

SYNTHESIS AND THERMAL DISSOCIATION OF TELLURATES OF THE THREE-COMPONENT SYSTEM KOH-H₆TeO₆-H₂O

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Abstract

Potassium hydrogen tellurate is used for the obtaining of zinc tellurates, silver nitrate (AgNO₃) and mercury nitrate (Hg(NO₃)₂). The synthesis and structural study of telluric acid derivatives have attracted much attention due to their physical properties, such as dielectric relaxation, proton conductivity, and ferroelectric properties. The synthesis of similar compounds and their structural studies seem to be important. The tellurates of a number of metals can be used as new materials in solar panel. Potassium hydrogen tellurate (K₂H₄TeO₆) is obtained by mixing of preliminarily heated solutions of potassium hydroxide (KOH) and orthotelluric acid (H₆TeO₆). Potassium tellurate (K₂TeO₄) is obtained by heating potassium hydrogen tellurate (K₂H₄TeO₆) until release of the constitutional water. The two tellurates are subjected to derivatographic analysis. The mechanism of thermal decomposition is determined.

Key words: tellurates, thermal dissociation, three-component system.

1. INTRODUCTION

The synthesis and structural study of telluric acid derivatives have attracted much attention due to their physical properties, such as dielectric relaxation, proton conductivity, and ferroelectric properties. At the same time, the number of alkali metal hydrogen tellurates characterized by X-ray crystallography is small. Therefore, the synthesis of similar compounds and their structural studies seem to be important. The tellurates of a number of metals can be used as new materials in solar panel. (Churakov et al., 2007; Vanek et al., 2000; Ranbo et al., 2004).

Potassium hydrogen tellurate is used for the obtaining of zinc tellurates (Gospodinov, 1994). The solubility isotherm of the system ZnSO₄ – K₂H₄TeO₆ – H₂O was studied and the conditions of synthesis of zinc tellurates were determined. The thermal and thermodynamic properties of the compounds obtained were determined.

Potassium hydrogen tellurate is used for the obtaining of silver nitrate (AgNO₃) (Gospodinov, 1992). The system AgNO₃ – K₂H₄TeO₆ – H₂O has been studied and its solubility isotherm is drawn at 100 °C. The composition of the phases in the system is determined by using the solubility isotherm and chemical, crystallo-optical and X-ray phase analyses after the phases are washed and dried. Derivatograph analysis is carried out and a scheme of thermal decomposition is suggested.

Potassium hydrogen tellurate is used for the obtaining of mercury nitrate (Hg(NO₃)₂) (Gospodinov, 1991). That compound was obtaining at fixed concentrations of an Hg(NO₃)₂ solution and alkaline orthotellurate. This study was made using the solubility method P_H measurements. The solid phase was analyzed after it was separated from the mother solution. By a chemicopreparative method. After washing and drying it was also subjected to chemical, X-ray phase, crystallo-optical and derivatograph analyses.

According to (Rosenheim and Jander, 1948), potassium tellurates can be obtained from orthotelluric acid (H₆TeO₆) and potassium hydroxide (KOH) solution by the wet method. The orthotellurate with composition K₆TeO₆ can not be obtained. Among hydrogen orthotellurates, the two-base salt is most widely investigated in the form of various hydrates (Mayer and Nilowaty, 1948).

According to (Rosenheim and Jander, 1948) K₂H₄TeO₆·5H₂O crystallizes from solution with excess of H₆TeO₆ and 20% potassium hydroxide at 0°C. Under longer period in native lye it is transformed into K₂H₄TeO₆·3H₂O. In dry air, the compound releases its crystallization water to become K₂H₄TeO₆ (Rosenheim and Jander, 1948).

K₂H₄TeO₆·3H₂O crystallizes at room temperature from the same solution which releases 5 hydrates as large transparent prisms at 0°C.

Previously, the compound K₂H₄TeO₆·3H₂O was considered to have composition K₂TeO₄·5H₂O. It crystallizes under very careful concentration of the potassium tellurate solution at room temperature. K₂H₄TeO₆ was considered to be actually K₂TeO₄·2H₂O, which crystallizes under cooling of H₆TeO₆ solution in concentrated solution of KOH as strongly double refracting crystals which always contain adsorbed excess of KOH.

