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SOLID PHASE REACTIVITY OF SODIUM OXOSALTS OF MANGANESE

Z. Gontarz, R. Grzybowska and R. Sabaliński

Department of Inorganic Chemistry, Technical University of Warsaw, ul. Noakowskiego 3, 00-664 Warszawa, Poland

Abstract

The observed relationships are presented of the solid phase reactivity of the following salts: $NaMnO_4$, Na_2MnO_4, Na_3MnO_4, Na_4MnO_4, Na_2MnO_3, $Na_2Mn_2O_5$, Na_5MnO_4, $Na_4Mn_2O_5$, $NaMnO_2$, Na_4MnO_3, Na_2MnO_2 and $Na_2Mn_2O_3$.

Keywords: solid state reactivity

Introduction

Manganese, an element of the first series of the dsp block, forms a considerable number of oxo-compounds – oxides and oxosalts, at oxidation states within +7–+2. The hitherto known oxides and anionic sublattices of oxosalts with various cationic counterions are presented in Fig. 1 in the Górski's classification system [1].

The oxo species of manganese collected in Fig. 1 are arranged in definite lattice structures [2–17]. The Górski's classification system enables also the analysis of the course of chemical reactions of compounds containing such species by demonstration of elementary acid-base processes (transfer of O^{2-} ligands) or red-ox processes (transfer of either electrons or oxygen atoms) [18]. The system enables therefore the comparison of relative reactivity of all oxo species of manganese containing a definite cationic counterion. It makes it possible also to determine the influence of cationic counterion on the structure and reactivity of a definite kind of anionic sublattice of a salt.

The aim of the present work was to determine the thermal stability of sodium oxosalts of manganese, their reactivity to molecular oxygen, and mutual reactivity in binary system. The results should give a consistent image of reactivity of oxides and sodium oxosalts of manganese. It will provide a base for analysis of the effect of various cationic counterions on changes in the structure and reactivity of individual oxomanganese sublattices. It may also serve a basis for analysis of reactions of oxocompounds of other dsp block elements.

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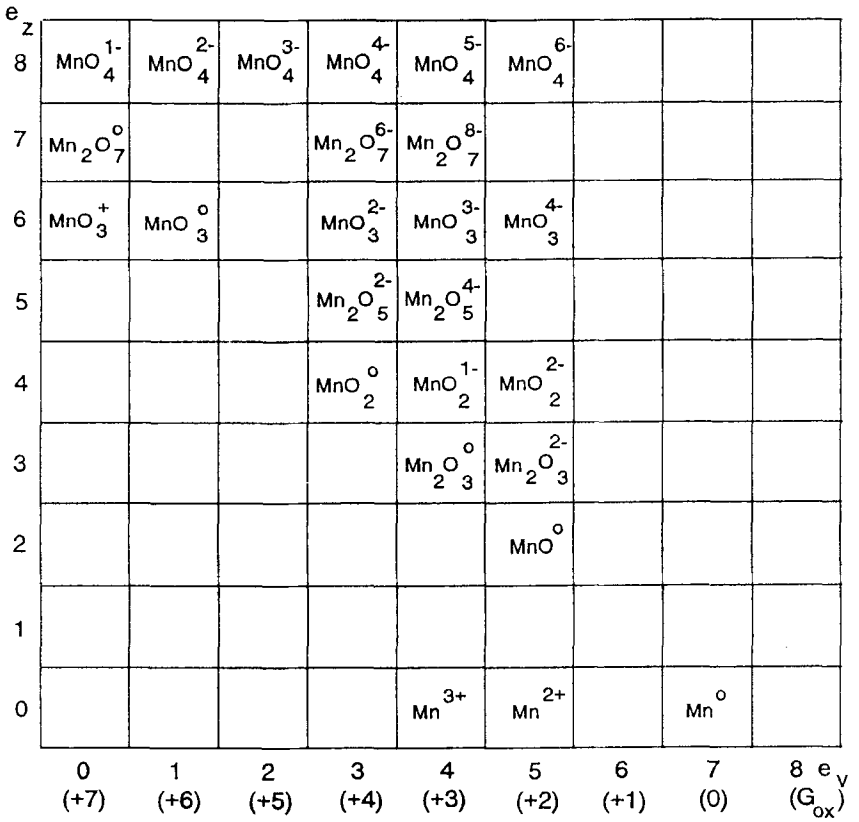

