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THERMAL STABILITY AND THERMODYNAMICS OF THE DECOMPOSITION OF FERROCENE AND SOME OF ITS ONE-, TWO-, AND TRINUCLEAR DERIVATIVES

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Abstract – Mono-, bi-, and trinuclear derivatives of ferrocene $(C_5H_5)Fe(C_5H_4)C(CH_3)_2OH$ (I), $[C_5H_5FeC_5H_4]_2CCH_3OH$ (II) and $C_5H_5FeC_5H_4]_3COH$ (III) were synthesized, the thermal stability and thermodynamics of their decomposition reactions were studied. It is shown that when the samples are heated from room temperature to 700 °C in an inert gas flow, the residual mass of compounds I-III is 2.05, 20.24 and 66.96% of the initial mass, respectively, and these compounds decompose with the formation of nanosized iron/iron oxide and carbon particles. The decomposition of these compounds in an air stream leads to the combustion of these compounds with the formation of only iron oxide (III) in the form of a solid residue and carbon dioxide and water as products of the gas phase. The temperature dependences of the Gibbs free energy of the decomposition reactions of ferrocene and its derivatives in the range 600-1500K have been determined.

Keywords – Ferrocene, Ferrocene Derivatives, Thermal Stability, Decomposition, Thermodynamics

Introduction

Due to their low toxicity and high thermal stability, ferrocene and its derivatives have found wide application in various fields of science and technology - the electronics industry, medicine, biochemistry, organic synthesis, and catalysis. Ferrocene and its derivatives are used in the creation of heat-resistant coatings and light-sensitive materials, liquid crystals, heat-resistant polymers, fuel combustion regulators, in the production of multilayer carbon nanotubes. Ferrocene is a promising starting material for obtaining iron oxide nanostructures by thermal decomposition, ferromagnetic micro/nanoparticles, thin films of iron oxide, carbon nanotubes with ferromagnetic fillers, etc. [1-6]. The widespread use of ferrocene and its derivatives requires, first of all, the study of the features of reactions with their participation, in particular, the thermodynamics of pyrolysis and combustion reactions. The most complete information on thermodynamic properties and thermodynamic functions is available only for ferrocene and some of its derivatives [7-11]. The heat capacity of isobutanoylferrocene, benzoylferrocene, and benzylferrocene was measured in the temperature range from 6 K to 372 K by low-temperature adiabatic calorimetry in [8, 9]. In [10] the heat capacities, entropy, enthalpy and free energy of formation were determined for a number of ferrocene derivatives - ferrocenylmethanol $C_5H_5FeC_5H_4$-CH_2OH, benzoylferrocene $C_5H_5FeC_5H_4$-COC_6H_5, benzylferrocene $C_5H_5FeC_5H_4$-COC_6H_5, propionylferrocene $C_5H_5FeC_5H_4$-COC_2H_5, n-propylferrocene $C_5H_5FeC_5H_4$-C_3H_7, isobutylferrocene $C_5H_5FeC_5H_4$-$CH_2CH(CH_3)_2$. In [12], the thermodynamics of ferrocene pyrolysis with the formation of iron clusters catalyzing the formation of carbon nanotubes is presented, and an expression is obtained for the size distribution function of clusters depending on the conditions of their formation.

In this paper the results of the study of thermal stability of ferrocene and some of its mono-, bi- and trinuclear derivatives - $C_5H_5FeC_5H_4C(CH_3)_2OH$ (I), $[C_5H_5FeC_5H_4]_2C(CH_3)OH$ (II), $[C_5H_5FeC_5H_4]_3C$-OH (III), the peculiarities of the decomposition of these compounds in the flow of inert and oxidizing gases, the calculation of the temperature dependences of thermodynamic parameters of these reactions are presented.

2. Objects and methods of research

The objects of study were ferrocene and its derivatives I-III.

2.1. Synthesis of ferrocene derivatives

The synthesis of the above ferrocene derivatives was carried out according to [13].

