Effect of β-Cyclodextrin on the Thermal Cis−Trans Isomerization of Azobenzenes

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The cis−trans thermal isomerization of *p*-methyl red **(1),** *o*-methyl red **(2),** and methyl orange **(3)** was inhibited by β-cyclodextrin (β-CD) at constant pH. Their isomerization rate decreased 4, 8, and 1.67 times, respectively, in a solution containing 0.01 M β-CD. This effect can be attributed to the formation of an inclusion complex between the substrate and β-CD which hinders the rotation of the N=N bond. The isomerization rate of methyl yellow **(4),** 4-(dimethylamino)-4′-methoxyazobenzene **(5),** and naphthalene-1-azo[4′-(dimethylamino)benzene] **(6)** was not affected by β-CD due to the presence of an organic cosolvent in the solution which displaces the azobenzene from the cavity, and the complex formed is probably equatorial. In addition, the transition state for the isomerization of compounds **1**−**3** involves rotation and that of **4**−**6**, which have only electron-donating groups, inversion. This latter process brings about less volume change than rotation so it is less hindered by the complexation with β-CD.

Introduction

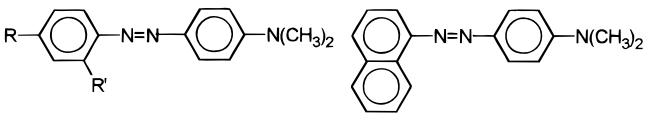
Cyclodextrins are largely used as hosts for organic molecules. They possess a hydrophobic cavity due to a cyclic arrangement of six (α-CD), seven (β-CD), and eight (γ-CD) D-(+)-glucopyranose units, linked by α-(1,4) glycosidic bonds. The macrocycle can be described as a truncated cone, the narrow rim bearing the primary −OH groups and the wide rim the secondary −OH groups.[1]

The binding of a molecule or ion to the cavity of a cyclodextrin results in the formation of an inclusion complex that involves relatively weak nonspecific interaction. The association of the guest molecule normally occurs by partial or full fitting of the cavity. The main driving forces for substrate and host binding are as follows: (a) Van der Waals forces, (b) hydrophobic interactions, and (c) hydrogen bonding. The inclusion phenomenon produces changes in the processes undergone by the guest due to steric effects as well as changes in the microenvironment.

Several kinetic and equilibrium studies have been reported on the inclusion complexes of cyclodextrins with azo dyes of variable structural complexities.[2,3] Azobenzene derivatives exhibit photoinduced reversible cis−trans isomerism, and the formation of an inclusion complex of azobenzene with α-CD or β-CD leads to a decrease in the quantum yield for the trans−cis isomerization of azobenzene.[4] The cis−trans photoisomerization of *p*-methyl red has been investigated in the host−guest Langmuir−Blodgett films prepared with amphiphilic β-CD derivatives.[5,6]

The isomerization of azobenzenes is a subject of great current interest due to their possible application in energy storage systems or in photochemical devices.[7] The thermal *Z*−*E* isomerization of *p*-aminoazobenzenes proceeds by two routes as shown in Scheme 1: (a) inversion of one or both of the nitrogen atoms through a linear (sp-hybridized) transition state in which the double bond is retained and (b) disruption of the nitrogen−nitrogen p-bond, with rotation around the remaining σ-bond giving the *E* isomer (rotation mechanism).[8,9]

Since the isomerization reaction takes place with a considerable volume change, we considered it of interest to determine the effect of β-cyclodextrin (β-CD) on the thermal cis−trans isomerization of azo compounds **1**−**6**, and these results are reported here.



1-5 **6**

1: R: -COO⁻, R': H , p-Methyl red.

2: R: H, R' : -COO⁻, o-Methyl red.

3: R: SO_3^- , R' : H, Methyl orange.

4: R: H, R': H, Methyl yellow.

5: R: -OMe, R': H, 4-dimethylamino-4'-methoxyazobenzene.

