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THERMOGRAVIMETRIC STUDIES OF BINARY AND TERNARY SYSTEMS CONTAINING SALICYLIC ACID, SODIUM SALICYLATE, SODIUM CARBONATE AND SODIUM HYDROGEN CARBONATE. PART II*

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The mechanism of thermal decomposition of binary and ternary systems containing salicylic acid, sodium salicylate and disodium salicylate sesquihydrate, sodium carbonate and sodium hydrogen carbonate were studied by means of thermogravimetric and differential thermal analysis. The possibility was demonstrated of analyzing ternary systems containing three unreactive or three reactive components. The results can be useful for monitoring the course of the commercial-scale manufacture of sodium salicylate and for checking declared compositions of salicylate mixtures.

This work provides an extension of our studies aimed at developing an effective monitoring of the course and conversion degree in the process of the commercial-scale manufacture of sodium salicylate [1]. Preliminary tests revealed the possibility of application of thermogravimetry to analyze binary systems whose components interact, and to check declared compositions of mixtures containing salicylic acid [2]. Ternary systems can be analyzed via reactions occurring at elevated temperatures, which eliminate one of the components, thereby leaving binary systems. In this work, further binary and ternary systems involving sodium carbonate and disodium salicylate sesquihydrate have been studied.

Experimental

Reagents

Disodium salicylate sesquihydrate was obtained by drying in air disodium salicylate obtained as reported previously [2].

As a result of heating disodium salicylate semihydrate was obtained between 60–90°.

The identities of the salts were confirmed by results of elemental analysis (C, H) [3] and sodium determination by acidimetric titration in aqueous ether solution with bromophenol blue as indicator. The semihydrate was identified by atomic absorption spectrophotometry.

Sodium carbonate was of analytical grade, and the remaining reagents were the same as in [2].

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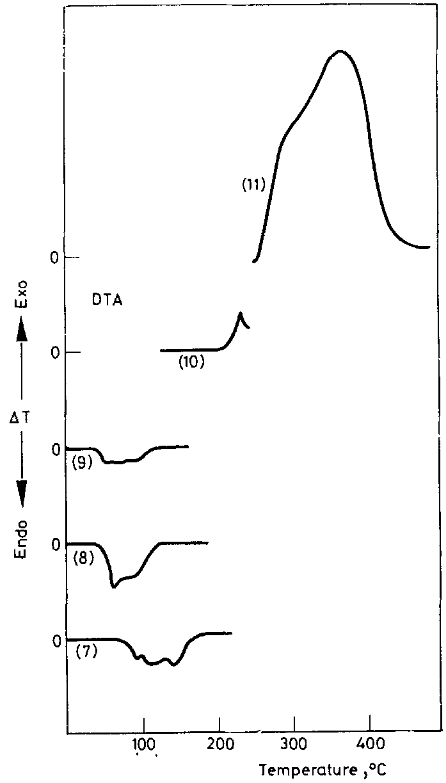

Fig. 1. DTA peaks corresponding to endothermic and exothermic reactions (7–11)

