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# REACTIONS OF TELLURATES(IV) OF SOME 2nd GROUP METALS WITH BASIC OXIDES

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## Abstract

Calcium, strontium and barium tellurates(IV) were heated, in $N_2$ atmosphere, with stoichiometric amounts of CaO, SrO and BaO, respectively. The products of reactions, proceeding at 380–620°C, contained orthotellurate and telluride anions formed in disproportionation.

**Keywords**: barium tellurate, calcium tellurate, strontium tellurate

## Introduction

The tellurate(IV) anion $TeO_3^{2-}$ belongs to the group of the so-called Ψ-anions formed by the more electronegative elements of the *sp* block and having a lone electron pair in their valency states. In all solid tellurates(IV) the shape of the $TeO_3^{2-}$ anion is typical for the Ψ-anions, i.e. a pyramid with lone electron pair in the apex.

Salts containing Ψ-anions undergo, on heating, specific reactions of thermal decomposition, which consists in disproportionation of the anionic sublattice. As a result, products containing species at higher and lower oxidation states are formed, e.g.:

$$4NaClO_3 \rightarrow 3NaClO_4 + NaCl$$

$$4Na_2SO_3 \rightarrow 3Na_2SO_4 + Na_2S$$

$$8Na_2HPO_3 \rightarrow 4Na_3PO_4 + Na_4P_2O_7 + 2PH_3 + H_2O$$

It has been found that the course of disproportionation process and, in particular, the kind of the products formed, depend on the sort of metal cations involved [1–6]. For example, in the presence of strongly acidic $Zn^{2+}$ cation, the sulfite anion decomposes as follows:

$$ZnSO_3 \rightarrow ZnO + SO_2$$

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In lower periods the scheme of decomposition of the Ψ-anions depends on both the kind of the anion-forming element and the cation involved. The aim of the present work was to study the course of decomposition of tellurate(IV) anion on heating in the presence of calcium, strontium and barium oxides.

## Experimental

### *Materials*

Solid anhydrous calcium, strontium and barium tellurates(IV) were obtained by dehydration of hydrous salts precipitated from aqueous solutions. These were prepared from solid salts: $K_2TeO_3$ (pure, Reakhim), $BaCl_2 \cdot 2H_2O$ (anal. grade, POCh), $SrCl_2 \cdot 2H_2O$ (anal. grade, POCh), $CaCl_2 \cdot 6H_2O$ (anal. grade, POCh). In solid phase reactions use was made of the following solid oxides: BaO (anal. grade, POCh), SrO obtained by decomposition of $Sr(OH)_2$ at 700°C, CaO obtained by decomposition of $CaCO_3$ at 900°C. The reaction mixtures were prepared by grinding stoichiometric amounts of tellurites(IV) with corresponding metal oxides in the atmosphere of nitrogen free of oxygen.

### *Apparatus*

Thermogravimetric analyses were performed with the aid of Derivatograph, produced by MOM, Budapest. The phase composition of the starting materials and of the products of reactions was determined by powder X-ray diffraction method using HZG-4 apparatus. The infrared absorption analyses were performed using the analyzer Specord IR by the method of KBr tablets.

## Discussion of results

Calcium, strontium, and barium tellurates(IV), obtained by precipitation in reactions of $K_2TeO_3$ with chlorides of the corresponding metals, were subjected to thermogravimetric analysis. All the salts, after having been dried at 105°C, contained still some amounts of crystallization water. For this reason, before being used for reactions with the oxides, they were dried at 300°C in a stream of nitrogen free of $O_2$. Thermogravimetric analyses of dehydrated $CaTeO_3$, $SrTeO_3$ and $BaTeO_3$ showed, that in inert gas atmosphere they were stable at temperature up to 900°C.

The DTA curves recorded in atmosphere of $O_2$-free nitrogen for mixtures of $CaTeO_3$, $SrTeO_3$ and $BaTeO_3$ with corresponding oxides CaO, SrO and BaO, revealed the existence of an exothermic effect at a temperature depending on the kind of the cation involved (Fig. 1). The temperatures are presented in Table 1.

