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THERMOANALYTICAL INVESTIGATION OF MIXTURES CONTAINING OXALIC ACID, SODIUM HYDROGEN OXALATE AND SODIUM OXALATE

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The ternary system containing $H_2C_2O_4 \cdot 2H_2O$, $NaHC_2O_4 \cdot$ and $Na_2C_2O_4$ was investigated. It was ascertained that the termal curves of the mixtures were not the algebraic sums of their component curves. All thermal decomposition stages were interpreted and the means of performing qualitative and quantitative analyses in the system were given.

When oxalic acid is produced from sodium oxalate in aqueous solution by the ion-exchange of sodium for hydrogen using a cation-exchange resin [1–3], crystallization of the solution obtained yields oxalic acid dihydrate. If the ion-exchange capacity of the cation-exchange columns is used up totally, sodium ions are also present in such a solution. Consequently, sodium hydrogen oxalate monohydrate and even sodium oxalate are crystallized.

A solid ternary system containing oxalic acid dihydrate, sodium hydrogen oxalate was subjected to thermoanalytical investigation to develop its full qualitative and quantitative analyses based on the following reactions of thermal decomposition of the individually heated compounds of this system [4–6]:

$$
\begin{aligned}
H_2C_2O_4 \cdot 2\,H_2O &\rightarrow H_2C_2O_4 + 2\,H_2O \\
NaHC_2O_4 \cdot H_2O &\rightarrow NaHC_2O_4 + H_2O \\
2\,NaHC_2O_4 &\rightarrow Na_2C_2O_4 + (H_2C_2O_4) \\
Na_2C_2O_4 &\rightarrow Na_2CO_3 + CO
\end{aligned}
$$

In the present paper the results of this investigation are described.

Experimental

Analar grade oxalic acid dihydrate and sodium oxalate were used. Sodium hydrogen oxalate monohydrate was prepared by evaporating the excess water from an aqueous solution of a stoichiometric mixture of oxalic acid and sodium oxalate and drying the precipitated salt at about 350 K till free from moisture.

Mixtures for examinations were prepared in amounts of about 50 mg by direct weighing of their individual compounds into a 0.9 cm^3 Pt crucible.

Thermal analyses were carried out in flowing air using a Mettler TA-2 thermal analyzer. TG, DTG and DTA curves were recorded over the temperature range 300 to 900 K at a constant heating rate. As low a heating rate as 0.025 K/s was chosen to avoid melting of $H_2C_2O_4 \cdot 2\,H_2O$ (at 370 K) and $H_2C_2O_4$ (at 460 K), which disturb the thermogravimetric analysis of mixtures containing oxalic acid, and to obtain a good resolution of the thermal decomposition stages.

Results and discussion

TG, DTG and DTA curves obtained during the heating of a mixture containing all three components of the examined system are shown in Fig. 1, and DTG curves of all possible mixture types of this system in Figs. 2a–2g.

It can be observed that only in the case of mixture (d) (notation of samples from Fig. 2) are the thermal curves the algebraic sums of the corresponding curves of its individually heated components; for the remaining mixtures the curves are more complicated. This is proof that chemical reactions take place during the heating of these latter mixtures.

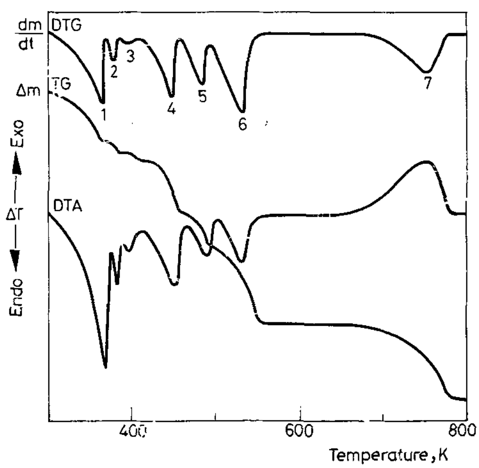

Fig. 1. TG, DTG and DTA curves of a mixture containing $H_2C_2O_4 \cdot H_2O$, $NaHC_2O_4 \cdot H_2O$ and $Na_2C_2O_4$

The establishment by X-ray analysis of a new, previously-unidentified crystalline phase apart from $Na_2C_2O_4$ in the mixture (f) heated up to 460 K confirms the above conclusion.