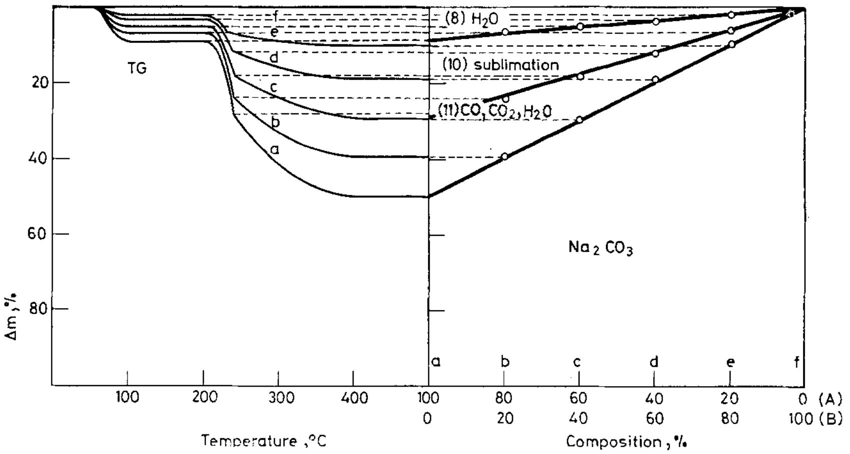

Fig. 2. Thermal decomposition of a system containing disodium salicylate sesquihydrate and sodium carbonate (system I). Loss in weight as a function of temperature (1) and composition (2). The decomposition of the sesquihydrate is described by Eqs (8), (10) and (11)

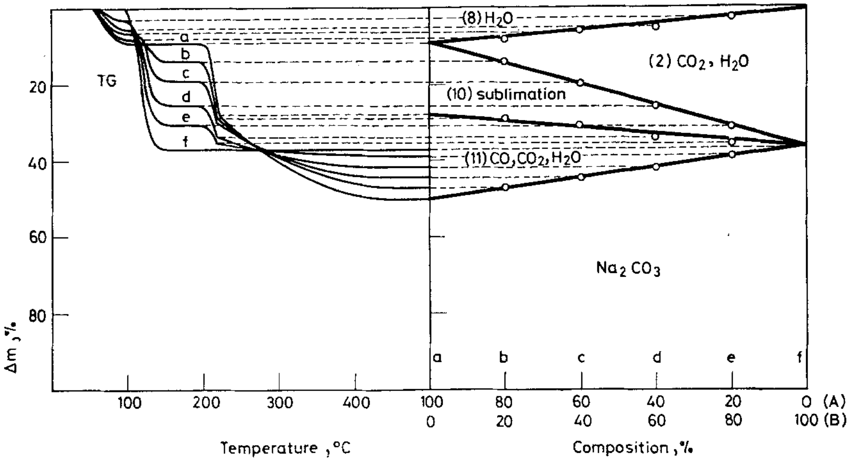

Fig. 3. Thermal decomposition of a system containing disodium salicylate sesquihydrate and sodium hydrogen carbonate (system II). Loss in weight as a function of temperature (1) and composition (2). The decomposition of sodium hydrogen carbonate occurs according to Eq. (2), and that of the sesquihydrate according to Eqs (8), (10) and (11)

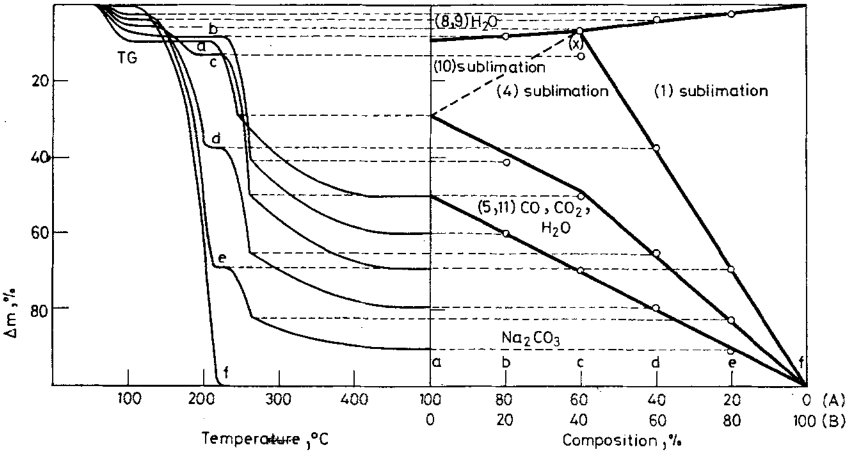

Fig. 4. Thermal decomposition of a system containing disodium salicylate sesquihydrate and salicylic acid (system III). Loss in weight as a function of temperature (1) and composition (2). Water is liberated in reaction (9). Sublimation of salicylic acid unreacted in reaction (9) occurs according to point (1). The decomposition of disodium salicylate sesquihydrate unreacted in reaction (9) occurs according to Eqs (8), (10) and (11). (x) denotes a stoichiometric point of reaction (9). The decomposition of sodium salicylate is described by Eqs (4) and (5)

