Molecular Dynamics of α-Cyclodextrin Inclusion Complexes

J. P. Behr and J. M. Lehn*

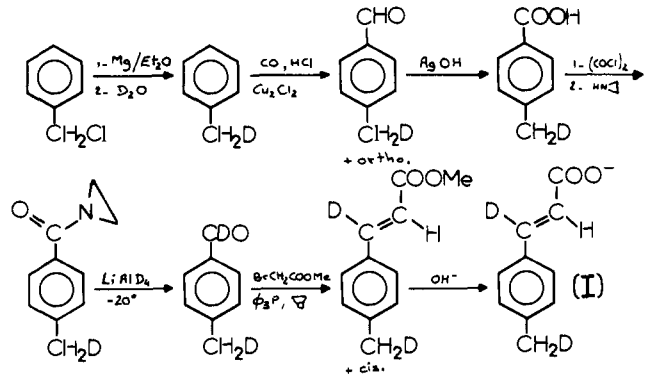
Contribution from the Institut Le Bel, Université Louis Pasteur, 67 Strasbourg, France.[1] *Received July 8, 1975*

Abstract: The molecular motions in the inclusion complexes formed by α-cyclodextrin (α-CD) with the *p*-methylcinnamate (I), *m*-methylcinnamate (II), and *p-tert*-butylphenate (III) anions have been studied by ^2H and ^{13}C nuclear relaxation. The results show that upon inclusion, the reorientation times of the substrates increase by a factor of ca. 4, whereas for α-CD the increase in overall tumbling motion depends on the substrate. The internal methyl group rotations of the substrates in [I, α-CD] and [II, α-CD] are hindered, showing that they are located inside or at least in contact with the macrocycle. In contrast, the bulky *tert*-butyl substituent in [III, α-CD] is probably located outside the hydrophobic core of α-CD since its internal motion is little affected upon complexation. None of the substrates is tightly bound to α-CD from the dynamic point of view; the best coupling between the substrate and cavity motions is seen in [II, α-CD], where the benzene ring substituents are in a meta arrangement. The results point out that in a general fashion a molecular complex should be described not only by its thermodynamic stability and its formation and dissociation kinetics, but also by its *dynamic rigidity*, defined by the coupling between the molecular motions of the two (or more) entities of which it is composed. Dynamic coupling coefficients of 0.16, 0.26, and 0.18 are obtained respectively for the complexes of substrates I, II, and III with α-CD.

The cyclodextrins are α-1,4-linked cyclic oligomers of D-glucopyranose which possess the remarkable property of forming inclusion complexes with a variety of small molecules of appropriate size.[2-4] One of the most fascinating and far-reaching aspects of their chemistry is their model enzyme behavior[5-15] both in terms of substrate complexation and reactivity (especially with attachment of a potential catalytic site). The α-cyclodextrin molecule (cyclohexaglucopyranose), α-CD, has the shape of a hollow truncated cone with 12 secondary hydroxyl groups around the larger circumference and 6 primary hydroxyl groups around the smaller side;[16] the cavity thus defined is relatively hydrophobic, and binds hydrophobic residues of compatible size, forming usually 1:1 complexes. This small water soluble "active site" catalyzes some reactions with the assistance of its hydroxyl groups, leading to substrate specificity, competitive inhibition, and Michaelis-Menten type kinetics. All these characteristics of enzyme-catalyzed reactions are obviously easier to relate to molecular events than in the case of macromolecules and further refinement comes from thermodynamic,[17] NMR,[4] ORD,[18,19] ESR,[20] or x-ray[16] studies. In an effort to gain insight into the dynamic properties of a substrate embedded in a large cavity, we have studied the molecular motions in three inclusion complexes of α-cyclodextrin using the rotational correlation times determined from the measurement of carbon 13 and deuterium relaxation times. As substrates we choose: (a) labeled *p*-methylcinnamic acid (I), for the ease of labeling and measuring ^2H relaxation times from proton line shape analysis; (b) *m*-methylcinnamic acid (II), where the change in methyl position should alter the geometry of the complex, the CH_3 group being a dynamic probe of binding tightness in both cases; (c) *p-tert*-butylphenol (III) for studying the effect of a bulky group on the benzene nucleus.

