

## **KINETICS OF THERMAL DECOMPOSITION OF METAL ACETATES**

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(Received September 21, 1990)

The acetates of magnesium, nickel, copper, manganese, sodium and barium were subjected to thermal decomposition by means of thermogravimetric techniques (TG) under a constant flow of nitrogen. The decompositions occurred in steps and the kinetics of every set of reactions was determined by the Coats and Redfern method. These results were analysed to establish the decomposition kinetics and hence to calculate activation energies. The activation energies were also determined by applying the Horowitz-Hugh method, which yielded similar results.

Thermogravimetric analysis (TG) has come into widespread use in the past decade for rapid assessment of the thermal decompositions of various substances. The thermal decomposition of metal acetates have been well documented [1-7]. Little information is available, however, on the kinetics of thermal decomposition of these metal acetates. In the present investigations, the orders of reaction ( $n$ ) and the activation energies ( $E$ ) of decomposition of the acetates of magnesium, nickel, copper, manganese, sodium and barium are determined.

The use of thermogravimetric data to evaluate the kinetic parameters of solid-state reactions involving weight loss has been investigated by a number of workers [8-11]. Determination of the order of reaction and activation energy with the above-mentioned methods suffered from a number of disadvantages. Therefore, an attempt was made to calculate the kinetic parameters by employing the Coats and Redfern method [12]. The activation energies were also calculated by employing the Horowitz method [11]. The acetates were chosen on the basis that decomposition occurs in steps; from the percentage weight losses, the volatile species were investigated and the kinetics of every set of reactions was determined.

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## Experimental

All metal acetate samples were of analar grade and were used as such.  $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Ba}(\text{CH}_3\text{COO})_2$  were all from E. Merck, whereas  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  was supplied by Riedel.

The TG curves were recorded on the Shimadzu TG-31 system with a temperature-programmed furnace (fitted with a voltage stabilizer), a thermocouple and an R-122T recorder. The heating rate employed was 10 deg / min. Since small sample weights of 10–15 mg were used, it was possible to operate at a heating rate of 10 deg/min without loss of resolution. All experiments were performed under a flow of nitrogen at a flow rate of 40 ml/min.

## Results and discussion

The TG curves of various metal acetates are shown in Fig. 1. A computer program in Basic language was applied for the equations [12]. The value of  $n$  was first changed to calculate the data, followed by plotting on a computer with the "ENEG" graphic system for each value of  $n$ . The best straight line was chosen with a low value of variance, and a computational approach was also made to select the value of  $n$  which gave the best straight line through

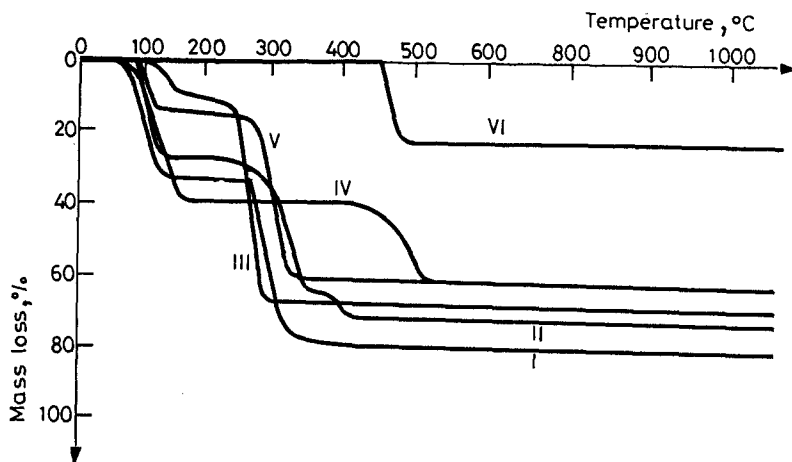


Fig. 1 TG curve of (I)  $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (II)  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$   
(III)  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (IV)  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  (V)  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$   
(VI)  $\text{Ba}(\text{CH}_3\text{COO})_2$ .

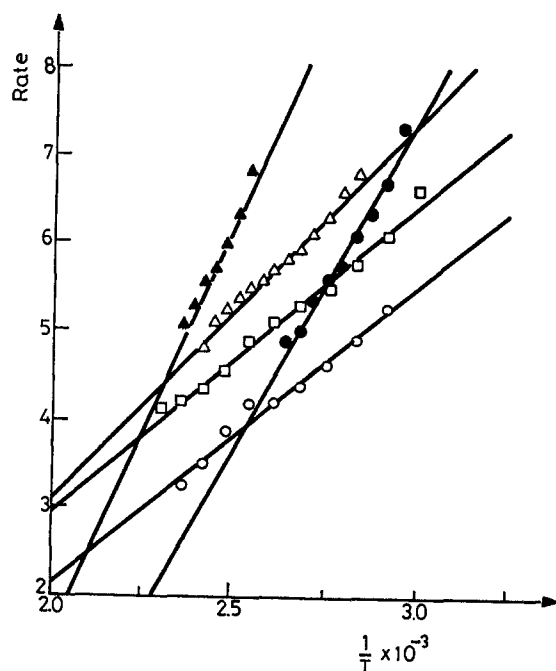


Fig. 2 Dehydration kinetics of metal acetates.

