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STAGES OF THERMAL DECOMPOSITION OF SODIUM OXO-SALTS OF SULPHUR

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Thermal behaviour of sodium oxo-salts of sulphur: Na_2SO_4, $Na_2S_2O_7$, $Na_2S_2O_6$, Na_2SO_3, $Na_2S_2O_5$, $Na_2S_2O_4$, $Na_2S_2O_3$, $Na_2S_3O_6$ and of sulphides Na_2S and Na_2S_2 was studied on heating up to 1000°C. The experiments were performed with anhydrous compounds obtained from commercial products by recrystallisation and dehydration. The stage mechanisms of decomposition of anionic sub-lattices of the salts have been proposed basing on the Górski's morphological classification of simple species. The thermal stability and the stage decomposition mechanisms were correlated with the structure and the potential chemical properties of the salt anions. The thermal decomposition processes were studied by means of thermal analysis, and the decomposition products were identified by means of X-ray phase analysis.

Keywords: *elementary transformations, Górski's morphological classification, sodium oxo-salts, thermal decomposition mechanism*

Introduction

Investigations on thermal decomposition of chemical compounds are usually reported in the form of single, individual studies. In the present paper we are going to show, basing on the example of sulphur oxo-salts, a complex approach to the problem of thermal decomposition of chemical compounds and their interpretation at the molecular level.

As a start point we shall use the atomic core-based definition of chemical elements, proposed by Górski, and the classification of simple species developed on that basis by the same author [1]. According to that conception all the simple species of sulphur (both oxy-anions and neutral molecules) can be located in a system obtained by filling the valence states of sulphur cores by electrons and oxide anions.

In such a system a simple species can be described by of a set of three numbers:

- number of free electrons in the valence states of sulphur pertaining to one sulphur core in the simple species (e_v),
- number of electric charges brought by the oxide anions into the sphere of sulphur core and calculated per one core (e_z),
- a number of sulphur cores in the simple species (n).

The three numbers enable to create a three-dimensional system of simple species, which for integral values of e_v and e_z can be represented in tabular form as a set of simple species of sulphur projected on the e_v–e_z plane as shown in Fig. 1.

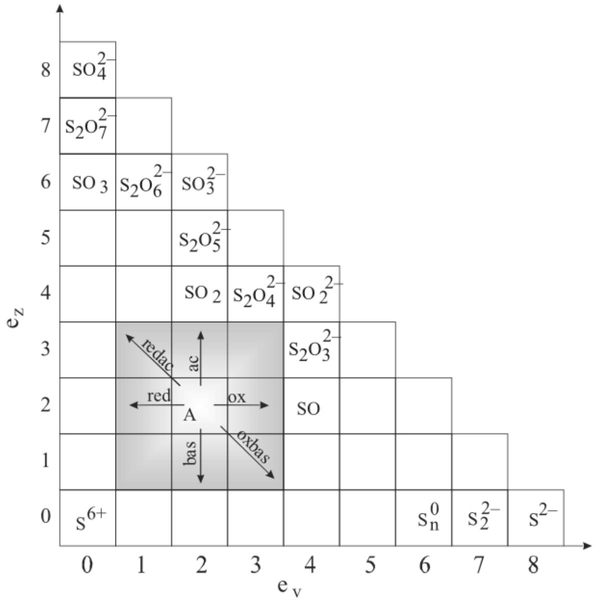

Fig. 1 Tabular version of classification of sulphur simple species and potential possibilities of the species as guided reactants

The positions of the simple species shown in Fig. 1 correspond to definite chemical properties, and thus also to a definite reactivity, which for monocentric species is represented by a set of arrows. The arrows show potential products of transformation of a given species transformed according to elementary processes resulting from the uniform definition of acids, bases, oxidizers and reducers [1]. Elementary reactions of individual species consist in either loss or acceptance of electrons in red–ox processes or

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Table 1 Elementary half-reactions in transformations of mono-centric sulphur species

