

Internal Rotation of Cyclopentadienyl Rings in Ferrocene Derivatives

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Abstract

The relaxation time of several ferrocene derivatives was measured, and the internal rotation was discussed. For almost all the derivatives, the degree of the internal rotation was constant in spite of the different molecular weights. However, for (triphenylmethyl)ferrocene, the rotation of the unsubstituted ring would be slower due to the bulkiness of the substituent. Furthermore, the derivatives that have a hydroxyl- or acetyl group on the substituent were also discussed. Their rotation would be influenced by the location of these substituents.

Keywords

Ferrocene, Internal Rotation, NMR Relaxation Time, Partial Molar Volume

1. Introduction

One of the interesting features of ferrocenes is the rotation of the cyclopentadienyl (Cp) ring around the Cp-Fe-Cp bond axis. On the unsubstituted ferrocene in solution, the two Cp rings freely rotate around the bond axis [1]. A change in the rotation property when some substituents were introduced into the Cp rings is very interesting.

For the 1,1'-disubstituted ferrocenes, many studies have mainly used the dipole moment measurement. The two Cp rings in 1,1'-diacetyl- or 1,1'-benzoyl-ferrocene freely rotate [2]. However, the rotation is restricted in the 1,1'-dihalo-ferrocenes, and the cis-like conformation, where the two halogen atoms are close, is very unstable [3]. The degree becomes greater according to the size of the halogen atoms. These results for the 1,1'-dihaloferrocenes were due to the electrostatic effect between the two halogen atoms.

The authors reported the Cp ring rotation on the following derivatives. The Cp rings of 1,1'-dit-butylferrocene freely rotate, but the rings of 1,1'-bis(triphenylmethyl)ferrocene having bulky substituents were restricted, and the *cis*-like conformation was very unstable [4].

On the other hand, a study of the monosubstituted ferrocenes was done by a longitudinal relaxation time NMR method instead of the dipolar moment [5]. In this study, the ¹H- and ¹³C-NMR relaxation time was measured. The rotation of the Cp rings was discussed by comparing the substituted and unsubstituted Cp rings.

2. Experimental

2.1. Synthesis

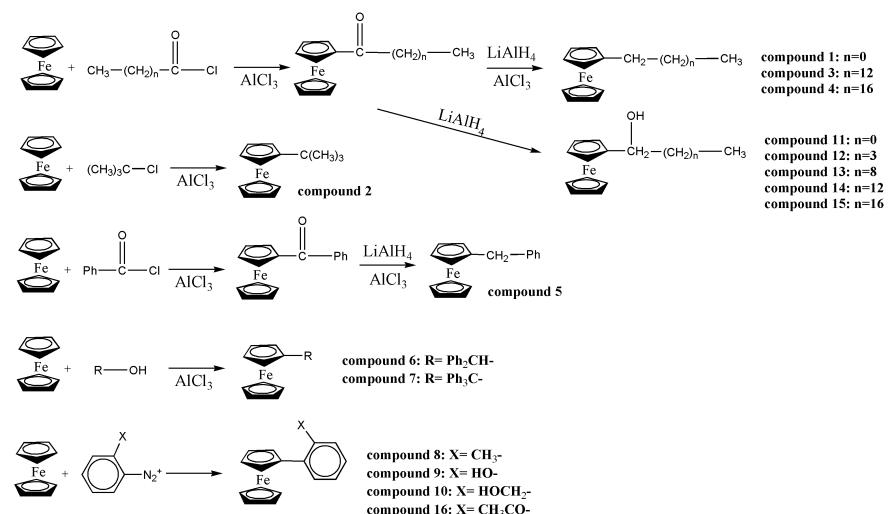
The ferrocene derivatives used in this study were synthesized by well-known methods [4] [6] [7] [8]. The compounds were identified by ¹H NMR, IR, and mass spectra as described in the previous paper [4] [6]. The synthetic routes were shown in **Scheme 1**.

2.2. Measurement of Relaxation Time

The longitudinal relaxation time was measured using JEOL A-400 and ECS-400 spectrometers. NMR samples consisted of 0.5 ml of solution in 5 mm o.d. tubes. After degassing by passing Ar gas, the spectra were recorded at ambient temperature. Longitudinal relaxation times values were measured under proton-noise-decoupling conditions by the inversion recovery method.

