Thermochimica Acta, 58 (1982) 191–198
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

THERMAL DECOMPOSITION OF OXALATES. PART 17 *. THERMAL DECOMPOSITION OF MANGANESE(II) OXALATE IN A NITROGEN ATMOSPHERE

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(Received 17 March 1982)

ABSTRACT

Comparative studies of the kinetics of the isothermal and nonisothermal dehydration and decomposition of manganese(II) oxalate in an atmosphere of nitrogen are reported. Agreement between the values of the energy of activation for the isothermal and the nonisothermal dehydration at high heating rates was obtained. At low heating rate, the value obtained for the energy of activation is comparable with the enthalpy of dehydration. Values of 143 and 242 kJ mole^{-1} were obtained for the energy of activation of the isothermal and nonisothermal decomposition, respectively. The difference is attributed to the condition of the anhydrous salt used in both cases. The theory of absolute reaction rate is applied and the parameters obtained are discussed.

INTRODUCTION

Application of the equations of nonisothermal processes to obtain kinetic parameters requires the obedience of the rate process concerned to a single rate equation over the whole range of reaction. Dollimore et al. [2–4] reported more than one straight line from rising temperature experiments which was attributed to the variation in the distribution of reaction sites as the reaction proceeds from one distribution of sites to the other. On the other hand, agreement between isothermal and nonisothermal values of the energy of activation has been reported for a number of decomposition reactions [5–7].

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* For Part 16, see ref. 1.

0040-6031/82/0000–0000/$02.75

The present study deals with the effect of heating rate on the values of the energy of activation of the nonisothermal dehydration and decomposition of commercial manganous oxalate dihydrate. Dehydration and decomposition of the salt under isothermal conditions were also investigated.

EXPERIMENTAL

Materials

Manganous oxalate dihydrate was supplied commercially as the purest available grade. The salt is a fine white powder and was used without further purification.

Apparatus

Dehydration and decomposition experiments were carried out in an atmosphere of nitrogen using a Stanton-Redcroft TG 750 thermobalance with a temperature programmer capable of heating rates from 1 to 100°C min^{-1} and an isothermal control between 0 and 1000°C with an accuracy of ±0.1°C. All experiments were carried out using a sample weight of ~9.5–10 mg.

Isothermal experiments were carried out at 99, 110, 115, 124 and 164°C for the dehydration, and 385, 391, 406 and 425°C for the decomposition ranges.

Nonisothermal dehydration and decomposition were carried out using heating rates of 5, 10 and 15°C min^{-1}. Nonisothermal decompositions were conducted by heating each sample for 15 min after complete dehydration.

DTA measurements were also carried out in an atmosphere of nitrogen using the Stanton-Redcroft DTA unit.

RESULTS AND DISCUSSION

DTA curves in a nitrogen atmosphere show two endothermic peaks at 131 and 396°C for the dehydration and decomposition reactions, respectively. The decomposition peak was assigned to the formation of manganous oxide, MnO, as an end product [8].

TG experiments gave values of 20 and 60 for the percentage loss in the sample weight upon dehydration and decomposition, respectively.

(1) Dehydration

The Arrhenius plots of log K vs. $1/T$ for the dehydration range are shown in Fig. 1. The rate constants, k, were obtained from the first order decay expression of the isothermal experiments at various temperatures (Fig. 2). Similar Arrhenius plots for the rising temperature (TG) data at the various heating rates studied are also shown in Fig. 1. The data shown in Fig. 1 for the nonisothermal experiments were calculated manually using the following equation [2] which yielded only one straight line for each plot.

$$\log\frac{\mathrm{d}\alpha/\mathrm{d}T\cdot\beta}{\mathrm{f}(\alpha)}=\log k=\log A-\frac{E}{2.303RT} \tag{1}$$

where $\mathrm{d}\alpha/\mathrm{d}T=$ the fraction decomposed per degree, $\beta=$ heating rate, $\mathrm{f}(\alpha)=(1-\alpha)$ for a first order reaction, $T=$ the temperature in Kelvin, $E=$ the energy of activation, $A=$ Arrhenius frequency factor, $R=$ the general gas constant.

