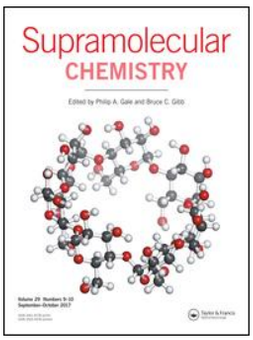

Supramolecular Chemistry

ISSN: 1061-0278 (Print) 1029-0478 (Online) Journal homepage: https://www.tandfonline.com/loi/gsch20

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To cite this article: Fred O. Garces , V. Pushkara Rao , M. A. Garcia-garibay & Nicholas J. Turro (1992) A comparison of ^{1}H-^{13}C cross polarization and magic angle spinning dynamics of the α-, β- and γ-cyclodextrin inclusion complexes of benzaldehyde, Supramolecular Chemistry, 1:1, 65-72, DOI: 10.1080/10610279208027442

To link to this article: https://doi.org/10.1080/10610279208027442

SUPRAMOLECULAR CHEMISTRY, Vol. 1, pp. 65–72
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A comparison of ^{1}H-^{13}C cross polarization and magic angle spinning dynamics of the α-, β- and γ-cyclodextrin inclusion complexes of benzaldehyde

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The solid state inclusion complexes of benzaldehyde with α-, β- and γ-cyclodextrins have been studied by cross-polarization and magic angle spinning solid state NMR techniques (CPMAS-NMR). The effects of complexation on the mobility of the guest have been analyzed in terms of nuclear relaxation parameters such as ^{13}C spin-lattice relaxation (T_1), ^{1}H spin-lattice relaxation in the rotating frame ($T_{1\rho}(H)$), and cross polarization transfer (T_{CH}). It is proposed that large variations observed in the T_{CH} values of the guest in the three complexes may be interpreted in terms of motion with correlation times in the range between ca. 0.1–5.0 msec. These motions may strongly affect the extent of the heteronuclear dipolar coupling partially responsible in determining the rates of cross polarization.

INTRODUCTION

The last few years have witnessed an increasing interest on the influence of rigid environments on organic photochemical reactivity.[1] Rigid environments studied include organic and inorganic supports such as polymer matrices, zeolites, clays, silica gel and organized entities such as molecular crystals and inclusion complexes.[1] Their impact on photochemical reactivity has now been well recognized and it is known that their influence may range from subtle to dramatic. Many examples reported in the literature ascribe the photochemical properties observed in these media to structural effects such as conformational control and steric interactions.[1] While these influences may predispose the excited states and the reactive intermediates to undergo specific decay pathways, sometimes the dynamics of the reactants determine the importance of competing photochemical processes. It is therefore desirable to characterize these reaction systems not only structuraly but also from a dynamic point of view including their diffusional, rotational and conformational motions.

In order to carry out the dynamic characterization of a model system we have studied the NMR properties of the inclusion complexes of benzaldehyde in α-, β- and γ-cyclodextrin (cyclohexaamylose, α-CD; cycloheptaamylose, β-CD and cyclooctaamylose, γ-CD).[2] The cross polarization and magic-angle-spinning (CPMAS) NMR spectral properties of the hosts, have been studied by several authors[3] and several inclusion complexes have also been analysed.[4] The photochemical properties of these complexes have been recently studied and their differences clearly reflect structural and perhaps dynamical properties.[5] While the depth of the binding cavity of all three cyclodextrins is about the same (7.8 Å), the diameter of their truncated-cone structure increases with increasing ring size[2] as shown in Scheme 1. Because of these differences, it is expected that the orientation and rotational motion of benzaldehyde in these complexes will vary with cavity size. Experimentally, the photochemical studies have revealed that while benzaldehyde is photostable in α-CD, intermolecular reactions between two benzaldehyde molecules leading to 4-benzoyl benzaldehyde and benzoin occur both in β-CD and γ-CD (Scheme 2). Furthermore, benzoin obtained in the

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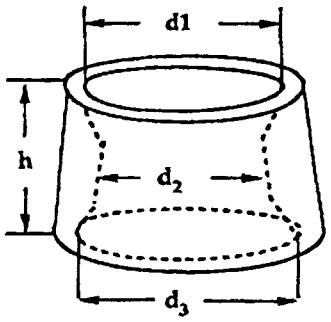
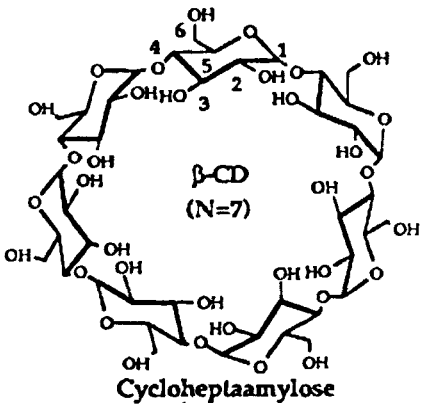
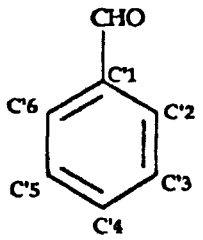




