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Thermodynamic Characteristics of Silver Perfluorobenzoates $C_6F_5COOAg{\cdot}0.5C_6F_5COOH$ and C_6F_5COOAg

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Abstract—The thermodynamic characteristics of silver perfluorobenzoates $C_6F_5COOAg{\cdot}0.5C_6F_5COOH$ and C_6F_5COOAg were studied by thermogravimetry, differential scanning calorimetry, and mass spectrometry. It was found that vaporization of these compounds occurs incongruently to give metallic silver and C_6F_5COOH, $C_{12}F_{10}$, CO_2, and $C_{18}F_{14}$ molecules. Using the 2nd and 3rd laws of thermodynamics, the standard enthalpy of formation of silver perfluorobenzoate was found to be $\Delta_f H^\circ_{298}(C_6F_5COOAg, cr) = -1195.6 \pm 15.7$ kJ/mol and the standard enthalpy of formation of the pentafluorobenzoic acid radical was estimated to be $\Delta_f H^\circ_{298.15}(C_6F_5COO^\bullet, cr) = -878.6 \pm 25.0$ kJ/mol.

Keywords: mass spectrometry, silver perfluorobenzoate, thermodynamics, vaporization, standard enthalpy of formation

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INTRODUCTION

Thermodynamic characteristics of compounds (enthalpy, Gibbs energy of formation, enthalpy of sublimation, partial pressures, etc.) are necessary for the development of methods of synthesis, use of functional materials, and modeling of various chemical engineering processes. For example, metallic, oxide, and carbide thin films and coatings and nanocrystalline material with unique optical, electrical, and mechanical properties are often produced using heterogeneous chemical processes [1, 2], which require knowledge of thermodynamic characteristics of the reactants and products. Coordination compounds of metals with organic ligands are often used as reactants in these reactions [3–6]; unfortunately, little is known about thermodynamic characteristics of these compounds. This is mainly due to experimental problems arising in the studies of the compounds. Previously we proposed a procedure for determination of the main energy characteristic of substances, that is, standard energy of formation of metal trimethylacetates (pivalates) based on DSC measurements of the enthalpy of the heterogeneous reaction of a metal with silver pivalate [7, 8]:

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

This method is characterized by relatively low Ag–Piv bond energy [8, 9].

The pivalate complex in this procedure can be replaced by other silver carboxylates with thermally stable anions and relatively low metal–ligand bond energy. The search for such compounds is fairly attractive, as this markedly expands the scope of applicability of this procedure.

Here we studied thermodynamic characteristics of silver pentafluorobenzoate C_6F_5COOAg (AgPfb) by the Knudsen effusion method with mass spectral analysis of the gas phase. Apart from the mass spectral approach, the thermal behavior of AgPfb was investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC).

EXPERIMENTAL

The following chemicals were used in the study: EtOH (96%), $Ag(NO_3)$ (analytical grade, Reachim), KOH (reagent grade, Reachim), C_6F_5COOH (99%, P&MInvest).

Synthesis of silver pentafluorobenzoate. A weighed portion of KOH (0.013 g, 2.358 mmol) was added to a solution of C_6F_5COOH (0.050 g, 2.358 mmol) in EtOH (15 mL), and the mixture was stirred for 15 min at 75°C. $AgNO_3$ (0.038 g) was added, and the reaction mixture was stirred at room temperature for 10 min until a white precipitate of potassium nitrate formed.

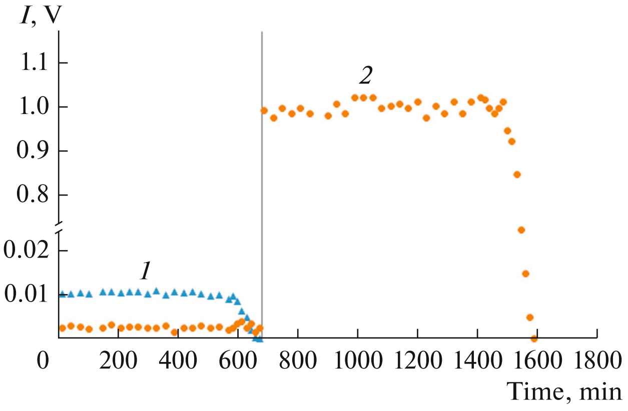

Fig. 1. Vaporization isotherms of (*1*) $C_6F_5COOAg\cdot 0.5C_6F_5COOH$: $C_6F_5COO^+$ and (*2*) $C_{12}F_{10}^+$.