Experimental Section

α-Cyclodextrin was obtained from Pierce Chemical Co. and recrystallized from water. *m*- and *p*-methylcinnamic acids were synthesized from the corresponding tolualdehydes (Fluka) and *p-tert*-butylphenol was obtained from Fluka AG. *p*-Methyl-*d-trans*-cinnamic-*d* acid was synthesized following the scheme below.



Each step is straightforward and described in the literature at least for a closely related compound. *o*-Toluic acid (8%) and *cis-p*-methylcinnamic acid (9%) were removed from the corresponding para and trans acids by recrystallization from water. The product (I) was >95% d_2, the trans configuration of the double bond resulting from the H,D coupling constant of 2.45 Hz, which corresponds to a trans H,H coupling of 16.0 Hz.

Uv spectra were taken on a Cary 14 spectrometer and NMR measurements were performed on a Varian XL-100-15-FT spectrometer using 12-mm sample tubes. ^2H spin-lattice relaxation times were measured by line shape analysis of the resonance of the protons spin-spin coupled to the deuterium following the method previously described.[21,22] ^{13}C spin-lattice relaxation times were measured by the modified inversion recovery method of Freeman.[23]

Unless otherwise stated, the molar concentrations of the solutions were as follows: ca. 0.15 M for the free substrates (as sodium carboxylate or phenoxide), 0.07 M in substrate and 0.1 M in α-CD (limit of solubility) to measure the relaxation times of the substrate, 0.1 M in substrate and 0.07 M in α-CD to measure the relaxation times of α-CD. The temperature was kept at 33 ± 2 °C for all experiments.

Results and Discussion

The association constants for the complexation of I-III with α-CD have been measured by two methods: first by the changes induced in the uv absorption spectrum of the substrates by the addition of α-CD, as also seen for other benzenoic compounds;[24] second by the chemical shifts induced in the ^{13}C NMR spectra of α-CD by addition of the substrates. These data treated by a least-squares program gave constants of 150 to 200 M^{-1} for [I, α-CD] and [II, α-CD], and ca. 250 M^{-1} for [III, α-CD]. There is good evidence from other physical data[3] and by analogy with closely related systems that these complexes are of the 1:1 inclusion type.

^2H Relaxation Times and Correlation Times. The relaxation of the deuterium nucleus has over the ^{13}C relaxation

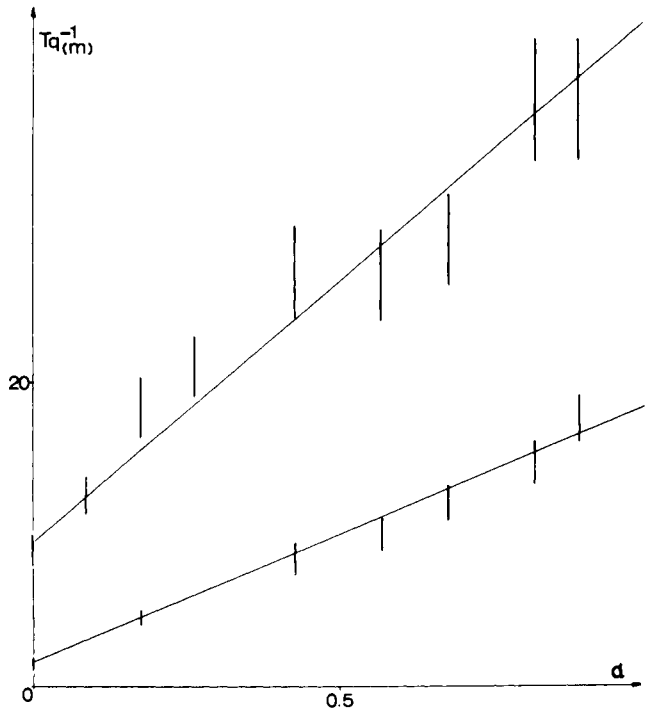


Figure 1. Plot of the measured relaxation rate $T_q^{-1}(m)$ of the -CD=CH- group (upper line) and the CH_2D group (lower line) in I vs. α, the complexed fraction of I; concentration of I = 0.05 M.