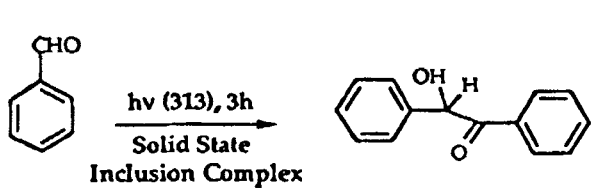
Cyclo dextrin	N	d_1	d_2	d_3	h
α	6	5.6	4.2	8.8	7.8
β	7	6.8	5.6	10.8	7.8
γ	8	8.0	6.8	12.0	7.8

N: Number of amylose units



Benzaldehyde

Scheme 1



α-Cyclodextrin	–	(No Reaction)	–
β-Cyclodextrin	56%	(e.e. = 15%)	24%
γ-Cyclodextrin	43%		35%

Scheme 2

photolysis of the β-CD complex showed measurable optical rotation (ca. 15% e.e.) while the benzoin formed in the γ-CD complex showed no optical rotation (Scheme 2).[5] It has been proposed that these differences result from the relative orientation and the translational and rotational mobility of benzaldehyde within these complexes.[1d,6] The objective of the present study is to probe all three complexes in a comparative manner by solid state NMR in order to obtain insights into their relative motions. From all the analytical techniques available to study solid systems, NMR offers the highest expectations regarding the simultaneous structural and dynamical characterization.[7a,b] Structural identity and heterogeneity can be readily measured by steady state NMR, while dynamical properties including correlation times extending from ca. 10^{-7} to 10^{1} sec can be obtained from analysis of nuclear magnetic relaxation and chemical exchange.[7]

The work presented here is preceded by reports by Kuan *et al.*[8] and by Ripmeester[9] where the inclusion complexes of benzaldehyde with α- and β-cyclodextrin have been studied in some detail. The inclusion compound of benzaldehyde in γ-cyclodextrin is reported here for the first time along with a number of relaxation properties of all three complexes. Structural assignments and partial dynamical information available in the literature for the α-CD and β-CD complexes indicate differences related to the relative mobility of the ring and benzaldehyde groups of the host.[8,9] In the case of β-CD, correlation times for motion have

been analyzed in terms of temperature effects and dipolar dephasing and have been proposed to be somewhere between 10^{-3} and $10^{-7}\,s^{-1}$.[9] In an attempt to determine the range of motion within narrower limits, we compare the dynamics of these three systems by taking advantage of well established solid state signal enhancement and line narrowing techniques based on the CPMAS technique:[10] (a) ^{13}C spin-lattice relaxation (T_1),[11] (b) ^{1}H spin lattice relaxation in the rotating frame [$T_{1\rho}(H)$][12] and (c cross polarization times (T_{CH}).[13,14] When values from the three complexes are compared, differences in these parameters should report on whether the motions prevailing in the guest have correlation times near the ^{13}C Larmor frequency (62 MHz), the frequency of the spin-locking field (40 kHz), or around the values given by the strength of the heteronuclear dipolar interaction, $\Delta\omega_{CH}$ (1–25 kHz).

EXPERIMENTAL

Preparation

Inclusion complexes were prepared by adding benzaldehyde (Aldrich) to saturated aqueous solutions of the cyclodextrins (α, β and γ). The solutions were magnetically stirred for 24 h at room temperature. A white precipitate was formed and was filtered and dried at 50 °C for 5 h. Complexes were characterized on the basis of their X-ray powder diffraction patterns, FT-IR spectra and stoichiometry ratios as in our previous photochemical work[5] and were used for solid state NMR studies.

Instruments

Solid state NMR measurements were carried out on a Bruker AF-250 FT-NMR spectrometer which included an IBM Instruments NMR solid accessory package. A broadband solid state probe designed by Doty Scientific tuned to the carbon resonance frequency at 62.896 MHz was used for all of our experiments. Signal averaging and processing were carried out with the Bruker Aspect 3000 computer and software.