The precipitate was filtered off and the resulting solution was allowed to slowly evaporate at room temperature without access of light. After 5 days, a white precipitate formed, which was separated from the mother liquor by decantation, washed with cold EtOH ($T \approx$ 5°C), and dried in air.

For $C_6F_5COOAg\cdot 0.5C_6F_5COOH$

Anal. calcd., %:	C, 29.65	H, 0.12
Found, %:	C, 29.81	H, 0.19

IR (ν, cm^{-1}): 2637 w, 1712 w, 1649 w, 1550 s, 1525 s, 1489 s, 1415 m, 1370 s, 1289 m, 1144 w, 1106 m, 990 s, 932 m, 818 w, 758 s, 705 w, 620 w, 512 w, 439 w.

Elemental analysis was performed on an EuroEA 3000 CHNS-analyzer. The IR spectrum was measured on a Spectrum 65 Fourier Transform spectrometer (Perkin Elmer) by the attenuated total reflectance (ATR) method in the frequency range of 4000–400 cm^{-1}.

The change in the sample weight was measured on a TG 209 F1 Iris thermobalance (NETZSCH) in the temperature range of 35–400°C. The measurements were carried out in alundum crucibles with an open surface at a constant heating rate of 10 K/min under argon (30 mL/min gas flow rate) with a protective inert gas flow of 10 mL/min. The heat absorption and release accompanying phase transitions and destruction processes were recorded on a DSC 204 F1 Phoenix differential scanning calorimeter (NETZSCH) in the temperature range of 20–300°C at a constant heating rate of 10 K/min under atmospheric pressure in a dynamic argon atmosphere (40 mL/min gas flow rate) with a protective inert gas flow of 70 mL/min. The instrument was pre-calibrated in temperature and sensitivity in the temperature range from –100 to 500°C against phase transition parameters of high-purity Hg, In, Sn, Zn, Bi, Pb, and CsCl standards (manufactured by NETSZCH) and C_6H_5COOH (99.99%) at a heating rate of 10 K/min according to the ASTM E967-08 (2014) and ASTM E968-02 (2014) procedures, respectively.

The samples were prepared in the following way: 1–2-mg powdered samples weighed to an accuracy of 0.02 mg were placed into aluminum crucibles with canted and punctured lids.

The process of vaporization was studied on an MS 1301 mass spectrometer meant for thermodynamic measurements in the temperature range of 370–461 K. Standard molybdenum Knudsen effusion cells with an evaporation to effusion area ratio ≥600 were used. The temperature was measured by a Pt-Pt/Rh thermocouple and maintained constant to an accuracy of ±2°C.

RESULTS AND DISCUSSION

The intensities of the major ions detected in the mass spectrum of the saturated vapor at different ionizing voltages are given in Table 1. Analysis of the experimental data given in Table 1 and known published data [10–13] indicate that the gas phase above the studied compound mainly consists of molecules of pentafluorobenzoic acid (C_6F_5COOH), perfluorobiphenyl ($C_{12}F_{10}$), carbon dioxide (CO_2), and a minor amount of perfluorotriphenyl ($C_{18}F_{14}$).

In order to determine the character of vaporization and calculate the partial pressures, experiment on complete evaporation of a known weight of silver pentafluorobenzoate was carried out at two constant temperatures. The results of this experiment are shown in Fig. 1.

The initial constant ion current intensities $I_{C_6F_5COOH}$, $I_{C_6F_5COO}$ at T= 375 K down to their almost complete vanishing correspond to vaporization of pentafluorobenzoic acid C_6F_5COOH molecules. The subsequent constant ion current intensities $I_{C_{12}F_{10}}$, $I_{C_6F_5}$ at T = 425 K up to the complete burning-out of the sample reflect vaporization of the $C_{12}F_{10}$ molecules. After completion of the experiment, a non-volatile residue identified as silver metal was left in the effusion chamber. The observed picture provides two important conclusions: the compound being tested is the solvate $C_6F_5COOAg\cdot nC_6F_5COOH$, which is vaporized in two stages. The first vaporization stage at T = 375 K is related to transition of pentafluorobenzoic acid molecules to the gas phase to give individual silver pentafluorobenzoate. In the second stage, taking place at 425 K, this compound thermally decomposes to give crystalline silver, while perfluorobiphenyl $C_{12}F_{10}$ and carbon dioxide CO_2 molecules pass to the gas phase. The complete sublimation experiment was used to find the weight of silver in the solvate and to determine the solvate composition, which was found to be $C_6F_5COOAg\cdot 0.5C_6F_5COOH$ (2 : 1). Thus, the process of vaporization of this compound can be described by the following reactions:

Table 1. Mass spectrum of the gas phase of silver pentafluorobenzoate

Ion	Relative intensity			T, K
	70 V	14 V	13.5 V	
$C_6F_5COOH^+$	0.95	Not measured	1.0	370
$C_6F_5COO^+$	1.0			
$C_6F_5^+$	0.60			
C_6CO^+	0.13			
$^*CO_2^+$	~0.5(40)	(1.5)		
$C_{12}F_{10}^+$	1.0	1.0	1.0	430
$C_6F_5^+$	0.65	1.0		
$C_{12}F_9^+$	0.15			
$C_{12}F_8^+$	0.15			
$C_{12}F_5^+$	0.14			
$C_{12}F_4^+$	0.08			
$C_6F_5COOH^+$	0.015			
$C_6C_2^+$	0.13			
$C_{18}F_{14}^+$	0.025			
$^*CO_2^+$	~0.3(35)	0.3(5)		

* The intensity of the target signal against the overall signal.

$$C_6F_5COOAg{\cdot}0.5C_6F_5COOH(cr) = C_6F_5COOAg(cr) + 0.5C_6F_5COOH(g), \quad (2)$$

$$C_6F_5COOAg(cr) = Ag(cr) + 0.5C_{12}F_{10}(g) + CO_2. \quad (3)$$

Similar results were obtained in a thermogravimetric study of the silver complex (Fig. 2). In the temperature range of 35–120°C, the sample lost 24.3% of the starting weight, while in the range of 120–240°C, the loss was 38.6% (Fig. 2). The weight loss in the first stage is associated with the removal of $0.5C_6F_5COOH$ (the calculated weight loss is 24.9%). Thus, the molar mass of the starting compound is 425 ± 4 g/mol, which corresponds to its chemical formula $C_6F_5COOAg{\cdot}0.5C_6F_5COOH$. Then C_6F_5COOAg decomposes to form AgF as the solid residue (the calculated weight of the solid residue is 29.9%) and the polycondensation product $(C_6F_{5-x})_n$, with CO_2 and $C_{12}F_{10}$ being removed

$$C_6F_5COOAg(cr) \rightarrow AgF(cr) + (C_6F_{5-x})_n(cr) + 0.5C_{12}F_{10}(g) + CO_2. \quad (4)$$

Decomposition products formed under atmospheric pressure differ from the products formed in vacuum in the mass spectral experiment. This is not surprising, since mass spectral studies, unlike DSC and TG measurements, are performed under equilibrium conditions.

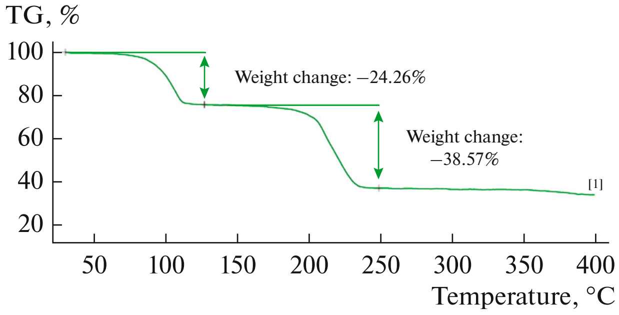

Fig. 2. Results of TG study of the thermolysis of silver perfluorobenzoate solvate. The scanning rate was 10 K/min; atmospheric pressure and a dynamic argon atmosphere were used.

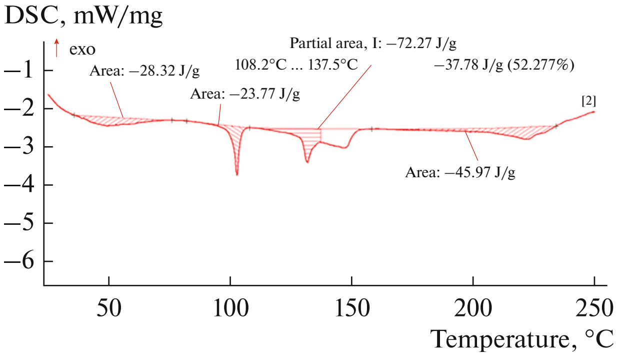

Fig. 3. Results of a DSC study of thermolysis of silver perfluorobenzoate solvate. The scanning rate was 10 K/min; atmospheric pressure and a dynamic argon atmosphere were used.