6: Naphthalene-1-azo-(4'-dimethylaminobenzene)

Results and Discussion

Equilibrium Studies. The spectrum of compounds **1**−**3** was determined in water, those of **4** and **5** in ethanol−water 20/80 v/v, and the one for **6** in ethanol−water 50/50 v/v. The solutions were prepared with NaOH at the same concentration used for the kinetic studies (see below). The fact that compounds **4**−**6** are too

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(2) Clarke, J. R.; Coates, J. H.; Lincoln, S. F. *Carbohydr. Res.* **1984**, *127*, 181−191.
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(6) Yabe, A.; Kawabata, Y.; Niino, M.; Ouchi, A.; Takahashi, H.; Tamura, S.; Tagaki, W.; Nakahara, H.; Fukuda, K. *Thin Solid Films* **1988,** *160,* 33
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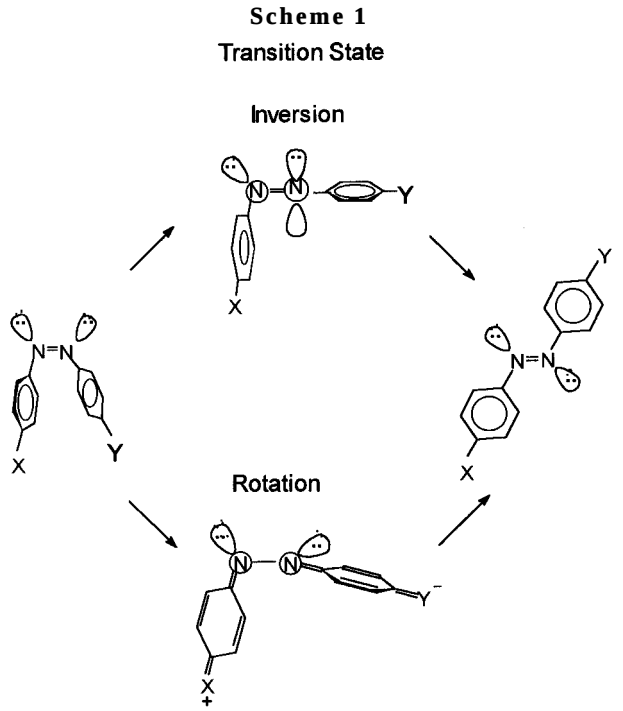
Scheme 1



insoluble in water precludes the determinations without an organic cosolvent. In all cases the addition of β-CD to the diluted solution of the different substrates shifted the maximum wavelength to the blue and decreased the extinction coefficient. The spectrum of compound **5** was also measured in water−acetonitrile 80:20 v/v containing NaOH 0.1 M where it has λ_{max} 444 nm and a shoulder at 412 nm. The ratio of extinction coefficients is 1.21, and the addition of 0.01 M of β-CD lowered this ratio to 1.07. The changes in the spectrum in the presence of β-CD show that there must be some specific interaction between compounds **1**−**6** and β-CD because a similar addition of soluble starch did not modify the spectrum. A well-defined isosbestic point was not obtained in any case, suggesting that there is more than one type of interaction.[10] The spectrum for compound **3** is shown in Figure 1.

If the interaction is of 1:1 stoichiometry, the system can be described as in eq 1 where S, β-CD, and S·β-CD

$$S + \beta\text{-CD} \overset{K_{11}}{\rightleftharpoons} S\cdot\beta\text{-CD} \qquad (1)$$

stand for the substrate molecules, β-cyclodextrin, and the β-cyclodextrin−substrate complex, respectively. The change in absorbance, ΔA, at constant wavelength is given by eq 2 which can be rearranged to eq 3 where

$$\Delta A = \frac{\Delta\epsilon_{11} K_{11} [\beta\text{-CD}]_o [S]_o}{1 + K_{11}[\beta\text{-CD}]_o} \qquad (2)$$

$$\frac{[\beta\text{-CD}][S]_o}{\Delta A} = \frac{1}{K_{11}\Delta\epsilon_{11}} + \frac{[\beta\text{-CD}]_o}{\Delta\epsilon_{11}} \qquad (3)$$