Species	Properties	Elementary half-reactions		
SO_4^{2-}	oxbas	$SO_4^{2-}+8\check{e}\rightarrow S^{2-}+4O^{2-}$	or	$SO_4^{2-}\rightarrow S^{2-}+4O^0$
	bas	$SO_4^{2-}\rightarrow SO_3^0+O^{2-}$		
SO_3	ac	$SO_3^0+O^{2-}\rightarrow SO_4^{2-}$		
	ox	$2SO_3^0+2\check{e}\rightarrow S_2O_6^{2-}$	or	$SO_3^0+2\check{e}\rightarrow SO_3^{2-}$
	oxbas	$SO_3+2\check{e}\rightarrow SO_2^0+O^{2-}$	or	$SO_3^0\rightarrow SO_2^0+O^0$
SO_3^{2-}	oxbas	$SO_3^{2-}+6\check{e}\rightarrow S^{2-}+3O^{2-}$	or	$SO_3^{2-}\rightarrow S^{2-}+3O^0$
	redac	$SO_3^{2-}+O^{2-}\rightarrow SO_4^{2-}+2\check{e}$	or	$SO_3^{2-}+1/2O_2\rightarrow SO_4^{2-}$
	bas	$SO_3^{2-}\rightarrow SO_2^0+O^{2-}$		
	red	$SO_3^{2-}\rightarrow SO_3+2?$	or	$2SO_3^{2-}\rightarrow S_2O_6^{2-}+2\check{e}$
SO_2	ac	$SO_2^0+O^{2-}\rightarrow SO_3^{2-}$		
	ox	$2SO_2^0+2\check{e}\rightarrow S_2O_4^{2-}$	or	$SO_2^0+\check{e}\rightarrow SO^{2-}$
	oxbas	$SO_2^0+4\check{e}\rightarrow S_0+2O^{2-}$	or	$SO_2^0\rightarrow S^0+2O^0$
	redac	$SO_2^0+O^{2-}\rightarrow SO_3^0+2\check{e}$	or	$SO_2^0+O^0\rightarrow SO_3^0$
S^{2-}	redac	$S^{2-}+4O^{2-}\rightarrow SO_4^{2-}+8\check{e}$	or	$S^{2-}+4O^0\rightarrow SO_4^{2-}$
	red	$2S^{2-}\rightarrow S_2^{2-}+2\check{e}$		
S_2^{2-}	red	$S_2^{2-}\rightarrow 2S_n+2\check{e}$		
	redac	$S_2^{2-}+3O^{2-}\rightarrow S_2O_3^{2-}+6\check{e}$	or	$S_2^{2-}+3O^0\rightarrow S_2O_3^{2-}$
	ox	$S_2^{2-}+2\check{e}\rightarrow 2S^{2-}$		

in loss or acceptance of oxide anions O^{2-} participating in the ac–bas processes.

There exists also a specific type of elementary reactions, which is a combination of the two processes. Such reactions proceed with either acceptance or loss of oxygen atoms and thus they are equivalent to either a loss of $2\tilde{e}$ and acceptance of O^{2-} or a loss of O^{2-} and acceptance of $2\tilde{e}$. Hence these reactions may be considered as coupled redac or oxbas reactions. The list of elementary half-reactions in transformations of mono-centric species of sulphur, as resulting from their positions in the classification system, is shown in Table 1.

Overall transformations of the anionic sub-lattices of the salts under study may be regarded as a sum of the series of elementary processes passed on the starting salt anions and on the intermediate species formed.

Sodium salts of the anions were used in the experiments because of the specific properties of the Na^+ cations. The large cationic radius (102 pm) [2], small charge, and low electron binding energy cause that during the decomposition of the salts the cations do not participate in the decomposition of the anionic sub-lattices neither as acid-base reactants nor as oxidants. Only at temperatures exceeding 1000°C, hence about the decomposition temperatures of Na_2SO_4 and Na_2S, sodium cations can participate in such processes as oxidizers, on passing to the gas phase as sodium metal, or as acids, on forming ion pairs in the gas products. Hence all salts containing this cationic counterion should form, as far as thermal stability and sequence of thermal dissociation stages are concerned, a consistent reaction series resulting from the properties of the species formed in the decomposition and products of steadily increasing stability.

Experimental

The tests were performed with the use of salts of the following origin: Na_2SO_4 (a.p., POCh), $Na_2S_2O_7$ obtained by thermal decomposition of $Na_2S_2O_8$ (a.p., POCh) at 220°C, $Na_2S_2O_6$ obtained by dehydration of $Na_2S_2O_6{\cdot}2H_2O$ (a.p., POCh) at 150°C, Na_2SO_3 (a.p., POCh), $Na_2S_2O_5$ (a.p., POCh), $Na_2S_2O_4$ (a.p., POCh), $Na_2S_2O_3$ obtained by dehydration of $Na_2S_2O_3{\cdot}5H_2O$ (a.p., POCh) at 150°C, $Na_2S{\cdot}9H_2O$ (a.p., POCh), $Na_2S_2{\cdot}2H_2O$ obtained by synthesis from $Na_2S{\cdot}9H_2O$ (a.p., POCh) and S (a.p., POCh), $Na_2S_3O_6$ obtained by synthesis from $Na_2S_2O_3$ and H_2O_2 (a.p., POCh), then twice recrystallized and dried at 70°C.

The thermal stability of the compounds was determined by means of complex thermal analysis using the OD 202 Derivatograph, system Paulik–Paulik–Erdey under the following conditions: DTA 1/5, DTG 1/10 and TG 100. The samples weighing several hundred mg were heated (in alumina crucibles) with a rate of 10°C min^{-1} in the stream of O_2-free nitrogen (flow rate 50 cm^3 min^{-1}). Solid products of thermal dissociation were identified by means of X-ray phase analysis using a Siemens HZG4 apparatus.

