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Novel photohydration of *trans*-stilbenes and *trans*-anethole inside cyclodextrin nanocavity in aqueous medium

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ABSTRACT

An unique photochemical hydration of *trans*-stilbene, *trans*-3-methoxystilbene and *trans*-anethole was observed inside cyclodextrin nanocavity in water. An excited-state proton transfer from cyclodextrin hydroxyl groups *via* a carbocation intermediate, which is stabilized by cyclodextrin secondary hydroxyl groups, is proposed.

1. Introduction

Photochemistry of olefins particularly stilbenes has been explored in detail by many research groups [1–8]. *trans–cis* isomerization (from either the lowest excited singlet or triplet state) of *trans*- and *cis*-stilbenes and electrocyclic ring closure of *cis*-stilbene to dihydrophenanthrene are the most common photoprocesses [9–14]. In suitable cases, photochemical solvent addition to olefinic double bond of *trans*-stilbene (**1a**) taken place in addition to isomerization and cyclization. To account for this two distinct competitive pathways: (a) 1,2-hydrogen shift *via* carbene intermediate and (b) direct addition of methanol to the alkenic bond are proposed [15]. In photochemical addition of methanol and 2,2,2-trifluoroethanol to **1a** and its methoxy derivatives [16–18], *m*-methoxy substituents were more reactive than others, since the photochemically generated carbocation intermediate was stabilized by excited-state electron-donating ability of methoxy substituents. Similarly efficient water addition was observed in hydroxystilbenes and 3-hydroxystyrylnaphthalenes [19–21] promoted by solvent-mediated excited-state proton transfer (ESIPT) from the phenolic hydroxyl group. Aromatic alkenes with electron-donating substituents undergo photohydration in aqueous sulfuric acid *via* S_1, if other photoprocesses do not compete favourably [22]. General acid catalysis and linear Brønsted plots are observed in these reactions [23]. Photochemistry of *trans*-anethole (**1c**) was also investigated in detail by several research groups [24–33]. Its excited-state behaviour is prototypical of simple conjugated alkenes, undergoing both unimolecular (*cis-trans* isomerization) and bimolecular (dimerization, solvolysis and electron transfer) reactions.

Cyclodextrins (CDs), form host–guest complexes with different guest molecules of appropriate size resulting in modified reactivity and selectivity [34]. In many cases, the photoreactivity of substrates is altered as the reaction is sensitive to CD nanoenvironment and this aspect has been exploited extensively [35–42]. CDs were also employed as photoreactors for solvolysis reactions such as photohydration of non-conjugated aryl olefin bichromophores. Upon inclusion into CD cavities, photocyclization for 2-allylphenol, 2-allylaniline and di-π-methane photorearrangement for 2-allylanisole, occurring in homogeneous solvents, are strongly depressed and photohydration of the acyclic olefin moiety is found to be the predominating photoprocess (*via* excited intramolecular interactions) [43,44]. Enantiodifferentiating photoaddition of methanol to 1,1-diphenylpropene in organic–aqueous binary media was reported [45]. [2+2] Photocycloaddition of a symmetrical stilbene derivative yielded a mixture of dimers in presence of γ-CD but in β-CD resulted only its *trans–cis* isomerization [46–49]. However, systematic reports are lacking on photosolvolysis of **1a**, **1b** and **1c** in presence of cyclodextrin under photochemical conditions. In the present work, we report the photohydration behaviour of stilbene **1a** and its 3-methoxy derivative **1b** in presence of cyclodextrin acting as a nanoregulating vessel. For comparison, photobehaviour of an unsymmetrical arene **1c** is also studied.

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2. Materials and methods

2.1. General

Cyclodextrins α-CD, γ-CD (American Maize Products, Indiana), β-CD (Aldrich) and HP-β-CD (American Maize Products, Indiana) were used as-received. Trimethyl-β-cyclodextrin was prepared by reported procedure [50]. *trans*-Stilbene (**1a**) and *trans*-anethole (**1c**) were purchased from Merck. *trans*-3-Methoxystilbene (**1b**) was synthesized by reported procedure [17]. All the solvents used in the reactions were distilled and purified prior to use. Double distilled water was used for all reaction.