Solid state NMR studies

Samples of the cyclodextrin-benzaldehyde inclusion complexes (ca. 250 mg) were packed in 7 mm o.d. sapphire (Al_2O_3) rotors with Kel-f end caps provided by Doty Scientific. Carbon-13 spectra were acquired with cross polarization and magic angle spinning. High power proton decoupling fields of ca. $\gamma B_1/2\pi = 40$ KHz were used in all our experiments. The Hartman-Hahn condition was achieved and contact times of 1.5 to 2 ms were used with recycled delays between 2–6 s (6 s for ^{13}C T_1 measurements). A minimum of 200 interferograms, with 4K datum points zero-filled to 8K, were collected to obtain the desired signal to noise ratio. Spinning rates were generally between 3–5 KHz and chemical shifts are relative to the methyl carbon of external hexamethylbenzene (Me = 16.7 ppm vs TMS). All measurements were taken at ambient temperatures, (20 ± 2 °C). Dipolar dephasing spectra, typically used to assign quaternary carbons,[7a,15] were obtained by allowing a 50 μs dephasing period after the cross polarization time.

The ^{13}C spin lattice relaxation times were measured by a CPMAS inversion recovery pulse sequence (90°-(^{1}H spin lock-^{13}C contact)-90°-t-90°-FID). In the absence of an exact value, a recycle delay of 6 s was chosen for proton relaxation as a compromise between sufficient signal intensity and reasonable experiment times. A minimum of nine delay times ranging from 0.01 to 60 sec were allowed for ^{13}C relaxation. All T_1 measurements were performed at room temperature (20 ± 2 °C) and relaxation times were calculated with a three parameter fitting algorithm with the Bruker software and Aspect 3000 computer.

The cross polarization times, T_{CH}, and the ^{1}H spin lattice relaxation in the rotating frame, $T_{1\rho}(H)$, were determined by double exponential fitting of the intensity data obtained using variable spin-locked contact times ranging from 10^{-5} to 10^{-2} sec. Fitting was obtained with a minimum of nine contact times according to the following relation:[10,14]

$$I(t) = Io/(1\text{-}T_{CH}/T_{1\rho}(H)) \times \{1\text{-exp-}(1\text{-}T_{CH}/T_{1\rho}(H))t/T_{CH}\} \times \exp[-t/T_{1\rho}(H)] \quad (1)$$

RESULTS AND DISCUSSION

^{13}C CPMAS and dipolar dephasing spectra

The transfer of spin magnetization of the abundant proton spin reservoir to the dilute ^{13}C nuclei is carried out coherently while the Hartman-Hahn condition is satisfied in a spin-lock experiment.[7,10,12] The strong spin-locking RF-fields also serve the purpose of decoupling the strong dipolar interactions of the carbon nuclei to the protons of the system. Proton decoupling, when continued during the acquisition time, offers the possibility of observing relatively narrow lines in solid samples when the experiment is carried out under magic angle spinning (MAS) conditions. However, when decoupling is suspended for relatively short periods time (e.g. 50 μs) before acquisition in a dipolar dephasing experiment, the

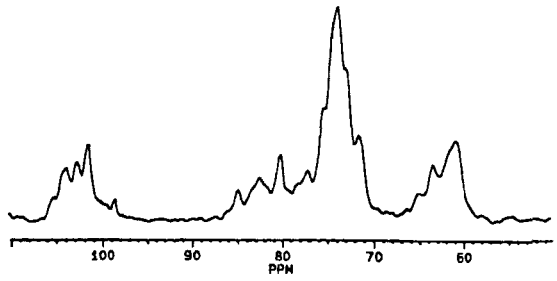


Figure 1 ^{13}C CPMAS spectrum of hydrated γ-cyclodextrin.

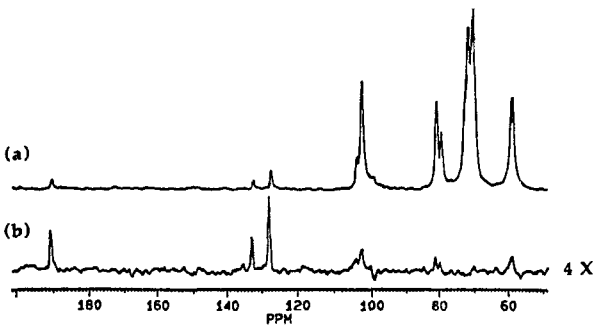


Figure 2 (a) ^{13}C CPMAS and (b) dipolar decoupled spectra (amplified 4 ×) of the inclusion complexes of benzaldehyde with γ-cyclodextrin.

strong spin-spin interactions may cause relaxation that destroys the intensity of the carbon signal.[7,15] Signals from non-protonated carbons usually survive the dipolar dephasing along with those which have their dipolar interactions reduced by molecular motion.[9,14a]