2.1.1. Synthesis of mononuclear dimethyl carbinol derivatives of ferrocene $C_5H_5FeC_5H_4$-$C(CH_3)_2OH$ (I).

For the synthesis of compound (I), a mixture of 0.1 mol of metallic lithium and 5 ml of mercury was intensively stirred at 50°C. 0.01 mol of ferrocene dissolved in 25 ml of tetrahydrofuran was added in portions to the amalgam thus obtained, and continuously stirred for 30 minutes. The obtained ferrosenyllithium intermediate $C_5H_5FeC_5H_4Li$ is easily oxidized and hydrolyzed. Decantation of the mixture was carried out by adding 8 ml of acetone, followed by stirring in a magnetic stirrer for 2-3 hours. Next, 3% HCl was added to the solution. After that, the color of the solution changed from light blue to light yellow and then remained unchanged. The reaction solution was then evaporated with heating to separate the desired product isopropylferrocenylcarbinol from the reaction mixture. After repeated washing of the residue with hot n-hexane (3-5 ml), it was extracted with 3-20 ml of ethanol. The extracts were mixed and the alcohol was removed. The residue was a light yellow compound $C_5H_5FeC_5H_4$-$C(CH_3)_2OH$ (I) with a melting point of 69-70°C and a yield of 87%. According to the results of elemental analysis, compound I corresponds to the general formula $C_{13}H_{16}FeO$. Calculated, %: Fe-22.96, C-63.93. H-6.55. O - 6.55. Found, %: Fe–22.48, C-63.05, H-6.37. O - 6.43. ^1H NMR ($CDCl_3$): $\delta C_5H_5(\alpha,\beta)$ - 4.09 ppm; $\delta C_5H_4(\alpha,\beta)$ - 3.95; 3.80 ppm $\delta(OH)$ - 4.19 ppm $\delta(CH_3)$ - 2.25 ppm; IR spectrum: (KBr) $\nu(OH)$ - 3050; 3098 cm^{-1}. $\nu(C_5H_4)$-C - 1105 cm^{-1}

2.1.2. Synthesis of diferrosenylmonomethyl carbinol $[C_5H_5FeC_5H_4]_2C(CH_3)OH$ (II).

To do this, a 5% solution of NaOH in interval 0-10°C and further stirred for 0.5 hour. Then, a 3% HCl aqueous solution was added to the reaction mixture and extracted with n-hexane 3 times. To purify the dark brown residue from primary substances, it was washed with n-pentane or a light fraction of gasoline in a ratio of 3:10 (in ml). As a result, 3.44 g of dark brown carbinol derivative $[C_5H_5FeC_5H_4]_2C(CH_3)OH$ (II) was obtained. The yield of the target product with melting temperature 119-120 °C was 83%. According to the results of elemental analysis, the compound corresponds to the chemical formula $C_{22}H_{22}Fe_2O$. Calculated, %: C - 63.76, H - 5.31; Fe - 27.05, O-3.86. Found, %: C - 63.51; H - 5.25; Fe - 26.95, O - 3.79. ^1H NMR ($CDCl_3$): δC_5H_5 - 4.08 ppm $\delta C_5H_4(\alpha,\beta)$ -3.79; 3.91 ppm δ(OH) - 4.29 ppm $\delta(CH_3)$- 2.17 ppm; IR spectrum (KBr): ν(OH) - 2995, 3032 cm^{-1}, $\nu(C_5H_4\text{-}C)$- 1107 cm^{-1}.

