

## Thermal decomposition of $\beta$ -cyclodextrin inclusion complexes of ferrocene and their derivatives

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### Abstract

The thermal decomposition of the solid inclusion complexes of ferrocene and its derivatives with  $\beta$ -CD was studied by DTA, TG and DTG. The inclusion complexes contain crystallization water and the first decomposition stage corresponds to the dehydration of the complexes. The second stage is related to the liberation of the ferrocene and its derivatives, and the degradation of the  $\beta$ -CD structure takes place in the third stage. However, the second and third stages of decomposition for some of the inclusion complexes occur in the same temperature ranges and are impossible to distinguish. The final decomposition products formed around 500°C consist mainly of  $\text{Fe}_2\text{O}_3$ . The thermal behaviour of physical mixtures of these ferrocene derivatives and  $\beta$ -CD was also investigated. The thermal analysis results show that the interaction of ferrocene and its derivatives with  $\beta$ -CD is a chemical phenomenon. The ferrocene derivatives gain an additional thermal stability after inclusion complexation into the  $\beta$ -CD cavity. Thermal analysis methods can be used satisfactorily for the recognition of inclusion complexation.

*Keywords:*  $\beta$ -Cyclodextrin; DTA; Ferrocene; Inclusion complex; TG

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### 1. Introduction

Cyclodextrins (CDs) are water-soluble macrocyclic oligosaccharides, the most widely used of which contain six, seven and eight D-glucose units for  $\alpha$ -,  $\beta$ - and  $\gamma$ -CD, respectively. Their most prominent feature is a rigid, well-constructed cylindrical cavity capable of including various guest molecules to form stable host–guest inclusion

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complexes in the solid state and aqueous solutions [1]. The necessary criteria for the formation of an inclusion complex are that the guest must be hydrophobic and have a suitable geometry. The driving force for inclusion complexation is the removal of high-energy water molecules from the CD cavities by guest molecules, release of strain energy of the ring and the presence of intermolecular interactions such as hydrogen-bonding and London dispersion forces [2]. The binding is usually very strong and inclusion complexation occurs not only in aqueous solution but also in organic media such as dimethyl sulphoxide and ethylene glycol [3,4].

CDs are used for a wide range of applications, including the stabilization of light-sensitive compounds, enantiomeric and isomeric separations, catalysis, improving pharmaceutical formulations and increasing solubility properties. Their applications have been summarized by Sybilska-Keulemansova [5] and Szejtli [6]. Considerable attention has also been given to CDs as enzyme models because of their similar chemical and physical properties, especially in relation to the function of biologically important substances [7].

Various methods such as UV, IR, NMR, X-ray spectroscopy and chromatography are widely used to demonstrate the formation of an inclusion complex. The application of thermal analysis has also been reported in this field [8–16]. Unfortunately, in most cases thermal data have been interpreted only from a qualitative point of view [8–12] and only very few studies have been published on the thermal decomposition, and the kinetic analysis of thermogravimetric data for inclusion complexes of CDs [13–16]. Harada and coworkers first reported the inclusion complexes of the ferrocene series with CDs [10–12,17,18] and later other organo-transition metal complexes were found to serve as guests in the CD inclusion complexes [19–21]. Recently we prepared the solid inclusion complexes of some ferrocene derivatives with  $\beta$ -CD [22]. This paper describes their thermal decomposition behaviour and the relative stability of ferrocene derivatives before and after inclusion into the  $\beta$ -CD cavity.

## 2. Experimental

### 2.1. Preparation of inclusion complexes

Analytical grade  $\beta$ -CD, ferrocene and its derivatives, acetylferrocene,  $\alpha$ -methylferrocenemethanol, 1,1'-dimethylferrocene, dimethylaminomethylferrocene, ferrocene-carboxaldehyde and benzoylferrocene were purchased from Aldrich Chemical Company and used without further purification.

The  $\beta$ -CD inclusion complexes of ferrocene and its derivatives were prepared by adding fine crystals of ferrocene and its derivatives to a saturated aqueous solution of  $\beta$ -CD at 60°C with stirring. The precipitated product was washed with warm water to remove the remaining  $\beta$ -CD and dried in vacuo. The uncomplexed ferrocene was removed by washing the dried residue with tetrahydrofuran and the product was recrystallized from water or aqueous alcohol. The other inclusion complexes were prepared in the same way.

