INVESTIGATION OF THERMAL DECOMPOSITION OF ANTHRANILATES OF ALKALI METALS

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The thermal properties of the anthranilates of the alkali metals Li, Na, K, Rb and Cs were studied. Thermal, chemical and X-ray analyses and infrared spectroscopy were used to determine the reactions of decomposition of these compounds. The thermal properties of the anthranilates of the alkali metals were compared with those of other metals.

Introduction

Thermal investigations of a number of complexes and salts of divalent metals with ligands forming chelate rings revealed that the first stage of decomposition involved the transformation of the di compounds into the mono compounds according to reaction (1):
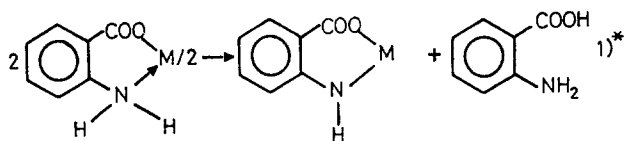

where *M* is a divalent metal ion.*

This decomposition course was observed for the Ni(II), Fe(II), Co(II), Mn(II), Zn(II), Cd(II) and Mg(II) complexes of salicylic acid [1, 2], the Zn(II) and Cd(II)

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*   In the case of different ligands, both *cis* and *trans* stuctures are possible.

complexes of anthranilic acid [3], the Zn(II) complex of 2-oxy-3-naphtalenic acid [2] and the Cd(II), Ni(II), Cu(II), Co(II), Zn(II), Mg(II) complexes of salicyloaldoxime [2, 4, 5] and the Ca, Sr and Ba salts of salicylic acid [6] and anthranilic acid [7].

It was interesting to investigate the decompositions of the salts of these ligands with alkali metals.

The decompositions of the salicylates of the alkali metals were studied by Wesolowski and Radecki [8]. They suggested that these compounds decomposed according to the reaction
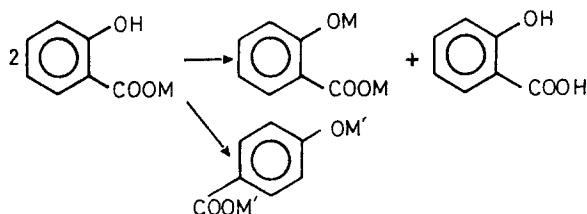
where M = Li, Na; M' = K, Rb, Cs.

The first decomposition stage leads to the formation of dimetal salicylates.

The present paper deals with an analysis of the thermal decompositions of alkali metal anthranilates.

Experimental

The analytically pure compounds Li_2CO_3, NaOH, KOH (POCh-Gliwice), Rb_2CO_3 (E. Merck) and $Cs_2CO_3 \cdot 2H_2O$ (Hopkin and Williams, Chadwell) were used without further purification. Anthranilic acid (Eastman) was purified by crystallization from hot water with the addition of active carbon. Metal anthranilates were obtained by treating anthranilic acid with a stoichiometric quantity of the appropriate metal carbonate or hydroxide. The reactions were carried out in aqueous solution at room temperature. The crude products were isolated by partial evaporation of the water, followed by crystallization from acetone.

The sodium and potassium salts were dried in air, while the lithium, rubidium and caesium salts were dried over $CaCl_2$ in a desiccator. Under these conditions, anhydrous lithium and caesium salts, and hydrated sodium, potassium and rubidium salts were obtained. The elemental analysis results are given in Table 1.

The elemental analysis data and the TG curves indicate that sodium anthranilate crystallizes with half a molecule of water, and the potassium and rubidium salts with one molecule of water.

Table 1 Results of elemental analysis of anthranilates of alkali metals

Compound	Calc. / %			Found / %		
	C	N	H	C	N	H
LiA	58.8	9.8	4.2	59.0	9.5	4.4
NaA·½H₂O	50.0	8.3	4.2	49.8	8.3	4.7
NaA	52.0	8.9	4.7	52.8	8.8	3.8
KA·H₂O	43.5	7.3	4.2	43.8	8.1	4.5
KA·(1-x)H₂O*	47.7	7.9	3.4	46.3	7.8	4.7
RbA·H₂O	35.1	5.8	3.3	36.4	5.7	3.6
RbA	37.9	6.3	2.7	37.8	5.7	2.8
CaA	31.1	5.2	2.2	31.5	5.7	2.3

*Calculated for the anhydrous compound

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 5 deg·min^{-1} in air. Galvanometer sensitivities for the respective curves were: DTA 1/10, DTG 1/10, TG 100. The standard substance was α-Al₂O₃. The samples weighed 100 mg each.

