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Reactions of manganese oxides with $K_2S_2O_7$

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Abstract The course of reactions of potassium disulphate(VI) with manganese oxides: MnO, Mn_2O_3 and MnO_2 was studied in solid phase. In the reactions all the manganese oxides were reduced to Mn^{2+} which then became a component of one of the reaction products namely $K_2Mn_2(SO_4)_3$. A classification scheme of the reaction path has been proposed.

Keywords Sodium disulphate(VI) · Manganese oxides · Thermal decomposition

Introduction

Chemical literature includes many papers dealing with reactions of various compounds with sodium and potassium disulphates(VI). In solid phase, and particularly in a state of molten solid, disulphates(VI) exhibit strongly acidic properties and they can also act as oxidants. Such properties of disulphates are used i.a. in analytic chemistry for solubilization of hardly soluble oxide materials with the aim of determination of some of their components. It has been shown [1] that the readiness of oxides to react with disulphates(VI) depends on their basicity. Strongly basic oxides such as BaO, SrO, CaO, react most readily, at lowest temperatures. The reaction is more difficult with ZnO, CdO, CuO and aluminium, iron, chromium or vanadium sesquioxides of stoichiometry M_2O_3 [2, 3]. There are also cases in which a reaction of an oxide with disulphate(VI) is accompanied by reduction, as in reaction with Pb_3O_4 where only $PbSO_4$ is formed [1]. In this paper we present our studies on solid phase reactions of potassium disulphate(VI) with manganese oxides MnO, Mn_2O_3 and MnO_2, of different acid–base and redox properties. Only the reactions of MnO_2 with $K_2S_2O_7$ and $Na_2S_2O_7$ producing $K_2Mn_2(SO_4)_3$ have been described in literature [4], but the included explanation of manganese reduction from Mn(IV) to Mn(II) with participation of disulphate(VI) ions seems to be not convincible.

Experimental

The following compounds were used in the studies:

- $K_2S_2O_8$ commercial (anal. grade, POCh),
- $K_2S_2O_7$ obtained by thermal decomposition of $K_2S_2O_8$ at 350 °C in nitrogen atmosphere [2–4],
- β-MnO_2, obtained by purification of commercial product (POCh) by boiling in concentrated nitric acid with subsequent heating at 450 °C,
- Mn_2O_3 obtained by thermal decomposition of MnO_2 at 700 °C in nitrogen atmosphere [5],
- MnO obtained by thermal decomposition of MnC_2O_4 at 500 °C in nitrogen atmosphere [6].

Thermal stability of the compounds and the temperature ranges of the reactions were determined by means of complex thermal analysis. Samples about 200 mg in weight were heated in standard alundum crucibles in a dynamic atmosphere of oxygen-free nitrogen, in a Derivatograph device type OD 202 system Paulik–Paulik Erdey. Solid reaction products were identified by differential X-ray analysis using a SIMENS HZG4 device. Larger amounts of the reaction product were obtained by heating the initial mixture in a tubular furnace under conditions settled in the thermal analysis.

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Results and discussion

Thermal decomposition of $K_2S_2O_8$

Figure 1 shows thermoanalytical curves of $K_2S_2O_8$ used for obtaining $K_2S_2O_7$, which was then used in the reactions tested. As can be seen from the DTA curve the decomposition proceeds with an exothermic point at 280 °C. The reaction follows the equation:

$$K_2S_2O_8 \rightarrow K_2S_2O_7 + {}^1\!/\!_2O_2$$

The solid reaction product $K_2S_2O_7$ undergoes a polymorphic transformation at 320 °C and melts at 420 °C. The processes are manifested as endothermic effects on DTA curves both in the case of a pure compound and under conditions of thermal analysis of mixtures with manganese oxides. They confirm the presence of $K_2S_2O_7$. The effects conform to literature data [3, 4]. After being melted $K_2S_2O_7$ undergoes a slow decomposition in a wide temperature range, with a maximum rate at 690 °C, according to the following balance equation:

$$K_2S_2O_7 \rightarrow K_2SO_4 + SO_3$$

Thermal decomposition of MnO_2

Figure 2 shows thermoanalytical curves of ß-MnO_2. The decomposition proceeds with a strong endothermic effect, seen on the DTA curve at 565 °C, according to the following equation:

$$2MnO_2 \rightarrow Mn_2O_3 + {}^1\!/\!_2O_2$$

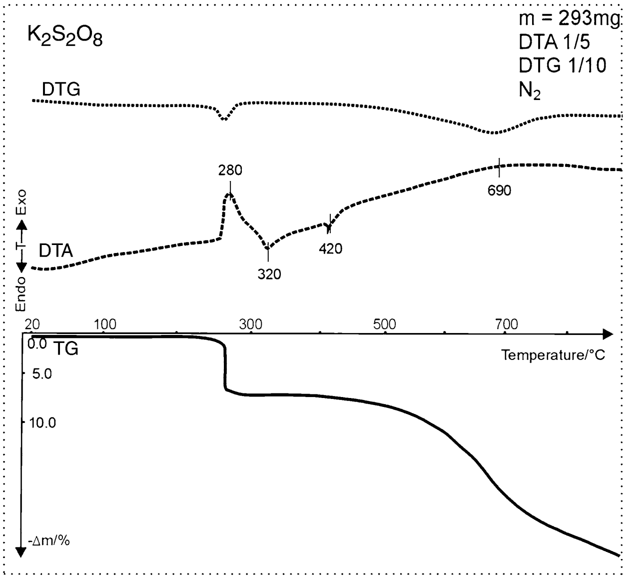

Fig. 1 TG, DTG, DTA curves of $K_2S_2O_8$

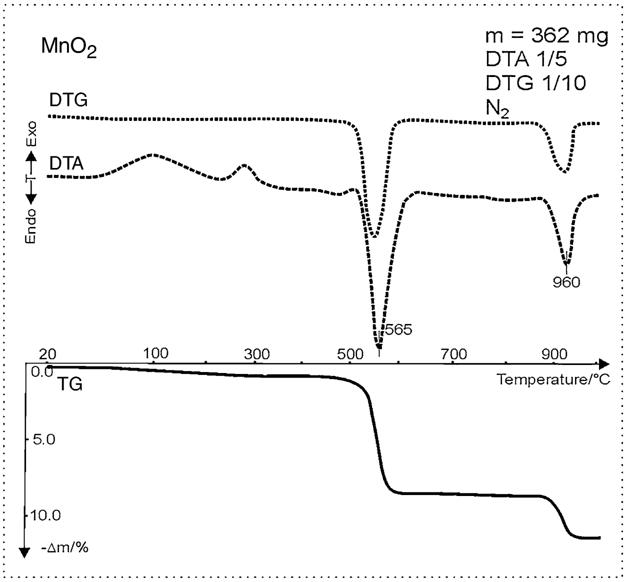

Fig. 2 TG, DTG, DTA curves of MnO_2

Another endothermic effect, seen on the DTA curve at 960 °C, corresponds to decomposition of manganese(III) oxide according to the following equation:

$$3Mn_2O_3 \rightarrow 2Mn_3O_4 + {}^1\!/\!_2O_2$$

The decomposition of manganese(IV) oxide conforms to the literature data [5] and formation of other oxides has been confirmed by the XRD of samples heated at 600 and 1000 °C.

Reactions of manganese oxides with $K_2S_2O_7$

$MnO + K_2S_2O_7$

Figure 3 shows thermoanalytical curves of an equimolar mixture of MnO and $K_2S_2O_7$. A DTA effect at 340 °C is due to a polymorphic transformation of potassium disulphate(VI). The reaction between the two initial compounds proceeds mainly at 450 °C, after melting of the disulphate at 410 °C, with an exothermic effect and with no loss in mass. Reaction products obtained by heating a sample at 750 °C in nitrogen atmosphere contained, as shown by XRD analyses, solid phases of $K_2Mn_2(SO_4)_3$ and K_2SO_4. The presence of $K_2Mn_2(SO_4)$ is also confirmed by the DTA effects: polymorphic transformation at 560 °C and melting at 710 °C, in conformity with [1–4]. The reaction may also by represented by the following balance equation:

$$2MnO + 2K_2S_2O_7 \rightarrow K_2Mn_2(SO_4)_3 + K_2SO_4$$

$Mn_2O_3 + K_2S_2O_7$

Figure 4 shows thermoanalytical curves for a 1:2 mixture of manganese(III) oxide and $K_2S_2O_7$. The rate of the