## 2.2. Instrumental

TG, DTG and DTA curves were obtained simultaneously on a Rigaku TG 1810 thermal analyser combined with a TAS 100 thermogravimetric analyser. Samples were heated in platinum crucibles under a flowing nitrogen atmosphere within the temperature range 20–600°C. The heating rate was 10 K min<sup>-1</sup> and sample weights ranged from 5 to 10 mg. Highly sintered  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as a reference material. The solid decomposition products formed at the end of the thermal decomposition were identified using a Philips PW 1710 X-ray powder diffractometer with Cu K $\alpha$  radiation.

## 3. Results and discussion

Table 1 presents the analytical results for the prepared inclusion complexes. These results show that all the complexes obtained in high yields are stoichiometric compounds. Most of the complexes have 1:1 (guest:  $\beta$ -CD) molar ratios, as deduced from elemental analysis and the spectroscopic data, whereas the interaction of benzoylferrocene with  $\beta$ -CD resulted in the formation of a 1:2 (benzoylferrocene:  $\beta$ -CD) complex [22].

The thermoanalytical results for ferrocene and its derivatives used in this work are given in Table 2. Among these compounds, ferrocene sublimes at 88°C while dimethylaminomethylferrocene, which is a viscous, dark brown liquid with a boiling point of 124–128°C at  $3.33 \times 10^{-4}$  MPa, boils with decomposition at 215°C at room temperature and normal atmospheric pressure. Most of the ferrocene derivatives exhibit a single-stage decomposition, except for  $\alpha$ -methylferrocenemethanol and benzoylferrocene which decompose in three stages. In fact the solid ferrocene derivatives

Table 1  
Analytical data for  $\beta$ -CD inclusion complexes of ferrocene and its derivatives<sup>a</sup>

Compound	Yield %	C %	H%	Fe %	$\beta$ -CD: guest
$\beta$ -CD-ferrocene	65	45.42 (46.02)	6.53 (6.19)	3.92 (4.12)	1:1
$C_{52}H_{80}O_{35}Fe \cdot 2H_2O$					
$\beta$ -CD-1,1'-dimethylferrocene	82	45.93 (46.83)	6.53 (6.40)	4.19 (4.03)	1:1
$C_{54}H_{84}O_{35}Fe \cdot 2H_2O$					
$\beta$ -CD-dimethylaminomet.ferr.	55	45.92 (46.71)	6.40 (6.49)	4.03 (3.95)	1:1
$C_{55}H_{87}O_{35}NFe \cdot 2H_2O$					
$\beta$ -CD-acetylferrocene	73	45.68 (46.36)	6.63 (6.20)	3.76 (3.99)	1:1
$C_{54}H_{82}O_{36}Fe \cdot 2H_2O$					
$\beta$ -CD- $\alpha$ -methylferr.methanol	81	46.17 (46.29)	6.26 (6.33)	4.29 (3.99)	1:1
$C_{54}H_{84}O_{36}Fe \cdot 2H_2O$					
$\beta$ -Cd-ferr.carboxaldehyde	90	45.92 (45.96)	6.09 (6.11)	4.38 (4.03)	1:1
$C_{53}H_{80}O_{36}Fe \cdot 2H_2O$					
$\beta$ -CD-benzoylferrocene	73	46.55 (46.09)	5.92 (6.20)	2.53 (2.12)	2:1
$C_{101}H_{154}O_{71}Fe \cdot 4H_2O$					

<sup>a</sup> Data in parentheses indicate the calculated values.

Table 2  
Thermal data for ferrocene and its derivatives

Compound	State	Melting point °C	Thermogravimetry temp. range °C	DTG <sub>max</sub> °C	Weight loss %
Ferrocene C <sub>10</sub> H <sub>10</sub> Fe	1	– <sup>a</sup>	88–202	180	99.99
Acetylferrocene C <sub>12</sub> H <sub>12</sub> OFe	1	83	109–227	216	95.50
1,1'-dimethylferrocene C <sub>12</sub> H <sub>14</sub> Fe	1	36	76–163	154	95.60
Ferrocenecarboxaldehyde C <sub>11</sub> H <sub>10</sub> OFe	1	123	127–220	206	86.30
Dimethylaminomethylferrocene C <sub>13</sub> H <sub>17</sub> NFe	1	– <sup>b</sup>	98–225	215	97.51
α-methylferrocenemethanol C <sub>12</sub> H <sub>14</sub> OFe	1	76	82–137	118	5.00
	2		137–213	165	11.60
	3		218–398	286	46.30
Benzoylferrocene C <sub>17</sub> H <sub>14</sub> OFe	1	108	164–262	242	26.10
	2		268–287	276	11.70
	3		289–328	302	61.60

<sup>a</sup> Sublimes at 88°C.

