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Remember that K_{12} is the exchange energy of the C–C bond. In the S_0 fragmentation, K_{23} is the exchange energy of the C=O bond that becomes the π bond in ground-state formaldehyde while in the T_1 fragmentation K_{23} is the exchange energy of the C=O π bond that becomes the n–π^* spin coupled pair in T_1 excited-state formaldehyde and is almost zero. Thus at any point along the reaction path $|K_{23}|$ for S_0 will always be greater than $|K_{23}|$ for T_1 (since $K_{23} \cong 0$ in T_1). Since $|K_{12}|$ is a simple function of C–C distance, the condition of eq 3 can only be met for the triplet at a smaller value of $|K_{12}|$ and thus at a larger value of R_{C-C}. This last observation also gives some insight into the origin of the larger resonance in the S_0 transition structure. The resonance energy represents the balance between bonded and uncoupled (nonbonded) exchange (see the general eqs 79–81 in ref 19a). In the region of the transition state the resonance energy is dominated by K_{12}. In fact K_{12} is an order of magnitude larger than the other K_{ij}. Since K_{ij} is a function of C–C distance, the larger resonance in the S_0 transition state is merely a result of the shorter C–C distance and larger K_{12}.

Conclusions

In this paper we have reported 4-31G MC-SCF geometry optimizations and analytical hessian (frequencies) computations for S_0, T_1, and S_1 states that are necessary in the description of the mechanism of the chemiluminescent decomposition of 1,2-dioxetane. The energetics have been confirmed by multireference MP2 computation at selected critical points. The origin of the S_0/T_1 surface degeneracy in the region of the biradical minimum and the different barrier heights in S_0/T_1 fragmentation are rationalized using a rigorous VB model.

Our results suggest a mechanism which involves (1) thermal (S_0) ring opening of dioxetane to produce a biradical almost without activation energy; (2) passage (via O–O bond breaking) though a S_0–T_1 *avoided* crossing in the region just before the biradical minimum controlled by strong spin–orbit coupling;[6a] (3) passage (in T_1 via C–C stretching) through a second *real* T_1–S_0 crossing immediately after the biradical minimum; (4) passage (in T_1 via C–C bond breaking) over a transition state for C–C fragmentation to produce triplet and ground-state formaldehyde. In contrast to previous suggestions,[3,5-7] the rate-determining step occurs on the T_1 surface. Our estimate of the activation energy at the MC-SCF/MP2/6-31G* level with a zero-point correction computed at the 4-31G level is 21.3 kcal mol^{-1} which is to be compared with the experimental activation energy of[3] 22.1 ± 0.3 kcal mol^{-1}. The experimental value for $\Delta S^{\ddagger}$ is small or negative. Since the rate-determining step occurs on T_1 and not on S_0, our results show that this negative or small experimental value for $\Delta S^{\ddagger}$ could be consistent with the short C=O bond length (and large force constant of the double bond) in one of the C=O bonds.

Finally the rationalization of the computed results using a rigorous VB model gives a simple explanation of the origin of the S_0/T_1 crossing and the barrier heights for fragmentation that lends additional credence to the results. The S_0/T_1 crossing is seen to arise from a competition between the fact that the lone pair closed shell repulsions are different in S_0 and T_1 and the fact that one of the destabilizing π orbital exchange integrals is zero in the triplet. The differing activation energies for S_0 and T_1 fragmentation arise from the difference in resonance energy between the two diabatic surface intersections.

The reason for the broad acceptance of the biradical mechanisms[7] (where the O–O bond rupture was the rate-determining step) was the realization that the activation energy (21 kcal mol^{-1}) could be understood in terms of the bond strength of the peroxy bond (~36 kcal mol^{-1}) and the strain energy of a 4-membered ring. The results presented in this work indicate that the rationalization of the O–O bond rupture and the subsequent C–C bond rupture cannot be made using simple two-center/two-orbital models. For example, the barrier in the passage from a to c via TS-b results from avoided crossing of the electronic configuration in Figure 7a and the electronic configuration in Figure 7b (but with singlet spin coupling) which becomes S_1 at c. Thus energetics must be rationalized in terms of different closed shell/lone pair repulsions and different destabilizing C–O π orbital exchange integrals in addition to the C–O bond exchange.

Finally, we should note that the nature and magnitude of the spin–orbit coupling has only been discussed qualitatively in this work. A more detailed study of the mechanism of this reaction must address the nature of the spin coupling quantitatively.

Acknowledgment. The support of the SERC (UK) under Grant No. GR/F 48029 and GR/F 46452 is gratefully acknowledged. Mar Reguero is pleased to acknowledge support from a NATO postdoctoral fellowship.