Numerous thermal analyses on mixtures having various compositions were carried out to determine the reactions involved.

It was found that:

(1) The weight loss Δm_1 always corresponds to the quantity of crystal water of $H_2C_2O_4 \cdot 2\,H_2O$ present in the mixture; this increases only if the sample also contains moisture.

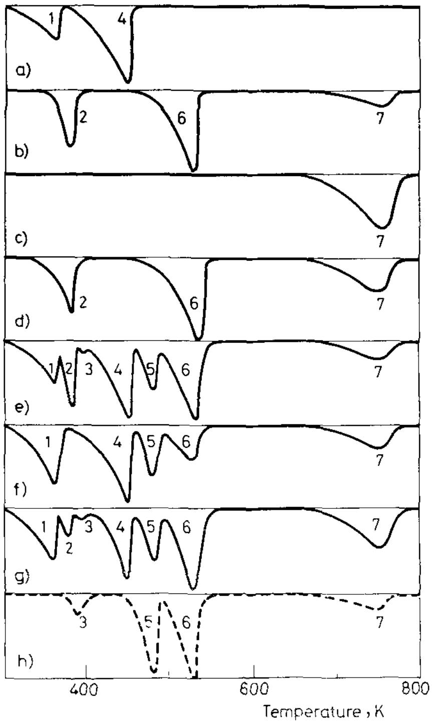

Fig. 2. DTG curves of: a) $H_2C_2O_4 \cdot 2H_2O$; b) $NaHC_2O_4 \cdot H_2O$; c) $Na_2C_2O_4$; d) mixture of $NaHC_2O_4 \cdot H_2O$ and $Na_2C_2O_4$; e) mixture of $H_2C_2O_4 \cdot 2H_2O$ and $NaHC_2O_4 \cdot H_2O$; f) mixture of $H_2C_2O_4 \cdot 2H_2O$ and $Na_2C_2O_4$; g) mixture of $H_2C_2O_4 \cdot 2H_2O$, $NaHC_2O_4 \cdot H_2O$ and $Na_2C_2O_4$; h) $3NaHC_2O_4 \cdot H_2C_2O_4 \cdot H_2O$

(2) The weight loss $\Delta m_2 + \Delta m_3$ in mixtures (e) and (g) is equal to the crystal water of $NaHC_2O_4 \cdot H_2O$.

(3) The weight losses $\Delta m_4 + \Delta m_5$ in mixture (e), $\Delta m_4 + \Delta m_5 + \Delta m_6$ in (f), and $\Delta m_4 + \Delta m_5 + \Delta m_6 - 2.5\,(\Delta m_2 + \Delta m_3)$ in (g) are equal to the amount of anhydrous $H_2C_2O_4$.

(4) In mixtures (e) and (g) $\Delta m_5 : \Delta m_3 = 5$, and in (f) $\Delta m_6 : \Delta m_5 = 1.5$.

(5) The weight loss Δm_6 in mixture (e) results exactly from the quantity of $NaHC_2O_4 \cdot H_2O$.

(6) The weight loss Δm_7 can always be explained by the amount of $Na_2C_2O_4$ present in the mixture and/or which can be formed from $NaHC_2O_4 \cdot H_2O$.