Nuclear magnetic resonance (NMR) spectra were acquired on a Bruker DRX-300 (300 MHz) instrument using TMS as internal standard. Gas chromatographic analysis was performed in Shimadzu 17A instruments, using ZB-5, 30 meter capillary column equipped with FID detector and high purity nitrogen as carrier gas. GC–MS analysis was performed in Thermo Fennigan instrument using RX-5, 30 meter capillary column and high purity helium as carrier gas. Absorption spectra were recorded in JASCO-550 UV–Vis spectrophotometer. Induced circular dichroic spectra are recorded in a JASCO J-810 spectropolarimeter, furnished with a 150 W xenon lamp. The measurements were performed under nitrogen flux at $25 \pm 1\,^{\circ}C$ and the samples contained in a quartz cuvette of path length of 0.1 cm.

2.2. Preparation and characterization of cyclodextrin complexes

1:1 CD complexes were prepared by mixing an equlimolar amount of the substrate **1a**, **1b** or **1c** and the appropriate CDs with little amount of water, stirred for 12 h, filtered and washed with small amount of ether to remove any uncomplexed substrate. This complex was dried in an air oven at 50 °C for 6 h and employed for photolysis. In case of higher order complexes excess proportion of guest or CDs is taken. A known amount of the solid complex was dissolved in a minimum amount of distilled water and the guest was extracted with warm chloroform. The amount of the recovered guest estimated gravimetrically after the removal of the chloroform. The values are closer to unity indicating that a 1:1 complex is formed in all the cases.

Binding constants of inclusion complexes were calculated by using Benesi–Hildebrand [51] method. Solution of substrates **1a–c** was prepared by dissolving a known mass in 10% acetonitrile–water mixture. 0.1 mL of this stock solution was transferred into 10 mL volumetric flasks, the respective cyclodextrin (from a 0.01 M from freshly prepared stock solution in water) was added, diluted to 10 mL with water and stirred for 6 h to ensure equilibrium upon complexation. Absorption spectra were recorded at room temperature by monitoring the absorption maximum for substrate **1a–c** at 300, 296 and 258 nm, respectively. Existence of an inclusion complex inside the cyclodextrins was evidenced by the measurement of formation constant using Benesi–Hildebrand method (Supplementary data). The formation constant values ($dm^3\ mol^{-1}$) for **1a**, **1b** and **1c** with various CDs are listed in Table 1. These higher formation constant values indicate the formation of strong inclusion complexes **1a–c** with all CDs.

Complex stoichiometry was obtained by the continuous variation method, named as Job's plot, based on the difference in absorbance changes ($\Delta OD = A_0 - A$) of the guest (**1a–c**) observed in the presence of cyclodextrin [52–54]. For this method a series of solutions was prepared and submitted to a spectrometer that contains the same total number of moles of the two (both **1a–c** and CD), but differs in the molar fraction of each. By this method it shows, all the guest **1a–c** forms 1:1 complex with all cyclodextrin (Supplementary data).

Table 1
Formation constants values ($dm^3\ mol^{-1}$) for **1a**, **1b** and **1c** with different cyclodextrins.[a].

Olefin	Cyclodextrin			
	α-CD	β-CD	γ-CD	Trimethyl-β-CD
1a[b]	146	322	409	675
1b[c]	665	725	401	720
1c[d]	281	695	892	–

[a] Formation constants are calculated using Benesi–Hildebrand method [51].
[b] [**1a**] = 4×10^{-5} M, [CD] = 4×10^{-5} to 8×10^{-4} M.
[c] [**1b**] = 4×10^{-5} M, [CD] = 4×10^{-5} to 8.8×10^{-4} M.
[d] [**1c**] = 7×10^{-4} M, [CD] = 7×10^{-4} to 13.2×10^{-3} M.

