Thermochimica Acta, 196 (1992) 503–509
Elsevier Science Publishers B.V., Amsterdam

Thermal decomposition of aqueous solutions of manganese(II) nitrate

J. Pelovski, O. Matova and St. Shoumkov
Technological University, Kl. Ohridski 8, Sofia 1156 (Bulgaria)

(Received 8 April 1991)

Abstract

The processes of dehydration and thermal decomposition of aqueous solutions of manganese(II) nitrate, which depend on the composition of the initial test samples during their treatment in natural gas atmosphere, have been investigated using thermogravimetric analysis. The kinetics data have been analysed.

It has been established that some impurities, such as calcium, magnesium and barium ions and crystal nuclei of manganese(IV) dioxide, influence the thermostability of manganese nitrate and the mechanism of its decomposition.

The vital influence of water vapour on the kinetic mechanism and the rate of decomposition of manganese nitrate solutions containing alkaline earth nitrates has been demonstrated.

The presence of a compensation effect in the alteration of the pre-exponential factor and the apparent activation energy has been recorded.

INTRODUCTION

The elaboration of a technological process for the preparation of manganese oxides from nitrate solutions requires that the mechanism and kinetics of their thermal decomposition be known. With regard to this, the process has been examined by different authors [1–4] and some differences in the experimental conditions have been discussed.

The present research work has the object of establishing the influence of some impurities, such as calcium, magnesium and barium ions and crystal nuclei of manganese(IV) dioxide, on the mechanism and kinetics regularities of the thermal decomposition of aqueous solutions of manganese(II) nitrate.

EXPERIMENTAL

The experiments were carried out in dynamic conditions at a heating rate of 6 °C min^{-1}, using a MOM derivatograph, model Q-1500-D. The apparatus is fitted with a gas-feeding appliance for purging at a flow rate of

TABLE 1

Composition (%) of the test samples

Test sample	$Mn(NO_3)_2$	H_2O	$Ca(NO_3)_2$	$Mg(NO_3)_2$	$Ba(NO_3)_2$	MnO_2
1	73.03	26.95	–	–	–	–
2	58.30	41.68	–	–	–	–
3	54.56	27.19	11.71	6.22	0.30	–
4	49.10	24.47	10.54	5.60	0.27	10.00
5	54.56	27.19	11.71	6.22	0.30	–
6	49.10	34.47	10.54	5.60	0.27	–

10 l h^{-1} and a relative humidity of about 70%. The weight of the test samples was 100 mg, the balance sensitivity was 0.1 mg and the recording speed was 2 mm min^{-1}. A closed labyrinth crucible 10 mm in diameter and 20 mm in height was used. For one of the test samples, the crucible was standard and open, and the processes were carried out in an air atmosphere.

Manganese(II) nitrate crystal hydrate, a quality, pure product of Riedel de Haën AG, containing less than 0.02% impurities was used as a basic material of the investigation. From this crystal hydrate, solutions were prepared containing 41.68%, 27.19% and 34.47% water, and with calcium, magnesium and barium nitrates. The ratio between the manganese and the other nitrates corresponds to the averaging ratio between these components in the solutions, prepared by nitric acid treatment of polymetallic ores. Calcium and magnesium nitrate crystal hydrates and barium nitrate of reagent purity (Reachim, USSR) were used to prepare the solutions. These materials contain respectively 69.30%, 60.43% and 99.98% of the basic salts. For one of the test samples, manganese dioxide of reagent purity was added to the manganese and alkaline earth nitrates, at a level of 10 wt.% with respect to the solution. The compositions of the examined test samples are given in Table 1.

RESULTS AND DISCUSSION

The thermogravimetric relationships obtained are shown in Figs. 1–5. The data were analysed using the kinetics equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{B}(1-\alpha)^n \exp\left(-\frac{E}{RT}\right) \qquad (1)$$

Table 2 gives the values for the pre-exponential factor A, the apparent activation energy E and the apparent order of the reaction n, with the corresponding correlation coefficient R for the different test samples.

