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THERMAL DECOMPOSITION OF SILVER(I) AND MERCURY(I) ANTHRANILATES AND SALICYLOALDOXIMATES

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Abstract

The processes of thermal decomposition of silver(I) and mercury(I) anthranilates and salicyloaldoximates were studied. Thermal, chemical and X-ray analyses and infrared spectroscopy were used to determine the mechanisms of decomposition of these complexes. The factor determining the decomposition is the character of the Ag^+ and Hg_2^{2+} ions, which are easily reduced to free metals. The final reaction product of the compounds of silver is the pure metal; the compounds of mercury are volatilized completely when heated.

Keywords: complexes, mercury(I) anthranilate, mercury(I) salicyloaldoximate, silver(I) anthranilate, silver(I) salicyloaldoximate

Introduction

This analysis of the thermal decompositions of Ag(I) and Hg(I) anthranilates and salicyloaldoximates is a continuation of studies on the thermal properties of complexes and salts of metals with chelate-forming organic ligands. Previous examinations have shown that, in the first stage of decomposition, a number of anthranilates [1, 2], salicylates [2], salicyloaldoximates [2] and 2-oxy-3-naphtholates [2] of divalent metals lose one ligand molecule and change from di- to mono-compounds. The salts of univalent metals, such as the salicylates of the alkali metals, change from mono- to dimetallic compounds [3], whereas in the case of the anthranilates [4] and salicyloaldoximates [5] of the alkali metals the anion is destroyed as soon as the firs stage of decomposition occurs.

Experimental

Ag(I) anthranilate and salicyloaldoximate were obtained according to methods described by Hill and Curran [6], and Lumme and Knuuttile [7], respectively.

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Hg(I) anthranilate: equal amounts of 1 *M* NaOH solution and purified anthranilic acid were mixed. The solution was filtered, and a slight excess of $Hg_2(NO_3)_2 \cdot 2H_2O$ solution acidified with nitric acid to *pH* 3–4 was then added. A white precipitate was formed immediately. It was filtered off, washed several times with water, and then dried in air in a dark place.

Hg(I) salicyloaldoximate: equal amounts of an alcoholic solution of salicyloaldoxime and a 0.5 *M* aqueous solution of NaOH were mixed and a stoichiometric amount of acidified $Hg_2(NO_3)_2 \cdot 2H_2O$ solution was added (a procedure similar to Hg(I) anthranilate preparation). The solution was left in a dark place. The white precipitate formed after several hours was filtered off, washed with several portions of water and dried in air. Hg(I) anthranilate and Hg(I) and Ag(I) salicyloaldoximates were stored in dark ampoules. The results of elemental analysis are presented in Table 1. The contents of silver and mercury in the compounds were obtained by Volhard's method.

Table 1 Results of analysis of silver(I) and mercury(I) anthranilates and salicyloaldoximates

Compound	Calculated /%				Found /%			
	C	H	N	M	C	H	N	M
$[C_6H_4(NH_2)COO]Ag$	35.4	2.5	5.7	44.2	34.3	2.5	5.6	44.5
$[C_6H_4(NH_2)COO]_2Hg_2$	25.0	1.8	4.2	59.6	24.9	1.7	4.1	59.7
$[C_6H_4(CHNOH)O]Ag$	34.5	2.5	5.7	44.2	33.6	2.6	5.3	43.7
$[C_6H_4(CHNOH)O]_2Hg_2$	25.0	1.8	4.2	59.6	25.7	2.1	4.0	59.4

Thermal analysis

Thermal tests were carried out on an OD-102 derivatograph (MOM, Budapest). The temperature range was 20–1000°C, with a heating rate of 10 deg·min^{-1}. The reference substance was α-Al_2O_3. The samples weighed 100 mg each. Thermal curves for the compounds are shown in Fig. 1.