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Alcohol Size as a Factor in the Ternary Complexes Formed with Pyrene and β-Cyclodextrin

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Abstract: The effect of alcohols on the β-cyclodextrin (CD)/pyrene complex has been examined by using steady-state fluorescence measurements. A 1:1 stoichiometric ratio has been found between the alcohol and β-CD. As the stoichiometry of the binary β-CD/pyrene complex is 2:1, a ternary complex of stoichiometry of 2:1:2 β-CD/pyrene/alcohol is proposed. Apparent formation constants in the presence of different alcohols have been determined by using the variation of the I/III vibronic band ratio of pyrene with increasing cyclodextrin concentration. The 2:1 β-CD/pyrene stoichiometry for the binary complex has also been confirmed. The present study demonstrates that proper size matching among the pyrene, the cyclodextrin, and the alcohol leads to substantially larger equilibrium constants for the ternary complexes.

Introduction

Hydrophobic interaction of cyclodextrins (CDs) in aqueous solution is one of the primary forces involved in the formation of inclusion complexes between these cyclic oligosaccharides and different guest molecules. The size of the guest relative to that of the CD cavity is also a critical parameter.

Upon inclusion of a fluorophore, CDs offer a more protective microenvironment and generally enhance the luminescence of the guest molecule by shielding the excited species from quenching and nonradiative decay processes that occur in bulk solution. In

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general, the guest molecule loses its hydration sphere upon entering the cyclodextrin cavity, and water molecules are simultaneously expelled from the cavity.

Most studies of CDs have focused on the binary complexes formed with various organic compounds.[1] Still other studies have described the formation of ternary cyclodextrin complexes in which two different guests are included in a single CD host molecule. Early studies on ternary complexes were directed toward the use of cyclodextrins as models for protein–ligand interactions and enzyme catalysis, where the cavity of the CD is utilized as a reaction medium in which reacting species can be effectively brought together. In this regard, Kano et al.[2-4] have reported the fluorescence-quenching effect of trimethylamine and dimethylamine on several polycyclic aromatic hydrocarbons (PAHs) included in β-CD. They showed that the formation of a three-component complex of β-CD requires the amine to be occluded onto the β-CD cavity, forming a guest molecule capped β-CD with the PAH inside the cavity.

Hamai[5] has reported the quenching of β-CD/sodium 1-pyrenesulfonate and β-CD/pyrene complexes by anilines, which was interpreted in terms of the formation of a 1:1:1 ternary complex. The existence of a 2:1:1 β-CD/2-methoxynaphthalene/1,2-dicyanobenzene complex has also been reported.[6] Other studies have exploited the changes in the chemical behavior of inclusion complexes of CDs in the presence of surfactants as third components.[7-10]

The effect of the presence of alcohols on the inclusion complexes of cyclodextrins with select guest molecules has also been reported. Ueno et al.[11] have showed that the fluorescence intensity of aqueous solutions of α-(naphthyloxy)acetic acid was only slightly enhanced in the presence of γ-CD, while a marked enhancement was observed when cyclohexanol was added. This effect was interpreted in terms of a 1:1:1 complex of γ-CD/α-(naphthyloxy)acetic acid/cyclohexanol. Kano et al.[12] have also reported the decrease on the excimer fluorescence of pyrene in γ-CD in the presence of *n*-butanol due to the formation of a ternary complex. Nakajima[13] has reported an increase in the formation constant of the β-CD/pyrene complex upon addition of ethanol, while the existence of 1:1:1 β-CD/pyrene/alcohol ternary complexes was shown by Hamai.[14]

In this laboratory, much attention has been given to the binding properties of cyclodextrins with PAHs in the presence of select third components such as alcohols.[15-23] A marked enhancement in fluorescence intensity of pyrene has been observed in the presence of aliphatic alcohols.[17] In these studies, different saturated alcohols were examined with β-CD, heptakis(2,6-di-*O*-methyl)-β-CD, and heptakis(2,3,6-tri-*O*-methyl)-β-CD to evaluate the role of both the alkyl chain size of various aliphatic alcohols and the role of the primary and secondary hydroxyl groups of cyclodextrins on the formation of the ternary complexes. It was concluded that the primary and secondary hydroxyl groups are crucial to the formation of the ternary complex. Fluorescence lifetime measurements have also been used to study the interactions of α-, β-, and γ-CDs and select naphthalene derivatives.[18] The presence of a second long-lived component indicated the formation of an inclusion complex. This technique was also available for the study of the effect of select alcohols on complexes of pyrene with γ-, β-, and substituted β-CDs. In addition, formation constants of the ternary complexes have been reported.[19-21]

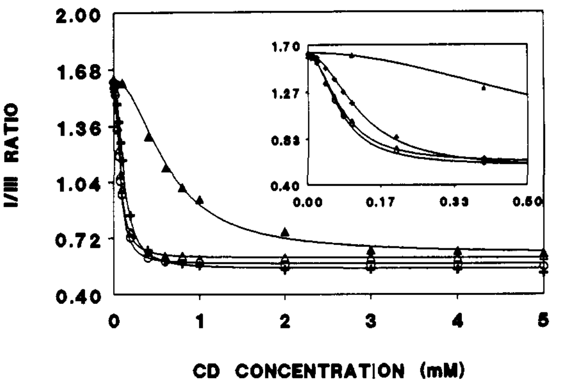

Figure 1. Influence of β-CD concentration on the I/III vibronic band ratio of pyrene, in the presence of different straight-chain alcohols. (▲) Ethanol; (△) *n*-propanol; (○) *n*-butanol; (+) *n*-pentanol.