<sup>b</sup> Boils with decomposition at 215°C.

have relatively low melting points and decomposition temperatures. For example, the melting point of 1,1'-dimethylferrocene is as low as 36°C and its decomposition begins at 76°C.

The DTA, TG and DTG curves of β-CD and its inclusion complexes with ferrocene and its derivatives are shown in Figs. 1–8; the melting points, temperature ranges, and experimental and calculated weight losses are summarized in Table 3.

Three endothermic peaks are observed in the thermal decomposition of β-CD (Fig. 1). The first peak between 30 and 100°C corresponds to the dehydration of β-CD. The experimental water content indicates that β-CD contains 10 moles of crystallization water which are lost up to 100°C; the dehydration is completed in one stage. These observations are consistent with the results reported by Szafranek [14]. However, Kohata et al. [16] claimed that due to the presence of a small endotherm, some of the water molecules included in the β-CD cavity escape below 64°C, while the rest are released between 64 and 100°C. The second small endothermic peak at 223°C, without any weight loss, clearly represents a physical process and is attributed to the reversible transformation of β-CD [13]; however, the nature of this transformation is not known. The third stage is related to the degradation of the β-CD structure. Decomposition starts at 248°C and the rapid weight loss continues up to 345°C, giving approx. 75% total weight loss. The weight loss of β-CD proceeds at higher temperatures (> 345°C) at a very slow rate so that no DTG peak corresponding to this process is recorded. The melting of β-CD also occurs in the third stage and thus the temperature range 250–300°C (DTG<sub>max</sub>) also corresponds to the endothermic changes of melting.

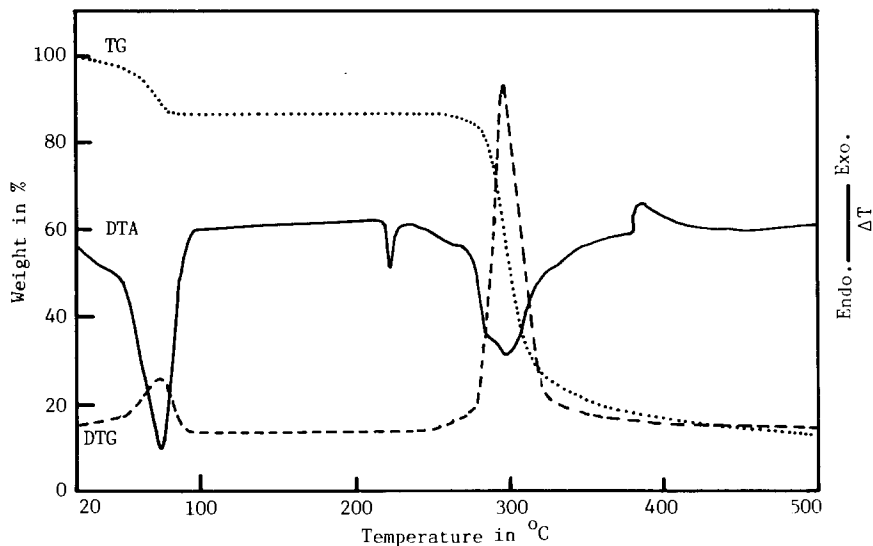


Fig. 1. DTA, TG and DTG curves of  $\beta$ -CD.

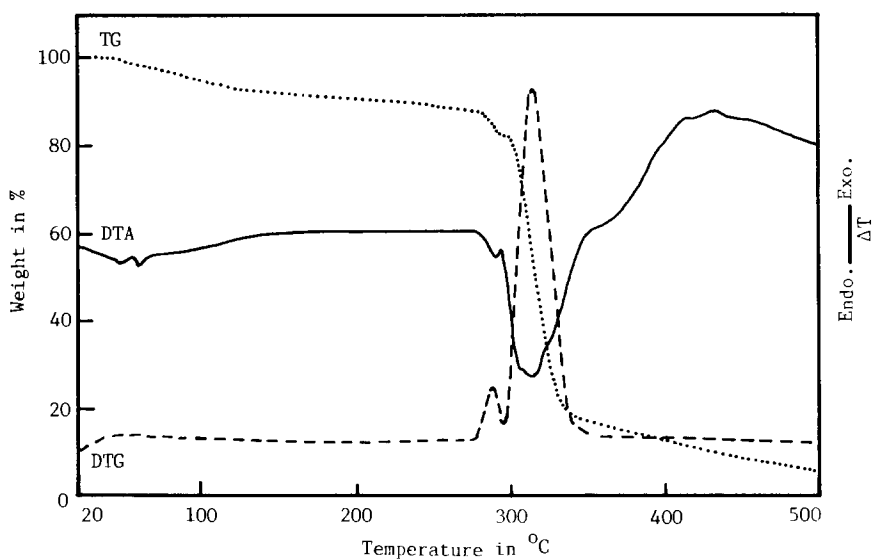


Fig. 2. DTA, TG and DTG curves of  $\beta$ -CD inclusion complex of ferrocene.