The thermogravimetric dependences of the solutions of manganese nitrate, treated in natural gas atmosphere, show clear differences that

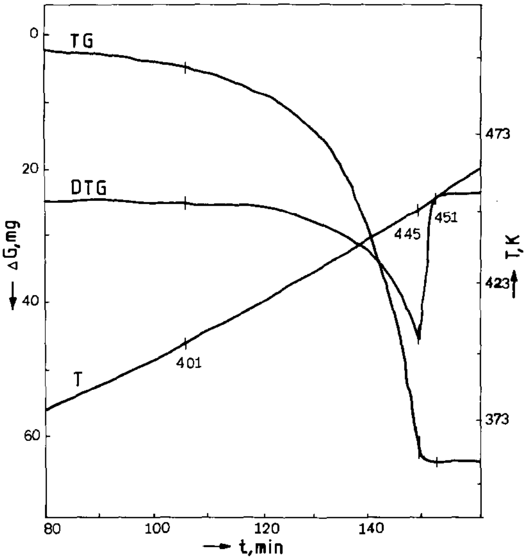

Fig. 1. Derivatogram of $Mn(NO_3)_2 \cdot xH_2O$ with 26.95% water (test sample 1).

depend on the composition of the initial test samples. For example, the decomposition interval of the manganese nitrate shifts towards higher temperatures for solutions containing calcium, magnesium and barium ions, when compared with pure manganese nitrate solution (Figs. 1 and 3, and Table 2). The temperatures of the decomposition are lowered and

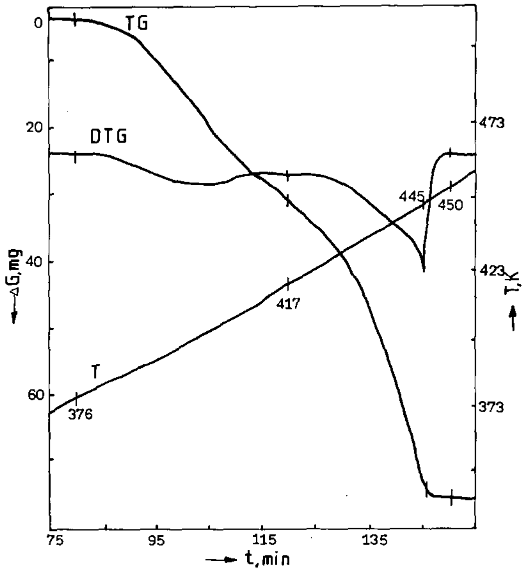

Fig. 2. Derivatogram of $Mn(NO_3)_2 \cdot xH_2O$ with 41.68% water (test sample 2).

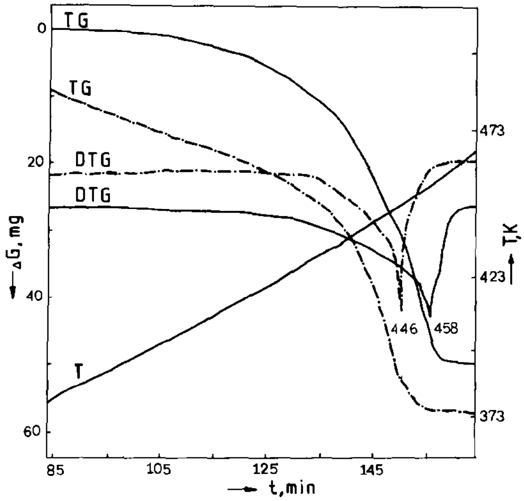

Fig. 3. Derivatogram of manganese nitrate solution containing calcium, magnesium and barium nitrates: ———, in natural gas atmosphere (test sample 3); and ·—·—·, in air atmosphere with about 70% relative humidity (test sample 5).