$[\beta\text{-CD}]_o$ and $[S]_o$ represent the initial concentration of β-cyclodextrin and that of the substrate, respectively; $\Delta\epsilon_{11}$ is the difference in the molar absorptivity between the free and complexed substrate. From the slope and intercept ratio of a plot according to eq 3, the equilibrium constant K_{11} for the association of the substrate with CD (eq 1) is obtained. Alternatively, a nonlinear fit of the data to eq 2 yields K_{11} and both methods should give the same results.[10] Only the data for compounds **1**−**3** fit to eqs 2 and 3 but for compound **1** and **3** the change in the wavelength of analysis yields significantly different equilibrium constants (Table 2) indicating that more than one type of complex is formed. In a previous study on the interaction of *p*-methyl red with α- and β-CD at pH 9.5, the same equilibrium constant was obtained at different

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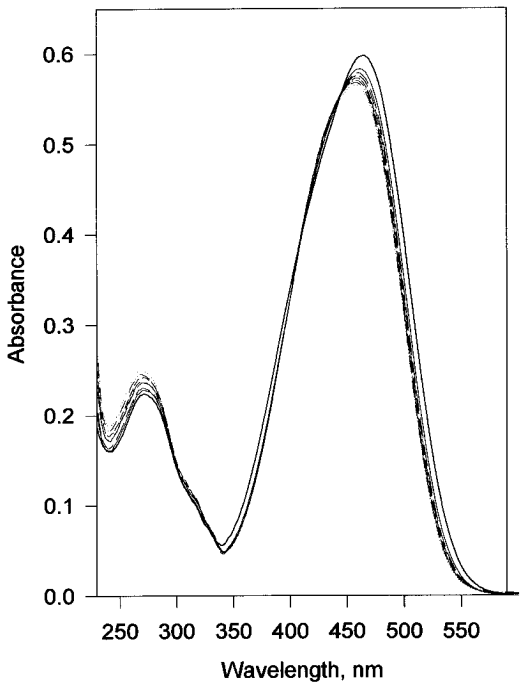


Figure 1. Spectra of **3** in the presence of β-CD. Temperature: 25 °C; solvent: H_2O; [methyl orange] = 6.8×10^{-5} M; [β-CD] = 0 (—) to 10 (···) mM; NaOH 0.1 M.

Table 1. Effect of β-Cyclodextrin on Cis−Trans Isomerization of Azobenzenes[a]

[β-CD], M	*o*-methyl red[b] k_{obs}, s^{-1}	*p*-methyl red[c] k_{obs}, s^{-1}	methyl orange[c] k_{obs}, s^{-1}
0.0000	0.297	0.100	0.179
	0.053[d]		
0.0001	0.216	0.0606	
0.0002			0.173
0.00025		0.063	
0.0003			0.170
0.0005	0.190		0.165
0.0008			0.161
0.0010	0.170	0.054	0.159
0.0020		0.039	
0.0030	0.117	0.0328	0.147
0.0040		0.0326	0.129
0.0050	0.090	0.024	0.127
0.0060		0.0247	0.122
0.0075	0.084		
0.0090			0.114
0.0100	0.034	0.024	0.109
	0.055[d]		
	0.239[e]	0.083[e]	
0.0120		0.022	0.101
0.0150	0.035	0.0231	0.098
0.0170		0.0203	

[a] Temperature, 25 ± 0.1 °C; ionic strength 0.20 M; rate constants are average of at least three determinations, and the mean deviation is less than 5%. [b] [NaOH], 0.01 M; solvent, water. [c] [NaOH], 0.1 N; solvent, water. [d] Solvent, EtOH/H_2O (20:80); [NaOH], 0.01 M. [e] Solvent, EtOH/H_2O (50:50); [NaOH], 0.01 M. [e] Soluble starch in concentration equivalent to the β-CD.