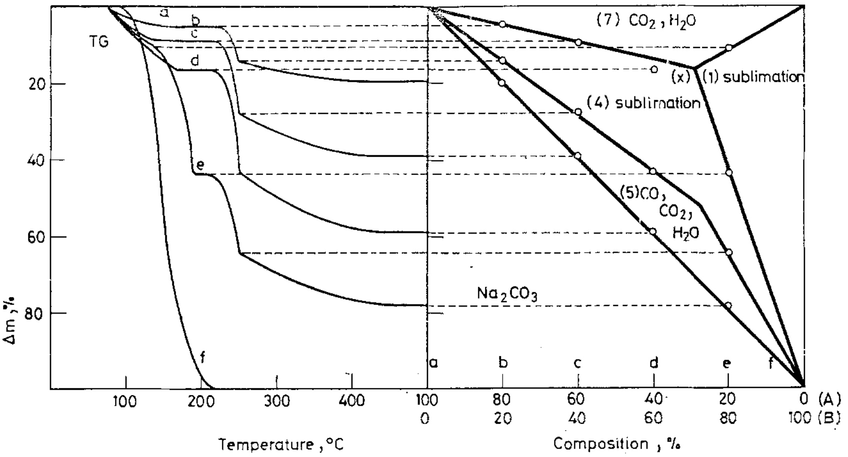

Fig. 5. Thermal decomposition of a system containing sodium carbonate and salicylic acid (system IV). Loss in weight as a function of temperature (1) and composition (2). Volatile products are formed in reaction (7). Sublimation of salicylic acid unreacted in reaction (7) occurs as in point (1). (x) denotes a stoichiometric point of reaction (7). The decomposition of sodium salicylate occurs according to Eqs (4) and (5)

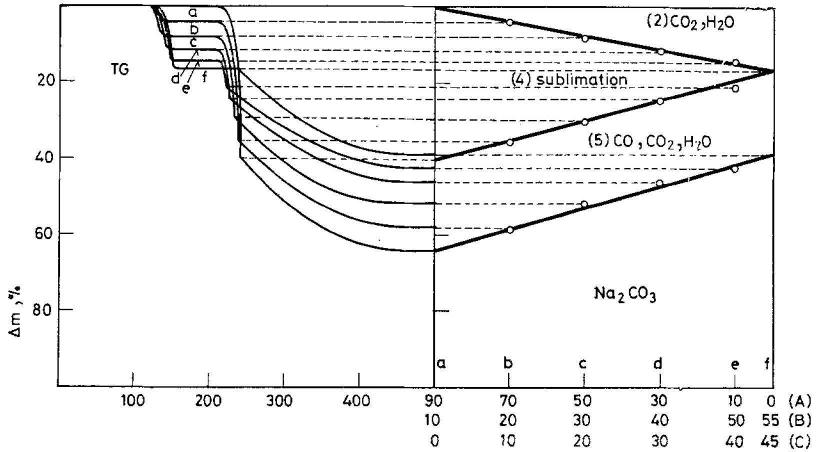

Fig. 6. Thermal decomposition of a system containing sodium salicylate, disodium salicylate and sodium hydrogen carbonate (system V). Loss in weight as a function of temperature (1) and composition (2). The decomposition of sodium hydrogen carbonate occurs according to Eq. (2), and those of sodium and disodium salicylates according to Eqs (4) and (5), and (5) respectively

