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HEAT CAPACITIES OF FERROCENE, ACETYL-, 1,1′-DIACETYL-, BENZOYL- AND 1,1′-DIBENZOYLFERROCENE BY DSC *

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SUMMARY

The values of the heat capacities of the ferrocene, acetyl-, 1,1′-diacetyl-, benzoyl- and 1,1′-dibenzoylferrocene have been obtained by DSC in the temperature range 20—100°C and the regression line equations in this temperature interval have been calculated. The data obtained for ferrocene agree with those reported in the literature and obtained by Jǿns and Gjaldbaek.

Some observations and correlations on the behaviour of the heat capacities are reported.

INTRODUCTION

In recent years, the interest in ferrocene derivatives, whether in theoretical research or in the applied field has increased. In particular, acetylferrocene and 1,1′-diacetylferrocene have been used in the synthesis of polymers which are stable up to 750 K and which have semiconductor properties [1] and benzoyl ferrocene derivatives have been used as protective ultraviolet absorbers in transparent organic coatings [2].

In the case of ferrocene, all the major physico-chemical parameters are well known, but the same is not true for its derivatives. There is a lack of data in the literature concerning the heat capacities of these compounds which would also be useful in obtaining information about their thermodynamic parameters. For this reason, the determinations of the heat capacities at different temperatures has been carried out by DSC.

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EXPERIMENTAL

Instrumentation

A Perkin-Elmer DSC-2 instrument was used with a heating rate of 5°C min^{-1} and an atmosphere of dry nitrogen at a flow rate of 100 ml min^{-1}. Weighings were carried out on a Perkin-Elmer Model AD-2Z autobalance electronic ultramicrobalance.

Preparation of compounds

Ferrocene

The ferrocene was supplied by Aldrich. Before use, it was purified by sublimation under vacuum at 130°C. The melting point of the solid compound obtained was 137.9 ± 0.5°C.

Acetylferrocene [3]

93 g of ferrocene, 250 ml of acetic anhydride and 20 ml of 85% phosphoric acid were allowed to react slowly with stirring and in a nitrogen atmosphere. The mixture was then refluxed at 100°C in an oil bath for 10 min and, after cooling, it was slowly poured into ice water, and then neutralized with 200 g of sodium carbonate monohydrate in 200 ml of water. Filtration gave a dark solid product which was purified on an alumina chromatographic column using benzene as eluant. Three fractions were obtained, the second of which was the acetylferrocene. The yield was 65%. The obtained solid was then sublimed under vacuum at 80°C to give a solid melting at 85.5 ± 0.5°C.

1,1'-Diacetylferrocene [4]

To a mixture of 53 g of aluminium trichloride and 32 g of acetyl chloride in 200 ml of dry methylene chloride was slowly added with stirring and in a stream of nitrogen a solution of 30 g of ferrocene in 130 ml of methylene chloride. The mixture was stirred for 2 h and then poured onto ice. The two phases obtained were separated and the aqueous phase extracted several times by chloroform. The chloroformic extract was mixed with the organic phase and evaporated to 100 ml. On cooling, the 1,1'-diacetylferrocene precipitates as red chips at a yield of 70%. The compound obtained was purified by sublimation under vacuum at 120°C to give a product with a melting point of 130.5 ± 0.5°C.

Benzoylferrocene [5]

A solution of 14 g of benzoyl chloride and 13 g of aluminium trichloride in 250 ml of dry methylene chloride was added dropwise over a period of 1 h under nitrogen to a vigorously stirred solution of 20 g of ferrocene in 300 ml of dry methylene chloride in a three-necked flask. The solution was then gently refluxed for another 30 min. After hydrolysis with 0.1 M hydrochloric acid, the product was worked up and the solid chromatographed on alumina using benzene as eluant. The dark-red needles were recrystallized from petroleum ether at a yield of 65%. The melting point of the solid obtained was 111.0 ± 0.5°C.