Fig. 1 Classification diagram of oxo-species of manganese

Experimental

The reagents used in experimental works were: Na_2O (pure, Merck), NaOH (anal. grade, POCh, Poland), $NaMnO_4$ (pure, Fluka) – dehydrated, MnO_2 (pure, POCh, Poland) – (purified by boiling in concentrated HNO_3 with subsequent ignition at 500°C). MnO was obtained by thermal decomposition of $Mn_2C_2O_4$ at 900°C in nitrogen atmosphere. Mn_2O_3 was obtained by thermal decomposition of MnO_2 at 700°C in nitrogen.

Sodium salts were synthesized in solid phase reactions in tubular furnace in the atmosphere of deoxidized nitrogen. The composition of the mixtures of sodium oxide with corresponding manganese oxides, of mixtures of sodium hydroxide with Na_2MnO_4 and $NaMnO_4$, temperatures and durations of heating the mixtures, as well as the oxidation state of manganese in the obtained compounds, found by means of chemical analysis, are collected in Table 1.

Table 1

Reagents	Composition of mixtures	Temperature /T, time /h	Products	Oxidation state of Mn
Na_2O, MnO	1:1	500°C, 3h	Na_2MnO_2	+2
Na_2O, MnO	1:2	500°C, 3h	$Na_2Mn_2O_3$	+2
Na_2O, MnO	2:1	500°C, 3h	Na_4MnO_3	+2
Na_2O, Mn_2O_3	1:1	650°C, 3h	$NaMnO_2$	+3
Na_2O, Mn_2O_3	2:1	650°C, 3h	$Na_4Mn_2O_5$	+3
Na_2O, Mn_2O_3	5:1	650°C, 3h	Na_5MnO_4	+3
Na_2O, MnO_2	1:1	600°C, 3h	Na_2MnO_3	+4
Na_2O, MnO_2	1:2	600°C, 3h	$Na_2Mn_2O_5$	+4
Na_2O, MnO_2	2:1	600°C, 3h	Na_4MnO_4	+4
NaOH, Na_2MnO_4	2:1	750°C, 2h		
		350°C, 8h	Na_3MnO_4	+5
NaOH, Na_2MnO_4	1:1	150°C, 10h	Na_2MnO_4	+6

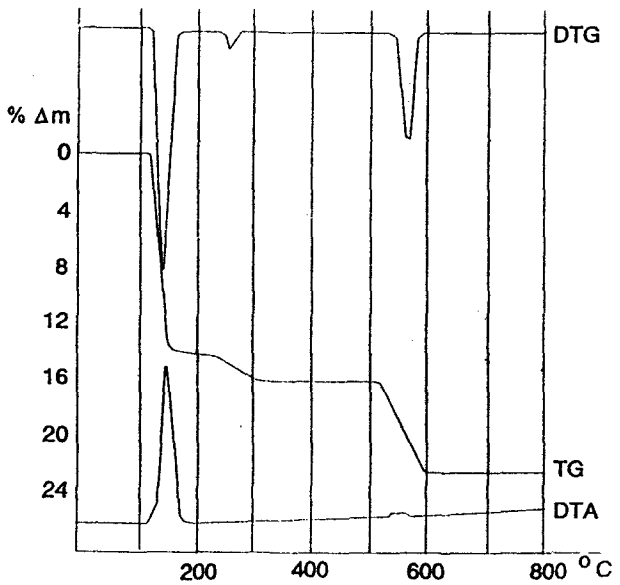

Fig. 2 TG, DTA and DTG curves of $NaMnO_4$

Measurement methods and equipment

The course of reactions of syntheses of the compounds, their thermal stability, and the path of solid phase reactions in mixtures of these compounds were