In cases where greater amounts of the decomposition products were needed the decomposition was carried out in a tubular furnace, in a stream of nitrogen, at specified temperatures determined from the data of thermal analysis.

Results and discussion

The highest thermal stability, among the sodium salts of sulphur oxy-acids, was obtained for Na_2SO_4, which did not decompose over the whole temperature region studied. It underwent a reversible polymorphic transformation at 255°C and melted without decomposition at 920°C. According to literature data sodium sulphate(VI) passes to the gas phase with thermal dissociation above 1200°C, and the gas products contain $Na_{(g)}$, $SO_{2(g)}$ and $O_{2(g)}$ [3]. The decomposition mechanism of pure Na_2SO_4 leading to Na_2O, SO_2 and O_2 as the end products, proposed by Lee [4] is of lesser probability.

Na_2S appeared to be thermally stable up to 920°C. Thermal analysis curves of $Na_2S{\cdot}9H_2O$ do not reveal any effect besides to the ones due to dehydration of the hydrous sulphide occurring below 200°C. According to literature data sodium sulphide melts at 1177°C, and a phase transition is observed at 1000°C [5].

A lesser thermal stability was for Na_2SO_3 which is decomposed without change of mass, with an exothermic effect with maximum at 660°C, to give a mixture of solid products Na_2SO_4 and Na_2S, conforming to the balance equation:

$$4Na_2SO_3 \rightarrow 3Na_2SO_4 + Na_2S \qquad (1)$$

$Na_2S_2O_7$ (Fig. 2) melts at 405°C, and its decomposition proceeds in a wide temperature range from 380 to 900°C, according to the balance equation:

$$Na_2S_2O_7 \rightarrow SO_3^0 + Na_2SO_4 \qquad (2)$$

Some endothermic effects were also observed at temperatures above 600°C. According to literature data $Na_2S_2O_7$ decomposes in the temperature range 380–790°C [6], and melting point of that compound is 402°C [7, 8]. Theoretically calculated loss of mass is 36.0%, and the value obtained in our experiments is 36.21%.

The decomposition of $Na_2S_2O_5$ (Fig. 3) proceeds at temperatures above 140°C, with a maximum on DTA curve observed at 200°C, conforming to equation:

$$Na_2S_2O_5 \rightarrow Na_2SO_3 + SO_2 \qquad (3)$$

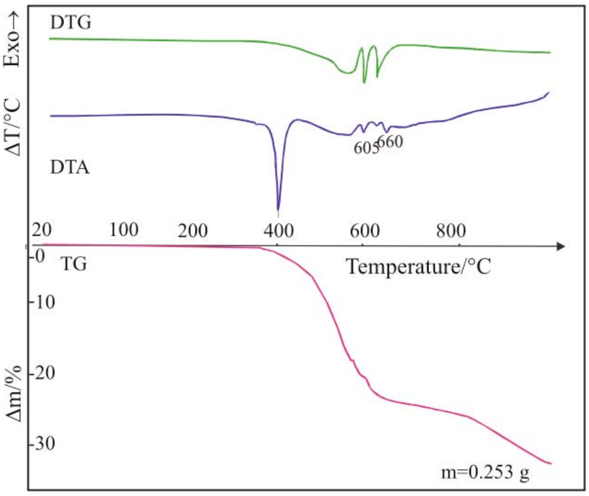

Fig. 2 TG, DTG, DTA curves of $Na_2S_2O_7$

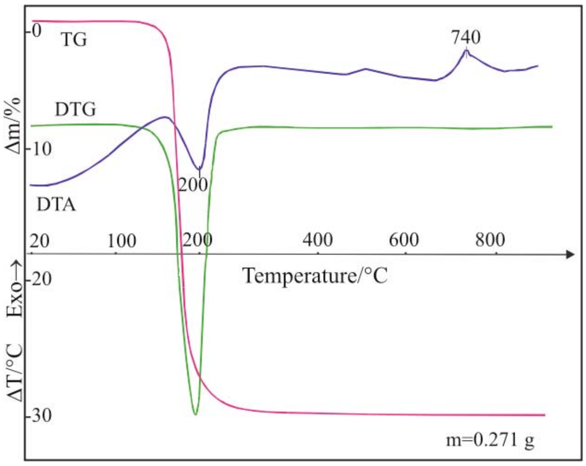

Fig. 3 TG, DTG, DTA curves of $Na_2S_2O_5$

A small exothermic effect due to the disproportionation of sulphate(IV) formed is observed at 740°C. According to Erdey [9] the decomposition of that compound in air atmosphere proceeds with a maximum on DTA curve at 170°C. Sulphate(IV) is oxidized to sulphate(VI) and the disproportionation effect is invisible. The theoretical loss of mass is 33.68%, and the one calculated from our experimental data is 30.07%.