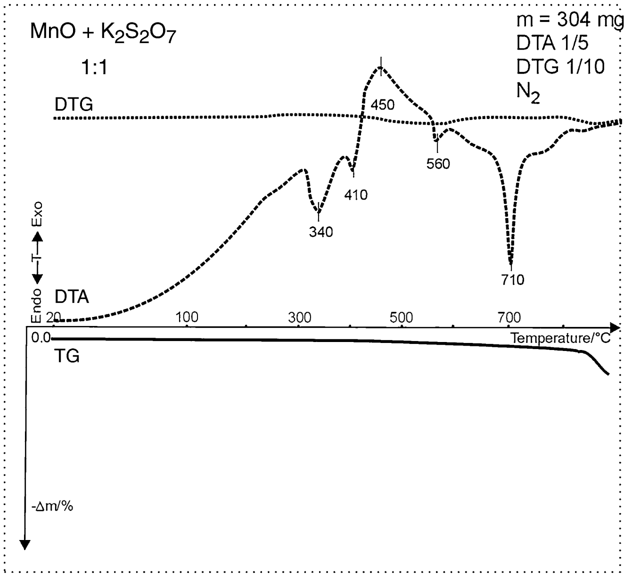

Fig. 3 TG, DTG, DTA curves of MnO mixed with $K_2S_2O_7$

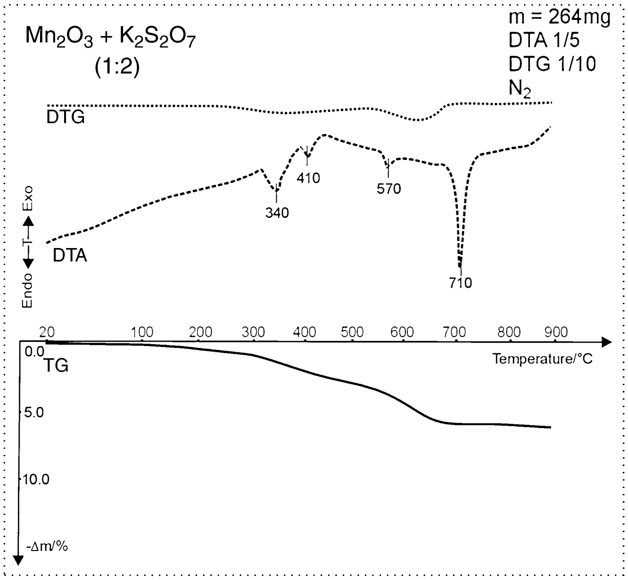

Fig. 4 TG, DTG, DTA curves of Mn_2O_3 mixed with $K_2S_2O_7$

reaction had a maximum at 400 °C. As shown by X-ray phase analysis the reaction products collected above 880 °C contained $K_2Mn_2(SO_4)_3$ and K_2SO_4. The presence of the $K_2Mn_2(SO_4)_3$ phase has been confirmed by the presence of DTA effects due to a phase transformation and melting of that compound, at temperatures 570 and 710 °C, respectively.

Since in the reaction proceeding at a stoichiometry of 1:2 the DTA curve had two overlapping effects: exothermic effect due to the reaction at 400 °C and endothermic effect due to melting of $K_2S_2O_7$ at 410 °C, the reaction was also carried out at a 2:1 molar ratio of the reactants. Under these conditions the DTA curve exhibited a clear exothermic effect at 400 °C. Besides, the DTA curve had an endothermic effect at 800 °C due to decomposition of excessive Mn_2O_3. The presence of Mn_3O_4, in addition to $K_2Mn_2(SO_4)_3$ and K_2SO_4 in the reaction products, was confirmed by the XRD method.Hence the balance reaction involving Mn_2O_3 may be presented by the following equation:

$$Mn_2O_3 + 2K_2S_2O_7 \rightarrow K_2Mn_2(SO_4)_3 + K_2SO_4 + {}^{3}\!/\!_{2}O_2$$

$MnO_2 + K_2S_2O_7$

Figure 5 shows thermoanalytical curves of reaction of manganese dioxide with $K_2S_2O_7$. As results from the DTA curve the reaction proceeds in temperature range 360–600 °C. It is preceded by melting of $K_2S_2O_7$, which is manifested by an endothermic effect at 380 °C. Maximum rate of the reaction is at about 400 °C. The results of the X-ray diffraction analyses confirmed the presence of $K_2Mn_2(SO_4)_3$ and K_2SO_4 in a sample heated at 900 °C. As in the former case, thermal effects at 560 and 680 °C on the DTA curve are due to polymorphic transformation and melting of $K_2Mn_2(SO_4)_3$.