△ Sodium acetate · 3H<sub>2</sub>O, ▲ Copper acetate · H<sub>2</sub>O, □ Magnesium acetate · 4H<sub>2</sub>O,  
○ Nickel acetate · 4H<sub>2</sub>O, ● Manganese acetate · 4H<sub>2</sub>O,

the points. The activation energy for the best fit was calculated. Plots of the dehydration and decomposition reactions of the above metal acetate are shown in Figs 2 and 3, respectively. The decomposition reactions were studied and volatile products were determined via loss in weight in particular temperature ranges and the intermediate species were also investigated from the percentage weight remaining and are tabulated in Table 1. The activation energy values calculated with the methods of both Coats and Redfern and Horowitz are tabulated in Table 2 and are in reasonable agreement.

Figure 1-I shows the TG curve of  $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , which indicates two types of decomposition reactions. In the first step of decomposition, a 34% loss in weight was observed in the temperature range 275–340°, which corresponds to the loss of four water molecules. The intermediate was anhydrous  $\text{Mg}(\text{CH}_3\text{COO})_2$ , which was stable up to 270°. This dehydration reaction was of first order and required an activation energy of 15.9 kcal per mole. Above this temperature, the intermediate decomposed, with a loss in weight of 47% up to 340°. This corresponds to the loss of one

Table 1 Decomposition process of metal acetates in inert N<sub>2</sub> atmosphere

No	Compound	Temp. range, °C	Wt. loss, %		Volatile evolved	Corresponding intermediate
			Found	Calc.		
1	Mg(CH <sub>3</sub> COO) <sub>2</sub> ·4H <sub>2</sub> O	50-150	34	33.6	4H <sub>2</sub> O	Mg(CH <sub>3</sub> COO) <sub>2</sub>
2		275-340	46	47.6	(CH <sub>3</sub> ) <sub>2</sub> CO + CO <sub>2</sub>	MgO
3	Mn(CH <sub>3</sub> COO) <sub>2</sub> ·4H <sub>2</sub> O	80-140	15	14.69	4H <sub>2</sub> O	Mn(CH <sub>3</sub> COO) <sub>2</sub>
4		270-320	45	42.13	(CH <sub>3</sub> ) <sub>2</sub> CO + CO <sub>2</sub>	MnO
5	Cu(CH <sub>3</sub> COO) <sub>2</sub> ·H <sub>2</sub> O	110-160	8.9	9.2	H <sub>2</sub> O	Cu(CH <sub>3</sub> COO) <sub>2</sub>
6		205-600	59	59.19	CH <sub>3</sub> COOH + C + H <sub>2</sub> + CO <sub>2</sub>	Cu
7	Ni(CH <sub>3</sub> COO) <sub>2</sub> ·4H <sub>2</sub> O	90-140	28	28.95	4H <sub>2</sub> O	Ni(CH <sub>3</sub> COO) <sub>2</sub>
8		250-360	36	34.54	CH <sub>3</sub> COCOCH <sub>3</sub>	NiO <sub>2</sub>
9		390-420	6	6.43	1/2O <sub>2</sub>	NiO
10	Na(CH <sub>3</sub> COO) <sub>2</sub> ·3H <sub>2</sub> O	60-160	40	39.70	3H <sub>2</sub> O	CH <sub>3</sub> COONa
11		160-410	21	21.32	(CH <sub>3</sub> ) <sub>2</sub> CO	Na <sub>2</sub> CO <sub>3</sub>
12	Ba(CH <sub>3</sub> COO) <sub>2</sub>	455-470	23	22.7	(CH <sub>3</sub> ) <sub>2</sub> CO	BaCO <sub>3</sub>

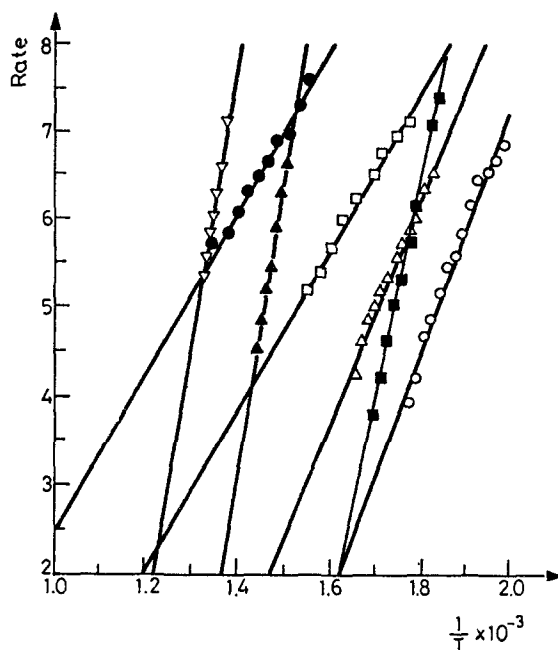


Fig. 3 Decomposition kinetics of metal acetates.