Investigation of sinters

Sinters were obtained under conditions similar to those of the thermal analysis. Weighed 100 mg samples of the compound were heated in an electric furnace at 10 deg·min^{-1}. The TG curves were used to choose appropriate temperatures for obtaining the sinters. The results of chemical analysis of the sinters are presented in Table 2.

IR spectrophotometric analysis

The IR spectra were taken on a Specord 80 spectrophotometer in the range 4000–200 cm^{-1}. Samples were prepared as pills in KBr.

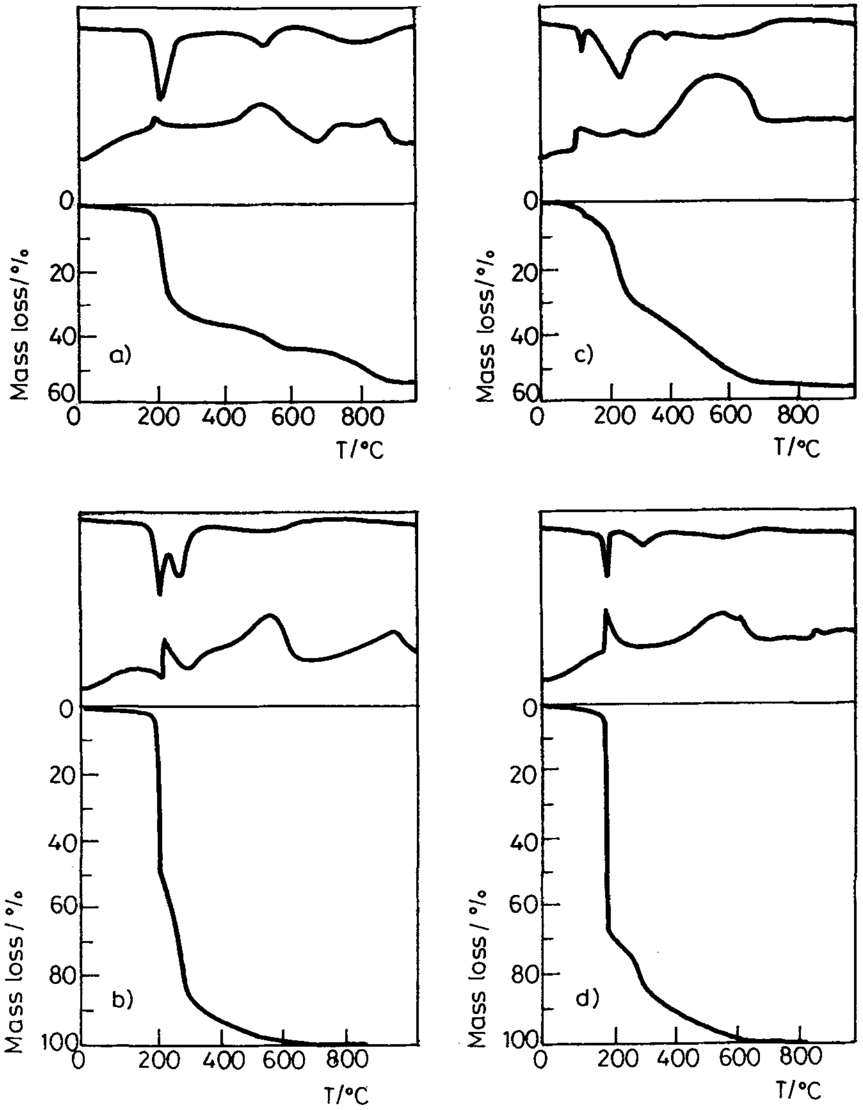

Fig. 1 Thermal analysis curves: a, silver(I) anthranilate; b, mercury(I) anthranilate; c, silver(I) salicyloaldoximate; d, mercury(I) salicyloaldoximate

