Decomposition Kinetics of Metal Acetates

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Summary: Thermal decomposition of acetates of potassium, cobalt, zinc, mercury and lead have been investigated using thermogravimetric technique (TGA), under constant flow of nitrogen. The results indicate that major products are acetone, carbon dioxide, oxygen, depending on whether the final solid products is that of oxide or the metal. Kinetic parameters of the thermal decomposition of these metal acetates were investigated on the basis of their respective thermal curves. Calculation of reaction order and an activation energy were carried out by the Coats-Redfern's method and also by Horowitz- Hugh's method giving comparable results.

Introduction

Thermogravimetric analysis have come into wide use in the last decade for rapidly assesing the thermal decomposition of various substances. The acetate of group IIA metals have been extensively studied [1-3]. The decomposition of calcium acetate has in fact long been used as student exercise to demonstrate the formation of acetone. Thermal analysis of rare earth acetates as well as acetates of lead and copper is reported earlier [4-5]. The thermal decomposition of calcium, sodium, silver, copper, nickel, and mangnesium is reported in literature [6-14]. The kinetic data of thermal decom position of metal acetate is scarce. Kinetics of thermal decomposition of metal nitrates [15], suphates [16], and acetates [17] is previously investigated by employing Coats and Redfern method [18]. Boguslawska and co-worker [19], also used this method for the measurement of kinetic parameters of thermal decomposition of nitritonickelates (II). Therefore effort has been made in the present investigations to determine the kinetic parameters of thermal decomposition of the acetates of potassium, cobalt, zinc, mercury and lead by using Coats and Redfern method. The kinetic parameters for the above aforesaid metal acetates decomposition were also determined by applying Hugh - Horowitz's method [20].

Results and Discussion

The TG curves of various metal acetates-shown in Fig. 1, indicate dehydration and decomposition process. Decomposition reactions were studied and volatile products were determined by the loss in weight in particular temperature range, and the intermediate species were also investigated from percent weight remained and are tabulated in Table 1. For the calculation of the kinetic parameters, a computer programmed in basic language is designed, for the equation (18). Detail is published elsewhere [15-17]. First changing the value of n to calculate the data and then it is plotted on computer using "ENEG", graphic system for each value of n. A best straight line is chosen having low value of standard deviation, and also computational approach to select the value of n, which gives the best straight line through the points.

Activation energy for the best fit is calculated. Plots of dehydration and decomposition of the aforesaid metal acetates are shown in Fig. 2 and 3 respectively.

Fig. 1-I) is the TG curve of $CH_3COOK\ 2H_2O$, indicates three types of decomposition reactions. In the first step, 15.73 % loss in weight is observed in temperature range of 30-120°C, corresponds to the loss of two molecules of water. This dehydration reaction is of first order and required an activation energy of 48.48 kJ/mol. The intermediate is anhydrous potassium acetate and is stable upto 395°C and decomposition start above 400°C upto 460°C, accompanying 24.30% loss in weight corresponds to the loss of one mole of acetone. This decomposition reaction is of second order kinetics and required an activation energy of 261.37 kJ/mol. The intermediate K_2CO_3, decomposes at 749-1000°C giving no residue. It means that the potassium metal has