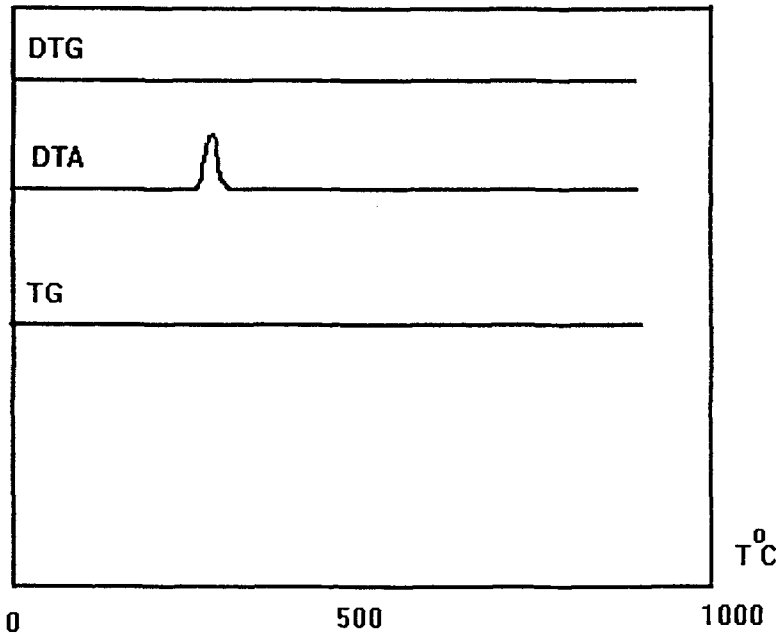


**Fig. 1** Thermal curves of a mixture of $2BaTeO_3 + 3BaO$ ($m$=480 mg, TG=100 mg, $v_g$= 10 deg·min$^{-1}$, $N_2$dyn)

**Table 1** Disproportionation temperatures of tellurates(IV) in presence of corresponding oxides

| Mixture | Disproportionation temperature/ °C |
|---|---|
| $2CaTeO_3 + 3CaO$ | 620 |
| $2SrTeO_3 + 3SrO$ | 420 |
| $2BaTeO_3 + 3BaO$ | 380 |

The phase composition of the reaction mixtures was analyzed by X-ray diffraction method both before and after the reaction.

In all cases the products of the solid state reactions contained the orthotellurate phases: $Ca_3TeO_6$, $Sr_3TeO_6$ and $Ba_3TeO_6$ . Because of the absence of oxidants in the reaction systems such products could not be formed as only due to disproportionation reactions. The other product of such a reaction should be either tellurite ion $Te^{-2}$ or free Te. In the latter case the reaction mixture should darken, but no such effect was observed. No presence of free tellurium in the reaction products was also detected by chemical methods. On the other side, X-ray diffraction analyses did not reveal the presence of telluride phases, probably because of their amorphous form. The presence of tellurides was confirmed, however, by chemical methods, using the reaction:

$$TeO_6^{6-} + 3Te^{2-} + 12H^+ \rightarrow 4Te + 6H_2$$

Small amount of the reaction mixture, treated with a HCl solution, dissolves with simultaneous precipitation of solid black Te. The obtained results enable to state, that anhydrous calcium, strontium and barium tellurites, heated in inert gas atmosphere in the presence of oxides of these metals, undergo disproportionation which proceeds according to the following scheme:

$$4MTeO_3 + 6MO \rightarrow 3M_3TeO_6 + MTe$$

The disproportionation does not take place, however, on heating in the absence of alkali oxides. In this respect tellurates(IV) behave similarly to other ψ-anions formed by the elements of the 5-th period.

## Conclusions

The studies performed enable to make the following conclusions:

1. Calcium, strontium, and barium tellurates(IV), precipitated from aqueous solutions of soluble salts, are strongly hydrated. On heating the hydration water is slowly liberated with rising temperature. For complete dehydration heating to about 300°C is necessary.

2. Anhydrous $CaTeO_3$, $SrTeO_3$ and $BaTeO_3$ heated in inert gas atmosphere do not decompose up to about 900°C.

3. Calcium, strontium and barium tellurates(IV), heated in the presence of corresponding oxides, undergo exothermic disproportionation reactions which yield corresponding orthotellurates(VI) ($M_3TeO_6$) and tellurides.

4. The temperature, at which the disproportionation reactions are effected, increases with increasing acidity of the metal cation involved.

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**Zusammenfassung** — In einer Stickstoffatmosphäre wurden Calcium-, Strontium- und Bariumtellurate(IV) mit stöchiometrischen Mengen von CaO, SrO und BaO erhitzt. Die Produkte der bei 380–620°C ablaufenden Reaktion enthalten in einer Disproportionierungsreaktion entstehende Orthotellurate und Tellurid-Anionen.