Investigation of sinters

Sinters were obtained under conditions similar to those of the thermal analyses. The TG curves were used to choose the temperatures at which the sinters were obtained.

Mass losses were determined for each decomposition stage and elemental analysis of the sinters was carried out. The results are given in Tables 1 (anhydrous salts), 2 and 3. Decomposition products occurring at temperatures above 850 °C were not analysed. Those compounds melted into both porcelain and corundum crucibles.

Infrared spectrophotometric analysis

The infrared spectra of the anthranilates and their sinters were taken on a Specord 80 spectrophotometer in the range 4000–200 cm^{-1}. Samples were prepared as pills in KBr. Changes in the region 3500–3300 cm^{-1}, corresponding to the valence vibrations of the NH₂ group, and in the region 1670–1370 cm^{-1}, corresponding to the vibrations of the COOH group, were analysed [9] (Table 4).

Table 2 The temperature and mass loss of sinters of anthranilates

Compound	Decom. stage	Temp. / °C	Formula	Mass loss Calc. / %	Mass loss Found / %
LiA	I	530	$Li_2CO_3 + C_xH_yN_zO_k{}^*$		64.0
	II	680	Li_2CO_3	74.0	71.0
$NaA \cdot \frac{1}{2}H_2O$	I	185	NaA	5.4	5.3
	II	515	$Na_2CO_3 + C_xH_yN_zO_k$		46.8
	III	850	Na_2CO_3	68.5	68.0
$KA \cdot H_2O$	I	165	KA	9.4	7.6
	II	560	$K_2CO_3 + C_xH_yN_zO_k$		52.6
	III	700	K_2CO_3	63.9	66.0
$RbA \cdot H_2O$	I	240	RbA	7.5	7.0
	II	530	$Rb_2CO_3 + C_xH_yN_zO_k$		43.3
	III	700	Rb_2CO_3	51.1	51.8
CsA	I	520	$Cs_2CO_3 + C_xH_yN_zO_k$		33.7
	II	640	Cs_2CO_3	41.4	40.5

*x, y, z, k – different values in the case of different compounds

Table 3 Results of elemental analysis of the sinters of the first stage decomposition of LiA and CsA the second stage of $NaA \cdot \frac{1}{2}H_2O$, $KA \cdot H_2O$, $RbA \cdot H_2O$

Compound	Temp. / °C	Found / % $C_{(x)}$	Found / % $N_{(y)}$	Found / % $H_{(z)}$
LiA	530	31.0	4.1	1.8
$NaA \cdot \frac{1}{2}H_2O$	515	37.1	5.8	1.7
$KaA \cdot H_2O$	560	23.1	1.9	2.3
$RbA \cdot H_2O$	525	19.5	1.1	2.0
CsA	520	14.2	2.5	2.1

In the salt spectra, slight shifts in the NH_2 group bands were observed, in the direction of lower frequencies in comparison with the positions of these bands for the acid (the largest for the lithium salt: 77 and 96 cm^{-1}, Table 4).

For the anthranilic acid compounds with transition metals, when coordinate bonds are formed the shift in the bands of the NH_2 group is about 150-200 cm^{-1} [9].

Table 4 Frequencies of absorption bands of NH_2 and COO^- groups of anthranilic acid and its compounds

Freq. / cm^{-1}	HA	LiA	NaA·½H₂O*	KA·H₂O*	RbA·H₂O	RbA	CsA
as (NH₂)	3472	3395	3440; 3408	3432	3448	3424	3448
s (NH₂)	3376	3280	3328	3328	3312	3304	3312
C=O	1672						
as (COO⁻)		1535	1532	1532	1532	1520	1532
		1510	1512	1512	1512		1508
s (COO⁻)		1398	1392	1384	1372	1384; 1364	1372

* The bands of the groups mentioned have the same position in the case of the salts of NaA and KA·xH₂O $(x < 1)$

Thus, for the alkali metal salts, analogously to the Ca, Sr and Ba salts [7], the influence of the metal ion on the NH_2 group is not significant. In the second of the investigated regions, valence vibration bands of the carboxyl group and the carboxylate ion occur. In the salt spectrum, the 1672 cm^{-1} band disappears altogether, but other bands appear, with frequencies corresponding to symmetrical and antisymmetrical vibrations of two carbon-oxygen bands (Table 4).