The spectra of α and β cyclodextrins obtained in our experiments are similar, but not identical to those reported in the literature[3,8] for the hydrated hosts. The spectrum of γ-cyclodextrin, shown in Fig. 1 as a representative example, closely resembles the spectrum of the hydrated host reported by Furo *et al.*[3b] The spectra of the α and β cyclodextrin complexes (not shown) are significantly broader than those of Gidley and Bociek[3a] and more closely resemble those reported earlier by other workers.[3b,c,8]

The CPMAS spectra of the inclusion complexes of α- and β-cyclodextrin with benzaldehyde have been investigated by Kuan *et al.*[8] and by Ripmeester,[9] who included dipolar dephasing and variable temperature studies. We have repeated the spectral measurements (CPMAS) for all three complexes along with the corresponding dipolar dephasing experiments. Those corresponding to the γ-CD complex are shown in Fig. 2. The spectra obtained for the α- and β-CD complexes were in good agreement with those published by Kuan *et al.* and we will only comment briefly on details of the spectrum of the γ-CD complex reported here for the first time.

Analysis of the spectra of Figs 1 and 2 indicates a decrease in resolution when the spectral features of the pyranose host carbons (C_1–C_6) in the free cyclodextrin (Fig. 1) are compared with those of the benzaldehyde complex (Fig. 2a). Each of the pyranose carbons C_1, C_2 and C_6, which appeared as multiple dispersed signals in the free hosts, appears as a set of superimposed bands in narrower region in the complex. The benzaldehyde (notice primes, C′) carbonyl carbon (C′ = O), ipso carbon (C'_1) and para-carbon (C'_4) are resolvable from one another at 193, 137 and 136 ppm respectively. However, the ortho and meta-carbons of benzaldehyde (C'_2, C'_3, C'_5 and C'_6) appeared as a single broad band at 131 ppm. In agreement with the trend expected to follow from the results of Ripmeester with the α- and β-cyclodextrin complexes, the dipolar dephasing of the γ-CD complex strongly decreases the signals of the host while those of the guest remain nearly unaffected.[9]

The efficiency of dipolar dephasing in reducing the signal intensity reflects the strength of the heteronuclear dipolar coupling.[15] The almost complete disappearance of the CD resonances indicates a strong dipolar interaction in the rigid molecules of the host (Fig. 2b). The small effect of a 50 μsec dipolar dephasing time in the spectra of the benzaldehyde molecules indicates that the strength of the C-H dipolar interaction is comparatively reduced ($\omega_{CH} \ll 20$ KHz) due to molecular motion. In fact, severe intensity reductions in the carbonyl carbon signal of the dipolar dephasing spectra of benzaldehyde of the α-CD complex were interpreted by Ripmeester in terms of a model where the aldehyde group of benzaldehyde is fixed in the lattice while the phenyl moiety performs two fold flips about the C_1–C_4 axis.[9] In the case of the β-CD, where all of the benzaldehyde resonances prevailed, a model was proposed where benzaldehyde undergoes general reorientation in both the phenyl and the aldehyde portion. The results for the γ-CD inclusion complex are therefore quite similar to those of β-CD as the C=O, C'_1 and C'_4 resonances observed at δ = 190.3, 136.2 and 133.2 ppm show only a small reduction while the intensity for the $C'_{2,3,5,6}$ at 128.19 ppm shows no appreciable change (Fig. 2b).

Furthermore, analysis of the chemical shifts obtained with the three inclusion complexes shows a trend in which the ^{13}C resonances for benzaldehyde in γ-CD resonate further up field than those in β-CD, which in turn are higher than those in α-CD (Table 1). These upfield shifts have been attributed to the orientation and penetration of the phenyl portion of the benzaldehyde into the cyclodextrin cavity.[8] The chemical shift pattern for the three systems suggest that penetration of the phenyl portion of the

benzaldehyde follows the order γ-CD > β-CD > α-CD.

^{13}C spin lattice relaxation (T_1)