Values of 144, 86 and another 86 kJ mole^{-1} were obtained for the energy of activation of the nonisothermal dehydration at heating rates of 5, 10 and 15°C min^{-1}, respectively, compared to 73 kJ mole^{-1} for the isothermal

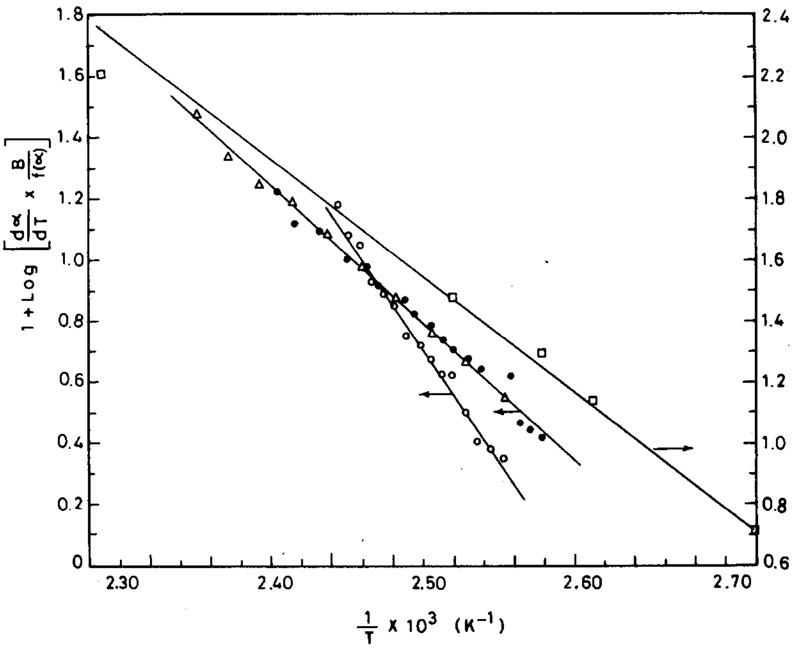

Fig. 1. Arrhenius plots for the isothermal and nonisothermal dehydration of ZnOX·2 H_2O. □, Isothermal; ○, nonisothermal at 5°C min^{-1} heating rate; △, nonisothermal at 10°C min^{-1} heating rate; ●, nonisothermal at 15°C min^{-1} heating rate.

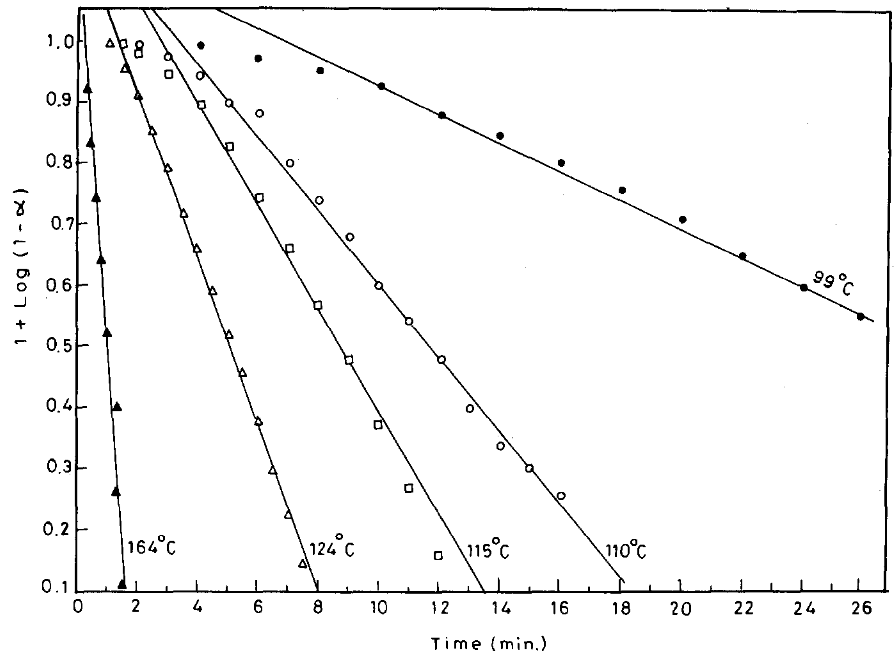

Fig. 2. First order plots for the isothermal dehydration of ZnOX·2 H_2O.

experiments (Table 1). The results obtained show good agreement between isothermal and nonisothermal reactions at high heating rates, namely at 10 and 15°C min^{-1}. Good agreement between isothermal and nonisothermal energies of activation was also reported by Dollimore et al. [5]. It was also pointed out that heating at high temperatures induces defects which decrease the energies of activation [9,10].