From the measured curves (Figs. 2–8) and thermoanalytical results (Table 3) for the inclusion complexes of ferrocene and its derivatives with  $\beta$ -CD, some general features can be recognized. All the complexes contain two moles of crystallization water, except  $\beta$ -CD–benzoylferrocene complex which has four moles of crystallization water. The

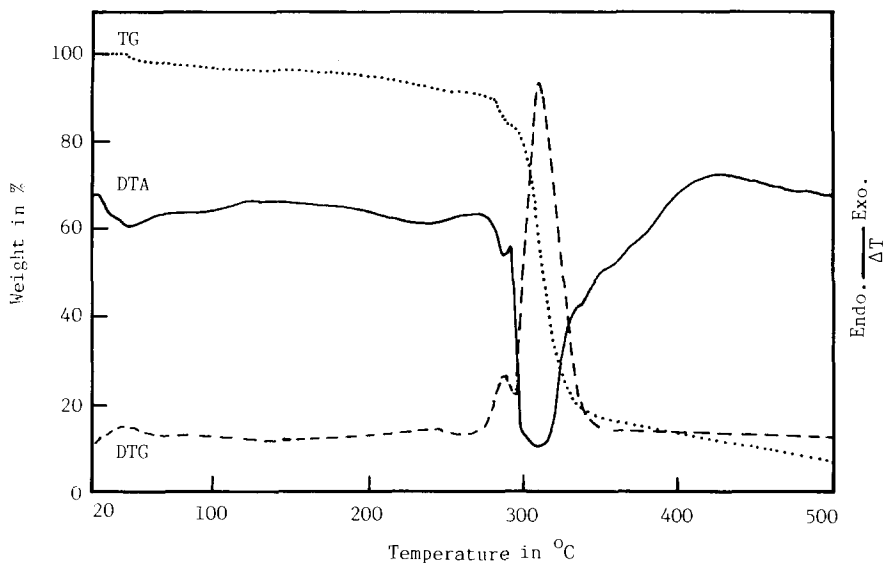


Fig. 3. DTA, TG and DTG curves of  $\beta$ -CD inclusion complex of 1,1'-dimethylferrocene.

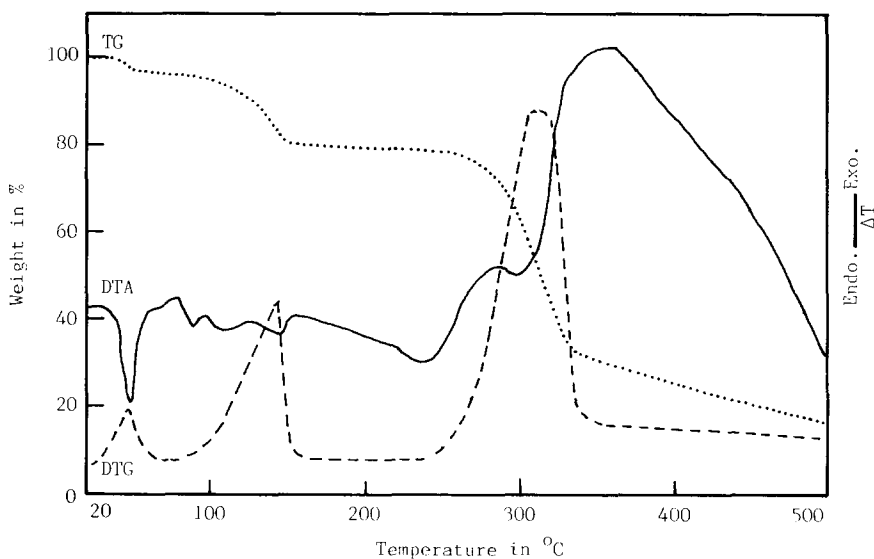


Fig. 4. DTA, TG and DTG curves of  $\beta$ -CD inclusion complex of dimethylaminomethylferrocene.

