Thermal decomposition of some silver(I) carboxylates under nitrogen atmosphere

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Abstract The thermal decomposition reactions of $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{COOAg}$ (**1**), $(\text{CH}_3)_3\text{SiCH}_2\text{COOAg}$ (**2**), CF_3COOAg (**3**), $(\text{CH}_3)_3\text{CCOOAg}$ (**4**), $\text{C}_2\text{H}_5\text{COOAg}$ (**5**), $\text{C}_3\text{F}_7\text{COOAg}$ (**6**), $\text{C}_6\text{F}_{13}\text{COOAg}$ (**7**) and $(\text{CF}_2)_3(\text{COOAg})_2$ (**8**) were studied in N_2 atmosphere using thermogravimetry (TG), derivative thermogravimetry and differential thermal analysis. Characterized compounds decomposed in one- or multi-step processes with metallic silver formation in the range 215–465 °C. TG-IR studies of gases evolved during thermolysis revealed products of decomposition, such as carboxylic acids, CO_2 and recombination reactions.

Keywords Silver carboxylate · Thermal analysis · Gaseous products

Introduction

‘Silver(I) carboxylates and their complexes with tertiary phosphines have found applications as precursors for chemical vapor deposition (CVD) [1–7]. Silver thin layers produced by this method can be applied in microelectronic circuits, catalysis, as a bactericidal coatings [8], as mirrors and other applications [4, 9]. The knowledge about thermal properties of precursors is important for the evaporation parameters and determination of the metallated species which can be transported in the gas phase. Furthermore, the weight loss during the experiment can be indicative of volatility and the cleanliness of the thermolysis mechanism.

The precursors should be volatile and decompose to a metal at relatively low temperature and pressure in CVD apparatus. The data on gas phase composition and stability during transport in the CVD equipment are used in selection of the appropriate conditions [10]. These parameters are necessary for ascertaining of the evaporation temperature, CVD heating regime and finally the precursor decomposition temperature on the substrate surface in the last stage of the layer formation. The thermal stability and thermodynamic data on compounds applied for CVD can also be useful in selection of the most promising precursors.

Generally, silver(I) carboxylates are thermally stable and decompose to the metallic silver and volatile organic and inorganic products at a wide range of temperatures [11–15] depending on the carboxylate residue. Reported informations of silver(I) carboxylates proposed the following scheme of the decomposition reaction:

However, other studies suggested formation of the silver(I) oxide (unstable greater than 300 °C) in the first stage of this process connected with formation of the anhydride of the corresponding acid. In the further stage, the anhydride and silver oxide undergo transformation giving final products: RCOOH and Ag^0 [11]. So far, only few studies reported concerning this matter and our study is intended to extend this issue.

Experimental

Materials and synthesis

Carboxylic acids: $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{COOH}$ (96 %), $(\text{CH}_3)_3\text{SiCH}_2\text{COOH}$ (99 %), CF_3COOH (99 %), $(\text{CH}_3)_3\text{CCOOH}$

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(99 %), $\text{C}_2\text{H}_5\text{COOH}$ (99.5 %), $\text{C}_3\text{F}_7\text{COOH}$ (98 %), $\text{C}_6\text{F}_{13}\text{COOH}$ (99 %) and $(\text{CF}_2)_3(\text{COOH})_2$ (97 %) were purchased from Aldrich, whereas AgNO_3 (>99.9 %), KNO_3 (99 %), NaHCO_3 (99.5 %), $\text{C}_2\text{H}_5\text{OH}$ from POCH (Poland) and were used as received. All salts were prepared according to previously reported procedures [16–18]. In the case of (1), (2), (4) and (5), appropriate carboxylic acids and potassium nitrate were suspended in a water–ethanol solution (1:1), heated to 40 °C and stirred, followed by silver nitrate addition. The obtained precipitate was filtered, washed with water, ethanol and dried. The salts (3) and (6)–(8) were synthesized by the reaction of fluorinated carboxylic acids and silver carbonate.