Thermal dissociation of $Na_2S_2O_6$ (Fig. 4) proceeds at temperatures above 250°C, with a maximum on DTA curve at 280°C, according to equation:

$$Na_2S_2O_6 \rightarrow SO_2 + Na_2SO_4 \qquad (4)$$

and the thermal analysis curves are identical with the ones obtained formerly by Zsakó *et al.* [10]. Theoretical loss of mass is 31.07%, and the one calculated from our experiments is 31.34%.

$Na_2S_2O_4$ decomposes above 130°C, with a strong exothermic effect and a maximum on DTA curve at 180°C (Fig. 5). The decomposition proceeds with a theoretical mass loss 18.39%, due to liberation

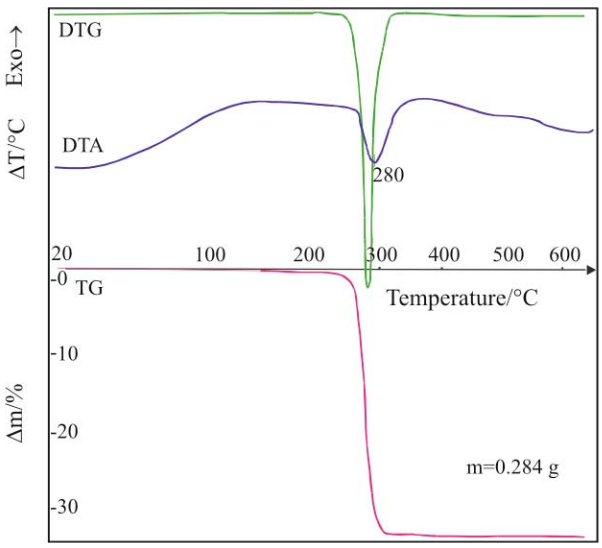

Fig. 4 TG, DTG, DTA curves of $Na_2S_2O_6$

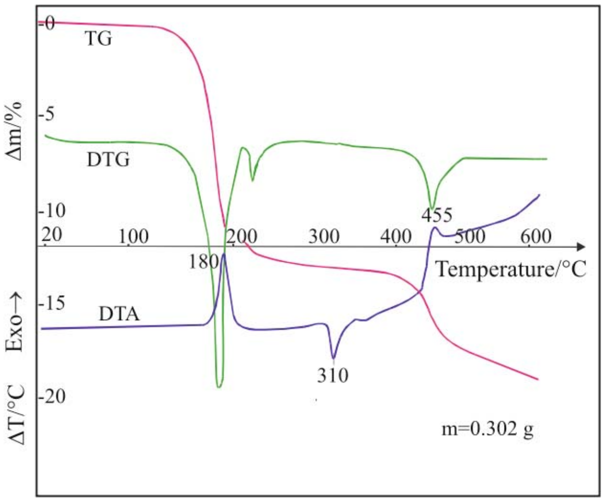

Fig. 5 TG, DTG, DTA curves of $Na_2S_2O_4$

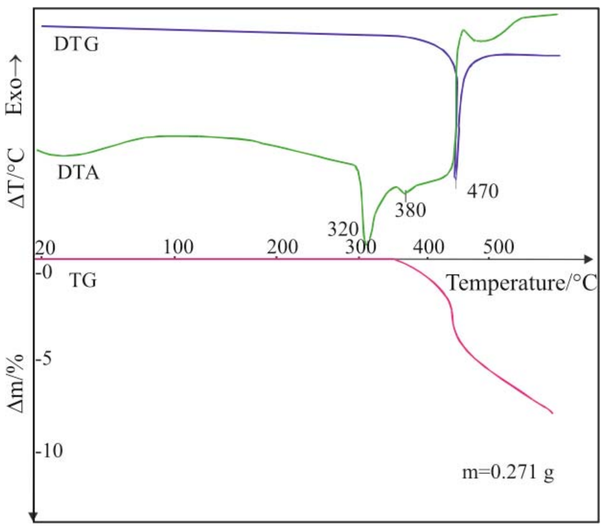

Fig. 6 TG, DTG, DTA curves of $Na_2S_2O_3$

of SO_2. The solid products were found to contain Na_2SO_3 and $Na_2S_2O_3$. The decomposition proceeds conforming to the following reaction:

$$2Na_2S_2O_4 \rightarrow SO_2 + Na_2S_2O_3 + Na_2SO_3 \quad (5)$$

Higher temperatures reveal some effects connected with transformations of the decomposition products: an endothermic effect at 310°C due to the melting of thiosulphate produced and another one above 450°C connected with its decomposition. The results of former studies [11] suggest that both the decomposition temperature and the mechanism of decomposition are connected with layer thickness of the compound. In cases where the sample was spread in a thin layer in the crucible two exothermic effects at 215 and 250°C, respectively, were observed, and for a thick layer the decomposition proceeded at 205°C. The loss in mass as calculated from the experimental data and equal to 13.33% deviates considerably from the theoretically calculated one, perhaps due to the complicated decomposition mechanism of $Na_2S_2O_4$.