become practically identical with that of pure manganese nitrate solution if manganese dioxide is added to the solution of manganese and alkaline earth nitrates (Figs. 1 and 3). The course of the thermogravimetric dependences of pure solutions of manganese nitrate changes as the water content increases from 26.95% to 41.68% (Figs. 1 and 2). Two steps in the curve of test sample 2 can be clearly distinguished: evaporation of the water up to a

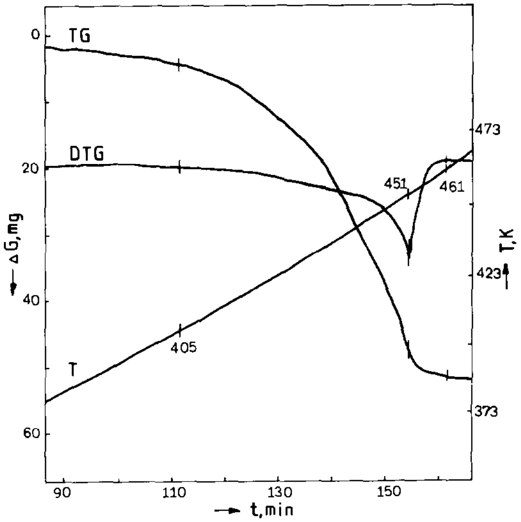

Fig. 4. Derivatogram of manganese nitrate solution containing calcium, magnesium and barium nitrates and manganese dioxide (test sample 4).

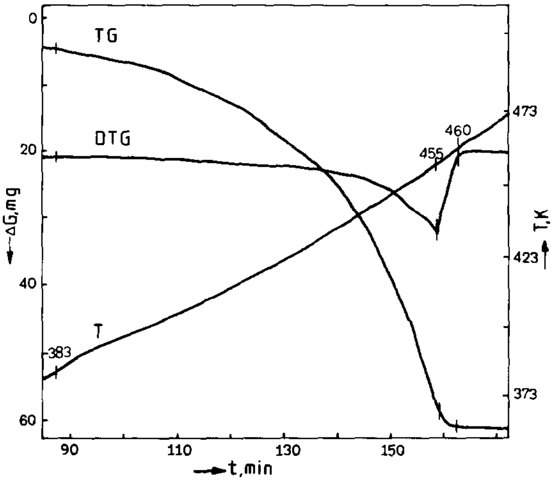

Fig. 5. A derivatogram of manganese nitrate solution containing calcium, magnesium and barium nitrates and 34.47% water (test sample 6).

temperature of 417 K and a molar ratio of $H_2O{:}Mn(NO_3)_2$ of 1.6; and a subsequent dehydration together with simultaneous decomposition of the manganese nitrate. The interval of destruction and the temperature of the maximum in the rate of the process for both test samples are equal. If the water content is increased from 27.19% to 34.47%, (Figs. 3 and 5), the decomposition temperatures are lowered by 10 K for solutions of manganese and alkaline earth nitrates. The decomposition mechanism of manganese nitrate solutions containing alkaline earth nitrates is the same as that of pure manganese nitrate solutions treated in an air atmosphere (Fig. 3, test sample 5). The states of evaporation and dehydration at temperatures of 365–414 K up to a molar ratio of $H_2O{:}Mn(NO_3)_2 = 1$ and the dehydration of the residual water, together with decomposition of the manganese nitrate at temperatures up to 455 K, are traced on the thermogravimetric curves as described by De Bruijn [3]. The influence of the atmosphere on the dehydration and decomposition of manganese nitrate,

TABLE 2

Temperature intervals and values of the kinetic parameters

Test sample	Temperature interval (K)	*A*	*E*	*n*	*R*
1	405–451	9.8	111.1	0	0.9865
2	417–450	8.8	102.0	0	0.9778
3	416–470	9.7	111.8	0.5	0.9938
4	405–455	8.2	97.5	0.75	0.9833
5	414–455	12.9	137.1	0	0.9750
6	383–460	3.1	57.0	0	0.9870

established in our previous investigations [5], was also demonstrated for solutions containing alkaline earth nitrates (Fig. 3, test samples 3 and 5).