TABLE 1

Physical and analytical data of the compounds investigated

Compound	Formula	Melting point		Ref.	C (%)		H (%)	
		Determined (°C ± 0.5)	Literature (°C)		Calcd.	Found	Calcd.	Found
Ferrocene	$C_{10}H_{10}Fe$	173.9	174	8	64.56	64.58	5.42	5.40
			173 –174	9				
Acetylferrocene	$C_{12}H_{12}OFe$	85.5	85 – 86	8	63.20	63.19	5.30	5.30
			83 – 85	4				
			85 – 86	3				
1,1'-Diacetylferrocene	$C_{14}H_{14}O_2Fe$	130.5	130 –131	8	62.25	62.27	5.22	5.20
			128.5–129.5	4				
			130 –131	10				
Benzoylferrocene	$C_{17}H_{14}OFe$	111.0	108.1–108.3	5	70.37	70.35	4.86	4.85
			111.5–112.0	11				
1,1'-Dibenzoylferrocene	$C_{24}H_{18}O_2Fe$	106.5	106.5–106.7	5	73.12	73.10	4.60	4.62
			105 –106	12				

1,1'-Dibenzoylferrocene [5]

The procedure was the same as that described for benzoylferrocene. The acylating solution added to ferrocene contained 29 g of benzoyl chloride and 27 g of aluminium trichloride in 400 ml of dry methylene chloride and the chromatographic purification was achieved on alumina with benzene followed by ether as eluants. The yield of purple needles, m.p. 106.5 ± 0.5°C, was 86%.

Purity control

The purity of the compounds was checked by thin layer chromatography on alumina plates using benzene as eluant. In addition to the melting points, elemental analyses for C and H were obtained and the corresponding data are collected in Table 1 which also gives the theoretical values and some values reported in the literature.

RESULTS AND DISCUSSION

The heat capacities of the compounds examined were obtained by DSC from the equation

$$C_{p,s} = \frac{W_{saph}}{W_s} \frac{D_s}{D_{saph}} c_{p,saph} M_s$$

where $C_{p,s}$ = heat capacity of the sample, $c_{p,saph}$ = specific heat of sapphire, W_s = weight of the sample, W_{saph} = weight of sapphire, D_s = sample displacement, D_{saph} = sapphire displacement, and M_s = molecular weight of the sample.

Earlier, the molar heat capacities of ferrocene were calculated in the temperature range 20—120°C, and compared with those obtained by the equation

$$C_p = 50.32 + 0.1627\ (T - 325)\ \text{cal mole}^{-1}\ \text{degree}^{-1}$$

proposed by Jøns and Gjaldbaek [6] and corresponding to the

$$C_p = 41.89 + 0.1627\ (\text{temp. in °C})\ \text{cal mole}^{-1}\ °\text{C}^{-1}$$

In Table 2, the molar heat capacities of ferrocene at ten degree intervals in the temperature range 20—120°C obtained experimentally by DSC are compared with those calculated from the above equation at the same temperatures. It can be seen that there is good agreement between the experimental and calculated values ($\Delta < 1\%$). Using the same operational parameters, we then obtained experimentally the molar heat capacities of acetylferrocene and 1,1'-diacetylferrocene (Table 3) and benzoylferrocene and 1,1'-dibenzoylferrocene (Table 4). These values were compared with those obtained at the same temperatures by the regression line equations given in Table 5, obtained by the least squares method, for the temperature ranges shown in the table. Analysing the tables it can be seen that

(a) for the ferrocene derivatives, the heat capacities were calculated up to

TABLE 2

Molar heat capacities of ferrocene determined by DSC and from the equation given in the literature in the temperature range 20—120°C
Experimental values (y) compared with the values calculated from the regression line [y(regr.)] and the values calculated from the equation reported in ref. 6 [y'(regr.)].

x (±0.5°C)	y (±0.5 cal mole^{-1} deg^{-1})	y(regr.) [a] (cal mole^{-1} deg^{-1})	y'(regr) [b] (cal mole^{-1} deg^{-1})	$100[y - y'(\text{regr.})]/y$
20.0	45.3	45.3	45.1	0.4
30.0	46.7	46.9	46.8	−0.2
40.0	48.6	48.5	48.4	0.4
50.0	50.1	50.0	50.0	0.2
60.0	51.5	51.6	51.7	−0.4
70.0	53.1	53.2	53.3	−0.4
80.0	54.9	54.8	54.9	0
90.0	56.3	56.4	56.5	−0.4
100.0	58.2	57.9	58.2	0
110.0	59.5	59.5	59.8	−0.5
120.0	60.9	61.1	61.4	−0.8

[a] $y(\text{regr.}) = 42.13 + 0.158x$ (this work).
[b] $y'(\text{regr.}) = 41.89 + 0.163x$ (reported in the literature).

