Synthesis and un-isotherm kinetic study of some ferrocene acids

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Abstract: The goal of this paper is to study thermal stability of some ferrocenes with acidic functional groups. Some other kinetic characteristics such as critical temperature and the rate constant corresponding to maximal degradation speed have been also evaluated. The type of functional units adjacent to the ferrocenyl unit determines thermal stability of ferrocene compounds. Groups with a powerful withdrawing effect determine a decreasing of the temperatures at which the material starts to lose weight. If a very long alkyl chain is connected to the ferrocene unit, a shielding effect in respect to the other carboxylic group was observed, with an increase of the thermal stability.

Keywords: Ferrocene acid, Thermogravimetry, kinetic parameters

1 Introduction

Both chemical and physical properties of materials are determined, in a great extent, by the combination of structural units in its molecules. In the case of organometallic molecules, the most important factor in inducing special properties is the presence of a metal, which could bring all the different metal properties and also new shapes that cannot be found in other organic compounds. Within a few years of its discovery, a number of functionalized ferrocene molecules had been prepared, with a great applicability in the homogeneous catalysis, enantioselective synthesis, as redox active materials, radiation

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In finding new properties, thermal stability of the compounds is one of the most important requirements. Because liquid crystals are materials in which mesomorphic properties appear at a certain temperature domain it is easy to understand the important role played by thermal stability for such compounds. For example, in the case of liquid crystals with the clearing point above the decomposition temperature a study of thermo degradation process is requested. Although initially was thought that metal-carbon bonds are unstable, the high thermal stability of ferrocene changed many of these ideas and the organoiron compounds become the focus of many investigations [3-7]. The rich chemistry of ferrocene stems from the nucleophilicity of the cyclopentadienyl rings, extremely reactive towards numerous electrophiles. An important factor in inducing thermal stability of ferrocene compounds is the type of functional groups adjacent to the ferrocenyl unit. Present study is focused on thermal stability of some ferrocene-containing acidic functions that are intermediates in liquid crystals synthesis. Although minor structural changes have been made, important modifications regarding thermal stability has been observed. These observations strongly suggest the fact that the structures and also other side reactions could be the reason of this behavior.

2 Experimental

2.1 Synthesis and samples preparation

The reactions performed are shown in Scheme 1:

Ketoacids 1 and 4 were obtained by classical Friedel-Crafts acylation of ferrocene, using anhydrous AlCl$_3$ as catalyst [7,8]. The reduction to the corresponding alkyl derivatives 2 was performed using Clemmensen reduction with Zn/Hg [9].

Ferrocene, stearoyl chloride, succinic anhydride and anhydrous aluminum chloride (Aldrich) were used without further purifications. Thin layer chromatography (TLC) was carried out on Silica gel 60 F$_{254}$ plates (Merck). The melting points were determined
on a Böetius microscope and are uncorrected. Infrared spectra were recorded on a Nicolet Magna 550 Fourier Transform IR spectrometer (NaCl crystal window) and NMR spectra on a Jeol ECA 600 MHz spectrometer.

1,1'-bis(3-carboxy-propionyl)-ferrocene, 1: To a solution containing 10 g (0.0537 moles) ferrocene and 10.7503 g (0.1075 moles) succinic anhydride in 350 mL anhydrous dichloromethane, cooled about 5 °C, 15.7847 g (0.1182 moles) anhydrous AlCl$_3$ was added in small portions, the temperature being kept under 10 °C. The reaction mixture was refluxed, under stirring, for an additional 7 h and then poured on ice, when 1 separates as an orange solid, while unreacted ferrocene and mono ketoacid remain in dichloromethane. The precipitate was filtered out, washed with dichloromethane, to produce practically pure 1 (TLC, ethyl acetate), 9.8 g yield 47 %, orange solid, mp: 179 °C (dec.), IR (KBr/cm$^{-1}$) 3103 (-OH), 2924 (C-H), 1705 (>C=O, carboxylic), 1668 (>C=O, ketonic), 1456, 1381, 1290, 1251, 1170, 1083, 939, 891, 837; $^1$H-NMR $\delta$ H (DMSO): 12.13 (s, 2H, -OH), 4.88 (s, 4H, ferrocene), 4.64 (s, 4H, ferrocene), 3.34 (s, 4H, C-CH$_2$-CO), 2.95 (s, 4H, -C-CH$_2$-).