We have also reported on the fluorescence quenching of cyclodextrin complexes of pyrene and naphthalene using potassium iodide.[22] In these studies, the ability of CDs in the presence of alcohols to further shield the fluorophores from interactions with strong quenchers was demonstrated. An analytical application of such protection was described for the selective enhancement of pyrene fluorescence in a mixture of pyrene and fluoranthene. Fluoranthene was quenched by iodide while the β-CD/pyrene/2-methyl-2-propanol complex was practically unaffected by the presence of the quencher.[23]

Recent studies using steady-state fluorescence measurements and molecular modeling have demonstrated that pyrene forms a 1:1 complex with γ-CD and 1:1 and 2:1 complexes with β-CD and that the 2:1 complex is predominant over the 1:1 complex for β-CD/pyrene.[24] The stoichiometry of the systems and the formation constants of the inclusion complexes were determined by monitoring the variation of the I/III vibronic band ratio of pyrene in the presence of the cyclodextrins.[25,26] In the studies reported in this paper, we examine the effect of select alcohols with varying alkyl chains (straight, branched, and cyclic) on the β-CD/pyrene complex.

Experimental Section

Apparatus. Steady-state fluorescence measurements were performed on a Perkin-Elmer LS-5 spectrofluorometer equipped with a Model 7500 data station. Solutions were excited at 335 nm, with excitation and emission bandwidths of 5 and 3 nm, respectively. All measurements were performed at 21 ± 0.1 °C. High-resolution NMR spectra were obtained with an NT-360 NB spectrometer.

Materials. Pyrene (99+%) was obtained from Aldrich and used as received. The β-cyclodextrin was obtained from American Maize Products (Hammond, IN) and was recrystallized twice from water before use. All alcohols (high purity grade) were obtained from Aldrich and used as received. Deuterium oxide (Aldrich, 99.9% atom D) was used

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Table I. I/III Ratio of Pyrene in 5.0 × 10^{-3} M β-CD in the Presence of Different Alcohols[a]

straight chain	I/III	branched, cyclic, and aromatic	I/III
ethanol	0.63	2-propanol	0.64
n-propanol	0.61	2-methyl-2-propanol	0.70
n-butanol	0.56	cyclopentanol	0.67
n-pentanol	0.52	cyclohexanol	0.63
n-hexanol	*b*	phenol	0.63
n-heptanol	*b*	benzyl alcohol	0.72

[a] Alcohol concentration is 1% v/v. [b] Solutions too turbid for measurement.

as the solvent in the NMR studies.

Method. A 5.0 × 10^{-4} M stock solution of pyrene was prepared in cyclohexane. Aqueous pyrene solutions were prepared by pipetting an aliquot of the stock solution into a 100-mL flask. The cyclohexane was then evaporated by using dry nitrogen, and the contents of the flask were diluted with deionized water (Continental Water Systems, Atlanta, GA) to give a 2.0 × 10^{-7} M pyrene solution.

(a) Influence of β-CD Concentration. Pyrene and alcohol concentrations were held constant at 1.0 × 10^{-7} M and 1% v/v, respectively, while β-CD concentrations were varied from 1.0 × 10^{-5} to 5.0 × 10^{-3} M. A 5-mL aliquot of the 2.0 × 10^{-7} M pyrene was transferred into a 10-mL flask, and the necessary amount of alcohol was added to give a 1% v/v alcohol–water solution. A β-cyclodextrin stock solution (1.0 × 10^{-2} M) was prepared, and appropriate volumes were transferred into the flasks to give the desired β-CD concentrations.

(b) Influence of Alcohol Concentration. In these experiments, β-CD and pyrene concentrations were held constant at 2.5 × 10^{-3} and 1.0 × 10^{-7} M, respectively, while the concentration of alcohol was varied from 0.001 to 2% by volume. A 5-mL aliquot of the 2.0 × 10^{-7} M pyrene and the appropriate volume of 1.0 × 10^{-2} M β-CD were transferred into a 10-mL flask, and the necessary amount of alcohol was added to give the desired alcohol concentration.

(c) NMR Studies. Proton NMR spectra were recorded in D_2O at ambient temperature. The samples were equilibrated in the probe for approximately 5 min before each run. Chemical shifts are expressed in parts per million (ppm) relative to HOD at 4.8 ppm.