Table 2 Results of sinters analysis

Compound	Stage	T°/C	Mass loss /%		Content determined /%			
			on TG	obtained	C	H	N	M
$[C_6H_4(NH_2)COO]Ag$	I	280	32.0	32.1	23.7	1.4	4.6	60.5
				28.3*	23.9*	1.4*	4.0*	61.5*
	II	590	43.0	43.0	4.2	–	–	78.0
				43.5**	4.3**	–	–	78.2**
	III	860	56.0	56.2	–	–	–	98.9
$[C_6H_4(NH_2)COO]_2Hg_2$	I	210	50.0	50.3	43.7	1.1	4.7	32.8
	II	300	85.0	85.0	58.8	1.2	5.6	86.6
	III			the sample volatilizes completely				
$[C_6H_4(CHNOH)O]Ag$	I	120	2.8	3.0	–	–	–	45.5
	II	220	26.0	26.6	23.8	1.4	4.0	61.8
				28.3***	23.9***	1.4***	4.0***	61.5***
	III	650	56.0	56.6	–	–	–	98.9
$[C_6H_4(CHNOH)O]_2Hg_2$	I	180	67.0	66.7	62.0	1.8	5.5	23.3
	II	320	86.0	85.3	71.8	2.5	8.3	13.6
	III			the sample volatilizes completely				

The values with signs correspond with theoretical loss of mass and content of elements when * $[C_6H_4(NH)COO]Ag_2$, ** Ag_2CO_3, *** $[C_6H_4(CHNO)O]Ag_2$ are formed.

Diffractometric analysis

X-ray tests were carried out on a DRON-1 diffractometer, using CuK$_\alpha$ radiation with a nickel filter. The intensities of rays reflected by the crystals were recorded in the 2Θ angle range 2 to 70°C. The results obtained for silver anthranilate sinters are presented in Table 3. Similar results were obtained for silver salicyloaldoximate sinters.

Table 3 Results of X-ray analysis of Ag(I) anthranilates sinters

Sinter			Silver	
d/n (experimental data)			*d/n* (literature data)	I
280°C	590°C	860°C		
2.350	2.360	2.350	2.350	90
2.040	2.040	2.035	2.040	50
1.440	1.440	1.439	1.440	40
1.231	1.232	1.227	1.228	60
1.180	1.179	1.178	1.176	20

Discussion and conclusions

Silver(I) and mercury(I) anthranilates

The spectra of Ag(I) and Hg(I) anthranilates are different from the spectrum of the free acid [6] in the range 3500–3100 cm^{-1} as regards the NH_2 group vibrations, and in the range 1670–1300 cm^{-1} as regards the vibrations of the COOH group and the COO^- ion. In the spectrum of the silver compound, the NH_2 group bands are shifted by about 50 cm^{-1} towards lower frequencies and occur at 3428 cm^{-1} and 3324 cm^{-1}. Their intensity is lower, and a new band appears at 3124 cm^{-1}, which is not present in the spectra of other univalent metal salts [4]. Similar differences are observed in this range in the band structure of compounds of transition metals with alanine (Fig. 2).

In the spectrum of mercury(I) anthranilate, the NH_2 group bands occur in the lower frequency range as a single wide band with two maxima at 3200–3030 cm^{-1}. In the second of the interesting ranges for both compounds, the intense band of valency vibrations of the carboxyl group disappears [1672 cm^{-1} (ν_{as})] whereas the ν_{as} and ν_s vibrations bands of the carboxylate ion appear at 1542 and 1360 cm^{-1} for the Ag(I) compound, and at 1512 and 1364 cm^{-1} for the Hg(I) compound. Analogous changes are observed in the spectra of other metal compounds [6]. It was accepted on the basis of the IR spectra that the silver(I) and mercury(I) ions react with the amine and the carboxyl group of anthranillic acid and form complex compounds $[C_6H_4(NH_2)COO]Ag$ and $[C_6H_4(NH_2)COO]_2Hg_2$.