dehydration of these inclusion complexes is completed at much lower temperatures than that of the parent  $\beta$ -CD. For example, the completion temperatures for the dehydration of  $\beta$ -CD–dimethylaminomethylferrocene,  $\beta$ -CD–benzoylferrocene and  $\beta$ -CD–acetylferrocene are 60, 62 and 65°C, respectively. During the inclusion process,

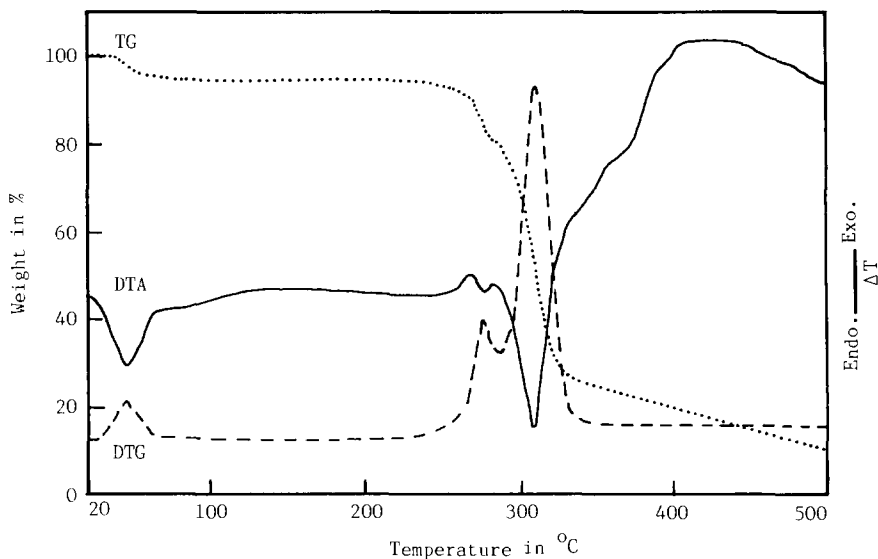


Fig. 5. DTA, TG and DTG curves of  $\beta$ -CD inclusion complex of acetylferrocene.

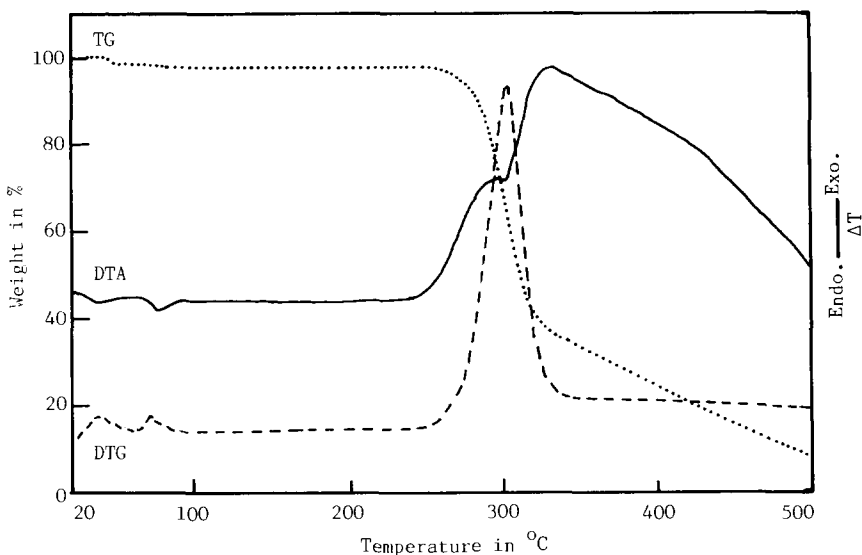


Fig. 6. DTA, TG and DTG curves of  $\beta$ -CD inclusion complex of  $\alpha$ -methylferrocenemethanol.

most of the water molecules in the  $\beta$ -CD cavity are replaced by the ferrocene derivatives which indicates that the inclusion of ferrocene and its derivatives into the  $\beta$ -CD cavity results in the weakening of the bonds between the remaining water molecules and  $\beta$ -CD so that their liberation needs much lower energy and corresponds to the lower