the advantage to be overwhelmingly dominated by the single quadrupolar mechanism. As a consequence, the relation between the measured quadrupolar relaxation time T_q and the molecular correlation time τ_q is straightforward when pseudoisotropic motion is assumed:[22]

$$T_q^{-1} = 0.43 \times 10^{12}\tau_q \quad (1)$$

This is probably not true for the ^{13}C relaxation of the methyl group in I and II where like in toluene[25] both dipole-dipole and spin-rotation interactions are important (see below). Therefore we preferred measuring ^2H relaxation times using the previously developed proton line shape analysis method[22] and specifically labeled *p*-methylcinnamate-d_2 (I). T_q was measured as a function of the fraction α of substrate complexed by α-CD; such data may in principle lead to the absolute values of the association-dissociation rate constants of the complex.[26,27] Indeed the mathematical form of the relation between the measured relaxation time $T_q(m)$ and the complexed fraction α depends on both these kinetic rate constants and on the correlation times for the free and complexed species. Particularly, when the rate constant for dissociation is small compared to the inverse of the correlation time for the complexed species, the general equation simplifies to:

$$T_q^{-1}(m) = \alpha T^{-1}(\text{complex}) + (1 - \alpha)T^{-1}(\text{free}) \quad (2)$$

Figure 1 shows the variation of $T_q^{-1}(m)$ in dilabeled I vs. α; both the methyl and acrylic ^2H relaxations are compatible with eq 2. The intercepts for $\alpha = 0$ and 1 are respectively T^{-1}(free) and T^{-1}(complex) and are listed in Table I together with the calculated correlation times using eq 1. From the observed linear relationship between $T_q^{-1}(m)$ and α we may therefore conclude that the dissociation rate constant of the complex is much smaller than 10^{10} s^{-1}. Computer simulations using the general relation between $T_q(m)$ and α show in fact that the rate of dissociation should be $<10^8$ s^{-1} but even this lower limit gives no information about how far from the diffusion control is the association process. *T*-jump measurements[3] have shown that this limit

Table I. ^2H Quadrupolar Relaxation Times T_q[a] and Correlation Times τ_q for Dilabeled I and Its Complex with α-Cyclodextrin

	-CD=CH-		CH_2D	
Compd	T_q, ms ± 10%	τ_q, ps ± 15%	T_q, ms ± 10%	τ_q, ps ± 15%
I	105	22	1000	2.3
[I, α-CD]	23	100	54	43

[a] Obtained from line shape analysis[21,22] of the vinyl and methyl protons NMR signals.

is never quite reached and that the rate constants vary over a wide range, depending on the nature and position of the substituents.

Table I shows that for the free molecule the methyl group reorientation is ca. ten times faster than the double bond reorientation. This is not unexpected if one makes the reasonable assumption of a rotation barrier between the double bond and the benzene ring, and a very fast unhindered internal rotation for the methyl group around its threefold axis. This agrees with previous results showing unhindered rotation for methyl groups linked to aromatic hydrocarbons.[25,28] Indeed internal rotations decrease local correlation times, and in the limiting case of an internal rotation very fast with respect to the overall reorientation, the local methyl motion is decoupled by a factor of ca. 10[28,29] from the remainder of the molecule. Thus, the correlation times of the cinnamic side chain and of the phenyl ring in I should be similar, i.e., they are approximately rigid from the dynamic point of view (slow internal motion; see also the case of II below), whereas the terminal methyl group displays free rotation.