Figure 6 shows the results of thermal analysis of sodium thiosulphate. The effect observed on the DTA curve at 320°C corresponds to the melting process. This is followed by a start of decomposition of $Na_2S_2O_3$ at 380°C, manifested by a strong exothermic effect. The decomposition may be presented by the following balance equation:

$$4Na_2S_2O_3 \rightarrow 3Na_2SO_4 + Na_2S_5 \quad (6)$$

Literature data concerning the decomposition of thiosulphate take notice of an endothermic effect at 330°C as being due to melting of the compound, and an exothermic effect at 470°C due to the decomposition [9]. Na_2S_2 does not decompose up to 920°C. After the end of dehydration at 250°C, Na_2S_2 melts at 470°C (literature data: 469.5°C [12], 475°C [13], 482° [14], 478°C [15]).

$Na_2S_3O_6$ was stable up to temperature 200°C. It decomposes in two stages with maxima on the DTA curve at 250 and 320°C (Fig. 7), conforming to the equation:

$$Na_2S_3O_6 \rightarrow SO_2 + S + Na_2SO_4 \quad (7)$$

Thermoanalytical curves obtained for that compound are identical with those obtained previously [11]. Theoretical loss of mass is 40.03%, and that obtained in our experiments was calculated as 39.16%.

While comparing the temperature regions of decomposition of sodium salts of sulphur anions presented in Fig. 8a it is possible to relate their stability with the structure of the anions. The stability of the compounds depends on the stability of sulphur species and this, in turn, on the binding energy of S–O bonds in species with single central core or of S–S

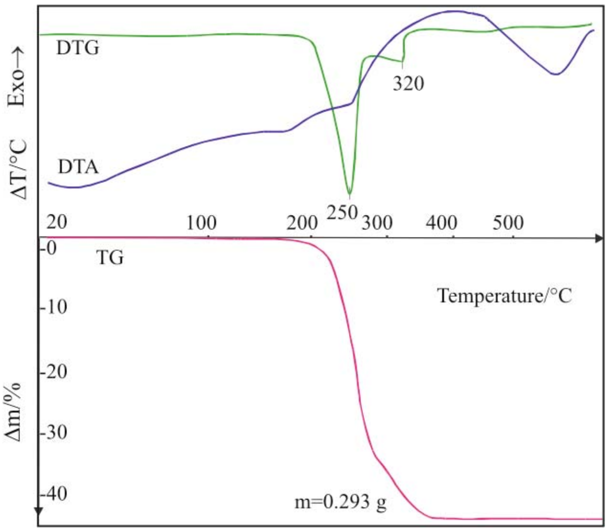

Fig. 7 TG, DTG, DTA curves of $Na_2S_3O_6$

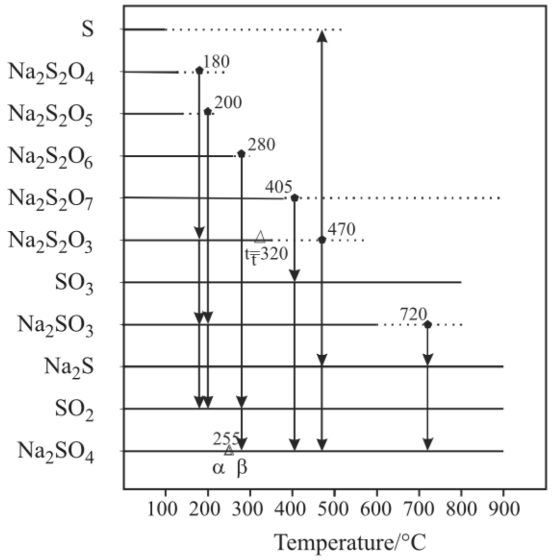

Fig. 8a Temperature ranges of decomposition of sulphur oxides and sodium salts

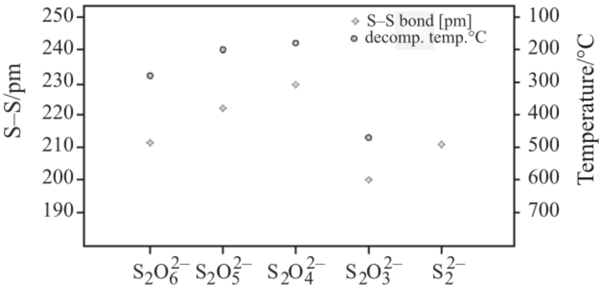

Fig. 8b Interrelation between S–S bond length and thermal stability of two-core sulphur species

