Thermodynamic Investigation of Precursors for MOCVD Processes: tris-Dipivaloylmethanate of Iron

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Abstract

The heat capacity for tris-dipivaloylmethanate of iron $Fe(C_{11}O_2H_{19})_3$ within the temperature range 57–316 K has been measured by the adiabatic method. An anomaly of heat capacity has been discovered with a maximum at ~115 K, which points to the phase transformation of the $Fe(C_{11}O_2H_{19})_3$ complex. Anomalous contributions to entropy and enthalpy have been revealed. Within an accuracy of experimental determination, the anomalous entropy has been found to be $R\ln 2$. Within the range 0–57 K the heat capacity C_p has been calculated using the characteristic behavior of the Debye temperature. The thermodynamic functions (entropy, enthalpy and reduced Gibbs' energy) have been calculated within the range 0–315 K.

INTRODUCTION

Dipivaloylmethanate of iron $Fe(C_{11}O_2H_{19})_3$, or $Fe(DPM)_3$, belongs to the class of complex of the transition metals with β-diketones. In solid state, β-diketonates of metals relate to crystals of molecular type. Because of high volatility, *i. e.* a substantial vapor pressure over the solid phase at moderate temperatures [1], β-diketonates are widely used for solving various applied problems [2], including the organization of ecologically safe technologies. At present, thermodynamic and other physicochemical properties of this class compounds are under intense investigation [3–7]. Thermodynamic properties are used to calculate the characteristics of equilibrium and stability for the crystal – gas systems; they are also used to investigate and optimize gas-phase technological processes. For reliable calculation of thermodynamic functions (enthalpy, entropy, *etc.*), one should know the low temperature heat capacity data. In the present work, we report experimental results of a heat capacity investigation for tris-dipivaloylmethanate of iron $Fe(C_{11}O_2H_{19})_3$ within the temperature range 57–316 K.

EXPERIMENTAL

The $Fe(C_{11}O_2H_{19})_3$ complex was synthesized in aqueous alcohol medium by reaction of $FeCl_3 \cdot 6H_2O$ with the neutralized by NaOH ligand $H \cdot DPM$, all taken in stoichiometric amounts. The formed $Fe(DPM)_3$ crystals were filtered off and washed with distilled water and then recrystallized in acetone-water system. The final purification of a product was performed by sublimation in a vacuum gradient furnace at the pressure of 10^{-2} mm Hg allocating the deposition zone 120–130 °C.

Visually, the $Fe(DPM)_3$ sample at room temperature is brick-red crystalline powder with the mean crystallite size of ~0.3 mm. The melting point determined on Boetius table is 164 °C (437 K), which is in good agreement with T_{melt} = 163 °C (438 K) obtained in [8]. The IR spectra and derivatogram support the conformity of the obtained compound to tris-

TABLE 1

Experimental heat capacity of $Fe(C_{11}O_2H_{19})_3$ (molar mass: 605.659 g/mol)

T, K	C_p, J/(mol K)	T, K	C_p, J/(mol K)	T, K	C_p, J/(mol K)
57.622	210.66	111.824	472.38	211.767	692.95
61.261	225.01	115.013	505.42	216.488	705.33
64.564	237.69	115.246	511.59	221.377	715.42
67.600	248.90	118.744	484.40	226.330	727.01
70.437	260.38	120.733	475.36	231.337	738.01
73.109	271.00	122.358	473.66	236.298	747.97
75.642	280.87	125.922	473.63	241.207	758.83
78.056	290.64	126.837	475.88	246.287	769.10
80.546	299.05	130.022	482.45	251.743	783.11
82.600	309.22	132.744	489.11	257.671	796.50
84.717	316.26	133.188	489.57	264.144	809.77
84.746	317.65	138.320	503.69	270.651	824.16
86.406	323.33	143.727	517.66	274.376	834.45
87.160	326.67	148.977	531.92	277.468	842.17
89.094	333.42	154.124	545.91	277.788	841.35
89.702	337.22	159.297	560.42	282.881	853.43
94.111	353.84	164.903	575.85	284.754	857.03
94.158	354.74	170.566	592.61	288.566	866.69
98.422	372.16	175.845	604.32	291.862	873.77
99.260	375.27	181.112	619.26	294.182	879.10
101.674	383.76	186.297	630.44	299.636	890.12
104.473	396.73	191.274	644.76	300.430	893.87
104.814	399.82	196.789	658.54	305.026	902.20
108.216	418.79	202.273	670.89	310.487	915.56
109.752	432.55	207.109	683.35	316.083	929.02