The observed changes point to the formation of an ionic metal-carboxylate ion bond. Analogous changes have been observed for the salts and complexes of other metals [9, 10]. There is no difference between the IR spectra of the hydrated and the anhydrous sodium and potassium salts. The bands of the vibrations of the NH_2 and COO^- groups appear at the same frequencies and exhibit similar widths and intensities. The spectrum of the anhydrous rubidium salt shows changes in relation to the spectrum of the hydrated compound. The bands of the NH_2 group are shifted towards lower frequencies (Table 4), and their intensity and sharpness are decreased considerably. In place of the doublet at 1532 and 1512 cm^{-1}, corresponding to asymmetrical vibrations of the COO^- group, a single 1520 cm^{-1} band appears, whereas the 1372 cm^{-1} band is shifted towards higher frequencies and its structure is changed (Table 4). Comparison of the spectra of all the analysed anthranilates obtained above 500 °C (Table 2) shows that they are the spectra of the corresponding carbonates [11].

X-ray analysis of the sinters

X-ray tests were carried out on a DRON-1 diffractometer, using CuK_α radiation, with a nickel filter. The intensities of rays reflected by the crystals were recorded in the 2θ angle range $2°–70°C$.
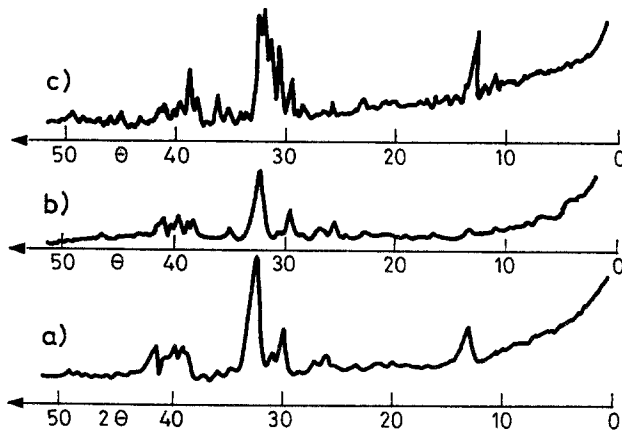
Fig. 1 X-ray analysis of potassium carbonate (a) and of sinters of potassium anthranilate (b, c)

In the diffractograms of lithium anthranilate sinters (560°, 680 °C) and sodium anthranilate sinters (518°, 860 °C), peaks characteristic of the corresponding carbonates were found [12]. The diffractograms of potassium anthranilate sinters differed from the literature data [12]. With the aim of identification, a diffractogram of analytically pure K_2CO_3 (POCh, Gliwice) was obtained. The diffractogram of a sinter obtained at 570 °C differed from the former only in respect of the intensities of the peaks, but for a sinter obtained at 700 °C new peaks appeared
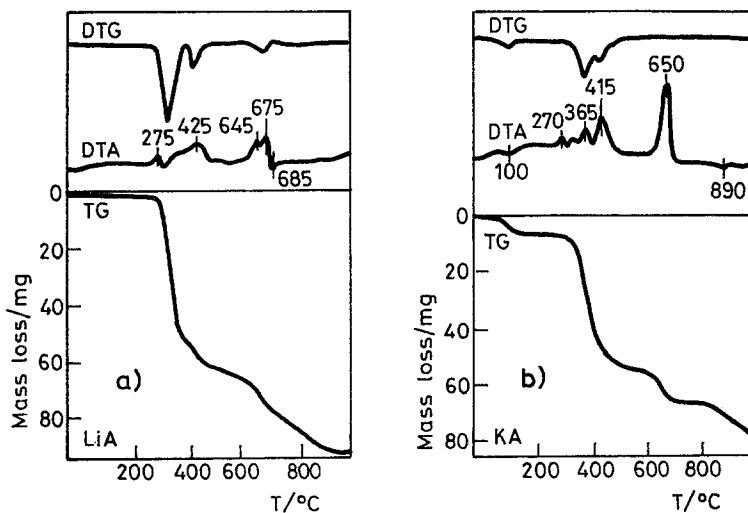

Fig. 2 Thermal curve: a - lithium anthranilate, b-potassium anthranilate

(Fig. 1). The differences may be due to different degrees of hydration of highly hygroscopic potassium carbonate [13]. (The mass loss and determined carbon content, $c_{calc.} = 8.6\%$, $c_{found} = 8.7\%$, point to the presence of K_2CO_3.)

Due to the high hygroscopicity of the compounds obtained, the diffractograms of RbA and CsA sinters turned out not to be helpful in the interpretation.

Results and discussion

Analysis of the TG curves indicates that the thermal decompositions of the lithium, sodium and caesium salts are three-stage processes, whereas the potassium and rubidium salts are decomposed in four stages. Thermal curves for the lithium and potassium compounds are shown in Fig. 2.