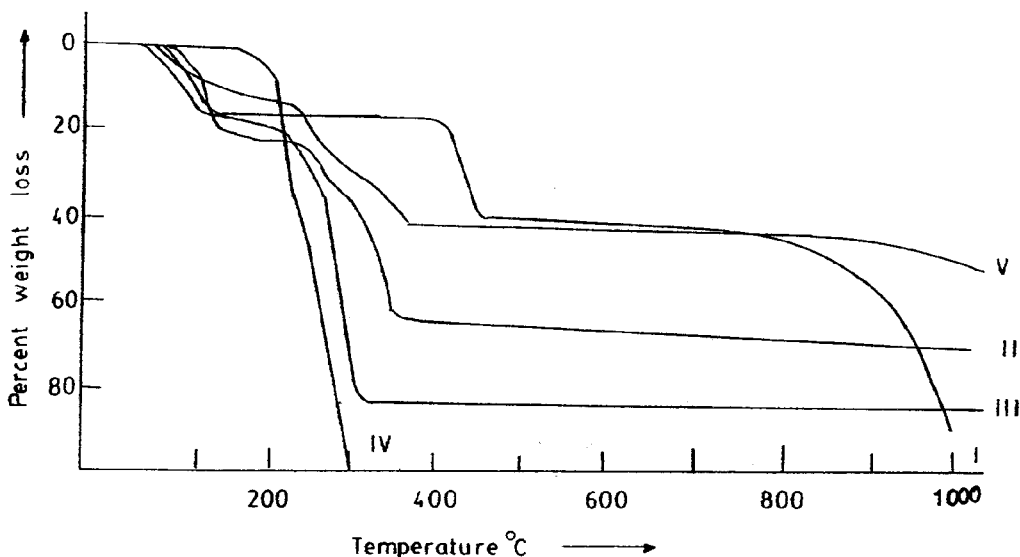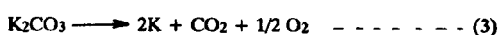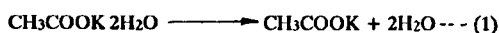Fig. 1: TG curve of metal acetate: (I) $KCH_3COO\ 2H_2O$ (II) $Co(CH_3COO)_24H_2O$ (III) $Zn\ (CH_3COO)_22H_2O$ (IV) Hg $(CH_3COO)_2$ (V) $Pb\ (CH_3COO)_23H_2O$

Table 1: Decomposition process of metal acetate in intert N_2 atmosphere.

No	Compound	Temp. range °C	%wt. loss found	calc.	volatile evolved	corresponding intermediate
1	$CH_2COOK\ 2H_2O$	30-120	15.73	15.5	$2H_2O$	CH_3COOK
2		400-460	24.30	25.00	$(CH_3)_2CO$	K_2CO_3
3		750-970	58.20	59.50	$2K + CO_2 + 1/2\ O_2$	-
4	$Co(CH_3COO)_2\ 4H_2O$	40-120	26.93	28.93	$4H_2O$	$Co(CH_3COO)_2$
5		180-260	20.2	23.3	$(CH_3)_2CO$	$CoCO_3$
6		263-300	17.32	17.68	CO_2	CoO
7	$Zn(CH_3COO)_2\ 2H_2O$	55-100	16.8	14.4	$2H_2O$	$Zn(CH_3COO)_2$
8		160-290	65.0	53.0	$(CH_3)_2CO + CO_2$	Zn
9	$Hg\ (CH_3COO)_2$	160-300	100	100	$(CH_3)_2CO +$	$CO_2 + 1/2\ O_2 + Hg -$
10	$Pb\ (CH_3COO)_2\ 3H_2O$	40-200	14.5	14.2	$3H_2O$	$Pb(CH_3COO)_2$
11		240-300	16.0	15.3	$(CH_3)_2CO$	$PbCO_3$
12		310-370	12.0	11.6	CO_2	PbO

also been volatilised. This decomposition reaction is of 2/3 order kinetics and required an activation energy of 326.50 kJ/mole. The proposed mechanism of decomposition is as follow.

