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Thermal and spectroscopic studies of the Ag(I) salts with fluorinated carboxylic and sulfonic acid residues

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Abstract

Silver(I) salts with RCOOH, where R is $CF_3(CF_2)_2$, $CF_3(CF_2)_6$, $CF_3(CF_2)_8$, C_6F_5, $C_6F_5CH_2$, with RSO_3H, where R is CF_3, $CF_3(CF_2)_3$, and with $HOOC(CF_2)_3COOH$ were synthesized. The thermal decomposition processes were studied and the activation energies calculated from thermal data. The decomposition mechanisms and thermal stabilities are discussed. From the IR, and ^{13}C and ^{19}F NMR measurements, it is proposed that the carboxylic acid residues have monodentate bonding.

INTRODUCTION

Silver(I) carboxylates are mainly studied because of their usefulness in the metathetical syntheses of complexes [1, 2] and as a source of metallic silver in chemical vapor deposition (CVD). This prompted us to study Ag(I) salts with carboxylic and sulfonate acids that were substituted to the highest degree with fluorine atoms. The fluoro-substituted acids should enhance the volatility of the salts which could be used as a future source of silver in chemical vapor deposition. The aim of this study is to analyze the thermal decompositions of the Ag(I) salts and their activation energies in order to establish their thermal stability. Carboxylic acid residues can act as ligands binding to the metal ion in different ways [3]. The binding of the acids to Ag(I) will be discussed in the present paper.

EXPERIMENTAL

Silver nitrate p.a. was purchased from P.O.CH., Poland, and used without further purification for the reaction with aqueous $NaHCO_3$ solution. The Ag_2CO_3 thus obtained was used in the reactions with the

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following acids: C_3F_7COOH, $C_7F_{15}COOH$, $C_9F_{19}COOH$, C_6F_5COOH, $C_6F_5CH_2COOH$, CF_3SO_3H, $HO_2C(CF_2)_3CO_2H$. Acids of analytical grade were purchased from Aldrich.

The silver salt of $CF_3(CF_2)_3SO_3H$ was obtained by dissolving potassium nonafluoro-1-butanesulfonate in water and passing the solution through a column filled up with cation exchange resin (Dowex 50W X8 50/100 mesh (H^+)). The eluted acid reacted immediately with the silver carbonate. The subsequent steps were identical to those described below.

Silver salts were prepared by the reaction of stoichiometric amounts of Ag_2CO_3 (5 mmol) with acid. Syntheses were carried out in water or in aqueous ethanol in a dark room. Reaction was usually completed within 24 h or earlier, according to the acid reactivity. The unreacted silver carbonate was filtered, washed with ethanol, and the clear filtrate was evaporated in a stream of cold air. The residues were recrystallized from water or from aqueous ethanol. The silver contents were determined by the argentometric method. Carbon was determined by semi-microanalysis. The analytical results (%) were $C_4F_7O_2Ag$, Ag (33.30/33.60) and C (15.50/15.00); $C_8F_{15}O_2Ag$, Ag (20.43/20.71) and C (18.35/18.44); $C_{10}F_{19}O_2Ag$, Ag (17.09/17.37) and C (19.48/19.34); $C_7F_5O_2Ag$, Ag (33.59/33.82) and C (26.20/26.36); $C_8F_5H_2O_2Ag$, Ag (31.94/32.40) and C (28.58/28.86); CF_3SO_3Ag, Ag (41.66/41.98) and C (4.50/4.67); $C_4F_9SO_3Ag$, Ag (15.81/16.11) and C (12.00/11.80); $C_5F_6O_4Ag_2$, Ag (47.40/47.54) and (13.10/13.23).

IR spectra were recorded with a Bruker 113 JFS FTIR spectrometer using KBr discs and 200 scans; below 400 cm^{-1}, polyethylene discs were used. Thermal studies were performed on a OD-102 derivatograph (Paulik and Paulik, MOM Budapest). The atmosphere over the sample was air pumped by a water pump, the heating range was up to 500°C and the heating rate was 2.5°C min^{-1}. The sample mass was 100 mg and the TG sensitivity was 50 mg; the reference material was Al_2O_3 of grain size <0.06 mm. NMR spectra were recorded with a Varian Gem 200-XL spectrometer. Samples were dissolved in $CDCl_3$, D_2O or DMSO-d_6. ^{13}C spectra were recorded at 50 MHz and ^{19}F spectra at 188 MHz. The references were TMS for ^{13}C and CCl_3F for ^{19}F resonance.