Dehydration of the hydrated anthranilates is the first decomposition stage. This process is not completed for the potassium compound. Loss of the water molecule from KA *· H_2O corresponds to a mass loss of 9.4%. The mass loss read from the TG curve is 7% (sinter 165 °C). The remaining water is removed together with fragments of the organic anion. Dehydration of the salts occurs in different ranges of temperatures. Rubidium anthranilate loses water most easily (40°–90 °C); next is potassium anthranilate (70°–140 °C), while the process is most difficult for the sodium compound (115°–170 °C).

The large differences in the temperature at which dehydration begins, the differences in the IR spectra of the hydrated and anhydrous rubidium salts and the lack of changes in the spectra of NaA·0.5H_2O and NaA all suggest that the water may be bound in different ways in these two salts. It was assumed that in the rubidium salt it is outer sphere water, whereas in the sodium salt it is inner sphere water. This conclusion is supported by the fact that rubidium salts crystallizing from aqueous solution do not contain crystallization water bound to the cation, whereas sodium salts may contain it [14].

All the anhydrous anthranilates decompose into the respective carbonates during the subsequent stage. This is indicated by the IR spectra [11], and also, in certain cases, by the results of diffractometric analysis.
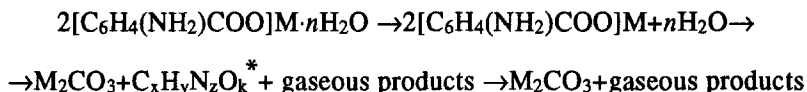
However, the results of elemental analysis and the observed mass losses (Tables 2 and 3) show that stable fragments of the decomposed anion remain in the sinters. They volatilize in the subsequent stage of decomposition, and pure carbonates are formed, as demonstrated by the calculated mass losses (Table 2), the determined contents of carbon and the IR spectra. Diffractometric analysis confirms these conclusions as related to LiA (680 °C) and NaA (860 °C) sinters.

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* $A = C_6H_4(NH_2)COO^-$

Salts heated to 1000 °C decompose further. The decomposition products were not examined as they melt into both porcelain and corundum crucibles.

On the basis of the above data, the thermal decompositions of the analysed anthranilates can be presented as follows:

$$2[C_6H_4(NH_2)COO]M \cdot nH_2O \rightarrow 2[C_6H_4(NH_2)COO]M + nH_2O \rightarrow$$

$$\rightarrow M_2CO_3 + C_xH_yN_zO_k{}^* + \text{gaseous products} \rightarrow M_2CO_3 + \text{gaseous products}$$

where M = metal ion, $n = 0$, 1/2, 1.

The courses of the DTA curves for all the analysed compounds indicate that for the hydrated salts, the first reaction is endothermic, while the following reactions are exothermic, which is a result of combustion of decomposition products of the organic ligand.

The last small peaks in the DTA curves are endothermic. They are connected with the melting and decomposition of carbonates. The temperatures ($T_\alpha = 0.01$ at which the decompositions of LiA, NaA, KA, RbA and CsA start are similar: 280°, 300°, 295°, 290° and 290 °C, respectively. The temperatures of decomposition of the anthranilates of alkaline earth metals are higher: 325°, 350° and 330 °C for CaA$_2$, SrA$_2$ and BaA$_2$, respectively [7], and for the anthranilates of heavy metals they are similar or lower (ZnA$_2$ - 300 °C, CdA$_2$ - 290 °C, MgA$_2$ - 160 °C, PbA$_2$ - 240 °C and SnA$_2$ - 200 °C) [3].

Sharp bends in the TG curves of the anthranilates of the alkali metals allow determination of the temperatures at which the pure carbonates are formed (Fig. 2):

840°, 670°, 650° and 640 °C for the carbonates of sodium, potassium, rubidium and caesium. Thus, the larger the ionic radius of the metal, the lower the temperature of formation of the pure carbonate. During a study of the thermal decomposition of the anthranilates of calcium, strontium and barium, analogous conclusions were drawn [7].

The temperature of pure Li$_2$CO$_3$ formation (680 °C) is also the temperature at which the sinter was obtained (only an inflection was noted in the TG curve, Fig. 2) and it does not fit into the series formed by the remaining alkali metals. This dissimilarity may result from differences between the lithium ion and the ions of the remaining alkali metals in this group as concerns the structure of the external electronic shell.

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* x, z, z, k = different values for the different compounds.

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Zusammenfassung — Es wurden die thermischen Eigenschaften von Anthranylaten der Alkalimetalle Li, Na, K, Rb und Cs untersucht. Zur Bestimmung der Zersetzungsreaktionen dieser Verbindungen wurde eine thermische, chemische und röntgenografische Analyse sowie IR-Spektroskopie angewendet. Die Eigenschaften der Alkalimetallanthranylate wurden mit denen von anderen Materialien verglichen.