The mode of inclusion of **1a–c** inside β-CD cavity was also evident from ICD spectra. ICD spectra (Supplementary data) shows a peak around 290–310 nm for **1a**, **1b** and 260 nm for **1c** which is due to π–π^* transition of phenyl group in **1a–c**. In all the three substrates positive ICD bands were observed since the electronic transition dipole moment of π–π^* transition of **1a–c** lies parallel to the symmetry axis of the β-cyclodextrin cavity (axial inclusion).

α-, β- and γ-CD complexes of substrate **1a–c** were also characterized by their ^1H–^1H NOESY spectra recorded in DMSO-d_6 at 25 °C on a Bruker 300 MHz instrument. 5×10^{-2} M of 1:1 complex was used to record the NOESY spectra with mixing time 300 ms. (Cross-peaks appeared between the CDs inner H3, H5 protons and corresponding aromatic protons of **1a–c** confirms the formation of inclusion complexes inside the CD cavity; Supplementary data.)

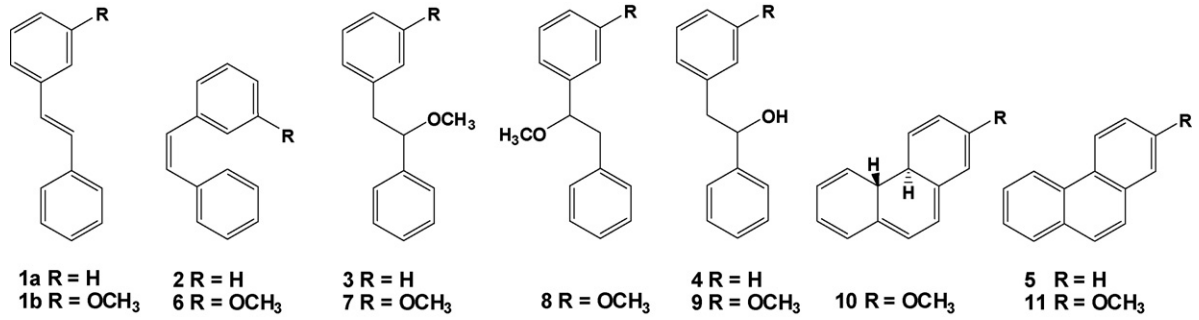
Energy minimized geometries of the complexes were obtained using molecular mechanics calculations by Accelrys Insight 2000 molecular modeling package on a Silicon Graphics IRIX workstation [55–57]. All minimizations were done with program Discover using a CVFF force field. The conjugate gradient algorithm was applied for minimization. Default values were assumed for all parameters. The initial structure of guest molecules (*trans*-stilbene (**1a**), *trans*-3-methoxystilbene (**1b**) and *trans*-anethole (**1c**)) and cyclodextrin were built in a Builder module from standard fragments and minimized initially. Calculations are done in a vacuum and structures are minimized using CVFF force field and RMS derivative 0.001 was achieved in each case. Complexation energies were calculated using the following equation $\Delta E = \Delta E_{complex} - \Delta E_{host} - \Delta E_{guest}$ (Supplementary data).