XRD analyses were also performed for samples heated in nitrogen atmosphere at 260 and 500 °C. The results confirmed the presence of $K_2S_2O_7$ and MnO_2 phases in the former sample, and phases $K_2Mn_2(SO_4)_3$ and K_2SO_4 in the latter one. The reaction of MnO_2 with potassium disulphate(VI) proceeds according to the following balance equation:

$$2MnO_2 + 2K_2S_2O_7 \rightarrow K_2Mn_2(SO_4)_3 + K_2SO_4 + O_2$$

As results from analyses of the products of reactions of $K_2S_2O_7$ with manganese oxides MnO, Mn_2O_3 and MnO_2

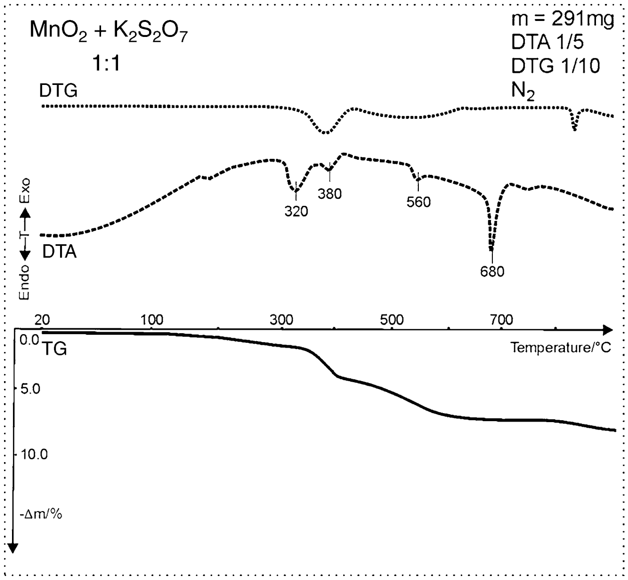

Fig. 5 TG, DTG, DTA curves of MnO_2 mixed with $K_2S_2O_7$

performed with various stoichiometric ratios of the reactants the real proportions of the reacting compounds correspond to the formerly given balance equations. In all cases the reaction ends with the complex salt $K_2Mn_2(SO_4)_3$ containing Mn^{2+} ions, and the reactions are practically completed at similar temperature ranges up to 550 °C, whereas thermal decomposition of pure manganese oxides (except MnO) proceeds at much larger temperature range. For MnO_2 the maximum rate of decomposition is observed at 565 °C, and for Mn_2O_3 at 960 °C, but in this case the end product is not MnO but Mn_3O_4. In the decomposition of manganese oxides the role of reducers is played by the O^{2-} ligands which supply the number of electrons necessary to reduce manganese cores to manganese at a lower oxidation degree, hence for the half reactions:

$$2MnO_2 + 2e \rightarrow Mn_2O_3 + O^{2-} \text{ or}$$
$$2MnO_2 \rightarrow Mn_2O_3 + \tfrac{1}{2}O_2$$

$$3Mn_2O_3 + 2e \rightarrow 2Mn_3O_4 + O^{2-} \text{ or}$$
$$3Mn_2O_3 \rightarrow 2Mn_3O_4 + \tfrac{1}{2}O_2$$

Mn_3O_4 produced in the latter reaction is regarded as a spinel-type compound containing manganese in two oxidation states as Mn(II) and Mn(III). The compound may be treated as a salt having Mn^{2+} cation and anionic sublattice MnO_2^-. Mn(III) present in the form of MnO_2^- sublattice is a weaker oxidant than that present in the oxide form of Mn_2O_3, hence Mn_3O_4 is decomposed to MnO at a temperature much above 1000 °C. It is a general rule, since in the cases of identical oxidation degree a species binding more oxide ligands is always a weaker oxidizer. For example, the oxidizing ability decreases in the following series: Mn_2O_7–MnO_4^-; CrO_3–$Cr_2O_7^{2-}$–CrO_4^{2-}; SO_3–SO_4^{2-}; SO_2–SO_3^{2-}, PbO_2–PbO_3^{2-}–PbO_4^{4-}, etc.

In the case of oxide reactions with disulphate(VI) the reduction of manganese takes place also with participation of oxide anions, but it leads always to formation of Mn^{2+}, hence the number of electrons transferred is different than the number oxide anions, as shown in Table 1. The second column shows the role played in these reactions by the disulphate(VI) and the required stoichiometry of these reactions, as every $S_2O_7^{2-}$ anion is capable of binding one oxide anion.