Spin lattice relaxation (parameter T_1) of the ^{13}C magnetization was determined by CPMAS inversion recovery experiments. The CPMAS method offers the advantage of having a recycle delay determined by the relaxation of the ^{1}H magnetization and not that of the ^{13}C nuclei which is normally much longer. Qualitative runs indicated no increase in signal intensity when recycle times of 4 sec were increased to 6 sec and it was assumed that satisfactory ^{1}H relaxation had occurred. The experimental results for the three inclusion complexes are shown in Table 2 for selected resonance positions. The T_1 values of benzaldehyde were found to be consistently shorter than those of the cyclodextrin carbons for all three inclusion complexes. This result is in agreement with the results obtained from the dipolar dephasing experiments separating the behavior of the two groups of signals from the host and the guest systems. In benzaldehyde, the unprotonated C'_1 show the longest relaxation times in all three complexes suggesting the importance of dipolar mechanisms.[11] The rigidity of the carbonyl group and restricted rotation along the C'_1–C'_4 axis proposed by Ripmeester[9] in the α-CD complex is supported by the larger T_1 values of the carbon atoms along the rotation axis (C=O, C'_1 and C'_4) as compared with those of the carbon atoms undergoing rotation in the periphery of the benzaldehyde ring ($C'_{2,3,5,6}$). The more general reorientation proposed for benzaldehyde in the β-CD is also suggested by the nearly equal T_1 values of all the protonated carbons. The same property is also observed for the γ-CD complex suggesting similar reorientation patterns. The relaxation times for all signals were found to decrease as the complex changes from α-CD to β-CD and to γ-CD.

The host carbons were found to present similar trends as those observed in the guest. From all the CD resonances analyzed, those of the hydroxymethylene groups (C_6), which may have a relatively free internal rotation, were found to have the shortest T_1 values. Accordingly, the changes in T_1 values observed for the amylose ring carbons as a function of the inclusion complexes is not paralleled by the primary hydroxyl group. The exception is notable in the case of the α-CD complex where a relatively large T_1 value of 6.67 sec is obtained as compared with values of 0.66 and 0.94 for the β-CD and γ-CD complexes. This suggests a tighter molecular packing which may be enforced either by crystal packing considerations or by the benzaldehyde guest. Although the variations in T_1 values for the three complexes are significant, it appears that they are not different enough to suggest motions with correlation times in the proximity of the inverse of the ^{13}C Larmor frequency. Unless very close correlation times were to occur for the three complexes, the behavior of the T_1 values approaching either from the rigid lattice or the extreme narrowing limits should probably be more different. Better suggestions can be made after analyzing the cross polarization dynamics of these complexes.

Table 1 ^{13}C chemical shifts[a] of benzaldehyde in its inclusion complexes with α-, β- and γ-cyclodextrins

Assignment	α ^{13}C (δ)	β ^{13}C (δ)	γ ^{13}C (δ)
Benzaldehyde			
C=O	193.1	191.9	190.3
C'_1	137.1	137.3	136.2
C'_4	135.7	134.6	133.2
$C'_{2,3,5,6}$	130.1	129.6	128.2

[a] Chemical shifts measured vs external hexamethyl benzene.

Cross polarization times (T_{CH}) and spin lattice relaxation in the rotating frame [$T_{1\rho}$(H)]

Experimentally, the intensity of the ^{13}C signals are measured as a function of the cross polarization

Table 2 ^{13}C spin-lattice relaxation times[a] (T_1) in benzaldehyde-cyclodextrine complexes

	Cyclodextrin[b]				*Benzaldehyde*[b]			
Complex	*C6*	*C2,3,5*	*C4*	*C1*	$C'_{2,3,5,6}$	C'_4	C'_1	*C'=O*
α: (δ)	61.1	74.0	80.8	103.0	130.0	135.7	137.1	193.1
T_1	6.67	13.2	20	20	0.67	1.12	11.7	1.9
β: (δ)	61.4	73.6	82.1	104.7	130.0	134.6	137.3	192.3
T_1	0.66	10.81	14.0	23.8	0.36	0.54	4.47	0.34
γ: (δ)	60.0	72.8	81.9	104.7	128.2	133.2	136.2	190.2
T_1	0.94	12.9	13.2	11.75	0.38	0.33	3.6	0.60

[a] Values in sec.

[b] See Scheme 1 for meaning of labels.

(δ) Chemical shifts, ppm.

