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INVESTIGATION OF THERMAL DECOMPOSITION OF ANTHRANILATES OF ALKALINE EARTH METALS

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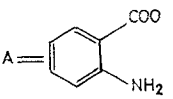
The thermal properties of calcium, strontium and barium anthranilates (general formula $MA_2 \cdot n H_2O$, where M = metal, and A = ) were studied. Thermal, chemical and X-ray analysis, as well as infrared spectra, were used to determine the mechanism of decomposition for these compounds. Calcium anthranilate is decomposed in four stages; the final reaction product is calcium oxide. The other anthranilates are decomposed in three stages; the final reaction products are strontium carbonate and barium carbonate.

Calcium, strontium and barium form salts with anthranilic acid. The compounds contain two molecules of the acid per metal ion. Infra-red tests have shown that an ionic bond is formed between the carboxyl group and the metal ion, whereas the amine group does not form a bond [1]. Thermal investigations of anthranilates of some heavy metals were carried out by Lumme [2], who found that anthranilates are decomposed in two or three stages, the end-products being oxides or metals. The thermal stability of the compounds analyzed gradually in the sequence $ZnA_2 > NiA_2 > CdA_2 > CoA_2 > CuA_2 > PbA_2$. So far there are no data in the research sources concerning the thermal stability of anthranilates of light metals.

Experimental

Material

$BaCl_2 \cdot 2 H_2O$, $CaCl_2 \cdot 6 H_2O$ and $SrCl_2 \cdot 6 H_2O$ were analytically pure reagents from POCh Gliwice. Anthranilic acid (Eastman) was purified by crystallization from hot water with the addition of active carbon. Calcium, strontium and barium anthranilates were prepared as suggested by Hill and Curran [1]. The elemental analysis results are given in Table 1.

Table 1

Results of elemental analysis of anthranilates of alkaline earth metals

Compound	Calc., %			Found, %		
	C	H	N	C	H	N
$[C_6H_4(NH_2)COO]_2Ca \cdot H_2O$	50.9	4.2	8.5	50.4	4.2	9.0
$[C_6H_4(NH_2)COO]_2Sr \cdot \frac{1}{2} H_2O$	45.5	3.5	7.6	44.5	3.8	7.6
$[C_6H_4(NH_2)COO]_2Ba \cdot H_2O$	39.4	3.3	6.6	39.4	3.4	7.0

Thermal analysis

Thermal tests were carried out on an OD-102 derivatograph (MOM, Budapest). The temperature range was 20–1000°, with a heating rate of 10°/min in air. Galvanometer sensitivities for the respective curves were: DTA 1/10; DTG 1/10; TG 100.

The standard substance was α-Al_2O_3. The samples weighed 100 mg each. Thermal curves for barium anthranilate 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 with SiC heating components at 10°/min.

Table

Results of elemental analysis and

Compound	Decom. stage	Temp., °C	Formula
$[C_6H_4(NH_2)COO]_2Ca \cdot H_2O$	I	230	$[C_6H_4(NH_2)COO]_2Ca$
	II	400	$[C_6H_4(NH)COO]Ca$
	III	700	$CaCO_3$
	IV	960	CaO
$[C_6H_4(NH_2)COO]_2Sr \cdot \frac{1}{2} H_2O$	I	200	$[C_6H_4(NH_2)COO]_2Sr$
	II	400	$[C_6H_4(NH)COO]Sr$
	III	670	$SrCO_3$
$[C_6H_4(NH_2)COO]_2Ba \cdot H_2O$	I	230	$[C_6H_4(NH_2)COO]_2Ba$
	II	400	$[C_6H_4(NH)COO]Ba$
	III	630	$BaCO_3$

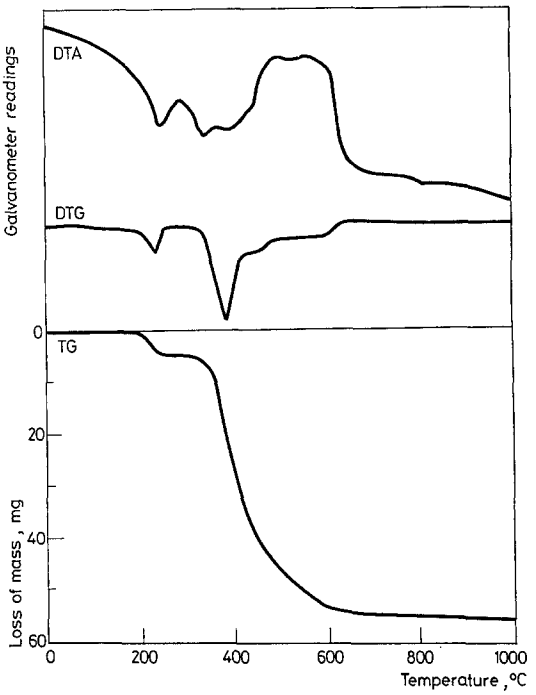


Fig. 1. Thermal analysis curves of barium anthranilate

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mass loss of sinters of anthranilates