Results and Discussion

Effect of β-CD Concentration. The relative intensities of the fluorescence emission vibronic bands of pyrene show considerable variation in different solvent media. This variation is generally reported in terms of the relative intensities of bands I and III. The effect of increasing concentrations of β-CD on the I/III ratio of pyrene in the presence of different alcohols with straight chains is shown in Figure 1. The initial addition of β-CD leads to a dramatic decrease in the I/III ratio, followed by a leveling off of the ratio at higher β-CD concentrations. It should be noted that the decrease of the ratio with increasing β-CD is significantly more pronounced in *n*-butanol than in ethanol. This in turn gives rise to a steeper slope for *n*-butanol (see insert). The presence of *n*-butanol in β-CD solutions appears to render the environment of included pyrene more nonpolar than ethanol. Since this is the case not only for *n*-butanol but also for *n*-propanol and *n*-pentanol, it suggests that the observed effect does not depend on the probes' inward migration into the CD cavity or its specific association with the alcohol. Rather, the alcohols may be positioned in the open end of the β-CD torus and/or extended into the cavity, thereby eliminating some of the ordered water and reducing the degree of fluorophore–water interaction. It can be inferred that the alcohol is effectively capping the CD and enhancing the hydrophobic environment of pyrene in the β-CD complex. It should be noted that the I/III ratio decreases with increasing alcohol carbon chain length, with the lowest ratio being obtained for *n*-pentanol (see Table I).

At 1% v/v alcohol and 5.0 × 10^{-3} M β-CD, the I/III ratio is between 0.5 and 0.6, which is similar to that of a nonpolar solvent such as cyclohexane. This low I/III value suggest that pyrene is located in a very nonpolar region of the CD cavity and is removed from the bulk aqueous environment. In the case of ethanol, pyrene may effectively interact with water, hence the slightly higher I/III ratio. The most plausible explanation for this trend should be in terms of the size and the volume of the alcohol. Large and bulky alcohols of suitable size compared to the open end of the host will completely cap the CD cavity, minimize pyrene interaction with water, and consequently create a more hydrophobic environment for pyrene.

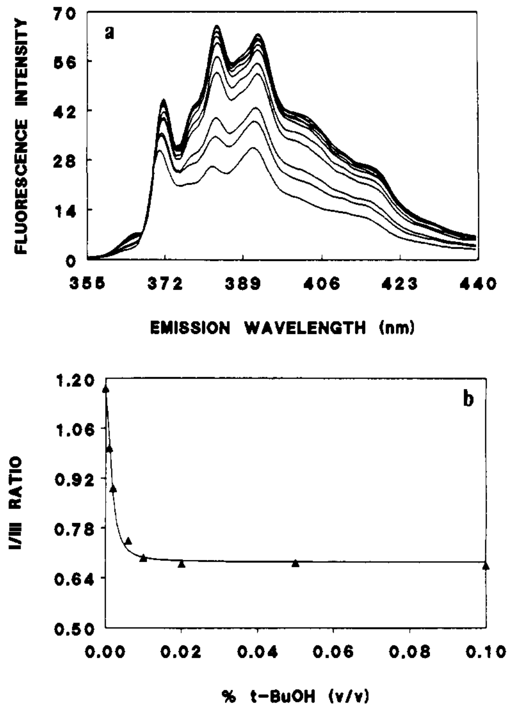

Figure 2. (a) Emission spectra of the β-CD/pyrene complex in the presence of 2-methyl-2-propanol. From bottom to top, % 2-methyl-2-propanol (v/v): 0.001, 0.002, 0.006, 0.01, 0.02, 0.05, 0.1, 0.2, 0.6, 1.0 and 2.0. (b) Influence of 2-methyl-2-propanol concentration on the I/III vibronic band of pyrene in 2.5 × 10^{-3} M β-CD.

The ratios in column 4 of Table I are similar to those in column 2, and there are relatively small variations in the values. In this case, branched, cyclic, and aromatic alcohols are used, and no systematic trend in the ratio relative to the size is observed. Following the rationalization given above, this suggests that the hydrophobic environment of pyrene in β-CD is slightly more polar with 2-methyl-2-propanol and cyclopentanol than with 2-propanol. Similarly, in the case of aromatic alcohols, a higher I/III ratio is obtained for benzyl alcohol when compared with phenol.

Effect of Varying Alcohol Concentration. To further investigate the β-CD/pyrene complexation process, the influence of varying the alcohol concentration has been examined. The decrease of the I/III ratio is similar to that obtained when the CD concentration is varied. It should be noted that in the absence of CD the alcohols do not have any significant influence on the I/III ratio. Upon addition of alcohol, the fluorescence intensity of the β-CD/pyrene complex is dramatically enhanced. Figure 2a shows the emission spectra of β-CD/pyrene in the presence of varying amounts of 2-methyl-2-propanol. An enhanced band, at around 364 nm, appears, and an isoemissive point appears at 368 nm. This suggests that a new complexation process is taking place. The variation of the I/III ratio with 2-methyl-2-propanol concentration is shown in Figure 2b. The decrease of the I/III ratio with increasing 2-methyl-2-propanol concentration levels off at about 0.01% v/v. Higher concentrations of the alcohol produce slight increases in the fluorescence intensity but do not significantly affect the I/III ratio.