^{13}C Relaxation Times and Correlation Times. For a ^{13}C nucleus directly linked to at least one proton, the major relaxation process comes usually from the $^{13}C,H$ dipolar interaction; the measured spin-lattice relaxation time T_1 of such a nucleus is related to the correlation time τ_c of its motion by

$$T_1^{-1} = 3.60 \times 10^{10}\, n r_{CH}^{-6}\tau_c \quad (3)$$

where n is the number of linked protons at distance r_{CH} (in Å). Except for the CH_3 carbon nuclei where the spin-rotation mechanism also contributes,[25] eq 3 holds for all proton bearing carbons of α-CD, of the substrates I-III, and of their complexes. Figure 2 shows some partially relaxed ^{13}C spectra[23] taken for the measurement of α-CD T_1's. The relaxation times measured for the free substrates and their mixtures with α-CD are listed in Table II. Taking into account the amount of free and complexed species present in the mixtures, the relaxation times (eq 2) and the correlation times (eq 3) of the complexes have been calculated (Table III).

For free and complexed α-CD, the ring ^{13}C T_1's (C_{1-5}) are equal within experimental error in each case. Thus, as expected, there is no fast internal motion in the cyclic framework and the mean value $\langle T_1 \rangle_{1-5}$ was taken to calculate (using eq 3) the correlation times given in Table III. The same comment holds for carbons 1-3,5,6 in II and 1,2 in III.

However, T_1 of carbon 4 in II is much shorter than the corresponding $\langle T_1 \rangle_{1-3,5,6}$, an effect similar to that found for monosubstituted benzenes where the difference between T_1 (para) and T_1 (ortho, meta) has been attributed to anisotropic reorientation.[25] Indeed for compound II (and certainly I and III too) reorientation will be easier around an axis going through the bulky hydrated anion and the benzene nucleus, since both the frictional and inertial resistances are lower than for the motions about the other axes. The C_4-H vector has the smallest angle with such an axis