The DSC curve (Fig. 3) shows an endotherm associated with the removal of adsorbed C_6F_5COOH or water in the temperature range of 20–65°C; this is followed by incongruent melting of $C_6F_5COOAg\cdot 0.5C_6F_5COOH$ (the melting heat is 11 ± 2 kJ/mol and the melting point is 102 ± 1°C) and delayed (relative to the open surface in the thermobalance measurements) evaporation of C_6F_5COOH through a small hole in the lid. This process overlaps with the incongruent melting of AgC_6F_5COO at 130°C; it can be stated that the heats absorbed during these processes are fairly similar in magnitude (approximately 15 ± 3 kJ/mol for each of the processes). Above 150°C, decomposition of C_6F_5COOAg takes place with absorption of approximately 20 ± 4 kJ/mol.

In each stage of the mass spectral experiment, the effusion chamber was calibrated against the thermodynamic characteristics of lithium pivalate with the goal to calculate the absolute values of the partial pressures of components during the vaporization of the silver pentafluorobenzoate solvate [14] (Table 2).

The enthalpies of reactions (2) and (3) were determined using the 2nd law of thermodynamics by investigating the temperature dependences of the equilibrium constants of reactions (2) and (3), $k\ (2) = P^{0.5}_{C_6F_5COOH}$, $k\ (3) = P_{CO_2}P^{0.5}_{C_{12}F_{10}}$ (Fig. 4). In view of the invariable ratio $P_{CO_2}/P_{C_{12}F_{10}} = 2$, the temperature dependence of the expression $k\ (3) = P^{1.5}_{C_{12}F_{10}}$ was studied. The standard enthalpies of reactions (2) and (3) were calculated from the isobaric equation of the chemical reaction by the least squares method in the temperature ranges of 375–405 and 410–445 K, respectively. The average standard enthalpies of reactions (2) and (3) obtained for three independent experiments were $\Delta_r H^\circ_T\ (2) = 82.6 \pm 12.6$ kJ/mol, $\Delta_r H^\circ_T\ (3) = 154.2 \pm 19.6$ kJ/mol. The enthalpy of reaction (3) was also calculated using the 3rd law of thermodynamics. The calculation made use of the absolute partial pressures of CO_2 and $C_{12}F_{10}$ molecules at $T = 425$ K (Table 2) and the entropy change in reaction (3) equal to the entropy change in the silver nitrate decomposition at $T = 298$ K: $\Delta S^\circ_T = 244.4$ J/(mol K) [15]. The standard enthalpy of reaction (3) calculated in this way was $\Delta_r H^\circ_T\ (3) = 180.1 \pm 12.3$ kJ/mol. Analysis of the results obtained using the 2nd and 3rd laws of thermodynamics makes it possible to recommend the value $\Delta_r H^\circ_T\ (3) = 167.2 \pm 23.1$ kJ/mol and to take $T = 298.15$ K (in view of low temperatures of measurements). Using the enthalpies of reaction (3) obtained in this way, together with the standard enthalpies of formation of carbon dioxide $\Delta_f H^\circ_{298}(CO_2, g) = -393.5 \pm 0.04$ kJ/mol [15] and perfluorodiphenyl $\Delta_f H^\circ_{298}(C_{12}F_{10},\ g) = -1264.2 \pm 5.2$ kJ/mol [16], we calulated the standard enthalpy of formation of crystalline silver pentafluorobenzoate by the Hess's law to be $\Delta_f H^\circ_{298}(C_6F_5COOAg,\ cr) = -1192.8 \pm 23.6$ kJ/mol. This value and analysis of the known published data on the enthalpy of formation of radicals from several carboxylic acids were used to estimate the standard enthalpy of formation of the pentafluorobenzoic acid radicals: $\Delta_f H^\circ_{298.15}(C_6F_5COO^\bullet, cr) = -878.6 \pm 25.0$ kJ/mol and the enthalpy of the heterogeneous reaction $\Delta_r H^\circ_{298.15}\ (4) = 314 \pm 34.4$ kJ/mol

$$C_6F_5COOAg(cr) = C_6F_5COO^\bullet(g) + Ag(cr). \quad (5)$$

Owing to high enthalpy of this reaction and the thermal instability of the $C_6F_5COO^\bullet$ radical, silver pentafluorobenzoate can be used in heterogeneous reactions as a carboxylating agent in the synthesis of

Table 2. Partial pressures (Pa) of components of the saturated vapor pressure of $C_6F_5COOAg\cdot 0.5C_6F_5COOH$