Mixed Alcohols. The effect of the addition of 2-methyl-2-propanol on the fluorescence of β-CD/pyrene (1.0 × 10^{-7} M pyrene and 1.0 × 10^{-3} M β-CD) solution, containing 1% v/v *n*-propanol, was examined (Figure 3). In the absence of 2-methyl-2-propanol, the I/III ratio of the solution containing *n*-propanol is 0.61. Addition of varying amounts of 2-methyl-2-propanol shows an increase in the I/III ratio, reaching a maximum value of 0.70. This value is characteristic of a β-CD/pyrene solution containing 1% v/v 2-methyl-2-propanol. In contrast, addition of varying amounts of *n*-propanol to the β-CD/pyrene

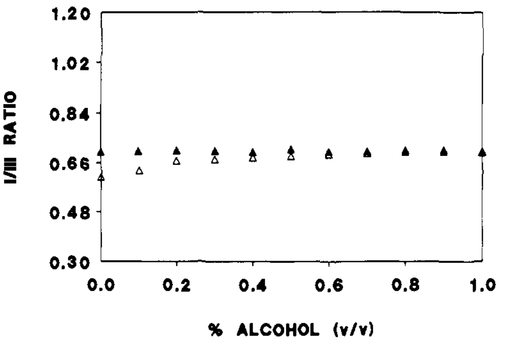

Figure 3. Effect of mixtures of alcohols on the I/III vibronic band ratio of pyrene in 1.0 × 10^{-3} M β-CD. (△) *n*-Propanol is fixed at 1% v/v, and the concentration of 2-methyl-2-propanol ranged from 0.0 to 1.0% v/v. (▲) 2-Methyl-2-propanol is fixed at 1% v/v, and the concentration of *n*-propanol ranged from 0.0 to 1.0% v/v.

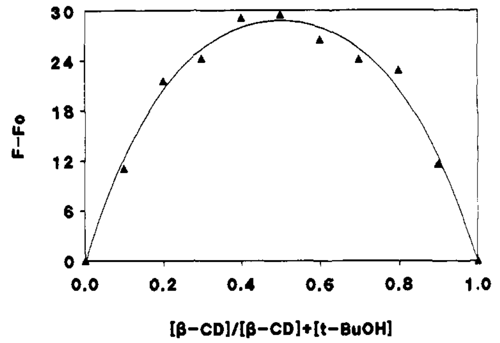

Figure 4. Continuous variation plot monitored at λ_{EM} = 383 nm, λ_{EX} = 335 nm. The pyrene concentration is 1.0 × 10^{-7} M. [β-CD] + [*t*-BuOH] = 2.5 × 10^{-3} M.

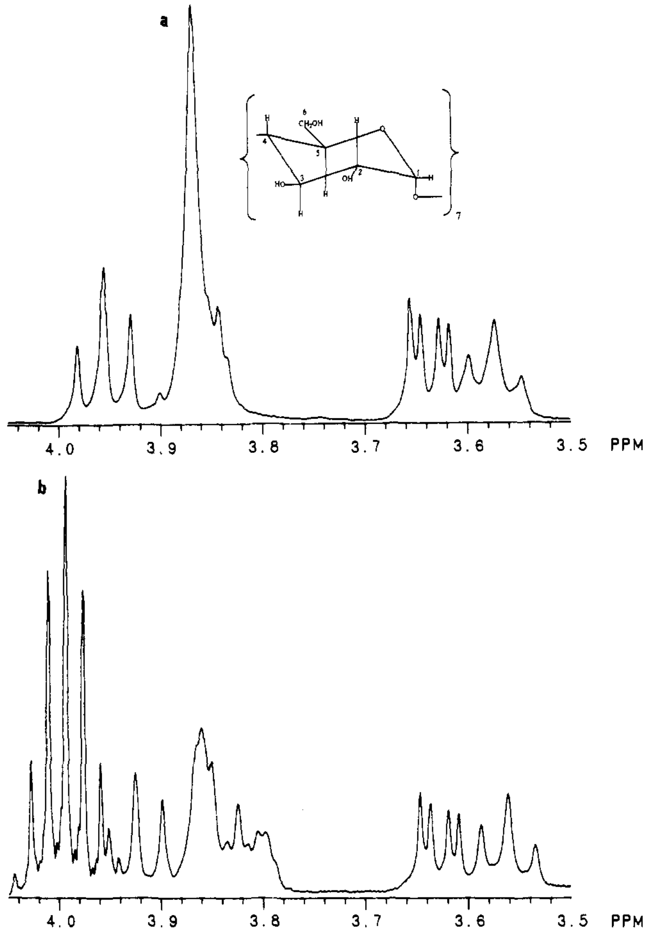

Figure 5. ^{1}H NMR spectra of β-CD (5.0 × 10^{-3} M) in D$_2$O. (a) Pure β-CD and (b) containing 1% 2-propanol.

solution containing 2-methyl-2-propanol (I/III = 0.70) does not affect the observed ratio. The I/III ratio remains constant through the addition of 1% v/v *n*-propanol. It can be inferred that 2-methyl-2-propanol has a stronger effect on the complexation process, displacing *n*-propanol from the complex. A similar effect was obtained with mixtures of ethanol/2-methyl-2-propanol, 2-propanol/2-methyl-2-propanol, and *n*-butanol/2-methyl-2-propanol. Clearly, the complexation in β-CD/pyrene/2-methyl-2-propanol is such that their mutual association is more favorable than with any of the other alcohols mentioned above. Similar experiments show that cyclopentanol has a stronger interaction with β-CD, displacing 2-methyl-2-propanol (*t*-BuOH) from the complex.