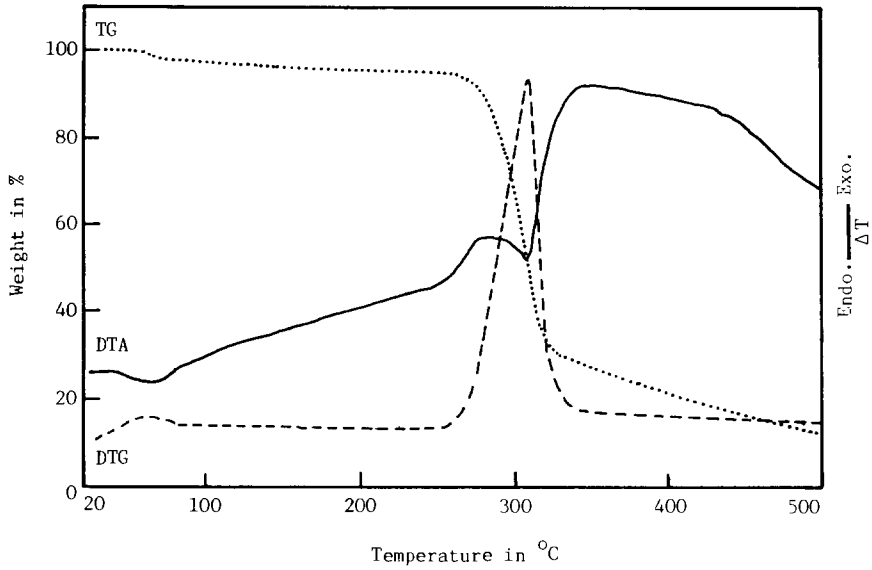


Fig. 7. DTA, TG and DTG curves of  $\beta$ -CD inclusion complex of ferrocenecarboxaldehyde.

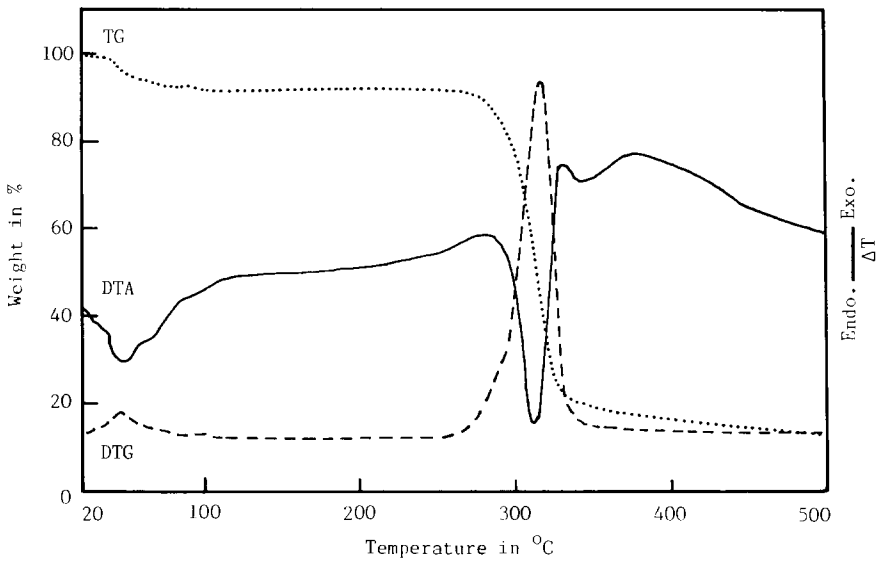


Fig. 8. DTA, TG and DTG curves of  $\beta$ -CD inclusion complex of benzoylferrocene.

temperatures. The determined and calculated water contents of these complexes were found to be in very good agreement.

After the dehydration stage, the decomposition of the inclusion complexes takes place in one or two stages; following inclusion complexation the endothermic trans-



Table 3  
Thermal data for  $\beta$ -CD and  $\beta$ -CD inclusion complexes of ferrocene and its derivatives