Condensed phase	Conditions of sublimation	$P_{C_6F_5COOH}$	$P_{C_{12}F_{10}}$	P_{CO_2}	T, K
		Pa			
$C_6F_5COOAg\cdot 0.5C_6F_5COOH$	Knudsen	8.8×10^{-4}			378
C_6F_5COOAg	Knudsen. Closed volume		9.4×10^{-2} 9.5×10^{-2}	6.8×10^{-2} 4.8×10^{-2}	425

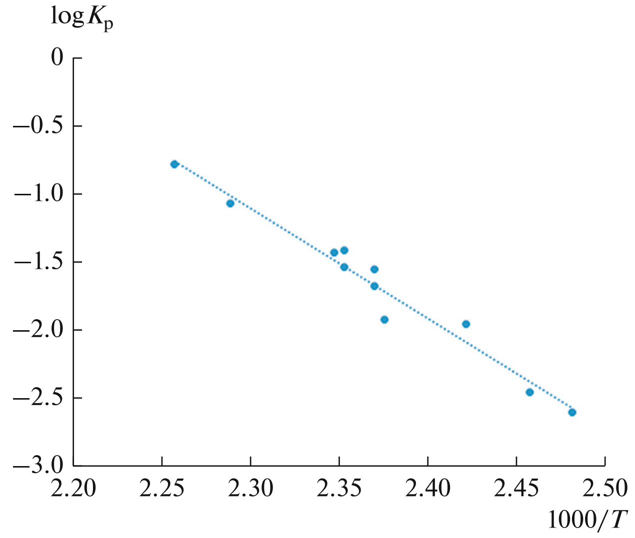

Fig. 4. Temperature dependence of the equilibrium constant of reaction (3).

salts at relatively low temperatures and with a high bond enthalpy: $\Delta_r H^\circ_{298}(C_6F_5COO{-}M) > 340$ kJ/mol.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Pierson, H.O., *Handbook of Chemical Vapor Deposition (CVD): Principles, Technology and Applications*, New York: Noyes, 1992.
2. Syrkin, V.G., *CVD-metod. Khimicheskoe parofaznoe osazhdenie* (CVD. Chemical Vapor Deposition), Moscow: Nauka, 2000.
3. Grodzicki, A., Lakomska, I., Piszcek, P., et al., *Coord. Chem. Rev.,* 2005, vol. 249, p. 2232.
4. Kretzschmar, B.S.M., Assim, K., Preub, A., et al., *RSC Adv.,* 2018, vol. 8, p. 15632.
5. Mungkalasiri, J., Bedel, L., Emieux, F., et al., *Chem. Vap. Deposition,* 2010, vol. 16, p. 35.
6. Puurunen, R.L., *J. Appl. Phys.,* 2005, vol. 97, p. 121.
7. Morozova, E.A., Dobrokhotova, Zh.V., and Alikhanyan, A.S., *J. Therm. Anal. Calorim.,* 2017, vol. 130, p. 2211.
8. Lukyanova, V.A., Papina, T.S., Didenko, K.V., and Alikhanyan, A.S., *J. Therm. Anal. Calorim.,* 2008, vol. 92, p. 743.
9. Lukyanova, V.A., Pimenova, S.M., Ilin, D.Yu., et al., *J. Chem. Thermodyn.,* 2019, vol. 131, pp. 336–339. https://doi.org/10.1016/j.jct.2018.11.016
10. Szlyk, E., Lakomska, I., and Grodzicki, A., *Thermochim. Acta,* 1993, vol. 223, p. 207.
11. Logvinenko, V., Polunina, O., Michailov, Yu., et al., *J. Therm. Anal. Calorim.*, 2007, vol. 90, no. 3, p. 813.
12. Bazhanova, Z.G., Tarasov, Yu.I., Kovtun, D.M., et al., *J. Struct. Chem.*, 2010, vol. 51, no. 3, p. 433.
13. Roberts, G.D. and Edward, W.V., *Org. Mass Spectrom.,* 1981, vol. 16, p. 546.
14. Kayumova, D.B., Malkerova, I.P., Kiskin, M.A., et al., *Russ. J. Inorg. Chem.*, 2021, vol. 66, p. 868. https://doi.org/10.1134/S0036023621060127
15. Database. Thermal Characteristics of Compounds. http://www.chem.msu.ru/cgi-bin/tkv.pl.
16. NIST Chemistry Webbook. http://webbook.nist.gov/chemistry/.

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