Thermal decomposition of manganese oxides and the role of disulphate anions may be interpreted in terms of classification diagram of oxygen-containing species of manganese, which gives a possibility to follow the transformations of manganese compounds, as shown in the papers [7–9].

The steps of thermal decomposition of manganese oxides shown in the classification system may be presented by means of a scheme shown in Fig. 6. Stoichiometric forms of the species shown in the scheme and in the step equations show manganese cores in the polymeric systems of oxides with corresponding number of oxide anions and valency electrons. The number of O^{2-} anions is defined by means of the e_z number of the species. The number of electrons bound in the d orbitals of manganese is a measure of electric charge of coordination centre of the species.

The first step of MnO_2 decomposition consists in a release of oxygen:

$$MnO_2 \rightarrow [MnO] + \tfrac{1}{2}O_2 \tag{1}$$

and corresponds to binding of two electrons by manganese(IV) which releases oxygen. The manganese is in a polymeric system where it is bound through oxygen bridges with other manganese cores of the initial oxide. These enable the transfer of electrons to one of the neighbouring cores of Mn(IV) thus leading to a production of manganese(III) oxide:

$$[MnO_2] + [MnO] \rightarrow Mn_2O_3 \tag{2}$$

Such a mechanism of formation of Mn_2O_3 as a result of synproportionation of Mn(II) with Mn(IV) has been confirmed in the studies of decomposition of γ-MnO_2 obtained by electrolysis [10–12]. The oxide decomposes at 470 °C (lower than does β-MnO_2), to form Mn_2O_3 and Mn_5O_8 (at various proportions depending on the conditions of decomposition) conforming to the approximate balance equation:

$$7MnO_2 \rightarrow Mn_5O_8 + Mn_2O_3 + 1,5O_2$$

The compound Mn_5O_8, isostructural with $Cd_2Mn_3O_8$, may be considered as a ionic compound with Mn^{2+} cations and anionic sublattice of $Mn_3O_8^{4-}$ [13]. That compound is formed from a part of primary species resulting from the decomposition of MnO_2 before they have a possibility to be synproportionated to Mn(III). The step of oxygen release according to (1) is followed by rearrangement of oxide ligands to form Mn_5O_8:

Table 1 Half reactions of manganese oxides modification

Half reactions of starting species	Modified half reactions	Stoichiometry
$MnO_2 + 2e \rightarrow Mn^{2+} + 2O^{2-}$	$MnO_2 \rightarrow Mn^{2+} + O^{2-} + 0{,}5O_2$	(1:1)
$Mn_2O_3 + 2e \rightarrow 2Mn^{2+} + 3O^{2-}$	$Mn_2O_3 \rightarrow 2Mn^{2+} + 2O^{2-} + 0{,}5O_2$	(1:2)
$MnO \rightarrow Mn^{2+} + O^{2-}$	$MnO \rightarrow Mn^{2+} + O^{2-}$	(1:1)

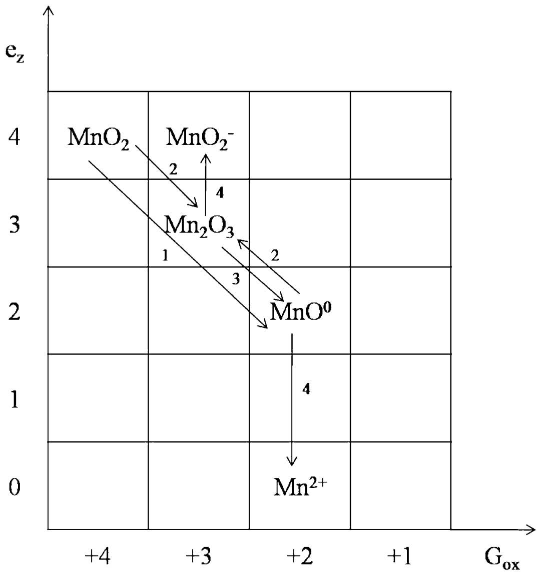

Fig. 6 Schemes of thermal decomposition of manganese oxides

$$2[\mathrm{MnO}] + 3\mathrm{MnO_2} \rightarrow \mathrm{Mn_2^{II}Mn_3^{IV}O_8}$$

The compound decomposes at about 500 °C to give Mn_2O_3 by reduction of a part of manganese(IV) to Mn(II) and simultaneous synproportionation of Mn(II) formed and existing Mn^{2+} cations and the residues of Mn(IV). The process may be presented by the following scheme of reactions taking place in the system:

$$\left[4\mathrm{Mn^{2+}},\ 2\mathrm{Mn_3O_8^{4-}}\right] \rightarrow \left[4\mathrm{Mn^{2+}}, \mathrm{Mn^{II}M_5O_{15}^{8-}}\right] + \tfrac{1}{2}\mathrm{O_2} \rightarrow \left[5\mathrm{Mn^{2+}},\ \mathrm{Mn_5O_{15}^{8-}}\right] \rightarrow\ 5\mathrm{Mn_2O_3}$$

At a higher temperature (900 °C) manganese(III) in Mn_2O_3 is also reduced by release of oxygen. It combines two electrons to become manganese(II):

$$\mathrm{Mn_2O_3} \rightarrow 2[\mathrm{MnO}] + \tfrac{1}{2}\mathrm{O_2} \qquad (3)$$

which is stabilized in the oxide Mn_3O_4 in the form of Mn^{2+} cations, since the O^{2-} anions from its surrounding are more firmly bound by Mn(III) from the undecomposed part of Mn_2O_3, which is thus converted into the anionic sublattice of $[MnO_2^{\,-}]$:

$$[\mathrm{MnO}] + [\mathrm{Mn_2O_3}] \rightarrow \left[\mathrm{Mn^{2+}}\right] + 2\left[\mathrm{MnO_2^-}\right] \qquad (4)$$

The oxide Mn_3O_4 may be considered as a salt consisting of Mn^{2+} cations and an anionic sublattice $MnO_2^{\,-}$. The increase of the e_z number of manganese in that sublattice results in the decrease of oxidizing properties of manganese(III) and the release of oxygen from that compound requires a temperature much exceeding 1000 °C. Such an approach has a structural confirmation. The structure of Mn_3O_4 can be described as a system of interpenetrating bands formed of square MnO_4 units (with the Mn–O distances of 193 pm) joined together through their edges, in which the octahedral coordination is supplemented by oxide anions of the bands lying below and above in a much larger distance of 193 pm [14]. Mn^{2+} cations have a tetrahedral coordination by oxide anions of the bands, with a Mn–O distance of 228 pm (see Fig. 7).

The reactions of manganese oxides with potassium disulphate (VI) proceeding at temperature range 350–600 °C give in all cases, according to a similar reaction scheme (see Fig. 8), Mn^{2+} cations present in the complex salt $K_2Mn_2(SO_4)_3$. In the case of MnO this is a typical acid–base reaction in which oxide anions from MnO are bound by the $S_2O_7^{\,2-}$ ions:

$$\mathrm{S_2O_7^{2-}} + \mathrm{MnO} \rightarrow 2\mathrm{SO_4^{2-}} + \mathrm{Mn^{2+}} \qquad (1)$$

In the case of Mn_2O_3, where manganese(III) is fully converted into manganese(II) at a much lower temperature than in thermal decomposition of the oxide, the oxide anions from Mn_2O_3 are bound by the disulphate anions and a part of manganese is converted into $[MnO^+]$:

$$\mathrm{S_2O_7^{2-}} + \mathrm{Mn_2O_3} \rightarrow 2[\mathrm{MnO^+}] + 2\mathrm{SO_4^{2-}} \qquad (2)$$

The oxidizing properties of manganese(III) present in $[MnO^+]$ are much higher than those of the initial oxide, for not to mention the $MnO_2^{\,-}$ sublattice in Mn_3O_4. Mn(III) is reduced by the oxide anions to unstable Mn(I) and the number of electrons is matched to Mn(II) by means of the bridging oxide anions:

$$[\mathrm{MnO^+}] \rightarrow [\mathrm{Mn^+}] + \tfrac{1}{2}\mathrm{O_2} \qquad (3)$$

$$[\mathrm{MnO^+}] + [\mathrm{Mn^+}] \rightarrow \left[\mathrm{Mn_2O^{2+}}\right] \qquad (4)$$

Oxide anions from the immediate surroundings of Mn(II) are bound with the disulphate anions:

$$\left[\mathrm{Mn_2O^{2+}}\right] + \mathrm{S_2O_7^{2-}} \rightarrow 2\left[\mathrm{Mn^{2+}}\right] + 2\mathrm{SO_4^{2-}} \qquad (5)$$