Table 2. Calculated Rates and Equilibrium Constant for the Cis−Trans Isomerization of Azobenzenes 1−6

compd	k_{ct}, s^{-1}	k_{ct}^{CD}, s^{-1}	K_c, M^{-1} [d]	K_{11}, M^{-1} [e]
p-methyl red[a]	0.100	0.025	4400 ± 1400	1300 ± 300[f]
				400 ± 100[g]
o-methyl red[a]	0.297	~0	654 ± 150	204 ± 35[h]
methyl orange[a]	0.179	0.072	105 ± 20	893 ± 80[i]
				699 ± 75[j]
				484 ± 78[k]
methyl yellow[b]	0.0088	0.0081[l]		
		0.0061[m]		
4-(dimethylamino)-4′-methoxyazobenzene[b]	0.0018	0.0021[m]		
naphthalene-1-azo-[4′-(dimethylamino)benzene][c]	0.002	0.0017[m]		

[a] Temperature, 25 ± 0.1 °C; solvent, water. [b] Solvent, H_2O/EtOH (80:20). [c] Solvent, H_2O/EtOH (50:50). [d] Kinetically determined from the fit to eq 6. [e] Spectrophotometric value determined from the fit to eq 2 and 3. [f] Measured at $\lambda = 500$ nm. [g] $\lambda = 424$ nm. [h] $\lambda = 479$ nm. [i] $\lambda = 510$ nm. [j] $\lambda = 480$ nm. [k] $\lambda = 465$ nm. [l] Observed rate constant in a solution containing β-CD = 0.006 M. [m] Observed rate constant in a solution containing β-CD = 0.01 M.

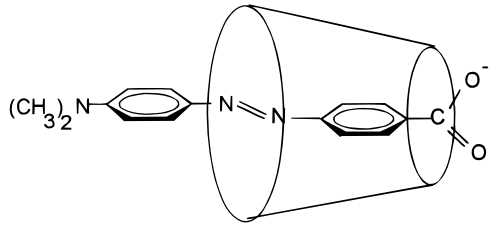


Figure 2. Schematic representation of one of the 1:1 complexes of **1** with β-CD (carboxylate inclusion).

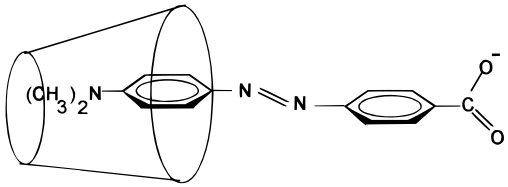


Figure 3. Schematic representation of one of the 1:1 complexes of **1** with β-CD (dimethylamino inclusion).

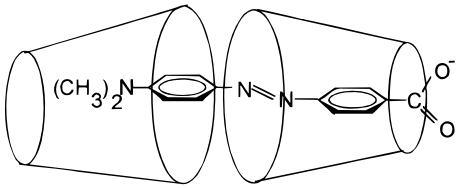


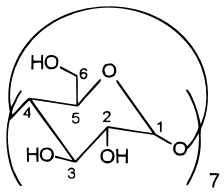
Figure 4. Schematic representation of the 1:2 complex of **1** with β-CD.

wavelengths[11] and the values of K_{11} reported, i.e., 3810 M^{-1} [10] and 6230 M^{-1},[12] are significantly higher than those of this work. The differences may be attributed to the fact that our values were determined at higher pH (see the Experimental Section) and under these conditions a significant amount of β-CD is ionized because its pK_a is 12.3.[13] In addition, our spectrophotometric values are apparent equilibrium constants since there is evidence that more than one type of complex is formed. Complexes of the type shown in Figures 2 and 3 or complexes of 1:2 stoichiometry such as the one shown in Figure 4 may also be formed. The lack of isosbestic points in the spectra is consistent with the formation of complexes of stoichiometry higher than 1:1. If complexes of 1:2 stoichiometry were formed the change in absorption with the addition of β-CD would be given by eq 4.[10]

$$\Delta A = \frac{[S]_o[\beta\text{-CD}]_o K_{11}(\Delta\epsilon_{11} + \Delta\epsilon_{12}K_{12}[\beta\text{-CD}])}{1 + K_{11}[\beta\text{-CD}]_o(1 + K_{12}[\beta\text{-CD}]_o)} \quad (4)$$