1,1'-bis(3-carboxypropyl) ferrocene, 2: In a two-neck flask, 0.1148 moles of zinc and 0.00274 moles of HgCl$_2$ were stirred for 5 minutes in 15 mL of water. Concentrated hydrochloric acid (1mL) was slowly added and the mixture was stirred for another 5 minutes. The freshly prepared amalgam was decanted and 50 mL of water, 11 mL of concentrated HCl and 250 mL of toluene, containing 0.017419 moles of diketoacid acid were added. The mixture was refluxed, under stirring, for 7 hours, every hour 1 mL of concentrated HCl being added. The completion of reduction was monitored, using TLC (chloroform:methyl ether – 2:1). The organic layer was separated and washed several times with water. The reduced ketoacid was extracted with a sodium hydroxide solution (5 %) and precipitated with a 20 % HCl solution, yield of pure acid 70 %, mp: 73 °C; IR (KBr/cm$^{-1}$): 3089 (OH), 2922 (C-H), 2850 (C-H), 1707 (C=O, carboxylic), 1409, 1249, 1153, 1039, 823, 806, 669, 484; $^1$H-NMR $\delta$ H (DMSO): very broad (2H, -OH), 4.05 (m, 8H, ferrocene), 3.37 (m, 8H, -CH$_2$-).

1-stearoyl-1'- (3-carboxy-propionyl)-ferrocene (4): The synthesis of 4 was made according to the lower route in the Scheme 1:

a) **Synthesis of stearoyl ferrocene:**
To a solution of 5 g of ferrocene (0.028 moles) and stearoyl chloride 8.1415 g (0.0268 moles) in anhydrous dichloromethane (200 mL), cooled around 5 °C, 3.935 g of anhydrous AlCl$_3$ (0.0308 moles) was added in small portions, maintaining the temperature under 10 °C. The reaction mixture was left at room temperature, under stirring, for an additional 10 h. The crude product was poured on ice and the organic layer was separated. The organic layer was washed several times with water and concentrated. Stearoyl ferrocene was purified by column chromatography on Al$_2$O$_3$ using a mixture of dichloromethane:hexane (1:1). The yield of pure brown stearoyl ferrocene was 92.9 % (11.3 g), mp: = 42–47 °C, IR (KBr/cm$^{-1}$): 2914 (C-H), 2850 (C-H), 1670 (C=O, ketonic), 1473, 1458, 1408, 1265, 1107, 1001, 817, 713, 532, 476, $^3$H-NMR $\delta$ H (CDCl$_3$): 4.77 (t, 2H, Fe ring),
4.47 (t, 2H, Fc ring), 4.18 (s, 5H, Fc ring), 2.66-2.70 (t, 2H, -COCH₂), 1.68-1.71 (m, 2H, -CO-CH₂C-), 1.25-1.34 (m, 28H), 0.86-0.89 (t, 3H, -CH₃).

b) Synthesis of 1-stearoyl-1’-(3-carboxy-propionyl)-ferrocene (4):
The synthesis of 4 was made accomplished using the same procedure of Friedel Crafts reaction with a large excess of AlCl₃ in a molar ratio stearoyl ferrocene, succinic anhydride and AlCl₃ of 1:1:5. After 12 h of stirring, the reaction mixture was poured on ice. The organic layer was concentrated and the crude product was purified on silica with a mixture of dichloromethane: ethyl acetate (1:5). The yield of pure red-brown 4 was 25%, mp: = 123 °C, (KBr/cm⁻¹) 3130 (very broad–OH), 2916 (C-H), 2850 (C-H), 1710 (-C=O, carboxylic), 1666 (-C=O – ketonic), 1629 (-C=O, ketonic), 1456, 1401, 1381, 1342, 1286, 1257, 1170, 1083, 889, 833, 480; ¹H-NMR δH (CDCl₃): 12.07 (very broad) (s, 1H, -OH), 4.72-7.75 (dd, 4H, Fc ring), 4.42-4.47 (dd, 4H, Fc ring), 2.93-2.96 (t, 2H, -CH₂-COO), 2.67-2.70 (t, 2H, -COCH₂), 2.55-2.57 (t, 2H, -CH₂-COO), 1.57-1.61 (q, 2H, C-CH₂-C), 1.17-1.28 (m, 28H), 0.78-0.81 (t, 3H, -CH₃).