The hydrates of potassium metatellurates are synthesized also as reported in (Party, 1936). The authors of (Duquenoy, 1971) obtained $K_2TeO_4 \cdot 5H_2O$ by precipitation of concentrated solution of tellurite with alcohol, with excess of KOH. $K_2TeO_4 \cdot 2H_2O$ is prepared by partial dehydration of the pentahydrate at $110^\circ C$. The anhydrous K_2TeO_4 is obtained by full dehydration of one of the crystallohydrates mentioned above.

The X-ray pattern of K_2TeO_4 allows concluding that it is isomorphic with K_2SeO_4 and crystallizes in the orthorhombic syngony with parameters $a=7.9 \text{ \AA}$, $b=10.5 \text{ \AA}$, $c=6.25 \text{ \AA}$ (Duquenoy, 1971).

The aim of the study is to define the conditions which is obtained $K_2H_4TeO_6$.

2. EXPERIMENTAL AND DISCUSSION

For the synthesis of potassium tellurates, KOH with purity of 99.99 mass % is used, as well as orthotelluric acid (H_6TeO_6) obtained by oxidation of tellurium dioxide (TeO_2) with hydrogen peroxide (Russian patent, 1967). According to data from spectral analysis, the product obtained had purity of 99.999 mass% by total content of impurities.

The tellurates preparation is carried out as follows: 50 ml of KOH solution of varied concentration are added to 50 ml 0.05M solution of orthotelluric acid, so as $n(H_6TeO_6:KOH)$ is in the range from 1 to 5. Both solutions are heated to boiling before mixing.

The solid phases obtained are subjected to chemical analysis. K^+ - ions are determined alkalimetrically (Sharlo, 1969) and tellurate ions – iodometrically and gravimetrically (Nazarenko and Ermakov, 1974).

The results obtained from the chemical analysis are presented in Table 1. They correlate well with theoretically calculated values which confirmed the stoichiometry of the products obtained. In the whole range of concentrations $n=0-5$, only one phase of $K_2H_4TeO_6$ is observed.

Table 1. Chemical analysis of potassium tellurates

Compound	Theoretical composition, mass %			Chemical analysis, mass %		
	K_2O	TeO_3	H_2O	K_2O	TeO_3	H_2O
$K_2H_4TeO_6$	30.80	57.42	11.78	30.81; 30.79; 30.84	57.50; 57.44; 57.40	11.82; 11.80; 11.76
K_2TeO_4	34.91	65.09	-	34.93; 34.91; 34.89	65.12; 65.10; 65.07	-

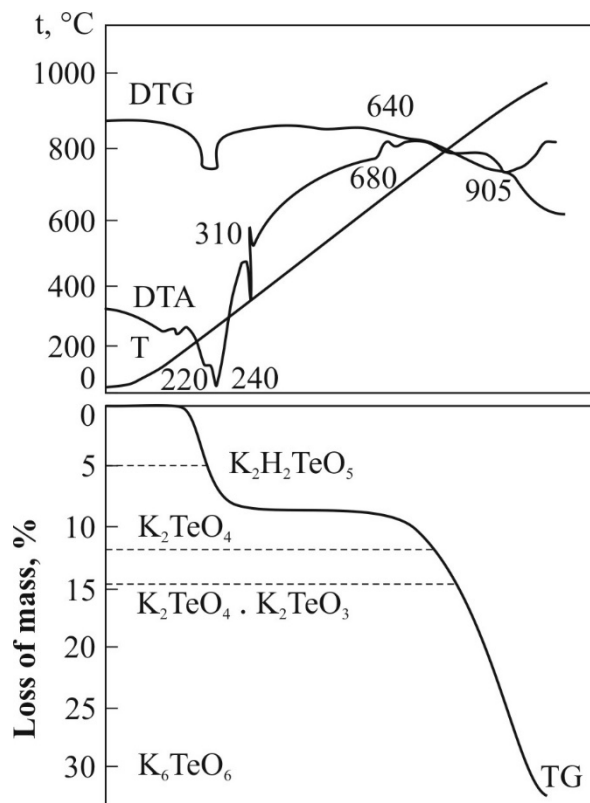
The other studies are carried out on apparatuses as follows: The X-ray analysis – on URD-6 (Germany), with anode Cu, K_α radiation and Ni - filter for β -radiation.

