>99	–	–	–	0.99	–
	β-CD (aqueous)[f]	2	43	–	9	46	0.95	0.8
	γ-CD (solid)[c]	–	>99	–	–	–	0.99	–
	γ-CD (aqueous)[e]	5	84	–	–	11	0.94	8.1
4	Hexane[c]	9	35	23	24	9	0.05	2
	H_2O[c,d]	12	43	27	11	7	0.04	4.5
	β-CD (solid)[e]	–	>99	–	–	–	0.99	–
	β-CD (aqueous)[f]	5	32	–	Trace	63	0.86	0.6
	γ-CD (solid)[e]	–	>99	–	–	–	0.99	–
	γ-CD (aqueous)[f]	2	88	–	–	10	0.98	9
5	Hexane[c]	10	54	21	12	3	0.27	5.7
	H_2O[c,d]	5	46	36	10	3	0.06	6.7
	β-CD (solid)[e]	–	>99	–	–	–	0.99	–
	β-CD (aqueous)[f]	4	18	–	–	78	0.82	0.3
	γ-CD (solid)[e]	–	>99	–	–	–	0.99	–
	γ-CD (aqueous)[f]	2	82	–	–	16	0.97	5.3

[a] For structures see Scheme 1.
[b] Cage effect = [AB–(AA + BB)]/[AA + AB + BB]
[c] Conversion = ∼30% (15 min of irradiation).
[d] The concentrations of ketones in water were exactly the same as the complexes mentioned in footnote (f). However, not all ketones dissolved in water. Most ketones remained as suspensions in water. Irradiations of suspensions were carried out.
[e] Conversion = ∼10% (24 h of irradiation).
[f] Conversion = ∼30% (15 min of irradiation). [β-CD-**1**], [β-CD-**2**], [γ-CD-**1**], [γ-CD-**2**] = 7.5×10^{-4} M. [β-CD-**3**], [β-CD-**4**], [γ-CD-**3**], [γ-CD-**4**] = 3.5×10^{-4} M. [β-CD-**5**], [γ-CD-**5**] = 8.8×10^{-5} M. Small amount of AA was observed as a result of secondary photoreaction of dibenzyl ketone (primary photoproduct).

is very slow in the solid state. Even after 24 h of irradiation, only 10% conversion was achieved. One possible reason is that the solid state sample is not uniformly exposed to light as compared to isotropic media. Another possibility is that the recombination of the primary radical pair, formed via α-cleavage of ketones, competes with the decarbonylation leading to regeneration of the reactant ketone. The decarbonylation rate constants of similar phenyl acyl radicals in organic solvents were calculated to be $\sim 10^7\ s^{-1}$ [35,36]. The recombination of the primary radical pair can compete with the decarbonylation provided the intersystem crossing to singlet state occurs faster than $10^7\ s^{-1}$. This argument assumes that the rate constants for cleavage within cyclodextrin cavities are the same as in solution and that in solid state and in solution are similar. At this stage we do not have sufficient data to support this assumption.

Irradiation of CD complexes in aqueous media gave both Type I and Type II products. Among the type I products, only AB was formed indicating that the primary radical pair is confined by β-CD cavity even in the solution phase. The type II products that are not formed during solid-state irradiation were predominant upon irradiation of β-CD inclusion complexes in aqueous solutions. The results suggest that the cavity of β-CD templates the α-alkyl dibenzyl ketone in a conformation favorable for γ-hydrogen abstraction (Fig. 3).

Dominance of cleavage product, dibenzyl ketone, in all α-alkyl dibenzyl ketones can be understood on the basis of the well established mechanism for similar systems such as benzoin alkyl ethers and alkyl deoxy benzoins [37,38]. The 1,4 diradical formed via Norrish type II reaction of α-alkyl dibenzyl ketone can exist in two conformations, namely, *cisoid* and *transoid*



Scheme 2. Mechanism of product formation via the Norrish Type II process.

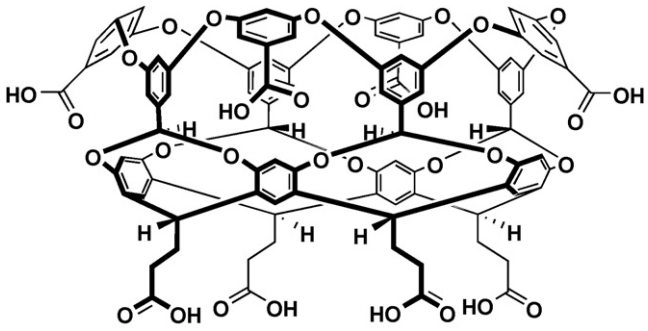
(Scheme 2). Cisoid can yield both cyclobutanol (cyclization) and dibenzyl ketone (cleavage), whereas transoid can yield only the elimination product, dibenzyl ketone (DBK). Transoid 1,4-diradical is unlikely to be formed within the cavity of CD. Amongst the two processes that the cisoid 1,4-diradical can undergo, cyclization is sterically more demanding and requires greater motion within the cavity of β-cyclodextrin. We speculate that the folding of the alkyl chain within the confining cavity of β-CD most likely templates the 1,4 diradicals to be in *cisoid* conformation and the restriction provided by the cavity allows only the cleavage process.

