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Heterophase Synthesis of Silver Trifluoroacetate with Copper, Indium, and Zinc. Standard Enthalpy of Formation of Copper Trifluoroacetate

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Abstract—Solid-phase reactions of silver trifluoroacetate CF_3COOAg with copper, indium, and zinc are studied by thermogravimetry, differential scanning calorimetry, and mass spectrometry. In a temperature range of 358–428 K, the reactions are found to afford trifluoroacetates of these metals without mass loss of the weighed samples. The obtained experimental data make it possible to calculate the enthalpy of formation of copper trifluoroacetate $\Delta_f H^\circ_{298}(CF_3COOCu, cr) = -1020.5 \pm 18.0$ kJ/mol.

Keywords: thermogravimetry, differential scanning calorimetry, mass spectrometry, silver trifluoroacetate, standard enthalpy of formation, vaporization

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INTRODUCTION

Processes based on heterophase chemical reactions are widely used for the preparation of metallic, oxide, and carbide films and coatings and nanocrystalline materials with interesting optical, electrical, and mechanical properties [1, 2]. Chemical vapor deposition (CVD) is the most frequently applied method. When using the CVD process, a substrate is almost always placed into the reactor to which vapors of one or several substances (precursors) are supplied. The precursors enter into the reaction and/or decompose on the surface or near the surface of the heated object/substrate, and the necessary substance deposits as a thin film on the object surface. All CVD processes differ in the method of conducting chemical reactions, for instance, thermal, laser, photo-, and microwave methods. An appropriate chemical precursor is very important for all these processes. The precursor can be gaseous, liquid, or solid. The precursor should be highly volatile to evaporate at a relatively low temperature giving a continuous thin film upon the interaction with the substrate. Many organometallic or coordination compounds of metals with organic ligands are characterized by similar properties. The main requirements imposed on an ideal precursor are volatility, sufficient thermal stability during evaporation, high purity, high volatility of decomposition products to avoid the contamination of the growing film, and stability during storage within a prolong period.

As can be seen from the parameters listed above, the main requirement for choosing a precursor is the knowledge of its main thermodynamic characteristics (volatility, standard enthalpy of formation, dissociation, and Gibbs energy). Coordination compounds of metals with organic ligands are often used as the main precursors in the Thermal CVD procedure [3–6]. Unfortunately, the thermodynamic characteristics of these compounds are poorly studied. This is mainly related to experimental problems appeared when studying these substances. This work is devoted to the development of the procedure for the determination of standard enthalpies of formation for these precursors.

EXPERIMENTAL

We have previously proposed a procedure for the determination of the main energy characteristic of the substance: the standard enthalpy of formation of metal trimethylacetates (pivalates) based on the measurement by differential scanning calorimetry (DSC) of the enthalpy of the heterophase reaction of the metal with silver pivalate [4, 5]

$$n\mathrm{AgPiv(cr)} + \mathrm{M(cr)} = \mathrm{MPiv}_n\mathrm{(cr)} + n\mathrm{Ag(cr)}, \quad (1)$$

which is characterized by a relatively low energy of the Ag–Piv bond [5, 6].

In this procedure, carboxylic silver salts with a thermally stable acid residue and a low energy of the metal–ligand bond can be used instead of the pivalate

Table 1. Measurement conditions and overall thermal effect

m, mg		*R**	$AgCF_3COO$, mol/g of mixture	*Q*, J/g	Δ*Q*, J/g
$AgCF_3COO$	Cu				
37.39	115.26	10.64	0.001108	32.5	1.5
22.75	114.30	17.33	0.000751	21.6	0.2
25.15	230.00	31.55	0.000446	13.0	0.8
20.60	135.90	22.76	0.000596	17.1	0.1
41.40	167.40	13.95	0.000897	27.2	0.7
44.37	42.13	3.28	0.002321	64.8	1.3

* Ratio of the amounts (in mol) of Cu to $AgCF_3COO$.

complex. Similar compounds make it possible to considerably extend the possibility of using this procedure. An analysis of the known published data on the standard enthalpies of formation of carboxylic and fluorocarboxylic acids [7], $RCOO^{\bullet}$ and $RF_nCOO^{\bullet}$ radicals, metal carboxylates, and enthalpies of the RCOO–H bond [7–11] allowed a rather reliable estimation (using the chemical similarity method [12]) of the standard enthalpy of formation of crystalline silver trifluoroacetate: $\Delta_f H°(298.15\text{ K}) = -992.0 \pm 18.0$ kJ/mol.