2.1.1 Methods section- thermogravimetric data

Thermal behavior was carried out with a MOM-Budapest Derivatograph, which allows simultaneous recording of thermogravimetric, derivative thermogravimetric and differential analysis, in statically air conditions. Aluminium Aluminium oxide as referring material, calcinated at 1000 °C, platinum melter, heating speed of 10 °C and a sample weight of 26±5 mg has been used. Kinetic processing of thermogravimetrically data was established using integral methods: Coats-Redfren [10] and Reich-Levi [11].

3 Results and discussions

The recorded thermograms for 1, 2 and 4 are presented in figures 1, 2, and 3:

The thermograms indicate that the thermal decomposition of ferrocene acids is very complex. Thermal degradation takes place in two steps for the 1 acid and in three steps in the case of the 2 and 4 acids.

Table 1 reveals the initials temperatures at which thermal degradation begins (Tᵢ) and ends (Tᵢ) for each step, weight loss (w, %), corresponding for each stage, and DTA characteristics.

The most important weight loss was observed in the last stage of thermal degradation, at temperatures over 360 °C for 1, and higher than 560 °C for 2 and 4, respectively. Using as thermal stability criteria the initial temperature of decomposition, the thermal stability series was established as being the following:

1 < 2 < 4

The thermostability of compound 1 could be justified by the presence of two strong electron-withdrawing groups, conjugated with the two-cyclopentadienyllic rings of ferrocene, which induce the decrease of the retroactive π bond between iron and the two cores, and, as a consequence, the decreasing of thermal stability as compared with the
Fig. 1 TG, DTA and DTG curves for 1.

Fig. 2 TG, DTA and DTG curves for 2.

other two acids. Beside that, in appreciating thermal degradation, not only a molecule should be considered, but also the neighboring molecules, so that the intermolecular
forces have an important role. These forces determine the melting point of material and, in consequence, the aggregation state of material at a certain temperature. Accordingly to the thermogram, in case of acid 1, thermal degradation starts at 100 °C, before the observed melting point on microscope (179 °C), so that the material is in the solid state. In solid state, molecules are stacked together and only vibrations are possible. The crystalline network could accumulate a large amount of energy and degradation could start earlier than in the case of acid 4, with the same functional groups connected next.

**Table 1** Thermogravimetric data.

| Sample | Thermal degradation stage | $T_i$(°C) | $T_f$(°C) | Characteristics DTA | Weight loss (w%) |
|--------|---------------------------|-----------|-----------|---------------------|-----------------|
| 1      | I                         | 100       | 360       | exo                 | 11.60           |
|        | II                        | 360       | 700       | exo                 | 69.00           |
|        | residue                   |           |           |                     | 19.40           |
| 2      | I                         | 180       | 480       | exo                 | 24.90           |
|        | II                        | 480       | 560       | exo                 | 21.90           |
|        | III                       | 560       | 760       | exo                 | 26.20           |
|        | residue                   |           |           |                     | 27.00           |
| 4      | I                         | 280       | 470       | exo                 | 15.98           |
|        | II                        | 470       | 570       | exo                 | 28.76           |
|        | III                       | 570       | 780       | exo                 | 38.35           |
|        | residue                   |           |           |                     | 16.91           |
to the ferrocene unit. The thermal degradation of 2 starts at a higher temperature than for the ketonic homologue 1, behavior that is probably the consequence of a much more complex degradation reaction. It is possible that during the process, some degradation products with a higher thermostability to appear. Although it has the same two strong electron-withdrawing groups, the most stable acid is 4, whose thermal degradation starts, unexpectedly, at a higher temperature (280 °C). One of the explanations is the fact that 4 have a single carboxylic group, which is known to be the weakest part of the chemical structure. Another explanation for the high degradation temperature is the presence of the long stearoyl chain, which could have a shielding effect to the carboxylic group. It seems that not only the nature of the functional groups adjacent to the ferrocene units, but also other factors interfere in evaluating thermal stability.

