Thermochimica Acta, 41 (1980) 265—268
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

KINETICS OF THE ISOTHERMAL DECOMPOSITION OF Cu(II) BUTYRATE

P.C. KALSI *, P.S. BASSI and C.M. KHAJURIA

Department of Chemistry, University of Jammu, Jammu, 180001 (India)

(Received 8 April 1980)

The isothermal decomposition of $Cu(CH_3CH_2CH_2COO)_2$ has been studied at 190, 200 and 210°C. The final decomposition product was identified as CuO by X-ray diffraction and chemical analysis. The kinetics of the isothermal decomposition follow a linear law, with an activation energy of 84.9 ± 5 kJ mole^{-1}. The simultaneous DTG, DTA and TG curves of the sample have been recorded at heating rates of 5 and 10°C min^{-1}.

INTRODUCTION

TG and DTA are extensively used to study the kinetics of decomposition reactions. Here, decomposition may depend on numerous physico-chemical factors and experimental conditions. In isothermal techniques, it is commonly assumed that at constant temperature the shape of the curve representing the degree of decomposition as a function of time depends only on the mechanism of reaction; hence, isothermal methods are preferred.

In continuation of our work on the isothermal decompositions of Cu(II) carboxylates [1—5], we describe here the kinetics of the isothermal decomposition of Cu(II) butyrate. For the isothermal decomposition, the rate of the reaction has been followed by the weight loss method. The end product has been found to be cupric oxide by X-ray diffraction and chemical analysis. Derivatographic studies of the sample have also been recorded at 5 and 10°C min^{-1}.

EXPERIMENTAL

Cu(II) butyrate · H_2O was prepared by the method of Martin and Waterman [6]. The anhydrous salt was obtained from the hydrated form by dehydration at 100° C over P_2O_5 in vacuum. The composition of the anhydrous salt was established by gravimetric analysis by precipitating Cu as CuSCN [7], by elemental analysis (found: Cu, 26.9; C, 40.3; H, 5.5%. calculated: Cu, 26.7;

---

* Present address: Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400 085, India.

C, 40.3; H, 5.8%). For the isothermal decomposition studies, a known amount (~0.5 g) of powdered sample (below 100 mesh sieves) was taken and studied by the method reported earlier [8]. The final decomposition product, CuO, was found to be crystalline under a polarizing microscope. Its identity was established by X-ray diffraction and chemical analysis.

DTG, DTA and TG of the sample were studied with a Paulik—Paulik—Erdey MOM derivatograph (Hungary). Heating rates were 5 and 10°C min^{-1}.

RESULTS AND DISCUSSION

The kinetics of the decomposition were studied isothermally at temperatures of 190, 200 and 210°C. At 190°C the final product after 12 h of reaction was identified as CuO by the X-ray diffraction using Cu-$K\alpha$ radiation. The *d* values with the corresponding relative intensities were calculated from X-ray diffraction study of the end product and compared with the values reported [9] for CuO. For each diffraction line from the powdered material its interplanar spacing (*d*) was calculated from Bragg's relation and the relative intensity of each line was measured by visual comparison of the intensity of the line with the standard scale.

The experimental *d* values and the corresponding intensities of the final product were found to be in good agreement with those reported in the literature [9] for CuO. The identity of the product was further confirmed by chemical analysis. To identify the intermediate products, samples were withdrawn from the thermostat at different time intervals. No stable intermediate could be isolated by X-ray diffraction during the isothermal decomposition studies between 190 and 210°C.

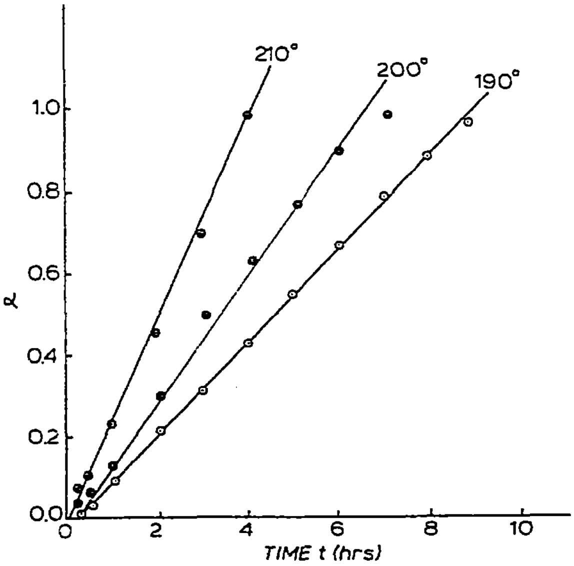

Fig. 1. Plot of α vs. *t* at different temperatures for the isothermal decomposition of Cu(II) butyrate.

The linear range of isothermal decomposition of Cu(II) butyrate has been expressed by the equation

$$\alpha = Kt + C \qquad (1)$$

where K, t and C are the rate constant, time, and a constant, respectively, for the isothermal decomposition of Cu(II) butyrate at different temperatures. The applicability of this equation is shown in Fig. 1, where the plots of α vs. t at various temperatures are the straight lines. The rate constants have been calculated from the linear portion of the plot of α vs. t and are 0.115 h^{-1}, 0.150 h^{-1} and 0.250 h^{-1} at 190, 200 and 210°C, respectively. It is observed that the rate constant increases with rise in temperature and the Arrhenius equation is followed in this temperature range. The activation energy is found to be 84.9 ± 5 kJ $mole^{-1}$. This behaviour is not due to induction and the indications are that the reaction centres [10—12] are already present in larger quantities. The fast linear reaction at 210°C and the absence of a sigmoid curve initially can be regarded as evidence in favour of the reaction centres.