The fact that the data for **1**−**3** give a reasonable fit to eqs 2 and 3 indicates that in the range of β-CD concentration used $K_{12}[\beta\text{-CD}] < 1$. The different values of the equilibrium constants obtained at different wavelengths may be due to different $\Delta\epsilon_{11}/\Delta\epsilon_{12}$ ratios. Attempts to fit the data to eq 4 failed. The reason may be that eq 4 has four adjustable parameters, namely $\Delta\epsilon_{11}$, $\Delta\epsilon_{12}$, K_{11}, and K_{12}, and the number of data points was 10−12. It was not possible to get more data because the maximum change in optical density (ΔA) which is obtained for solutions containing β-CD 0.01 M is smaller than 0.1.

NMR Determinations. To obtain more direct evidence for the β-CD inclusion complex structure, we measured the ^{1}H-NMR spectra of **1** with and without β-CD in D_2O/NaOD 0.1 M. The chemical shifts were determined relative to water which appears at 4.63 ppm relative to external tetramethylsilane. In Table 3 are tabulated the changes in chemical shift ($\Delta\delta$) of **1** and CD in the mixed solutions relative to their values in separated solutions. The NMR spectrum of pure β-CD consists of peaks due to five kinds of protons H-1 (4.78 ppm, doublet), H-3 (3.75 ppm, triplet), H-5,6 (3.64−5.58 ppm, unresolved), H-2 (3.35 ppm doublet of doublets), and H-4 (3.26 ppm, triplet).[14] The numbering of protons is indicated in structure **7**.



7

There is a significant upfield shift of the H-3 and H-5 signal of β-CD (the two hydrogens inside the cavity) and H-6. This shift can be attributed to diamagnetic anisotropy of the benzenoid moiety of the included azo compounds. The resonances of the H-1, H-2, and H-4 located outside of the β-CD torus are relatively unaffectd ($\Delta\delta$ < 0.01 ppm) by the addition of the guest suggesting that the association does not take place at the exterior of the torus. Since splitting of the β-CD signals is not observed,

(11) Tawarah, K; Khouri, S. *Carbohydr. Res.* **1993**, *245*, 165.
(12) Tawara, K. *Ber. Bunsen Ges.* **1993**, *97*, 727.
(13) Van Etten, R. L.; Clowes, G. A.; Sebastian, J. F.; Bender, M. L. *J. Am. Chem. Soc.* **1967**, *89*, 3253.
(14) The hydrogen has been assigned on the basis of literature data: Guo, Q-X.; Li, Z.-Z.; Ren, T.; Zhu, X-Q.; Liu, Y.-C. *J. Incl. Phenom. Mol. Rec.* **1994**, *17*, 149.

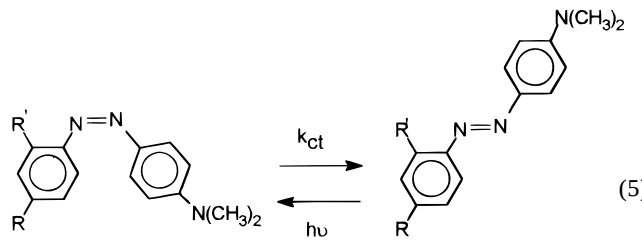
Table 3. Chemical Shift Variations ($\Delta\delta$) in ppm of the Cyclodextrin and *p*-Methyl Red Protons Induced by Complexation at 300 K

p-methyl red	β-CD[a]	$\Delta\delta$
H-5,5′		0.05
H-4,4′		0.03
H-3,3′		0.00
H-2,2′		−0.01
$-CH_3$		0.03
	H-1	−0.01
	H-2	−0.01
	H-3	−0.05
	H-4	−0.01
	H-5	−0.10
	H-6	−0.06

