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THERMAL ANALYSIS OF BINARY AND TERNARY SYSTEMS OF SALICYLIC ACID, SODIUM SALICYLATE AND SODIUM HYDROGEN CARBONATE

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The thermal decompositions of binary and ternary systems of salicylic acid, monosodium salicylate, disodium salicylate and sodium hydrogen carbonate were studied by thermogravimetry and differential thermal analysis. The possibility was shown of analyzing systems involving components which react with each other upon heat treatment. Use can be made of results of this work to follow the course and extent of the reaction employed in the commercial method of manufacturing sodium salicylate and to check declared compositions of salicylate mixtures.

The thermal decomposition of salicylates has been studied by Pirisi and Mattu [1, 2], Yasutake and co-workers [3, 4] and Radecki and co-workers [5, 7]. The objective of this work was to develop a procedure for following the course and extent of the commercial process of manufacturing sodium salicylate [8] and for analyzing mixtures containing salicylic acid and its salts.

Experimental

Materials

Pure, sublimed salicylic acid and AnalaR grade sodium hydrogen carbonate were used.

Monosodium and disodium salicylates were obtained by neutralizing an ethanolic and aqueous solution, respectively, of salicylic acid with a stoichiometric quantity of sodium hydrogen carbonate. The monosodium salt was crystallized from water. The disodium salt was additionally washed with 75° ethanol to remove excess of salicylic acid. The identity of the salts was confirmed by results of elemental analyses performed by a flash-combustion method [9].

Methods

Thermogravimetry was carried out in air using a Paulik—Paulik—Erdey (MOM, Budapest) Derivatograph [10]. Samples (200 mg) of powdered and intimately mixed components were analyzed. Decomposition was carried out in platinum crucibles at a rate of 5 deg/min up to 500°, using α-Al_2O_3 as reference material.

Results and discussion

Results are shown in Tables 1–3 and in Figs 1–8.

A general course of the thermal decomposition of the systems studied can be presented by the following reactions:

1. evaporation of $o\text{-}\mathrm{HOC_6H_4COOH}$
2. $\mathrm{2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O}$
3. $o\text{-}\mathrm{HOC_6H_4COOH + NaHCO_3} \rightarrow o\text{-}\mathrm{HOC_6H_4COONa + CO_2 + H_2O}$
4. $2o\text{-}\mathrm{HOC_6H_4COONa} \rightarrow o\text{-}\mathrm{NaOC_6H_4COONa} + o\text{-}\mathrm{HOC_6H_4COOH}$ subl.
5. $o\text{-}\mathrm{NaOC_6H_4COONa} \rightarrow \mathrm{1/2Na_2CO_3}$ + volatile products ($\mathrm{CO, CO_2, H_2O}$)
6. $o\text{-}\mathrm{NaOC_6H_4COONa} + o\text{-}\mathrm{HOC_6H_4COOH} \rightarrow 2o\text{-}\mathrm{HOC_6H_4COONa}$

Reactions (1–4) are endothermic, as shown by the DTA traces in Fig. 1. Reaction (1) is characterized by two peaks in the DTA trace. The first (120–190°) is due to melting of salicylic acid, and the other (190–250°) to its evaporation. Pirisi and Mattu [1] have found as many as four endothermic peaks and one exothermic one for this transformation. The peaks were ascribed to the melting of salicylic

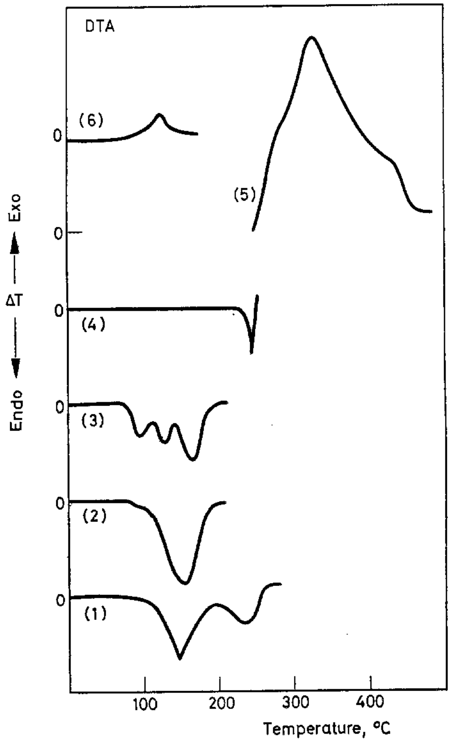

Fig. 1. DTA peaks corresponding to endothermic and exothermic reactions (1)–(6)