DERIVATOGRAPHIC STUDY OF Cu(II) BUTYRATE

The combined DTG, DTA and TG curves of a 200 mg sample of anhydrous Cu(II) butyrate heated at a rate of 5°C min^{-1} with 200 mg sensitivity in a circular platinum crucible are given in Fig. 2.

The thermal decomposition of Cu(II) butyrate begins at 220°C and ends at 430°C, as shown by DTG. In this temperature range, DTG indicates two closely spaced peaks. The TG curve shows a rapid loss which corresponds to the formation of Cu_2O. The corresponding DTA shows two closely spaced endotherms at 275 and 310°C in this region, indicating multiple-step decom-

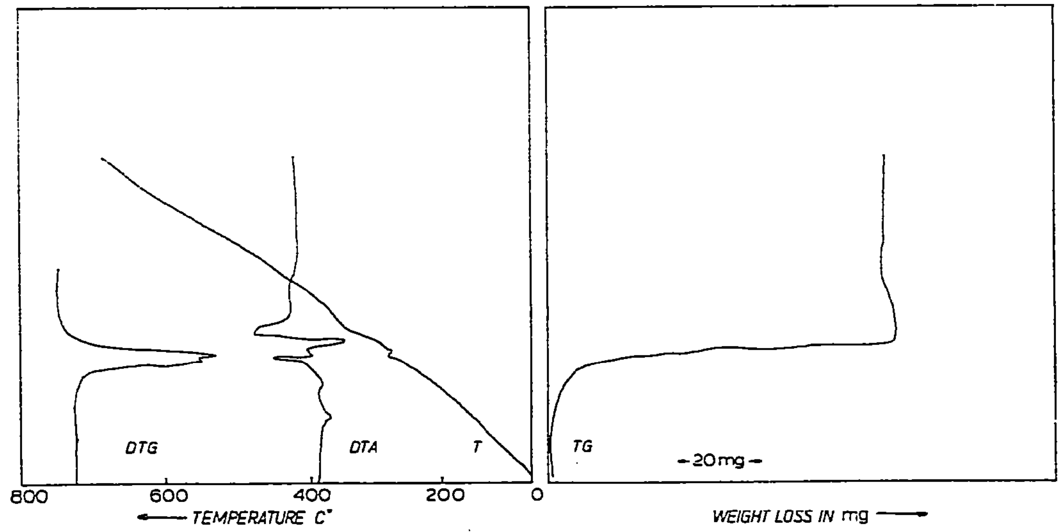

Fig. 2. Derivatogram for Cu(II) butyrate at a heating rate of 5°C min^{-1}.

position. Finally, there is an increase in weight in the TG curve. This weight increase is due to the oxidation of Cu_2O to CuO by atmospheric oxygen. This increase in weight due to oxidation of Cu_2O is indicated by a broad exothermic peak in DTA. There are two more small endotherms in DTA with about 1.0% loss in weight. These may be due to decomposition of adsorbed gases or moisture. The thermogram was also recorded at the heating rate of 10°C min^{-1}. All these steps were indicated in the DTG, DTA and TG fairly and clearly when the heating rate was maintained at 10°C min^{-1}. It was not possible to calculate the activation energy from these curves due to multiple-step decomposition.

ACKNOWLEDGEMENTS

P.C.K. is grateful to CSIR, New Delhi, for the award of a Post Doctoral Fellowship.

REFERENCES

1 P.S. Bassi and P.C. Kalsi, Indian J. Chem., 14A (1976) 967.
2 P.S. Bassi and P.C. Kalsi, J. Therm. Anal., 10 (1976) 375.
3 P.S. Bassi, P.C. Kalsi and C.M. Khajuria, Indian J. Chem., 15A (1977) 399.
4 P.S. Bassi and P.C. Kalsi, J. Therm. Anal., 13 (1978) 363.
5 P.C. Kalsi and P.S. Bassi, J. Therm. Anal., 17 (1979) 543.
6 R.L. Martin and H.J. Waterman, J. Chem. Soc., (1957) 2545.
7 A.I. Vogel, Quantitative Inorganic Analysis, Longmans, Green, London, 1962, p. 497.
8 P.S. Bassi and P.C. Kalsi, Acta Ciencia Indica, 4 (1975) 303.
9 Swanson and Tatge, Natl. Bur. Stand. U.S. Circ. 539, 1 (1953) 49.
10 D. Dollimore, J. Dollimore and D. Nicholson in J.H. De Boer (Ed.), Reactivity of Solids, Elsevier, New York, 1961 p. 634.
11 D. Dollimore and K.H. Tonge, in G.M. Schwab (Ed.), Reactivity of Solids, Elsevier, New York, 1965 p. 502.
12 P.S. Bassi, P.C. Kalsi and C.M. Khajuria, Thermochim. Acta, 34 (1979) 183.