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THERMAL DECOMPOSITION STAGES OF POTASSIUM, RUBIDIUM AND CAESIUM PERMANGANATES

Z. Gontarz and *B. Pisarska*

INSTITUTE OF BASIC CHEMISTRY, FACULTY OF CHEMISTRY, WARSAW UNIVERSITY OF TECHNOLOGY, POLAND

Thermal decomposition of $KMnO_4$, $RbMnO_4$ and $CsMnO_4$ have been investigated. Stage mechanisms of the thermal decomposition on the basis of the morphological classification have been proposed.

This work is an attempt to put a hypothesis of a step mechanism of $KMnO_4$, $RbMnO_4$ and $CsMnO_4$ decomposition, on the basis of earlier studies on the decomposition of chromates [1].

The following reagents were used: $KMnO_4$ (p.a. POCH, Poland), $RbMnO_4$ and $CsMnO_4$ - obtained in exchange reactions between solutions of chlorides (RbCl and CsCl p.a. POCH, Poland) and $KMnO_4$.

Thermal decomposition studies were carried out by thermal analysis methods (T, TG, DTA, DTG) on derivatograph (MOM, Budapest).

Thermal curves of the investigated compounds are shown in Fig. 1. Decomposition of these compounds takes place in the temperature range 200°-300° with a maximum rate at 260°, 275°, 295° for $KMnO_4$, $RbMnO_4$ and $CsMnO_4$ respectively.

Mass losses are connected with oxygen evolution and were estimated to be 11.7, 8.0 and 6.5 wt. % for $KMnO_4$, $RbMnO_4$ and $CsMnO_4$, respectively.

According to literature data [2-11] and obtained results, the decomposition of the MnO_4^- sublattice is a complicated process. It proceeds via a series of elementary transformations consisting in the evolution of oxygen and transfer of electrons or oxide anions between oxo-species of manganese.

Manganates (VI) containing MnO_4^{2-} anions are products of the permanganates decomposition as well as cryptomelane which is a complex compound of the $K_xMn_8O_{16}$ ($x \leq 2$) stoichiometry and cryptomelane like compounds of the $K_xMn_7O_{16}$ ($x \leq 4$) stoichiometry.

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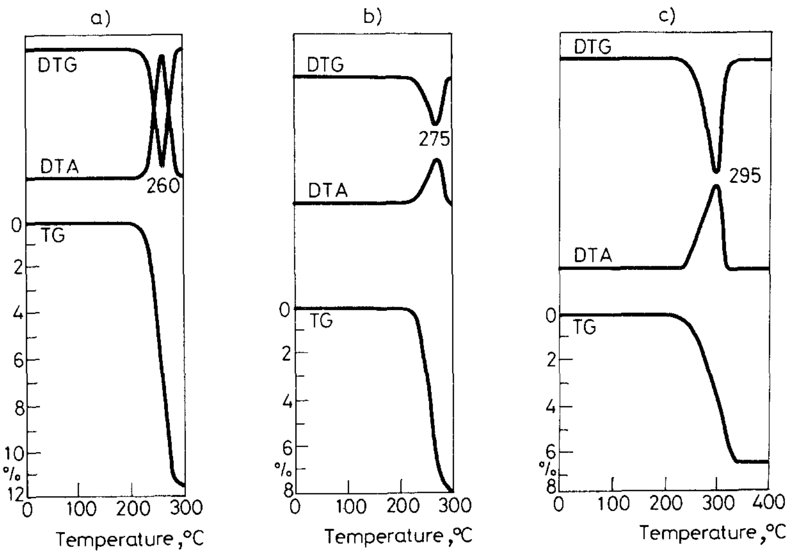

Fig. 1 TG, DTG and DTA curves of a) $KMnO_4$, b) $RbMnO_4$ and c) $CsMnO_4$

The two latter compounds are formed during the decomposition of $KMnO_4$ and their anion's sublattices can be presented by simple species $(8-x)MnO_2 \cdot xMnO_2^-$ and $(7-x/2)MnO_2 \cdot x/2\, MnO_3^{2-}$.

The following simple oxo-species of manganese: MnO_4^{2-}, MnO_2^0, MnO_3^{2-} and MnO_2^- are involved in the structure of the final products during the decomposition of MnO_4^-.