acid, formation of phenyl salicylate, phenol and xanthone, and to combustion of the compounds. We could not confirm these results, however.

A broad DTA peak over the range 80 – 190°, observed in reaction (2), is due to heat absorption by gaseous CO_2 and H_2O leaving the system.

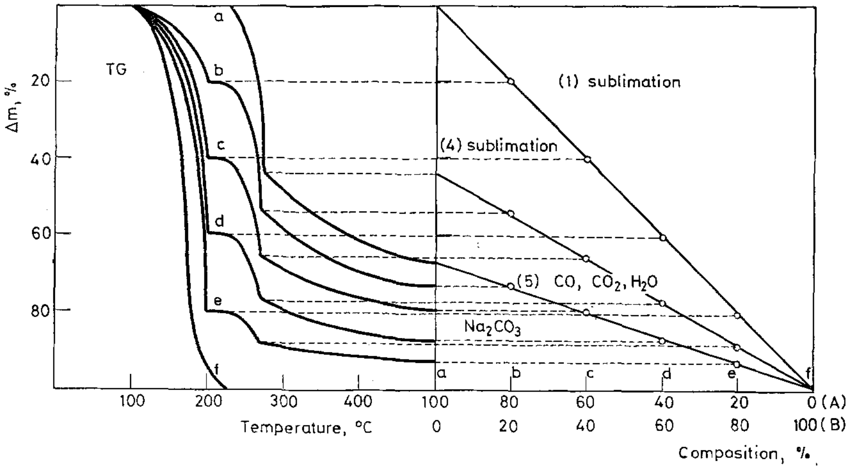

Fig. 2. Thermal decomposition of a mixture of sodium salicylate (A) and salicylic acid (B) (system I). Weight losses as a function of temperature (1) and composition (2)

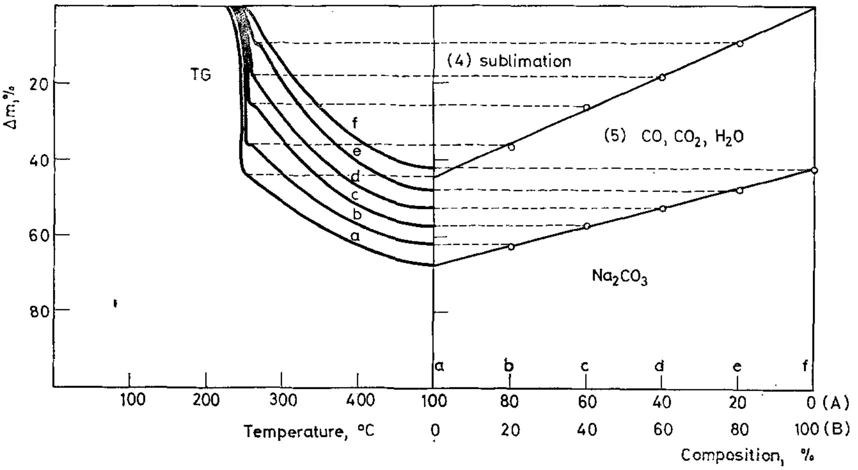

Fig. 3. Thermal decomposition of a mixture of monosodium (A) and disodium salicylates (B) (system II). Weight losses as a function of temperature (1) and composition (2). Decomposition of the monosodium salt obeys equations (4) and (5)

Three endothermic peaks in reaction (3) (Fig. 1, curve 3) are likely to be due to evolution of CO_2 and H_2O, as can be judged by their position over the same temperature range as that of the DTA peak in reaction (2). However, the peak is split