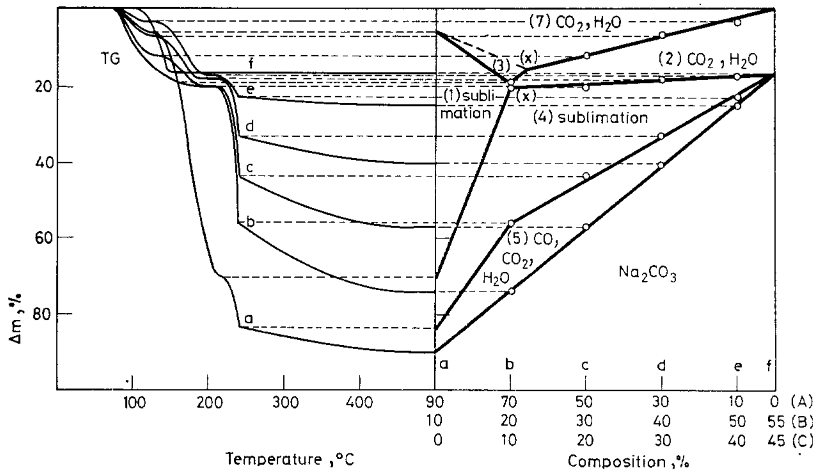

Fig. 7. Thermal decomposition of a system containing salicylic acid, sodium carbonate and sodium hydrogen carbonate (system VI). Loss in weight as a function of temperature (1) and composition (2). Volatile products are formed in reactions (3) and (7). Sublimation of salicylic acid unreacted in reactions (3) and (7) occurs according to point (1). The decomposition of sodium hydrogen carbonate unreacted in reaction (3) occurs according to Eq. (2). (x) denotes a stoichiometric point of reactions (3) and (7). The decomposition of sodium salicylate is described by Eqs (4) and (5)

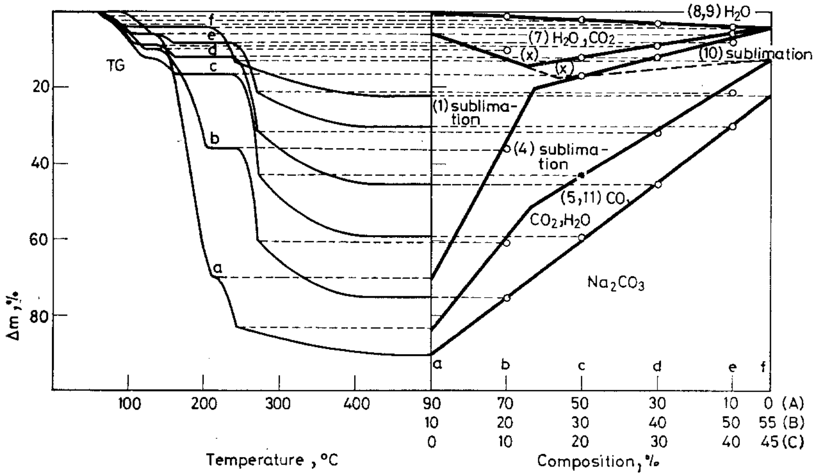

Fig. 8. Thermal decomposition of a system containing salicylic acid, sodium carbonate and disodium salicylate sesquihydrate (system VII). Loss in weight as a function of temperature (1) and composition (2). Water is liberated according to Eq. (9). Volatile products are formed in reaction (7). Sublimation of salicylic acid unreacted in reactions (7) and (9) occurs according to point (1). The decomposition of disodium salicylate sesquihydrate unreacted in reaction (9) occurs according to Eqs (8), (9) and (11). (x) denotes a stoichiometric point of reactions (7) and (9). The decomposition of sodium salicylate occurs according to Eqs (4) and (5)

Table 1

Results of thermogravimetric investigations of systems I and II containing

No.	System	De-compn. stage	Temp. range, °C	Residue in crucible
I	*(A)* Disodium salicylate $1.5H_2O$	1.	60– 90	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ Na_2CO_3
		2.	210–240	$[C_6H_4(O)COO]Na_2$ Na_2CO_3
	(B) Na_2CO_3	3.	240–420 240–440*	Na_2CO_3
II	*(A)* Disodium salicylate $1.5H_2O$	1.	60– 90	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $NaHCO_3$
		2.	110–150	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ Na_2CO_3
		3.	210–240	$[C_6H_4(O)COO]Na_2$ Na_2CO_3
	(B) $NaHCO_3$	4.	240–420 240–440*	Na_2CO_3

