

Molecular Motions and the Structure of β -cyclodextrin Inclusion Complexes with Ferrocene, [3]-Ferrocenophane-1,3-dione and Ruthenocene

ZDZISLAW NARANKIEWICZ, ALEXANDR L. BLUMENFELD, VERONICA L. BONDAREVA, IRINA A. MAMEDYAROVA, MARINA N. NEFEDOVA, and VIATCHESLAV I. SOKOLOV

Institute of Organoelement Compounds, USSR Academy of Sciences, 28 Vavilov St. 117813 Moscow, U.S.S.R.

(Received 6 February 1991; in final form: 12 June 1991)

Abstract. Spin-lattice relaxation time measurements in laboratory and rotating frames as well as proton second moment analysis have been used to investigate molecular motions in β -cyclodextrin (CD) and its solid inclusion complexes with the title organometallic compounds. Different dynamical processes have been identified in the host lattice along with high mobility of the ferrocene and ruthenocene guest molecules. The Arrhenius parameters of all motions were obtained. The assumption based on the second moment measurements was made about the axial structure of the ferrocene complex and the equatorial one of the ruthenocene complex at low temperatures. The bridged ferrocenophane molecule was shown to be rigid on the NMR time scale. The ternary inclusion complex of β -CD with ruthenocene and iodine was also studied and no evidence of redox reactions was observed.

Key words. Inclusion complexes, β -cyclodextrin, ferrocene, ruthenocene, NMR, spin-lattice relaxation, second moments.

1. Introduction

The β -cyclodextrin (CD) molecule built from 7 D-glucose residues has the form of a tapered cylindrical tube (Figure 1). Though the inclusion complexes of β -CD with various organometallic compounds are known [1, 2], data concerning their structure and molecular mobility are limited. We report here the results of our study of the solid β -CD complexes with ferrocene (I), [3]-ferrocenophane-1,3-dione (II) and ruthenocene (III). In 1984 Harada and Takahashi [3] reported the preparation of solid α -, β - and γ -CD complexes with ferrocene and discussed briefly their possible structure. Since the Cotton effect in the β -CD and γ -CD complexes was found to have opposite signs the authors [3] assumed that the ferrocene molecules had different orientations inside the host lattice. From simple geometrical considerations they postulated the axial structure for the β -CD complex and an equatorial one for γ -CD. However, more recently an extensive study has been performed of all cyclodextrins, including the smallest one, α -CD, complexed with ferrocene itself and several acylferrocenes [4]. It turned out that the signs of the Cotton effect exhibited no simple correlation with the proposed geometry. So, β -CD + FcH showed a negative sign whereas both γ -CD + FcH and, remarkably, α -CD + FcH show a positive effect. By the way, the Cotton effect sign changes for acylferrocenes in an irregular way. Therefore, the initial hypothesis [3] has to be considered as erro-

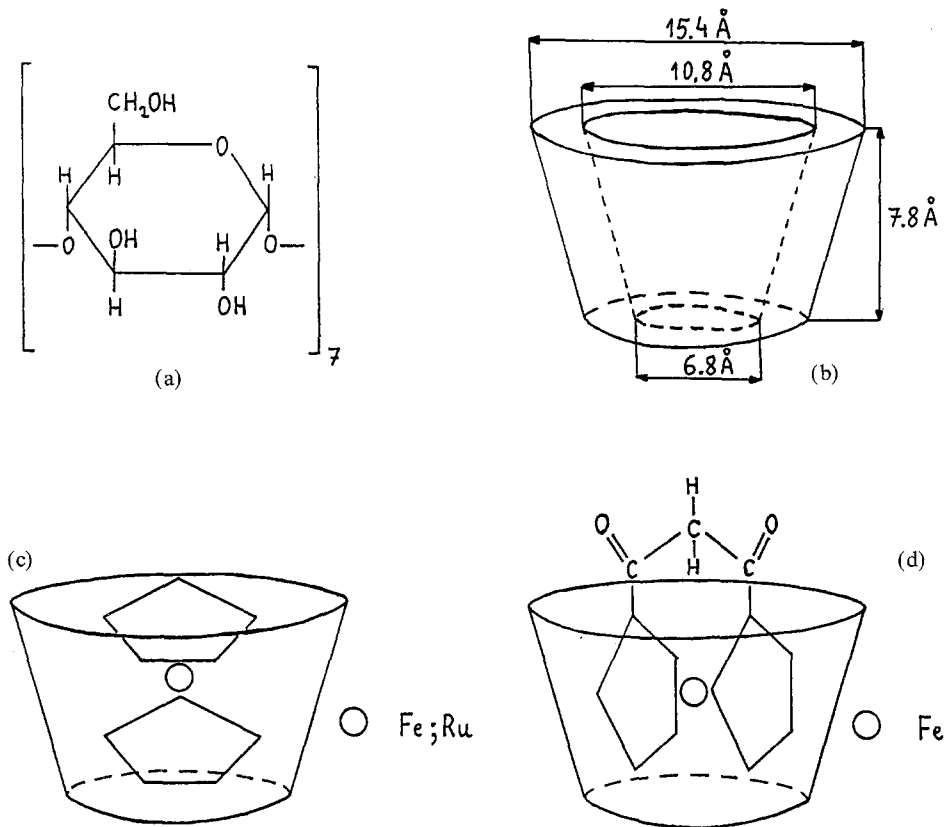


Fig. 1. The schematic structure of β -CD and its complexes. (a) The D-glucose residue. (b) The structure of the β -CD unit. (c) The axial structure of complexes **I** and **III**. (d) The equatorial structure of complex **II**.

neous. Recently two research groups [5, 6] have published detailed calculations for the above complexes by the use of molecular mechanics with an optimization scheme. They found that the axial and equatorial structures of the β -CD complexes differed in energy only slightly (2 kJ mol^{-1}) and could hardly be distinguished. Indirect evidence based on Mössbauer data [7] favoured the isotropic rotation of the ferrocene molecule in the α -CD complex at room temperature.