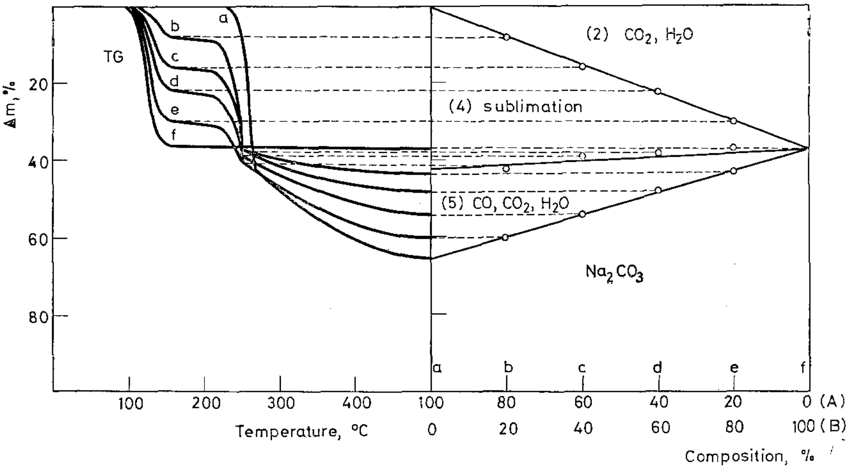

Fig. 4. Thermal decomposition of a system of sodium salicylate (A) and sodium hydrogen carbonate (B) (system III). Weight losses as a function of temperature (1) and composition (2). Decomposition of sodium hydrogen carbonate obeys equation (2), and that of sodium salicylate equations (4) and (5)

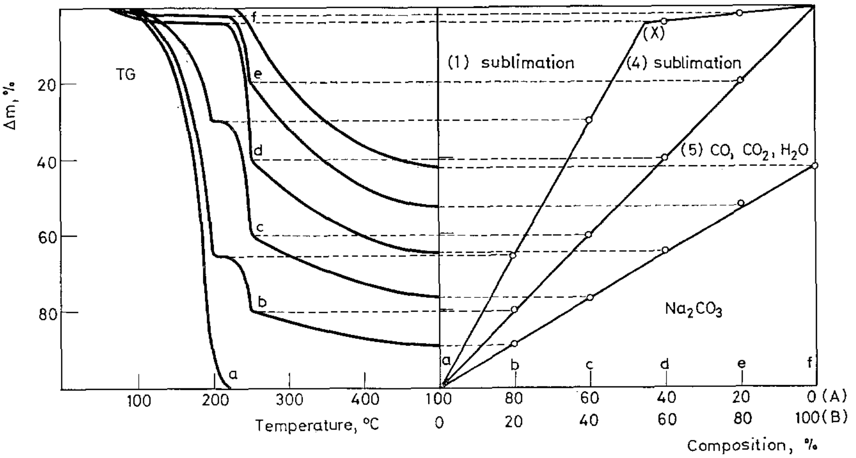

Fig. 5. Thermal decomposition of a system of salicylic acid (A) and disodium salicylate (B) (system IV). Weight losses as a function of temperature (1) and composition (2). Sublimation occurs of salicylic acid unreacted in reaction (6)

(×) Stoichiometric point of reaction (6). Decomposition of sodium salicylate obeys equations (4) and (5)