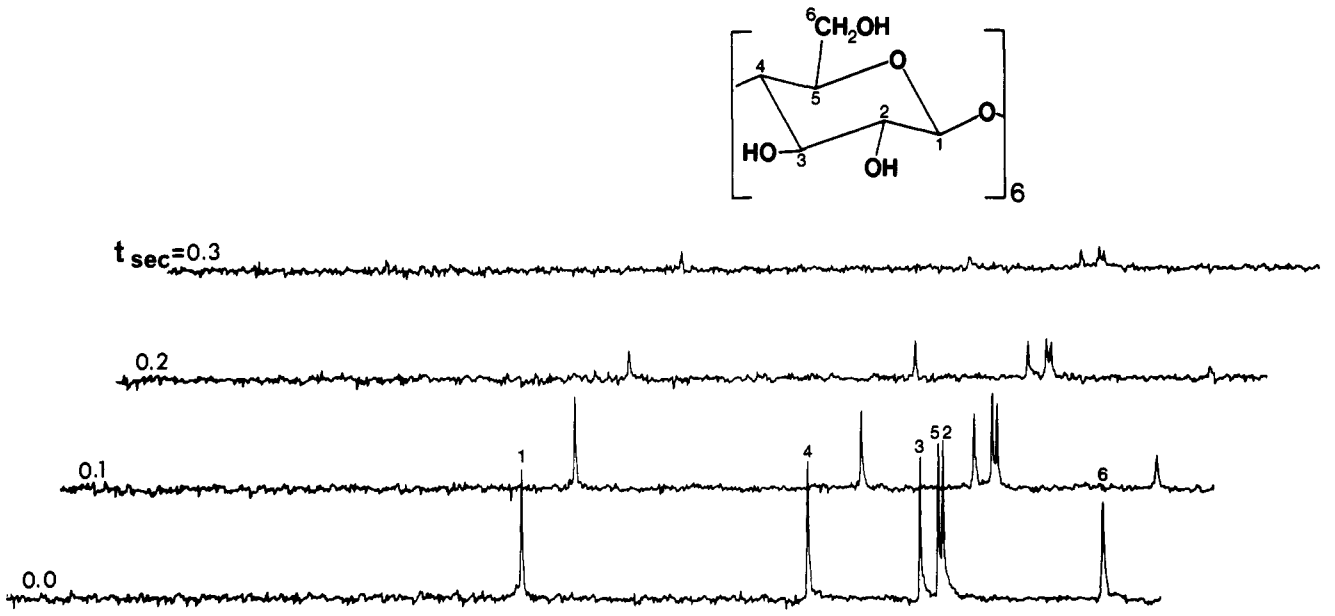


Figure 2. Measurement of ^{13}C T_1's for α-cyclodextrin (α-CD) by the $(90°-5T_1-180°-t-90°-5T_1)_N$ method; only four spectra out of ten are shown for clarity, [α-CD] = 0.1 M. Assignment following ref 34.)

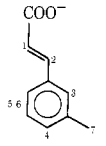
Table II. ^{13}C Relaxation Times for α-Cyclodextrin (α-CD) and Mixtures with *p*-Methylcinnamate (I), *m*-Methylcinnamate (II), and *p-tert*-Butylphenate (III)

Compd[a]	^{13}C relaxation times T_1 s ± 10%						
	1	4	3	5	2	6	$\langle T_1\rangle_{1-5}$
[α-CD][b]	0.135	0.145	0.150	0.155	0.135	0.105	0.144
[α-CD, I]	0.075	0.085	0.080	0.090[c]		0.045	0.082
[α-CD, II]	0.125	0.120	0.110	0.120	0.125	0.075	0.120
[α-CD, III]	0.100	0.095	0.105	0.105[c]		0.055	0.101

	1	2	3	4	5	6	7	$\langle T_1\rangle_{1-3,5,6}$
(II)[d]	1.70	1.65	1.35	0.80	1.50	1.40	2.95	1.52
[α-CD, II]	0.45	0.40	0.45	0.30	0.45	0.60	0.34	0.47

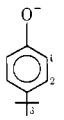
	1	2	3	$\langle T_1\rangle_{1,2}$
(III)[e]	2.45	2.40	1.25	2.42
[α-CD, III]	0.65	0.50	0.60	0.57

[a] The measured T_1's correspond to the underlined species. [b] Assignment as in Figure 2. [c] Lines overlapped. [d] Assignment as follows



II

(based on off-resonance decoupling and chemical shift consideration). [e] Assignment as follows



III

(based on off-resonance decoupling and chemical shift considerations).

Table III. ^{13}C Relaxation Times T_1 (s) and Rotational Correlation Times τ_c[a] (10^{-12} s, ps) for α-CD and Its Molecular Inclusion Complexes[b] with I, II, and III

Compd[c]	T_1	τ_c	T_1	τ_c
	α-CD overall		Primary hydroxyl	
[α-CD]	0.14	340	0.10	235
[α-CD, I]	0.08	630	0.06	430
[α-CD, II]	0.12	420	0.07	340
[α-CD, III]	0.10	500	0.05	470
	Substrate overall		Methyl	
II	1.5	32	2.9	<5.6[d]
[α-CD, II]	0.45	110	0.30	52
	Substrate overall		*tert*-Bu	
(III)	2.4	20	1.2	13
[α-CD, III]	0.54	91	0.6	28

[a] Calculated following eq 3 with r_{CH} = 1.10 ± 0.02 Å; accuracy ±25%. [b] With the concentrations used for α-CD/substrate mixtures (see Experimental Section) and the roughly measured association constants, one calculates that ca. 90% of the underlined species is complexed; this has been taken into account using eq 2 for calculating T_1 and τ_c. [c] T_1 and τ_c correspond to the underlined species. [d] Because of the spin–rotation contribution, only an upper limit can be given.

and the modulation of the C_{13},H dipole–dipole interaction by this motion will be the least effective.