A value of 130 kJ $mole^{-1}$ was obtained for the enthalpy of dehydration of manganous oxalate dihydrate [10]. The values of the energy of activation obtained in the present study for the isothermal and nonisothermal kinetics at high heating rates may be attributed to the participation of a single water molecule in the activated complex [11], whereas the high value of 144 kJ $mole^{-1}$ obtained for the nonisothermal dehydration at 5°C min^{-1} agrees fairly well with the 130 kJ $mole^{-1}$ reported value of the enthalpy of the reaction, and hence the two molecules of water are expected to participate in the activated complex.

The Arrhenius frequency factor, A, was evaluated from eqn. (1) at 130°C and is given in Table 1. Values of Q^*/Q calculated by the use of the theory of absolute reaction rates, i.e.

$$A = \frac{kT}{h} Q^*/Q \qquad (2)$$

TABLE 1

Values of the Arrhenius parameters for the dehydration and decomposition of manganese(II) oxalate

Reaction	Kinetic parameters	Isothermal	TG at		
			5°C min^{-1}	10°C min^{-1}	15°C min^{-1}
Dehydration	E (kJ mole^{-1})	73	144	86	86
	A (s^{-1})	4.7×10^{6}	4.6×10^{16}	1.7×10^{8}	1.7×10^{8}
	Q^*/Q	$\approx 5 \times10^{-7}$	$\sim 5 \times10^{3}$	$\sim 2 \times10^{-5}$	$\sim 2 \times10^{-5}$
Decomposition	E (kJ mole^{-1})	143	242	242	242
	A (s^{-1})	4.3×10^{10}	4.6×10^{16}	4.6×10^{16}	4.6×10^{16}
	Q^*/Q	$\approx 3 \times10^{-3}$	$\sim 3 \times10^{3}$	$\sim 3 \times10^{3}$	$\sim 3 \times10^{3}$

where Q is the complete partition function for the activated complex excluding the reaction coordinates and Q is the complete partition function for the reactants are also given in Table 1. Utilization of eqn. (2) to solid state reactions was first applied by Cordes [12] and Shannon [13]. The values of E, A and Q^*/Q given in Table 1 indicate a single mechanism to be operative for the isothermal and nonisothermal dehydration at 10 and 15°C min^{-1} which is, according to Shannon, the loss of gases from the reaction interface, and the activated complex is less restricted in rotation compared to the reactants [13] ($Q^*/Q < 1$). High values of $Q^*/Q > 10^3$ as in the case of the nonisothermal dehydration at 5°C min^{-1} is attributed to a free rotation and translational degrees of freedom of the activated complex in two dimensions [14].

(2) *Decomposition*

The kinetics of this reaction were determined from experiments in which the anhydrous oxalate was heated at 160°C for 15 min in an atmosphere of nitrogen prior to the decomposition experiments. The first order plots for the isothermal decomposition are shown in Fig. 3 and their Arrhenius plot is shown in Fig. 4. Figure 4 also shows the results of the rising temperature