The derivatographic studies are carried out on a derivatograph MOM, type OD-102. Crystallographic observations are performed on an optical microscope "Docuval" (Carl Zeiss Jena, Germany).

All the lines registered by the X-ray analysis corresponded to $K_2H_4TeO_6$ by interplanar distances and intensities. Lines for the initial substances and alloys are not observed (Table 2).

Table 2. X-ray data for potassium tetrahydrogen orthotellurate $K_2H_4TeO_6$

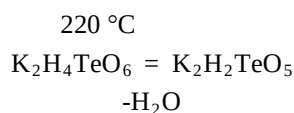
I/I_0	$d, \text{ \AA}$	I/I_0	$d, \text{ \AA}$
78	7.8933	72	3.0763
58	6.7015	50	2.9955
89	6.0619	58	2.7368
78	5.4172	64	2.5474
72	4.5026	50	2.3120
72	4.0368	56	2.1741
83	3.8062	39	2.1444
45	3.5172	100	2.0342
45	3.3359	45	1.9317

Fig. 1 Derivatogram of $K_2H_4TeO_6$

DTA- Differential thermal analysis: temperature difference,

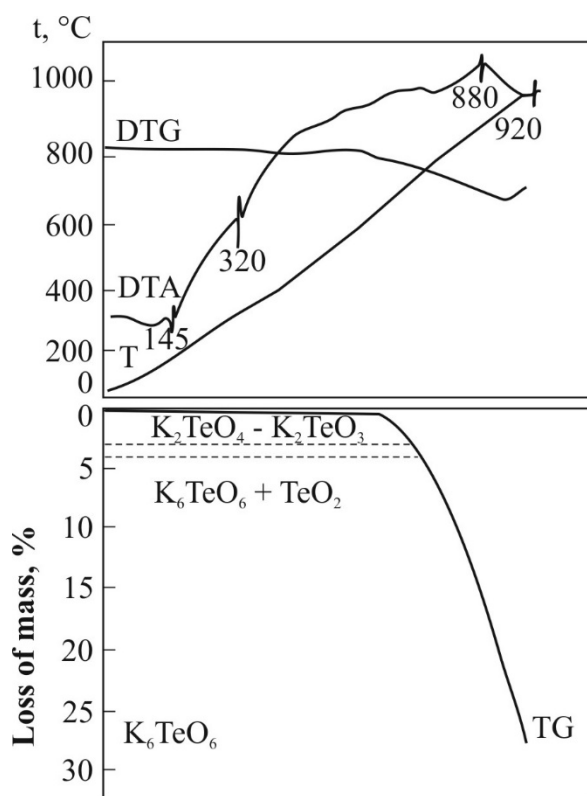
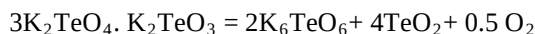
TG – Thermogravimetric analysis

The derivatogram of potassium tetrahydrogen orthotellurate is shown in Fig.1. The compound is thermally stable up to 135 °C. Above this temperature, a two-stage process of release of constitutional water. The endothermic effect at 220 °C is attributed to release of 1 mol of constitutional water according to:



The mass loss corresponding to this transformation is 6.02 mass % while theoretical value is 5.89 mass %. The data obtained from the chemical analysis showed that K_2O content is 32.70 mass %, TeO_3 – 61.12 mass %, H_2O – 6.18 mass %, while theoretical values K_2O is 32.68 mass %, TeO_3 – 61.06 mass % and H_2O – 6.26 mass %.