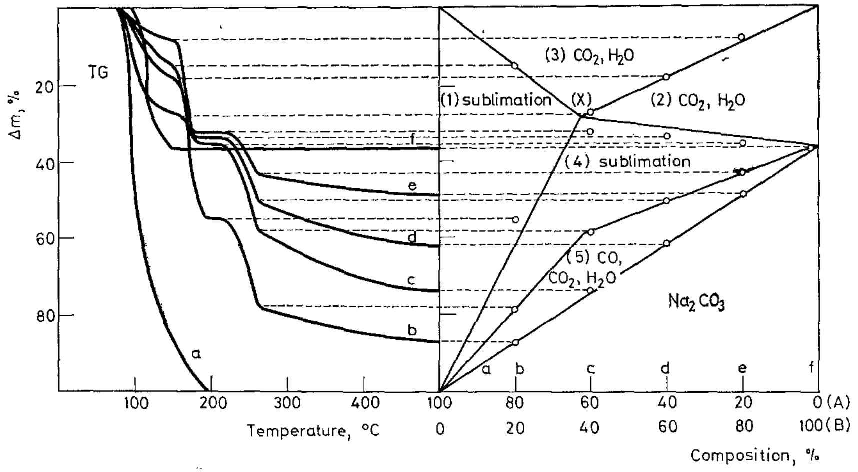

Fig. 6. Thermal decomposition of a system of salicylic acid (A) and sodium hydrogen carbonate (B) (system V). Weight losses as a function of temperature (1) and composition (2). Gaseous products follow reaction (3). Sublimation occurs of salicylic acid unreacted in reaction (3). Decomposition of sodium hydrogen carbonate unreacted in reaction (3) follows reaction (2)

(×) Stoichiometric point of reaction (3). Decomposition of sodium salicylate obeys equations (4) and (5)

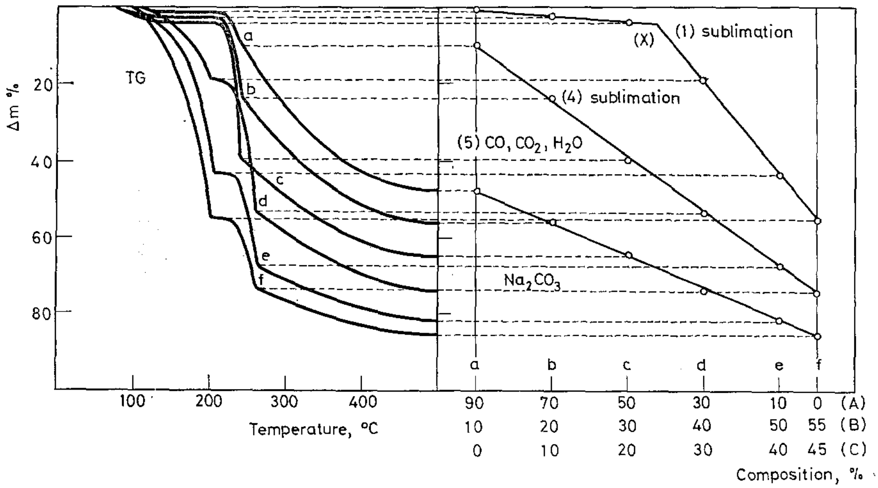

Fig. 7. Thermal decomposition of a system of disodium salicylate (A), salicylic acid (B) and monosodium salicylate (C) (system VI). Weight losses as a function of temperature (1) and composition (2). Sublimation occurs of salicylic acid unreacted in reaction (6)

(×) Stoichiometric point of reaction (6). Decomposition of sodium salicylate obeys equations (4) and (5) into three components, which is possibly due to simultaneous occurrence of an exothermic effect associated with the formation of sodium salicylate.

Reaction (4) is accompanied by a single endothermic effect occurring over the range 240–260° (curve 4). It is due to sublimation of salicylic acid.

Reaction (5) is exothermic, as shown by a broad DTA peak over the range 260–470° (curve 5). A small heat loss due to desorption of gases is overlapped by a strong exothermic effect due to partial combustion of organic matter.

