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THERMAL DEHYDRATION AND DECOMPOSITION OF OXYGEN-TELLURIUM(VI) COMPOUNDS WITH ALKALI METALS AND AMMONIUM

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Abstract

In the framework of a systematic study of compounds with hydrogen bonds, thermoanalitycal methods were employed to study four groups of hydrogen tellurates: a) $Li_2H_4TeO_6 \cdot 3H_2O$, $Na_2H_4TeO_6$, $K_2H_4TeO_6$; b) LiH_5TeO_6, $NaH_5TeO_6 \cdot 2H_2O$, $KH_5TeO_6 \cdot 2H_2O$; c) NH_4HTeO_4; d) $K_4H_4Te_2O_{10} \cdot 7.3H_2O$. The individual steps in the thermal degradation were described and the intermediates formed were characterized by analytical, infrared spectrometry, powder X-ray and, for NH_4HTeO_4, also mass spectrometry methods.

Keywords: decomposition products, hydrogen tellurates, thermal stability

Introduction

The thermal decomposition of hydrogen tellurates of the alkali metals of the $M_2H_4TeO_6$ (M=Li, Na, K, Rb, Cs, Tl) [1, 2] type, which yield tellurates of the M_2TeO_4 type as decomposition products has been described in the literature. Of the $MH_5TeO_6 \cdot nH_2O$ ($0 \leq n \leq 3$ type, the thermodynamical properties of only the sodium salts have been studied, but the published results differ [3, 4]. The thermal decomposition of the $LiH_5TeO_6 \cdot nH_2O$ and $KH_5TeO_6 \cdot nH_2O$ (where $0 \leq n \leq 3$) types has not been described. The purpose of the present study is to confirm the decomposition mechanisms published for hydrogen tellurates and to elucidate the thermoanalytical properties of substances that have not yet been studied. The results obtained permit a more detailed interpretation of the results of study of these compounds from the standpoint of possible transitions to a phase with important physical properties, for example, with proton conductivity.

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Experimental

Preparation

LiH_5TeO_6 and $Na_2H_4TeO_6$ were prepared by dissolving solid H_6TeO_6 in a solution of the corresponding hydroxide. $NaH_5TeO_6{\cdot}2H_2O$ and $K_2H_4TeO_6$ were prepared by mixing solutions of hexa-hydrogen telluric acid and the corresponding hydroxide in equivalent amounts. $KH_5TeO_6{\cdot}2H_2O$, $Li_2H_4TeO_6{\cdot}3H_2O$ and NH_4HTeO_4 were obtained by mixing solutions of the corresponding carbonate with a solution of H_6TeO_6. $K_4H_4Te_2O_{10}{\cdot}7.3H_2O$ was prepared by diluting a saturated solution of telluric acid with water and heating, with drop-wise addition of a solution of potassium hydroxide [5]. The products were filtered and washed with water and ethanol in all cases.

Characterization

Tellurium was determined gravimetrically and also by AAS method using the flame technique (air–acetylene) with a Varian Techtron Model 1200 instrument. Elemental analysis for the alkali metals was carried out by the AAS method under the same conditions as for Te. The ammonia content in NH_4HTeO_4 was determined by elemental analysis of samples for the contents of nitrogen and hydrogen.

Infrared spectra were recorded with an ATI Mattson Genesis Fourier Transform Spectrometer, using KBr discs or nujol suspensions in the 4000 to 400 cm^{-1} range (with a resolution of 2 cm^{-1}). The spectra were analysed using WinFirst 3.1 software.

X-ray powder diffraction patterns were obtained with an URD-6 diffractometer and CuK_α radiation. The results of the X-ray measurements were analysed using ZDS software.

Thermogravimetry (TG) was performed with a Derivatograph OD 102 instrument (MOM, Budapest), in static air, using sample masses of approximately 250–300 mg in platinum sample pans, and heating at 10°C min^{-1} (or 5°C min^{-1}) from ambient temperature to a maximum temperature of 800°C. TG, DTA and DTG curves were recorded.

Decomposition of NH_4HTeO_4 was followed by mass spectroscopy by using a Finnigam MAT INCOS 50 instrument. The substance was dissolved in methanol and injected directly into the instrument. The carrier gas was helium and a sample heating rate of 30°C min^{-1} was used.