The endothermic effect at 240 °C is attributed to the release of the second mol of constitutional water and transformation of potassium tetrahydrogen orthotellurate into potassium metatellurate. The total mass loss by full dehydration is 11.84 mass % while theoretical value is 11.78 mass %. Data obtained from the chemical analysis showed that potassium metatellurate has the following composition: K_2O – 34.93 mass % and TeO_3 65.07 mass % while theoretically calculated K_2O is 34.91 mass % and TeO_3 – 65.09 mass %. The endothermic effect at 310 °C is not related to mass loss but to polymorphic transformation. This suggestion is confirmed by the fact that the X-ray pattern of a sample heated to this temperature differs from that taken at 500 °C. At temperature of 680 °C, the metatellurate transformed into mixed double salt $K_2TeO_4 \cdot K_2TeO_3$ as a result of intermolecular regrouping. The total mass loss resulting from all the transformations described so far is 14.44 mass %, while theoretical value is 14.40 mass %. Decomposition with transformation of the mixed tellurate-tellurite into potassium orthotellurate is observed at 905 °C. The decomposition occurs by the following mechanism:

Fig. 2. Derivatogram of K_2TeO_4

DTA- Differential thermal analysis: temperature difference,

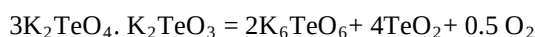
TG – Thermogravimetric analysis

The TeO_2 released becomes volatile at temperatures higher than 800 °C. For this reason, up to the final temperature of 950 °C of the derivatographic analysis carried out, the mass loss is as low as 35 mass % while the full process ending with obtainment of pure K_6TeO_6 phase should result in loss of 50.08 mass %.

Fig.2 shows the derivatogram of K_2TeO_4 . The compound is thermally stable up to temperature of 600 °C. Above this temperature, a two-stage decomposition took place. At 700-780 °C, decomposition occurs by the scheme:



The mass loss corresponding to this transformation was 3.02 mass% vs. theoretical value 2.97 mass%. The data obtained from the chemical analysis showed that K_2O content was 36.02 mass%, TeO_3 – 33.58 mass%, and TeO_2 30.49 mass%, vs. theoretical values K_2O – 35.93 mass%, TeO_3 – 33.56 mass% and TeO_2 30.51 mass%. At 905 - 920°C, decomposition occurs by the scheme:



At 950°C, the final temperature of the derivatographic analysis performed, the total mass loss from all the processes discussed above and related to mass reduction is as low as 29.3 mass % while theoretical value is 43.42 mass %. The discrepancy between theoretically calculated and really expected mass loss is due to TeO_2 becoming volatile at temperatures higher than 800 °C and the derivatigraphic analysis being performed and comparatively high heating rate. The scheme of thermal dissociation proposed is confirmed by the X-ray analysis. The pattern of the product registered at 950 °C showed phases of K_2TeO_4 , K_2TeO_3 and K_6TeO_6 .

3. CONCLUSION

Potassium hydrogen tellurate ($\text{K}_2\text{H}_4\text{TeO}_6$) is obtained by mixing of preliminarily heated solutions of potassium hydroxide (KOH) and orthotelluric acid (H_6TeO_6). Potassium tellurate (K_2TeO_4) is obtained by heating potassium hydrogen telluride ($\text{K}_2\text{H}_4\text{TeO}_6$) until release of the constitutional water. The two tellurates are subjected to derivatographic analysis. The mechanism of thermal decomposition is determined.

The derivatogram of potassium tetrahydrogen orthotellurate is shown that the compound is thermally stable up to 135 °C. Above this temperature, a two-stage process of release of constitutional water. The endothermic effect at 220 °C is attributed to release of 1 mol of constitutional water. The endothermic effect at 240 °C is attributed to the release of the second mol of constitutional water and transformation of potassium tetrahydrogen orthotellurate into potassium metatellurate.

The derivatogram of K_2TeO_4 shows that the compound is thermally stable up to temperature of 600 °C. Above this temperature, a two-stage decomposition took place. At 700-780 °C, after decomposition is obtained K_2TeO_4 , K_2TeO_3

The pattern of the product registered at 950 °C showed phases of K_2TeO_4 , K_2TeO_3 and K_6TeO_6 .

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