2.1.3. Synthesis of trisferrosenyl carbinol $[C_5H_5FeC_5H_4]_3C\text{-}OH$ (III).

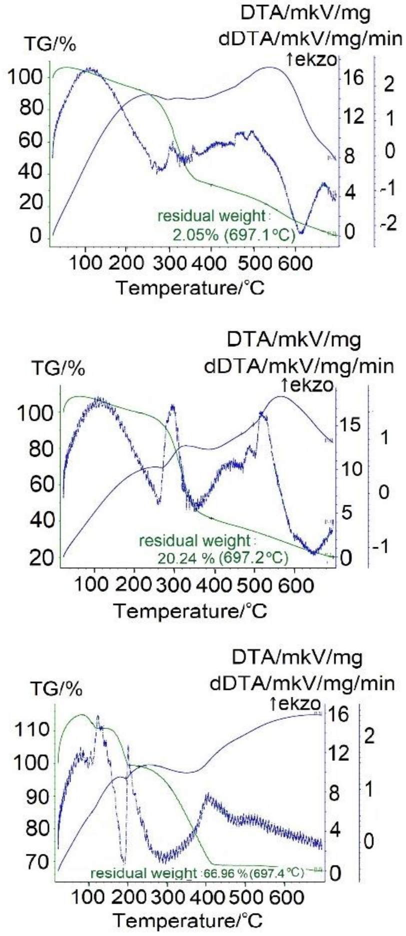
To 0.01 mol 5.72 g of tris-ferrocenylmonochloromethane $[C_5H_5FeC_5H_4]_3CCl$ and 100 ml of n-heptane were added 25 ml of 1.14 g of KOH diluted in 0.2 mol of water and stirred continuously for 30 min. As a result, a dark yellow (III) compound was obtained. The yield of this compound was 79%, melting point 142-143°C, decomposition $T_{dec.}$> 296°C. According to the results of elemental analysis, the resulting compound corresponds to the chemical formula $C_{31}H_{28}Fe_3O$. Calculated, %: Fe-28.76, C - 63.69, H - 4.79, O -2.73. Found, %: Fe-28.70, C - 63.50. H - 4.68, O -2.63, ^1H NMR ($CDCl_3$): δC_5H_5 - 4.07 ppm, $\delta C_5H_4(\alpha,\beta)$ - 3.88; 3.96 ppm, δ(OH) - 4.18 ppm; IR spectrum (KBr): ν(OH) -2965, 3022 cm^{-1}, $\nu(C_5H_4\text{-}C)$- 1107 cm^{-1}.

2.2. Methods of research

The elemental composition of the synthesized compounds was determined using an AAS iCE 3000 Thermo Fisher Scientific atomic absorption spectrometer and a LECO CHNOS analyzer, TruSpec Micro, USA. The structure of the synthesized compounds was established by IR and NMR spectroscopy. IR spectra were recorded on an Alfa Bruker IR Fourier spectrophotometer in KBr tablets; electronic absorption spectra of solutions of these compounds in organic solvents (n-hexane, heptane, acetone, ethyl alcohol) were recorded on a Specord 50 plus spectrophotometer, Jena Analytical, Germany. NMR spectra were recorded in deuterated acetone and chloroform at room temperature using an AM-300 spectrometer, Bruker with an operating frequency of 300 MHz. X-ray diffraction patterns were recorded using an XRD D2 PHASER diffractometer at room temperature. Thermal analysis experiments (TG/DTA) were carried out using a NETZSCH, F3 Jupiter, Germany thermal analyzer in dynamic mode in a nitrogen flow. A programmable temperature regime was used with a heating rate of 10°C per minute. In all TG/DTA experiments, about 10 mg of powders of ferrocene and its derivatives of the above composition were taken in a corundum crucible and subjected to thermal analysis in the temperature range from 20 to 700°C. Thermodynamic parameters were calculated using the Origin 2019 program.

3. Results and discussion

Ferrocene is stable in air and does not decompose when heated to 743 K. Starting from 770 K, ferrocene decomposes intensively in air as a result of combustion. The reaction proceeds with the formation of iron(III) oxide and the release of carbon dioxide and water into the gas phase. The synthesized derivatives of ferrocene I-III melt and decompose at lower temperatures than ferrocene. The final decomposition products of these derivatives in the N2 gas flow are mainly the carbonized formations of cyclopentadienyl fragments and iron/iron(II) oxide particles. Figure 1, a-c shows thermograms of the compounds I-III.



a) $C_5H_5FeC_5H_4C(CH_3)_2OH$ b) $[C_5H_5FeC_5H_4]_2C(CH_3)OH$

c) $[C_5H_5FeC_5H_4]_3C\text{-}OH$

Fig. 1. Thermograms of ferrocene derivatives: a) I, b) II and c) III.