and S–O–S bonds in species with two or more central atoms of sulphur. The energies of these bonds are in correlation with their length. Among the mono-core species under consideration the shortest S–O bond is observed in the SO_4^{2-} anion (147 pm [16] as compared with 151 pm [17] in SO_3^{2-}). The shortest S–O bonds in the oxides are 141 pm in SO_3 [18] and 143 pm in SO_2 [19]. The $S_2O_7^{2-}$ anion in $Na_2S_2O_7$ with 163 pm S–O bond length [20] is the sole species with an S–O–S oxide bridge. Other bi-coric sulphur species contain only S–S bonds with the lengths of: 214 pm in $S_2O_6^{2-}$ [21], 222 pm in $S_2O_5^{2-}$ [22], 239 pm in $S_2O_4^{2-}$ [23], 200 pm in $S_2O_3^{2-}$ [24] and 213 pm in S_2^{2-} [12]. As results from Fig. 8b a correlation exists between their bond lengths and thermal stability. The highest stability is observed in the SO_4^{2-}, and a lesser one in SO_3^{2-}. In bicentric anions having the S–S bond the least stability is observed in the $S_2O_4^{2-}$ anion with the longest S–S bond, and the highest stability in $S_2O_3^{2-}$ anion with the shortest S-S bond. Among bicentric sulphur species the highest stability was found in $S_2O_7^{2-}$ anion having an oxide bridge. All the sulphur oxy-anions, both the charged species and oxide molecules, are interconnected through elementary reactions that consist on transfer of either electrons of oxide ligands. Hence there is a question, whether thermal transformations of anionic sub-lattices in sodium salts can be built from the elementary reactions that link the anions cited with the species of end products of the decomposition?

As can be seen in Fig. 8a the highest stability is observed in the series of species with monocoric coordination centre disposed in the line e_z+e_v=8, namely: SO_4^{2-}, SO_3^{2-}, S^{2-} and the oxide species: SO_3 and SO_2. The species of Na_2SO_4 and Na_2S that have the anions with symmetrically equilibrated fields of sulphur cores (in SO_4^{2-} the sulphur core has a purely ligand environment, and in S^{2-} the environment is purely electronic) when heated above 920°C, pass to the gas phase thus becoming an equilibrium state of various species unstable in the solid phase [3, 4]. SO_2 molecules and S atoms are also stable at temperatures above 1000°C.

A lower stability is observed in SO_3^{2-} anions in Na_2SO_3. This compound decomposes at 720°C in a complex disproportionation accompanied by a strong exothermic effect. The products obtained in the decomposition of sodium sulphate(IV) are the more stable, formerly discussed compounds, containing more stable species SO_4^{2-} and S^{2-} (reaction 1). The complex disproportionation consists in a cascade reaction of oxygen transfer effected within the line e_z+e_v=8, in which a part of SO_3^{2-} anions play the role of redac reactants transformed then into SO_4^{2-} anions, and the other part are oxbas reactants being transformed into S^{2-}, as shown in Fig. 9 (equations in Table 1). Hence the decomposition consists in a transfer of oxygen atoms between SO_3^{2-} anions. The anions, while acting as

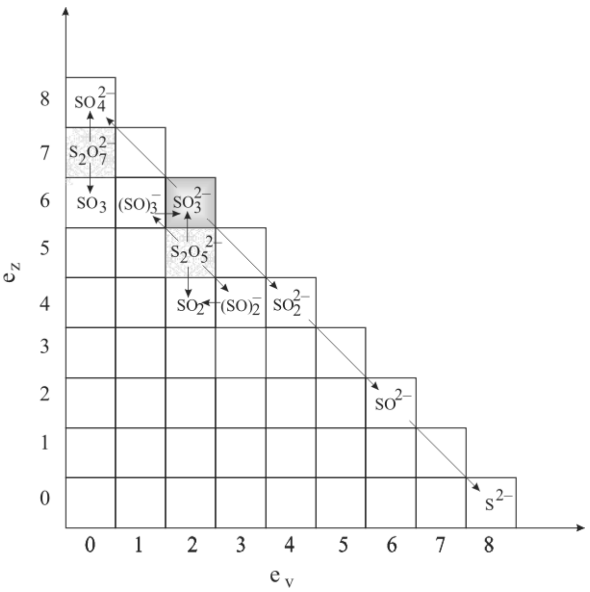

Fig. 9 Schemes of thermal decomposition of $S_2O_7^{2-}$ in $Na_2S_2O_7$, SO_3^{2-} in Na_2SO_3 and $S_2O_5^{2-}$ in $Na_2S_2O_5$

the oxbas reactants must pass, successively, though SO_2^{2-} and SO^{2-}, two unstable sulphur oxy-anions having still stronger oxbas properties (analogous changes in the oxbas properties are observed in the series of chlorine oxy-anions occupying the places along the line $e_z+e_V=8$, namely: ClO_4^-, ClO_3^-, ClO_2^- and ClO^-). Hence the decomposition leads to obtaining of sulphur species with purely electron and ligand environment, the most stable in the system. Despite of the increase of basic properties the unstable species SO_2^{2-} and SO^{2-} do no react with Na^+ cations.