Results and discussion

For compounds of the $M_2H_4TeO_6{\cdot}nH_2O$ (M=Li, Na, K; $0\leq n\leq 3$) type, thermoanalytical curves demonstrated that decomposition leads to the compound M_2TeO_4. The DTA curves, characterized by marked endothermic peaks, are depicted in Fig. 1. For anhydrous $Na_2H_4TeO_6$ compounds, this process, in which constitutional water is released, occurs in the temperature range 245–265°C (calculated loss of H_2O 13.2%, experimental loss 14.3%). A similar process occurs for $K_2H_4TeO_6$ in the 260–275°C range (calculated loss of H_2O 11.78%, experimental loss 11.9%). For the lithium salt, which was prepared as the trihydrate, $Li_2H_4TeO_6{\cdot}3H_2O$, 3 molecules of water of crystallization are first lost in the temperature range 50–90°C. This corresponds to a mass loss of 17.8% on the TG curve (theoretical values: 18.29%). The actual decomposition to $Li_2H_4TeO_6$ occurs in the temperature range 125–180°C (experimental value 16.4% H_2O, calculated loss 14.92%). The progress of the above decomposition is similar to that described in the literature [1]; however, the temperature of the process differs considerably. This difference can be explained by the fact that the decompositions described in the literature were carried out a high heating rates (73°C min^{-1}), so that these processes occurred at much higher temperatures, especially for the lithium and sodium salts.

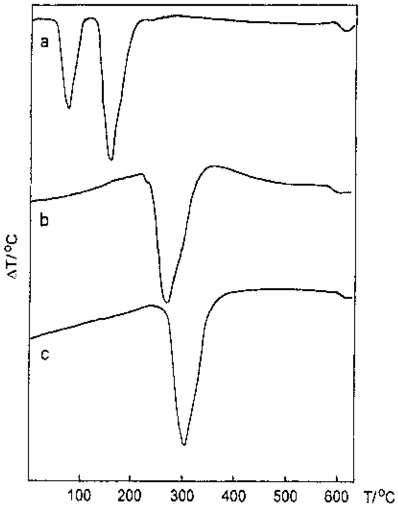

Fig. 1 DTA curve of $Li_2H_4TeO_6{\cdot}3H_2O$ (a), $Na_2H_4TeO_6$ (b) and $K_2H_4TeO_6$ (c)

It is also clear from Fig. 1 that the temperature of decomposition of anhydrous salts increased with a gradual increase in the size of the cation ($Li^+<Na^+<K^+$). This is a result of the stabilizing action of the cations in ionic compounds with large anions, which increases with increasing ionic diameter.

The gradual thermal decomposition of the second group of the studied salts (LiH_5TeO_6, $NaH_5TeO_6{\cdot}2H_2O$ and $KH_5TeO_6{\cdot}2H_2O$) can be described schematically as

$$MH_5TeO_6{\cdot}nH_2O\ (0\le n\le 2) \rightarrow MH_5TeO_6 \rightarrow MHTeO_4$$

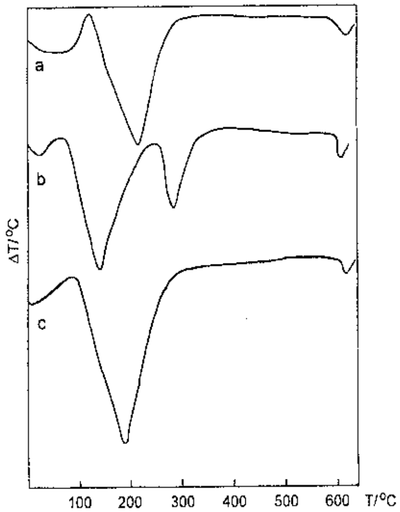

Fig. 2 DTA curve of LiH_5TeO_6 (a), $NaH_5TeO_6{\cdot}2H_2O$ (b) and $KH_5TeO_6{\cdot}2H_2O$ (c)

The DTA curves of these decompositions are depicted in Fig. 2 Compared to anhydrous LiH_5TeO_6 whose decomposition to $LiHTeO_4$ occurs in a single step in the temperature range 120–210°C (calculated loss in the mass of H_2O, 15.29%, experimental 15.29%), the beginning of the decomposition of the hydrated sodium and potassium salts is shifted towards lower temperatures. In the case of $NaH_5TeO_6{\cdot}2H_2O$, the decomposition occurs in two steps, in which two molecules of water of crystallization are first released in the temperature range 80–140°C (calculated decrease in the mass of H_2O, 12.53%, experimental 14.3%); in the second step in the temperature range 250–270°C, the actual decomposition of NaH_5TeO_6 occurs (calculated decrease in the mass of H_2O, 25.05%, experimental 23.7%). The hydrated salt $KH_5TeO_6{\cdot}2H_2O$ decomposes in a single step which includes dehydration and decomposition of the anhydrous salt in the temperature range 100–200°C (calculated mass loss 23.7%, experimental 23.7%). The decomposition temperatures of the anhydrous salts, LiH_5TeO_6 and NaH_5TeO_6 are once again affected by the size of the cation, similarly to tellurates of the $M_2H_4TeO_6$ type, where the decomposition of the lithium salt occurs at a lower temperature. However, the decomposition temperatures are also affected by the structural ordering of these substances. While the structure of the sodium salt consists of TeO_6 octahedra interconnected by oxygen atoms [3], the structure of LiH_5TeO_6 consists of isolated octahedra interconnected by weaker hydrogen bonds [7]. The temperature of decomposition of the potassium salt K_5HTeO_6 could not be found because of the shape of the thermal curves.