2.3. Measurement of Partial Molar Volume

The partial molar volumes were measured using a Lipkin-Devison type pycnometer. The ferrocene derivatives were dissolved in benzene, and the solution was



Scheme 1. Synthetic routes of the ferrocene derivatives.

added in the pycnometer. The concentration of the solutions was 0.5 - 3.0 wt%. The pycnometer was sintered in a thermostatic tank at 30°C, and the volume of solution were measured. From this volume and weight of the solution, the partial molar volumes were calculated.

3. Results and Discussion

The relaxation time is a parameter for the mobility of molecule or its part. The ferrocene Cp rings rotate around the Cp-Fe-Cp bond axis. The Cp carbon relaxation times are influenced by the degree of the Cp ring mobility. However, the degree contains several mobility modes; rotation, vibration, translation, and so on. For discussion of the internal rotation, the relaxation times of the two Cp rings must be compared.

For comparing the substituted and unsubstituted Cp rings, the values of the 1'- and β -positions were used. Because the 1'-position carbon on the unsubstituted Cp ring has hydrogen atoms on both side carbons, the β -position carbon on the substituted Cp ring is similar.

The longitudinal relaxation time of the Cp group carbon is summarized in **Table 1**. The partial molar volumes are listed in **Table 2**.

Table 1. ^{13}C longitudinal relaxation time of ferrocene derivatives^{a,b}.

Compound	Substituent	Longitudinal relaxation time (T1)/s			$1'/\beta$
		1'	α	β	
1	ethyl	14.50	10.30	10.70	1.36
2	<i>t</i> -butyl	13.50	8.58	9.06	1.49
3	pentadecyl	6.14	3.72	3.87	1.59
4	octadecyl	5.23	3.13	3.55	1.47
5	benzyl	9.91	-	6.84	1.45
6	diphenylmethyl	6.38	4.60	4.69	1.36
7	triphenylmethyl	6.97	3.12	3.12	2.23
8	<i>o</i> -methylphenyl	8.44	5.59	5.78	1.46
9	<i>o</i> -hydroxyphenyl	5.66	2.83	4.24	1.33
10	<i>o</i> -(hydroxymethyl)phenyl	7.08	3.03	3.86	1.83
11	1-hydroxyethyl	9.51	7.21	7.59	1.25
12	1-hydroxpentyl	7.13	3.35	4.26	1.67
13	1-hydroxydecyl	7.32	3.61	4.61	1.59
14	1-hydroxypentadecyl	6.11	2.89	4.00	1.53
15	1-hydroxybenzyl	6.46	—	3.31	1.95

^aSolvent: benzene, ^bTemperature: ambient.

Table 2. Partial molar volume of ferrocene derivatives^{a,b}.

Compound	Substituent	Partial molar volume/cm ³ /mol
	ethyl	66.7
2	<i>t</i> -butyl	62.5
3	pentadecyl	64.0
4	octadecyl	61.7
5	benzyl	89.7
6	diphenylmethyl	93.0
7	triphenylmethyl	111.3
8	<i>o</i> -methylphenyl	91.5
9	<i>o</i> -hydroxyphenyl	122.3
10	<i>o</i> -(hydroxymethyl)phenyl	115.4
11	1-hydroxyethyl	94.7
12	1-hydroxypentyl	94.6
13	1-hydroxydecyl	82.3
14	1-hydroxypentadecyl	73.6
15	1-hydroxybenzyl	149.5

^aSolvent: benzene, ^bTemperature: ambient.

3.1. Alkyl- and Arylferrocenes

The relationship between the molecular weight and $1'/\beta$ value is shown in **Figure 1**. (*o*-Methylphenyl)ferrocene and benzylferrocene are isomers (molecular weight 276), and their $1'/\beta$ values were almost equal (**Table 1** Compounds 5 and 8). This shows that the kind of substituent does not affect the rotation properties. The $1'/\beta$ values of almost all the derivatives containing these two derivatives were about 1.5. However, for (triphenylmethyl)ferrocene, the $1'/\beta$ value was higher (**Figure 1**). Based on this result, the unsubstituted Cp ring of this derivative would rotate faster than the rings of the other derivatives.