RESULTS AND DISCUSSION

Thermal analysis

The results of the thermal analysis are presented in Table 1. The thermal decomposition of the studied salts is at least a two-step process. The initial temperature of the first step is in the range 85–320°C. The lowest

TABLE 1

Results of the thermal analysis

Compound	Heat effect	Temperature range/°C			Weight loss/%		Detached group	E_a/kJ mol^{-1}
		t_f	t_m	t_f	Found	Calc.		
$CF_3(CF_2)_2COOAg$	Endo	225	245	350	9.0	8.7	CO	
	Exo	350	388	470	57.0	57.0	$CF_3(CF_2)_2$–	362
$CF_3(CF_2)_6COOAg$	Endo	140	325	–	15.0			
	Exo	–	385	460	64.0	79.2	$CF_3(CF_2)_6COO$–	217
$CF_3(CF_2)_8COOAg$	–	130	–	265	8.5			
	Exo	265	340	430	73.9	82.6	$CF_3(CF_2)_8COO$–	103
C_6F_5COOAg	Endo	210	250	–				
	Exo	–	270	280	68.5	68.7	C_6F_5–, CO_2	264
$C_6F_5CH_2COOAg$	–	130	–	220	9.0	9.0	HCHO	
	Exo	220	298	340	58.2	58.6	C_6F_5–, CO	219
CF_3SO_3Ag	–	20	–	210	5.0			
	Endo	210	255	360	10.0			
	Endo	360	510	–	10.0	24.9	SO_2	
	Exo	–	580	590	30.0	30.0	CF_3–, $0.25O_2$	142
$CF_3(CF_2)_3SO_3Ag$	Endo	85	105	140	2.5			
	Endo	140	165	430	13.0	15.7	SO_2	
	Exo	430	465	–	50.0			
	Exo	–	485	500	7.5	57.8	$CF_3(CF_2)_3O$–	450
$AgO_2C(CF_2)_3CO_2Ag$	Exo	320	365	375	41.5	41.4	–$O_2C(CF_2)_2CO_2$–	352
	Exo	375	400	415	11.5	11.4	–CF_2–	

temperature is observed for $CF_3(CF_2)_3SO_3Ag$ while the highest is observed for silver glutarate. The first step is endothermic with the exception of silver glutarate. The mass loss in the first step is clearly connected with the detachment of SO_2 from trifluoromethanesulfonate and nonafluorobutanesulfonate salts. Salts with sulfonates exhibit two endotherms on the DTA curve, followed by exotherms, as with the rest of salts. The carboxylate salts decompose in such a way that it is difficult to connect the first step with the detachment of CO or CO_2. This is caused by the close subsequent exothermic decomposition reactions observed on the DTA, DTG and TG curves. The exothermic reaction starts in the range from 220°C (for $C_6F_5CH_2COOAg$) up to 430°C (for $CF_3(CF_2)_3SO_3Ag$). The mass loss on the TG curves is connected with the dissociation of the carboxylic acid residue, or perfluorinated chain in the case of silver sulfonates. The final product of the decomposition processes is metallic silver, as demonstrated by the powder diffractogram of the residue taken from the crucible after thermal analysis.

The lowest temperature of silver formation is in the case of C_6F_5COOAg (280°C). The temperatures of silver formation change in the order $C_6F_5COOAg < C_6F_5CH_2COOAg < C_3F_6(COO)_2Ag_2 < C_9F_{19}COOAg < C_7F_{15}COOAg < C_3F_7COOAg < C_4F_9SO_3Ag$. The most stable appeared to be silver methanesulfonate. Analysing the length of the aliphatic chain of the perfluorinated salts revealed that the temperature of silver formation increased with decreasing numbers of fluorine and carbon atoms in the aliphatic residue. Salts with fluorinated aromatic acids and dicarboxylic acid show the lowest temperatures of silver formation.

The activation energies were calculated from the TG curve using a method based on the general Horowitz–Metzger [4] equation. Activation energy values are listed in Table 1. The highest value was found for $CF_3(CF_2)_3SO_3Ag$, and the lowest for $CF_3(CF_2)_8COOAg$, which confirms that an increase in the number of fluorine atoms causes a decrease in the thermal stability. From the thermal studies, it is evident that the silver salts of fluorinated carboxylic acid residues readily decompose to metallic silver.