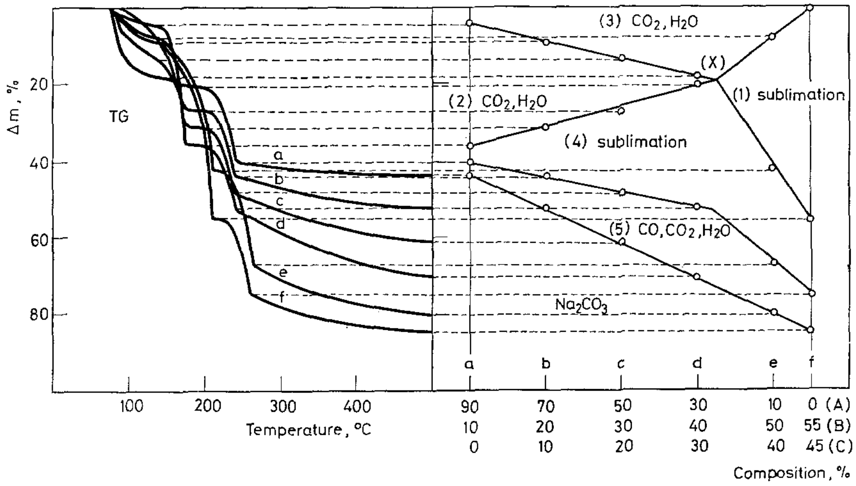

Fig. 8. Thermal decomposition of a system of sodium hydrogen carbonate (A), salicylic acid (B) and sodium salicylate (C) (system VII). Weight losses as a function of temperature (1) and composition (2). Gaseous products are formed according to equation (3). Decomposition of sodium hydrogen carbonate unreacted in reaction (3) follows equation (2). Sublimation occurs of salicylic acid unreacted in reaction (3)
(×) Stoichiometric point of reaction (3). Decomposition of sodium salicylate obeys equations (4) and (5)

Reaction (6) is accompanied by a weak exothermic effect (curve 6).

Inspection of results shown in Tables 1–3 and Figs 2–8 reveals some correlations between the contents of the individual components in a system and their thermal decomposition. A characteristic features of the systems studied is the reactivities of their components upon heating. This is exemplified by reactions (3) and (6), which afford sodium salicylate. Analysis of these reactions showed that in the latter, component (B) is completely consumed in systems IVb and c and VIa, b and c. Component (A) is consumed in systems IVd and e and VId and e, too. In reaction (3), components (B) and (A) are eliminated in systems Vb and VIIa, b, c and d, and in Vc, d and e and VIIe, respectively.

As a result of quantitative reactions occurring between individual components of the systems studied, the final thermal decomposition of the products proceeds according to equations [4] and [5].

Table 1

Results of thermogravimetric analyses of systems I—III, containing two non-interacting components

No.	System	Decompn. stage	Temp. range, °C	Residue in crucible	Composition of systems, %											
					a (*A*) 100 (*B*) 0		b 80 20		c 60 40		d 40 60		e 20 80		*f* 0 100	
					Weight loss, %											
					F.	C.	F.	C.	F.	C.	F.	C.	F.	C.	F.	C.
I	(A) Sodium salicylate (B) Salicylic acid	1.	100—220	$[C_6H_4(OH)COO]Na$	0.0	0.0	19.0	20.0	39.0	40.0	59.0	60.0	79.0	80.0	100.0	100.0
		2.	240—270	$[C_6H_4(O)COO]Na_2$	45.0	43.1	54.0	54.5	65.5	65.9	77.0	77.2	88.0	88.6	100.0	100.0
		3.	270—470	Na_2CO_3	67.5	66.9	72.5	73.5	79.0	80.1	86.5	86.8	92.0	93.4	100.0	100.0
II	(A) Sodium salicylate (B) Disodium salicylate	1.	240—260	$[C_6H_4(O)COO]Na_2$	45.0	43.1	36.0	34.5	26.0	25.9	18.0	17.3	9.5	8.6	0.0	0.0
		2.	260—470	Na_2CO_3	67.5	66.9	62.0	61.9	57.0	56.9	52.5	51.8	47.5	46.8	42.0	41.8
III	(A) Sodium salicylate (B) $NaHCO_3$	1.	100—150	$[C_6H_4(OH)COO]Na$ Na_2CO_3	0.0	0.0	8.0	7.4	16.0	14.8	22.0	22.2	30.0	29.5	37.0	36.9
		2.	220—250	$[C_6H_4(O)COO]Na_2$ Na_2CO_3	45.0	43.1	42.0	41.9	39.0	40.6	38.0	39.2	37.5	38.2	37.0	36.9
		3.	250—470	Na_2CO_3	67.5	66.9	60.0	60.9	54.0	54.9	48.0	48.9	43.0	42.9	37.0	36.9

