

THERMAL BEHAVIOR OF THE SACCHARINATES OF K, Na, Rb, Cs AND NH₄

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Abstract: The saccharinates: K₃(sac)₃· 2H₂O, Na₃(sac)₃· 2H₂O (the triclinic form), Rb₂(sac)₂· H₂O, Cs(Hsac)(sac)· H₂O and NH₄(sac) were prepared from the corresponding carbonates and saccharin, and their thermal decomposition was investigated by thermogravimetric (TG, DTG, DTA) methods in static atmosphere of helium and by DSC in a flow of nitrogen.

All compounds, excluding the anhydrous ammonium salt, were dehydrated prior to the decomposition of the saccharinato ligands. Except for the Cs salt, the decomposition of the dehydrated saccharinates started for about 150 K higher than the decomposition of the saccharin itself.

Key words: Alkali salts, DSC, saccharinates, TG analysis, thermal decomposition

1. Introduction

Besides the commercial importance of the alkali saccharinates (mainly owing to their high solubility in water), the structural data for these compounds are rather scanty. To date, only the crystal structures of one of the two hydrates of Na saccharinate [1] as well as that of K₂Na saccharinate [2] have been published. Recently, we have synthesized the saccharinates of K, Rb and Cs (structure determination and refinement is in progress). In this paper we report the thermal behavior of the saccharinates of K, Na, Rb, Cs and NH₄.

2. Experimental

Starting from the respective carbonates and saccharin, the following salts were prepared from warm EtOH/H₂O mixtures: K₃(sac)₃· 2H₂O (KSAC), Rb₂(sac)₂· H₂O (RBSAC), Cs(Hsac)(sac)· H₂O (CSSAC) and NH₄(sac) (ASAC). Commercial Na saccharinate was recrystallized from EtOH to give the triclinic Na₃(sac)₃· 2H₂O (NASAC) [3]. For the TG/DTG/DTA analyses Setaram TG-DTA92 instrument and a static atmosphere of helium were used (Al₂O₃ crucibles). The DSC measurements were performed with Mettler DSC20 oven connected to a Mettler TA 400 temperature controller, using Al containers (air, heating rate 5 K/min).

3. Results and Discussion

3.1. Dehydration of the Salts

All compounds (except the anhydrous ASAC) are dehydrated prior to the decomposition of the saccharinato ions.

The dehydration of NASAC and KSAC (Figs. 1 and 2) proceeds in two steps, along with the existence of only *two* structurally different types of water molecules in the structure

of NASAC. At the same time, this is an indication that there are *two* structurally non-equivalent types of water molecules in case of KSAC. The mass loss ratio of the two dehydration steps of KSAC inevitably shows that the molar ratio of the structurally different water molecules is 2:1, 2/3 of the water molecules in its structure being more weakly bonded than the rest. The higher dehydration temperature of KSAC compared to that of NASAC, on the other hand, indicates that the water molecules in the structure of the first are more strongly bonded than those in the latter compound. The anhydrous NASAC and KSAC undergo melting prior to the further decomposition (Figs. 1 and 2).

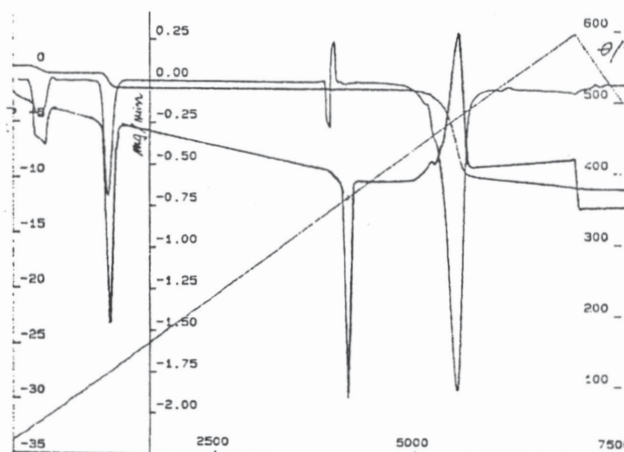


Fig. 1. Thermal Decomposition Curves of NASAC

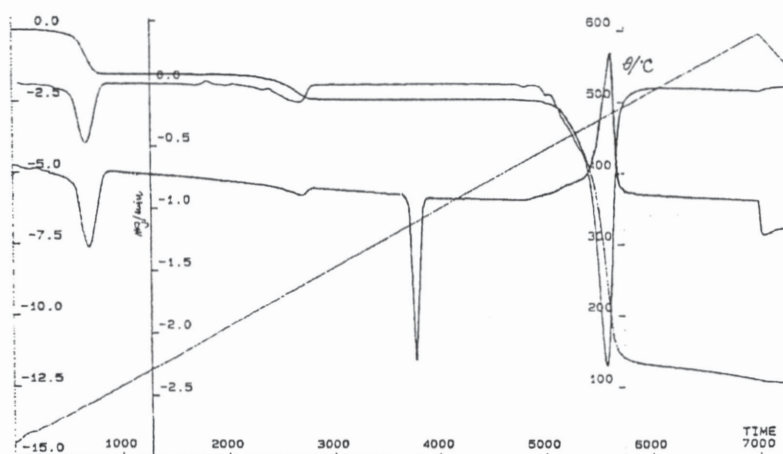


Fig. 2. Thermal Decomposition Curves of KSAC

Contrary to NASAC and KSAC, RBSAC initially melts (at 473 K) upon heating and afterwards is dehydrated (Fig. 3).