Effect of Complexation on the Molecular Motions of the Substrates and of the α-Cyclodextrin Ligand. Despite the uncertainty (mostly due to the lack of accurate r_{CH} distances) in the τ_c's, the results given in Tables II and III allow a few general comments to be made.

(1) The overall reorientation of the three *substrates* in water (assumed pseudo-isotropic) is about the same, τ_c ranging from 2 to 3.2 × 10^{-11} s. This is not surprising if one compares the structures of these compounds: all are disubstituted benzenes with one substituent bearing a negative charge. In addition, the decrease in molecular dimensions by going from *tert*-butyl to methyl substitution is compensated by the attachment of the acrylic side chain. A small anisotropy in the tumbling motion of II is indicated by the ^{13}C relaxation times (see above).[25] The same is probably true for I and III but cannot be seen experimentally because there is no C–H vector lying nearly parallel to the preferred rotation axis. In I the methyl group is free to rotate as seen by deuterium relaxation measurements, while in III the

CH_3-C as well as the $(CH_3)_3C$-C rotations are severely hindered (overall and local motions differ only by a factor of 1.5 whereas free rotation about two bonds would lead to a factor of ca. 100).[28] For II only an upper limit to the methyl correlation time can be given by ^{13}C relaxation, but this group is certainly free to rotate as in I; similarly in 2-methylfluorene, the methyl group is fully decoupled from overall motion.[28]

The similarity of the ^{13}C relaxation times for the acrylic side chain and for the phenyl ring in II (Table II) confirms that these two groups are dynamically strongly coupled in agreement with the conclusion reached for I (see above).

(2) *Upon inclusion* in α-CD, the overall tumbling motion of the three substrates slows down by a factor of ca. 4 as a consequence of coupling of their motions to those of the α-CD ligand. The reorientation of the *p*- and *m*-methyl groups slows down by a factor of 20 in [I, α-CD] and [II, α-CD] as compared to the free substrates. Using the correlation times of the aromatic ring and of the CH_3 group for describing the overall and the local molecular motions, the correlation time τ_i for internal reorientation about the C-CH_3 bond may be calculated.[28] τ_i is very large in the complexes [I, α-CD] (55 ps) and [II, α-CD] (75 ps) as compared to the free substrates I and II (smaller than about 2 ps). This is indication for a strong hindrance of the C-CH_3 reorientation in the complexes. The motions of the CH_3 groups are not fully decoupled anymore from those of the benzene ring, showing that these groups are also included in the hydrophobic core or at least in contact with it. The *m*-methyl group seems the most affected, although this may not be significant (if we assume the same C-H bond length for the methyl groups in I and II, the relative error is about ±10%). The C-4 relaxation time of II is still smaller than the mean $\langle T_1 \rangle_{1\text{-}3,5,6}$ in the complex, suggesting that the tumbling of the substrate in [II, α-CD] remains anisotropic. τ_i of the *t*-Bu group is similar in III and [III, α-CD] (about 30 ps); this should indicate that in the complex, the bulky substituent is located outside the cyclodextrin ring.

(3) For α-CD itself the overall reorientation time is in the range expected for a molecule of this size and is similar to that found from EPR measurements on spin-labeled β-CD.[20] There is no internal motion faster than the overall one, except for the primary alcohol groups which reorient slightly faster than the rigid skeleton, due to internal rotation about the C(5)-C(6) bond. After inclusion of a substrate, the overall correlation time increases in the order [α-CD] < [II, α-CD] < [III, α-CD] < [I, α-CD]. Although the change in molecular dimension is small between α-CD and its inclusion complex with one of the substrates, τ_c increases by a factor of ca. 2 in [I, α-CD]. This quite large change may be rationalized by considering that the carboxylate group remains fully hydrated in the complex, thus lowering its reorientation rate (the introduction of a charged ammonium or carboxylate group may change drastically the correlation time of a molecule, as seen for glycine derivates[30]). The increase in τ_c (α-CD) is the smallest for [II, α-CD] where the *m*-methyl group may orient the carboxylate group in such a way that it is partly hydrogen bonded with the hydroxyls of α-CD; this would agree with the hypothesis proposed by Bender et al.[6] for explaining the large meta/para selectivity observed for the α-CD catalyzed hydrolysis of substituted phenyl acetates.