TABLE 3

Molar heat capacities of acetylferrocene and 1,1'-diacetylferrocene determined by DSC in the temperature range 20—120°C
Experimental values (y) compared with the values calculated from the regression line [y(regr.)].

x (±0.5°C)	Acetylferrocene		1,1'-Diacetylferrocene	
	y (±0.5 cal mole^{-1} deg^{-1})	y(regr.) [a] (cal mole^{-1} deg^{-1})	y (±0.5 cal mole^{-1} deg^{-1})	y(regr.) [b] (cal mole^{-1} deg^{-1})
20.0	57.0	57.3	68.4	68.2
30.0	60.5	60.2	70.1	70.6
40.0	62.9	63.0	72.9	73.1
50.0	66.1	65.8	76.0	75.5
60.0	68.7	68.7	78.2	78.0
70.0	71.3	71.5	80.1	80.5
80.0	74.3	74.3	83.3	82.9
90.0			85.1	85.4
100.0			88.2	87.9
110.0			90.1	90.3
120.0			92.8	92.8

[a] y(regr.) = 51.67 + 0.283x
[b] y(regr.) = 63.22 + 0.247x

TABLE 4

Molar heat capacities of benzoylferrocene and 1,1'-dibenzoylferrocene determined by DSC in the temperature range 20—120°C
Experimental values (y) compared with the values calculated from the regression line (y(regr.)].

x (±0.5°C)	Benzoylferrocene		1,1'-Dibenzoylferrocene	
	y (±0.5 cal mole^{-1} deg^{-1})	y(regr.) [a] (cal mole^{-1} deg^{-1})	y (±0.5 cal mole^{-1} deg^{-1})	y(regr.) [b] (cal mole^{-1} deg^{-1})
20.0	89.6	89.7	108.2	108.0
30.0	95.8	95.8	114.5	115.0
40.0	101.3	101.9	121.8	121.9
50.0	108.8	107.9	128.9	128.8
60.0	114.4	114.0	136.3	135.7
70.0	119.4	120.1	142.9	142.7
80.0	126.2	126.2	149.1	149.6
90.0	132.4	132.3		

[a] y(regr.) = 77.50 + 0.609x
[b] y(regr.) = 94.17 + 6.93x

a temperature 10—20°C below the melting point, at which point, sublimation began to affect the accuracy of measurement;

(b) as can be clearly seen in Table 2, the data obtained from the Jǿns and Gjaldbaek equation [6] for the heat capacities of ferrocene also agree very well with the experimental data for temperatures lower than those suggested by the authors and particularly in the range 20—120°C;

(c) Tables 2—4 show that, at the same temperatures in the examined temperature ranges, there is a sequence

C_p(1,1′-dibenzoylferrocene) > C_p(benzoylferrocene) > C_p(1,1′-diacetylferrocene) > C_p(acetylferrocene) > C_p(ferrocene)

i.e. at the operational temperature, the heat capacities of the 1,1′-disubstituted ferrocenes are higher than those of the monosubstituted ferrocenes which are higher than the values for ferrocene. It can be seen that the heat capacity is higher for the derivatives with the higher steric hindrance;

(d) the increase in C_p as a function of temperature is higher for the benzoyl derivatives than for the acetyl derivatives and these, in turn, are higher than for ferrocene. In fact, the angular coefficients b of the regression lines given in Table 5 show that b(benzoylferrocene) ($\simeq$0.6—0.7) > b(acetylferrocenes) ($\simeq$0.2—0.3) > b(ferrocene) (=0.16).

(e) Finally, the usefulness of the determined heat capacities for obtaining information about some thermodynamic functions of these compounds must be considered. In fact, the obtained C_p values for ferrocene, acetylferrocene and 1,1′-diacetylferrocene allowed us, in a recent paper [7], to calculate the enthalpic functions for the solid phase, and knowing the enthalpic function for the gas phase, it has been possible to obtain the sublimation enthalpies at 298 K for these compounds and, finally, the free energy function for the solid phase.

TABLE 5

Regression line: analytical forms $y = a + bx$
y in cal mole^{-1} degree^{-1} ± 0.5 cal mole^{-1} degree^{-1}; x in °C ± 0.5°C

Compound	Range (°C)	a (cal mole^{-1} deg^{-1})	b (cal mole^{-1} deg^{-2})	R
Ferrocene				
This work	20.0—120.0	42.13	0.158	0.999
Ref. 6	132 —172	41.89	0.163	
Acetylferrocene	20.0— 80.0	51.67	0.283	0.998
1,1′-Diacetylferrocene	20.0—120.0	63.22	0.247	0.998
Benzoylferrocene	20.0— 90.0	77.50	0.609	0.999
1,1′-Dibenzoylferrocene	20.0— 80.0	94.17	0.693	0.999

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