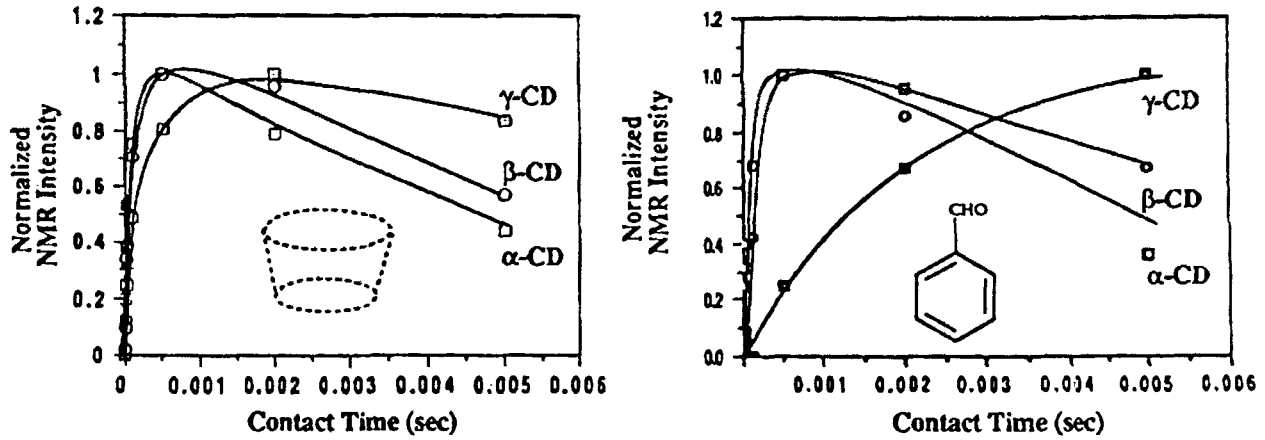


Figure 3 Plots of the signal intensity versus contact time for representative signals of (a) the three cyclodextrin hosts (signal of C4), and (b) the guest benzaldehyde (signal of $C'_{2,3,5,6}$).

(contact) time which in our experiment ranges from 25 μsec to 10 msec. Measurements were carried after the Hartman-Hahn condition ($\gamma B_{1C} = \gamma B_{1H}$) had been optimized with the sample spinning at 3.5 KHz and a delay of 6 sec between consecutive pulses to allow for ^1H relaxation. The growth and decay of the ^{13}C magnetization as a function of the contact time in the CPMAS reflects the dynamics of the spin-locked magnetization transfer and the decay of the ^1H magnetization in the rotating frame.[7,10,13-19] The intensity data as a function of contact time was analyzed by fitting according to Eq. 1 to obtain cross polarization times (T_{CH}) and decay due to spin-lattice relaxation in the rotating framt [$T_{1\rho}(H)$]. Given the signal-to-noise values obtained and the limited number of data points, relatively good fits were obtained for a qualitative analysis purposes. The typical behavior of the ^{13}C signal intensities as a function of contact time is represented in Figs 3a and 3b for signals corresponding to the three cyclodextrin guests and their benzaldehyde hosts respectively. Differences in the growth and subsequent decay of the ^{13}C signals, due to the T_{CH} and $T_{1\rho}(H)$ processes respectively, are clearly discernible in the plots.

The values of T_{CH} and $T_{1\rho}(H)$ obtained for the CD and benzaldehyde signals in the three inclusion complexes, summarized in Table 3, contain more detailed information. The uncertainties in the values of Table 3 is estimated to range on the order of 20–50%. Errors come mainly from the signal intensity of the original data in the case of the smallest signals and from the reduced number of data points involved in the fitting procedure. Our analysis is focused on differences that are larger than the estimated error. Notably, the T_{CH} values obtained for the benzaldehyde carbon nuclei present the largest and most informative differences. In the case of the ortho and meta carbons

Table 3 Cross polarization parameters [T_{CH} and $T_{1\rho}(H)$] in benzaldehyde/cyclodextrin complexes

	Cyclodextrin				*Benzaldehyde*	
	C6	*C2,3,5*	*C4*	*C1*	*C2,3,5,6*	*C=O*
Alfa (δ, ppm)	61.1	74.0	80.8	103.0	130.0	193.0
T_{CH}*	31	59	53	32	82	64
$T_{1\rho}(H)$†	10.6	4.8	6.6	5.4	6.0	5.4
Beta	61.4	73.6	82.1	104.7	130.0	192.3
T_{CH}	62	92	94	105	248	317
$T_{1\rho}(H)$	4.8	5.5	5.5	5.2	6.5	4.1
Gamma	61.0	73.6	81.5	102.7	130.3	191.5
T_{CH}	88	133	119	123	4350	3800
$T_{1\rho}(H)$	16.2	16.3	4.7	5.9	4.4	—

* Values in sec.

† See Scheme 1 for meaning of labels.

(δ) Chemical shifts, ppm.