Compared to free α-CD, the internal motion of the CH_2OH groups is increasingly affected by going from [I, α-CD] to [II, α-CD] to [III, α-CD], but the direction in which each substrate enters the α-CD ring not being known, no correlation with the structures can be made. This direction may not even be the same for I, II, and III; indeed the hydrolysis of phenyl acetates (noncharged molecules) has been found to be catalyzed via the secondary hydroxyls[6] whereas in the crystal, the acetate anion is hydrogen bonded to four primary hydroxyls.[31]

(4) The most striking result is the existence in the three complexes studied of an independent and probably highly anisotropic *motion of the substrates with respect to the cavity*. Indeed in the complexes, the correlation times of the included molecules are about four to six times shorter than the correlation time of the receptor α-CD molecule (Tables I and III). The nondirective and weak nature of the forces involved in the complexation, the symmetry of the cavity, as well as possible deformations of the macrocycle may be responsible for this independent motion which probably takes place around the sixfold symmetry axis of α-CD. Thus the cyclodextrins and their complexes, although being worthwhile models for the study of enzyme-like behavior in relatively small systems (see the introductory section), have dynamic properties far from an enzyme-substrate complex where stronger and more directive interactions probably maintain the substrate.[32,33]

Conclusion

Insofar as the present results also hold for other benzene derivatives, the inclusion complexes of mononuclear aromatic substrates with α-cyclodextrin are of the *weakly coupled* type from the dynamical point of view, i.e., substrate and ligand have different molecular motions. This contrasts with the notion of tightness usually associated with complexation. Although weak addition complexes of the donor-acceptor type are still much more dynamically labile,[27,35] the present complexes display appreciable motion of the substrate with respect to the ligand in the complexed state, despite their "inclusion" nature. They result from association of two species with only weak directional interactions. These relatively simple systems illustrate the fact that complex formation should be described not only by a thermodynamic association constant but also by a *dynamic coupling coefficient* similar to that defined for intramolecular motions.[28] Such a parameter, taken as the ratio of substrate correlation time to ligand correlation time, would be equal to or smaller than 1 depending on whether the substrate motions are the same as those of the ligand or faster. Values of 0.16, 0.26, and 0.18 are obtained from the data in Tables II and III for the α-CD complexes of I, II, and III, respectively; thus appreciable decoupling is observed.

It would be of interest to study other complexes of α-cyclodextrin or β-cyclodextrin or of modified cyclodextrin,[36] since such systems are clearly well suited for the detection of dynamical coupling in molecular complexes. Furthermore in these and other chemical or biological systems the study of dynamic coupling also provides a means of defining *structural complementarity* in the formation of selective molecular complexes.

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Metal–Metal Interactions Involving Metalloporphyrins. III. Conversion of Tetraphenylporphinatoiron(III) Azide to an N-Bridged Hemin Dimer[1]

David A. Summerville and Irwin A. Cohen*[2]

Contribution from the Departments of Chemistry, Polytechnic Institute of New York, Brooklyn, New York 11201, and Brooklyn College of the City University of New York, Brooklyn, New York 11210. *Received May 16, 1975*

Abstract: The high temperature solution decomposition of tetraphenylporphinatoiron(III) azide ($TPPFe^{III}N_3$) in the absence of added base and oxygen has been examined. In addition to N_2 the only reaction product observed is formulated as TPPFeNFeTPP analogous to $(TPPFe)_2O$. The room temperature Mössbauer spectrum is sharp (δ = 0.10, rel Fe; Δ = 1.08 mm/s) and is compared to that of $(TPPFe)_2O$. Magnetic studies reveal a temperature independent moment indicative of one unpaired electron per dimer. The FeNFe infrared mode is observed at 910 (vs) and 885 (m) cm^{-1}. Kinetic studies of the solution thermolysis indicate first-order decomposition of $TPPFeN_3$ with E_a = 33.7 kcal/mol. This appears to be the first example of a nitrogen atom bridge between two metals of the first transition series.