Compound	Stage	Thermogravimetry temp. range/ $^{\circ}$ C	DTG peak temp./ $^{\circ}$ C	Weight loss %		$\Delta T/C^a$
				Found	Calculated	
$\beta$ -CD	1	30–100	75	13.66	13.69	
$C_{42}H_{70}O_{35} \cdot 10H_2O$	2	248–343	300	64.50		
$\beta$ -CD-ferrocene	1	38–72	60	2.84	2.65	
$C_{52}H_{80}O_{35}Fe \cdot 2H_2O$	2	268–294	288	5.10	13.71	180
	3	295–354	315	66.95	–	
$\beta$ -CD-1,1'-dimethylferrocene	1	25–68	46	2.30	2.60	
$C_{54}H_{84}O_{35}Fe \cdot 2H_2O$	2	249–295	288	14.05	15.46	173
	3	295–356	310	65.65	–	
$\beta$ -CD-dimethylaminomet.ferr.	1	35–60	48	2.30	2.55	–
$C_{53}H_{87}O_{35}NFe \cdot 2H_2O$	2	82–162	144	15.54	17.19	
	3	252–343	316	46.95	–	
$\beta$ -CD-acetylferrocene	1	35–65	48	3.36	2.58	
$C_{54}H_{82}O_{36}Fe \cdot 2H_2O$	2	240–288	278	15.91	16.30	131
	3	288–337	310	62.90	–	
$\beta$ -CD- $\alpha$ -methylferr. methanol	1	26–100	73	2.40	2.57	
$C_{54}H_{84}O_{36}Fe \cdot 2H_2O$	2	253–348	304	63.00	–	171
$\beta$ -CD-ferr.carboxaldehyde	1	35–85	71	2.25	2.60	
$C_{53}H_{80}O_{36}Fe \cdot 2H_2O$	2	255–348	307	67.40	–	128
$\beta$ -CD-benzoylferrocene	1	40–62	48	3.52	2.74	
$C_{101}H_{154}O_{71}Fe \cdot 4H_2O$	2	252–360	316	73.15	–	88

<sup>a</sup> Indicates the increase in the thermal stability of the parent ferrocene derivatives.

formation peak of  $\beta$ -CD at around 220°C is removed. The release of ferrocene from the  $\beta$ -CD–ferrocene complex begins at 268°C, and before the completion of this stage, the decomposition of the  $\beta$ -CD structure in the complex takes place. Thus these two processes overlap each other.  $\beta$ -CD–acetylferrocene,  $\beta$ -CD–1,1'-dimethylferrocene and  $\beta$ -CD–dimethyl aminomethylferrocene lose their respective ferrocene derivatives with decomposition in a single step. The weight loss values found for this decomposition stage (stage 2 in Table 3) of these inclusion complexes are consistent with the calculated values. Thus, it is possible to determine the guest-to-host molar ratios of these inclusion compounds, which are usually determined by means of elemental analysis or spectroscopic methods, such as NMR or UV, and to suggest the use of thermal analysis as an alternative method to determine the stoichiometry of some inclusion complexes. After the release of the guest, the decomposition of the host,  $\beta$ -CD, begins and the decomposition temperature of the  $\beta$ -CD part of these compounds becomes significantly higher than that of the parent  $\beta$ -CD (third stage in Table 3). The decomposition of benzoylferrocene, ferrocenecarboxaldehyde and  $\alpha$ -methylferrocene methanol contained in the  $\beta$ -CD cavity occurs in the same temperature range as  $\beta$ -CD (approx. 250–350°C) and in a single step so that it is almost impossible to distinguish between the decompositions of ferrocene derivatives and  $\beta$ -CD.

The decomposition and melting of all the inclusion complexes proceed simultaneously. The decomposition temperatures of the ferrocene derivatives are greatly increased by inclusion complexation. The temperature differences between free ferrocene derivatives (Table 2) and included ferrocene derivatives (Table 3) were taken as a parameter to express the increase in the thermal stability and are also given as  $\Delta T$  in Table 3. The  $\Delta T$  values indicate that all the inclusion complexes studied are thermally stable and that ferrocene and its derivatives gain additional thermal stability in the  $\beta$ -CD cavity. For example, the sublimation temperature of ferrocene is 88°C and in the case of the ferrocene inclusion compound, there is no change at around 90°C except for the loss of the crystallization water at lower temperatures. It is stable up to 268°C and starts to decompose above 268°C. Thus the  $\Delta T$  value of ferrocene is 180°C which shows that ferrocene and its derivatives are held tightly in the  $\beta$ -CD cavity. Since dimethylaminomethylferrocene is a liquid decomposing at its boiling point, its  $\Delta T$  value could not be calculated in the same way and is not, therefore, included in Table 3. The value of  $\Delta T$  may be due to the polarity of the guest and intermolecular interactions between the guest and the host.

The solid decomposition products of the inclusion complexes formed at 500°C consist of mainly  $\text{Fe}_2\text{O}_3$  (hematite). The X-ray powder diffraction pattern of the solid decomposition products formed in nitrogen atmosphere is illustrated in Fig. 9.