($C'_{2,3,5,6}$) plotted in Fig 3b, T_{CH} increases over a 53-fold range from 82 to 248 to 4350 μs on going from α-CD to γ-CD complexes. Interestingly the $T_{1\rho}(H)$ obtained along with those values ranges from 6.0 to 6.5 to 4.4 ms and do not present an experimentally significant variation. A similar trend is observed for all of the benzaldehyde signals including those of the carbonyl carbon also included in Table 3. In contrast to the variations in T_{CH} values observed for benzaldehyde, the signals of cyclodextrin only present relatively small differences in their T_{CH} and $T_{1\rho}(H)$ values. Variation in T_{CH} values within the different CD signals are constrained within less than a two-fold variation and are too close to the experimental error of our measurements and fitting to make any compelling argument. However, changes in T_{CH} values for the different CD complexes clearly show a systematic increase as the complex changes from α-CD to β-CD to γ-CD. Although relatively less reliable, the values of $T_{1\rho}(H)$ do not show significant variations either as a function of carbon atom groups or as a function of

cyclodextrin. All values were found to occur in the neighborhood of 6 to 10 msec and suggest the equilibration of the proton reservoir in all three samples.[10,13]

It is evident from Fig. 2b and Table 3 that the most striking variations occur in the T_{CH} values of the carbon signals of the benzaldehyde guests. Qualitatively, the cross polarization transfer rates depend on the strength of heteronuclear dipolar interaction between the abundant ^{1}H spins and dilute ^{13}C nuclei.[10,14] These interactions depend on the distance and orientation between the two dipoles and on the effect of molecular mobility in decreasing the strength of their interaction.[14a,17] Both intramolecular and intermolecular contributions to the dipolar coupling are expected to play a role in the case of the inclusion complexes involved in this study. Only minor effects are observed on the T_{CH} values of the CD carbon atoms which make up a relatively static spin system in all three samples. In contrast, the mobility of the guest reduces the strength of both intramolecular and intermolecular heteronuclear dipolar interactions involving its own carbon nuclei.

An approximate and useful expression for the rate of cross polarization is given by:[10]

$$T_{CH}^{-1} = C_{AB}(M_{CH}/M_{HH}^{1/2}) \qquad (2)$$

where M_{CH} and the M_{HH} are the second moments of the dipolar C-H and homonuclear H-H spectral interactions and C_{AB} is a geometric factor including the gyromagnetic ratios of the nuclei under consideration. In general terms, molecular mobility has the effect of reducing the strength of the dipolar interactions of both homonuclear and heteronuclear origin.[14a,17] However, the strength of these two interactions is significantly different. Motions with decreasing correlation times, starting from a static molecular frame towards correlation times in the tens of KHz regime, should affect first the weaker heteronuclear interactions (C-H) followed then by the homonuclear ones (H-H). While molecular motion may have the ability of affecting all of the terms involved in Eq. 2, it appears reasonable that the difference in T_{CH} values may result mainly from a reduction of the heteronuclear C-H dipolar coupling. The constant $T_{1\rho}(H)$ values suggest that the motions of the guest in all three complexes at room temperature are not near the 40 KHz domain of the spin-locking fields used in our experiments. Motions occurring near this frequency would accelerate relaxation in the rotating frame, reduce the $T_{1\rho}(H)$ values of the proton system increasing the differences in their values. Our results suggest that it is motions occurring mainly in the 0.5–10 KHz frequency domain which have a tremendous effect on the T_{CH} values of the guest. This result, in agreement with the analysis of Ripmeester who proposed the range of molecular motion in the β-CD complex, should roughly be in the much broader 1 kHz–10 MHz domain.

CONCLUSIONS

The combined and comparative analysis of the ^{13}C-T_1, ^{1}H-$T_{1\rho}$ and T_{CH} values of the inclusion complexes of benzaldehyde in α-, β- and γ-cyclodextrins suggests that correlation times for motion should be in the ca. 0.1–5 msec region. This is manifested in the large differences in T_{CH} values of the carbon nuclei of the guest which follow the trend expected to occur with increased mobility in the series α-CD, β-CD and γ-CD. The results from these experiments suggest that techniques based on the measurement of spin alignment[19] and 2-D exchange,[20] which are most suitable for measuring correlation times in this time domain should be of great value in pinning down the dynamics of benzaldehyde in the CD complexes.

ACKNOWLEDGEMENTS

The authors acknowledge the NSF, AFSOR and DOE for their generous support of this research.

(Received 7 May 1992)

