Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 3, 743–746

THE STANDARD ENTHALPY OF FORMATION OF SILVER PIVALATE

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The standard enthalpy of combustion of crystalline silver pivalate, $(CH_3)_3CC(O)OAg$ (AgPiv), was determined in an isoperibolic calorimeter with a self-sealing steel bomb, Δ_cH^0 (AgPiv, cr)= –2786.9±5.6 kJ mol^{-1}. The value of standard enthalpy of formation was derived for crystalline state: Δ_fH^0(AgPiv,cr)= –466.9±5.6 kJ mol^{-1}. Using the enthalpy of sublimation, measured earlier, the enthalpy of formation of gaseous dimer was obtained: Δ_fH^0(Ag_2Piv_2,g)= –787±14 kJ mol^{-1}. The enthalpy of reaction $(CH_3)_3CC(O)OAg(cr)=Ag(cr)+(CH_3)_3CC(O)O^{\cdot}(g)$ was estimated, Δ_rH^0=202 kJ mol^{-1}.

Keywords: *calorimetry, enthalpy of combustion, enthalpy of formation, silver pivalate, thermochemistry*

Introduction

Metal carboxylates are one of the most commonly used types of precursors for MOCVD technique in putting on surfaces of thin and epitaxial films or different protective coatings. Despite this fact, reliable data on gaseous phase composition, sublimation enthalpies are quite rare; as concerns the basic thermodynamic characteristic that is standard formation enthalpy, the data are practically missed. Analyzing literature data on thermodynamic constants of this type of compounds it can be concluded, that there is a huge mismatch between the results of different investigations. It may be related to a complicacy of such investigations.

Silver pivalate was chosen for our work due to the low value of metal-ligand bond enthalpy. This fact gives an opportunity to produce quite high concentrations of free pivalate radical in gaseous phase at relatively low temperatures. It makes possible to synthesize numerous arid metal pivalates in different oxidation numbers under certain conditions. There is possibility of in-situ synthesis of arid metal pivalates in Knudsen cell of the high-temperature mass-spectrometer with simultaneous definition of enthalpies of reactions between silver pivalate and metals after the second principle of thermodynamics; this enables calculating standard formation enthalpies of these substances.

Experimental

Silver pivalate was synthesized using the method described in [1]. 20 mmol of pivalic acid (chem. pure) dissolved in 7.5 mL of water were mixed with 20 mmol of potassium hydroxide (chem. pure) dissolved in 7.5 mL of water. Obtained solution was mixed with 10 mmol of silver nitrate (chem. pure) dissolved in 15 mL of water. White precipitate was filtered on a Buchner funnel, washed out by 50 mL of water and dried under vacuum. Yield of silver pivalate made up 25% of the theoretical.

Three samples of AgPiv were prepared. Their composition was controlled by laser mass-spectrometry and by chemical analysis for C and H. First of these methods detected in sample II the following metallic impurities (in mass%): Na-0.014, Mg-0.002, K-0.064, Ca-0.007, Cu-0.0001. The sample III contained only the traces of the same metals, and their presence could be neglected in thermochemical calculations. The metals are supposed to be present in the form of pivalates. Samples I and II were submitted to chemical analysis; it was obtained, in mass%: C-28.73, H-4.50 (I) and C-28.48, H-4.38 (II). The theoretical values are: C-28.74, H-4.34 (I, calculated for pure AgPiv) and C-28.77, H-4.35 (II, calculated taking into account admixtures of metals pivalates).

The density of AgPiv, 1.1 g cm^{-3}, was estimated from X-ray data; the molecular mass, 208.99196, was calculated from relative atomic masses 1995 recommended by IUPAC [2].

The energy of combustion of AgPiv in oxygen was determined using isoperibolic calorimeter with a self-sealing steel bomb described elsewhere [3]. The temperature rise was measured with a copper resistance thermometer and a bridge circuit [4]. The sensitivity of the temperature measurements corresponded to $\pm5\cdot10^{-5}$ K.

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1388–6150/$20.00

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The energy equivalent *W* of the calorimeter was determined by combustion of the thermochemical standard benzoic acid and was equal to 58254.9±10.6 J Ω^{-1} for the calorimeter with the empty bomb. The massic combustion energy of benzoic acid was –26432.5±1.9 J g^{-1} under certificate conditions.