The relationship between the molecular weight and the partial molar volume is indicated in **Figure 2**. In this figure, the derivatives were classified into three groups. The first group is the alkylferrocenes, and the partial molar volumes are about 65 (**Figure 2**). The second group is the derivatives having phenyl groups, and their values are about 90 (**Figure 2**). The last one is (triphenylmethyl)ferrocene, and its value is 110 (**Figure 2**). This classification shows that the derivatives possessing phenyl group(s) have larger volumes than the derivatives possessing no phenyl group. Especially the (triphenylmethyl)ferrocene's volume is significantly large.

These results would be interpreted as follows. The bulky triphenylmethyl group exists to hang over unsubstituted Cp ring protons. As a result, the space in which the solvent is difficult to approach is produced (**Figure 3**). Therefore, the

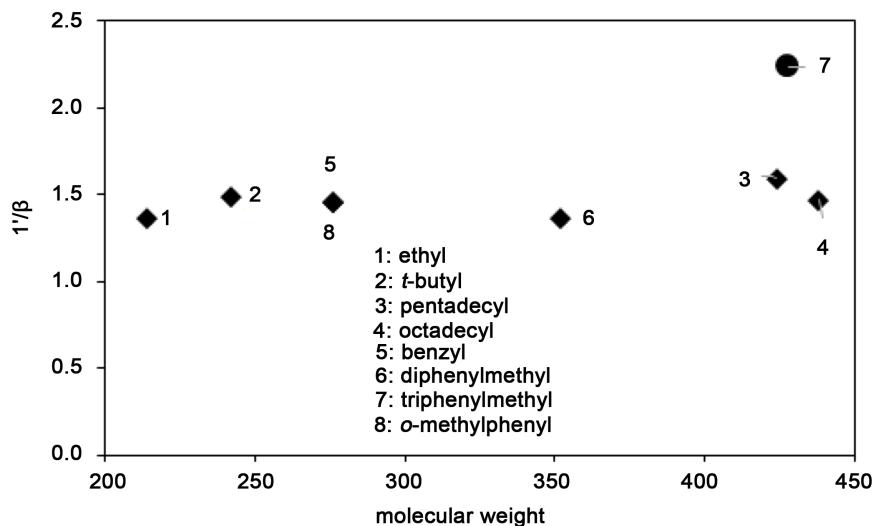


Figure 1. The relationship between the molecular weight and $1'/\beta$ value on alkyl- and arylferrocenes.

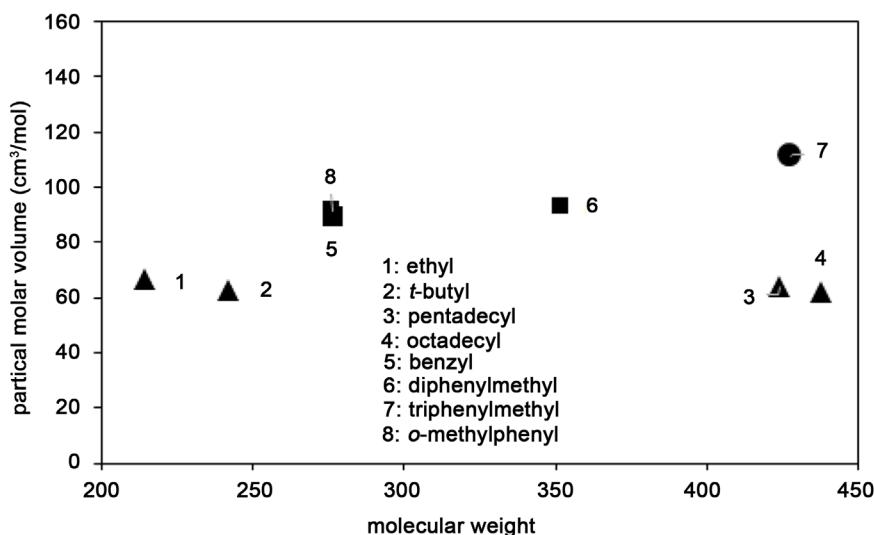


Figure 2. The relationship between the molecular weight and the partial molar volume on alkyl- and arylferrocenes.