In this paper we present the results of our study of the complexes **I**, **II** and **III** by the use of ^1H solid state NMR spectroscopy. Ternary cyclodextrin complexes with two different kinds of molecules included are of some interest. One of the few known complexes, containing both ruthenocene and iodine, has been studied in this work. The temperature dependence of the spin-lattice relaxation times in the laboratory frame (T_1), the spin-lattice relaxation times in the rotating frame (T_{1e}) and the proton second moments (M_2) were measured in the range 100–400 K. In order to facilitate the interpretation of the complex relaxation curves we also investigated complexes precipitated from D_2O – complexes **I-d**, **II-d** and **III-d**.

2. Experimental

The cyclodextrin complexes of the metallocenes were prepared in water on gentle warming. The ruthenocene-CD complex was then treated with iodine vapour to afford the ternary complex.

All NMR measurements were made with a Bruker SXP-2-100 pulse spectrometer operating at 90 MHz (proton resonance frequency). The sample temperature was controlled by a home-made device which assured an accuracy of ± 1 K in the range 100–400 K. The samples were studied in sealed glass tubes under gaseous Ar. The 90° pulse width was of the order of $2 \mu\text{s}$. Different techniques were used for measuring relaxation times: inversion-recovery, saturation-recovery and null-point methods for T_1 and multiple-pulse spin-locking for T_{1e} . The proton second moments were measured either by Fourier transform of the second half of the solid-echo or by measuring the slope of the initial part of the free induction decay. All data obtained by different methods were consistent. The adjustment of durations, phases and amplitudes of rf pulses was made according to standard procedures [8].

3. Discussion

In order to understand the complex dynamical behaviour of **I**, **II** and **III**, as well as of their deuterioanalogues, we have included in our investigation the study of molecular motions in the host lattice of β -CD.

3.1. LINE SHAPE MEASUREMENTS

Figure 2 represents free induction decays (FID) after 90° pulses of β -CD, β -CD-d, **I** and **I**-d at room temperature. It is obvious from the plot that the β -CD signal is a superposition of two components with $T_{2b} = 15 \mu\text{s}$ (broad component) and $T_{2a} = 150 \mu\text{s}$ (narrow component). Comparing this observation with the signal from the deuterated sample, β -CD-d, where only the broad component was observed, one can assign the narrow component to H_2O molecules included within the host CD lattice. When the sample was cooled, the width of the narrow component increased and at low temperatures ($T < 240$ K) the FID became a single-component. From the amplitude ratio of the two components one can conclude that each molecule of β -CD contains 11 molecules of H_2O . We deconvoluted the complex FIDs into two components by the least squares procedure and thus obtained the temperature dependence of the narrow component second moment. Two approaches were used to obtain the activation parameters of the motional process of water molecules. According to the Waugh-Fedin equation [9] the activation energy, E_a , is connected with the approximate value of the line-narrowing temperature, T_c :

$$E_a = 37T_c \quad (1)$$

The more accurate approach of Gutovsky and Pake [10] takes into account the experimental data in the wider temperature range near T_c :

$$\tau_c = (4\pi\alpha\gamma\sqrt{M_2})^{-1} \tan\left\{\frac{\pi}{2}\left[\frac{M_2 - M_{2h}}{M_{2l} - M_{2h}}\right]\right\} \quad (2)$$