In order to discuss the interactions between ferrocene derivatives and  $\beta$ -CD, physical mixtures of these compounds were prepared in stoichiometric ratios and their thermal behaviour also studied. Only one example is given in Fig. 10 for the physical mixture of benzoylferrocene with  $\beta$ -CD and this should be compared with the thermal curves for the inclusion complex of the same compound (Fig. 8). In the case of a physical mixture, each component behaves independently, that is, benzoylferrocene melts at around 110°C and decomposes at around 160°C (stage II). The dehydration (40–90°C, stage I), transformation (220°C) and decomposition (250–340°C, stage III) temperatures of

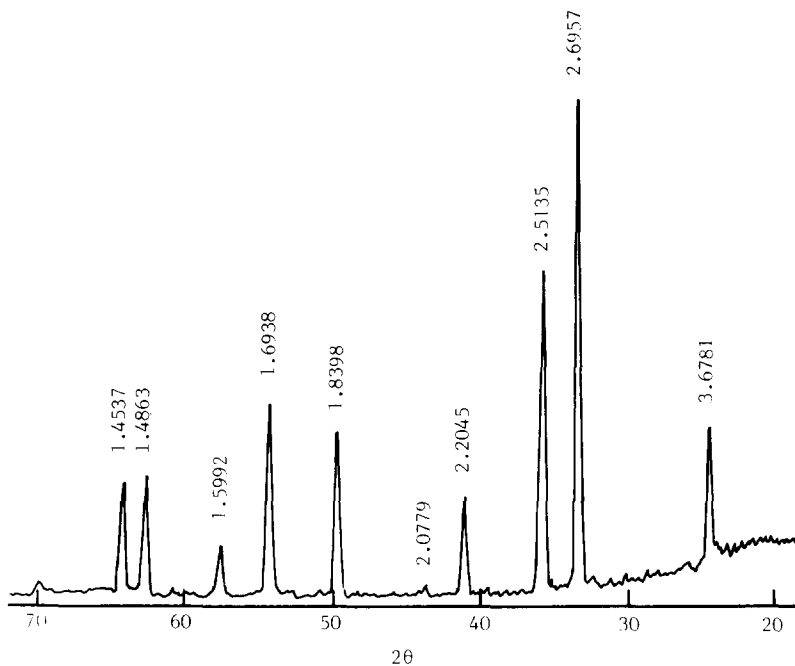


Fig. 9. X-ray powder diffraction pattern of the solid decomposition product of the inclusion complexes at 500°C.

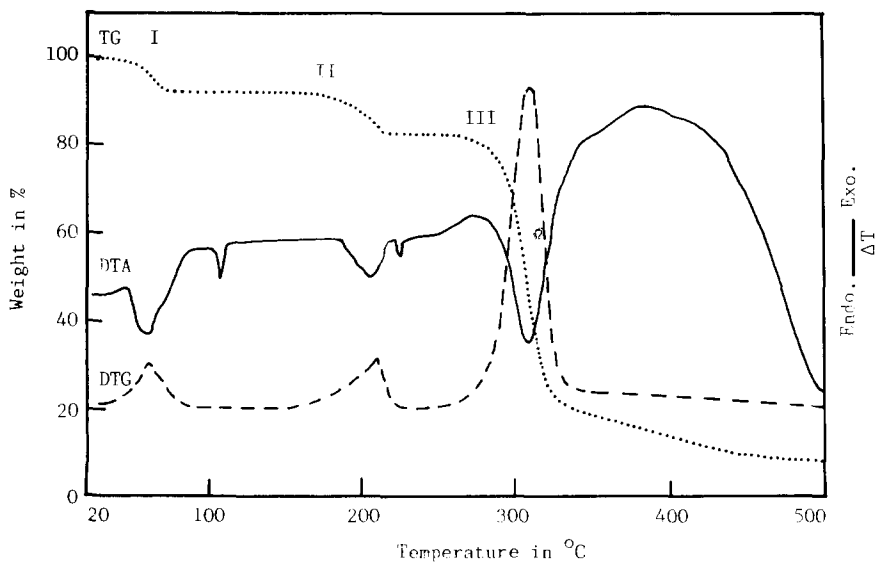


Fig. 10. DTA, TG and DTG curves of the physical mixture of  $\beta$ -CD and benzoylferrocene.

$\beta$ -CD are clearly seen in Fig. 10. However, in the case of the inclusion complex of benzoylferrocene, after the removal of the crystallization water, there is no change and the decomposition of the complex begins at 250°C. The thermal analysis data show that the inclusion of ferrocene and its derivatives into the cavity is a chemical complexation phenomenon rather than a physical interaction and this chemical phenomenon can satisfactorily be identified by thermal analysis methods.

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