* decomposition point of systems Ia and Ib
F = found, C = calculated

Apparatus

Thermogravimetry of systems containing the above-mentioned components, taken in the proportions shown in Tables 1–3 was carried out by means of the OD-130 (MOM-Budapest) Derivatograph [4]. Samples (200 mg) consisted of finely-powdered and intimately-mixed components. Decompositions occurred in platinum crucibles at a temperature increase of 5°/min up to 500°, using α-Al_2O_3 as the reference material. Results of the thermal decompositions of the systems are shown in Tables 1–3 and in Figs 1–8.

Discussion

Steps characterizing the course of thermal decomposition of the systems can be written as follows:

two unreactive components

Composition of system, %											
a		b		c		d		e		f	
(A) 100		80		60		40		20		0	
(B) 0		20		40		60		80		100	
Percentage weight loss of crucible content											
F	C	F	C	F	C	F	C	F	C	F	C
9.0	8.6	6.5	6.9	5.0	5.2	3.0	3.5	2.0	1.7	0.0	0.0
29.0	31.1	24.0	24.9	18.0	18.7	12.0	12.5	6.5	6.2	0.0	0.0
50.0	49.3	39.5	39.5	29.5	29.6	19.0	19.7	10.0	9.0	0.0	0.0
9.0	8.6	8.0	6.9	6.0	5.2	5.0	3.5	2.0	1.7	0.0	0.0
9.0	8.6	14.0	14.3	19.5	19.9	25.5	25.6	30.5	31.3	37.0	36.9
29.0	31.1	29.5	32.3	31.5	33.4	34.0	34.6	35.5	35.8	37.0	36.9
50.0	49.3	47.0	46.8	44.0	44.5	42.0	41.9	39.0	39.4	37.0	36.9

(1) sublimation of salicylic acid, $C_6H_4(OH)COOH \uparrow$

(2) $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

(3) $C_6H_4(OH)COOH + NaHCO_3 \rightarrow C_6H_4(OH)COONa + CO_2 + H_2O$

(4) $2C_6H_4(OH)COONa \rightarrow C_6H_4(ONa)COONa + C_6H_4(OH)COOH \uparrow$ (sublimation)

(5) $2C_6H_4(ONa)COONa \rightarrow Na_2CO_3$ + volatile products (CO, CO_2, H_2O)

(6) $C_6H_4(ONa)COONa + C_6H_4(OH)COOH \rightarrow 2C_6H_4(OH)COONa$

(7) $2C_6H_4(OH)COOH + Na_2CO_3 \rightarrow 2C_6H_4(OH)COONa + CO_2 + H_2O$

(8) $C_6H_4(ONa)COONa \cdot 1.5H_2O \rightarrow C_6H_4(ONa)COONa \cdot 0.5H_2O + H_2O$

(9) $C_6H_4(ONa)COONa \cdot 0.5H_2O + C_6H_4(OH)COOH \rightarrow 2C_6H_4(OH)COONa + 0.5H_2O$

(10) $4C_6H_4(ONa)COONa \cdot 0.5H_2O \rightarrow 2C_6H_4(ONa)COONa + 2Na_2CO_3 + C_6H_4(OH)COOH \uparrow$ (sublimation) + volatile products (CO, CO_2, H_2O)

(11) $2C_6H_4(ONa)COONa + 2Na_2CO_3 \rightarrow 4Na_2CO_3$ + volatile products (CO, CO_2, H_2O)