F. — found, C. — calculated

Table 2

Results of thermogravimetric analyses of system IV—V, containing two interacting components

No.	System	Decompn. stage	Temp. range °C	Residue in crucible	Composition of systems, %											
					a (*A*) 100 (*B*) 0		b 80 20		c 60 40		d 40 60		e 20 80		f 0 100	
					Weight loss, %											
					F.	C.	F.	C.	F.	C.	F.	C.	F.	C.	F.	C.
IV	(A) Salicylic acid (B) Disodium salicylate	1.	60–130* 90–200**	$[C_6H_4(OH)COO]Na$ $[C_6H_4(O)COO]Na_2$	100.0	100.0	65.5	64.8	30.0	29.7	4.0	0.0	2.0	0.0	0.0	0.0
		2.	220–250	$[C_6H_4(O)COO]Na_2$	100.0	100.0	80.0	80.0	60.0	60.0	40.0	40.0	20.0	20.0	0.0	0.0
		3.	250–470	Na_2CO_3	100.0	100.0	89.0	88.4	76.5	76.7	64.5	64.7	49.5	50.8	42.0	41.8
V	(A) Salicylic acid (B) $NaHCO_3$	1.	80–150	$NaHCO_3$ $C_6H_4(OH)COOH$ $[C_6H_4(OH)COO]Na$	0.0	0.0	15.0	14.8	27.5	27.0	18.0	18.0	8.5	9.0	0.0	0.0
		2.	100–190* 160–180**	Na_2CO_3 $[C_6H_4(OH)COO]Na$	100.0	100.0	55.0	61.9	32.0	28.3	33.5	31.1	35.0	34.0	37.0	36.9
		3.	230–260	Na_2CO_3 $[C_6H_4(O)COO]Na_2$	100.0	100.0	78.5	78.3	58.0	58.2	50.0	51.1	43.0	44.0	37.0	36.9
		4.	260–470	Na_2CO_3	100.0	100.0	87.0	87.4	73.5	74.8	61.5	62.2	48.5	49.5	37.0	36.9

F. — found, C. — calculated.

* temperature range of decomposition of systems IV d, e and f and V a and b

** temperature range of decomposition of systems IV a, b and c and V c, d, e and f

Table 3

Results of thermogravimetry of ternary systems VI—VII, containing two interacting components

No.	System	Decompn. stage	Temp. range, °C	Residue in crucible	Composition of systems, %											
					a (*A*) 90 (*B*) 10 (*C*) 0		b 70 20 10		c 50 30 20		d 30 40 30		e 10 50 40		f 0 55 45	
					Weight loss, %											
					F.	C.	F.	C.	F.	C.	F.	C.	F.	C.	F.	C.
VI	(A) Disodium salicylate (B) Salicylic acid (C) Sodium salicylate	1.	100—200* 70—130**	$[C_6H_4(OH)COO]Na$ $[C_6H_4(O)COO]Na_2$	1.0	0.0	2.5	0.0	4.0	0.0	19.0	18.8	43.0	43.0	55.0	55.0
		2.	230—260* 210—240**	$[C_6H_4(O)COO]Na_2$	9.5	10.0	25.0	24.3	39.5	38.6	53.5	53.9	67.5	67.2	74.0	74.4
		3.	260—470* 240—470**	Na_2CO_3	47.5	47.6	56.5	55.9	64.5	64.2	73.5	73.2	81.5	81.1	84.5	85.1
VII	(A) $NaHCO_3$ (B) Salicylic acid (C) Sodium salicylate	1.	70—140	$C_6H_4(OH)COOH$ $NaHCO_3$ $[C_6H_4(OH)COO]Na$	4.5	4.5	9.0	9.0	14.0	13.5	18.0	18.0	8.0	7.4	0.0	0.0.
		2.	140—175* 140—210**	Na_2CO_3 $[C_6H_4(OH)COO]Na$	35.5	35.5	31.5	30.3	27.0	25.2	20.5	20.1	42.0	41.0	55.0	55.0
		3.	210—240* 230—260**	Na_2CO_3 $[C_6H_4(O)COO]Na_2$	40.0	40.5	44.0	44.6	48.0	48.8	52.0	53.0	67.5	66.4	74.0	74.4
		4.	240—470* 260—470**	Na_2CO_3	43.5	43.2	52.0	52.6	61.0	61.8	70.0	71.2	80.0	80.5	84.5	85.2