Apparatus and experimental methods

TG/DTG–DTA measurements were performed on SDT 2960 TA analyser. Decomposition processes were studied in dynamic atmospheres of N_2 (99.999 %) at 100 ml min^{-1} . The heating rate was 10 °C min^{-1} and samples mass was 3–12 mg. Gaseous products of thermal decomposition were detected by a FT-IR BioRad Excalibur spectrophotometer equipped with thermal connector for gases evolved from TA SDT 2960 analyser. Powder X-ray diffraction data for the residues from thermal analysis were obtained with a Philips X'PERT diffractometer using Cu K α radiation.

Results and discussion

Thermal analysis results

The TG/DTG–DTA analyses of (1)–(8) were carried out to give an information of the possible decomposition temperatures and also the relative stability of the salts. The results are summarized in Table 1. Decomposition of (1) proceeds in one endothermic stage started at 150 °C (DTA curve: $T_{\text{max}} = 195$ °C) and is completed at 250 °C (Fig. 1a). The metallic silver is the final product with the presence of carbonaceous species, what is evident from XRD studies of the residue in the crucible [19]. Salt $(\text{CH}_3)_3\text{SiCH}_2\text{COOAg}$ (2) is thermally stable up to 135 °C and decompose greater than this temperature (Fig. 1b). This process is connected with one exothermic effect (DTA) with the maximum appeared at 210 °C. Metallic silver is formed greater than 215 °C. In the case of CF_3COOAg (3), DTA curve indicates four peaks (Fig. 1c). The first one is a strong endothermic transition at 260 °C, which is connected with a slight mass loss and probably corresponds to the melting point. The next stage (DTA: exo, $T_{\text{max}} = 350$ °C) is resulted from the main thermal decomposition process, and weight loss is about 48 %. Then, two small endothermic peaks appear at 415 and

430 °C. The corresponding mass loss on the TG is about 3 %. Silver pivalate (4) decomposes in one-stage process with T_{max} on DTA curve at 235 °C (exothermic peak) (Fig. 1d). As distinct from the others, thermolysis of (5)–(6) proceeds in two stages. Figure 2a shows the characteristic features of heating silver propionate (5). The first stage occurs between 80 and 130 °C (TG) and involves a mass loss of 3.2 %. The second one is associated with a mass loss amount to 39.2 % (160–265 °C). Three peaks are observed in the DTA curve; peaks 1 (endo, 100 °C) and 3 (exo, 245 °C) are well defined in both the DTA and DTG curves, but the weak peak 2 (endo, 175 °C) is visible only on DTA data.

The TG, DTA and DTG curves of silver heptafluorobutyrate (6) are presented in Fig. 2b. Analysis of the DTA data revealed two exothermic effects at 320 and 345 °C that are connected with a rapid weight loss. Furthermore, endothermic peak occurs at 290 °C. In the case of $\text{C}_6\text{F}_{13}\text{COOAg}$ (7), DTA curve displays three peaks maximized at 100, 145 and 275 °C (Fig. 2c). All peaks are linked with weight loss: ~4.5, ~3 and 61.9 %, respectively. Silver hexafluoroglutarate (8) undergoes decomposition in three steps with the DTA peak temperatures at 325, 350 and 370 °C (Fig. 2d). The first of them is very sharp. Thermolysis gives rise to the three weight losses in TG curve (about 37, 6 and 9 %).

The results point to higher thermal stability of fluorinated carboxylates. For most of analysed salts, mass of residue remaining is close to expected for the formation of metallic silver. Occurred slight discrepancy derived from the presence of small amounts of carbon in the solid product. Differences between calculated and experimental data are more significant for the compounds (4) and (5) and may be caused by the specificity of decomposition mechanism. From the above-presented results, it can be seen that described carboxylates can be potentially precursors in CVD process because they decomposed in a relatively low temperatures. However, it is noteworthy that this is only one of several necessary attributes of a good precursor.