2.3. General procedure for photolysis of *1a–c* in solution and as cyclodextrin complex

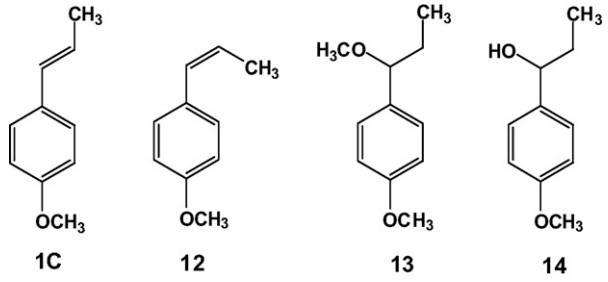
For solution photolysis 0.05 mmol of **1a**/**1b**/**1c** in 10 mL of the respective solvents was irradiated in nitrogen atmosphere at 312 nm. Microcrystalline CD complexes of **1a–c** (150 mg) were dissolved in 25 mL of respective solvents in Quartz tubes and degassed with high purity nitrogen gas for 30 min. The tubes were then placed in a HEBER multilamp photoreactor fitted with (4×12 W) 312 nm lamps and irradiated. All the solid-state photoreactions of CD complexes were carried out by placing the solid complexes in Quartz tubes, degassed with nitrogen gas and then sealed and then irradiated with periodic rotation for every 30 min. After irradiation, the products were extracted with hot chloroform and the resultant reaction mixture was analyzed by gas chromatography. Products were identified by coinjection with authentic samples and GC–MS and were also characterized by ^1H and ^{13}C NMR.

3. Results and discussion

CD complexes were prepared by mixing equimolar amounts of **1a–c** and the appropriate CD in aqueous solution. The formation of CD inclusion complexes was evident from host–guest



Scheme 1. Structures of products obtained in photolysis of **1a** and **1b**.



Scheme 2. Structures of products in photolysis of **1c**.

ratio, Job's plots, ICD spectra and dissociation constants using Benesi–Hildebrand [51] method and the mode of inclusion was identified by ^{1}H–^{1}H NOESY spectra as well as energy minimization studies (given as Supplementary data). The reaction mixture was irradiated at 312 nm (which excites the π, π* state of the olefinic double bond). The photoproducts, analyzed by GC, are listed in Schemes 1 and 2.

The reactions are also carried out inside the hydrophobic environment of CDs in water medium resulting in interesting selectivities. The results of the photoreaction of **1a–c** in different cyclodextrins, both in solution and also in the solid state are presented in Tables 2–4. Irradiation of **1a** in isotropic solvents had resulted mainly in *trans* to *cis* isomerization along with cyclization giving phenanthrene **5** [11]. In methanol medium (entries 1 and 3, Table 2) methanol addition product **3** was also formed. In both binary mixtures isomerization yield had decreased than in pure solvents.

An interesting change in photoreactivity was noticed when CD complexes of **1a** and **1b** were irradiated in aqueous media. A dramatic reduction in *trans* to *cis* isomerization was observed. In addition to **5**, photohydrated product **4** [60] was also formed in all cyclodextrins with secondary hydroxyl groups.

Higher conversion of **1a**/β-CD complex to **4** is noticed compared to isotropic media. Cyclization and isomerization are suppressed.

Table 2
Products distribution upon photolysis of *trans*-stilbene **1a** in solution and in different cyclodextrins.[a]

Entry	Medium	Time (h)	**1a**	**2**	**3**	**4**[b]	**5**
01	MeOH	4	11	70	9	–	10
02	ACN	4	16	60	–	–	24
03	MeOH:H_2O (50%, v/v)[c]	4	30	25	19	–	26
04	ACN:H_2O (50%, v/v)[c]	4	30	42	–	–	28
05	α-CD/H_2O	10	39	11	–	11	39
06	β-CD/H_2O	10	29	12	–	35	24
07	β-CD/H_2O	20	33	8	–	41	18
08	γ-CD/H_2O	10	12	18	–	31	39
09	γ-CD/H_2O (1:2)[d]	10	29	19	–	32	20
10	HP-β-CD/H_2O	10	53	4	–	24	19
11	Trimethyl-β-CD/H_2O	10	87	6	–	–	7
12	α-CD/solid	75	71	13	–	–	16
13	β-CD/solid	75	90	5	–	–	5
14	γ-CD/solid	75	75	21	–	–	4

[a] Reaction mixtures are analyzed by GC (error limit ±3%) and products are characterized by GC–MS; yield of photoproducts are normalized to 100. For structures of **1a**, **2–5**, refer Scheme 1.
[b] Characterized by ^{1}H and ^{13}C NMR [58].
[c] Solvent ratio.
[d] Host–guest ratio of CD and **1a**.

