Russian Journal of General Chemistry, Vol. 74, No. 3, 2004, pp. 341–345. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 3, 2004, pp. 379–383.
Original Russian Text Copyright © 2004 by Kozlova, Karyakin, Sheiman, Larina, Kamelova.

Thermodynamic Properties of Formylferrocene

M. S. Kozlova, N. V. Karyakin, M. S. Sheiman, V. N. Larina, and G. P. Kamelova

Research Institute of Chemistry, Lobachevskii Nizhni Novgorod State University, Nizhni Novgorod, Russia

Received March 12, 2002

Abstract—The enthalpies of combustion and formation, heat capacity, and related thermodynamic functions of formylferrocene were determined. The temperature dependence of the heat capacity of formylferrocene revealed anomaly in the range 217–291 K, interpreted as a λ transition in the solid state. The transition enthalpy and entropy were estimated.

At present much attention is given to searching for new application fields of ferrocene derivatives, elaborating synthetic approaches to these compounds, and elucidating their reaction mechanisms and structures and the nature of chemical bonding in them [1]. This necessitates research into physicochemical, particularly thermodynamic properties of ferrocene derivatives. However, there has been little work on their thermodynamics [2–4]. In this connection in the present work we determined the enthalpies of combustion and formation, heat capacity, and related thermodynamic functions of formylferrocene (**I**).

Heat capacity and thermodynamic functions. The experimental heat capacities of compound **I** (a total of 66 points) in the range 60–301 K are presented in Table 1 and in the figure. The temperature dependence of the heat capacity of compound **I** showed an anomaly in the range 217–291 K, which looks like a characteristic “hump” peaking at 281 K. According to McCallagh [5], this transition can be classed with solid-state λ transitions. From the area between the $C_p = f(\mathrm{T})$ and $C_p f(\ln T)$ curves with the λ transition and the corresponding interpolation curves we estimated the enthalpy ($\Delta_{\mathrm{tr}}H^0$ 365 ± 3 J mol^{-1}) and entropy ($\Delta_{\mathrm{tr}}S^0$ 1.36 ± 0.02 J mol^{-1} K^{-1}) of the transition. It should be noted that similar anomalies were observed with other ferrocene derivatives and almost all dicyclopentadienyl derivatives of 3*d* transition metals [6]. The anomaly in the temperature dependence of heat capacity is probably explained by the fact that the hindered internal rotation about the iron–cyclopentadienyl bond results in a transition in the above temperature range from a one-configuration state to two- or higher configuration states. However, the nature of the transition is impossible to elucidate from calorimetric data only.

The enthalpy of heating and the absolute entropy of compound **I** were calculated by numerical integration of smoothened $C_p = f(\mathrm{T})$ and $C_p f(\ln T)$ curves; the $[G^0(T) - H^0(0)]$ function was calculated by the Hibbs–Helmholtz equation. The heat capacities of compound **I** in the range 0–60 K, required for the calculations, were obtained by extrapolation by the Kelley–Parks method [7]. For the reference we used acetylferrocene (**II**) whose heat capacities in the range 5–300 K are available [3]. The equation $C_p^{\mathbf{I}} = (0.000625T + 0.8208)C_p^{\mathbf{II}}$ was obtained, whose coefficients were found using the experimental heat capacities of compounds **I** and **II** in the range 60–110 K. This equation fits the experimental heat capacities of compound **I** in the above temperature range to an accuracy of no more than 0.3%. We assume that the heat capacities at lower temperatures are fitted to the same accuracy. The calculated thermodynamic functions of crystalline ferrocene **I**, as well as the averaged heat capacities are listed in Table 2.

Standard enthalpy of combustion and thermodynamic functions of formation. By combustion calorimetry we determined the standard enthalpy of combustion of compound **I** at 298.15 K: $\Delta_c H_{\mathbf{I}}^0$ (298.15, c.) –6152.6 ± 7.0 kJ mol^{-1}. It was assumed that the process that occurs in the bomb is described by the following equation.

$$\mathrm{FeC_{11}H_{10}O(c.)} + 82/6\mathrm{O_2(g.)}$$
$$\rightarrow 11\mathrm{CO_2(g.)} + 5\mathrm{H_2O(l.)} + 1/3\mathrm{e_3O_4(c.)}.$$

From the standard enthalpy of combustion of compound **I** and reported standard enthalpies of formation of gaseous CO_2 (–393.51 ± 0.13 kJ mol^{-1}), liquid water (–285.830 ± 0.040 kJ mol^{-1}), and crystalline Fe_3O_4 (–1117.1 ± 2.1 kJ mol^{-1}) [8] we calculated the standard enthalpy of formation of crystalline formylferrocene at 298.15 K: $\Delta_f H_{\mathbf{I}}^0$(298.15, c.) 22.5 ± 7.0 kJ mol^{-1}. From the resulting absolute entropy of compound **I** at 298.15 K, as well as the absolute