[a] The numbers refer to structure **7**.

the inclusion process must be fast in the NMR time scale. The more affected signals for **1** are those ortho to the carboxylate group. This may indicate that the major type of interaction occurs as shown in Figure 2 with the carboxylate group protruding out of the smaller rim of the β-CD cavity. The protons bonded to the ring bearing the dimethyl amino group are not greatly affected but the methyl signals are shifted downfield significantly. Since under the conditions of the NMR experiment equal concentrations of β-CD and **1** are used, it is very unlikely that complexes of 1:2 stoichiometry are formed; therefore, the modification of the hydrogens bonded to the two aromatic rings probably means that complexes of the type shown in Figures 2 and 3 are formed.

Kinetic Studies. Solutions of compounds **1**−**6** in the same solvent as those used for the spectroscopic studies and at constant pH were irradiated with a medium-pressure mercury lamp (wavelength emitting maximally at 365 nm) until a photostationary state was reached. A bleaching of the solution occurs at the wavelength of maximum absorption but the spectrum returns to its original shape in the dark. The thermal isomerization reaction of methyl yellow is slow enough to allow for the determination of the UV−vis spectra as a function of time and good isosbestic points are obtained.[15,16] The solutions can be irradiated several times, always returning to the original spectrum which is indicative of a wholly reversible reaction and that the only reaction taking place is the cis−trans isomerization, eq 5. In the presence of β-CD similar results are obtained.



(5)

8

The observed rate constant for **1**−**3** decreases when β-cyclodextrin is added and it reaches a platteau (Table 1, Figure 5 is representative). The k_{obs} decreases 8.7-fold for *o*-methyl red, 4.16-fold for *p*-methyl red, and 1.64-fold for methyl orange at β-CD 10^{-2} M. On the other hand, the presence of 0.01 M β-CD does not change the rate of isomerization of compounds **4**−**6** within the experimental error (Table 2).

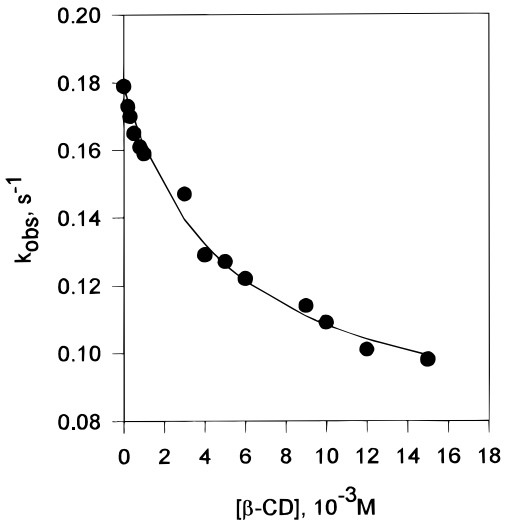
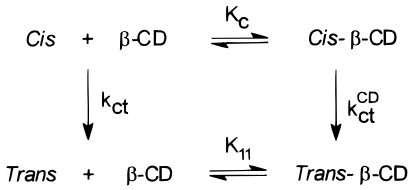


Figure 5. Dependence of the observed rate constant with the β-CD concentration for the cis−trans isomerization of methyl orange.

Scheme 2



The mechanism of cis−trans isomerization in the presence of β-cyclodextrin can be described as shown in Scheme 2.

The observed rate constant for Scheme 2 is given by eq 6 which predicts nonlinear dependence on β-CD concentration. The data for methyl orange and *o*- and

$$k_{obs} = \frac{k_{ct} + K_c k_{ct}^{CD}[\beta\text{-CD}]}{1 + K_c[\beta\text{-CD}]} \qquad (6)$$

p-methyl red were fitted to eq 6. For **2** the best fitting was obtained when the isomerization rate for the included substrate is considered zero which indicates that $k_{ct} > 10K_c k_{ct}$CD[β-CD], and consequently the ratio k_{ct}/k_{ct}-CD must be higher than 65.