$CH_3COOK\ 2H_2O \longrightarrow CH_3COOK + 2H_2O --- (1)$

$2CH_3COOK \longrightarrow K_2CO_3 + (CH_3)_2CO --- (2)$

$K_2CO_3 \longrightarrow 2K + CO_2 + 1/2\ O_2\ ------- (3)$

TG curve of $Co(CH_3COO)_24H_2O$ is shown in Fig. (1-II). It is evident from the TG curve that decomposition occurs in three steps. First step is that of dehydration in which four water molecules are eliminated in temperature range of 40-120°C. This dehydration reaction is of first order kinetics and required an activation energy of 67.53 kJ/mol. At temperature range of 180-260°C, the anhydrous cobalt acetate decomposes to yield one mole of acetone as volatile material and cobalt carbonate as residue. This decomposition reaction is of 2/3 order kinetics and required an activation energy of 93 kJ/mol. The cobalt carbonate is unstable and decomposes to yield CoO as residue and carbon dioxide as volatile. This reaction is of 1/2 order kinetics and required an activation energy of 303.12 kJ/mol. Similarly CoO as residue was also reported
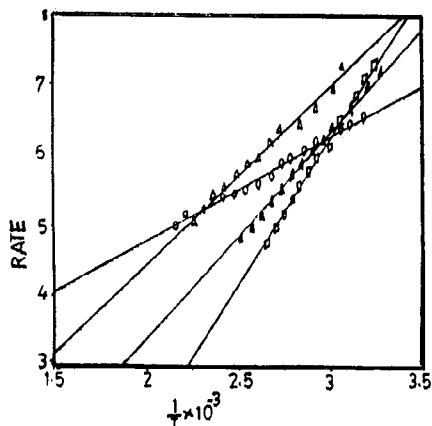
Fig.2: Dehydration kinetics of metal acetate: (Δ) KCH₃COO   2H₂O   (▲)   Co(CH₃COO)₂4H₂O   (□) Zn(CH₃COO)₂2H₂O (O) Pb(CH₃COO)₂3H₂O
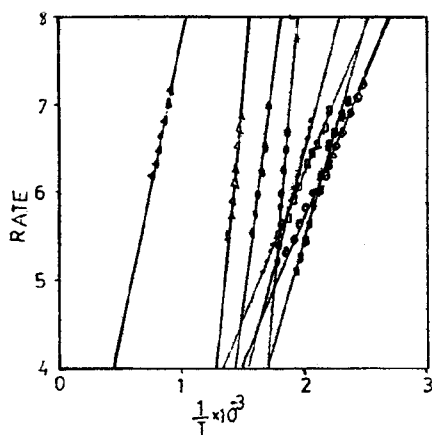
Fig.3: Decomposition kinetics of metal acetate:
(Δ) 2CH₃COOK (▲)K₂CO₃ (■) Co(CH₃COO)₂ (O) CoCO₃ (◨) Zn (CH₃COO)₂ (o) Hg (CH₃COO)₂ (•) Pb (CH₃COO)₂ (◉) PbCO₃

by other workers by the thermal decomposition of nitrogen ligand complexes of cobalt [21] and in thermal decomposition of sodium nitrogen hexacobaltate [22]. The decomposition process may be represented by the following stoichiometric equation.

$$Co(CH_3COO)_2 \, 4H_2O \longrightarrow CO(CH_3COO)_2 + 4H_2O \quad (4)$$

$$Co(CH_3COO)_2 \longrightarrow CoCO_3 + (CH_3)_2CO \text{ - - - -} \quad (5)$$

$$CoCO_3 \longrightarrow CoO + CO_2 \quad \text{- - - - - - -} \quad (6)$$

The TG curve of Zn(CH₃COO)₂2H₂O is shown in Fig. (1-III), showing two types of decomposition processes. Two water molecules are

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

No	Range of α studied	standard deviation	order n	Activation energy (E) kJ per mole Redfern's method	Hugh's method
1	0.15-0.82	0.0720	1	48.48	47.97
2	0.16-0.88	0.0795	2	261.37	260.42
3	0.13.093	0.1156	2/3	326.50	327.12
4	0.23-0.87	0.0669	1	67.63	67.11
5	0.14-0.87	0.0854	2/3	93.00	93.40
6	0.28-0.88	0.1360	1/2	303.12	302.95
7	0.12-0.79	0.660	1	76.42	76.12
8	0.15-0.89	0.0592	2/3	93.53	93.13
9	0.16-0.85	0.0402	1/2	61.87	61.79
10	0.16-0.87	0.0714	1	27.96	27.43
11	0.12-0.85	0.0624	2/3	104.78	103.98
12	0.19-0.91	0.0720	1/2	193.0	193.21