1070-3632/04/7403-0341 ©2004 MAIK “Nauka/Interperiodica”

Table 1. Experimental heat capacities of crystalline formylferrocene

T, K	C_p, J mol^{-1} K^{-1}	T, K	C_p, J mol^{-1} K^{-1}	T, K	C_p, J mol^{-1} K^{-1}
60.06	58.41	150.07	119.59	249.40	201.03
62.19	60.30	154.85	122.96	254.39	206.53
65.74	63.28	158.38	125.30	257.92	209.69
69.33	66.16	163.21	128.71	262.98	214.51
73.08	68.74	167.98	132.40	268.01	220.19
76.99	71.78	172.78	136.25	272.99	226.71
80.07	74.67	177.69	139.93	276.75	230.10
84.64	77.66	182.63	143.66	278.01	233.12
88.64	80.66	186.39	146.49	278.74	232.91
93.14	82.99	191.41	150.24	280.76	235.30
97.80	85.79	196.39	154.12	282.78	237.27
102.49	88.63	201.32	157.98	283.09	237.25
105.66	91.16	206.27	162.09	284.10	237.19
109.98	94.21	211.26	166.13	284.79	236.71
114.45	96.30	215.94	169.62	286.10	234.94
118.94	100.00	220.84	173.97	286.33	234.72
123.46	102.30	222.05	175.47	288.10	233.41
127.96	105.38	225.69	177.90	290.10	233.45
132.51	108.35	230.59	182.27	291.37	233.74
135.89	110.32	235.53	187.01	292.10	234.41
140.59	113.54	240.04	190.57	296.49	239.11
145.28	116.48	244.57	195.47	301.63	244.97

entropies of graphite (5.74 ± 0.13 J mol^{-1} K^{-1}), crystalline iron (27.15 ± 0.13 J mol^{-1} K^{-1}), and gaseous hydrogen (130.570 ± 0.033 J mol^{-1} K^{-1}) and oxygen (205.037 ± 0.033 J mol^{-1} K^{-1}) we obtained the standard entropy of formation of crystalline compound **I** at 298.15 K: $\Delta S_{\mathrm{I}}^{0}$(298.15, c.) –604.4 ± 1.1 J mol^{-1} K^{-1}.

From the standard enthalpy and entropy of formation of crystalline formylferrocene at 298.15 K by the Gibbs–Helmholtz equation we estimated its standard Gibbs function at the same temperature: $\Delta_f G_{\mathrm{I}}^{0}$(298.15, c.) 202.7 ± 7.1 kJ mol^{-1}.

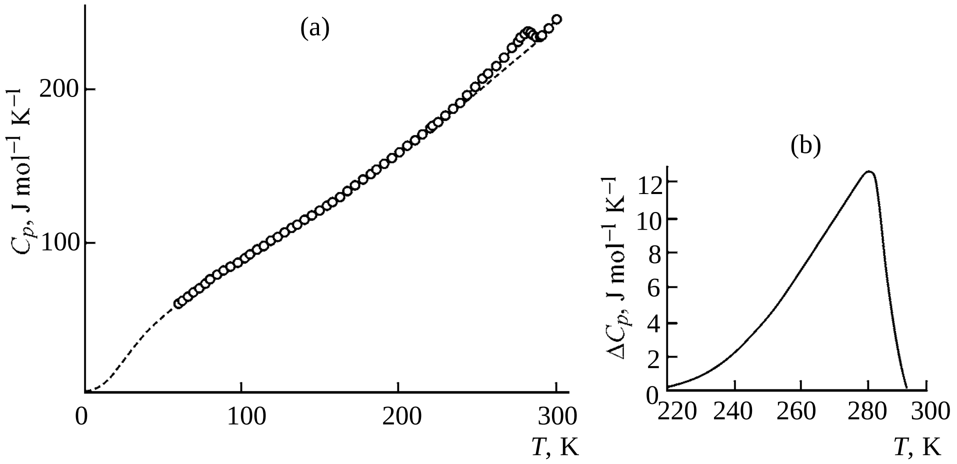

Fig. 1. (a) Temperature dependence of the heat capacity of formylferrocene and (b) temperature dependence of the difference between experimental and interpolated heat capacities in the transition range.