Stoichiometric Ratio between β-CD and Alcohol. The "continuous variation method" has been used to determine the stoichiometry of the ternary systems.[27,28] This method is usually applied to binary systems; however, it can be applied to this three-component system to determine the stoichiometry between the CD and the alcohol.[6,14] In this case, the pyrene concentration was fixed at 1.0 × 10^{-7} M. Under the conditions of [CD] + [t-BuOH] = 2.5 × 10^{-3} M, the observed fluorescence intensity, corrected for the contribution from the fluorescence of the binary complex, is plotted as a function of the CD molar fraction.

Figure 4 shows a plot for the β-CD/pyrene/2-methyl-2-propanol system. The difference in the fluorescence intensity goes through a maximum value at a CD molar fraction of 0.5. This result provides clear evidence of a 1:1 stoichiometry between β-CD and the alcohol. The same results have been found for the ternary complexes formed in the presence of *n*-propanol and cyclopentanol. This is in agreement with the 1:1 stoichiometric ratio reported by Hamai[14] between β-CD and *n*-pentanol and β-CD and ethanol; however, in that study, the existence of a 1:1:1 ternary complex of β-CD/pyrene/alcohol was erroneously concluded because of the assumption of a 1:1 β-CD/pyrene stoichiometry. As has been previously shown, the β-CD/pyrene complex is predominantly 2:1,[20] which will give a 2:1:2 β-CD/pyrene/alcohol stoichiometry for the ternary complex. Similar stoichiometric ratios between β-CD and aniline have been reported for the β-CD/pyrene/aniline and β-CD/sodium 1-pyrenesulfonate/aniline systems.[5]

NMR Studies of the β-CD/Alcohol System. The mechanism of interaction between the alcohol and β-CD was investigated by using nuclear magnetic resonance (NMR) spectroscopy. The interaction was assessed by comparing the NMR spectra of β-CD and β-CD/alcohol complex. Figure 5 shows the qualitative features concerning the interaction of 2-propanol with β-CD. The NMR spectrum of β-CD (Figure 5a) consists of peaks from five kinds of protons: the H-1 doublet (at δ 5.06), the H-3 triplet (at δ 3.96), a strong unresolved broad peak consisting of H-6 and H-5 (at δ 3.87–3.85), the H-2 appearing as two doublets (at δ 3.64), and the H-4 triplet (at δ 3.58). The addition of 2-propanol to the β-CD solution gives a slight up-field shift (−0.04 ppm) of the H-3 signal (Figure 5b). The signals between 3.80 and 3.85 ppm that appear on addition of 2-propanol are most likely due to H-5 proton shifting up-field from the region where H-5 and H-6 signals overlap in the pure β-CD. The H-3 and H-5 protons are located in the interior of the CD cavity, and it is therefore likely that H-3 and H-5 protons would shift in the same manner, thus providing a rationale for this assignment. In light of these assignments, the change in both shifts in the presence of the alcohol suggests that 2-propanol comes into considerable contact with the interior protons of β-CD. This is in agreement with the observations of Demarco and Thakkar,[29] who reported a strong shielding of protons inside the β-CD cavity for inclusion complexes formed with aromatic substrates. This is also consistent with Turro et

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al.,[30] who observed that the detergent probe [5-(4-bromo-1-naphthoyl)pentyl]trimethylammonium bromide is included in the inner cavity of γ-CD. The H-1, H-2, and H-4 protons located at the exterior of the β-CD torus are relatively unaffected, indicating that the association does not take place at the exterior of the torus. As expected, the NMR spectrum of β-CD/2-propanol containing pyrene solution did not show any qualitative differences since the pyrene should theoretically complex with less than 1% of the β-CD because of the low pyrene solubility. Additional NMR studies to evaluate these complexes are in progress in this laboratory.

Equilibrium Constants of the Ternary Complexes. The overall equilibrium constant (K_2) for the 2:1 association between cyclodextrin (CD) and pyrene (P) is given by

$$\mathrm{P} + 2\mathrm{CD} \rightleftharpoons \mathrm{P(CD)_2} \tag{1}$$

and

$$K_2 = [\mathrm{P(CD)_2}]/[\mathrm{P}][\mathrm{CD}]^2 \tag{2}$$

where $[\mathrm{P(CD)_2}]$ is the equilibrium concentration of the inclusion complex for a given CD concentration and [P] and [CD] are the equilibrium concentrations of pyrene and cyclodextrin, respectively. In the presence of an alcohol (A), assuming that the stoichiometry of the β-CD/pyrene complex does not change and taking into account the stoichiometric ratio found between β-CD and the alcohol, we have $[\mathrm{P(CD)_2A_2}] \gg [\mathrm{P(CD)A}]$, since the 2:1 complex is predominant. Then, the formation constant of the ternary complex is given by

$$\mathrm{P} + 2\mathrm{CD} + 2\mathrm{A} \rightleftharpoons \mathrm{P(CD)_2A_2} \tag{3}$$

and

$$K_3 = [\mathrm{P(CD)_2A_2}]/[\mathrm{P}][\mathrm{CD}]^2[\mathrm{A}]^2 \tag{4}$$