The DTA curves of the studied tellurates of the M_5HTeO_6 type, exhibit small endothermic peaks at temperatures above 600°C, corresponding to the decomposition of these substances to a mixture of TeO_2 and the corresponding oxides M_2O, as was confirmed by the powder X-ray patterns of the decomposition products.

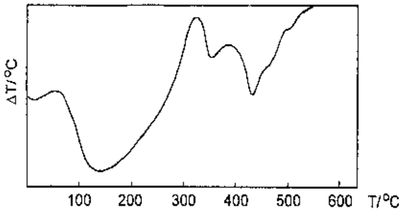

Fig. 3 DTA curve of NH_4HTeO_4

A further compound studied consisted of the hydrogen tellurate NH_4HTeO_4, which can be written from a structural point of view as $NH_4TeO_3(OH)$. The shape of the DTA curve, obtained at a heating rate of 5°C min^{-1}, is depicted in Fig. 3. It can be seen that decomposition begins at 60°C and progresses in five separate steps. The curve is dominated by the first broad endothermic peak, which lies in the broad temperature interval of 60–340°C. The other thermal effects are less marked. In contrast to the DTA curve, the TG curve exhibits a continuous shape and does not permit differentiation of the intermediate stages of the decomposition. However, it is apparent that, at a temperature of 240°C, the intermediate in the thermal decomposition contains, on the basis of elemental analysis, half the amount of nitrogen and water. A further increase in temperature leads to complete release of hydrogen and nitrogen from the sample. The substance is converted to the yellow semi-crystalline substance TeO_3, which is gradually decomposed in TeO_2 at a temperature of 395°C.

In order to explain the individual intermediates in the thermal decomposition of NH_4HTeO_4, this substance was studied using mass spectroscopy. At a heating rate of 30°C min^{-1}, the decomposition products were found to contain primarily nitrogen compounds (N_2, N_2H_4) and hydrogen telluride. In spite of the differences between the methods of mass spectrometry and thermal analysis, it can be demonstrated that the thermal decomposition of NH_4HTeO_4 will also lead to the formation of a number of nitrogen compounds, however, their identification would require the use of other methods, such as evolved gas analysis.

The last substance studied was $K_4H_4Te_2O_{10}{\cdot}7.3H_2O$. The DTA curve of the compound is depicted in Fig. 4. This is a three-step process in which 3.3 water

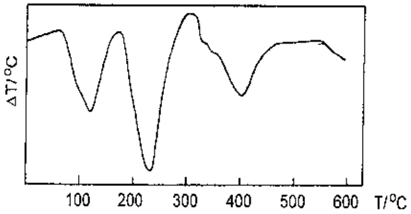

Fig. 4 DTA curve of $K_4H_4Te_2O_{10}{\cdot}7.3H_2O$

molecules are released in the first step in the temperature interval 60–140°C, appearing in the TG curve as a mass loss of 8.8% (calculated loss 8.41%). A further loss of 4 water molecules occurs in the temperature range from 180 to 230°C and corresponds to a measured mass loss of 18.6% (calculated value 18.6%). Finally, in the temperature range 320–440°C, the anhydrous salt $K_4H_4Te_2O_{10}$ decomposes according to the scheme.

$$K_4H_4Te_2O_{10} \rightarrow K_4Te_2O_8 + 2H_2O$$

A mass loss of 23% was found on the TG curve for this process (calculated value 23.69%).

Conclusions

The TG and DTA curves of the studied hydrogen tellurates of the alkali metals indicate dehydration (for the hydrated salts) and subsequent decomposition of the anhydrous compounds to form tellurates of the M_2TeO_4 type (for compounds of the $M_2H_4TeO_6{\cdot}nH_2O$ type), or of the $MHTeO_4$ type (for compounds of the $MH_5TeO_6{\cdot}nH_2O$ type). On heating the compound $K_4H_4Te_2O_{10}{\cdot}7.3H_2O$ undergoes dehydration, followed by decomposition to $K_4Te_2O_8$. The decomposition of NH_4HTeO_4 yields a number of unspecified compounds of nitrogen and TeO_3; the latter is converted to TeO_2 at higher temperatures.

Knowledge of the thermoanalytical properties of the studied compounds is essential for evaluation of their possible phase transitions connected with changes in hydrogen bonds.

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