dipivaloylmethanate of iron. According to the X-ray phase analysis, the compound is single-phase; the structure of the obtained crystals corresponds to the $Fe(DPM)_3$ structure determined in [9], with lattice parameters a = (20.325 ± 0.008) Å, b = (17.350 ± 0.007) Å, c = (23.171 ± 0.009) Å, β = (111.98 ± 0.03) deg; space group $C2_1/c$; coordination number $Z = 8$. The calculated X-ray density, according to the data of [9], is (1.061 ± 0.001) g/cm^3, the experimental density is (1.060 ± 0.003) g/cm^3. According to the results of elemental analysis, the carbon content in the sample is 51.08 % (the calculated is 51.02 %), the hydrogen content is 6.03 % (the calculated is 5.99 %) which corresponds to the stoichiometric composition of $Fe(C_{11}O_2H_{19})_3$ within the experimental accuracy.

A heat capacity of the sample within the temperature range 57–316 K was measured by the adiabatic method using the installation described in [3, 10]. The substance in amounts of 4.326 g was loaded into calorimetric ampoule. The molar mass (605.659 g/mol) for the molar heat capacity calculating was obtained using the formula $Fe(C_{11}O_2H_{19})_2$. In the pulse heating mode 75 experimental points of heat capacity were measured.

Values of experimental heat capacity for the compound $Fe(DPM)_3$ are shown in Table 1. Root-mean-square deviation of the experimental points from the smoothed curve $C_p(T)$ is 0.13 % within the range 57–115 K and 0.08 % within the range 115–316 K. An anomaly with a sharp maximum at T_c = 115.25 K is observed on the $C_p(T)$ curve (Fig. 1). In maximum the anomalous part (76.32 J/(mol K)) represents 17.5 % of a regular heat capacity. The appearance of the anomaly points to the phase transition in $Fe(DPM)_3$. No indications of the I kind phase transition were detected in the

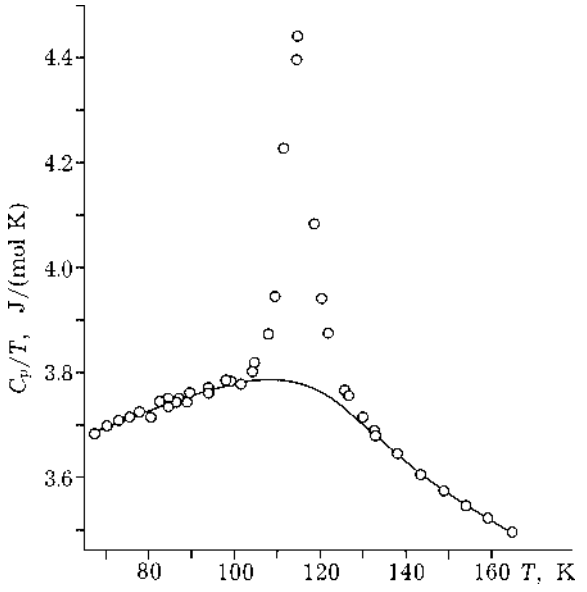

Fig. 1. Heat capacity of $Fe(C_{11}O_2H_{19})_3$ as $C(T)/T$ *vs.* T in the region of the anomaly. Points are experimental values, the solid line is an assumed regular behavior; $T_c = 115.25$ K.

thermogram recorded within the range 105–129 K.

In order to reveal the nature of this anomaly, we measured a static magnetic susceptibility χ of the investigated compound by means of SQUID magnetometer within the temperature range 2–300 K. It is represented in Fig. 2 in coordinates $1/\chi$ (T) and T. One can see that experimental points do not deviate from the linear dependence (Curie–Weiss law) within the whole temperature range.