The photochemical behavior of γ-CD inclusion complexes of ketones **1**–**5** in the solid state are exactly the same as that of β-CD inclusion complexes, giving exclusively AB coupling product suggesting that the confinement provided by the γ-CD cavity is same as that of β-CD in the solid state. However, the solution behaviors of the two differ. Photolysis of γ-CD inclusion complexes of ketones **1**–**5** in an aqueous solution gave predominantly the Type I product, AB. The amount of type II products obtained was in the range of 15%. Larger γ-CD most likely allows the α-alkyl dibenzyl ketones to adopt their most favored conformation that may not be the one favoring γ-hydrogen abstraction.

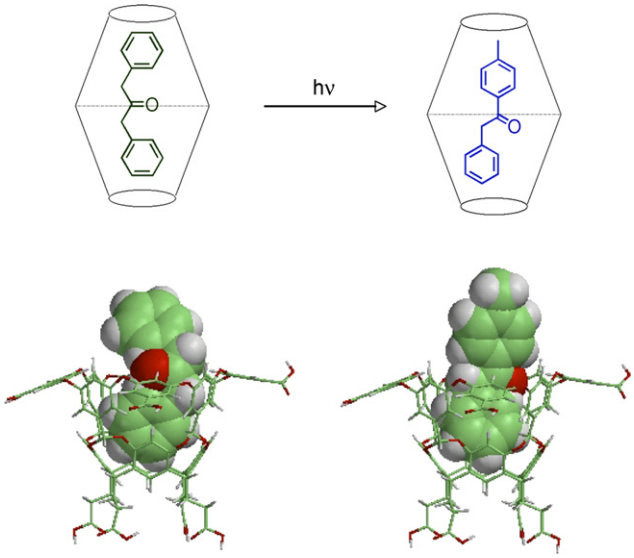
This could facilitate the decarbonylation to occur over the competing γ-hydrogen abstraction.

Influence of cyclodextrins on competition between Type I and Type II reactions of alkyl benzoin ethers, α-alkyl deoxy benzoins and α-alkly dibenzyl ketones has been investigated previously [37–39]. In the former two cases the normally less favored Type II process is enhanced within cyclodextrins. However, our observation that this did not happen with α-alkyl dibenzyl ketones was an anomaly. Even more puzzling was the formation of the rearrangement product as the major product of the Type I process within cyclodextrins in aqueous media. In our previous study, we had investigated the photochemistry of cyclodextrin complexed α-alkyl dibenzyl ketones both in solid state and in solution. Previous results on the photochemistry of β-CD-α-alkyl dibenzyl ketone inclusion complexes in solid state are identical to the current work. However, our current observation on their photochemistry in aqueous solutions is different from what was observed previously. The exact reason for the difference is not clear. We speculate that the GC column used two decades was not sophisticated enough to separate the rearrangement product and the type II products.

During the last two decades the photoreaction of dibenzylketones has been investigated in a variety of confined media and



Scheme 3. Structure of octa acid used as a host in water. Note the presence four COOH groups on the top and bottom rims.



Scheme 4. A cartoon representation suggesting the role of C–H· · ·π interaction in the rearrangement process. Newly formed CH_3 group interacts with the π-cloud of the four aryl groups at the bottom of the octa acid. The C–H bond projects itself on top of the π-cloud and this results in a weak stabilization.

in no case except within the octa acid capsule (Scheme 3) [8,40] the rearrangement product was formed in substantial yield. Within the octa acid capsule we believed that the existence of C–H. . .π interaction favored the rearrangement process (∼50%) (Scheme 4). The interaction occurs between the C–H of the methyl group and the p-cloud of the aromatic groups at the bottom part of the octa acid. No such aryl groups exist in cyclodextrin. Lack of such type of interaction within cyclodextrins and the open nature of the cyclodextrin cavity should not in principle favor rearrangement over decarbonylation of the Type I radical pair (Scheme 1). These reasoning prompted us to reinvestigate the α-alkyl dibenzyl ketones within cyclodextrins. Results presented here are consistent with the excited state behavior of related systems such as alkyl benzoin ethers and α-alkyl deoxy benzoins in a variety of organized media.

4. Summary

The results on α-alkyl dibenzyl ketones presented here clearly illustrates that the hydrophobic cavities of cyclodextrins (β-

CD and γ-CD) impose restrictions on the guest molecules and thereby alter their photochemical behaviors. Our results are consistent with previously reported results on benzoin alkyl ethers and alkyl deoxy benzoins. The difference in photochemical behaviors of the inclusion complexes of dibenzyl ketones **1**–**5** between solid state and solution phase photolysis suggests that the photoreaction of cyclodextrin inclusion complexes can follow two different mechanisms depending on the degree of freedom available for the guest molecules within the hydrophobic cavity. Overall, the conformational control exerted by the hydrophobic cavities of cyclodextrin on encapsulated molecules is appealing. The knowledge gained from this study could be used to better control excited state processes with organic hosts that are becoming available almost daily.