Table 3
Products distribution upon photolysis of *trans*-3-methoxystilbene **1b** in solution and in different cyclodextrins.[a,b].

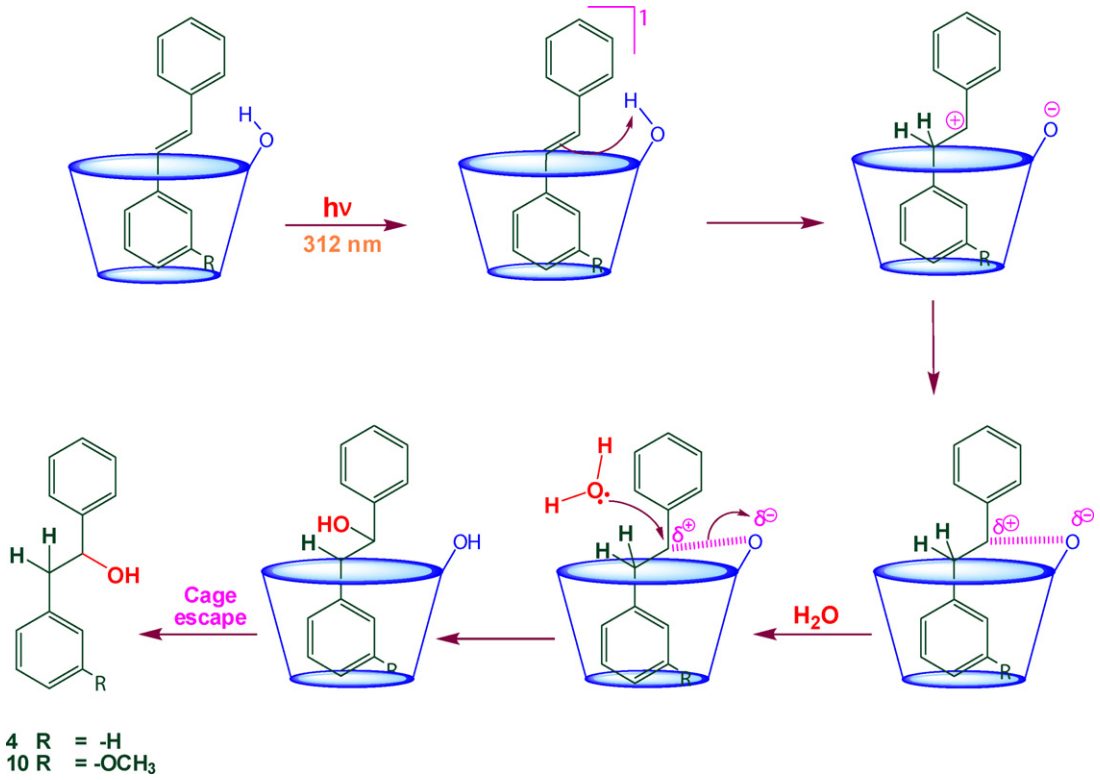
Entry	Medium	Time (h)	**1b**	**6**	**7**	**8**	**9**	**10**	**11**
01	ACN	4	4	14	–	–	–	24	58
02	MeOH	4	9	65	6	2	–	7	11
03	ACN:H_2O (50%, v/v)	4	5	27	–	–	–	23	45
04	MeOH:H_2O (50%, v/v)	4	12	56	–	–	–	10	22
05	α-CD/H_2O	10	–	74	–	–	18	2	6
06	β-CD/H_2O	10	2	3	–	–	42	10	43
07	γ-CD/H_2O	10	7	17	–	–	10	24	42
08	Trimethyl-β-CD/H_2O	10	14	59	–	–	–	8	19
09	α-CD/solid	75	63	6	–	–	–	19	12
10	β-CD/solid	75	65	25	–	–	–	2	8
11	γ-CD/solid	75	69	18	–	–	–	5	8

[a] Reaction mixtures are analyzed by GC (error limit ±3%) and products are characterized GC–MS. For structures of **1b** and **6–11** refer Scheme 1; yield of photoproducts are normalized to 100.
[b] Host–guest ratio of CD and **1b** is 1:1.