Table 1

Phase and chemical transformations taking place in a heated mixture of $H_2C_2O_4 \cdot 2\,H_2O$, $NaHC_2O_4 \cdot H_2O$ and $Na_2C_2O_4$

No. of weight loss stage	Temperature range, K	Transformations
1	300–365	$H_2C_2O_4 \cdot 2\,H_2O \rightarrow H_2C_2O_4 + H_2O$ vaporization of moisture
2	365–385	$NaHC_2O_4 \cdot H_2O \rightarrow NaHC_2O_4 + H_2O$
3	385–405	$3\,NaHC_2O_4 \cdot H_2C_2O_4 \cdot H_2O \rightarrow 3\,NaHC_2O_4 \cdot H_2C_2O_4 + H_2O$
4	405–460	sublimation of $H_2C_2O_4$
5	460–485	$3\,NaHC_2O_4 \cdot H_2C_2O_4 \rightarrow 3\,NaHC_2O_4 + H_2C_2O_4$
6	485–540	$2\,NaHC_2O_4 \rightarrow Na_2C_2O_4 + H_2C_2O_4$
7	660–770	$Na_2C_2O_4 \rightarrow Na_2CO_3 + CO$

The above findings permit the conclusion that a mixed salt of chemical constitution $3\,NaHC_2O_4 \cdot H_2C_2O_4$ (as indicated by the TG data) is formed when mixtures (e) and (g) are heated, the monohydrate of this salt is obtained. The salt and its monohydrate are likely to form only during the dehydration of oxalic acid dihydrate. The mixed salt monohydrate undergoes a four-stage thermal decomposition – its hypothetical DTG curve is shown in Fig. 2h.

The interpretation of all the thermal decomposition stages observed in the ternary system examined is given in Table 1. It is based on the above findings and data relating to the thermal decompositions of the investigated compounds [4–6]. The given interpretation affords a possibility, based on TG data, of complete qualitative and quantitative analyses of the following substances: oxalic acid dihydrate, sodium hydrogen oxalate monohydrate, sodium oxalate, or any mixture of these, even if moisture too is present in the examined sample (Table 2).

The qualitative analysis is based on the occurrence of specific weight loss stages (the comparison of the DTG curve of the examined sample with DTG curves shown in Fig. 2) with regard to the conditions in the second column of Table 2; and the quantitative analysis on the evaluation of the masses of the components (Table 2, column 4).

The accuracy of the determinations depends on the achieved resolution of thermal decomposition stages. When mixtures (DTG curves of which are shown in Fig. 2) were examined the results shown in Table 3 were obtained.

Similar agreements were observed when the single compound content was more then 5 per cent.

Table 2

Qualitative and quantitative analysis of the ternary system: $H_2C_2O_4 \cdot 2\ H_2O$, $NaHC_2O_4 \cdot H_2O$, $Na_2C_2O_4$

TG/DTG data		Sample composition	
Type of sample	variant	compounds	quantity (mass)
1	2	3	4
a	$2.5\Delta m_1 = \Delta m_4$	$H_2C_2O_4 \cdot 2\ H_2O$	m_s
	$2.5\Delta m_1 < \Delta m_4$	$H_2C_2O_4 \cdot 2\ H_2O$ $H_2C_2O_4$	$3.5\Delta m_1$ $m_s - 3.5\Delta m_1$
	$2.5\Delta m_1 < \Delta m_4$	$H_2C_2O_4 \cdot 2\ H_2O$ moisture	$1.4\Delta m_4$ $\Delta m_1 - 0.4\Delta m_4$
b	$\Delta m_6 = \frac{45}{14}\Delta m_7$	$NaHC_2O_4 \cdot H_2O$ moisture	m_s or $m_s - \Delta m_1$ Δm_1
or d	$\Delta m_6 < \frac{45}{14}\Delta m_7$	$NaHC_2O_4 \cdot H_2O$ $Na_2C_2O_4$ moisture	$2.89\Delta m_6$ $4.79\Delta m_7 - 1.49\Delta m_6$ Δm_1
c	–	$Na_2C_2O_4$	m_s
e	$\Delta m_6 = \frac{45}{14}\Delta m_7$	$H_2C_2O_4 \cdot 2\ H_2O$ $NaHC_2O_4 \cdot H_2O$ moisture	$1.4(\Delta m_4 + \Delta m_5)$ $2.89\Delta m_6$ $\Delta m_1 - 0.4(\Delta m_4 + \Delta m_5)$
or g	$\Delta m_6 < \frac{51}{44}\Delta m_7$	$H_2C_2O_4 \cdot 2\ H_2O$ $NaHC_2O_4 \cdot H_2O$ $Na_2C_2O_4$ moisture	$1.4[\Delta m_4 + \Delta m_5 + \Delta m_6 - 2.5(\Delta m_2 + \Delta m_3)]$ $7.22(\Delta m_2 + \Delta m_3)$ $4.79\Delta m_7 - 3.72(\Delta m_2 + \Delta m_3)$ $\Delta m_1 - 0.4[\Delta m_4 + \Delta m_5 + \Delta m_6 - 2.5(\Delta m_2 + \Delta m_3)]$
f	–	$H_2C_2O_4 \cdot 2\ H_2O$ $Na_2C_2O_4$ moisture	$1.4(\Delta m_4 + \Delta m_5 + \Delta m_6)$ $4.79\Delta m_7$ $\Delta m_1 - 0.4(\Delta m_4 + \Delta m_5 + \Delta m_6)$