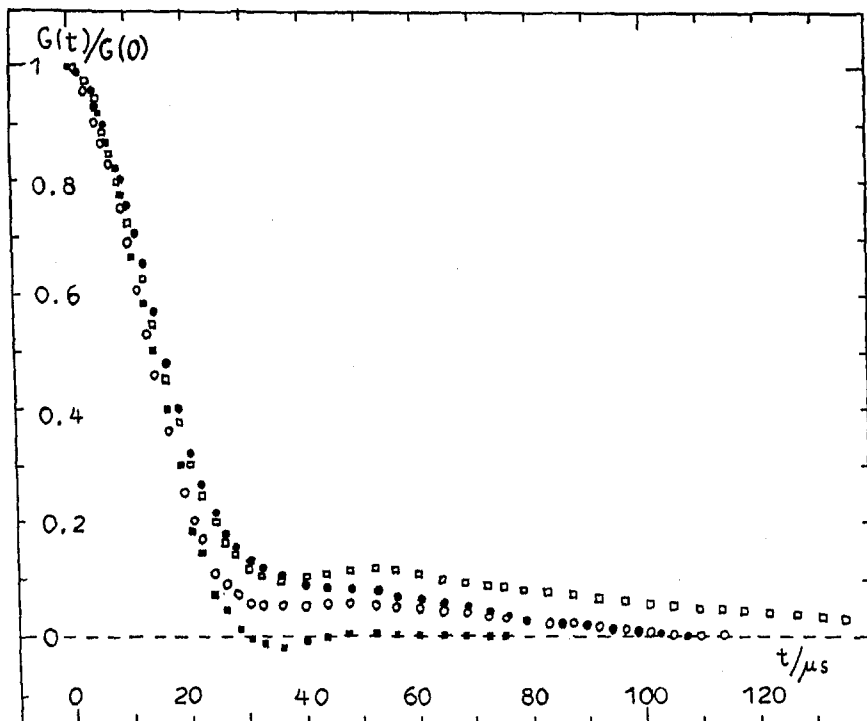


Fig. 2. The free induction decays at room temperature in β -CD (\square), β -CD-d (\blacksquare), I (\circ) and I-d (\bullet).

where M_{2h} , M_{2l} are the second moment values at the high and low temperature plateaux, respectively, and τ_c is the correlation time. From both equations similar values were obtained for E_a of the motion of the water molecules ($\approx 42 \text{ kJ mol}^{-1}$, see Table I, motion 1').

In complexes I and III the narrow components were also observed at room temperature (see Figure 2) but their nature was quite different from that of β -CD. First, the narrow components still existed at the lowest temperature (120 K) and second, deuterated samples I-d and III-d also contained narrow components. The deuterated complexes contained water molecules only in the form of D_2O and all hydroxyl protons were changed for deuterons, so it seemed reasonable to assume that at high temperatures the narrow components in I-d and III-d were due to the rapidly and isotropically rotating ferrocene (and ruthenocene) guest molecules. Such an assignment is supported by the experimental intensity ratio of the two components. These narrow components could be observed down to 120 K with broadening processes in the 253–313 K range (for I-d) and the 250–290 K range (for III-d). The activation parameters of these processes are listed in Table I (Motion 1). The second moment values of the narrow components at the high temperature plateau are very low: 0.3 G^2 for I-d and 0.5 G^2 for III-d. This led us to the conclusion that at high temperatures ferrocene and ruthenocene guest molecules exhibit rapid and isotropic reorientations and at low temperatures only reorienta-

Table I. Arrhenius parameters ($\tau_c = \tau_0 \exp(E_a/RT)$), ΔM_2 values, inverse temperatures of relaxation minima and distribution parameters for different molecular motions.

Compound	a	b	E_a [kJ mol ⁻¹]	ΔM_2 [G ²]	$10^3/T_{\min}$ [K ⁻¹]	$\tau_0 \times 10^{-13}$ [s]	β^c	
β -CD (H ₂ O)	1'	T_{1e}	41.9	2.20	3.50	1.49		
		M_2	42.5					
	2	T_{1e}	29.3	4.43	4.80	3.04		
		T_1	31.0	(4.40) ^d	(2.15)	(3.52)		
		T_1	22.6	2.60	3.28	1.41		
4	T_1	16.3	0.35	4.30	2.28			
5	T_1	6.3	0.16	6.20	99.3			
β -CD (D ₂ O)	2	T_1	31.4	(2.00)	(2.10)	(3.82)		
	3	T_1	22.2	0.12	3.10	2.71		
β -CD + Fc (H ₂ O)	2	T_1	30.8 ^e	(4.50)	(2.45)	(1.22)		
	3	T_1	21.8	1.36	3.23	2.25		
	4	T_1	16.3	0.35	4.30	2.28		
(I)	5	T_1	6.3	0.42	6.20	99.3		
	6	T_1	3.3	(1.30)	(9.00)	(314)		
β -CD + Fc (D ₂ O)	1	T_{1e}	44.8	1.16	3.11	3.57		
		M_2	44.0					
(I-d)	2	T_{1e}	37.1	2.82	3.80	2.99	0.49	
		T_1	37.1	(2.82)	(2.07)	(1.04)	0.49	
	3	T_1	21.4	0.20	3.05	4.21		
	6	T_1	3.3	(0.57)	(9.00)	(314)		
β -CD + Fc' (H ₂ O)	2	T_{1e}	33.9	7.30	4.05	3.78	0.60	
		T_1	33.9	(7.30)	(2.10)	(2.04)	0.60	
(II)	3	T_1	20.1	0.40	3.45	2.53		
	4	T_1	8.4	0.16	4.70	94.4		
	5	T_1	4.4	(0.22)	(9.00)	(92.0)		
β -CD + Fc' (D ₂ O)	2	T_{1e}	35.1	5.67	3.98	3.51	0.60	
		T_1	35.1	(5.67)	(2.15)	(1.22)	0.60	
(II-d)	3	T_1	20.1	0.20	3.50	2.24		
	4	T_1	8.4	0.11	4.90	77.1		
	5	T_1	4.4	(0.17)	(9.00)	(92.0)		
β -CD + Rc (H ₂ O)	2	T_1	28.5 ^e	(1.50)	(2.65)	(1.21)		
		T_1	21.4	0.90	3.35	1.94		
	4	T_1	16.3	0.20	4.15	3.06		
	(III)	5	T_1	6.3	0.08	5.20	211	
		6	T_1	3.5	(0.58)	(9.00)	(239)	
β -CD + Rc (D ₂ O)	1	T_{1e}	43.2	0.40	3.18	6.22		
		M_2	41.9					
(III-d)	2	T_{1e}	37.7	2.50	3.78	3.28	0.50	
		T_1	36.9	(2.50)	(2.15)	(0.77)	0.50	
	3	T_1	21.4	0.20	3.15	3.26		
	4	T_1	16.3	0.015	4.30	2.28		
	5	T_1	6.3	0.09	5.20	211		
	6	T_1	3.4	(0.51)	(9.00)	(261)		
β -CD + Rc + I ₂ (D ₂ O)	1	T_{1e}	47.8	0.74	2.85	7.10		
		T_{1e}	37.7	3.15	3.62	6.79	0.40	
(III-I ₂)	2	T_1	36.9	(3.15)	(2.20)	(0.62)	0.40	
		T_1	7.5	0.15	5.60	66.9		
	6	T_1	3.4	(0.43)	(9.00)	(261)		