At 1% v/v alcohol, the concentration of alcohol ($\approx 10^{-1}$ M) is in large excess compared to β-CD and pyrene. The apparent equilibrium constant under these conditions is given by

$$K' = [\mathrm{P(CD)_2A_2}]/[\mathrm{P}][\mathrm{CD}]^2 \tag{5}$$

When one is working at β-CD concentrations in large excess over the pyrene concentration, the following simplification can be applied: $[\mathrm{CD}] = [\mathrm{CD}]_0 - [\mathrm{P(CD)_2A_2}] \approx [\mathrm{CD}]_0$.

Under the assumption that the observed I/III ratio is the weighted average of the I/III ratio from complexed and free pyrene,[24-26] we have

$$\frac{[\mathrm{P(CD)_2A_2}]}{[\mathrm{P}]_0} = \frac{R_0 - R}{R_0 - R_2} \tag{6}$$

where the parameters R_0 and R_2 denote the ratio for pyrene in water and in the complex, respectively, and R is the measured ratio at a given CD concentration. The following equation is then applicable:

$$\frac{1}{R_0 - R} = \frac{1}{K'(R_0 - R_2)[\mathrm{CD}]_0^2} + \frac{1}{R_0 - R_2} \tag{7}$$

Thus, a plot of $1/(R_0 - R)$ versus the reciprocal of the square of the analytical concentration of CD should give a straight line. Figure 6 shows the plot of $1/(R_0 - R)$ vs $1/[\mathrm{CD}]_0^2$ for the β-CD/pyrene complex in the presence of 1% cyclopentanol. The linear relationship obtained confirms the 2:1 stoichiometry between β-CD and pyrene and strongly supports a 2:1:2 stoichiometry for the β-CD/pyrene/cyclopentanol ternary complex. The same stoichiometric ratios were also obtained for the other alcohols examined in this work.

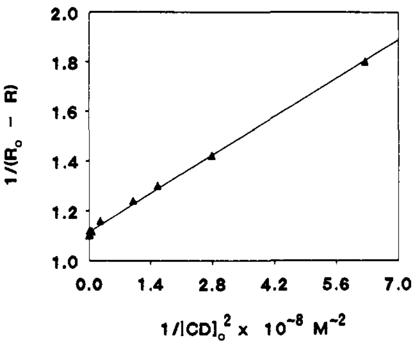

Figure 6. Plot of $1/(R_0 - R)$ vs $1/[\mathrm{CD}]_0^2$ for the β-CD/pyrene complex in the presence of 1% (v/v) cyclopentanol.

Table II. Estimated Formation Constants of β-CD/Pyrene in the Presence of Alcohols[a]

straight chain	log K'	branched, cyclic, and aromatic	log K'
ethanol	6.40	2-propanol	8.45
n-propanol	8.22	2-methyl-2-propanol	8.76
n-butanol	8.26	cyclopentanol	9.07
n-pentanol	7.84	cyclohexanol	8.10
n-hexanol	*b*	phenol	8.21
n-heptanol	*b*	benzyl alcohol	7.36

[a] Alcohol concentration is 1% v/v. [b] Solutions too turbid for measurements.

The formation constants were calculated from the changes in the I/III vibronic band ratio of pyrene with β-CD concentration by using nonlinear regression analysis.[31] The initial parameters used for the nonlinear regression method were estimated from the linear plots. Statistical analysis was performed by using Marquadt's iterative method[32] to fit the data directly to the equation

$$R = \frac{R_0 + R_2K'[\mathrm{CD}]_0^2}{1 + K'[\mathrm{CD}]_0^2} \tag{8}$$

The estimated apparent formation constants for the different alcohols are summarized in Table II.

Note in column 2 of Table II that log K' increases with increasing carbon chain length, reaching a maximum for *n*-butanol and then decreasing for *n*-pentanol. The *n*-butanol must show the optimum fit, suggesting that its size is the most appropriate to completely cap the open end of the β-CD cavity. Presumably, the hydrophobic part extends into the cavity. This results in a stronger association for *n*-butanol with the β-CD/pyrene system. Hamai[14] has noted that *n*-propanol is the best alcohol to fit into the void space unfilled by pyrene inside the β-CD cavity. The effect was rationalized in terms of the length of the alkyl chain. However, in view of our findings the formation constants for *n*-propanol and *n*-butanol are in the same relative range, with *n*-butanol giving a slightly more enhanced fit. The smaller formation constant found for *n*-pentanol suggests that it is too large compared with the open end of the β-CD cavity. It is interesting to note that *n*-pentanol gives the lowest I/III ratio (see Table I). However, the formation constant is not directly related to the I/III ratio obtained in the presence of the alcohol. This suggests that, in addition to the hydrophobic interactions between the β-CD and the alcohol, the stability of the ternary complex is also the product of the size and volume of alcohol.