Thermal stability of the salts containing bicentric sulphur species (disposed along the line $e_z+e_V=7$) is smaller than that observed in the former group of salts, although also in this group the highest stability is observed in salts having the anions with purely ligand ($S_2O_7^{2-}$) or purely electron (S_2^{2-}) environment of both atomic cores and with both ligand and electron environment at individual sulphur cores in $S_2O_3^{2-}$. The salt with $S_2O_7^{2-}$ anions was the most stable among the oxy-salts in this group. The decomposition of that salt following its melting consists in rupture of the oxide bridge (Fig. 9) hence in an ac–bas disproportionation due to volatility of SO_3^0:

$$S_2O_7^{2-}\rightarrow SO_3^0+SO_4^{2-}$$

The stability of the other oxy-salts containing bicentric anions with S–S bonds is diverse according to the strength of the S–S bonds, which are the weakest in each of those anions. The simplest way of decomposition of the S–S bonds consists in the homolytic rupture leading to formation of monocentric radical species:

$$S_2O_6^{2-}\rightarrow 2SO_3^-$$

$$S_2O_5^{2-}\rightarrow SO_3^-+SO_2^-$$

$$S_2O_4^{2-}\rightarrow 2SO_2^-$$

$$S_2O_3^{2-}\rightarrow 2SO_3^-+S^-$$

The formation of free radicals in the primary decomposition can be traced by means of the EPR technique. Literature data show that formation of radicals was found in the decomposition of $Na_2S_2O_6$ (SO_3^-) [25], $Na_2S_2O_5$ (only SO_2^- radicals were found) [26], and $Na_2S_2O_4$ (SO_2^-) [26], and no radicals were detected in the decomposition of thiosulphate. None of the radicals formed was stable. They undergo successive reactions proceeding with a transfer of electrons and oxide anions owing to the differences in ac–bas properties of the species resulted after the transfer of electrons. In the case of $S_2O_6^{2-}$ anion (Fig. 10) the decomposition proceeds through the following successive stages:

$$S_2O_6^{2-}\rightarrow 2SO_3^- \quad \text{(I)}$$

$$2SO_3^-\rightarrow SO_3^0+SO_3^{2-} \quad \text{(IIa)}$$

$$SO_3^0+SO_3^{2-}\rightarrow SO_4^{2-}+SO_2 \quad \text{(IIb)}$$

among which the stages IIa (electron transfer) and IIb (transfer of oxide ligand) can proceed simultaneously to give the final products:

$$S_2O_6^{2-}\rightarrow SO_4^{2-}+SO_2$$

In the case of $S_2O_5^{2-}$ the decomposition leads to formation of SO_2 and SO_3^{2-}. The asymmetrical struc-

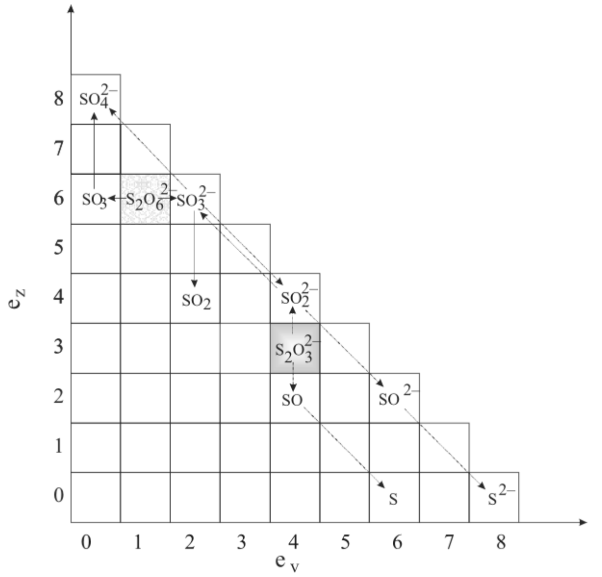

Fig. 10 Schemes of thermal decomposition of $S_2O_6^{2-}$ in $Na_2S_2O_6$ and $S_2O_3^{2-}$ in $Na_2S_2O_3$

ture of $S_2O_5^{2-}$ and the presence of SO_2^- radicals [26] detected in the decomposition suggest that the first stage of decomposition of $S_2O_5^{2-}$ anions consists in formation of the radicals:

$$S_2O_5^{2-} \rightarrow SO_3^- + SO_2^-$$

and electron transfer takes place in the successive stage (Fig. 9):

$$SO_3^- + SO_2^- \rightarrow SO_3^{2-} + SO_2$$

A single stage heterolytic decomposition, leading directly to formation of the end products, should also not be excluded:

$$S_2O_5^{2-} \rightarrow SO_3^{2-} + SO_2$$

The decomposition of anions in $Na_2S_2O_4$ may be presented as a scheme the following elementary transformations (Fig. 11):