^a Type of motion (see text).

^b Method of determination.

^c The Fuoss-Kirkwood distribution parameter.

^d Values in brackets mean that corresponding relaxation minima were not achieved.

^e The value is slightly understated since the distribution of correlation times has not been taken into account in this case.

tions of the Cp rings occurs. The latter motion will be considered later during the discussion of the relaxation data. The above conclusion is consistent with the study of the β -CD complex with perdeuterioferrocene by the use of ^2H NMR spectroscopy [13]. In complex **II** no narrow component was observed up to 400 K which means that the ferrocenophane guest molecules are motionless on the NMR time scale.

3.2. T_1 MEASUREMENTS

In order to obtain dynamical parameters from spin-lattice relaxation time measurements we have used the standard Blombergen–Purcell–Pound (BPP) approach [10]. The dependence of the relaxation rate T^{-1} and the correlation time τ_c of any molecular motion is given by the following equation:

$$T_1^{-1} = \frac{2}{3}\gamma^2\Delta M_2 \left\{ \frac{\tau_c}{1 + (\omega_0\tau_c)^2} + \frac{4\tau_c}{1 + (2\omega_0\tau_c)^2} \right\} \quad (3)$$

where $\omega_0 = 2\pi 90$ MHz is a proton resonance frequency and ΔM_2 is a part of the proton second moment which is averaged by a given molecular motion.

All temperature dependencies of spin-lattice relaxation times T_1 obtained in this work are shown in Figures 3 and 4. One can see that the relaxation in all the samples proceeds in a complex way and is determined by several motional processes with distinct parameters. We have determined the individual contributions to the net relaxation according to the standard BPP procedure [10] and the corresponding results are displayed in Figure 5(a–d). First we shall discuss the results obtained for the β -CD matrix (Figure 5a). Four dynamical processes (motions 2, 3, 4 and 5) are needed for an accurate fit to the experimental data. The activation parameters for all motions are given in Table I. The necessity to include high-temperature motion 2 (as well as motion 1, not shown here) followed from the T_{1e} measurements which will be discussed later. Motion 3 should be assigned to H_2O molecular reorientation for the following reasons. First, this motion in the deuterated sample of β -CD had significantly less relative intensity due to residual HDO molecules (see ΔM_2 values in Table I) and second, after heating the sample to over 390 K, when H_2O molecules leave the host lattice, this motion disappeared. Motion 4 can be attributed to proton exchange along inter and/or intramolecular hydrogen bonds since it is characterized by a very low ΔM_2 value and disappears completely in the deuterated sample (see Table I). We are of the opinion that the least hindered motion 5 ($E_a = 6.3$ kJ mol $^{-1}$) should be the small-amplitude tumbling of β -CD molecules or/and bending-like transitions between different conformational states. Motion 5 was not observed in β -CD-d because of the strong relaxation process which governed the relaxation at low temperatures (perhaps due to dissolved molecular oxygen) in this compound. However, Gidley and Bociek [14] discussed this motion in view of their ^{13}C CP MAS study of β -CD and its complexes.

Spin-lattice relaxation in complexes **I** and **III** proceeds basically in the same manner as in β -CD. The corresponding curves are shown in Figures 5b and 5d. The only distinctive feature is the presence of a low-temperature motion with a low activation barrier of roughly 3.3 kJ mol $^{-1}$ – motion 6 in Table I. This motion is