TG-IR results

Thermolysis is in many cases a one-particle reaction, but in fact apparently simple reactions are complicated processes [20, 21]. Our earlier TG-IR studies confirmed that $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{COOAg}$ (1) and $(\text{CH}_3)_3\text{SiCH}_2\text{COOAg}$ (2) decomposed with formation of several products originating from direct decomposition of molecules such as CO_2 , and from recombination reactions [12, 18]. The present examination (with a higher heating rate) point to carbon dioxide and carboxylic acids emission. In the case of silver 2,2-dimethylbutyrate, the following bands were present: νCH , 2981/2946/2895; CO_2 , 2360, 2332; $\nu\text{C=O}$, 1767; δCH_2 ,

Table 1 Results of thermal analysis of (1)–(8) in N₂ atmosphere

Compound	Heat effect DTA	Temperature/°C			Residue/%	
		T_{init}	T_{max}	T_{f}	Calc.	Found
CH ₃ CH ₂ C(CH ₃) ₂ COOAg (1)	Endo	150	240	250	48.4	48.0
(CH ₃) ₃ SiCH ₂ COOAg (2)	Exo	135	200	215	45.1	46.9
CF ₃ COOAg (3)	Endo	200	260	—	48.8	48.6
	Exo	—	335	—		
	Endo/endo	—	410/430	465		
(CH ₃) ₃ CCOOAg (4)	Exo	155	225	235	51.6	59.1
C ₂ H ₅ COOAg (5)	Endo	80	100	130	59.6	57.6
	Exo	160	240	265		
C ₃ F ₇ COOAg (6)	Endo/exo	250	320	—	33.6	32.8
	Exo	—	335	355		
C ₆ F ₁₃ COOAg (7)	Endo	70	95	—	29.1	30.7
	Endo	—	140	165		
	Endo	265	280	310		
(CF ₂) ₃ (COOAg) ₂ (8)	Endo	110	325	—	47.5	47.3
	Endo	—	355	—		
	Endo	—	375	385		

T_{init} initial temperature, T_{max} maximum temperature, T_{f} final temperature

Fig. 1 TG, DTG and DTA curves of CH₃CH₂C(CH₃)₂COOAg (1) (a), (CH₃)₃SiCH₂COOAg (2) (b), CF₃COOAg (3) (c) and (CH₃)₃CCOOAg (4) (d)

1473; δCH_3 or δOH , 1394; νCCO , 1115; $\gamma\text{C=O}$, 578 cm^{-1} (Fig. 3).

The result of TG-IR measurement performed for (3) is presented in Fig. 4. In this case, bands derived from carbon dioxide (2359 and 688 cm^{-1}) were observed in the maximum decomposition rate. The second main volatile product was CF₃CFO, which was also identified in earlier studies concerning transitions metals trifluoroacetates [22, 23]. This assumption is confirmed by the presence of bands at: 1896, 1240, 1210 and 1097 cm^{-1} [24, 25]. These results indicate that for this compound, recombination processes

within CF₃COO[−] also take place. Furthermore, two small peaks at 2180 and 2108 cm^{-1} seemed to be evidence of the presence of carbon monoxide [26].

The IR spectra for (CH₃)₃CCOOAg (4) reveal absorption bands derived from carbon dioxide (2359, 669 cm^{-1}) and bands at 2981 and 2946 cm^{-1} (νCH). Besides that intensive signals occur at 1,771 (asymmetric band of COO), 1117 cm^{-1} and the others at 1315, 1032, 888 and 577 cm^{-1} . These spectra are more similar to the spectra of pivalic acid than for anhydride, so we presume the presence of (CH₃)₃CCOOH.

Fig. 2 TG, DTG and DTA curves of $\text{C}_2\text{H}_5\text{COOAg}$ (**5**) (a), $\text{C}_3\text{F}_7\text{COOAg}$ (**6**) (b), $\text{C}_6\text{F}_{13}\text{COOAg}$ (**7**) (c) and $(\text{CF}_2)_3(\text{COOAg})_2$ (**8**) (d)

Fig. 3 FT-IR spectrum of the volatile products evolved during thermal decomposition of $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{COOAg}$ (**1**) (230–245 °C)

Fig. 4 FT-IR spectrum of the volatile products evolved during thermal decomposition of CF_3COOAg (**3**) (325–350 °C)

In the case of silver propionate (**5**), thermolysis consists of two isolated processes. In the first stage, the intensity of the bands is very small and only two of them at 1790 and 1773 cm^{-1} (νCOO) are detected. Unfortunately, based on this data, it was impossible to determine the composition of a vapor phase. Above-mentioned signals also appeared in spectra recorded at the second step of decomposition. Additionally, broad bands at 1148 and 1060 cm^{-1} (C–O stretching absorption) and bands resulted from CH and CO_2 vibrations also appear. The above results indicate the presence of diluted monomeric propionic acid in the vapor phase.