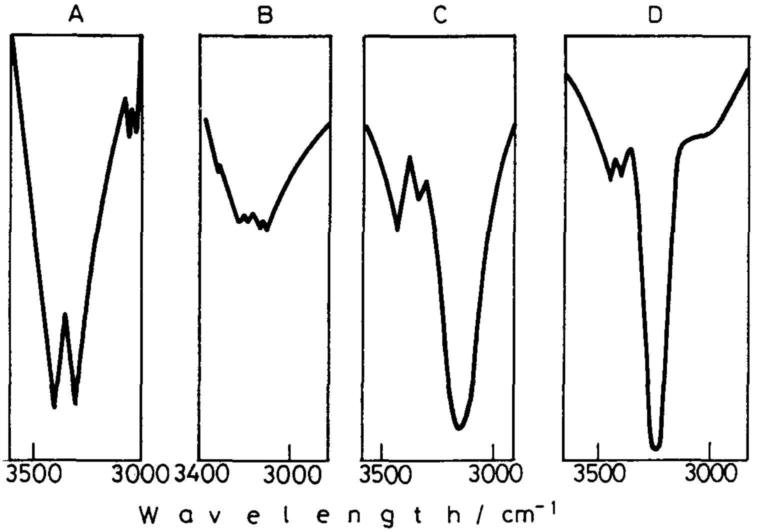

Fig. 2 The NH_2 group bands in the 3500–3000 cm^{-1} region: A, potassium anthranilate; B, mercury(I) anthranilate; C, silver(I) anthranilate; D di-(DL-α-alanino)-nickel(II)

Silver anthranilate undergoes thermal decomposition in three stages in the temperature range 190–860°C (Fig. 1a). The mass losses in the TG curve correspond to exothermic peaks in the DTA curve. They result mainly from the combustion of the organic fragments of the heated compound and obscure other thermal effects connected with the transformation. The rate of reaction is highest in the first stage, while the third stage is the slowest. At the temperatures determined on the basis of the TG curve, sinters were prepared. The mass losses and chemical analysis indicate that, in the first stage of decomposition, a dimetallic compound $[C_6H_4(NH)COO]Ag_2$ is formed, while in the second stage Ag_2CO_3 is formed, as was the case in the decomposition of alkali metal salicylates [3]. However, the heterogeneity of the sample, the IR spectral analysis and the X-ray analysis (Table 3) do not confirm this conclusion. The IR spectra of the sinters obtained at each stage of decomposition do not exhibit bands. Transmission over the whole range of analysed remains at approximately the same level of about 50%, and the only peaks observed in the diffraction patterns of the sinters are characteristic of metallic silver. In the sinters of the first and second stages, fragments of decomposed ligand are present besides metallic silver, and pure silver is the product of the third stage of decomposition.

Mercury(I) anthranilate decomposes in three stages (Fig. 1b) over the temperature range 150–590°C. The first two stages are rapid, overlapping processes, while the third is slow and results in complete volatilization of the sample. Four peaks are observed in the DTA curve: one endothermic peak, at 190°C, and three exothermic ones, at 210, 390 and 560°C. The endothermic peak is probably connected with the reduction of mercury and decomposition of the compound (the sinter obtained at this temperature is a black powder). The loss in mass and the chemical analysis of sinters (Table 2) indicate that both mercury and ligand fragments volatilize in the course of decomposition. The proportional content of metal in the sinter decreases, while those of carbon and nitrogen rise (compared with the composition of the sample before heating), and the metal volatilizes faster. No definite formula can be attributed to the sinters on the basis of the chemical analysis. The changes in the IR spectra indicate destruction of the ligand and X-ray analysis shows that the successive sinters are amorphous materials.