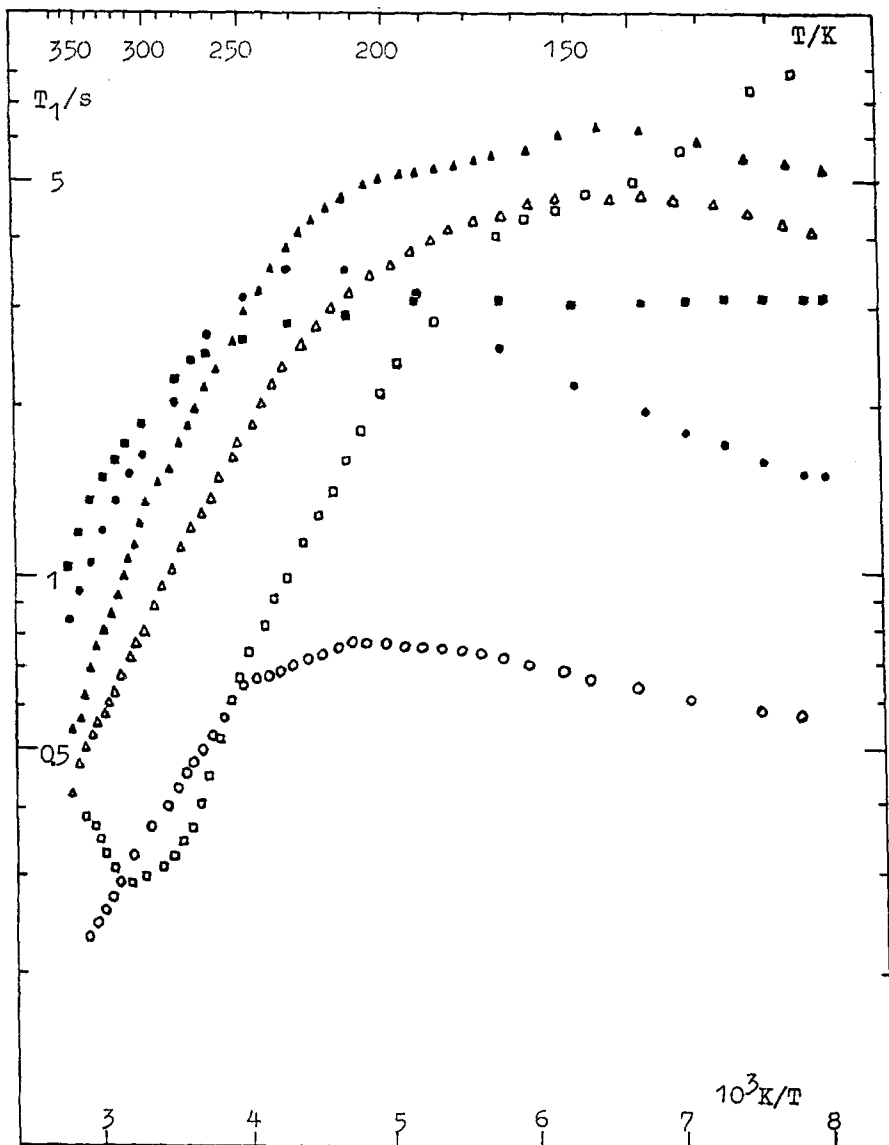


Fig. 3. Temperature dependences of the ^1H spin-lattice relaxation times T_1 observed for $\beta\text{-CD}$ (\square), $\beta\text{-CD-d}$ (\blacksquare), **I** (\circ), **I-d** (\bullet), **II** (\triangle) and **II-d** (\blacktriangle).

undoubtedly intrinsic to metallocene guest molecules and should be the reorientation of the 5-membered cyclopentadienyl (Cp) rings around the C_5 symmetry axis. The value of the activation energy is to our knowledge the lowest of all known for C_5 reorientations in different metallocene systems where the typical values lie in the range of 10–38 kJ mol^{-1} (see [11] and references therein). Whereas the barrier values are the same for complexes **I** and **III**, the $T_{1\text{min}}$ (and, hence, the corresponding ΔM_2 value) in **I** is approximately twice as large as in **III**. What is more, the ΔM_2 values for motion 6 in **III** and **III-d** are the same, whereas the difference between

