Thermochimica Acta, 176 (1991) 57–62
Elsevier Science Publishers B.V., Amsterdam

KINETIC STUDIES ON THE THERMAL DECOMPOSITION OF γ-IRRADIATED AND UNIRRADIATED COBALT CROTONATO COMPLEX

M.A. MOUSA *

Chemistry Department, Centre of Science and Mathematics, Taif (Saudi Arabia)

(Received 25 April 1990)

ABSTRACT

The kinetics of thermal decomposition of the γ-irradiated and the unirradiated cobalt crotonato complex have been studied using isothermal and dynamic thermogravimetric methods. The isothermal study indicated that the decomposition reaction proceeds in accordance with the three-dimensional phase boundary mechanism (R_3). Irradiation enhances the decomposition reaction but does not modify its mechanism. The activation energy decreases as the radiation dose increases.

INTRODUCTION

Currently, unsaturated organic acid compounds, e.g. fumaric and crotonic compounds, are used in many industrial applications. They are used in the manufacture of adhesives, emulsions, optical fibres and polyester resins [1–6]. Literature references concerning the kinetics of the unsaturated organic acids and their compounds are very scanty. Recently a study on the thermal stability of crotonic acid and some of its chelated compounds has been reported [7], but no details on the kinetics or mechanisms of thermal decomposition of the compounds were included. Therefore the present work was designed to study the kinetics and mechanism of thermal decomposition of the cobalt crotonato complex as one of these unsaturated organic acid salts. It is well known that the kinetic parameters of thermal decomposition reactions are highly affected by both the nature of the investigated samples and the conditions under which the decomposition takes place [8–11]. It was also our aim, therefore, to examine the effect of chemical defects induced by γ-irradiation on the decomposition mechanism and on the kinetic parameters calculated by isothermal and dynamic thermogravimetric techniques.

---

* Present address: Chemistry Department, Faculty of Science, Benha University, Benha, Egypt.

0040-6031/91/$03.50

EXPERIMENTAL

The cobalt crotonato complex, $Co(ca)_2$, was prepared by dissolving pure cobalt carbonate in a hot aqueous solution of crotonic acid (ca.) The solution was then filtered and concentrated on a water bath until a solid product was obtained on cooling. The product was filtered off and kept over anhydrous calcium chloride.

The identification of the complex was achieved by IR and chemical analysis [7]. The percentage of cobalt ion was confirmed by atomic absorption spectrophotometry.

The thermogravimetric (TG) analyses were recorded on a Mettler TA 3000 thermal analyser using samples of about 7 mg to ensure linear heating. In the isothermal studies the reaction temperature was varied between 463 and 668 K, and the heating rates used in the dynamic studies were 5, 10, 15 and 20 K min^{-1}.

Samples sealed in glass ampoules were irradiated at room temperature with ^{60}Co γ-rays at different doses between 20.2 and 40.1 Mrad.

RESULTS AND DISCUSSION

The DTA and TG curves for the unirradiated cobalt crotonato complex, $Co(ca)_2$, are presented in Fig. 1. The DTA curve shows an exothermic peak centred at 665 K due to the decomposition of the complex. The TG curve showed that the complex decomposes in a single stage process beginning at

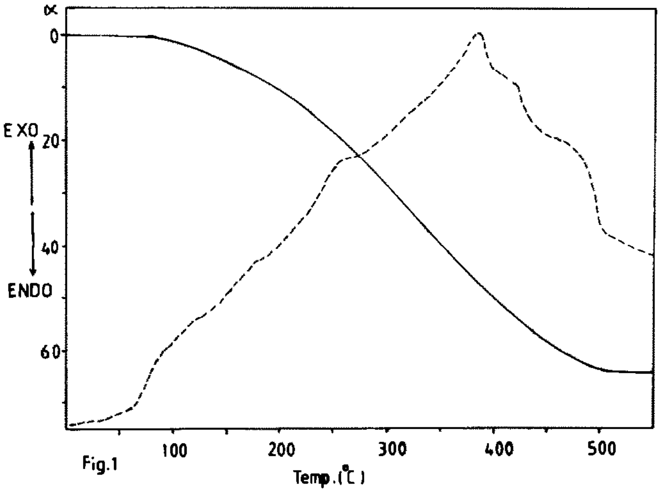

Fig. 1. DTA (— — —) and TG (———) curves for unirradiated cobalt crotonato complex, $Co(ca)_2$.