▽ Barium acetate, ▲  $\text{NiO}_2 = \text{NiO} + 1/2\text{O}_2$ , □ Nickel acetate, ○ Copper acetate,  
● Sodium acetate, △ Magnesium acetate, ■ Manganese acetate

molecule each of acetone and carbon dioxide, and agrees well with the results of Burriel-Marti [13]. This decomposition reaction follows a 2/3 order and required an activation energy of 57.59 kcal/mol. The weight residue of 19% was stable up to 1000° and corresponds to MgO. The proposed mechanism of decomposition is as follows:



The TG curve of  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  is shown in Fig. 1-V. It is evident from the curve that this decomposition also followed a two-step process [14]. The first step was that of dehydration, in which four molecules of water were eliminated in the temperature range 80–140°. This followed first-order kinetics and required an activation energy of 34.18 kcal/mol. In the second step of decomposition, the anhydrous manganese acetate decomposed to manganese oxide(s) and one molecule each of acetone and carbon dioxide were evolved as volatile products. This decomposition was of 1/2 order and

required an activation energy of 114.26 kcal/mol. The decomposition process may be represented by the following stoichiometric equation:



Table 2 Values of activation energy of thermal decomposition of metal acetates

No	Range of $\alpha$ studied	Standard deviation	Order $n$	Activation energy, $E$ kcal/mol	
				Redfern's method	Hugh's method
1	0.14–0.80	0.072	1	15.92	15.63
2	0.17–0.86	0.0795	2/3	57.59	57.41
3	0.12–0.9	0.1156	1	34.185	33.89
4	0.20–0.77	0.0669	1/2	114.26	112.54
5	0.12–0.83	0.0854	1	42.27	44.52
6	0.25–0.78	0.136	2	63.21	63.35
7	0.14–0.76	0.966	1	15.32	15.19
8	0.13–0.79	0.0592	2/3	40.79	40.86
9	0.12–0.75	0.0402	2	149.18	146.56
10	0.10–0.83	0.0714	1	19.42	20.21
11	0.14–0.87	0.0624	2	41.48	40.98
12	0.11–0.88	0.0892	1	147.08	145.36

The TG curve of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  is shown in Fig. 1-III, and again involves two types of decomposition [7]. The first step was that of dehydration, in which one molecule of water was eliminated in the temperature range 110–160°, with a 9% weight loss. The dehydration reaction was of first order and required an activation energy of 42.27 kcal per mole. In the second step, decomposition of the anhydrous copper acetate started above 200°; a slow loss in weight was observed up to 230°, whereas above this temperature there was an exponential loss in weight up to 300° and at the end of this decomposition process, in the interval 300–600°, only a 2% loss in weight was observed. In this decomposition step, a 59% loss in weight was observed and the overall reaction was of second order, with an activation energy of 63.21 kcal/mol. It is difficult to understand by what mechanism the

acetate group yields acetic acid as a product, but the process may be represented by the following stoichiometric equation:

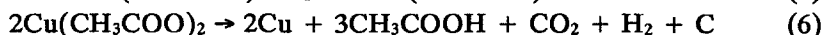
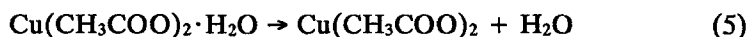
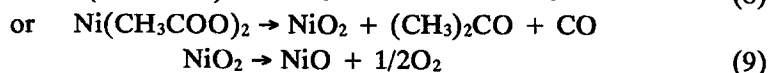
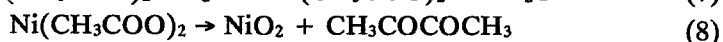
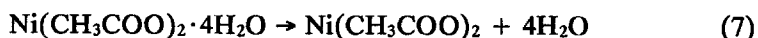
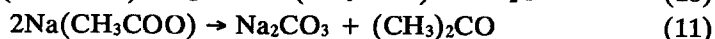
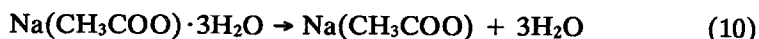