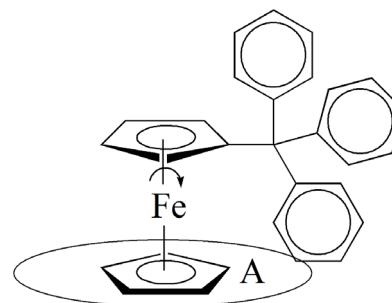


Figure 3. The space (A) in which the solvent is difficult to approach on (triphenylmethyl)ferrocene.

rotation of the Cp group is not prevented by the solvent, thus the $1'/\beta$ value becomes high. For diphenylmethyl group, a conformation in which the phenyl groups do not exist near the unsubstituted Cp proton is possible by the rotation around Cp-Ph bond axis. Such a conformation would result in the smaller $1'/\beta$ value and middle partial molar volume (**Figure 2**).

3.2. Ferrocene Derivatives Having AHydroxyl Group

For the alkyl- and arylferrocenes, the $1'/\beta$ value was mostly fixed except for (triphenylmethyl)ferrocene (**Figure 4**). Of the ferrocene derivatives having a hydroxyl group, only (1-hydroxybenzyl)ferrocene showed a high value (**Table 1** Compound 15). Furthermore, the derivative has a largerpartial molar volume than the other derivatives (**Figure 5**). In (1-hydroxybenzyl)ferrocene, the benzene ring is twisted by the formation of the OH- π type hydrogen bond [9]. Therefore, the substituent would produce a space in which the solvent is difficult to approach. On the other hand, (1-hydroxyalkyl)ferrocene has no such hydrogen bond, thus it would have similar values for $1'/\beta$ and the partial molar volume.

When (*o*-hydroxyphenyl)ferrocene and [*o*-(hydroxymethyl)phenyl]ferrocene were compared, the former showed a low $1'/\beta$ value. In (*o*-hydroxyphenyl)ferrocene, a strong OH-d type hydrogen bond is formed, so that the hydroxyl group exists near the unsubstituted Cp ring [6]. Therefore, the rotation of the Cp ring would be disturbed. On the other hand, [*o*-(hydroxymethyl)phenyl]ferrocene does not have such a hydrogen bond, because the hydroxyl group and iron atom are too close.

3.3. (*o*-Acetylphenyl)Ferrocene

As mentioned in a previous paper [10], (*o*-acetylphenyl)ferrocene has a chelate

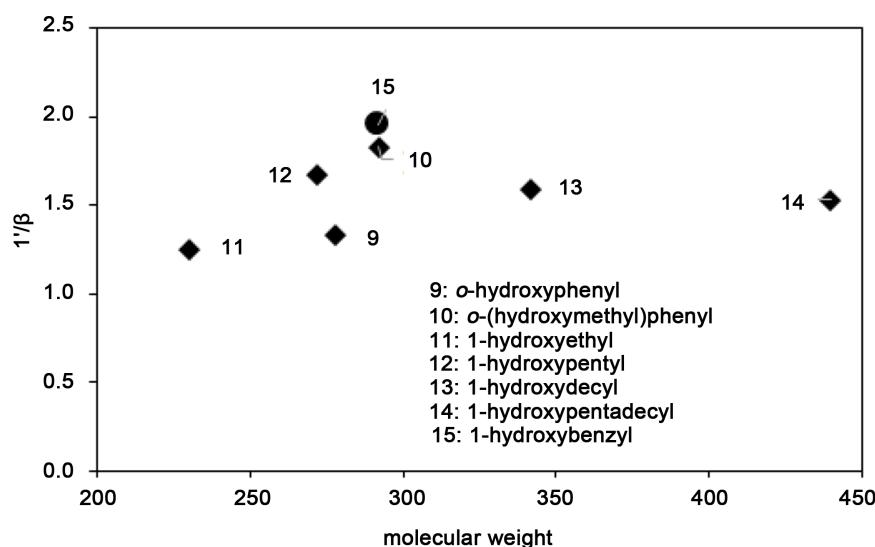


Figure 4. The relationship between the molecular weight and $1'/\beta$ value on ferrocenes derivatives having a hydroxyl group.

structure in which a metal cation is incorporated between the carbonyl oxygen and iron atom. In this section, the effect on the relaxation time by such a chelate ring formation is discussed. Here, acetonitrile-d₃ was employed as the solvent to dissolve the metal salts, but the solubility is low. Therefore, the ¹H relaxation time was used for the following discussion. The longitudinal relaxation time of the Cp group proton is summarized in **Table 3**.