Calc., %				Found, %			
mass loss	C	H	N	mass loss	C	H	N
5.4	53.7	3.8	9.0	4.6	52.7	4.0	9.2
41.2	47.6	2.9	8.0	45.0	43.4	2.9	6.5
69.9	12.0			69.5	11.8		
83.6				86.0			
2.4	46.8	3.3	7.8	2.3	46.0	3.1	7.7
37.9	37.7	2.3	6.3	39.0	35.3	2.4	5.9
59.7	8.2			60.0	8.3		
4.2	40.8	2.9	6.8	4.0	40.1	3.1	6.8
32.0	30.8	1.8	5.1	35.0	26.6	1.8	4.0
54.1	6.1			55.0	8.6		

The TG curves were used to choose the following temperatures at which the sinters would be obtained:

230, 400, 700 and 960° for the calcium compound, 200, 400, and 670° for the strontium compound, and 230, 400 and 630° for the barium compound. Mass losses were determined for each decomposition stage and elemental analysis of the sinters was carried out. The results are given in Table 2.

Spectrophotometric infra-red analysis

Infrared spectra were taken on a Spectromom 2000 spectrophotometer at $5000-700\ cm^{-1}$. Samples were prepared as pills in KBr. Spectra of calcium, strontium and barium anthranilates and of the sinters were taken. The spectra of the non-heated anthranilates and those of the respective sinters obtained at about 200° do not differ. They are the same as the spectra described by Hill and Curran [1]. The spectra obtained at 400° show some changes as compared to those of the non-heated anthranilates. All characteristic groups of bands do occur, however. The partly split band of the valence vibrations of the NH_2 group is shifted some 50 cm^{-1} in the region of 3400 cm^{-1} (the shift is not observed in the case of the strontium salt); the band is no longer split and its intensity is reduced.

In the region of $1600-1400\ cm^{-1}$, the bands attributed to C=C ring vibrations and to the antisymmetric COO^-s tretching vibration overlap more intensely. In the region of $900-700\ cm^{-1}$, some bands connected with out-of-plane deformation vibrations of the C–H bond and deformation vibrations of the NH_2 group have changed intensities. A comparison of the spectra of the sinters obtained from calcium, strontium and barium anthranilates at 700°, 670° and 630°, respectively, with literature data proves that they are the spectra of the carbonates. The spectrum of a sinter obtained by heating calcium anthranilate up to 960° showed the presence of calcium oxide [4].

X-ray analysis of the sinters

X-ray tests were carried out on a DRON-1 diffractometer, using $Cu-K_\alpha$ radiation with a nickel filter. The intensities of rays reflected by the crystals were recorded between 2 and 70° in the 2θ angle range. Diffractograms of non-heated compounds and of sinters were produced and compared with data given in the literature [5]. Carbonates of calcium, strontium or barium were found in sinters at 700°, 670° and 630°, respectively. Calcium oxide was present in sinters at 960°. Diffractograms of barium anthranilate and its sinter are shown in Fig. 2.

Results and discussion

The thermal curves indicate that the thermal decomposition of calcium anthranilate is split into 4 stages, whereas strontium and barium anthranilates are decomposed in 3 stages. Dehydration of the hydrated anthranilates is the first decomposition stage, which corresponds to a gradual mass loss in the TG curves

and to endothermic peaks in the DTA curves for calcium anthranilate (150°) and barium anthranilate (240°). No endothermic peak is observed in the case of hydrated strontium anthranilate; this may be due to the very small thermal effect accompanying the release of half a molecule of water. At about 330°, endothermic peaks without corresponding mass losses are observed in the DTA curves. They correspond to melting of the samples. The second decomposition stage then

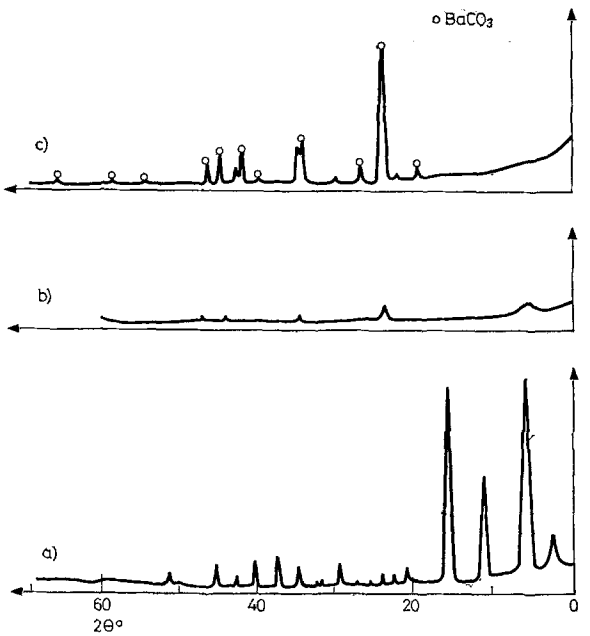
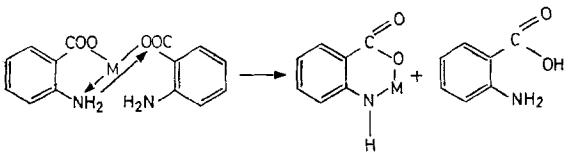