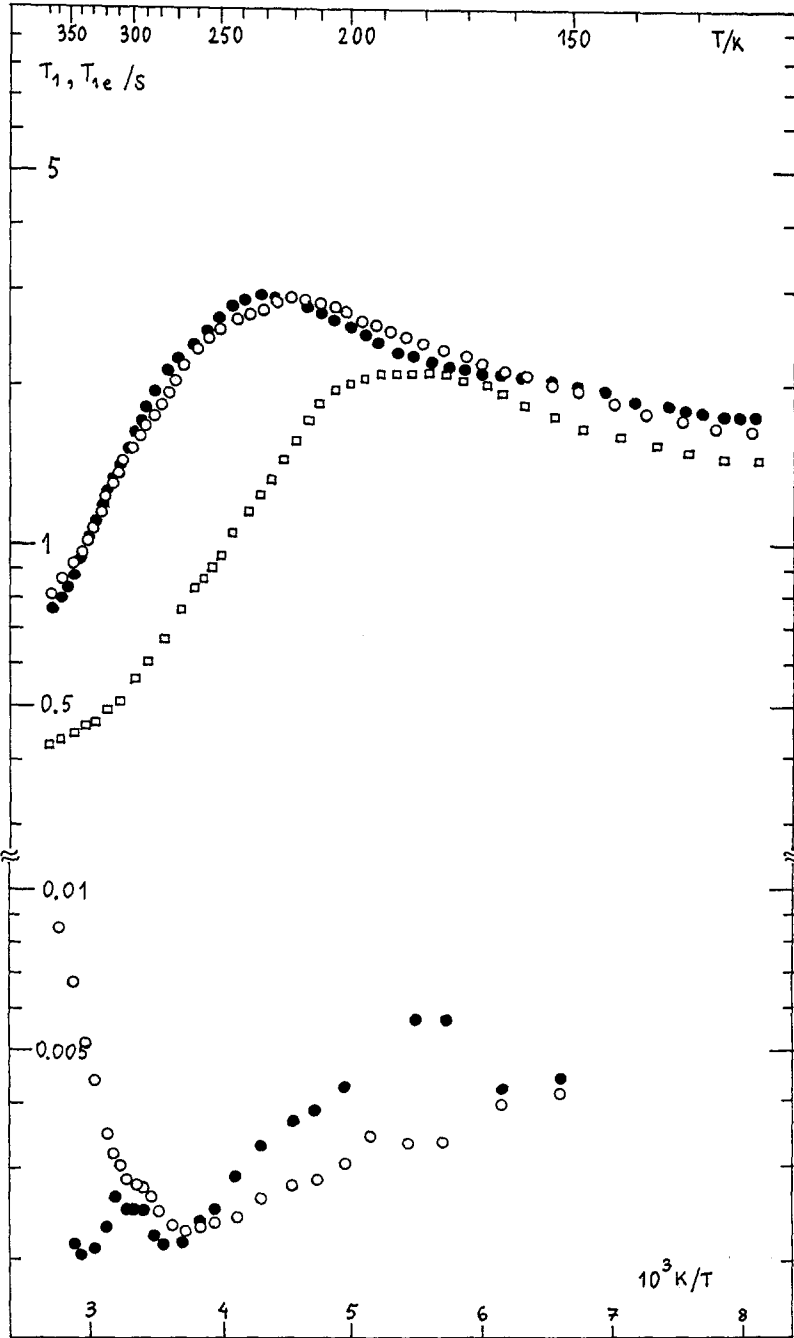


Fig. 4. Temperature dependences of the ^1H spin-lattice relaxation times T_1 (upper trace) of **III** (\square), **III-d** (\circ) and **III + I₂** (\bullet) and the spin-lattice relaxation times in an effective magnetic field ($B_{1\text{eff}} = 2.0\text{ G}$) T_{1e} (lower trace) of **III-d** (\circ) and **III + I₂** (\bullet). Note the break in the ordinate axis separating these plots.