Thermal degradation of the studied ferrocene acids is an exothermic process. TG curves are presented in Figures 1, 2 and 3, together with the differential thermal analysis curves (DTA).

In the purpose of getting some information regarding the degradation mechanism of the three acids, some theoretical values of the thermogravimetric data, calculated admitting that some small compounds leave in the different stages of thermal degradation, are presented in Table 2. A good correlation between the calculated data and those determined by thermo-gravimetical analysis, especially regarding the residue and fragments resulting from the first stage, has been established. The residue is FeO for 1 and a mixture of FeO and Fe$_2$O$_3$ for 2 and 4 in different ratio (2:1) and (3:1), respectively.

For the second and third steps of thermal degradation, in the case of 2 and 4 acids, the small molecular compounds released during the thermal degradation could not be identified because of the much more complex degradation mechanism, so that an ATG coupled with mass spectrometry is necessary.

| Sample | Stage of thermal degradation | I ATG% | Calc% | II ATG% | Calc% | III ATG% | Calc% | Residue |
|--------|------------------------------|--------|-------|---------|-------|----------|-------|---------|
| 1      | Fragments                    |        |       |         |       |          |       | FeO     |
|        | Percentage                   | 11.60  | 11.34 | 69.00   | 63.34 | 19.40    | 18.53 |         |
| 2      | Fragments                    | CO$_2$ |      | CH$_3$CHO, C$_2$H$_4$ | - | FeO and Fe$_2$O$_3$ (2:1) |
|        | Percentage                   | 24.90  | 24.44 | 21.90   | 26.2  | 27.00    | 28.11 |         |
| 4      | Fragments                    | CO$_2$ and CH$_3$CHO | - |         | FeO and Fe$_2$O$_3$ (3:1) |
|        | Percentage                   | 15.98  | 15.80 | 28.76   | 38.35 | 16.91    | 16.94 |         |

Table 2 ATG Data compared with theoretical data.

The evaluation of kinetic parameters from thermogravimetric data, in dynamic conditions of temperature, is based on differential and integrals methods, which need a higher number of experimental data evaluated. Accordingly, the evaluation of kinetic
parameters has been done using “Matchad 2000” programs, which allows determination of these parameters using two integral methods: Coats-Redfren (C-R) and Reich-Levi (R-L). The obtained results together with other kinetic characteristics such as: rate constant corresponding to maximal degradation speed \( k_{\text{max}} \) and critical (isokinetic) temperature \( T_{\text{cr}} \), are presented in Table 3.

In C-R method, the reaction order has been established from \( F(\alpha) \) function so that the graphical function \([\log F(\alpha)/T^2, 1/T]\) is linear; the activation energy and pre-exponential factor were obtained from the graphical parameters of the linear function.

In Reich-Levi case, the activation energy and pre-exponential factor were determined from \([\log F(\alpha), 1/T]\) linear function for a certain value of reaction order.

The rate constant, corresponding to maximal degradation speed \( k_{\text{max}} \) and critical temperature \( T_{\text{cr}} \) for the second degradation step, was calculated by applying Gorbachev equations [12], [13]. The results are presented in Table 4.

By comparing \( T_{\text{cr}} \) with \( T_{\text{max}} \), similar values were founded, which suggest the possibility of using these as criteria of thermostability and verify the series: 1 < 2 < 4. The different values of rate constants for this stage of thermal degradation suggest the fact that degradation took place with releasing of small different molecules.