F. — *found*, C — calculated

* Temperature range of decomposition of systems VId, e and f and VIIa, b, c and d.
** Temperature range of decomposition of systemsVIa, b and c, and VIIe and f.

Conclusions

1. Investigation of the thermal decompositions of systems of salicylic acid, sodium hydrogen carbonate, monosodium salicylate and disodium salicylate showed that the thermogravimetric method can be employed for determination of two components in binary mixtures.
2. Weight losses up to the appearance of a horizontal have been found to be proportional to the percentage of the components in a mixture.
3. A horizontal has been found to appear 2–5 times during the thermal decomposition of a sample, depending on its composition. This offers the possibility of verifying 2–5 times the reliability of an analysis of a single sample over various temperature ranges, without the necessity of discontinuing the decomposition.
4. Results of this work offer the possibility of analyzing mixtures of components which are able to react with each other during the course of the thermal decomposition. Analyses of ternary mixtures could be carried out owing to reactions (3) and (6). Sodium salicylate formed in these reactions increased the percentage of the salt already present in the system. Moreover, it eliminated one of the components of a ternary system, thereby giving a binary one.
5. Both DTG and DTA traces well reflect the thermal effects of reactions occurring in the systems considered upon heating. A correlation was found between the percentages of individual components in a system and the magnitudes of the DTA peak. The character of this correlation could not be established, however.
6. Results of this work show the possibility of using binary and ternary systems to check declared compositions of mixtures containing salicylates (systems I–IV), and extents of reaction (system VII), and to follow the course of the commercial method of manufacturing sodium salicylate (systems V and VI).

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RÉSUMÉ — Etude par thermogravimétrie et analyse thermique différentielle de la décomposition thermique de systèmes binaires et ternaires constitués d' acide salicylique salicylate monosodique, de salicylate disodique et d'hydrogénocarbonate de sodium. On montre la possibilité d'analyser des systèmes dont les composants réagissent entre eux lors du traitement thermique. Les résultats de cette étude permettent de suivre le déroulement et le degré d'avancement de la réaction utilisée dans le procédé commercial de fabrication du salicylate de sodium et de contrôler la composition déclarée des mélanges de salicylates.

ZUSAMMENFASSUNG — Die thermische Zersetzung binärer und ternärer Systeme, die Salicylsäure, Mononatriumsalicylat, Dinatriumsalicylat und Natriumhydrocarbonat enthalten, wurde untersucht. Die Möglichkeit der Analyse von Systemen, deren Komponenten bei Hitzebehandlung miteinander reagieren, wurde gezeigt. Die Ergebnisse dieser Arbeit gestatten den Verlauf und das Ausmaß der Reaktionen zu untersuchen, welche bei dem Herstellungsverfahren von handelsüblichen Natriumsalicylat ablaufen und die deklarierte Zusammensetzung von Salicylatmischungen zu prüfen.

Резюме — Используя термогравиметрию и ДТА, изучено термическое разложение двойных и тройных систем, включающих в себя салициловую кислоту, мононатрийсалицилат, динатрийсалицилат и бикарбонат натрия. Показана возможность анализа систем с такими компонентами, которые реагируют друг с другом при тепловой обработке. Результаты работы могут быть использованы для анализа хода и степени реакции, применяемой в промышленном методе получения салицилата натрия и для проверки предполагаемого состава салицилат- ных смесей.