The kinetic mechanism of the decomposition of the manganese nitrate changes under the influence of the alkaline earth nitrates; this is illustrated by the differences in the differential thermogravimetric curves and in the apparent order of the process for test samples 1, 2 and 3 (Figs. 1–3 and Table 2). The mechanism of the decomposition in the presence of manganese dioxide is different from that of the pure manganese nitrate solutions, as well as from those for solutions containing calcium, magnesium and barium nitrates. At the same time, the apparent activation energies for test samples 1–4 are approximately equal, within the range of the accuracy of the method. The increased water content of the solutions of manganese and alkaline earth nitrates lowers the apparent activation energy from 111.8 to 57 kJ mol^{-1} (test samples 3 and 6) and also changes the mechanism of the decomposition of the manganese nitrate. It is evident that the increased partial pressure of water vapour in the gas phase also accelerates the decomposition of manganese nitrate in a natural gas atmosphere. These results are in conformity with those obtained by Gallagher et al. [1,2], De Bruijn [3] and in our previous investigations [5]. Dehydration in the labyrinth crucible proceeds at a lower rate and at higher temperatures, compared with that in the open crucible and air atmosphere.

When comparing the kinetic parameters for the different initial test samples, the dependence observed between the pre-exponential factor and the apparent activation energy confirmed the presence of a compensation effect [6]. A change in the pre-exponential factor is balanced by a corresponding change in the apparent activation energy, according to

$$A = B + CE \tag{2}$$

where the constants have the values $B = 30$ and $C = 8.3$, determined

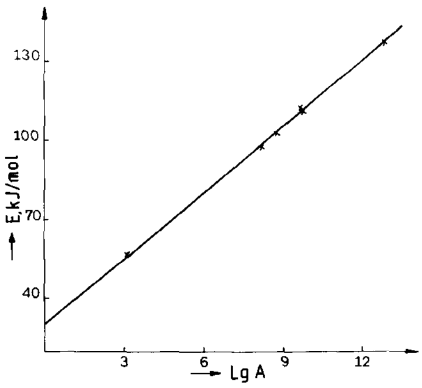

Fig. 6. Compensation effect.

graphically from Fig. 6. The different theories that explain the compensation effect do not provide a physical interpretation of the equation. The fact that eqn. (2) may be satisfied by kinetic data may be an indication for the presence of a general rate-controlling factor. In the present case, we may assume that this is the partial pressure of the water vapour in the gas phase.

CONCLUSIONS

The derivatographic and kinetic investigations of the decomposition of manganese(II) nitrate in natural gas atmosphere with different conditions prevailing in the initial test samples have demonstrated the influence of the impurities calcium, magnesium and barium ions and of crystal nuclei of manganese(IV) dioxide on the thermostability of the manganese nitrate and its decomposition mechanism. The important influence of water vapour on the kinetics of the decomposition of manganese nitrate solutions containing alkaline earth nitrates has been established. These facts should be taken into consideration in the development of the process.

REFERENCES

1 P.K. Gallagher, F. Schrey and B. Presscott, Thermochim. Acta, 2 (1971) 405–412.
2 P.K. Gallagher and D.W. Jonson, Thermochim. Acta, 2 (1971) 413–422.
3 T.J.W. De Bruijn, Battery-Grade Manganese Dioxide by Thermal Decomposition of Aqueous Manganese Nitrate Solutions: An Exploratory Study, Delft Univ. Press, 1980.
4 B.A. Belov, E.V. Gorozhankin, V.P. Efremov, N.S. Salnikova and A.L. Suris, J. Inorg. Chem., 10 (1985) 2520–2523.
5 J. Pelovski, O. Matova and St. Shoumkov, in press.
6 M.E. Brown, D. Dollimore and A.K. Galwey, Reactions in the Solid State, Mir, Moscow, 1983.