For the combustion experiment a weighed amount of AgPiv was pressed into pellet on hydraulic press, sealed in a Terylene-film bag and placed into a quartz crucible above the pellet of benzoic acid. Benzoic acid served as an auxiliary material. Its standard massic energy of combustion $\Delta_c u^0$= –26412.0±1.9 J g^{-1} was derived from that at the certificate conditions. The value of $\Delta_c u^0$ of Terylene film –22927.9±6.3 J g^{-1} and the mass of CO_2, formed from 1 g of the film 2.2897±0.0006 g were determined in [5]. The uncertainty intervals of presented values as well as everywhere in this paper are given as $\pm t\cdot s$, where *s* is the standard deviation of the mean and *t* is the Student's coefficient for the 0.05 significance level.

1 cm^3 of the water was introduced into the bomb. The initial pressure of oxygen was 3.5 MPa. The sample was ignited with a platinum wire heated by the discharge of a capacitor. The energy of ignition was constant in all experiments both with the investigated substance and in the calibration runs. Under these conditions the substance was burnt down to CO_2, H_2O and metallic silver. It was shown by laser mass-spectrometry, that 99.99% of solid product of combustion represented pure silver. Most part of silver was in the quartz crucible as an ingot (about 98%), and some part – as thin powder on the walls and bottom of the bomb. In some experiments traces of soot were observed in crucible, and the corresponding energy correction (0.3 to 1.7 J) was introduced. The initial temperature did not differ from 298.15 K by more than 0.02 K, the temperature rise was about 1.2 K. The energy of combustion of auxiliary materials (Terylene film and benzoic acid) was about 80% of the total amount of the energy evolved.

After the calorimetric experiments the gaseous products of combustion were analyzed for CO_2 and CO. The contents of CO_2 were determined after Rossini method [6] with the accuracy $\pm 4\cdot 10^{-4}$ g. Qualitative tests for CO(g) with indicator tubes were negative within the limits of their sensitivity $6\cdot 10^{-6}$ g. The amount of HNO_3, formed from N_2, O_2 and H_2O, was determined by titrating the bomb solution with a 0.1 N solution of NaOH.

Results and discussion

The results of seven combustion experiments are reported in Table 1.

The contents of CO_2 in the combustion products of the sample I proved to be close to 100.00%, (run 1) in perfect accordance with the above mentioned result of chemical analysis for C, so that mass *m* of the burnt substance in runs 1, 2 is just the result of weighing the tablet.

In runs with samples II and III deficit of CO_2 was observed. Assuming that traces of moisture (or other incombustible admixture) were present in these samples, the mass of the burnt substance was calculated from the results of the CO_2 analysis.

The influence of admixture of KPiv on the energy of combustion the sample II was estimated on the assumption that $\Delta_f H^0$ (KPiv) is equal to $\Delta_f H^0$ (AgPiv). Then the combustion energy of KPiv by equation: $K(C_5H_9O_2)(cr)+6.5O_2(g)+aq= KHCO_3(sol\text{-}n)+4CO_2(g)+4H_2O(l)$ is equal to –22715 J g^{-1}, and the correction amounts to 11 J g^{-1}. This correction is rather small even for the maximal admixture, hence there is no need to take into account all other minor admixtures

The *q*(HNO_3) correction was calculated as the energy of formation of nitric acid from N_2(g), O_2(g) and H_2O(l).

The q(st) correction was calculated according to Hubbard *et al.* [7]. The enthalpies of dilution of HNO_3, vaporization of H_2O and solution of O_2 and CO_2 in water were taken from the handbook [8].

The massic energy of combustion was calculated in each run by the following equation:

$$\Delta_c u^o = -(W\Delta R - q(b.a.) - q(f) - q(HNO_3) + \\ + q(s) - q(st))/m\text{-corr.(KPiv)}$$

The value $\Delta_c u^o$= –13320±27 J g^{-1} is obtained as the mean of 7 runs with all three samples. The molar energy of combustion according to the reaction: $Ag(C_5H_9O_2)(cr)+6.25O_2(g)=5CO_2(g)+4.5H_2O(l)+Ag(cr)$ was found to be $\Delta_c U^o$(AgPiv, cr)= –2783.8±5.6 kJ mol^{-1}. Based on this value, the standard enthalpies of combustion and formation of silver pivalate were derived: $\Delta_c H^0$(AgPiv, cr)= –2786.9±5.6 kJ mol^{-1} and $\Delta_f H^0$(AgPiv, cr)= –466.9±5.6 kJ mol^{-1}; the standard enthalpies of formation of CO_2(g), H_2O(l) were taken from [9].