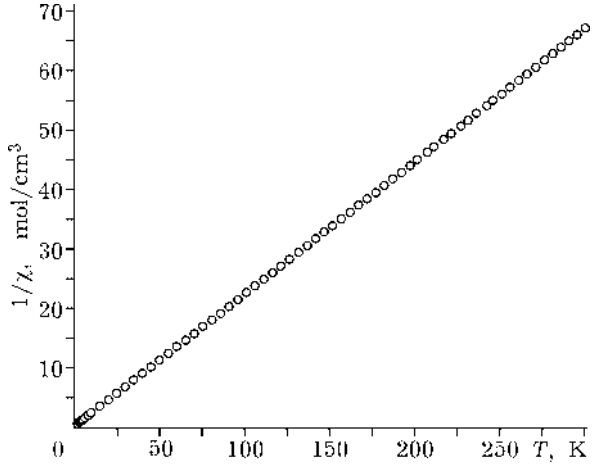

Fig. 2. Experimental points of an inverse magnetic susceptibility $1/\chi(T)$ within the range 2–300 K for $Fe(C_{11}O_2H_{19})_3$.

RESULTS AND DISCUSSION

In order to calculate thermodynamic functions at standard temperature 298.15 K, we extended the $C_p(T)$ dependence to 0 K. For this purpose, we used the dependence of Debye temperature $\Theta_D(T)$ within the range 57–316 K (Fig. 3) obtained on the basis of experimental data $C_p(T)$. A steep temperature dependence of $\Theta_D(T)$ is the evidence of a broad phonon spectrum of the compound, which is due to a large dispersion of the interatomic interaction energies in this compound. One can see in Fig. 3 that the dependence $\Theta_D(T)$ is a linear function below the anomaly (within the range 57–100 K). This dependence was extrapolated to 0 K. The Debye temperature at 0 K turned out to be 235 K. In Fig. 3, one can also see that the dependence $\Theta_D(T)$ for $Fe(DPM)_3$ and the dependence $\Theta_D(T)$ for $Cr(AA)_3$ obtained on the basis of experimental heat capacity [3] within the range 5–315 K exhibit the same behavior within the whole temperature range. This confirms correctness of the chosen method for obtaining $C_p(T)$ at temperature below 57 K.

Using the obtained dependence $Q_D(T)$ we calculated the heat capacity within the range 0–57 K. The entropy $S°(T)$, the difference of enthalpies $H°(T) - H°(0)$ and the reduced Gibbs' energy $\Phi°(T)$ were obtained by numerical integration of $C_p(T)$ within the range 0–315 K taking into account the contribution from the anomalous component $\Delta C_p(T)$. A smoothed dependence $C_p(T)$ and thermodynamic functions are listed in Table 2.

The following values of thermodynamic functions at standard temperature (298.15 K) were obtained:

C_p (298.15 K) = (887.7 ± 0.8) J/(mol K),

$S°$(298.15 K) = (961 ± 10) J/(mol K),

$H°$(298.15 K) − $H°$(0) = (147 500 ± 300) J/mol,

$\Phi°$(298.15 K) = (466 ± 9) J/(mol K).

Errors of the listed thermodynamic values are mainly due to the error of $C_p(T)$ extrapolation to 0 K. They are determined by the possible deviation of $\Theta_D(T)$ within (235 ± 23) K.

Debye temperature of the compound under investigation in the vicinity of phase tran-