350 K. The total weight loss of this process amounts to about 64.9%, which conforms with the formation of Co_3O_4 as residual material. The decomposition of irradiated samples started at lower temperatures than did that of the unirradiated one, and further reduction in decomposition temperature was observed with increasing radiation dose. At a heating rate of 10 K min^{-1} the inception temperature of the decomposition reaction was found to be lowered by 12 and 20 K for samples irradiated with 20.2 and 40.1 Mrad respectively. This behaviour was also observed for other materials [12–14]. The ionizing radiation creats chemical damages and crystal defects in cobalt compounds due to the following interaction [14–16]

$$Co^{2+} + \gamma \rightarrow Co^{3+} + e$$

These defects produce a strain in the crystal matrix of the complex. This strain, which is increased by heating, causes the acceleration of the reaction and, in turn, the onset of decomposition of the irradiated samples at lower temperatures than that for the unirradiated one.

The kinetics of the thermal decomposition reaction of the irradiated and non-irradiated cobalt crotonato complex were studied by thermogravimetric analysis using both the isothermal and the dynamic method. The isothermal decomposition was performed at temperatures between 463 and 668 K. Under isothermal conditions, the rate constant, k, is independent of reaction time and so $g(\alpha) = kt$, where α is the fraction of the cobalt crotonato complex decomposed at time t. The plots of α versus t for unirradiated samples are given in Fig. 2. The isothermal α/t data were analysed by linear regression analysis according to various kinetic model functions $g(\alpha)$ [17], as listed in Table 1. The results showed that the phase boundary controlled

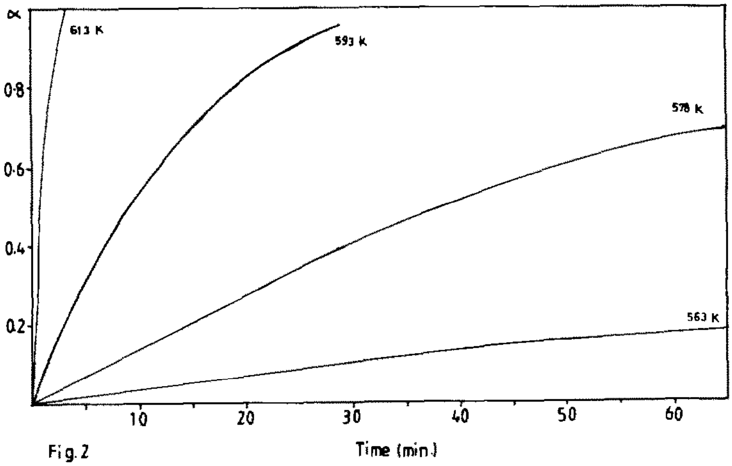

Fig.2

Fig. 2. Plot of α vs. t at different temperatures for decomposition of the unirradiated cobalt crotonato complex, $Co(ca)_2$.

TABLE 1

Kinetic model functions for solid decomposition

$g(\alpha)$	Symbol	Rate controlling process
α^2	D_1	One-dimensional diffusion
$\alpha+(1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion
$[1-(1-\alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion (Jander function)
$(1-2\alpha/3)-(1-\alpha)^{2/3}$	D_4	Three dimensional diffusion (Ginstling–Brownshtein function)
$\ln[\alpha/(1-\alpha)]$	Au	Autocatalytic reaction (Prout–Tompkins function)
$1-(1-\alpha)^{1/n}$	R_n	Phase-boundary reaction; $n=1$, 2 and 3 (one-, two-, and three-dimensional respectively)
$[-\ln(1-\alpha)]^{1/m}$	A_m	Random nucleation and its subsequent growth; $m=2$, 3 and 4 (Avrami–Erofeev function)
$-\ln(1-\alpha)$	F_1	First order kinetics

reaction (R_3) is the model which best coincides with our decomposition data, with a correlation coefficient higher than 0.981. According to this mechanism, the nucleation of the reactant occurs instaneously, and the reaction is controlled by movement of a sphere interface at constant velocity. However, the linear regression analysis method showed that the correla-

TABLE 2

Kinetic parameters for thermal decomposition of the cobalt crotonato complex estimated by isothermal and dynamic thermogravimetric methods using the R_3 model

