Journal of Organometallic Chemistry, 358 (1988) 401–403
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The cyclodextrin inclusion complexes of acylferrocenes: their preparation, and the induced Cotton effects in their circular dichroism spectra

V.I. Sokolov *, V.L. Bondareva, I.F. Golovaneva

Institute of Organo-Element Compounds, Academy of Sciences Institute of General and Inorganic Chemistry, Academy of Sciences, Moscow (U.S.S.R.)

(Received May 15th, 1988)

Abstract

Complexes of α-, β-, γ-cyclodextrins (CyD's) with acylferrocenes ($C_5H_5FeC_5H_4$-COR, R = H, CH_3, CF_3; $XC_5H_4FeC_5H_4Y$, X = Y = $COCH_3$, X, Y = $COCH_2CH_2$, $COCH_2CO$), prepared in situ in ethylene glycol or by dissolution of the 1/1 solid complexes have been investigated by use of circular dichroism (CD). Wavelengths for extrema, signs, molecular ellipticity $[\theta]$, and the rotatory strenghts, R_k, of the induced Cotton effects (ICE) have been determined, and were found to correspond to the metallocene chromophores.

Natural oligosaccharides, cyclodextrins (CyD) having the shape of a truncated cone are able to hold in the molecular cavity, a variety of single organic molecule of suitable size and shape [1]. Harada and Takahashi first reported in 1984 the solid inclusion complexes of CyD's and organometallics of the ferrocene series [2]. Later other organo-transition metals were found to serve as guests in the CyD inclusion complexes as reviewed recently [3].

Circular dichroism (CD) is one of the most useful tools for evaluating asymmetric interactions between host and guest molecules in solution. It has been used to study organometallic CyD complexes, with ethylene glycol being the solvent of preference [4].

Recently we prepared the solid complexes of some acylferrocenes with β-CyD and have studied the CD spectra in ethylene glycol for the three CyD's at equal concentrations of reagents. The results for the longest wavelength induced Cotton effect (ICE) are shown in Table 1. A more complete discussion will be given in due course.

This ICE corresponds to an electron transition in the metallocene which is mainly *d–d* in character. Some of the data obtained are significant. The greatest values of molecular ellipticity $[\theta]$ and rotatory strength, R_k, have been observed for

0022-328X/88/$03.50

Table 1

Some data on the cyclodextrin complexes of arylferrocenes (The rotatory strengths R_k are multiplied by a factor of 10^{40}. Concentrations of both reagents were 1.0×10^{-2} mol l^{-1})

$C_5H_4XFeC_5H_4Y$		λ_{max}	α			β			γ		
X	Y		λ	$[\theta]$	R_k	λ	$[\theta]$	R_k	λ	$[\theta]$	R_k
H	H	445	460	−24	−0.007	460	+495	+0.61	460	−58	−0.074
H	Ac	460	475	−25	−0.028	495	−154	−0.19	490	−46	−0.05
Ac	Ac	470	485	−18	−0.021	430	+30	+0.02	515	−79	−0.19
						490	−63	−0.06			
H	CF_3CO	490	490	−33	−0.06	465	+90	+0.15	530	−20	−0.018
H	CHO	470	[a]	[a]	[a]	495	+92	+0.06	490	−52	−0.04
$COCH_2CH_2$		450	480	−43	−0.14	470	−66	−0.08	465	+40	+0.03
$COCH_2CO$		455	395	−142	−0.22	400	−158	−0.19	410	−96	−0.29

[a] For this complex the ICE appeared to be too small at high absorption, to be measured.

the FcH-β-CyD combination and this probably reflects the best match of the size of cavity with that of the ferrocene molecule. When the ferrocene nucleus bears a substituent or the cavity becomes wider (γ) or narrower (α), the ideal situation is upset.

It is noteworthy that the introduction of an acyl group into the ferrocene does not lead to a change of sign of ICE for α-CyD at all, does lead to one in a single case for γ-CyD, and in contrast, does not lead to a change in sign of ICE in a single case for β-CyD. At present there is very little to indicate why this should be. One can conclude, however, that the hypothesis about the different orientations [2] of the FcR molecule inside the cavities of β- and γ-CyD as a reason for the change in sign of ICE is incorrect. Inclusion complexes of ferrocene itself with α-CyD and γ-CyD have an opposite sign when compared with that of β-CyD.

One should be emphasized that the positive charge in the metallocene molecule does not prevent the formation of an inclusion complex. Ferricinium hexafluorophosphate exhibits less ellipticity, $[\theta]_{460}+257$, than ferrocene itself which may indicate that it is a less stable complex. Of interest is the absence of an ICE due to the "ferricinium" absorption band near 600 nm which is attributed to charge transfer. Cobalticinium hexafluorophosphate exhibits a weaker ICE, $[\theta]_{410}+18.8$.

Finally, the equilibrium constants for the complexes between several ferrocene and β-CyD have been determined in ethylene glycol by CD. The dissociation constants have been found to be 2.44 mmol for ferrocene itself, 4.76 mmol for acetylferrocene, and 570 mmol for [3]ferrocenophanone-1 (cf. [4]).

$$\mathrm{CyD} + \mathrm{FcR} \rightleftharpoons \mathrm{CyD}\cdot\mathrm{FcR}$$

$$K_{\mathrm{diss}} = \frac{[\mathrm{CyD}][\mathrm{FcR}]}{[\mathrm{CyD}\cdot\mathrm{FcR}]}$$

It is evident that the existence of a heteronuclear bridge in a phanone molecule dramatically decreases the ability of the molecule to be included into the CyD cavity. However, the solid complex of [3]ferrocenophanone-1 with β-CyD has been obtained and its asymmetric reduction in solution has been described [5].

References

1 M.L. Bender, M. Komiyama, Cyclodextrin Chemistry, Springer, Berlin, 1978.

2 A. Harada, S. Takahashi, Chem. Commun., (1984) 645.

3 V.I. Sokolov, Metalloorg. Khim. (Russ.), 1 (1988) 25.

4 A. Harada, S. Takahashi, Chem. Lett., (1984) 2089.

5 V.I. Sokolov, V.L. Bondareva, P.V. Petrovskii, B. Gautheron, Metalloorg. Khim. (Russ.), 1 (1988) 71.