(*o*-Acetylphenyl)ferrocene alone showed a 1.77 1'/β value. In the presence of Ca²⁺, which does not form a strong chelate, the value did not significantly change. However, Al³⁺ forming a strong chelate structure (**Figure 6**) reduces the 1'/β value. These results would be due to the chelate structure in which the metal cation and carbonyl oxygen exist in the neighborhood of the unsubstituted Cp group. Therefore, the Cp ring rotation would be prevented in a manner similar to that for the (*o*-hydroxyphenyl)ferrocene mentioned in Section 3.2.

4. Conclusion

By comparing the relaxation time of substituted and unsubstituted Cp rings, the internal rotation of substituted ferrocenes was discussed. For almost all the

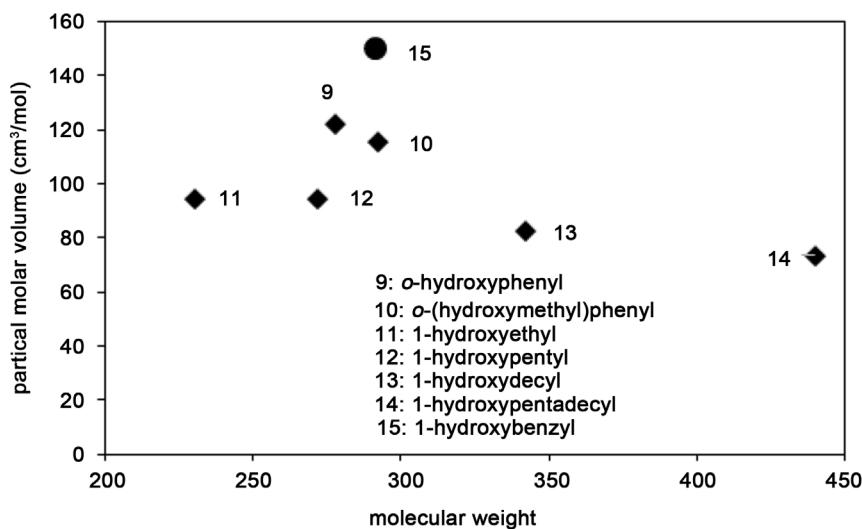


Figure 5. The relationship between the molecular weight and the partial molar volume on ferrocenes derivatives having a hydroxyl group.

Table 3. ¹H longitudinal relaxation time of (*o*-acetylphenyl)ferrocene (16) in the absence metal ions.^{a,b}

Entry	Metal ion	Longitudinal relaxation time (T1)/s		1'/β
		1'	β	
1	none	6.97	3.93	1.77
2	Ca ²⁺	4.72	2.55	1.85
3	Al ³⁺	3.36	2.54	1.32

^aSolvent: acetonitrile-d₃, ^bTemperature: ambient.

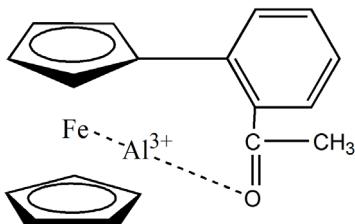


Figure 6. Plausible coordination of (*o*-acetylphenyl)ferrocene with Al^{3+} [10].

derivatives, the degree of the internal rotation was constant in spite of the different molecular weights. However, for (triphenylmethyl)ferrocene, the rotation of the unsubstituted ring would be slower. Furthermore, such a slow internal rotation is found for some derivatives that have a hydroxyl- or acetyl group on the substituent. These slow rotations would result in the existence of space in which the solvent is difficult to approach.

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