studied on the base of complex thermal analysis using Derivatograph apparatus (MOM Budapest). The reactions were carried out either in a dynamic atmosphere of deoxidized nitrogen or under static conditions in air, at temperature up to 900°C, with heating rate of 9 deg·min^{-1}. Samples of 200–300 mg in weight were placed in alundum crucibles. On the bases of the results of thermal analysis the experiments were carried out with greater samples using tubular furnace. Identifications of the intermediate compounds and of the reaction products were carried out by means of X-ray phase analysis using a HZG-4 device (Karl Zeiss, Jena), and by infrared absorption analysis on Specord IR 75 using KBr tablets or suspensions in nujol.

Results and discussion

Among the sodium oxosalts of manganese synthesized in our work only $NaMnO_4$ and Na_2MnO_4 were found to decompose on heating below 600°C. Sodium permanganate decomposes (Fig. 2), with evolution of oxygen, in temperature region 120–180°C, and the solid products of the decomposition are Na_2MnO_4 and MnO_2:

$$2NaMnO_4 \rightarrow Na_2MnO_4 + MnO_2 + O_2$$

The scheme of decomposition is similar to that observed in decompositions of $KMnO_4$, $RbMnO_4$ and $CsMnO_4$ [19]. It may be represented in terms of step equations of decomposition of the anionic sublattice – Fig. 3.

$$MnO_4^- \rightarrow MnO_3^- + 1/2O_2 \qquad (1)\ \text{Fig. 3}$$

$$MnO_4^- + MnO_3^- \rightarrow Mn_2O_7^{2-} \qquad (2)\ \text{Fig. 3}$$

$$Mn_2O_7^{2-} \rightarrow MnO_4^{2-} + MnO_3 \qquad (3)\ \text{Fig. 3}$$

$$MnO_3 \rightarrow MnO_2 + 1/2O_2 \qquad (4)\ \text{Fig. 3}$$

$$2MnO_4^- \rightarrow MnO_4^{2-} + MnO_2 + O_2$$

The decomposition of Na_2MnO_4 proceeds in temperature range 540–580°C probably following the reaction:

$$Na_2MnO_4 \rightarrow Na_2MnO_3 + 1/2O_2$$

In this case only the loss of oxygen from the MnO_4^{2-} sublattice takes place to yield a compound with MnO_3^{2-} anionic sublattice shown in Fig. 3.

$$MnO_4^{2-} \rightarrow MnO_3^{2-} + 1/2O_2 \qquad \text{(5) Fig. 3}$$

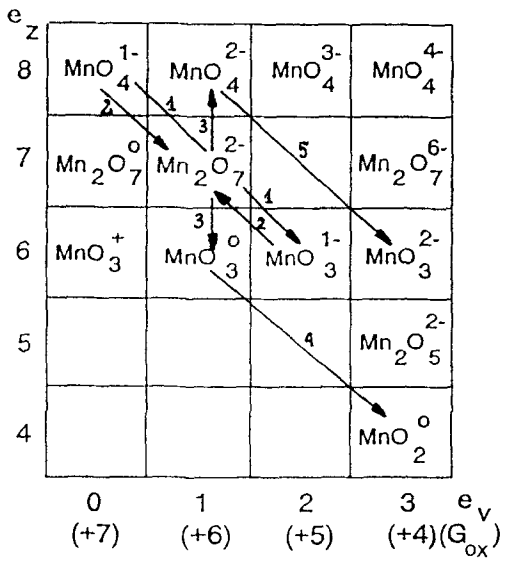

Fig. 3 Classification scheme of decomposition of MnO_4^- and MnO_4^{2-}

All the other sodium salts studied proved to be thermically stable up to 900°C in inert gas atmosphere. In heating in air atmosphere only salts of Mn (+4): $Na_2Mn_2O_5$, Na_2MnO_3 and Na_4MnO_4 were stable. All the other salts were oxidized in exothermic reactions to yield Mn (+4) compounds:

$$Na_2Mn_2O_3 + O_2 \rightarrow Na_2Mn_2O_5 \text{ (Fig. 4a)}$$

$$Na_2MnO_2 + 1/2O_2 \rightarrow Na_2MnO_3 \text{ (Fig. 4b)}$$

$$Na_4MnO_3 + 1/2O_2 \rightarrow Na_4MnO_4 \text{ (Fig. 4c)}$$

$$2NaMnO_2 + 1/2O_2 \rightarrow Na_2Mn_2O_5 \text{ (Fig. 4d)}$$

$$Na_4Mn_2O_5 + 1/2O_2 \rightarrow 2Na_2MnO_3 \text{ (Fig. 4e)}$$

Also Na_5MnO_4 was found to undergo oxidation, but the end products of the reaction have not been identified as yet. The temperature of oxidation of the above

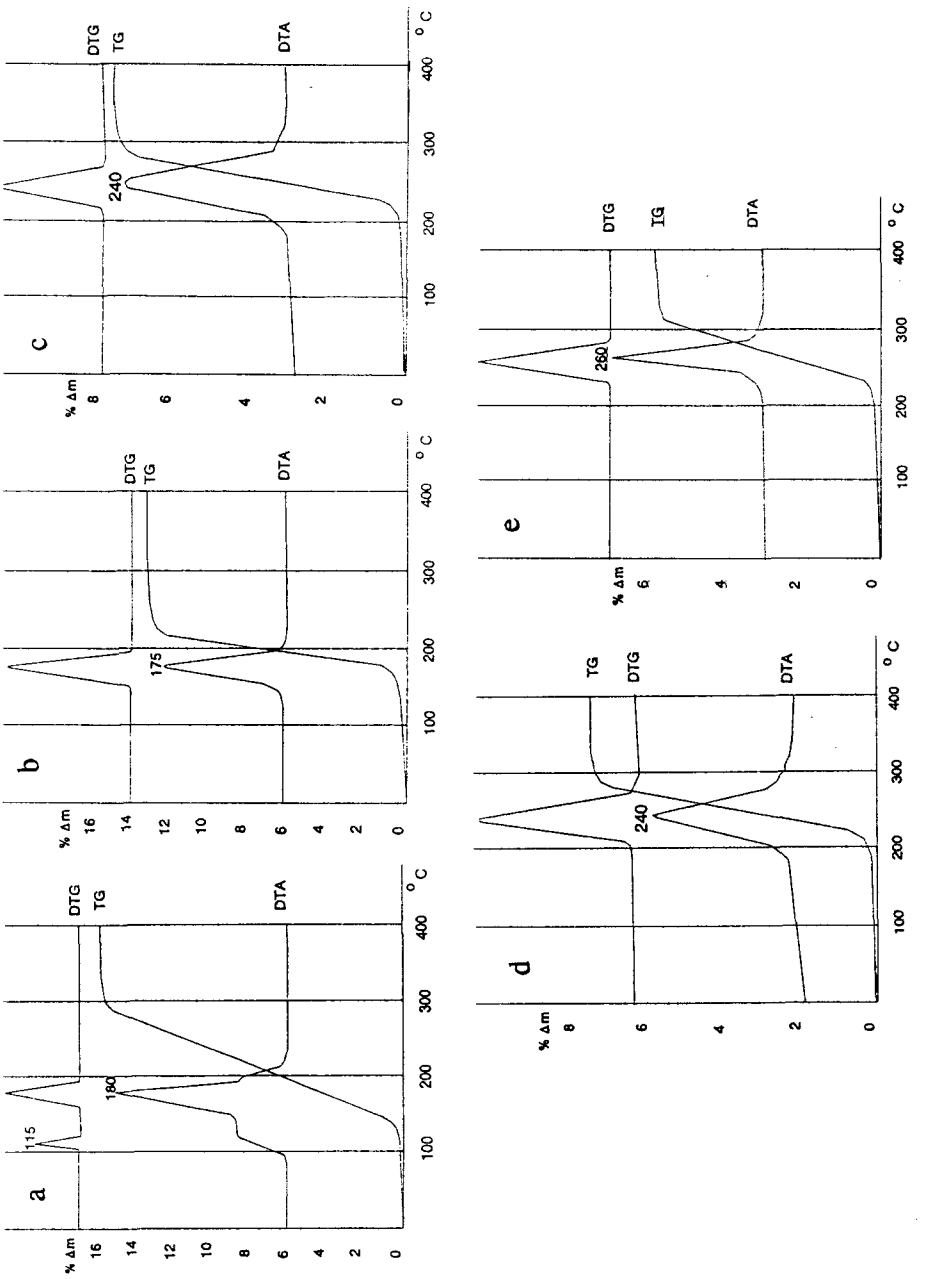

Fig. 4 TG, DTG and DTA curves of oxidation: $Na_2Mn_2O_3$ (a), Na_2MnO_2 (b), Na_4MnO_3 (c), $NaMnO_2$ (d), $Na_4Mn_2O_5$ (e)

compounds is relatively low. Among Mn (+2) compounds $Na_2Mn_2O_3$ reacts at 180°C, Na_2MnO_2 at 175°C, and Na_4MnO_3 at 240°C. For Mn (+3) compounds the oxidation proceeds at slightly higher temperatures: 240°C for $NaMnO_2$, 260°C for $Na_4Mn_2O_5$, and 265°C for Na_5MnO_4. The classification schemes of the oxidation reactions are shown in Fig. 5.