Thermograms of fig.1, a-c show that, unlike ferrocene, the above-mentioned derivatives decompose not in one stage, but at least in three stages. And the temperature intervals of thermal decomposition of compounds I-III are determined by the features of their composition. The formation of iron/iron(II) oxide as the final product during the thermal decomposition of ferrocene derivatives with oxygen-containing ligands is due to the oxidation of iron by these ligands formed during their thermal decomposition.

Above 770 K in an inert medium, ferrocene and its derivatives with hydrocarbon ligands decompose, forming particles of iron and carbon. The resulting carbon formation is almost 50% by weight and most likely represents a multiwalled nanocarbon tube [9, 10]. As can be seen from the thermograms shown in Fig. 1, when the samples are heated from room temperature to 700 °C in an inert gas flow, the residual mass for compounds I-III is, respectively, 2.05, 20.24, and 66.96% of the initial mass. And if we assume that the residue of thermal decomposition of compounds I-III consists of a mixture of iron, iron oxides and carbon, then, in accordance with equations (3) - (5), the mass of the solid residue should be, respectively, 78.69, 88.89 and 89.04% of the initial mass. This circumstance is mainly due to the difference in the volatility of compounds I-III. Under the conditions of the experiment, when heated from room temperature to 700 °C in an inert gas flow, at least 76, 68 and 22% of the initial mass of compounds I-III flies, respectively. The decomposition of ferrocene and its derivatives I-III under the above conditions can most likely be represented in the form of the following equations:

$(C_5H_5)_2Fe(g) \rightarrow Fe(s) + 3.7H_2(g) + 0.5CH_4(g) + 0.1C_5H_6(g) + 9[C](s)$ (1)

$C_5H_5FeC_5H_4\text{-}CH_2CH(CH_3)_2 \rightarrow Fe(s) + 7.1H_2(g) + 0.5CH_4(g) + 0.3C_5H_6(g) + 12[C](s)$ (2)

$C_5H_5FeC_5H_4\text{-}C(CH_3)_2OH \rightarrow FeO(s) + 2.7H_2(g) + 2.5CH_4(g) + 0.1C_5H_6(g) + 10[C](s)$ (3)

$[C_5H_5FeC_5H_4]_2CCH_3OH(g) \rightarrow Fe(s) + FeO(s) + 7.4H_2(g) + CH_4(g) + 0.2C_5H_6(g) + 20[C](s)$ (4)

$[C_5H_5FeC_5H_4]_3COH(g) \rightarrow 2Fe(s) + FeO(s) + 10.1H_2(g) + 1.5CH_4(g) + 0.3C_5H_6(g) + 28[C](s)$ (5)

To determine the temperature dependences of the free energy of these reactions, the Ulich equation was used, which, despite its simple form, has a fairly high reliability [14, 15]:

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_{298}^0 - \Delta C_{P,298}^0 T\left[\ln\left(\frac{T}{298}\right) + \frac{298}{T} - 1\right] \quad (6)$$

In equations (6): ΔG_T^0; ΔH_T^0; ΔS_{298}^0 - free energies, enthalpies and entropies of reactions; which are determined on the basis of the thermodynamic functions of the substances involved in the reactions. $\Delta C_{p,298}^0$ is the difference between the molar isobaric heat capacities of the products and initial substances of the reactions. The thermodynamic parameters of ferrocene and derivatives are borrowed from [9, 10]; (Table 2).

Table 2. Thermodynamic parameters of ferrocene and its derivatives [8, 9].