Table 2

Results of thermogravimetric investigations of systems III and IV containing

No.	System	De-compn. stage	Temp. range, °C	Residue in crucible
		1.	60- 90	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$
			60-140**	$C_6H_4(OH)COOH$
III	(*A*) Disodium	2.	130-220	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$
	salicylate		130-180***	$[C_6H_4(OH)COO]Na$
	$1 \cdot 5H_2O$	3.	210-240*	$[C_6H_4(O)COO]Na_2$
			230-260	Na_2CO_3
				$[C_6H_4(OH)COO]Na$
	(*B*) Salicylic acid	4.	230-260	$[C_6H_4(O)COO]Na_2$
				Na_2CO_3
		5.	240-440*	Na_2CO_3
			260-460	
	(*A*) Na_2CO_3	1.	80-140	$[C_6H_4(OH)COO]Na$
			80-170*	$C_6H_4(OH)COOH$
				Na_2CO_3
IV		2.	140-190	$[C_6H_4(OH)COO]Na$
			140-220**	Na_2CO_3
		3.	220-250	$[C_6H_4(O)COO]Na_2$
				Na_2CO_3
	(*B*) Salicylic acid	4.	250-470	Na_2CO_3

* decomposition point of systems IIIa and IVd

** decomposition point of systems IIIb and IVf

Reactions (1–6) have been discussed in the preceding publication [2]. Reactions (7–9) are endothermic, as can be seen from the DTA curves (Fig. 1). Reaction (7) is accompanied by three peaks over the range 80–160° (Fig. 1). Similarly as in reaction (3), they are likely to be due to evolution of CO_2 and H_2O and to an exothermic effect associated with the formation of sodium salicylate. A broad, split DTA peak at 40–120° in reaction (8) (Fig. 1) is due to heat absorption, one mole of crystallization water being evolved. In reaction (9) (Fig. 1), a DTA peak due to liberation of the crystallization water occurs over the same temperature range as that of the DTA peak in reaction (8). It probably overlaps an exothermic peak due to formation of sodium salicylate. A small exothermic peak (210–240°, DTA) (Fig. 1) in reaction (10) is due to changes occurring within the molecule caused by hydrolysis of disodium salicylate by its own water of two reactive components

Composition of system, %											
a (A) 100 (B) 0		b 80 20		c 60 40		d 40 60		e 20 80		f 0 100	
Percentage weight loss of crucible content											
F	C	F	C	F	C	F	C	F	C	F	C
9.0	8.6	8.0	8.2	6.5	7.8	4.0	5.2	2.5	2.6	0.0	0.0
9.0	8.6	8.0	8.2	13.0	8.1	37.5	38.8	69.0	69.4	100.0	100.0
29.0	31.1	41.0	21.7	13.0	8.1	37.5	38.8	69.0	69.4	100.0	100.0
29.0	31.1	41.0	41.8	50.0	47.8	65.0	65.2	82.0	82.6	100.0	100.0
50.0	49.3	60.0	59.5	69.0	69.6	79.0	79.7	90.0	89.9	100.0	100.0
0.0	0.0	5.0	4.5	9.5	9.0	16.5	13.5	10.5	11.7	0.0	0.0
0.0	0.0	5.0	4.5	9.5	9.0	16.5	13.5	43.5	39.5	100.0	100.0
0.0	0.0	14.5	14.5	28.0	29.0	43.0	43.5	64.5	65.6	100.0	100.0
0.0	0.0	20.0	20.0	39.0	40.0	59.0	60.0	78.0	80.0	100.0	100.0

*** decomposition point of system IIIc
F = found, C = calculated

crystallization. This peak is likely to overlap another endothermic one due to sublimation of liberated salicylic acid. Reaction (11) (Fig. 1) is reflected in the DTA trace by a broad exothermic effect over the range 240–450°. The heat loss caused by evolution of volatile products is balanced by the strong exothermic effect of the combustion of the organic moiety and probably by the heat of reaction between sodium hydroxide and CO_2 over the temperature range considered. Sodium carbonate did not decompose.