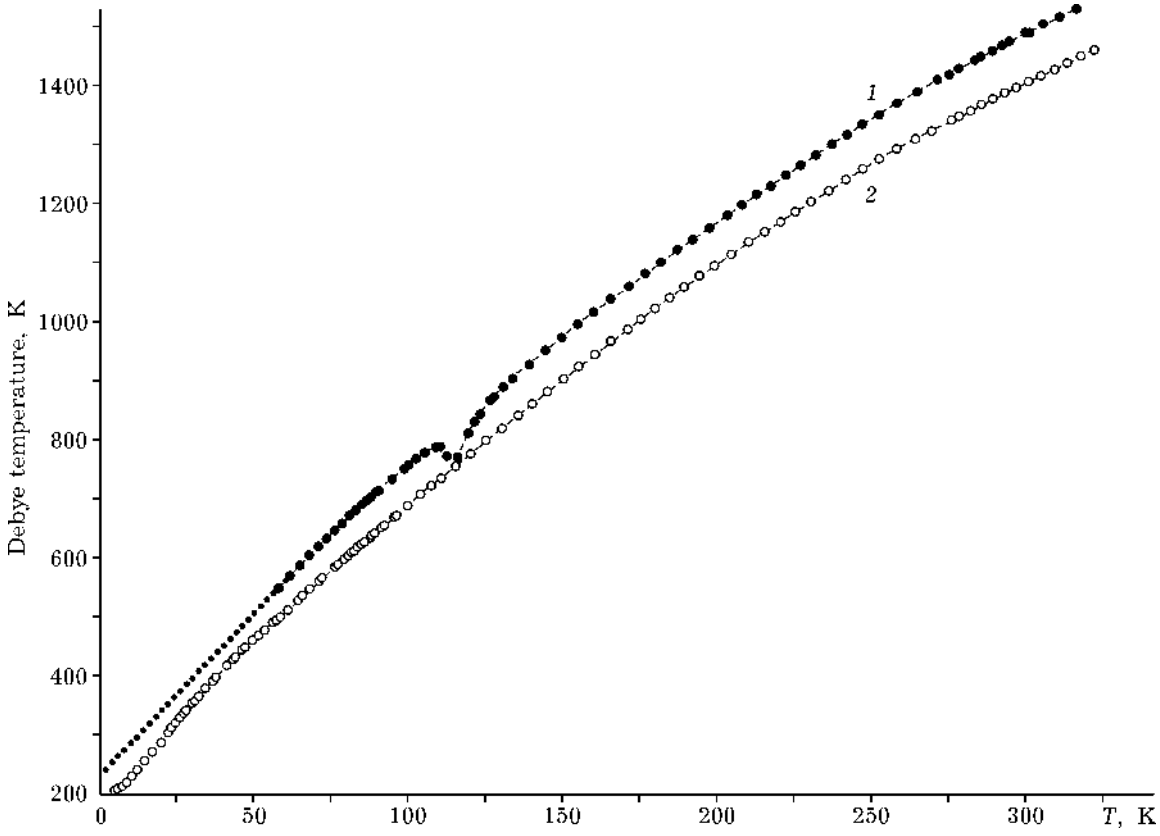

Fig. 3. Debye temperature $\Theta_D(T)$ for $Fe(C_{11}O_2H_{19})_3$ (*1*) and $Cr(C_5O_2H_7)_3$ (*2*). Points are an extrapolation of $\Theta_D(T)$ dependence.

sition is shown in Fig. 4. One can see that regular behavior of $\Theta_D(T)$ is described very well by a linear function; no jump of Debye temperature being observed in the phase transition. The linear dependence of Θ_D on temperature was used to separate the anomalous contribution to heat capacity.

In the region of the anomaly, the interpolated function $\Theta_D(T)$ (see Fig. 4) was recalculated into heat capacity, which was accepted as a regular constituent of C_p(reg.). Subtracting C_p (reg.) from experimental heat capacity we obtained the anomalous part $\Delta C_p(T)$ (Fig. 5). Entropy ΔS and enthalpy ΔH of the anomaly were obtained by integrating $\Delta C_p(T)$; the resulting values were (5.75 ± 0.11) J/(mol K) and (663 ± 12) J/mol, respectively.

The absence of both a jump of Debye temperature at T_c and any indicationes of the I kind phase transition on the thermogram gives us reasons to believe that we observe phase transition of the II kind. The entropy of transition ΔS coincides to a high accuracy with the value Rln 2 (5.76 J/(mol K)). This is the evidence for a possible transformation of two equally probable states (low-temperature phase) into one identical state (high-temperature phase).

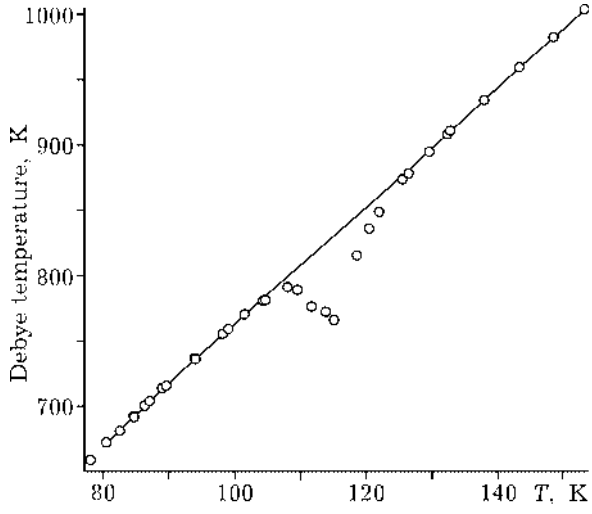

Fig. 4. Debye temperature $\Theta_D(T)$ for $Fe(C_{11}O_2H_{19})_3$ in the vicinity of phase transition. Points are experimental values; a solid line is a regular behavior of $\Theta_D(T)$.