Compound	$\Delta S^0_{298}(g)$, J/(K mol)	$\Delta H^0_{298}(g,$ kJ/ mol	$\Delta G^0_{298}(g)$,kJ /mol	$C^0_{P,298}(g)$,J /(K mol)
Ferrocene $(C_5H_5)_2Fe$	-3718 ±26	230 ±6	3387 ± 10	*255.9±6
Ferrocenylmethanol $C_5H_5FeC_5H_4$-CH_2OH	-5147 ± 26	52 ± 10	205 ±10	199 ±5
Isobutylferrocene $C_5H_5FeC_5H_4$ -$CH_2CH(CH_3)_2$	-7654 ± 2 0	133 ± 10	361 ±10	255 ±5
Monoferrocenyl dimethyl carbynol $C_5H_5FeC_5H_4$-$C(CH_3)_2OH$	- 6396± 26	98± 10	267±10	232±5
Diferrocenylmonomethyl carbynol (**) $[C_5H_5FeC_5H_4]_2C(CH_3)OH$	-1037±.30	655± 2 0	964± 25	578± 10
Triferrocenylcarbinol (**) $[C_5H_5FeC_5H_4]_3COH$	-1445± 30	982± 2 0	1446±30	763± 10

*This value is estimated according to the Neumann-Kop rule [16,17]; **Thermodynamic parameters of the noted compounds were estimated based on the thermodynamic parameters of ferrocene and ligands, taking into account their conversion to the corresponding radicals.

The thermodynamic parameters of other substances involved in reactions (1-5) are borrowed from [15]. Thermodynamic parameters for carbon nanotubes are taken from [7]. The following quantities were used in the calculations:

ΔH^0_{298} [$(C_5H_5)_2Fe$ (g)] = 230±6 kJ/mol; ΔH^0_{298} [(C_5H_6) (g)]= 105.9±1 kJ/mol

ΔH^0_{298} [(CH_4(g)] = –74.85 kJ/mol; ΔH^0_{298} [C](s)= –2.03 kJ/mol

ΔH^0_{1000} [C](s) = –1.98 kJ/mol; ΔH^0_{298} [(H_2(g)]= 0 ; ΔH^0_{298} [α-Fe]= 0

ΔS^0_{298} [$(C_5H_5)_2Fe$ (g)] = -371.8±2.6 J/(mol.K); S^0_{298} [$(C_5H_5)_2Fe$ (g)]= 361.1±2.1 J/(mol.K)

ΔS^0_{298} [(C_5H_6) (g)] = -237.8 J/(mol.K); S^0_{298} [(C_5H_6) (g)]= 182.7 J/(mol.K)

ΔS^0_{298} [(CH_4(g)] = -80.0 J/(mol.K); S^0_{298} [(CH_4(g)]= 186.19±85 J/(mol.K)

ΔS^0_{298} [C](s) = 0.44 J/(mol.K); ΔS^0_{1000} [C](s)= 0.55 J/(mol.K); S^0_{298} [(C(s)]= 6.25 J/(mol.K)

ΔS^0_{298} [(H_2(g)] = 0 ; S^0_{298} [(H_2(g)]= 130.6 ; ΔS^0_{298} [α-Fe]= 0 ;S^0_{298} [α-Fe]= 27.5 J/(mol.K)

$C^0_{P,298}$ [$(C_5H_5)_2Fe$ (g)] =255.9 J/(mol.K) – calculation

ΔH^0_{298} [(Fe_2O_3 (s)]= -822.2±4; ΔH^0_{298} [(CO_2(g)]= -393.5 kJ/mol; ΔH [(H_2O (g)]=-241.8

ΔG^0_{298} [(Fe_2O_3 (s)]= -740.3±4; ΔG^0_{298} [(H_2O (g)]= -228.6; ΔG^0_{298} [(CO_2 (g)]= -394.4

ΔS^0_{298} [(Fe_2O_3 (s)]= -274.8 J/mol.K; ΔS^0_{298} [(CO_2(g)]= 3.02; ΔS^0_{298} [(H_2O (g)]= -44.29