An inspection of the results in Tables 1–3 and Figs 1–8 reveals a correlation between the proportions of the individual components in the system and their thermal behaviour. Reactions between the components alter the course of decomposition of a given system. This can be illustrated by reactions (3), (7) and (9), which yield sodium salicylate. An analysis of the systems showed that in

Table 3

Results of thermogravimetric investigations of system V containing three unreactive

No.	System	De-compn. stage	Temp. range, °C	Residue in crucible
V	*(A)* Sodium salicylate	1.	110–140 110–150*	$[C_6H_4(O)COO]Na_2$ $[C_6H_4(OH)COO]Na$ Na_2CO_3
	(B) Disodium salicylate	2.	220–240	$[C_6H_4(O)COO]Na_2$ Na_2CO_3
	(C) $NaHCO_3$	3.	240–470	Na_2CO_3
VI	*(A)* Salicylic acid	1.	80–130 80–160*	$[C_6H_4(OH)COO]Na$ $C_6H_4(OH)COOH$ Na_2CO_3, $NaHCO_3$
		2.	140–180 110–150**	$[C_6H_4(OH)COO]Na$ $C_6H_4(OH)COOH$ Na_2CO_3
	(B) Na_2CO_3	3.	140–210 160–210*	$[C_6H_4(OH)COO]Na$ Na_2CO_3
	(C) $NaHCO_3$	4.	220–240	$[C_6H_4(O)COO]Na_2$ Na_2CO_3
		5.	240–460	Na_2CO_3
VII	*(A)* Salicylic acid	1.	60– 90	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $C_6H_4(OH)COOH$ Na_2CO_3
		2.	80–130* 90–120	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $[C_6H_4(OH)COO]Na$ $C_6H_4(OH)COOH$, Na_2CO_3
		3.	140–210* 130–200	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $[C_6H_4(OH)COO]Na$ Na_2CO_3
	(B) Na_2CO_3	4.	140–160 210–240**	$[C_6H_4(O)COO]Na_2$ Na_2CO_3 $C_6H_4(OH)COO]Na$
	(C) Disodium salicylate $1.5H_2O$	5.	220–240* 240–260	$[C_6H_4(O)COO]Na_2$ Na_2CO_3
		6.	240–460* 240–420** 260–450	Na_2CO_3

* decomposition point of systems Vf, VIb and VIIa
** decomposition point of systems VIf and VIIf
F = found, C = calculated

components and of systems VI and VII containing three reactive components

Composition of system, %											
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	
Percentage weight loss of crucible content											
F	C	F	C	F	C	F	C	F	C	F	C
0.0	0.0	4.0	3.7	8.0	7.4	11.5	11.1	14.5	14.8	16.5	16.6
40.0	38.8	35.0	33.9	29.5	29.0	24.5	24.0	21.0	19.1	16.5	16.6
64.0	64.4	58.0	58.9	51.5	53.4	46.0	47.9	42.0	42.4	39.0	39.6
6.0	5.9	19.0	11.7	12.0	11.2	7.0	6.7	3.0	2.3	0.0	0.0
6.0	5.9	19.0	19.1	20.0	18.6	18.0	17.8	17.0	17.0	16.5	16.6
70.0	69.8	20.0	20.5	20.0	18.6	18.0	17.8	17.0	17.0	16.5	16.6
83.0	82.8	56.0	55.5	43.0	43.6	33.0	32.8	23.0	23.0	16.5	16.6
90.0	90.0	74.0	73.7	57.0	57.4	40.5	41.1	25.0	24.8	16.5	16.6
0.0	0.0	1.0	1.3	2.0	1.7	3.0	2.6	3.5	3.5	4.0	3.9
6.0	5.9	11.0	13.0	12.5	13.0	9.0	9.3	6.0	5.7	4.0	3.9
70.0	69.8	34.0	24.3	12.5	13.0	9.0	9.3	6.0	5.7	4.0	3.9
70.0	69.8	34.0	24.3	17.0	17.5	12.5	16.1	8.0	14.7	13.0	14.0
83.0	82.8	59.5	56.9	42.5	42.5	31.0	31.1	21.0	19.7	13.0	14.0
90.0	90.0	75.0	74.9	59.0	59.9	45.0	44.8	30.0	29.7	22.0	22.2

reaction (3), component *C* was completely consumed in system VIb. Similarly, in reaction (7), component *A* was completely consumed in systems IVe and VIc, d, e, and component *B* in systems IVb, c, d, VIa, b and VIIa, b. In reaction (9) the same was noted with components *A*, *B* and *C* in systems IIIc, d, e; IIIb, c and VIIb, respectively.