Table 4
Products distribution upon photolysis of *trans*-anethole **1c** in solution and in different cyclodextrins.[a,b].

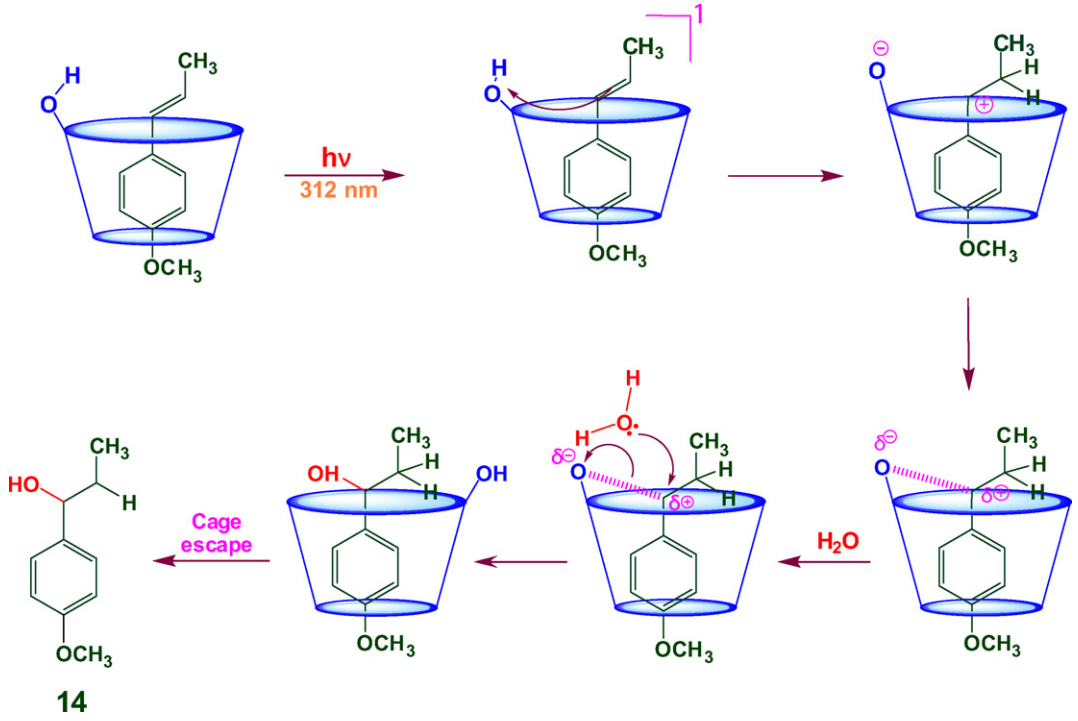
Entry	Medium	Time (h)	**1c**	**12**	**13**	**14**[d]
01	ACN	2	66	34	–	–
02	MeOH	2	66	22	12	–
03	*n*-Hexane	2	72	28	–	–
04	ACN:H_2O (50%, v/v)[c]	2	68	32	–	–
05	MeOH:H_2O (50%, v/v)[c]	2	55	25	19	1
06	α-CD/H_2O	10	–	11	–	89
07	β-CD/H_2O	10	9	11	–	80
08	β-CD/H_2O:MeOH (50%, v/v)[c]	10	–	–	76	24
09	β-CD/H_2O:ACN (50%, v/v)[c]	10	7	12	–	81
10	β-CD/H_2O:ACN (70%:30%, v/v)[c]	10	–	–	–	100
11	β-CD/H_2O:ACN (80%:20%, v/v)[c]	10	–	–	–	100
12	γ-CD/H_2O	10	30	16	–	54
13	α-CD/solid	25	65	35	–	–
14	β-CD/solid	25	13	87	–	–
15	γ-CD/solid	25	24	76	–	–

[a] Reaction mixtures are analyzed by GC (error limit ±3%) and products are characterized GC–MS; yield of photoproducts are normalized to 100. For structures of **1c**, **12–14** refer Scheme 2.
[b] In all CD complexes, H:G ratio is 1:1.
[c] Solvent ratio.
[d] Characterized by ^{1}H and ^{13}C NMR [59].