Silver(I) and mercury(I) salicyloaldoximates

In the IR spectra of the compounds formed by Ag(I) and Hg(I) with salicyloaldoximate, the range analysed related to the valence vibrations of two OH groups, phenol and oxime, and the C=N–O group. The OH groups of salicyloaldoximate involved in hydrogen-bonds produce a very intense band at 3380 cm^{-1} [7]. This band is entirely absent from the spectrum of silver salicyloaldoximate, while in the spectrum of the mercury compound a very broad band of slight intensity is observed at 3300–2900 cm^{-1}. Similar changes were observed in the case of divalent metals and accounted for by the formation of a bond between the metal and the oxygen of the phenol group, and also by the fact that the oxime group was involved in hydrogen-bonds of different strengths, depending on the structure of the complex being formed [7]. The C=N–O group, where the nitrogen atom forms a coordination bond with the metal, produces a number of bonds in the spectrum of the free ligand [7] and its salts [5]. The interpretation of the changes in the spectrum as concerns metal-ligand bond formation is not so explicit as in the case of the metal-anthranilate ion bonds. It was accepted that the changes observed in the range 1000–900 cm^{-1} may indicate the formation of bonds between Ag(I) or Hg(I) and the nitrogen atom of the C=N–O group. In this range, free salicyloaldoxime produces two intensive bands at 992 cm^{-1} and 900 cm^{-1} and a third band, of medium intensity, at 960 cm^{-1}. The spectrum is similar in the case of alkali metal salts [5]. One intensive band at 968 cm^{-1} is observed for the silver compound, while for the mercury compound there is an intense band at 1000 cm^{-1} and a weak one at 928 cm^{-1}. On the basis of the described changes in the IR spectra, it was accepted that, as in the case of the anthranilates, the salicyloaldoximates of silver(I) and mercury(I) are complex compounds, and the bonds are formed between the metal ion and the phenol and oxime group: $[C_6H_4(CHNOH)O]Ag$ and $[C_6H_4(CHNOH)O]_2Hg_2$.

The thermal decomposition of silver salicyloaldoximate proceeds in three stages in the temperature range 70–650°C (Fig. 1c). The first stage involves a slight mass loss, at first slow and then rapid. It corresponds to the exothermic peak at 130°C and a sharp peak in the DTG curve (120°C). The next two stages of decomposition are also exothermic processes. The exothermic peaks at 220 and 550°C are related to mass loss in the TG curve. The endothermic peak at 960°C, similarly to that in the DTA curve of Ag(I) anthranilate, corresponds to the melting of silver. In the first stage of decomposition, the white silver compound becomes darker and changes its consistency. Only the content of silver was determined in it (Table 2). The mass loss and chemical analysis of the product of the second stage of decomposition indicate the formation of $[C_6H_4(CHNO)O]Ag_2$, but this is not confirmed by the IR and X-ray analyses. The IR spectrum is analogous to that of silver anthranilate sinters. Transmission in the range examined is maintained at a constant level of about 50%. The diffraction pattern of the sinter demonstrates the presence of metallic silver. Thus, the sample contains the metal and solid fragments of decomposition of the ligand. The product of the third stage of decomposition is pure silver (Table 2).

The thermal decomposition of mercury salicyloaldoximate is also a three-stage process, taking place in the temperature range 120–640°C (Fig. 1d). The first stage ends at 200°C. It is a rapid exothermic process, corresponding to sharp peaks at 180°C in the DTG and DTA curves. The following reactions are much slower. The second and third stages of decomposition correspond to a broad exothermic peak with two maxima, at 540 and 620°C. The determined mass losses and chemical composition of the sinters do not allow definite formulas to be attributed to the decomposition products. The results obtained indicate that the proportional content of mercury in the successive sinters decreases, while the amounts of carbon and nitrogen increase (Tables 1 and 2). Mercury volatilizes from the sample faster than the ligand fragments. IR spectral analysis shows that the destruction of the ligand occurs even in the first stage of decomposition, and X-ray tests confirm that the products of all stages are amorphous materials. Analysis of the solid decomposition products showed that the course of the decomposition is determined by the character of the metal. As the temperature rises, Ag^+ and Hg_2^{2+} ions, which have low stability, are transformed to the metallic state. Their reduction is followed by decomposition of the ligand. X-ray analysis of the silver compound sinters confirms the presence of metallic silver in the products at all stages of decomposition. The absence of bands from the IR spectrum indicates that the ligand is decomposed and that the spectral bands are damped by the free metal, which does not exhibit IR absorption [12].