$$2S_2O_4^{2-} \rightarrow 4SO_2^-$$

$$4SO_2^- \rightarrow 2SO_2 + 2SO_2^{2-}$$

$$2SO_2^0 + 2SO_2^{2-} \rightarrow 2SO_3^{2-} + 2SO$$

$$2SO \rightarrow S + SO_2$$

$$SO_3^{2-} + S \rightarrow S_2O_3^{2-}$$

$$2S_2O_4^{2-} \rightarrow S_2O_3^{2-} + SO_2 + SO_3^{2-}$$

The process depends on the properties of the species formed successively in the course of the decomposition. The SO_2^- radicals, formed in the rupture of the S–S bond, react with one another, like in the case of $S_2O_6^{2-}$, by transfer of electrons and oxide ligands, thus leading to formation of SO_3^{2-} and SO. The unstable SO disproportionates into SO_2 and S, and the latter reacts with SO_3^{2-} anions to produce $S_2O_3^{2-}$ anions.

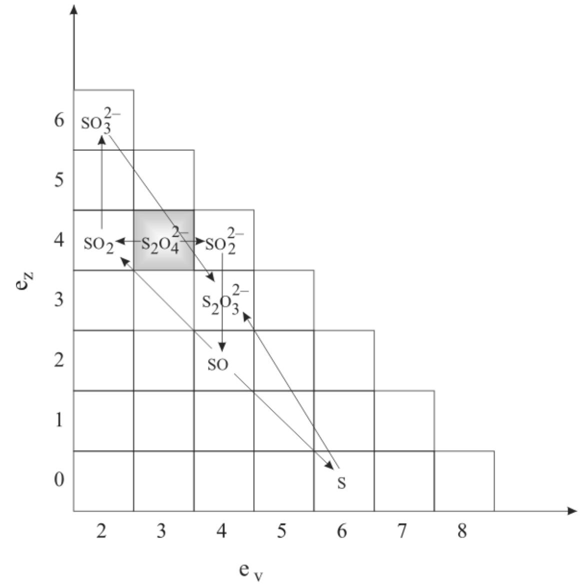

Fig. 11 Scheme of thermal decomposition of $S_2O_4^{2-}$ in $Na_2S_2O_4$

The salt of the $S_2O_3^{2-}$ anion, which is the most stable among the bicoric sulphur salts (Fig. 10), decomposes to SO_4^{2-} and S_5^{2-} (4S and S^{2-}). At the decomposition temperature the $S_2O_3^{2-}$ anion dissociates:

$$S_2O_3^{2-} \rightarrow S + SO_3^{2-}$$

and then the SO_3^{2-} anion disproportionates to SO_4^{2-} and S^{2-} with simultaneous binding of sulphur by S^{2-} to form S_5^{2-}:

$$4SO_3^{2-} + 4S \rightarrow 3SO_4^{2-} + S_5^{2-}$$

Thermal dissociation of sodium trithionate, containing a complex $S_3O_6^{2-}$ anion and representing a series of salts having thionate anions, proceeds in conformity with the following equation:

$$Na_2S_3O_6 \rightarrow SO_2 + S + Na_2SO_4$$

Thermal decomposition of multicentric species such as $S_3O_6^{2-}$ proceeds in a way analogous to the thermal decomposition of $Na_2S_2O_6$. The mechanism of that reaction may be interpreted as follows:

$$S_3O_6^{2-} \rightarrow S_2O_3^- + SO_3^- \qquad \text{(I)}$$

$$S_2O_3^- + SO_3^- \rightarrow S_2O_3^{2-} + SO^3 \qquad \text{(IIa)}$$

$$S_2O_3^{2-} + SO_3 \rightarrow S_2O_2 + SO_4^{2-} \qquad \text{(IIb)}$$

$$S_2O_2 \rightarrow SO_2 + S \qquad \text{(III)}$$

$$\Sigma S_3O_6^{2-} \rightarrow SO_2 + S + SO_4^{2-}$$

Conclusions

The morphological classification of sulphur oxycompounds, which joins their structures and their transformations into a coherent system that enables to divide the real, often complex transfosrmations of anionic sublattices of the salts, by making use of the regularity of variation of chemical properties observed in the system, into a sequence of elementary transformations consisting in transfer of electrons or oxide ligands between simple species in the systems of decomposing anionic sublattices of the salts. In the decomposition of sodium oxosalts of sulphur the role of Na^+ cations is limited principally to stabilisation of the anionic sublattices. The oxidizing and acidic properties of these salts are too weak to enable them to participate as reagents in transformation of the species in decomposition. The presented scheme of decomposition of anionic sublattices of sodium oxosalts may serve a basis for analysis of the effect of other cationic counterions, having stronger acidic, oxidizing or reducing properties, as well as of the effect of other reactants on modification of transformations of anionic sublattices in the salts.

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