m_s = mass of the examined sample.

The described method is rather time-consuming. To decrease the time of measurement a higher heating rate may be used over the temperature range 550–800 K without any worsening of the accuracy.

Differential thermal analysis too may be used to perform the qualitative analysis in the investigated system. As regards the DTA curves, reasoning analogous to

Table 3

Mixture	Composition, %	Composition, % from TG curves	Fig.
$NaHC_2O_4 \cdot H_2O$	65.2	64.1	2d
$Na_2C_2O_4$	35.8	34.7	
$H_2C_2O_4 \cdot 2\,H_2O$	36.5	36.9	2e
$NaHC_2O_4 \cdot H_2C$	63.5	61.6	
$H_2C_2O_4 \cdot 2\,H_2O$	54.0	54.8	2f
$Na_2C_2O_4$	46.0	46.9	
$H_2C_2O_4 \cdot 2\,H_2O$	36.4	35.9	
$NaHC_2O_4 \cdot H_2O$	11.8	12.6	2g
$Na_2C_2O_4$	51.8	50.3	

that for the DTG curves is applied, but the differentiating of sample (a) from (g), and of (b) from (d) and variants of (a) type is more difficult than in the case of TG data.

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RÉSUMÉ — On a étudié le système ternaire contenant $H_2C_2O_4 \cdot 2\,H_2O$, $NaHC_2O_4 \cdot H_2O$ et $Na_2C_2O_4$. On a établi que les courbes thermiques des mélanges ne correspondaient pas à la somme algébrique de leurs courbes composantes. On a interprété toutes les étapes de la décomposition thermique et donné les moyens d'effectuer des analyses qualitatives et quantitatives du système.

ZUSAMMENFASSUNG — Das $H_2C_2O_4 \cdot 2\,H_2O$, $NaHC_2O_4 \cdot H_2O$ und $Na_2C_2O_4$ enthaltende ternäre System wurde untersucht. Es wurde festgestellt, daß die thermischen Kurven der Gemische nicht den algebraischen Summen ihrer Komponentenkurven entsprachen. Sämtliche Stufen der thermischen Zersetzung wurden zugeordnet und die Möglichkeiten der Durchführung qualitativer und quantitativer Analysen im System angegeben.

Резюме — Исследована тройная система, содержащая $H_2C_2O_4 \cdot 2H_2O$, $NaHC_2O_4 \cdot H_2O$ и $Na_2C_2O_4$. Установлено, что термические кривые смесей не являются алгебраической суммой кривых отдельных компонент. Были объяснены все стадии термического разложения и даны пути проведения количественного и качественного анализов.