REFERENCES

1. (a) Ramamurthy, V. Ed. (1992). *Photochemistry in Organized Media and Constrained Environments*, VCN: New York; (b) Thomas, J.K. (1988). *Acc. Chem. Res.* **21,** 275; (c) Turro, N.J. (1987). *Tetrahedron* **43,** 1589; Scheffer, J.R., Garcia-Garibay, M. and Nalamazu, O. (1987). *Organic Photochemistry* **8,** 249; (d) Ramamurthy, V. and Eaton, D.F. (1988). *Acc. Chem. Res.* **21,** 200; (e) Kalyanasundaram, K. (1987). *Photochemistry in Microheterogeneous Systems*, Academic Press: New York; (f) Guillet, J. (1985). *Polymer Photophysics and Photochemistry*, Cambridge Univ. Press: Cambridge.
2. (a) Saenger, W. (1980). *Angew. Chem. Int. Ed. Engl.* **19,** 344; (b) Saenger, W. (1984). *Structural Aspects of Cyclodextrins and their Inclusion Compounds*, Atwood, J.L., Davies, J.E.D., MacNicol, D.D. Eds., Academic Press: New York.
3. (a) Gidley, M.J. and Bociek, S.M. (1986). *J. Chem. Soc., Chem. Commun.* 1223; (b) Furo, I., Pocsik, I., Tompa, K., Teeaar, R. and Lippmaa, E. (1987). *Carbohyd. Res.* **166,** 27; (c) Hewitt, J.M., Linder, M. and Perez, S. (1986). *Carbohyd. Res.* **154,** 1.
4. (a) Hall, L.D. and Lim, T.K. (1986). *J. Am. Chem. Soc.* **108,** 2503; (b) Ripmeester, J.A. (1986). *J. Incl. Phenom.* **4,** 129; (c) Inoue, Y., Okuda, T., Kuan, F.-H. and Chujo, R. (1984). *Carbohyd. Res.* **129,** 9; (d) Inoue, Y., Okuda, T., Chujo, R. (1983). *Carbohyd. Res.* **116,** C5; (e) Saito, H., Izumi, G., Mamizuka, T., Suzuki, S. and Tabeta, R. (1982). *J. Chem. Soc. Chem.* 1386.

5. Pushkara Rao, V. and Turro, N.J. (1989). *Tetrahedron Lett.* **30,** 4641.
6. (a) Sharat, S., Usha, G., Tung, C.H., Turro, N.J. and Ramamurthy, V. (1986). *J. Org. Chem.* **51,** 941; (b) Rao, B.N., Turro, N.J. and Ramamurthy, V. (1986). *J. Org. Chem.* **51,** 460; (c) Ramamurthy, V. Ref 1a, Ch. 7, p. 703.
7. (a) Fyfe, C.A. (1983). *Solid State Chemistry for Chemists*, C.F.C. Press: Guelph, Ontario, Canada; (b Leyrla, J.R. and Yannoni, C.S. (1982); *Acc. Chem. Res.* **15**, 208; (c) (1982). Sandstrom, J. *Dynamic NMR Spectroscopy*, Academic Press: London; (d) Kaplan, J.I. and Fraenkel, G. (1980). *NMR of Chemically Exchanging Systems*, Academic Press; (e) Voelker, R. (1988). *Angew. Chem. Int. Ed. Engl.* **27,** 1468.
8. (a) Kuan, F.H., Inoue, Y. and Chuho, R. (1986). *J. Incl. Phenom.* **4,** 4641.
9. Ripmeester, J. (1986). *J. Incl. Phenom.* **6,** 31.
10. Pines, A., Gibby, M.G. and Waugh, J.S. (1973). *J. Chem. Phys.* **59,** 569.
11. Torchia, D.A. and Szabo, A. (1982). *J. Mag. Res.* **49,** 107.
12. McBrierty, V.J. and Douglas, D.C. (1981). *Macromol. Rev.* **16,** 295.
13. Demco, D.E., Togenfeldt, J. and Waugh, J.S. (1975). *Phys. Rev. B* **11,** 4133.
14. (a) Schaefer, J. and Stejskal, E.O. (1979). *Topics in Carbon-13 NMR of Solid Polymers* **3,** 283; (b) Laupretre, L., Monnerie, L. and Virlet, J. *Macromolecules* **17,** 1397; (c) Poliks, M.D. and Schaefer, J. (1990). *Macromolecules* **23,** 682.
15. Opella, J.J. and Frey, M.H. (1979). *J. Am. Chem. Soc.* **101,** 5854.
16. (a) Beher, J.P. and Lehn, J.-M. (1976). *J. Am. Chem. Soc.* **98,** 1743; Morris, G.A. and Hall, L.D. (1982). *Can. J. Chem.* **60,** 2431.
17. Stejskal, E.O. and Schaefer, J. (1977). *J. Mag. Res.* **28,** 105.
18. Schaefer, Stejskal, E.O. and Buchdahl, R. (1977). *Macromolecules* **10,** 384.
19. Spiess, H.W. (1980). *J. Chem. Phys.* **72,** 6755.
20. (a) Blumich, B. and Spiess, H.W. (1988). *Angew. Chem. Int. Ed. Engl.* **27,** 1655; (b Hagemeyer, A., Schmidt-Rohr, K. and Spiess, H.W. (1989). *Adv. Mag. Res.* **13**, 85.