Sodium salicylate formed in reactions (3), (7) and (9) decomposes according to reactions (4) and (5).

In some of the systems studied, e.g. IIIb and VIb, certain decomposition stages overlap owing to the close decomposition points of the components.

Conclusions

1. Results of thermal decomposition of systems I–VII confirm the validity of conclusions made in the preceding work [2].
2. Under the thermal analysis conditions the ease of interaction with salicylic acid decreases in the following sequence: sodium carbonate > disodium salicylate > sodium hydrogen carbonate (systems III, IV, VI, VII).
3. This study showed that it is possible to analyze ternary systems whose components do not interact during thermal decomposition (system V). It is also possible to analyze systems containing three reactive components (VI, VII). As a result of reactions (3), (7) and (9) a new component is formed (sodium salicylate) and the system consists of three unreactive components.
4. The results of this work show the possibility of an extensive use of binary and ternary systems in chemical analysis. Each of the systems studied can be separate or in combination with any other system. One such possibility is given below:

$$\begin{array}{ccc}
\xrightarrow{50\%\ (A)\ 90\%} & \xleftarrow{90\%\ (A)\ \ 0\%} & \\
\xleftarrow{50\%\ (B)\ 10\%} & \xrightarrow{10\%\ (B)\ 55\%} & \xleftarrow{55\%\ (B)\ 50\%} \\
 & \xrightarrow{0\%\ (C)\ 45\%} & \xrightarrow{45\%\ (C)\ 50\%}
\end{array}$$

(*A*) salicylic acid, (*B*) sodium carbonate, (*C*) disodium salicylate sesquihydrate.

References

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Résumé — On a étudié par thermogravimétrie et par analyse thermique différentielle le mécanisme de la décomposition thermique de systèmes binaires et ternaires contenant de l'acide salicylique, du salicylate monosodique et du salicylate disodique sesquihydraté, du carbonate de sodium et de l'hydrogénocarbonate de sodium. On montre la possibilité d'analyser des systèmes ternaires comprenant trois composants réactifs ou non. Les résultats peuvent être utilisés pour commander le déroulement de la fabrication du salicylate de sodium à l'échelle commerciale et pour contrôler les compositions déclarées des mélanges de salicylates.

ZUSAMMENFASSUNG — Ein Mechanismus der thermischen Zersetzung Salicylsäure, Natriumsalicylat und Dinatriumsalicylat Sesquihydrat, Natriumcarbonat und Natriumhydrocarbonat enthaltender binärer und ternärer Systeme wurde mittels Thermogravimetrie und Differentialthermoanalyse untersucht. Die Möglichkeit, drei unreaktive oder drei reaktive Komponenten enthaltende ternäre Systeme zu untersuchen, wurde gezeigt. Die Ergebnisse können dazu eingesetzt werden den Verlauf der Natriumsalicylatfabrikation im Handelsmaßstab zu verfolgen und deklarierte Zusammensetzungen von Salicylatmischungen zu überprüfen.

Резюме — С помощью термогравиметрии и дифференциального термического анализа изучен механизм термического разложения двух- и трехкомпонентных систем, содержащих салициловую кислоту, салицилат натрия и полуторный гидрат динатрий салицилата, а также карбонат- и гидрокарбонат натрия. Показана возможность анализа трехкомпонентных систем, содержащих три нереагирующих или три реагирующих компонент. Полученные результаты можно использовать для контроля процесса промышленного производства салицилата натрия и для проверки объявленных составов салицилатных смесей.