Scheme 3. Proposed mechanism for photohydration of **1a** and **1b** within CD nanocavity.

The yield of **4** is lower with other cyclodextrins. In α-CD and HP-β-CD, photohydration is not efficient compared to β- and γ-CDs and this is in accordance with results already reported in non-conjugated aryl olefins [43,44]. The presence of excess **1a** in γ-CD complex does not affect the hydration process and no dimerization is observed [48]. The crucial role of secondary hydroxyl groups of CD in photolysis is evident in presence of trimethyl-β-CD, wherein no solvent addition product is obtained. Photolysis of solid CD complexes of **1a** has resulted in significant reduction in photoreactivity and only **2** and **5** are formed. This may be attributed to the restricted mobility and reduced absorption of light (due to scattering) in solid state compared to solution irradiation. The higher ratio



Scheme 4. Proposed mechanism for photohydration of **1c** within CD nanocavity.

of **5** in the conversion products (despite the low yield of **5** in solid-state reactions) particularly in α-CD (compared to β- and γ-CDs) is attributed to the tighter fit of substrate **1a** in α-CD. This restricts the reverse process, namely, conversion of *cis*-isomer **2** back to the original *trans*-isomer **1a**, enabling the former to cyclize readily to give **5**.

In photolysis of *trans*-3-methoxystilbene **1b**, various photoproducts were formed in methanol medium which are in accordance with reported results [16–18]. As with **1a**, isomerization and cyclization are the major photoprocesses in isotropic media (Table 3). In photolysis of **1b**/CD complexes in aqueous medium, in addition to isomerized **6** and cyclized products **10** and **11**, hydration product **9** is also formed in considerable amounts. β-CD gives better yield of **9** than the other CDs as in **1a**. On the other hand, γ-CD gives poor yield of **9** and this may be due to its weaker binding with **1a**/**1b**. In solid-state irradiation of **1b**/CD, only primary photoprocesses such as isomerization and cyclization are found to be significant.

To justify that the strong binding of substrate into CD cavity is essential for photohydration, studies are also extended to photolysis of an unsymmetrical arene namely *trans*-anethole **1c**. Presence of *p*-methoxy group in **1c** is expected to form a stronger complex which brings the double bond nearer to the secondary hydroxyl rim of cyclodextrin.

In photolysis of **1c** (Scheme 2), isomerization to *cis*-anethole **12** is the major photoprocess in isotropic media, as reported earlier [22]. In methanol medium, small amount of methanol addition product **13** is formed. In methanol–water (1:1) binary mixture, along with **13**, trace amount of hydration product **14** [59] is also observed. This is not observed in acetonitrile–water mixture. However, an interesting change in photoreactivity is noticed in irradiation of **1c**/CD complex in aqueous medium. While, isomerization has considerably decreased, hydration product (Markovnikov adduct **14**) is formed in good yield in all the three CDs (Table 4). With β-CD, photolysis in acetonitrile–water leads to 100% yield of **14** and other photoproducts are totally suppressed. Photolysis in methanol–water medium in presence of β-CD results in higher yield of methanol addition product **13** along with **14**. When the same CD complexes are irradiated in solid state without water, only isomerization is noticed.

Photohydration products **4** and **14** are reported for the first time in photolysis of **1a** and **1c** respectively in cyclodextrin medium. Hence, though they are known compounds their ^{1}H and ^{13}C NMR data are reported [58,59] to ensure unambiguous assignment. Their photostability under the present experimental conditions (both in presence and absence of CDs) is confirmed by analyzing during different irradiation times (2, 5 and 10 h) thus ruling out possible thermal and photochemical reversibility during photolysis. These results suggest that the reported yields are proportional to the addition rate.