The DSC study of the reaction of copper with silver trifluoroacetate similar to the reaction with silver pivalate described earlier [4] was carried out to check and elaborate a procedure with a new carboxylating agent. The CF_3COOAg complex synthesized via a known procedure [13, 14] and finely dispersed electrolytic copper (99.99% purity) were used in this work. Powders of the reagents were carefully triturated in a Teflon mortar periodically stirring with a spatula for 5 h. Sample preparation for further studies was conducted without pellet pressing. The thermal behavior of the [CF_3COOAg–Cu] system was studied by DSC on a 204 HP Phoenix instrument (NETZSCH) in a temperature range of 358–428 K at a constant heating rate (5 or 10 K/min). The temperature range from room temperature to the temperature of CF_3COOAg decomposition onset [14] equal to 473 K was chosen initially, but further the range was corrected on the basis of the stability of the product of the reaction of silver trifluoroacetate with copper. The measurements were carried out in aluminum crucibles with punctured covers under atmospheric pressure in a dynamic nitrogen atmosphere (gas flow rate 40 mL/min) at a protective inert gas flow of 70 mL/min. The instrument was beforehand calibrated to the temperature and sensitivity from 173 to 773 K by the phase transition parameters of the highly pure standards Hg, In, Sn, Zn, Bi, Pb, and CsCl.

RESULTS AND DISCUSSION

The conducted studies and mass spectral analysis of the reaction products showed that the solid-phase reaction of copper with silver trifluoroacetate in the 358–428 K temperature range proceeded as follows:

$$\begin{aligned} &CF_3COOAg(cr) + Cu(cr) \\ &= CF_3COOCu(cr) + Ag(cr), \end{aligned} \tag{2}$$

i.e., below the temperature of $AgCF_3COO$ decomposition onset at a heating rate of 5–10 K/min [14]. A similar run of the experiment excludes the side process of silver trifluoroacetate decomposition without copper salt formation. As shown by the experimental data, almost no mass loss of the sample occurred when heating was ceased below *T* = 433 K.

To estimate the heat of reaction (2) (Fig. 1), mixtures with different component ratios (Cu, $AgCF_3COO$) were used, and two to three measurements were carried out for each mixture to determine the average thermal effect (*Q*, J/g) of the reaction and the standard deviation of this value Δ*Q* (Table 1). The thermal effect of reaction (2) (*Q*) is directly proportional to the enthalpy of the reaction (if this value is temperature-independent) $\Delta_r H$ and the amount of $AgCF_3COO$ (mol) ($m_{AgCF_3COO}/M_{AgCF_3COO}$) per 1 g of the mixture ($m_{Cu} + m_{AgCF_3COO}$)

$$Q = \Delta_r H \frac{\dfrac{m_{AgCF_3COO}}{M_{AgCF_3COO}}}{m_{Cu} + m_{AgCF_3COO}}.$$

The change in *Q* (J/g) depending on the amount (mol) of silver trifluoroacetate per 1 g of the mixture (*x*) is shown in Fig. 2

$$x = \frac{\dfrac{m_{AgCF_3COO}}{M_{AgCF_3COO}}}{m_{Cu} + m_{AgCF_3COO}}.$$

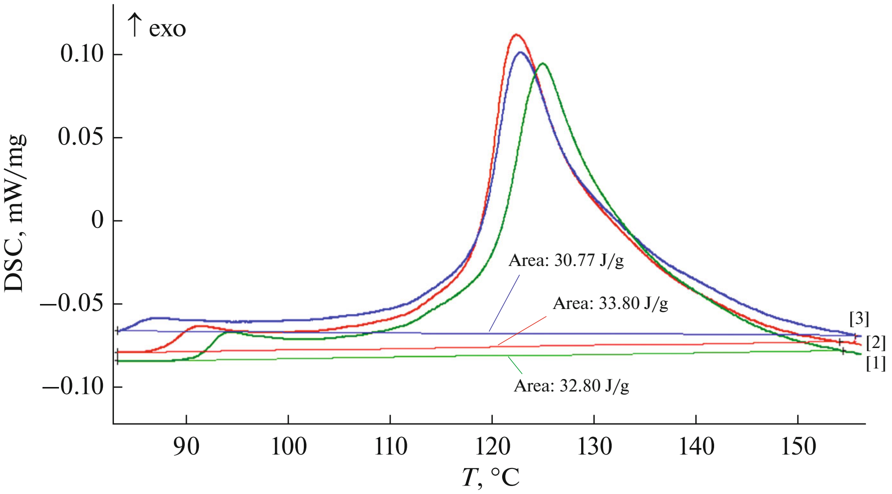

Fig. 1. DSC curves for the mixture with $R = 10.2$.