5. Experimental

Materials: α, β and γ cyclodextrins were obtained from Wacker Cyclodextrins and dibenzyl ketone was obtained from Aldrich and used as received. α-Alkyl dibenzyl ketones were synthesized following the procedure reported in the literature [41] and purified by column chromatography (silica gel, petroleum ether/dichloromethane). Doubly distilled and deionized water was used for performing aqueous reactions.

Preparation of cyclodextrin-α-alkyl dibenzyl ketone complex: A stock solution of α-alkyl dibenzyl ketone (10 mg/mL) in dichloromethane was prepared and from it the desired amount of α-alkyl dibenzyl ketone was pipetted out into clean dry test tube. The dichloromethane solution was then concentrated approximately to 0.1 mL. To it, excess of β-cyclodextrin (3 equiv.) in 4 ml of deionized water was added. The resulting suspension was stirred for 6 h. The precipitate thus formed was filtered, washed with excess of dichloromethane to remove any ketone that was adsorbed on the surface. The complex was then dried under reduced pressure and taken for photolysis. γ-CD inclusion complexes of ketones **1**–**5** were prepared following the same procedure adapted for β-CD complexes.

Photolysis and analysis procedures: The β-cyclodextrin-α-alkyl-dibenzyl ketones complexes were irradiated both as solid samples and as aqueous solutions. The aqueous solution was prepared by suspending the solid complex in calculated amount of deionized water, following which the solution was stirred for 12 h at 60 °C (warm water bath) to make it homogenous suitable for photolysis. The amount of deionized water required to solubilize the complex varied with substrate. For example, the β-CD inclusion complex of dibenzyl ketone is completely soluble in 10 mL of deionized water, whereas that of α-octyl dibenzyl ketone requires 100 mL of deionized water. After photolysis the product and the unreacted starting material were extracted with ethyl acetate/dichloromethane and analyzed in GC using SE-30 column. The photoproducts AA, AB, BB and CB for all α-alkyl-dibenzyl ketones were identified from their solution reactions. The photoproduct DBK was identified by comparing the spectral data with commercially available authentic sample.

GC conditions: The following conditions were used for GC analysis of the photoproducts. The temperature of the injection and the detection ports were maintained at 250 and 270 °C.

Substrate **1**. Column: SE-30. Temperature program: initial temp., 100 °C; initial time, 1 min; rate, 5 °C/min; final temp., 270 °C; final time, 20 min. Retention times: 1, 18.8 min; AA, 12.2 min; AB, 14.4 min; BB (Diastereomer), 16.3 min, 16.7 min; CB, 19.1 min; DBK, 17.2 min.

Substrate **2**. Column: SE-30. Temperature program: initial temp., 100 °C; initial time, 1 min; rate, 5 °C/min; final temp., 270 °C; final time, 20 min. Retention times: 2, 20.5 min; AA, 12.2 min; AB, 16.1 min; BB (Diastereomer), 19.3 min; CB, 21.6 min; DBK, 17.2 min.

Substrate **3**. Column: SE-30. Temperature program: initial temp., 100 °C; initial time, 1 min; rate, 5 °C/min; final temp., 270 °C; final time, 20 min. Retention times: 3, 24.1 min; AA, 12.2 min; AB, 20.0 min; BB (Diastereomer), 25.5 min, 25.7 min; CB, 24.8 min; DBK, 17.2 min.

Substrate **4**. Column: SE-30. Temperature program: initial temp., 100 °C; initial time, 1 min; rate, 5 °C/min; final temp., 270 °C; final time, 20 min. Retention times: 4, 25.8 min; AA, 12.2 min; AB, 21.9 min; BB (Diastereomer), 28.6 min, 28.8 min; CB, 26.6 min; DBK, 17.2 min.

Substrate **5**. Column: SE-30. Temperature program: initial temp., 100 °C; initial time, 1 min; rate, 5 °C/min; final temp., 270 °C; final time, 20 min. Retention times: 5, 29.1 min; AA, 12.2 min; AB, 25.6 min; BB (Diastereomer), 34.4 min, 34.6 min; CB, 29.9 min; DBK, 17.2 min.

Stability of the inclusion complexes: UV–vis titration study was carried out to determine the stability constant of CD inclusion complexes. In this study, the concentration of DBK was kept constant and the host concentration was varied. Typical procedure followed to achieve this is about 20 ml of a stock solution of **1** (1×10^{-4} M) was prepared in water. The stock solution was divided into two portions. To one portion, 22.7 mg of β-CD (2×10^{-3} M) was added and the resultant complex solution was stirred overnight. Known volume of DBK stock solution from the second portion was taken in UV cuvette, absorption spectrum was recorded (A_0). To the same solution, β-CD complex solution was added in 5 μl amount. Absorption spectrum was recorded after each addition. Increase in absorption intensity was plotted against the concentration of β-CD. Linear Benesi–Hildebrand plot suggests the formation of 1:1 complex. The stability constant was calculated from the slope and intercept. The stability constants for γ-CD inclusion complexes were estimated adapting similar procedure except that the γ-CD-complex solution was added in 10 μl portions.

Acknowledgments

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