The same reaction order of 1 was obtained for all the degradation steps in the case of all compounds. The activation energy for samples with the same mechanism of degradation, in the final step (2 and 4) is around 100-110 kJ/mol.

| Method Sample | C-R | R-L | C-R | R-L | C-R | R-L | C-R | R-L |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|
|               | n   |     |     |     |     |     |     |     |
| Stage I       |     |     |     |     |     |     |     |     |
| 1             | 1   | 1   | 14.27 | 13.80 | 5.07 | 4.92 | 0.96 | 0.98 |
| 2             | 1   | 1   | 37.00 | 36.75 | 9.38 | 9.33 | 0.98 | 0.99 |
| 4             | 1   | 1   | 64.03 | 63.25 | 13.94 | 13.79 | 0.98 | 0.99 |
| Stage II      |     |     |     |     |     |     |     |     |
| 1             | 1   | 1   | 59.33 | 53.43 | 10.26 | 11.10 | 0.99 | 0.99 |
| 2             | 1   | 1   | 262.96 | 215.38 | 42.32 | 34.96 | 0.97 | 0.98 |
| 4             | 1   | 1   | 152.42 | 145.78 | 24.19 | 23.22 | 0.97 | 0.99 |
| Stage III     |     |     |     |     |     |     |     |     |
| 2             | 1   | 1   | 104.15 | 96.44 | 14.60 | 13.59 | 0.97 | 0.99 |
| 4             | 1   | 1   | 121.52 | 115.97 | 16.65 | 15.94 | 0.97 | 0.99 |

\( n = \) reaction order,  
\( E_a = \) activation energy,  
\( \Lambda = \) pre-exponential factor,  
\( r^2 = \) correlation coefficient,  
C-R= Coats-Redfern integral method,  
R-L= Reich-Levi integral method.

**Table 3** The kinetic data.

The activation energy variation with conversion degree (\( \alpha \)) has been determined by
Table 4 Other kinetic data for second stage of thermal degradation.

| Sample | \(k_{\text{max}} \cdot 10^3 \text{ (s}^{-1}\text{)}\) | \(T_{\text{cr}} \text{ (°C)}\) | \(T_{\text{max}} \text{ (°C)}\) |
|--------|----------------|----------------|----------------|
| 1      | 2.27           | 481            | 450            |
| 2      | 8.70           | 503            | 505            |
| 4      | 4.45           | 563            | 555            |

\(k_{\text{max}}\) = rate constant for a maximal degradation rate,  
\(T_{\text{cr}}\) = critical temperature,  
\(T_{\text{max}}\) = temperature corresponded to the maximal degradation rate

using the Reich-Levi analytical method for the entire degradation domain.

A modification of the activation energy with the conversion degree has been found, confirming the complexity of the degradation mechanism and the tendency of closely values of the activation energy corresponding to the final degradation step for 2 and 4. These are mutually consistent with the observations from the ATG data. The obtained results are marked out in figure 4 and confirm the series established from thermogravimetric data, respectively \(1 < 2 < 4\).

![Fig. 4 The activation energy variation with the conversion degree.](image)

4 Conclusions

- Thermal behavior of some ferrocene acids with several structural changes has been studied.
- The thermal degradation process of 1, 2 and 4 acids has a complex mechanism by successive reactions.
- The following stability series of the compounds has been established:
  \[1 < 2 < 4\]
The compound’s thermal stability depends not only on the type of functional groups adjacent to the ferrocenyl unit, but also on other parameters. These include side reactions or the materials aggregation states in which the degradation begin (solid or liquid) or shielding effects on the carboxylic group.

Kinetic parameters obtained by using the Coats-Redfren (C-R) and Reich-Levi integration methods are mutually consistent.

The critical (isokinetic) temperature is comparable with $T_{\text{max}}$, suggesting the use of this thermal characteristic in establishing thermostability.

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