Ever since the preparation of dinitrogen complexes of ruthenium(II)[3] the decomposition of coordinated azide has been of interest. Basolo and co-workers have been able to characterize the decomposition of Ru(III)[4] and Ir(III)[5] azides as proceeding through a strongly electrophilic protonated nitrene (e.g., $[(H_3N)_5Ru^{III}NH]^{3+}$ or $[(H_3N)_5Ir^{III}NH]^{3+}$). The fate of the intermediate depends in part on the available oxidation states of the metal ion. In the case of the ruthenium(II) catalyzed decomposition of azide[6] the corresponding intermediate has been proposed as $[(H_3N)_5Ru^{II}\ddot{N}H]^{2+}$ Because of the apparent nucleophicity of that intermediate Basolo and co-workers have pointed out that a $Ru^{II}\ddot{N}H$ (nitrene) may be better represented as a $Ru^{IV}\ddot{N}H$ (protonated nitride or imido) species.

The only reported decomposition of a hemin azide was by McCoy and Caughey.[7] They observed that the infrared spectrum in the 2000-cm^{-1} region of azido protoporphyrin diethyl ester iron(III) in pyridine underwent a slow change at room temperature which was not inconsistent with the formation of a porphyrin $Fe^{II}N_2$ species. The spectral changes were not observed in the absence of pyridine or with other porphyrins. Because that product has not been fully characterized we investigated the decomposition of azidotetraphenylporphinatoiron(III) in the presence of bases and found the reaction to be extremely complicated. However, at high temperature, in the absence of added bases, the azide decomposition proceeded smoothly in pure xylene and provided an interesting product, $(TPPFe)_2N$, containing a nitrogen atom bridge analogous to the well-characterized μ-oxo dimer $(TPPFe)_2O$.[8-11] This appears to be the first example of a nitrogen bridged complex of a first transition series metal.

Experimental Section

All solvents and chemicals were reagent grade and used without further purification. Xylene was Fisher certified xylenes containing a mixture of ortho, meta, and para isomers which were dried and distilled from calcium hydride immediately prior to use.

Spectra were recorded on Perkin-Elmer Model 521 and Cary Model 14 spectrophotometers. Mass spectra were observed on a Hitachi Perkin-Elmer Model RMU-6E spectrometer. Mossbauer data were collected on a Ridl 400 channel analyzer, Model 34-12B, using an Elscint Mossbauer drive, Model MFD-4 in the sawtooth mode. Pulse height discrimination was performed with a high count rate amplifier (Elscint, Model CAV-N-1) and single channel analyzer (Elscint, Model SCA-N-2A). The data were analyzed by a conventional least-squares fit to individual Lorentzian shaped absorption peaks on an IBM 360-168 computer. The maximum error calculated for the position of any one absorption peak was ±0.002 mm/s. Low temperature spectra were obtained with an Air Products cryostat and a proportional temperature controller. Although the sample temperatures were held constant to within ±0.2 K the actual temperatures were known to only ±1.0 K. All spectra were observed using powders and isomer shifts are reported relative to iron metal.

Magnetic suceptibilities were measured on powdered samples by the Faraday method using an Ainsworth electronic balance and an Alpha cryostat between 77 and 300 K. $HgCo(SCN)_4$ was used as a standard and the magnetic field was measured using metallic nickel. Suceptibilities were corrected for diamagnetism using the value -386×10^{-6} cgs units/mol for tetraphenylporphine and the standard values for other elements present.[12]

Molecular weights were determined by vapor pressure osmome-