The obtained value of $\Delta_f H^0$(AgPiv, cr) was used to calculate the enthalpy of breaking bond Ag-Piv by the reaction: $Ag(CH_3)_3CC(O)O(cr)=Ag(cr)+(CH_3)_3CC(O)O^{\cdot}(g)$, ($\Delta_r H$). The value $\Delta_f H^0$ of pivalic acid radical ($(CH_3)_3CC(O)O^{\cdot}$), necessary for this calculation, is not known. It was estimated on the assumption that the difference between the $\Delta_f H^0$ values of pivalic acid and its radical is the same as for *n*-butanoic acid. The enthalpies of formation of *n*-butanoic and pivalic acids –475.8±4.1 and –491.3±6.6 kJ mol^{-1} correspondingly were taken

Table 1 Results of combustion experiments on $(CH_3)_3CC(O)OAg$ at T=298.15 K

Run no.	m/g	$W'\cdot\Delta R$/J	q (b.a.)/J	q (f)/J	q (HNO_3)/J	q (s)/J	q (st)/J	corr.(KPiv)/J	[CO_2]/%	$-\Delta_c u^o$/J g^{-1}
					Sample I					
1	0.211345	13686.2	10536.9	320.5	1.0	0.0	10.1	–	99.96	13332
2	0.223353	13346.0	10083.5	287.1	0.8	0.0	9.7	–	–	13275
					Sample II					
3	0.231336	13819.2	10425.7	306.9	1.8	1.7	10.1	11	98.91	13287
4	0.232047	13731.2	10304.3	321.1	3.4	1.7	9.9	11	99.14	13323
5	0.224836	13510.0	10200.7	294.6	3.0	0.0	9.8	11	99.03	13340
					Sample III					
6	0.217825	13413.0	10162.4	337.7	0.6	0.3	9.8	–	99.31	13326
7	0.220941	13555.5	10259.0	333.0	2.2	0.0	9.9	–	99.58	13358

m is the mass of the burnt substance; W' is the energy equivalent of the calorimeter corrected for heat capacity of the bomb contents, ΔR is the increase of the thermometer resistance, q (b.a.), q (f) are the energies of combustion of benzoic acid and Terylene film, q(HNO_3) is the energy of HNO_3 formation, q (s) is the correction for the energy of combustion of soot, q (st) is the correction to standard states, corr.(KPiv) is the correction for the combustion energy of the admixture KPiv, [CO_2] the ratio of the amounts of CO_2 determined experimentally to that calculated theoretically, $\Delta_c u^0$ is the standard massic energy of combustion of AgPiv from [10], the enthalpy of formation of *n*-butanoic acid radical –249.4 kJ mol^{-1} from [11]. As a result of the evaluating, the enthalpy of formation of pivalic acid radical, –265 kJ mol^{-1}, and the enthalpy of breaking bond Ag-Piv, 202 kJ mol^{-1}, were obtained.

The enthalpy of sublimation of AgPiv as dimer was determined in [12]: $2AgPiv(cr)=Ag_2Piv_2(g)$, $\Delta_s H^0=146.9\pm8.8$ kJ mol^{-1}. On basis of this value and the above value $\Delta_f H^0$ (AgPiv,cr) the enthalpy of formation of gaseous dimer $\Delta_f H^0(Ag_2Piv_2,g)=$ -787 ± 14 kJ mol^{-1} was obtained.

Before now no investigation of silver organic compounds by combustion calorimetry have been reported. Meanwhile, this method is just convenient for silver compounds due to the fact, that they form pure silver as a result of combustion in oxygen. Compounds of most other transition metals give a mixture of combustion products of variable valence; this circumstance hinders from obtaining accurate data by this method. The value of $\Delta_f H^0$(AgPiv), derived in our work, can be used for determination of $\Delta_f H^0$ of many other metals pivalates by mass-spectrometric investigation of equilibrium of reactions of AgPiv and these metals.

Acknowledgements

This work was supported by the program of the Presidium of the RAS ‘Development of Methods of Preparation of Chemical Substances and Creation of New Materials (Targeted Synthesis of Inorganic Compounds with Specified Properties and Creation of Functional Materials Based on them)’.

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DOI: 10.1007/s10973-008-9019-x