SPECTROSCOPICAL STUDIES

IR spectra

A carboxylate ion, $RCOO^-$, can coordinate to metals in a number of ways, including monodentate [5], chelating [6, 7] or bridging [8, 9].

Some reported correlations between the nature of the carboxylate coordination and the carbon–oxygen stretching frequencies will be used here to determine the Ag(I) coordination number and the composition

TABLE 2

Characteristic IR spectral frequencies in cm^{-1} [a]

Compound	ν_{as}(COO)	ν_s(COO)	Δ	δ_d(COO)	Π_{CO}
$CF_3(CF_2)_2COOH$	1772	1433	339	925	–
$CF_3(CF_2)_2COOAg$	1678	1400	278	–	–
$CF_3(CF_2)_6COOH$	1713	1421	292	–	538
$CF_3(CF_2)_6COOAg$	1658	1400	258	–	525
$CF_3(CF_2)_8COOH$	1700	1466	234	925	525
$CF_3(CF_2)_8COOAg$	1656	1400	256	919	519
C_6F_5COOH	1720	1488	232	920	–
C_6F_5COOAg	1610	1470	140	–	–
$C_6F_5CH_2COOH$	1716	1410	306	–	–
$C_6F_5CH_2COOAg$	1663	1381	282	925	550
$HO_2C(CF_2)_3CO_2H$	1769	1410	359	941	552
$AgO_2C(CF_2)_3CO_2Ag$	1700	1400	300	941	–
	$\nu_{as}(SO_3)$	$\nu_s(SO_3)$	$\delta_{as}(SO_3)$	$\delta_s(SO_3)$	
CF_3SO_3Ag	1250	1025	620	569	
$CF_3(CF_2)_3SO_3K$	1256	1025	622	563	
$CF_3(CF_2)_3SO_3Ag$	1260	1028	624	565	

[a] $\Delta = \nu_{as} - \nu_s$.

of the coordination sphere [10–12]. The selected absorption bands and their assignments are presented in Table 2.

Monodentate coordination should increase the separation (Δ) between the $\nu(CO_2)$ frequencies relative to the values of the free carboxylate ion [13], usually taken as those of the sodium or potassium salts. The separations for sodium and potassium trifluoroacetates are 223 and 241 cm^{-1} respectively [14, 15]. The observed separation is significantly higher than for ionic salts, and monodentate binding can be postulated for the salts under discussion. The exception is C_6F_5COOAg where the 140 cm^{-1} separation may be caused by chelating or bridging binding. Bands from the Ag–O stretching vibrations in the range below 500 cm^{-1} confirmed unidentate bonding of the carboxylates.

Absorption bands from SO_3 stretching and deformation frequencies are in the range characteristic for ionic salts, because there is no significant shifting of the bands in relation to potassium salt.

Analysis of NMR spectra

The ^{13}C NMR resonance of the carboxylate carbon in the free fluorinated aliphatic acids and salts under discussion appears in the range 159.1–165.7 ppm. The signal of the COO carbon in the spectra of the studied salts is shifted downfield by about 1 ppm in comparison to the value of the free acid, e.g. 159.6 to 160.5 ppm in C_6F_5COOAg. The highest shift (6.7 ppm) is observed in the spectrum of $CF_3(CF_2)_2COOAg$. The chemical shift of the α-carbon is located downfield about 3 ppm in the silver salts spectra in relation to the free acids, e.g. $CF_3(CF_2)_2COOAg$, 122.9 ppm; free acid, 119.9 ppm. The ^{19}F resonance of fluorine on the CF_2 group in the α-position is shifted slightly upfield by approx. 1 ppm. The resonance of the fluorine atoms in the CF_3 group is affected even more in the presence of the silver ions because they are shifted upfield by approx. 2 ppm, e.g. $CF_3(CF_2)_8COOAg$, −2.3; acid, −4.7 ppm).

The NMR spectral parameters and the analysis of the vibrational spectra lead to the conclusion that fluoro-substituted carboxylic acid residues are bonded with silver as unidentate ligands, with the exception of the silver pentafluorobenzoate.

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