eliminated at temperature range of 55-100°C. This dehydration reaction is of first order kinetics and required an activation energy of 76.42 kJ/mol. The second stage commences at 160°C, proceeds rapidly until 190°C, leading to the final weight loss of (65%). This value is much higher than predicted for the formation of one mole of each acetone and carbon dioxide. 18% weight remained as residue is very much less than the weight of metallic zinc (29.80%). It means that a part of zinc metal has been volatilized during decomposition reaction. This reaction is of 2/3 order kinetics and required an activation energy of 93.83 KJ/mol. This observation was also given by Judd *et al* [9] during the decomposition of copper acetate a part of metallic copper had also been volatilized. The decomposition process may be represented by the following stoichiometric equation:
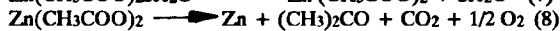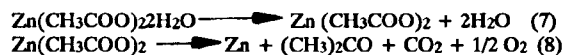
$$Zn(CH_3COO)_22H_2O \longrightarrow Zn (CH_3COO)_2 + 2H_2O \quad (7)$$
$$Zn(CH_3COO)_2 \longrightarrow Zn + (CH_3)_2CO + CO_2 + 1/2 O_2 \quad (8)$$

Fig. (1-IV) is the TG curve of Hg(CH₃COO)₂ and its decomposition is single step processes. No loss in weight is observed before 160°C, indicating the anhydrous nature of the compound. Mercuric acetate decomposed at temperature range of 160-300°C, and nothing is left as residue. This decomposition reaction is of first order kinetics and required an activation energy of 61.87 kJ/mole. The proposed mechanism of decomposition is as follows:
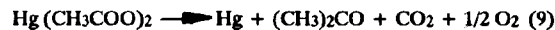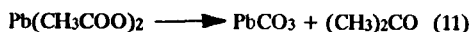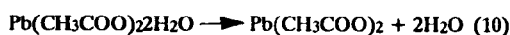
$$Hg(CH_3COO)_2 \longrightarrow Hg + (CH_3)_2CO + CO_2 + 1/2 O_2 \quad (9)$$

Fig. (1-V) is the TG curve of Pb(CH₃COO)₂3H₂O. It is evident from the curve

that its decomposition is a three steps process. In the first step 14.5% weight loss is observed in temperature range of 40-200°C, which corresponds to the loss of three molecules of water. The dehydration reaction follows first order kinetics and required an activation energy 27.96 kJ/mol. In the second step of decomposition 16% loss in weight in temperature range of 240- 300°C corresponds to the loss of one mole of acetone and lead carbonate is left as residue. This decomposition reaction is of 2/3 order kinetics and required an activation energy of 104.78 kJ/mol. The PbCO₃ is unstable and decomposed at temperature range of 310-370°C corresponds to the loss of one molecule of CO₂. The PbO is left as residue and is in good agreement with the work of Patil and co-workers [4]. This reaction is of 1/2 order kinetics and required an activation energy of 193 kJ/mol. PbO as residue was also obtained by the thermal decomposition of potassium lead hexanitritokelates [22]. PbO is stable upto 600°C and slowly loss in weight is observed upto 1000°C. Since this decomposition reaction is not completed upto 1000°C and hence the kinetics of this step is not studied. Therefore the proposed mechanism of decomposition is as follows:

$$Pb(CH_3COO)_2 2H_2O \longrightarrow Pb(CH_3COO)_2 + 2H_2O \quad (10)$$

$$Pb(CH_3COO)_2 \longrightarrow PbCO_3 + (CH_3)_2CO \quad (11)$$

$$PbCO_3 \longrightarrow PbO + CO_2 \quad (12)$$

Note: In Figs. (2 and 3) thermogravimetric data of metal acetates were used to calculate the relationship between

Rate = - log $[1-(1-\alpha)^{1-n}/T^2(1-n)]$ and $1/T .10^3$
for n = 1 and

when n = 1 Rate = - log $[-\log 1-(1-\alpha)/T^2]$

Experimental

All samples of metal acetates were of Analar grade and used as such. TG curves were recorded on Shimadzu TGA-31 system with temperature programmed furnace (fitted with voltage stabilizer), thermocouple and R-122T recorder. The heating rate employed was 10°C/min. Since small sample weight 10-15 mg were used, it was possible to operate at heating rate of 10°C/min without any loss of resolution. All experiments were performed under constant flow of nitrogen at flow rate of 40 ml/min.

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