The calculated equilibrium and rate constants are shown in Table 2. The values for K_c obtained from the kinetic measurements are not in good agreement with the value determined spectrophotometrically (Table 2). It should be noted that the kinetically determined values pertain to the inclusion of the cis isomer whereas the spectrophotometric values correspond to the inclusion of the trans isomer. Besides, if there is more than one type of complex formed, the value of K_c kinetically determined pertains to the complex which more strongly influences the isomerization rate.

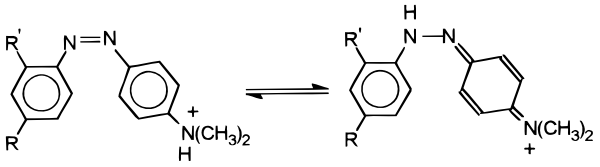
A significant decrease in the isomerization reaction rate of *p*- and *o*-methyl red is observed in presence of β-cyclodextrin and a smaller decrease in methyl orange. Several factors may contribute to the observed effect. The mechanism proposed for cis−trans isomerization of substrates having electron-donor and electron-acceptor substituents is rotation around the N−N bond through a dipolar transition state[8] which is favored in polar solvents. Inclusion places the substrate in a more hydro-

(15) Sanchez, A. M.; de Rossi, R. H. *J. Org. Chem.* **1993**, *58*, 2094.
(16) Sanchez, A. M.; de Rossi, R. H. *J. Org. Chem.* **1995,** *60*, 2974.

phobic medium which unstabilizes the polar transition state.[17] The substrates **1**−**3** can form hydrogen bonding with the OH of the rims of the cyclodextrin through the dimethylamino and/or the anionic substituent (−COO^- or −SO_3−) which hinders the rotation around the N−N bond so it contributes to lower the value of the isomerization rate constant of the complexed substrate.

Azo compounds bearing a dimethylamino group in the para-position form inclusion complexes with β-CD with the other ring inside the cavity, even when the ring has a carboxylic or a SO_3^{2-} group as substituent.[18] The degree of penetration in the cavity must be an important factor in determining the decrease in the reaction rate. Our NMR data indicate that in the case of **1** the inclusion takes place with the carboxylate group as well as the dimethylamino group inside the cavity (Figures 2 and 3). Literature data regarding the type of complex formed by methyl orange also indicates that the inclusion takes place with the SO_3^{2-} within the cavity.[18] The ortho-substituted compound is probably less deep in the cavity than the 4-substituted compound due to steric constrain. CPK molecular models indicate that **1** can penetrate the cavity and the carboxylate can protrude from the narrow rim of β-CD. On the other hand, **2** that has the carboxylate group in the ortho position can penetrate into the β-CD cavity about half the total deepness of the cavity. In the *cis*-isomer the carboxylate as well as the dimethylamino group can form hydrogen bonds with the OH groups located at the wider rim of β-CD. In the inclusion complexes of the *cis* isomers of **1** and **3**, hydrogen bond formation between both substituents and the hydroxyls of β-CD is not possible. The differences in the structures of the complexes of **1** and **3** compared with that of **2** may be responsible for the stronger effect of the complexation on the rate of isomerization of the later compound than for **1** and **3**.

Azobenzenes bearing electron-donating groups exist in acidic solution in two tautomeric forms, i.e., the azonium and amonium,[19−22] eq 7.