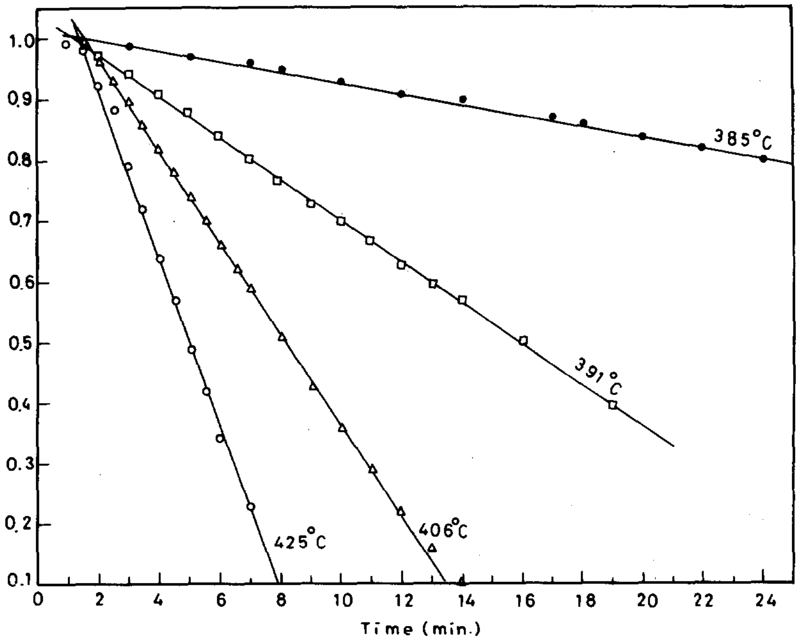

Fig. 3. First order plots for the isothermal decomposition of ZnOX.

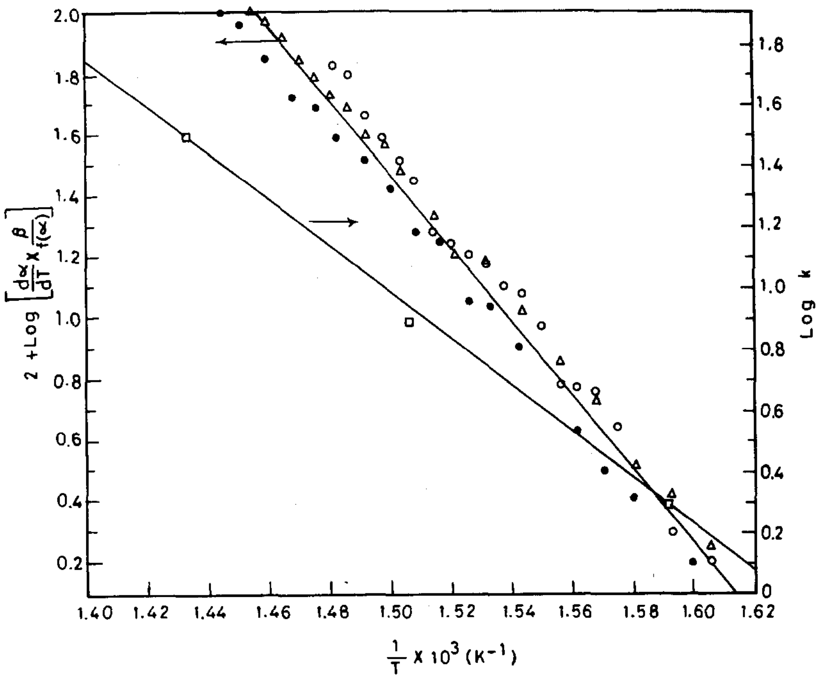

Fig. 4. Arrhenius plots for the isothermal and nonisothermal decomposition of ZnOX. □, Isothermal; ○, nonisothermal at 5°C min^{-1} heating rate; △, nonisothermal at 10°C min^{-1} heating rate; ●, nonisothermal at 15°C min^{-1} heating rate.

(TG) data obtained for the decomposition at heating rates of 5, 10 and 15°C min^{-1} using eqn. (1) which gave a single straight line. Values of 143 and 242.5 kJ mole^{-1} were obtained for the energy of activation from isothermal and nonisothermal plots, respectively. The difference could be a reflection of the condition of the anhydrous oxalate used in the isothermal and nonisothermal experiments. Values of 141 and 180 kJ mole^{-1} were reported for the isothermal decomposition to MnO in a nitrogen atmosphere [12–15].

A value of 250 kJ mole^{-1} was reported for the enthalpy of decomposition of the anhydrous manganese(II) oxalate in an atmosphere of nitrogen [11], which, compared with the range of the reported activation energies (140–265 kJ mole^{-1}), still allows for one oxalate ion in the activated complex, subject to reservations expressed by Garn [16]. Boldyrev et al. [17] have identified the activation energy for decomposition with the energy required to break the C–C bond in the oxalate ion.

Values of A and Q^*/Q were also evaluated, using eqn. (2), and are given in Table 1. Values of E and A obtained from the TG plots indicate a normal rate process which is characterized by A values $\approx 10^{15}$ sec^{-1} and energy of activation of the order of the enthalpy of the reaction. The value of $\approx 10^{-3}$ obtained for Q^*/Q for the isothermal decomposition indicate a mechanism governed by the loss of gases from the reaction interface.

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