Branching in the chain (column 4) gives higher formation constants than the straight-chain alcohols. The formation constants increase from 2-propanol to 2-methyl-2-propanol and to cyclopentanol, decreasing for cyclohexanol or phenol and further decreasing for benzyl alcohol. The most plausible explanation for higher formation constants is that the stability of the ternary complexes is directly related to the proper geometry and volume of the alcohol to fill the residual void space unoccupied by pyrene. It could be inferred that cyclopentanol has the most compatible size with β-CD. This is shown by the higher formation constant found for cyclopentanol when compared with the other alcohols.

It is interesting to note that cyclohexanol and phenol, two alcohols of very different chemical characteristics but of around

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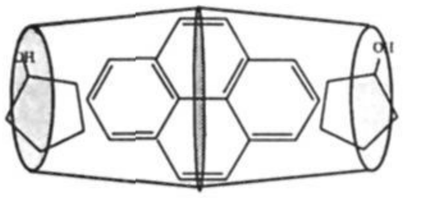
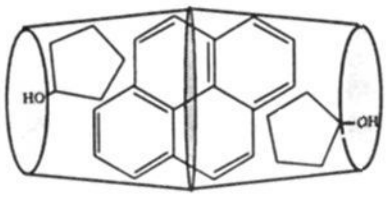
the same size and geometry, show comparable formation constants. These two alcohols must be too large compared to the β-CD cavity and hence give smaller formation constants compared to cyclopentanol. Benzyl alcohol, still larger, shows an even smaller formation constant. In contrast, 2-propanol is of smaller size than the open end of the β-CD cavity and also gives rise to less interaction than in the case of cyclopentanol.

Conclusions

Our data clearly demonstrate that proper size matching between the β-CD/pyrene complex and the alcohol strongly affects the stability of the ternary complex. Alcohols too small or too large compared to the open end of the β-CD cavity give formation constants that are smaller than those with the proper size such as *n*-butanol and cyclopentanol. Two of the most probable configurations for the β-CD/pyrene/cyclopentanol complex are shown below (not drawn to scale), with the hydrophobic part of the alcohol extending inside the cavity. For type I configuration, the pyrene is oriented axially inside the cavity with the alcohol capping the open end of each β-CD. In type II configuration, pyrene is positioned at an angle inside the two CDs. This allows for a stronger interaction between the alcohol and the protons located on the interior of the β-CD torus. The 2:1:2 β-CD/pyrene/alcohol stoichiometry suggests that the alcohol is on the primary side of the β-CD molecule. It should be noted that the orientation for the pyrene and alcohol in our depiction of the type II interaction is somewhat arbitrary and is not meant to depict the exact configuration of the complex.



Type I



Type II

From the mixed-alcohol results, it is evident that 2-methyl-2-propanol displaces ethanol, *n*-propanol, *n*-butanol, or 2-propanol from the complex, independent of the I/III ratios obtained for the different ternary complexes formed. This observation strongly supports the role of the size and volume of the alcohol and is in agreement with the trend found in the values for the formation constant. Other experiments performed with different mixtures are also consistent with these observations.

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Diimide Formation on Rhodium Surfaces: A Temperature-Programmed Reaction Spectroscopy Study

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Abstract: Diimide (N_2H_2) formation has been detected as a gas-phase product over the 180–500 K temperature range from a clean rhodium surface during decomposition of both hydrazine and ammonia. The diimide was identified on the basis of mass spectrometry of the parent ion (30 amu) and a single-dehydrogenation fragmentation product (29 amu) that is 6% of the parent. The formation of diimide was confirmed chemically for both precursors by observing substantial increases in yield in the presence of coadsorbed hydrogen and a substantial decrease in the presence of coadsorbed oxygen. Adsorbed NH from N_2H_4 or NH_3 decomposition is proposed as a potential surface intermediate.

Diimide (N_2H_2), the parent of azo compounds, is of great interest to chemists because of its important role as an active reducing agent in synthetic chemistry[1-4] and as a transient intermediate in a variety of gas-phase reactions.[2] Previous studies relating to diimide formation and characterization have been in solution, or low-temperature matrices where the diimide was formed in microwave discharges.[5-8] We report in this paper, to the best of our knowledge, the first observation of diimide formation mediated by a clean rhodium surface during decomposition of both hydrazine and ammonia. The diimide formation has been detected over the 180–500 K temperature range as a gas-phase product resulting from hydrazine and ammonia decomposition on a Rh surface.

The experiments were performed in a UHV system equipped with Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and a multiplexed mass spectrometer for temperature-programmed reaction spectroscopy (TPRS). The base pressure after bakeout was 3.2×10^{-11} Torr. The rhodium foil was mounted on a manipulator, which allowed resistive heating

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