S^0_{298} [(Fe_2O_3 (s)]= 87.44; S^0_{298} [(CO_2(g)]= 213.7; S^0_{298} [(H_2O (g)]=188.7

$C^0_{P,298}$ [$(C_5H_5)_2Fe$ (g)]=255.9 J/(mol.K); $C^0_{P,298}$ [(CO_2 (g)]=37.2

$C^0_{P,298}$ [(Fe_2O_3 (s)]= 103.76; $C^0_{p,298}$ [(H_2O (g)]= 33.58

$C^0_{p,298}$ [(O_2 (g)]= 29.35.

The equations for the temperature dependence of the Gibbs energy of the pyrolysis reaction of ferrocene and its derivatives (reactions 1-5) are given in Table 3, Fig.2 and visualized in Fig. 3.

Table 3. Equations for the temperature dependence of the Gibbs energy of the reaction of decomposition of ferrocene and its derivatives (reactions 1-5), obtained by equation (6). The equations are presented in computerized form.

Reaction	Compound	Equation ΔG_T^0(kJ/mol)= f(x); x=T
1	$(C_5H_5)_2Fe$	$-274.655-0.313*x-0.0982*x*(\ln(x/298)+298/x-1)$
2	$C_5H_5FeC_5H_4$ - $CH_2CH(CH_3)_2$	$-162-0,660*x-0,255*x*(\ln(x/298)+298/x-1)$
3	$C_5H_5FeC_5H_4$-$C(CH_3)_2OH$	$-364.8-0,2582*x-0,0756*x*(\ln(x/298)+298/x-1)$
4	$[C_5H_5FeC_5H_4]_2C(CH_3)OH$	$-1014+0,425*x+0,0549*x*(\ln(x/298)+298/x-1)$
5	$[C_5H_5FeC_5H_4]_3COH$	$-1383+0,242*x+0,036*x*(\ln(x/298)+298/x-1)$

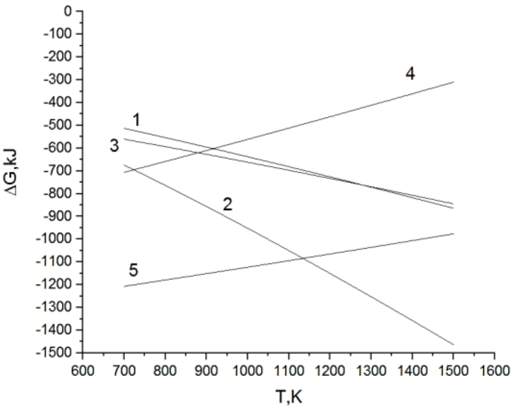


Fig. 2. Temperature dependences of the Gibbs energy of pyrolysis reactions (1-5) of ferrocene and its derivatives.

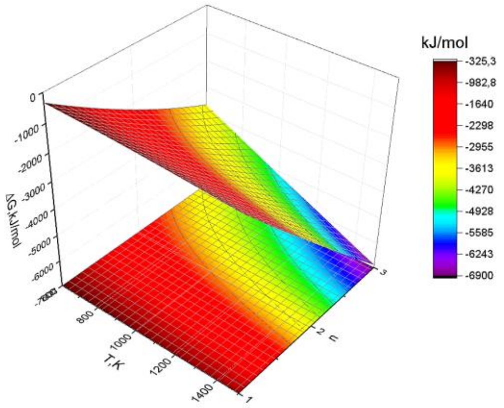


Fig.3. 3D visualization of the dependence of the free energy of the pyrolysis reactions of ferrocene and its derivatives (1-5) on temperature and the number of ferrocene cores based on the equations given in table 3 and equation (7).

$$\Delta G_{298}^0(kJ/mol) = 588.5-1068.75*y + 139.75*y^2 + (2.639-2,6965*y + 0.1695*y^2)*x + (-1,639+1.475*y-0.277*y^2)*x*(\ln(x/298)+298/x-1) \quad (7)$$