For $\text{C}_3\text{F}_7\text{COOAg}$ (**6**) (at a temperature about 280 °C), carbon dioxide and fluorocarbon species (1251 and 1213 cm^{-1} , respectively) are observed. At 290 °C, additional bands at 1391 and 1334 cm^{-1} (s) (from C–F groups) and 1792, 1148 and 1035 cm^{-1} (m) occur, which can be assigned to the heptafluorobutyric acid. It should be noted that the intensity of the νCOO band is much lower than for others carboxylates (Fig. 5).

The next salt (**7**), with longer fluorocarbon chain, decomposed in a different mode. At the two first stages of thermolysis, only bands from carbon dioxide are observed. Greater than 280 °C, strong sharp bands at 1,244 ($\nu\text{C–F}$),

Fig. 5 FT-IR spectrum of the volatile products evolved during thermal decomposition of C_3F_7COOAg (**6**) (300–320 °C)

Fig. 6 FT-IR spectrum of the volatile products evolved during thermal decomposition of $(CF_2)_3(COOAg)_2$ (**8**) (355–370 °C)

1781 cm^{-1} (νCOO) and additional bands at 1367, 1318, 1141, 1091, 861, 813 and 743 cm^{-1} are found on spectra of the volatile products. During the decomposition process of silver heptafluoroglutarate (**8**), only CO_2 and small bands at 1187 and 1050 cm^{-1} are registered less than 335 °C. Increasing the temperature causes the formation of additional bands at 1885 and 1849 cm^{-1} (νCOO). Simultaneous changes in the range $1000\text{--}1300\text{ cm}^{-1}$ are detected (bands at 1201 (s), 1137, 948, 894 cm^{-1}). Furthermore, C=O absorption bands appear. These results allow to assume that CO_2 and $(\text{CF}_2)_3(\text{COOH})_2$ are the main gaseous products at temperature less than 350 °C. The spectra registered greater than 350 °C correspond to the two successive stages of the thermal decomposition (see Fig. 6). In this case, there is no evidence of the presence of the COO group. The spectrum revealed bands derived from carbon dioxide and two doublets at 1339/1325 and $1194/1183\text{ cm}^{-1}$, indicating the presence of C_2F_4 [27].

TG-IR spectra analyses do not determine the presence of silver-containing species in the gas phase. However, these results may derive not only from the absence of them but also from too small concentration to be detected by an applied method. On the other hand, variable temperature mass spectra [28] pointed on $[\text{Ag}_2(\text{OOCR})]^+$ as main stable silver species and this dimeric system may be a volatile precursor in CVD reactor. We can also conclude that for both aliphatic and fluorinated silver(I) carboxylates, thermolysis resulted primarily in the formation of acids and carbon dioxide in the gas phase. It is also worth mentioning that in all cases, CO_2 is always recorded as the first gaseous product of thermal decomposition. Furthermore, the fragmentations and transformations of the acid residue take place.

Conclusions

Thermal decomposition of studied salts resulted in silver, what is evident from the TG calculation, XRD and results of the previous studies. The data indicate that carboxylates usually decompose without a melting point (or a melting point is connected with thermolysis) and cannot be efficiently evaporated. Aliphatic salts decompose in lower temperatures than fluorinated ones. This feature most probably comes out from the lower stability of Ag-O bond. In the case of aliphatic acids, they became less covalent than in perfluorinated analogs.

Analysis of the composition of vapors, formed during thermolysis in nitrogen atmosphere, indicates carbon dioxide and appropriate acids as the main products. Presence of RCOOH might correspond with a theory that R-CO-O-CO-R and Ag_2O undergo transformation to RCOOH and Ag^0 . In this case, there is a chance that the described transitions are so fast, that we cannot register the anhydride.

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