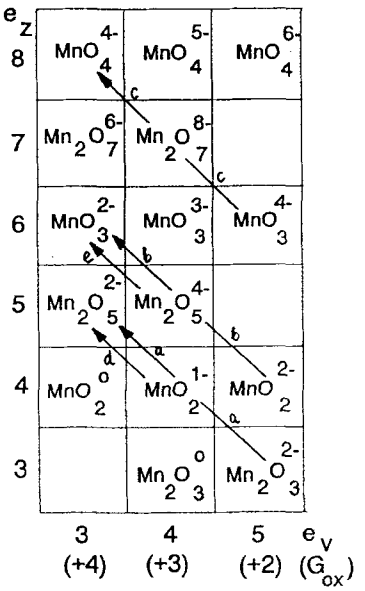

Fig. 5 Classification scheme of oxidation of: $Na_2Mn_2O_3$ (a), Na_2MnO_2 (b), Na_4MnO_3 (c), $NaMnO_2$ (d), $Na_4Mn_2O_5$ (e)

We have also carried out synproportionation reactions among the sodium oxosalts of manganese. Among many reactions possible only a certain number of these reactions have been realised as examples. DTA curves obtained for selected reaction systems are shown in Fig. 6.

Synproportionation reaction of Na_4MnO_4 with $Na_2Mn_2O_5$ proceeds with an exothermic effect in a broad range of temperature between 200 and 700°C, without a change in oxidation state, conforming the reaction:

$$Na_4MnO_4 + Na_2Mn_2O_5 \rightarrow 3Na_2MnO_3 \qquad (1)\ \text{Fig. 7}$$

The reaction of $Na_2Mn_2O_3$ with $Na_2Mn_2O_5$ proceeds in a narrow temperature range within 120–200°C, with a strong exothermic effect, according to reaction:

$$Na_2Mn_2O_3 + Na_2Mn_2O_5 \rightarrow 4NaMnO_2 \qquad (2)\ \text{Fig. 7}$$

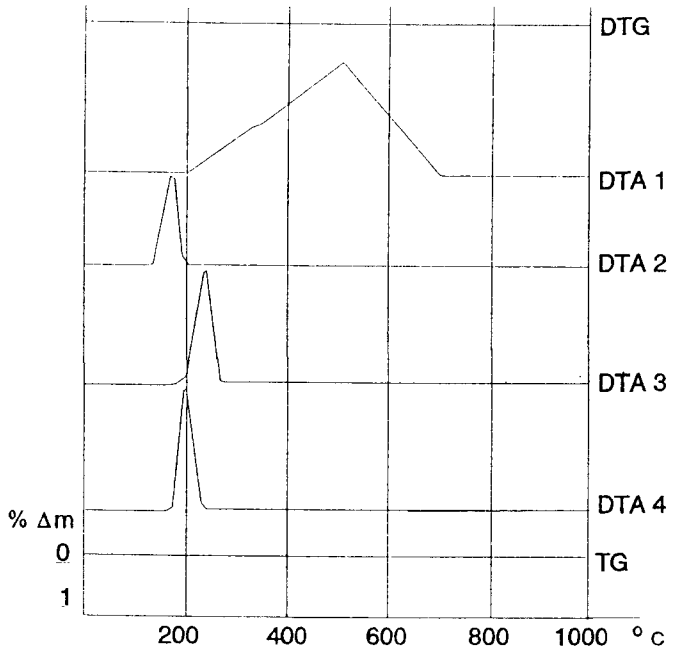

Fig. 6 DTA curves of synproportionation reactions:(1) $Na_4MnO_4+Na_2Mn_2O_5$, (2) $Na_2Mn_2O_3+Na_2Mn_2O_5$, (3) $Na_2MnO_2+Na_2MnO_4$,(4) $Na_5MnO_4+Na_3MnO_4$

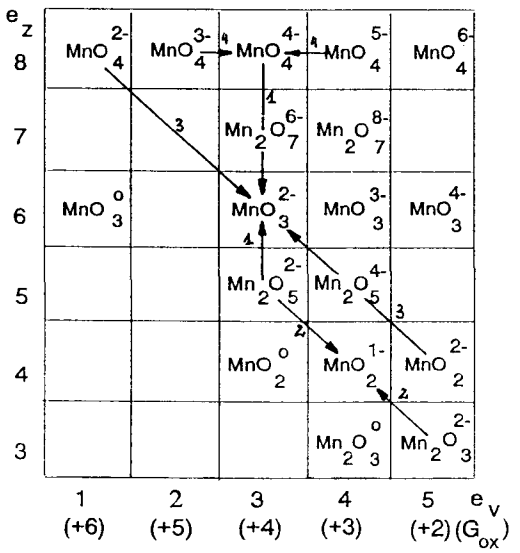

Fig. 7 Classification scheme of synproportionation reactions: (1) $Na_4MnO_4+Na_2Mn_2O_5$, (2) $Na_2Mn_2O_3+Na_2Mn_2O_5$, (3) $Na_2MnO_2+Na_2MnO_4$, (4) $Na_5MnO_4+Na_3MnO_4$

Also the reactions of Na_5MnO_4 with Na_3MnO_4 and of Na_2MnO_2 with Na_2MnO_4 proceed at low temperature range within 160–240°C with DTA maximum at 210°C and within 180–260°C with DTA maximum at 230°C, respectively, following the schemes:

$$Na_5MnO_4 + Na_3MnO_4 \rightarrow 2Na_4MnO_4 \qquad (3)\ \text{Fig. 7}$$

$$Na_2MnO_2 + Na_2MnO_4 \rightarrow 2Na_2MnO_3 \qquad (4)\ \text{Fig. 7}$$

The schematic representation of synproportionation of the anionic sublattices is shown in Fig. 7.

The reactions performed have shown that synproportionations involving the transfer of O^{2-} anions proceed in wide temperature ranges and at higher temperatures, than synproportionations of redox type where both electrons and oxide ligands are transferred.

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Zusammenfassung — Es wird die beobachtete Ähnlichkeit der Festphasenaktivität folgender Salze dargelegt: $NaMnO_4$, Na_2MnO_4, Na_3MnO_4, Na_4MnO_4, Na_2MnO_3, Na_2MnO_5, Na_5MnO_4, $Na_4Mn_2O_5$, $NaMnO_2$, Na_4MnO_3, Na_2MnO_2 und $Na_2Mn_2O_3$.