Analysis method	Irrad. dose (Mrad)	Heating rate ($K\ min^{-1}$)	E ($kJ\ mol^{-1}$)	A[a] (s^{-1})
Isothermal	–		284	4.0×10^{21}
	20.2		266	8.0×10^{20}
	40.1		253	5.5×10^{20}
Dynamic: calculated according to Coats and Redfern	–	5	281	2.4×10^{21}
	20.2		259	8.1×10^{20}
	40.1		248	4.1×10^{20}
	–	10	264	9.1×10^{20}
	20.2		249	5.3×10^{20}
	40.1		241	2.2×10^{20}
	–	15	251	4.3×10^{20}
	20.2		238	1.8×10^{20}
	40.1		232	7.4×10^{20}
	–	20	234	6.4×10^{19}
	20.2		220	3.8×10^{19}
	40.1		213	1.2×10^{19}

[a] A is a frequency factor.

tion coefficients obtained for the random nucleation model (A_3) are very close to those found for the R_3 model. All kinetic parameters obtained for irradiated and non-irradiated samples using the R_3 model are listed in Table 2.

In order to investigate the effect of one of the experimental conditions on the kinetic data obtained, the decomposition reaction has been studied using a thermogravimetric dynamic method. The kinetic parameters were calculated in this method according to Coats and Redfern [18,19] using the R_3 model, which gave the highest correlation coefficients in the isothermal studies. From the results obtained, which are given in Table 2, it can be seen that the apparent activation energy, E, decreases with increase in the heating rate.

Comparison of the data listed in Table 2 shows that the kinetic parameters evaluated according to the dynamic method show some differences from those evaluated according to the isothermal method. Such differences increase as the heating rate increases. However, these results indicate that the two methods give results in agreement at lower heating rates.

Table 2 shows that the E values decrease to a small extent with an increase in irradiation dose, which indicates that the ionizing radiation has not affected the mechanism governing the decomposition reaction. However, this lowering in the E values may be attributed to the induction effect of crystal defects produced in the crystal matrix during the irradiation process. Generally speaking the results obtained in this work indicate that γ-irradiation enhances the thermal decomposition of the cobalt crotonato complex.

REFERENCES

1 K. Taki, P.H. Kim and S. Namba, Bull. Chem. Soc. Jpn., 43 (1970) 1450.
2 A.K. Galwey, P.M. Jamieson, M.E. Brown and M.J. McGinn, in P. Barret (Ed.), Reaction Kinetics in Heterogeneous Chemical Systems, Amsterdam, 1975, p. 520.
3 A.V. Tobolosky, Properties and Structure of Polymers, Wiley, New York, 1960.
4 M. Fuku, K. Fukushi and T. Deguchi, Jpn. Kokai Tokkyo Koho, Patent 86 293255, 1986.
5 T. Shinohara and H. Oda, Jpn. Kokai Tokkyo Koho, Patent 87 30172, 1987.
6 S. Mase, M. Yoshida, A. Takigawa, K. Maeda, Y. Aoki and I. Tago, Jpn. Kokai Tokkyo Koho, Patent 87 98303 (1987).
7 J.R. Allan, J.G. Bonner, H.J. Bowley, D.L. Gerrard and S. Hoey, Thermochim. Acta, 141 (1989) 227.
8 A.K. Galwey, in H.J. Emeleus (Ed.), International Review of Science, Inorganic Chemistry, Vol. 10, Solid State Chemistry, Butterworths, London, 1975, p. 147.
9 C.H. Bamford and C.H. Tipper, Comprehensive Chemical Kinetics, Elsevier, Amsterdam, Vol. 22, 1980.
10 P.K. Gallagher and D.W. Johnson, Thermochim. Acta, 6 (1973) 67.
11 W.W. Wendlandt, Thermal Methods of Analysis, Wiley, New York, 2nd edn., 1974, p. 45.
12 El.M. Diefallah, S.N. Basahl and A.Y. Obaid, J. Radioanal. Nucl. Chem., 109 (1987) 177.
13 S.M.K. Nair, K.K. Malayil and P.D. Jacob, Thermochim. Acta, 141 (1989) 61.

14 M.A. Mousa, A.M. Summan and G.N. Al-Sousi, Thermochim. Acta, in press.
15 M.A. Mousa and A.M. Summan, Radiat. Phys. Chem., 33 (1989) 87.
16 M.A. Mousa, M.A. Ahmed, A.M. Summan and A.M. Badawy, Thermochim. Acta, 146 (1989) 87.
17 J. Sestak and G. Bergern, Thermochim. Acta, 3 (1971) 1.
18 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
19 G.M. Bancroft and H.D. Gesser, J. Inorg. Nucl. Chem., 27 (1965) 1545.