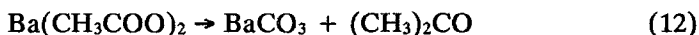
Figure 1-II is the TG curve of  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ . The decomposition occurred in three steps. In the first step, a loss in weight of 29% was observed in the temperature range 90–140°, indicating the loss of four water molecules [15]. This dehydration reaction was of first order and required an activation energy of 15.32 kcal/mol. The anhydrous nickel acetate was stable up to 250°. Above this temperature, a 36% loss in weight occurred, the weight remaining corresponding to  $\text{NiO}_2$  as an intermediate. There are two possibilities: either the acetate decomposed and  $\text{CH}_3\text{COCOCH}_3$  was eliminated, or the volatile products were in the form of one molecule each of acetone and carbon monoxide. This decomposition reaction was of 2/3 order and required an activation energy of 40.79 kcal/mol. The intermediate  $\text{NiO}_2$  was unstable and decomposed within the temperature range 390–420°. This decomposition reaction followed second-order kinetics and required an activation energy of 149.18 kcal/mol. The 40% weight residue was  $\text{NiO}$ . Therefore, the decomposition of nickel acetate may be described as follows:



Sodium acetate underwent two types of decomposition reactions, as shown in Fig. 1-IV. It is evident from the curve that in the first step 40% weight was lost and three water molecules were evolved [7]. The anhydrous sodium acetate was stable between 160° and 410°. Above this temperature, the anhydrous acetate decomposed: one mole of acetone was evolved and the residual 39% weight was sodium carbonate. This reaction followed second-order kinetics and required an activation energy of 41.48 kcal/mol. The decomposition of sodium acetate may therefore be represented as follows:



The TG curve of  $\text{Ba}(\text{CH}_3\text{COO})_2$  is shown in Fig. 1-VI. It was stable up to  $450^\circ$ . Above this temperature, loss in weight started and decomposition was completed up to  $470^\circ$ , with a loss in weight of 22%, corresponding to the loss of one molecule of acetone. The 77.3% residue was  $\text{BaCO}_3$ . The decomposition was of first order and required an activation energy of 147.10 kcal/mol. Therefore, the decomposition of barium acetate may be described as follows:



Note: In Figs 1 and 2, the thermogravimetric data on the metal acetates were used to calculate the relationship between

$$\text{rate} = -\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2 (1 - n)} \right] \text{ and } 1/T \cdot 10^3 \text{ for } n \neq 1$$

$$\text{and for } n=1 \text{ rate} = -\log \left[ \frac{-\log 1 - (1 - \alpha)}{T^2} \right]$$

## References

- 1 K. C. Patel, G. V. Chandrashekar, M. V. George and C. N. R. Rao, *Canad. J. Chem.*, 46 (1968) 257.
- 2 C. Dual, *Anal. Chim. Acta*, 13 (1955) 32.
- 3 M. A. Bernard and F. Busnot, *Bull. Soc. Chim. Fr.*, 5 (1968) 2000.
- 4 C. Dual, *Anal. Chim. Acta*, 20 (1959) 264.
- 5 L. Walter-Leavy and J. Laniece, *Comp. Rend.*, 250 (1960) 332.
- 6 D. R. Glasson, *J. Appl. Chem.*, 13 (1963) 124.
- 7 M. D. Judd, B. A. Plunkett and M. I. Pope, *J. Thermal Anal.*, 6 (1974) 555.
- 8 D. W. Kureben, D. W. van, Heerden, C. Van and F. J. Huntjens, *Fuel*, 30 (1951) 253.
- 9 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1968) 394.
- 10 C. D. Doyle, *J. Appl. Polymer Sci.*, 5 (1961) 285.
- 11 H. H. Horowitz and G. Metzger, *Anal. Chem.*, 35 (1963) 1464.
- 12 A. W. Coats and J. P. Redfern, *Nature*, 201 (1964) 68.
- 13 F. Burriel-Marti, S. Jimenez-Gomes and C. Alvarez-Herrero, *An. Edafol. Fissiol. Veg.*, 14 (1955) 221.
- 14 A. E. Newkirk, *Thermochim. Acta*, 2 (1971) 1.
- 15 W. R. Pease, R. L. Segall, R. St. C. Smart and P. S. Turner, *J. Chem. Soc. Faraday Trans.*, 82 (1982) 747.



**Zusammenfassung** — Mittels TG in konstantem Stickstoffstrom wurde die thermische Zersetzung von Magnesium-, Nickel-, Kupfer-, Mangan-, Natrium- und Bariumazetat untersucht. Es erfolgte eine schrittweise Zersetzung, die Kinetik für jede der Reaktionen wurde mit Hilfe der Methode von Coats und Redfern bestimmt. Diese Ergebnisse wurden genutzt, um die Kinetik der Zersetzung und anschließend die Aktivierungsenergien festzustellen. Ähnliche Werte für die Aktivierungsenergien erhielt man auch mit Hilfe der Methode von Horowitz Hugh.