The evolution of oxygen is the first stage of the MnO_4^- decomposition:

$$MnO_4^- \rightarrow MnO_3^- + O^o, \qquad (1) \text{ Fig. 2.}$$

The liquidation of one oxygen anion takes places in this stage. The oxygen atoms are formed and the remaining two electrons are connected into valency states *d* of manganese in the unstable MnO_3^- molecule.

Ac-bas synproportionation with the undecomposed MnO_4^- anions is most probably the next transformation of this anion:

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

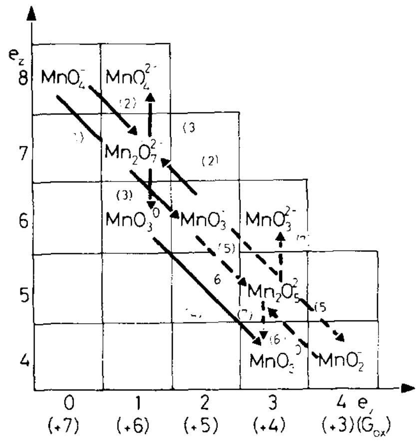

Fig. 2 e_z - e_v dependence of MnO_4^- anion

In the next stage the unstable $Mn_2O_7^{2-}$ anion is ac-bas disproportioned. MnO_4^{2-} - one of the final products of the primary salt decomposition appears in this step:

$$Mn_2O_7^{2-} \rightarrow MnO_4^{2-} + MnO_3^0, \qquad (3)\ \text{Fig. 2.}$$

MnO_3^0 appearing in the following stage decomposes to MnO_2^0:

$$MnO_3^0 \rightarrow MnO_2^0 + O^0, \qquad (4)\ \text{Fig. 2.}$$

The MnO_4^- decomposition would proceed in this way if stoichiometric β-MnO_2^0 of rutyl structure would be formed:

$$2MnO_4^- \rightarrow MnO_4^{2-} + MnO_2^0 + O_2^0$$

Actually, β-MnO_2^- is not formed during the decomposition of $KMnO_4$, $RbMnO_4$ and $CsMnO_4$, but cryptomelane compounds are formed. The formation of $Mn_8\,O_{16}^{x-}$ ($x \leq 2$) instead of MnO_2^0 requires the formation of MnO_2^- from MnO_3^-:

$$xMnO_3^- \rightarrow x\,MnO_2^- + xO^0, \qquad (5)\ \text{Fig. 2.}$$

MnO_2^- molecules are combined with MnO_2^0 and from the $Mn_8O_{16}^{x-}$ phase:

$$(8-x)MnO_2^0 + xMnO_2^- \rightarrow Mn_8O_{16}^{x-}.$$

This process can be presented by the equation:

$$(16-x)MnO_4^- \rightarrow (8-x)MnO_4^{2-} + Mn_8O_{16}^{x-} + 8\ O_2^0$$

The creation of cryptomelane like compounds requires the absence of MnO_3^{2-} anions. These molecules are formed as a result of the transfer of electrons. A reaction occurs between the coordinationally unsaturated MnO_3^- and MnO_2^- anions. These anions react with other species, but they are also able to react with each other:

$$MnO_3^- + MnO_2^- \rightarrow Mn_2O_5^{2-}, \qquad (6)\ \text{Fig. 2.}$$

$Mn_2O_5^{2-}$, after equalization of the number of electrons at the manganese core includes simple molecules:

$$Mn_2O_5^{2-} \rightarrow MnO_2^0 + MnO_3^{2-}, \qquad (7)\ \text{Fig. 2.}$$

$Mn_2O_5^{2-}$, in connection with MnO_2^0, forms cryptomelane like compound $(7-x/2)MnO_2^0 \cdot x/2MnO_3^{2-}$. This discussed process can be presented by the following equation:

$$2MnO_4^- \rightarrow (1-x)MnO_4^{2-} + MnO_2^0 \cdot x\,MnO_3^{2-} + (1+0.5x)O_2^0,$$

where $x \leq 2/5$.

Thus, the thermal decomposition proceeds with the simultaneous participation of all the elementary reactions described above, but the share of partial reactions depends on the conditions of the process and kind of cation.

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Zusammenfassung — Es wurde die thermische Zersetzung von $KMnO_4$, $RbMnO_4$ und $CsMnO_4$ untersucht. Auf der Basis der morphologischen Klassifizierung wurde ein Mechanismus für die thermische Zersetzungsreaktion vorgeschlagen.