The slope ratio of the straight line (obtained by the linear regression method with the intersection with the y axis at 0 for $x = 0$) is numerically equal to the heat of reaction (2) $Q = 28450 \pm 360$ J/mol. Taking into account low experimental temperatures, we accepted that the enthalpy of reaction (2) determined in the 358–428 K temperature range corresponds to a temperature of 298.15 K: $\Delta_r H^\circ_{298} = -28.5 \pm 0.5$ kJ/mol. Using the Hess law and the known (estimated) enthalpy of formation of crystalline silver trifluoroacetate, the standard enthalpy of formation of the crystalline copper(I) complex was calculated for the first time: $\Delta_r H^\circ_{298}$(cr, $CuCF_3COO$) = -1020.5 ± 18.0 kJ/mol.

The obtained results show that the apparatus used and thermodynamic characteristics of the carboxylating agent (CF_3COOAg) correspond to the methodical requirements necessary for the determination and calculation of standard enthalpies of formation of coordination compounds of metals with trifluoroacetate ligands.

Therefore, we carried out preliminary studies of the reactions of CF_3COOAg with metallic zinc and indium in order to synthesize their volatile coordination compounds necessary for the synthesis of thin indium–tin oxide (ITO) films. Thin oxide ITO films demanded by the modern industry are expensive prompting to search for cheaper analogs, and zinc oxide [15–19] and fluorine-doped zinc oxide (FZO) were proposed as such analogs among other materials [20–25]. As compared to zinc oxide, FZO has a number of advantages: an anomalously high linear electrooptic effect and more uniform cathode-luminescence properties that make this material still more attractive for commercial use. Various combinations of precursors, sources of ZnO and fluorinating agents, for instance, diethylzinc and hexafluoropropene or zinc acetate and ammonium fluoride, are often used for the preparation of FZO. A possibility of preparing oxide films with the fluorine content about 1.2% from one precursor rather than from two precursors (fluorinated zinc ketoiminates) was demonstrated [26]. The use of similar precursors gives a number of advantages: they are volatile, require no oxygen during deposition, deposit at a precursor temperature of 523 K and a substrate temperature of 673 K, and have very low contamination with carbon in the volume. The precursors of coordination compounds of zinc and indium based on trifluoroacetic acid can be characterized by similar properties. Therefore, studies on the determination of standard enthalpies of formation and the thermodynamics of vaporization of zinc and indium trifluoroacetates are very important. The mass

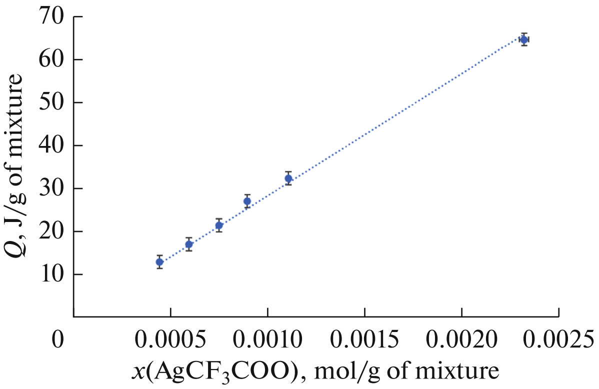

Fig. 2. Heat of the reaction per 1 g of the mixture as a function of the amount (mol) of $AgCF_3COO$ per 1 g of the mixture.

Table 2. Mass spectrum* of the gas phase [$AgCF_3COO$–In], $T = 540$ K ($U_{\text{ioniz}} = 60$ eV)

Ion	In^+	InL_2^+**	InL_3^+	$InFL^+$	$In_2L_4^+$	$In_2L_5^+$
Relative intensity, %	250	100	2.5	10	3	0.5

* The mass spectrum is given with allowance for the isotope composition.
** L = CF_3COO.

spectral analysis of the gas phase above the Zn–$AgCF_3COO$ and In–$AgCF_3COO$ systems (Table 2) showed that the following heterophase reactions occur in a temperature range of 350–520 K:

$$2CF_3COOAg(cr) + Zn(cr) = (CF_3COO)_2Zn(g) + 2Ag(cr), \quad (3)$$

$$3CF_3COOAg(cr) + In(cr) = (CF_3COO)_3In(g) + 3Ag(cr). \quad (4)$$

These reactions make it possible to successfully use the procedure considered in the work for the determination of standard enthalpies of formation and dissociation of zinc and indium trifluoroacetates and thermodynamic calculation of conditions for the formation of thin oxide films based on the In–Zn–O system doped with fluorine.

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CONFLICT OF INTEREST

The author of this work declares that they has no conflicts of interest.

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