(7)

9Azo **9Amo**

It is known that the isomerization reaction is catalyzed by acids,[23] and in previous work we determined that the isomerization rate of the protonated form of compounds **1**−**6** is ~10^8 times faster than that of the unprotonated compound. This has been attributed to the decrease in the double bond character of the N=N bond in the azonium tautomer which favors the rotation mechanism.[8]

Under our experimental conditions the concentration of the protonated species is very small, but due to the differences in reaction rate of the two species the contribution to the overall rate is important.[15,16] In the presence of β-CD the azonium and amonium tautomers may be included (Scheme 3), and it was shown that the inclusion shifts the equilibrium toward the amonium form.[24] Therefore, another factor that may contribute to the decrease in the isomerization rate of the included compound may be the shift of the equilibrium shown in Scheme 3 toward **9**Azo·CD

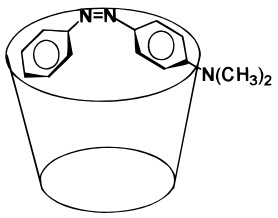
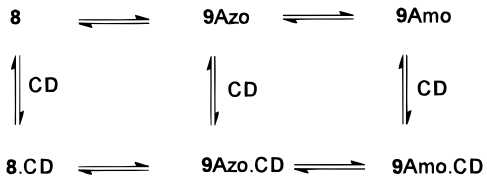


Figure 6. Schematic representation of an equatorial complex of *cis*-methyl yellow with β-CD.

Scheme 3



The fact that the reactions of **4**−**6** are not affected by cyclodextrin can be attributed to the presence of an organic cosolvent since it is known that the addition of organic solvents decreases the equilibrium constant for the association with cyclodextrin. For instance, the association constant of α-cyclodextrin with methyl red decreases 27-fold when the percentage of methanol in the solution is increased from 0 to 13%.[25]

The presence of a high percentage of ethanol, 20 and 50%, would avoid the formation of the inclusion complex, since the substrate would find in solution an environment similar to the one offered by the microenvironment of the cyclodextrin cavity. The presence of β-CD does not affect the rate constant of the compound 4-(dimethylamino)-2′-carboxyazobenzene when ethanol is added to the aqueous solution (see Table 1). However, the spectra of compounds **4**−**6** changes when β-CD is added**,** indicating some kind of interaction. One reasonable possibility is the formation of an equatorial complex where the azobenzene is located in one of the rims of the β-CD and not in the cavity (Figure 6). There are precedents in the literature which indicate that in the presence of organic cosolvents equatorial instead of inclusion complexes are formed.[26] In an equatorial complex the substrate is more exposed to the solvent and less steric hidrance for the isomerization is expected. Besides, compounds **4**−**6** have only electron-donating groups, and the mechanism of isomerization may be by inversion and not by rotation. In an included compound the torsional movement about the N=N double bond is expected to be much more hindered than the in-plane inversion.

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Experimental Section

Materials. The substrates **2**−**4** were commercial samples and were recrystallized form ethyl alcohol, whereas substrates **1, 5,** and **6** were prepared as described in the literature.[27] Their purity was controlled by HPLC and thin layer chromatography, and the compounds were identified by IR, NMR, and melting point.

The solutions for the substrates **1**−**3** were prepared in pure water, for **4** and **5** in ethanol 20%, and for **6** in ethanol 50%. The water used was obtained from a Millipore apparatus. β-CD Roquette was a gift from Ferromet, Buenos Aires, Argentina, and was used as received. Its purity was determined by UV−vis spectrophotometry (UV).

NMR Determinations. **1** (5.37 mM) and β-CD **(**4.08 mM) were dissolved in 0.5 mL of D_2O (99%) containing 0.01 mL of NaOD 40% p/v, and the spectra were taken on a Bruker 200FT spectrometer with the probe at 300 K.

Kinetics. Solutions of appropriate substrate at constant NaOH concentration and with variable concentrations of β-CD were irradiated with a medium-pressure Hg lamp for 10 min, and the cuvette was placed in the thermostated cell of a spectrophotometer (Shimadzu UV 260 or 2101 PC). The absorbance at the maximum of the substrate (463, 429, 461, 450, 448, 436 nm for **1**−**6**, respectively) was measured as a function of time. The experiments were repeated at least three times. The spectrum of the final solution matches that of the solution without irradiation.

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