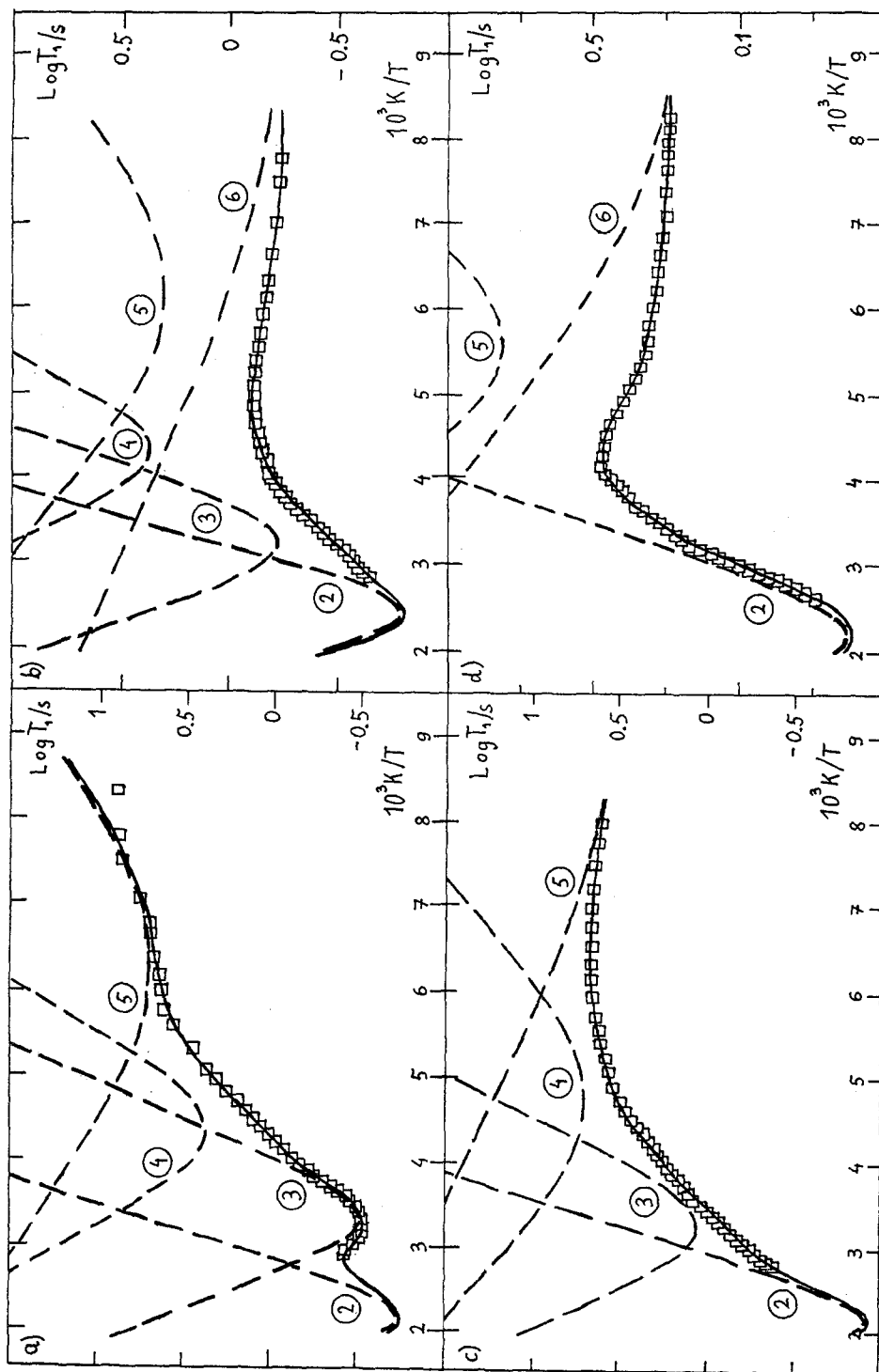


Fig. 5. Deconvolution of the experimental relaxation dependences into contributions from separate molecular motions (dashed lines). The net theoretical curve (solid line) is a sum of all the contributions. (a) β -CD. (b) Complex I. (c) Complex II. (d) III + I₂.

ΔM_2 in **I** and **I-d** is $0.7 G^2$ (see Table I). This becomes clearer if one recalls that metallocene protons, which contribute to the overall relaxation, account only for a small portion of all the protons of the sample. That means that in order to compare the results with e.g. crystalline ferrocene, the ΔM_2 values determined from the relaxation measurements should be multiplied by the corresponding factors, which depend on the modulated intermolecular contribution and are in the range of 2–10. In our opinion this is due to a different arrangement of metallocene molecules in **I** and **III** at low temperatures. The fact that proton second moments in **III** and **III-d** are the same and of low value can result from the equatorial position of the guest molecule. In this case the intermolecular contacts between Cp protons and the protons of the O—H(D) host hydroxyl groups are less pronounced than in the axial position, which could be the case for complex **I** with ferrocene (the tilted position of the guest molecule could not be ruled out). The latter conclusion is supported by several investigations where X-ray analysis [12], molecular mechanics calculations [5] and ^2H NMR [13] were used.

One can see from Figure 5c and Table I that the molecular dynamics in complex **II** looks very similar to that in pure β -CD. No additional motions were observed in **II** which indicates the 'rigid' arrangement of the guest ferrocenophane molecules. We think that the most probable structure of this complex is the one shown in Figure 1.

3.3. T_{1e} MEASUREMENTS

The study of spin-lattice relaxation processes in an effective magnetic field $B_{1\text{eff}}$ is a method to shift the experimental time scale towards low frequencies. The characteristic relaxation minimum is observed at the temperature where the condition $\gamma B_{1\text{eff}}\tau_c \approx 0.5$ is fulfilled rather than the above mentioned condition for relaxation in the laboratory frame. That means that the motion which is too hindered to be measured in the given temperature range by the T_1 method now becomes apparent in the same temperature range on the T_{1e} time scale. The theory of relaxation in a rotating frame is well developed [15, 16] and the following expression was used:

$$T_{1e}^{-1} = \Delta M_2 \tau_c \left\{ 1 - \frac{\sinh(2\alpha)(1 - \cos(2\theta))}{2\alpha[\cosh(2\alpha) - \cos(2\theta)]} \right\} \quad (4)$$

Here θ is the angle of pulse rotation in the multiple-pulse sequence, $2\alpha = 2\tau/\tau_c$ (2τ is the pulse spacing in the sequence).

The temperature dependences of the relaxation times T_{1e} of all substances except complexes **I** and **III** (precipitated from D_2O) are shown in Figures 4 and 6. One can see that in β -CD-d and complex **II** (with 'rigid' guest molecules) only one relaxation minimum was observed (motion 2), while in all other cases presented there is an additional high temperature minimum (motion 1). The fact that the latter minimum was observed in complexes with mobile guest molecules and that the corresponding activation energy coincides with the value obtained from our line shape measurements (see Section 3.1 and Table I) resulted in the assignment of motion 1 to isotropic reorientations of enclathrated metallocene molecules within the β -CD cage. By the same reason the high temperature minimum in β -CD (motion 1') should be assigned to reorientations of H_2O molecules.