The formation of the hydration product inside CD nanocavity in aqueous medium is rationalized by proposing the following mechanism (Schemes 3 and 4).

The mode of inclusion of **1a**–**c** inside CD cavity is supported by ^{1}H–^{1}H NOESY spectroscopy (Supplementary data). In case of **1a**, as both the rings are symmetrical, one of it is included inside the cavity. But in the case of **1b**, presence of cross-peaks between H3, H5 protons of CDs and methoxy substituted phenyl ring protons reveal that the substituted phenyl ring penetrates deeper inside the cavity. The same type of inclusion is also evident in **1c**. These modes of inclusion of **1b** and **1c** are also supported by energy minimization studies. In **1b**, both in β- and γ-CD, methoxy substituted phenyl ring goes inside the cavity as this mode has lower energy. Similarly in **1c** also, methoxy substituted phenyl ring goes inside the cavity with a lower complexation energy (Supplementary data). Binding constant values of **1a**, **1b** and **1c** show that they form stronger complexes with all the CDs. Formation of 1:1 complex in all the cases is also inferred from Job's plot of continuous variation.

Irradiation at 312 nm results in short-lived singlet excited state of **1a**–**c**, which abstracts a proton from the secondary hydroxyl group (C2) of CD. It is relevant to note that among the three CD hydroxyl groups (C2, C3 and C6), the C2 hydroxyls are more acidic (pK_a value is 12.1) [60,61] than the others. The resulting carbocation is stabilized by secondary hydroxyl groups present in wider rim of CD cavity. This stabilization may be either an ionic linkage or hydrogen bonding type [40,62]. The CD-stabilized carbocation is further attacked by the solvent, resulting in hydration across the alkenic bond of the **1a**–**c**. Absence of hydration product in photolysis with trimethyl-β-CD (Table 2, entries 11 and Table 3, entry 8) clearly suggests an active participation of CD's secondary hydroxyl group in the excited-state proton transfer process. Similarly the role of water in photohydration is evident in the absence of hydration products in solid-state irradiation of CD complexes of **1a**–**c**.

4. Conclusion

In conclusion, a novel photohydration of aryl olefins, namely *trans*-stilbene **1a**, *trans*-3-methoxystilbene **1b** and *trans*-anethole **1c** is achieved inside CD nanocavities in aqueous medium. This takes place only in presence of CDs and is reported for the first time, though the system was investigated extensively in previous literature [48–51]. This photohydration is proposed to occur *via* an excited-state proton transfer resulting in a carbocation intermediate which is stabilized by the CD secondary hydroxyl groups. *trans*-Anethole undergoes more efficient photohydration than *trans*-stilbene and *trans*-3-methoxystilbene, which is in accordance with the previously reported reactivity order, *i.e.*, arylpropene > stilbene [17]. β-CD enhances photohydration more efficiently than other CDs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.05.011.

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[58] Photoproduct **4** is characterized by NMR and GC–MS analysis. 1,2-Diphenylethanol (**4**): ^{1}H NMR (300 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm) 3.00 (m, 2H), 4.87 (dd, J = 8.2 and 5.2 Hz, 1H), 7.14–7.29 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm) 46.0, 125.8, 126.5, 127.5, 128.3, 128.4, 129.4, 138.0, 143.7. GC–MS: m/z 198.3 (M+).
[59] Photoproduct **14** is characterized by NMR and GC–MS analysis. 1-(4-Methoxyphenyl)propan-1-ol (**14**): ^{1}H NMR (300 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm) 0.88 (t, J = 7.2 Hz, 3H), 1.68–1.82 (m, 2H), 3.80 (s, 3H), 4.59 (t, J = 6.6, 1H), 6.87 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm) 10.2, 31.7, 55.2, 75.6, 113.7, 127.2, 136.7, 158.9. GC–MS: m/z 166.0 (M+).
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