The essential process in the decomposition on the mercury(I) compounds is the reduction of Hg_2^{2+} ion to metallic mercury rather than disproportionation. Analysis of the decomposition products does not indicate the presence of Hg(II) compounds in the sinters (X-ray and IR analyses).

The thermal decompositions of silver(I) and mercury(I) anthranilates and salicyloaldoximates take a different course from the decompositions of analogous compounds of other univalent metals, e.g. alkali metals [4, 5]; the thermal stabilities of these compounds are different. Alkali metal anthranilates are much more stable: for sodium anthranilate, $T_{\alpha=0.01} = 290°C$ [4]*. The most stable of the compounds under study is silver anthranilate ($T_{\alpha=0.01} = 190°C$) and the least stable is silver salicyloaldoximate ($T_{\alpha=0.01} = 70°C$). The thermal stabilities of the two mercury(I) compounds are similar ($T_{\alpha=0.01} = 150$ and 135°C for the anthranilate and salicyloaldoximate, respectively).

It is noteworthy that, in the process of decomposition of the silver compounds, a sinter appears with a metal to ligand ratio of 2:1. However, it is not a chemical compound. Compounds with this composition, but with definite structure, appear in the first stage of decomposition of alkali metal salicylates [3], e.g.:

$$2\,[C_6H_4(OH)COO]Na \rightarrow [C_6H_4(O)COO]Na_2 + C_6H_4(OH)COOH \qquad (1)$$

The decompositions of the salts of alkaline earth metals and some complexes of heavy metals proceed is a similar manner [10–12], e.g.:

$$[C_6H_4(NH_2)COO]_2Ca \rightarrow [C_6H_4(NH)COO]Ca + C_6H_4(NH_2)COOH \qquad (2)$$

In the case of some divalent metal compounds [10], as in the case of silver compounds, an intermediate compounds of the metal and ligand is not formed, but one molecule of free ligand is evolved, as in reaction (3):

$$[C_6H_4(NH_2)COO]_2Sn \rightarrow SnO + C_6H_4(NH_2)COOH+ \qquad \mathrm{W0J59}(3)$$
$$+\ \text{solid decomposition products of 1 ligand molecule}$$

In the whole series of analysed cases, the evolution of a ligand molecule from the compounds is observed, when intermediate metal–ligand compounds

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[*] Hydrated alkali metal salicyloaldoximates were obtained; dehydration and ligand decomposition are simultaneous.

are formed (reactions (1) and (2)), and when these compounds are destroyed (tin compounds reaction (3), and silver compound). The process itself depends to a small extent upon the character of the metal–ligand bond, which was suggested earlier [13]. It occurs both for the compounds of alkaline earth metals [1, 14], which form salts, and in the case of the complexes of transition metals [2, 10, 13, 15]. This problem requires further profound investigation.

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Zusammenfassung — Es wurde der thermische Zersetzungsprozeß von Silber(I)- und Quecksilber(I)-anthranylaten und -salicylaldoximaten untersucht. Zur Untersuchung des Zersetzungsmechanismus dieser Komplexe wurden eine thermische, eine chemische und eine Röntgenanalyse ausgeführt. Derjenige Faktor, der die Zersetzung bestimmt, ist der Charakter der Ag^{+}- bzw. Hg_2^{2+}-Ionen, die schnell zu freien Metallen reduziert werden. Das Reaktionsendprodukt der Silberverbindung ist reines Metall; die Quecksilberverbindungen wurden beim Erhitzen vollständig verflüchtigt.