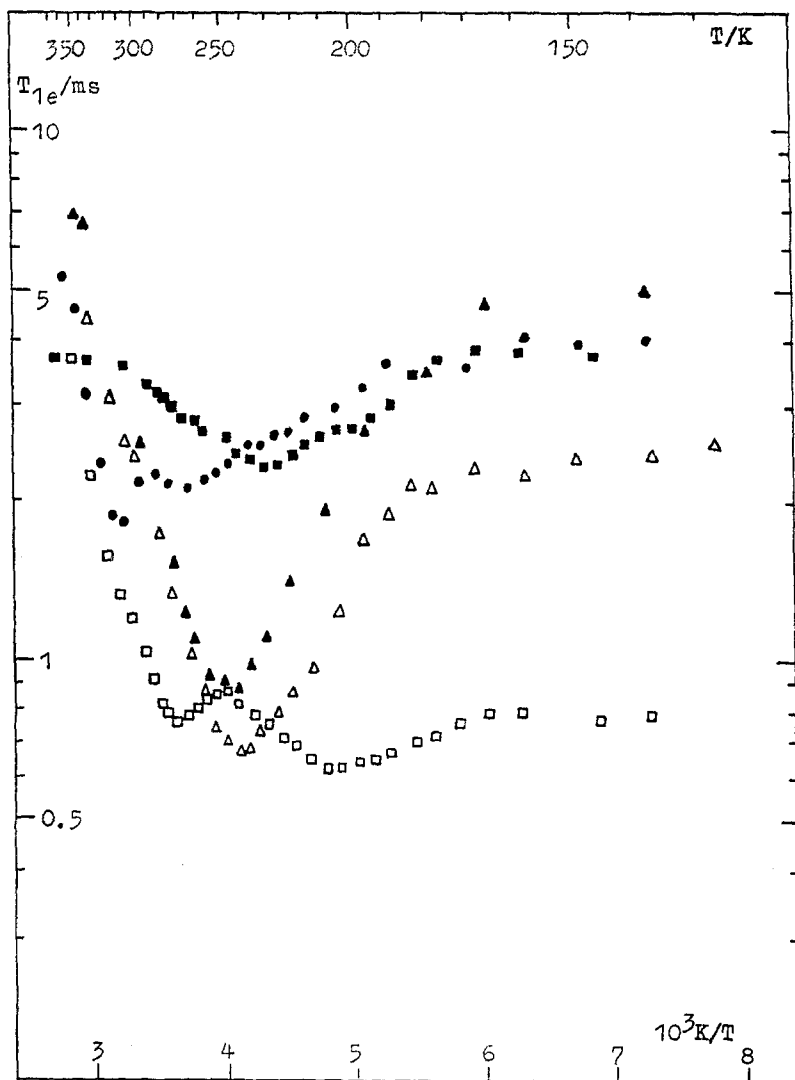


Fig. 6. Temperature dependences of spin-lattice relaxation times in an effective magnetic field ($B_{1\text{eff}} = 2.5 \text{ G}$) T_{1e} of β -CD (\square), β -CD-d (\blacksquare), I-d (\bullet), II (\triangle) and II-d (\blacktriangle).

A somewhat different situation occurred with complex **III** prepared in the presence of molecular iodine (complex **III-I₂**). In this case the I₂ molecules evidently enclathrated into the β -CD matrix along with ruthenocene molecules which led to the further hindering of their reorientations (see Table I). In all other respects the molecular dynamics in the **III-I₂** complex is very close to that in **III**. No evidence was observed of the redox reaction between iodine and ruthenocene.

The last motion to be considered here is motion 2 which is present in all samples. The large magnitudes of the ΔM_2 values obtained for this motion clearly indicate that it should be assigned to quasi-3-fold reorientations of the 7 CH₂OH (or CH₂OD) groups. In order to obtain the proper fit of the theoretical curve with

experimental points we had to include in this case the distribution of correlation times into Equations 3 and 4. Such a procedure is rather common with the investigations of molecular motions in organic glasses, solid solutions and polymers [17, 18]. In our case the best fit was obtained with the help of the Fuoss–Kirkwood distribution [18] with the parameters listed in Table I. The appearance of the distribution for motion 2 was not surprising since 7 (probably non-equivalent) CH₂OH groups could be in different crystallographic surroundings.

4. Conclusions

α , β , and γ -cyclodextrins (CD) are known to form stable inclusion complexes with ferrocene and its derivatives. Here we present new data concerning molecular dynamics in β -CD complexes with ferrocene (**I**), [3]-ferrocenophane-1,3-dione (**II**), ruthenocene (**III**), and the ternary complex of β -CD with ruthenocene and I₂ (**III-I₂). All these compounds were investigated in the 100–400 K temperature range by use of proton spin-lattice relaxation (T_1 and T_{1c}) and second moment measurements. In all complexes we observed very rich motional patterns which included up to six different molecular motions. The combined analysis of relaxation data and line shape calculations of the samples precipitated from H₂O and D₂O resulted in the following assignments. In pure β -CD the most hindered motions were reorientational jumps of H₂O molecules included within the CD framework ($E_a \approx 41.9$ kJ mol⁻¹). The other motions were the rotation of the CH₂OH group around the C—C bond ($E_a \approx 29.3$ kJ mol⁻¹), the reorientations of H₂O molecules located within the β -CD host lattice ($E_a \approx 22.6$ kJ mol⁻¹) and the proton transfer along the H-bond ($E_a \approx 16.3$ kJ mol⁻¹). All these motions are also present in complexes **I–III**, with qualitatively the same parameters. We also observed the following additional motions in these complexes. Complex **I**: the C₅ reorientations of cyclopentadienyl rings ($E_a \approx 3.3$ kJ mol⁻¹) and the overall isotropic rotation of the ferrocene molecule ($E_a \approx 44.8$ kJ mol⁻¹). Complex **II**: no mobility of the ferrocenophane molecule on the T_1 (90 MHz) time scale (rigid structure). Complex **III**: C₅ reorientation ($E_a \approx 3.4$ kJ mol⁻¹) and isotropic rotation ($E_a \approx 43.2$ kJ mol⁻¹). Complex **III-I₂: C₅ reorientations ($E_a \approx 3.4$ kJ mol⁻¹) and isotropic rotation ($E_a \approx 47.8$ kJ mol⁻¹). The assumption based on the second moment calculations was made that the low temperature structure of complex **I** was axial, and that of complexes **III** and **III-I₂ are equatorial. No evidence for redox reactions between ruthenocene and I₂ in the **III-I₂ complex was observed in this study.********

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