From Fig. 2 it follows that the pyrolysis reactions of ferrocene and its derivatives (1-5) with the production of carbon structures in the range of 700-1500K are characterized by negative values of free energy. The reactions are endothermic. Reactions (1,2) with the production of iron (1) and iron oxide (2) proceed with an increase in entropy. Consequently, with increasing temperature, their negative values of free energy increase. Reactions with the simultaneous production of iron and iron oxide proceed with a decrease in entropy, therefore, with increasing temperature, the negative values of their free energy greatly decrease.

Figure 3 visualizes the dependence of the free energy of pyrolysis on temperature in the range of 700-1600 K and on the number of ferrocene cores, respectively, for one-, two- and three-nuclear ferrocene compounds $C_5H_5FeC_5H_4\text{-}CH_2OH$, $[C_5H_5FeC_5H_4]_2CCH_3OH$, $[C_5H_5FeC_5H_4]_3COH$. Depending on the number of nuclei, the negative values of the decomposition free energy increase from -300 kJ/mol to -3000 kJ/mol.

Fig. 4 shows the dependences of the Gibbs energy on the temperature of the combustion reactions of ferrocene and a number of its derivatives.

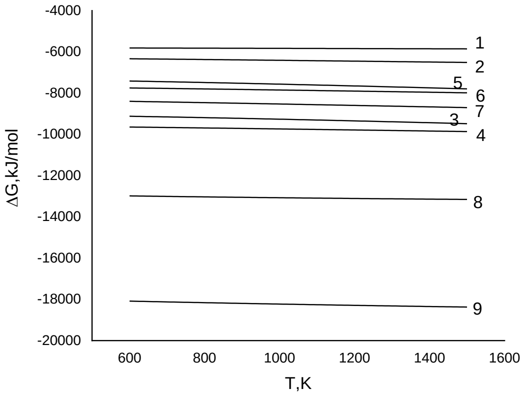


Fig. 4. Temperature dependences of the Gibbs energy of the combustion reactions of ferrocene (1) and its derivatives: 2- $C_5H_5FeC_5H_4\text{-}CH_2OH$, 3 - $C_5H_5FeC_5H_4\text{-}COC_6H_5$, 4 - $C_5H_5FeC_5H_4\text{-}CH_2C_6H_5$, 5- $C_5H_5FeC_5H_4\text{-}COC_2H_5$, 6 - $C_5H_5FeC_5H_4\text{-}C_3H_7$, 7- $C_5H_5FeC_5H_4\text{-}CH_2CH(CH_3)$, 8 - $[C_5H_5FeC_5H_4]_2CCH_3OH$, 9 - $[C_5H_5FeC_5H_4]_3COH$.

As can be seen from Fig. 4, the free energy of the combustion reactions of ferrocene and its derivatives with the production of iron(III) oxide weakly depends on temperature in the range of 600 -1500 K.

Conclusion

One-, two- and three-nuclear carbinol derivatives of ferrocene $C_5H_5FeC_5H_4\text{-}C(CH_3)_2OH$ (I), $[C_5H_5FeC_5H_4]_2C(CH_3)OH$ (II), $[C_5H_5FeC_5H_4]_3C\text{-}OH$ (III) have been synthesized. It has been established that these compounds have lower melting points than ferrocene and are readily soluble in many organic solvents. It is shown that when the samples are heated from room temperature to 700 °C in an inert gas flow, the residual mass of compounds I-III is 2.05, 20.24 and 66.96% of the initial mass, respectively, and these compounds decompose with the formation of nanosized iron particles. /iron oxide and carbon. The values of the Gibbs energy as a function of temperature of the decomposition reactions of these compounds under N_2 gas and air flow conditions were calculated. These compounds are supposed to be used as precursors for the production of iron-containing catalysts on carbon and oxide supports with nanosized active components.

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