The release of oxygen takes place at a lower temperature than in the decomposition of Mn_2O_3 as a result of impossibility of creating $MnO_2^{\,-}$ sublattice in the acid

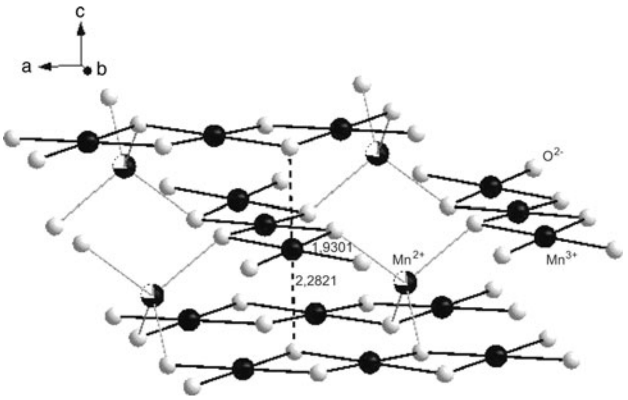

Fig. 7 Part of Mn_3O_4 structure

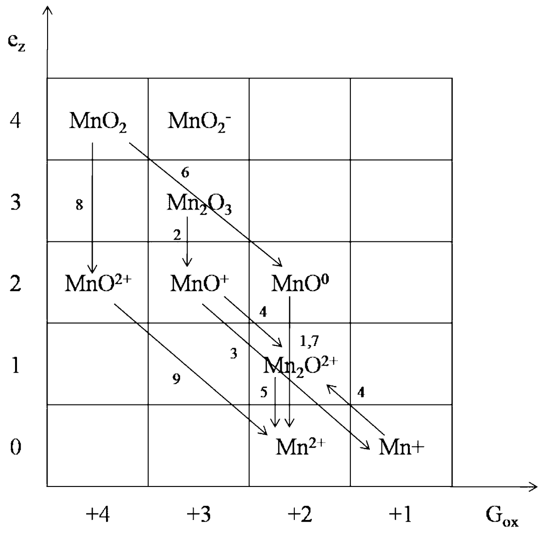

Fig. 8 Schemes of reactions of manganese oxides with potassium disulphate(VI)

medium. Finally, the reaction with MnO_2, which proceeds at a temperature range only slightly lower than that of the decomposition of oxide, will consist either in binding oxide anions from the [MnO], formed after the release of oxygen, by the disulphate:

$$MnO_2 \rightarrow [MnO] + {}^{1}\!/_{2}O_2 \tag{6}$$

$$[MnO] + S_2O_7^{2-} \rightarrow \left[Mn^{2+}\right] + 2SO_4^{2-} \tag{7}$$

or in direct binding O^{2-} by the disulphate anion and release of oxygen by the $[MnO^{2+}]$ formed:

$$MnO_2 + S_2O_7^{2-} \rightarrow \left[MnO^{2+}\right] + 2SO_4^{2-} \tag{8}$$

$$\left[MnO^{2+}\right] \rightarrow \left[Mn^{2+}\right] + {}^{1}\!/_{2}O_2 \tag{9}$$

Conclusions

Thermal stability of manganese oxides and temperature ranges of their thermal decomposition are functions of redox relations between the oxide anions, that play the role of reducers, and the manganese coordination centres acting as oxidizers. The lower is the oxidation degree (the higher the e_v value), the weaker are its oxidizing properties. The decomposition temperature thus rises in the series: $Mn_2O_7 < MnO_2 < Mn_2O_3 < Mn_3O_4$. The differences in oxidizing properties occurring at identical oxidation degree of manganese as observed in Mn_2O_3 and Mn_3O_4 are the result of difference in the e_z number depending on the number of oxide ligands shared by the manganese coordination centre of Mn(III). In Mn_2O_3 the value of e_z of Mn(III) is 3, but in Mn_3O_4 the manganese(III), located in the anionic sublattice of MnO^{2-}, is equal to 4. This fact is responsible for decrease of its oxidizing properties and increase of stability of the oxide. The presence of strongly acidic reactant $S_2O_7{}^{2-}$ in the reaction system causes that oxide ligands from the manganese core environment are engaged thus leading to increase of their oxidizing properties. As a consequence, the temperature of manganese oxide reduction decreases in reactions performed in the presence of disulphate anions and manganese(II) is the sole product of the reduction.

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