Table 2. Heat capacities and standard thermodynamic functions of formylferrocene

T, K	C_p, J mol^{-1} K^{-1}	$H^0(T) - H^0(0)$, kJ mol^{-1}	$S^0(T)$, J mol^{-1} K^{-1}	$-[G^0(T) - H^0(0)]$, kJ mol^{-1}
5	0.4060	0.0005	0.1415	0.0002
10	2.871	0.0076	1.020	0.0026
15	8.040	0.0340	3.091	0.0124
20	14.31	0.0901	6.277	0.0354
25	20.80	0.1790	10.06	0.0724
30	27.97	0.3010	14.34	0.1292
35	34.18	0.4560	19.13	0.2135
40	39.98	0.6440	24.42	0.3330
45	45.28	0.8516	29.24	0.4643
50	50.10	1.087	34.17	0.6217
60	58.56	1.641	44.37	1.022
70	66.66	2.266	54.00	1.514
80	74.56	2.972	63.41	2.101
90	81.10	3.750	72.57	2.781
100	87.48	4.593	81.44	3.551
110	93.85	5.499	90.08	4.409
120	100.2	6.470	98.52	5.352
130	106.6	7.504	106.8	6.379
140	113.0	8.602	114.9	7.488
150	119.7	9.765	122.9	8.677
160	126.7	11.00	130.9	9.946
170	133.9	12.30	138.8	11.29
180	141.4	13.68	146.7	12.72
190	149.2	15.13	154.5	14.23
200	157.0	16.66	162.4	15.81
210	165.0	18.27	170.2	17.47
220	173.2	19.96	178.1	19.22
225	177.5	20.84	182.0	20.12
230	181.9	21.74	186.0	21.04
235	186.5	22.66	189.9	21.98
240	191.2	23.60	193.9	22.94
245	196.1	24.57	197.9	23.92
250	201.2	25.56	201.9	24.91
255	206.4	26.58	205.9	25.93
260	211.8	27.63	210.0	26.97
265	217.3	28.70	214.1	28.03
270	222.9	29.80	218.2	29.12
273.15	226.6	30.51	220.8	29.81
275	228.7	30.93	222.3	30.22
280	234.5	32.09	226.5	31.34
285	236.5	33.27	230.7	32.48
290	233.5	34.44	234.8	33.65
298.15	241.1	36.37	241.3	35.59
300	243.1	36.82	242.8	36.03
301	244.2	37.06	243.6	36.28

Table 3. Experimental data related to the determination of the enthalpy of combustion of compound **Ia**[a]

m, g	Q, J	q(b. a.), J	q(t.), J	$q(HNO_3)$, J	$q(Fe_2O_3)$, J	$-\Delta_cU$, J g^{-1}	$-\Delta_cU$ kJ mol^{-1}
0.2637	35432.0	27798.2	35.2	19.3	4.6	28724.9	6148.5
0.3355	37498.4	27772.5	33.1	28.1	5.9	28785.7	6161.5
0.3626	35854.4	25365.5	32.1	25.8	6.4	28744.2	6152.6
0.2396	34231.2	27299.7	31.0	18.7	4.2	28698.6	6142.9
0.1795	33690.9	28470.6	43.5	21.1	3.1	28696.7	6142.4
					Average value		6149.6 ± 7.0

[a] (m) Sample weight; (Q) total energy evolved; [q(b. a.), q(t.), $q(HNO_3)$, $q(Fe_2O_3)$] corrections for the energies of combustion of benzoic acid, cotton thread, and the energies of formation of aqueous HNO_3 and crystalline Fe_2O_3, respectively; and (Δ_cU) energy of combustion of the sample in the calorimetric bomb.

EXPERIMENTAL

Formylferrocene purchased from Strem chemicals (purity 99.0 wt%) was used. The heat capacities were measured in an adiabatic vacuum calorimeter with a platinum ampule 7.5 cm^3 in volume. The temperature was measured with germanium (5–15 K) and platinum (15–300 K) resistance thermometers. The energy equivalent of the calorimeter was determined by measuring the heat capacity of an empty ampule filled with gaseous helium to a pressure of 8.5 kPa. The calorimeter design and measurements and calibration procedures have been described in [9]. The measurements accuracy was tested using as reference benzoic acid of K-1 brand. The resulting values fitted those reported in [10] within 1.5 (5–10 K), 0.5 (10–30 K) and 0.2–0.3% (>30 K). Ferrocene **I**, 4.5723 g, was placed in an ampule; the heat capacity of this sample was ~40–80% of the total heat capacity of the ampule with the sample. Heat capacities were measured in series by 3–11 points. The temperature rise in the experiments was no more than 3.5–4 K; therefore, no corrections for the curvature of the $C_p = f(T)$ function were applied.