Fig. 2. X-ray analysis of barium anthranilate. a — before sintering, b — after sintering at 400°, c — after sintering at 630°

begins. Rapid mass losses are observed in the TG curves for calcium, strontium and barium anthranilates. The endothermic peaks are indicated at about 400° in the DTA curves. The determined mass losses and the results of elementary analysis of the sinters (Table 2) prove that the second decomposition stage leads to the formation of a compound with one acid molecule per metal ion. This conclusion is supported by the infra-red spectra of the sinters. The spectra of the sinters contain the same bands as those occurring in the spectra of the non-heated anthranilates. The aromatic structure is maintained. Changes in band positions and structures at about 3400 cm^{-1}, and changes in the intensities of some bands between 900 and 700 cm^{-1}, were attributed to substitution of NH for the NH_2 group, and subsequent bonding of the NH group with metal ion. There is no distinct transition from the second to the third decomposition stage, characterized by a continued, but slower, mass loss. The process is endothermic as concerns

the further decomposition of the anthranilates, and exothermic as concerns the partial combustion of the decomposition products. The data in Table 2, as well as the results of infrared spectra and X-ray analysis of the sinters, indicate the formation of carbonates. The decomposition of the strontium and barium salts ends at 670° and 630° respectively. The endothermic peaks observed at 945° and 830° in the DTA curves correspond to phase transformations of the respective carbonates formed in the decomposition [6]. The further heating of calcium anthranilate, however, causes a rapid mass loss on the TG curve up to 810°, with an endothermic peak at 795°. The decomposition product was found to contain calcium oxide. The results suggest the following decomposition mechanism:

1. $[C_6H_4(NH_2)COO]_2M \cdot nH_2O \longrightarrow [C_6H_4(NH_2)COO]_2M + nH_2O$

2. 

3. $[C_6H_4(NH)COO]M \xrightarrow{O_2} MCO_3 + \text{combustion products}$

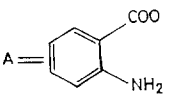
4. $MCO_3 \longrightarrow MO + CO_2$

The thermal curves were used to compare the thermal stabilities of the anthranilate monohydrates and the anhydrous anthranilates. Barium monohydrate is more stable than calcium monohydrate. The sequence of stabilities of the anhydrous anthranilates is Ca < Sr < Ba. The conclusion is that the stability of the salts increases with increase in the metal ion radius. The TG curves were used to determine the temperatures at which the carbonates were formed. These temperatures follow the sequence Ba < Sr < Ca. A higher metal ion radius corresponds to a lower temperature of carbonate formation. Calcium carbonate exists only at 696–810° and subsequently decomposes to calcium oxide. Strontium and barium carbonates do not decompose within the investigated temperature range (up to 1000°), which proves their good thermal stability [6].

References

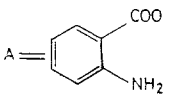
1. A. G. HILL and C. CURRAN, J. Phys. Chem., 64 (1960) 1519.
2. P. LUMME, Chem. Abstr., 55 (1961) 15 209a.
3. R. M. SILVERSTEIN and C. C. BASSLER, Spektroskopowe metody identyfikacji zwiazków organicznych, (Spectrometric Identification of Organic Compounds), PWN, Warszawa 1970.
4. R. A. NYGNIST and R. O. KAGEL, Infrared Spectra of Inorganic Compounds, Academic Press, New York 1971.
5. E. PRZYBORA, Rentgenostrukturalne metody identyfikacji mineralów i skal (X-ray Structural Identification of Minerals and Rocks), Wydawnictwo Geologiczne, Warszawa 1957.
6. A. BLAZEK, Thermal Analysis, Van Nostrand Reinhold Co., London 1973.

ZUSAMMENFASSUNG — Die thermischen Eigenschaften von Kalzium-, Strontium- und Bariumanthranilat (mit der allgemeinen Zusammensetzung

$MA_2 \cdot n\,H_2O$, M = Metall, A = 

wurden untersucht.
Die Zersetzungsmechanismen dieser Verbindungen wurden durch thermische, chemische- und Röntgenanalyse und mit Infrarotspektroskopie ermittelt. Kalziumanthranilat zersetzt sich in vier Stufen. Das Endprodukt ist Kalziumoxyd. Die anderen Anthranilate zersetzen sich in drei Stufen und geben Strontiumkarbonat und Bariumkarbonat als Endprodukt.

Резюме — Изучены термические свойства антранилатов кальция, стронция и бария общей формулы

$MA_2 \cdot nH_2O$, где M = металл, A = 

Термический, химический и рентгенографический анализы, а также ИК спектры были использованы для определения механизма реакции разложения этих соединений. Антранилат кальция разлагается в четыре стадии и конечным продуктом реакции является окись кальция. Другие антранилаты разлагаются в три стадии. Конечными продуктами реакции были карбонат стронция и карбонат бария.