TABLE 2

Thermodynamic functions of $Fe(C_{11}O_2H_{19})_3$ (molar mass: 605.659 g/mol)

T, K	C_p°, J/(mol K)	$S°$, J/(mol K)	$H°(T) - H°(0)$, J/mol	$\Phi°$, J/(mol K)
		Calculation		
10	8.2	3.2	23	0.9
15	20.9	8.7	93	2.5
20	38.3	17.0	240	5.0
25	59.1	27.6	482	8.5
30	81.9	40.5	834	12.7
35	105.8	54.9	1303	17.7
40	129.8	70.6	1892	23.3
45	153.6	87.3	2601	29.5
50	176.7	104.7	3427	36.1
		Experiment		
60	219.91	140.77	5413	50.55
70	258.70	177.57	7805	66.06
80	298.00	214.69	10589	82.32
90	337.70	252.09	13768	99.10
100	377.62	289.77	17348	116.28
110	437.32	328.02	21366	133.78
120	478.70	370.23	26220	151.73
130	482.41	408.32	30979	170.02
140	507.86	444.98	35927	188.36
150	534.63	480.93	41139	206.67
160	562.43	516.31	46622	224.91
170	589.82	551.24	52385	243.09
180	615.81	585.69	58414	261.16
190	640.92	619.66	64697	279.14
200	665.82	653.17	71233	297.01
210	689.56	686.24	78011	314.75
220	712.68	718.85	85022	332.38
230	734.91	751.03	92261	349.89
240	756.31	782.75	99716	367.26
250	778.32	814.07	107388	384.51
255	789.76	829.59	111309	393.09
260	801.07	845.04	115286	401.63
265	812.09	860.40	119319	410.14
270	823.43	875.69	123407	418.62
280	846.79	906.06	131760	435.49
290	869.62	936.17	140341	452.23
298.15	887.70	960.52	147503	465.79
300	891.72	966.03	149149	468.86
310	914.62	995.64	158180	485.38
315	926.16	1010.36	162782	493.60

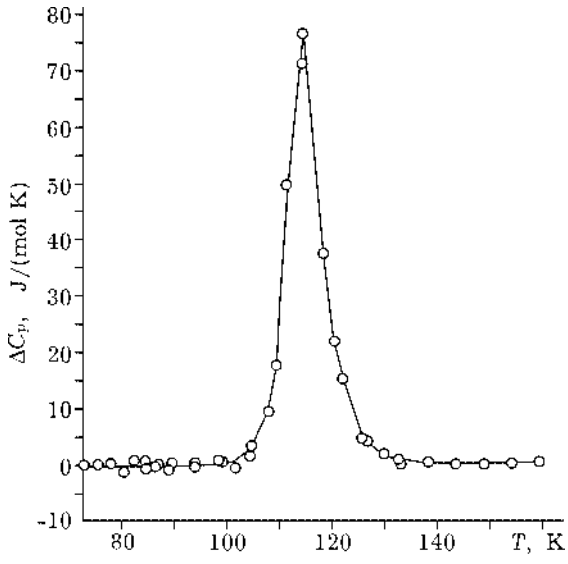

Fig. 5. Anomalous contribution to heat capacity of $Fe(C_{11}O_2H_{19})_3$: ΔS = 5.75 J/(mol K), ΔH = 663 J/mol.

Since the dependence of magnetic susceptibility on temperature does not deviate from Curie–Weiss law, one can exclude from consideration the change of the state of magnetic ion Fe^{3+} as a reason of the observed phase transition. It can be assumed that molecules $Fe(C_{11}O_2H_{19})_3$ being equivalent (indistinguishable) in high-temperature phase have got some distinguishing features in low-temperature phase.

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