The enthalpy of combustion of compound **I** was determined in a V-08 calorimetric device with a stationary bomb [11]. Samples were ignited with discharge of a capacitor bank to a platinum wire connected with a cotton thread (energy of combustion 16736 J g^{-1}). The capacity of the bank was 8000 μF, and its initial voltage was 30 V in all experiemnts. The temperature was measured with a platinum resistance thermometer (R 50 Ω) incorporated in a bridge circuit. The energy equivalent of the calorimeter was estimated at 14.847 ± 0.006 kJ V^{-1}, reference benzoic acid of K-1 brand ($-\Delta_cU$ 26.46 kJ g^{-1}, weighing in air). Crystalline compound **I** was combusted as pellets 0.3 g in weight in a thin-wall quartz crucible having holes in walls. To provide for the required temperature rise and complete combustion of the sample, a benzoic acid pellet of the same weight was placed in the crucible. Combustion was performed in a special-purity oxygen (initial pressure 3×10^6 Pa) [12]. Gaseous combustion products were analyzed for carbon dioxide whose quantity was used to estimate the sample weight. The completeness of combustion was judges about by the lack of carbon(II) oxide in gaseous combustion products using special indicator tubes. No carbon dioxide was found within the experimental accuracy (6×10^{-6} g). Moreover, visual inspection of the internal surface of the bomb after experiments revealed no signs of incomplete combustion (for instance, dark spots). The composition of solid products was determined by X-ray phase analysis. It was shown that the major product was always Fe_3O_4 with an admixture (on average, about 10 wt%) of Fe_2O_3.

The experimental data related to the determination of the enthalpy of combustion are presented in Fig. 3. Since solid combustion products comprised Fe_2O_3 along with Fe_3O_4, correction for incomplete oxidation of compound **I** was also applied [12]. The Washburn correction [13] (π –0.0584%), as well as correction for changing number of moles of gaseous combustion products were also applied (Δn –2.67 mol).

REFERENCES

1. Lemenovskii, D.A., *Soros. Obraz. Zh.*, 1997, no. 2, p. 64.
2. Tomassetti, M., Curini, R., D'Ascenzo, G., and Ortaggi, G., *Thermochim. Acta*, 1981, vol. 49, nos. 1–2, p. 333.
3. Domracheva, L.G., Karyakin, N.V., Sheiman, M.S., and Kamelova, G.P., *Vestn. Nizhegorod. Univ., Ser. Khim.*, 1998, no. 1, p. 145.

4. Domracheva, L.G., Karyakin, N.V., Sheiman, M.S., Kamelova, G.P., Larina, V.N., Suvorova, O.N., and Domrachev, G.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1999, no. 9, p. 1668.

5. *Fizika i khimiya tverdogo sostoyaniya organicheskih soedinenii* (Physics and Chemistry of the Solid State of Organic Compounds), Fox, D., Leibs, M., and Weissbereger, A., Moscow: Mir, 1967.

6. Rabinovich, I.B., Nistratov, V.P., Tel'noi, V.I., and Sheiman, M.S., *Termodinamika metalloorganicheskih soedinenii* (Thermodynamics of Organometallic Compounds), Nizhni Novgorod: Nizhegorod. Gos. Univ., 1995.

7 Kelley, K.K., Parks, G.S., and Huffman, H.M., *J. Phys. Chem.*, 1929, vol. 33, no. 11, p. 1802.

8. *Termicheskie konstanty veschestv* (Thermal Constants of Subatances), Glushko, V.I., Moscow: VINITI, 1965–1981, Vols. I–X.

9. Rabinovich, I.B., Sheiman, M.S., Nistratov, V.P., Kamelova, G.P., and Zorin, A.D., *Zh. Obshch. Khim.*, 1985, vol. 59, no. 10, p. 2414.

10. Rybkin, N.G., Orlova, M.P., Baranyuk, A.K., Nurullaev, N.R., and Rozhnovskaya, L.N., *Izmer. Tekh.*, 1974, vol. 7, p. 29.

11. Kir'yanov, K.V. and Tel'noi, V.I., *Tr. Khim. Khim. Tekhnol.*, Gorki: Gor'kov. Gos. Univ., 1975, no. 4, p. 109.

12. Tel'noi, V.I., Kir'yanov, K.V., Ermolaev, V.I., and Rabinovich, I.B., *Dokl. Akad. Nauk SSSR*, 1975, vol. 220, no. 5, p. 1088.

13. Skuratov, S.M., Kolesov, V.P., and Vorob'ev, A.F., *Termohimiya* (Thermochemistry), Moscow: Mosk. Gos. Univ., 1966, part 2.