The decomposition of CSSAC (Fig. 4) starts (at 368 K) with partial dehydration, yielding $\text{Cs}(\text{Hsac})(\text{sac}) \cdot 0.5\text{H}_2\text{O}$. This step represents an interconversion between the two forms of Cs saccharinate, CSSAC and $\text{Cs}(\text{sac}) \cdot 0.5\text{H}_2\text{O}$. The product thus can be formally

considered as a "solid mixture" of the latter form and saccharin. The hemihydrate afterwards melts and undergoes complete dehydration. The sharp endothermic peak at 489 K corresponds with the melting of the molecular saccharin, in agreement with the proximity of this temperature value with that of the melting of the saccharin itself (502 K).

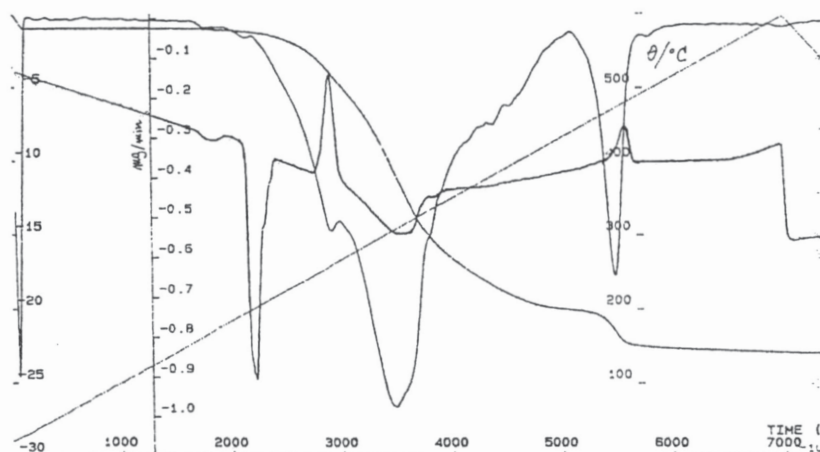


Fig. 3. Thermal Decomposition Curves of RBSAC

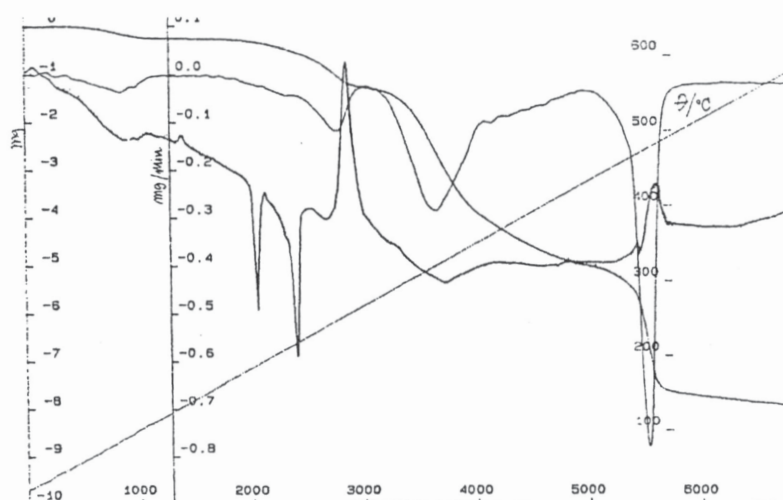


Fig. 4. Thermal Decomposition Curves of CSSAC

3.2. Decomposition of the anhydrous salts

The anhydrous NASAC and KSAC are decomposed in a single step (Figs. 1 and 2), corresponding with endothermic peaks at 760 K.

The decomposition of the anhydrous RBSAC and CSSAC is similar and, at the same time, different from that of the dehydrated NASAC and KSAC. RBSAC and CSSAC, namely, adopt *three-step* decomposition pathway (Figs. 3 and 4). Presumably due to the difference between the decomposition temperatures of the saccharinato *molecules* and *ions*, the decom-

position steps in case of CSSAC are well separated. Two of the steps in the case of RBSAC overlap, but since one of them is exo- and the other endothermic, they could be clearly resolved from the DTA curve.

In agreement with what is intuitively expected, the decomposition pathway of ASAC is different from those of the alkali saccharinates. The decomposition of this salt namely, is accompanied with sublimation, the overall process being finished around 673 K.

4. Conclusions

The present study shows a degree of similarity of the structures of NASAC and KSAC and, at the same time, a dissimilarity with that of RBSAC and especially with CSSAC. The results show that there are two structural types of water molecules in a molar ratio 2:1 in KSAC. The existence of molecular saccharin in CSSAC is confirmed.

5. References

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ТЕРМИЧКО РАЗЛОЖУВАЊЕ НА САХАРИНАТИТЕ НА K, Na, Rb, Cs и NH₄

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Апстракт: Поаѓајќи од соодветните карбонати и сахарин, синтетизирани се следните сахаринатни соли: K₃(sac)₃ · 2H₂O, Na₃(sac)₃ · 2H₂O (триклинична форма), Rb₂(sac)₂ · H₂O, Cs(Hsac)(sac) · H₂O и NH₄(sac). Испитувано е нивното термичко разложување во статичка атмосфера на хелиум со термогравиметриски методи (TG, DTG, DTA), како и со диференцијална сканинг калориметрија во динамичка атмосфера на азот.

Освен кај безводното амониумово соединение, кај сите соединенија доаѓа до дехидратација пред разложувањето на сахаринатните лиганди. Со исклучок на цезиумовата сол, температурата на разложување на дехидратираниите сахаринати е за околу 150 K повисока од онаа на сахаринот.