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KINETICS OF ISOTHERMAL DECOMPOSITION OF γ-IRRADIATED AND UNIRRADIATED COBALT(II) MALONATO COMPLEX

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ABSTRACT

The thermal decomposition of γ-irradiated and unirradiated cobalt(II) malonato complex $Na_2[Co(C_3H_2O_4)_2]\cdot 2H_2O$ has been studied by thermogravimetry (isothermal conditions). The reaction order, activation energy and frequency factor were computed by different models. The effect of γ-irradiation on the kinetic parameters of the thermal decomposition reaction is discussed. Radiation did not modify the mechanism of the reaction but accelerated the dehydration step due to the generation of more dislocations in the crystal lattice of the complex. The kinetics of the dehydration is controlled by a phase-boundary (R_2 and R_3 functions) mechanism, while the decomposition reaction is controlled by a first-order mechanism (F_1 function).

INTRODUCTION

The kinetic studies of solid decompositions have proceeded in two directions: using powdered materials and using single crystals. The former studies are much more extensive than the latter. The essential features of solid-state decompositions are: the destruction of the crystal lattice of the reactant, the breaking and redistribution of chemical bonds, the formation of the crystal lattice of the reaction product and, lastly, the diffusion of one component or

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the other through the product layer for further propagation of the dissociation reaction.

In dynamic thermogravimetric analysis, the weight changes of a sample are continuously recorded as a function of time (isothermal) or temperature (non-isothermal) as the sample is heated. Thermograms provide information relating kinetic data to the chemical changes which occur on heating [1]. There has been considerable discussion in the literature concerning the validity of kinetic data obtained by thermal analysis under non-isothermal conditions [2,3]. Therefore, in the present investigation an isothermal method was used.

Ionising radiation has frequently been used in studies of the thermal decomposition of crystalline solids to increase the number of reaction nucleation sites at the surface and in the bulk [2]. There are well known mechanisms whereby structural defects can be introduced by ionising radiations. Severe disruption of the lattice of a crystalline solid is possible, with the formation of a large number of vacancies. Vacancy migration and aggregation in a solid is known to lead to the formation of dislocation loops, an increase in the number of existing dislocations and colloid formation. Several studies [4–6] have shown that the defects induced by irradiation enhance the decomposition rate, the effect increasing with dose.

Literature references concerning the thermal stability of transition metal malonato complexes are very scanty [7–9]. Previous study [8] on the thermal stability of $Na_2[Co(C_3H_2O_4)_2] \cdot 2H_2O$ has been reported, but no details on the kinetics or mechanism of its thermal decomposition were included. Therefore, the present work was designed to study the effect of γ-irradiation on the kinetics of the thermal decomposition of $Na_2[Co(C_3H_2O_4)_2] \cdot 2H_2O$ and to determine the detailed mechanisms as well as the relevant kinetic parameters.

EXPERIMENTAL

The cobalt malonato complex, $Na_2[Co(C_3H_2O_4)_2] \cdot 2H_2O$, was prepared using cobalt nitrate and the sodium salt of malonic acid, according to a method reported elsewhere [10]. The chemicals used were obtained from B.D.H. and the complex was characterised by elemental analysis and by IR spectroscopy.

Thermogravimetric (TG) and differential thermal analysis (DTA) were recorded simultaneously by a DT-30 thermal analyser (Shimadzu, Japan), keeping the heating rate at 10 K min^{-1} for each run and using about 5 mg to ensure a linear heating of the sample.

Samples sealed in glass ampoules were irradiated at room temperature with ^{60}Co rays at different doses between 1.1 and 20.0 Mrad.

RESULTS AND DISCUSSION

Figure 1 shows DTA and TG curves for $Na_2[Co(C_3H_2O_4)_2] \cdot 2H_2O$. The DTA curve shows two endothermic peaks at 480 and 560 K followed by one exothermic at 610 K. The TG curve shows mass losses at 480 and 610 K but no change in weight could be observed at the endothermic peak appearing at 560 K. This peak is attributed to melting the compound [8]. The complex undergoes a dissociation in two steps (dehydration and decomposition) leading to a residual weight corresponding to CoO and Na_2CO_3 as confirmed by X-ray diffraction. The weight loss at the end of the first step (dehydration at 480 K) was 10.4% and at the end of the second step (decomposition) was 58.5% which can be easily explained by the following scheme

$$Na_2[Co(C_3H_2O_4)_2] \cdot 2H_2O \rightarrow Na_2[Co(C_3H_2O_4)_2] \quad (1)$$

$$Na_2[Co(C_3H_2O_4)_2] \rightarrow Na_2Co_3 + CoO \quad (2)$$

The kinetics for the dehydration and decomposition reactions were determined under isothermal conditions. The α–t curves for the isothermal decomposition at temperatures within the dissociation steps are shown in Fig. 2. The kinetic parameters were determined on the basis of the kinetic relation

$$d\alpha/dt = k(T)f(\alpha) \quad (3)$$

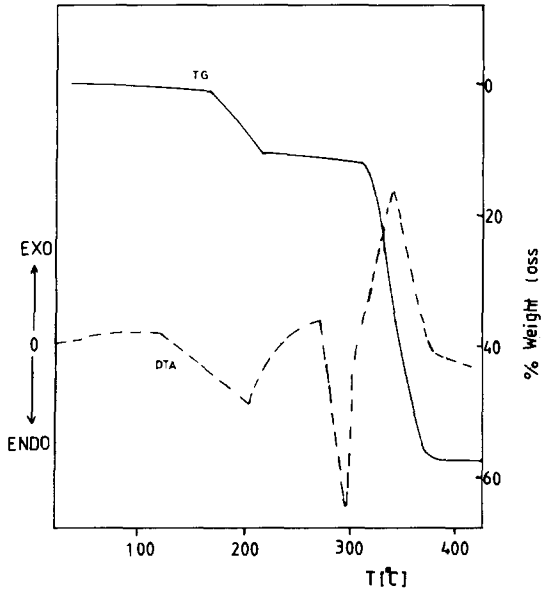

Fig. 1. DTA (— — —) and TG (———) curves for $Na_2[Co(C_3H_2O_4)_2] \cdot 2H_2O$.

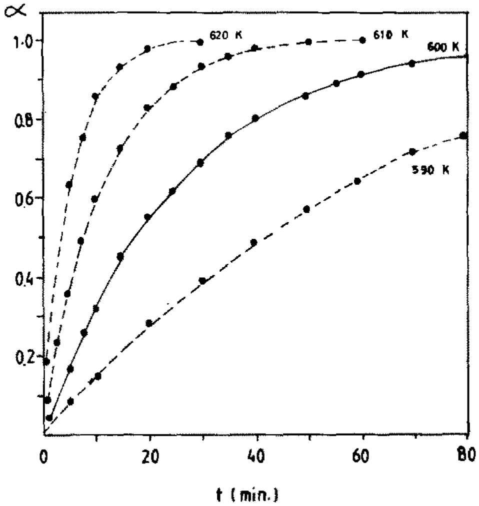

Fig. 2. Plot of α vs. t at different temperatures for the decomposition of $Na_2[Co(C_3H_2O_4)]$.

where α is the decomposed fraction and $k(T)$ is the specific rate constant of the reaction. Integrating eqn. (3) and replacing $d\alpha/f(\alpha)$ by the function $g(\alpha)$, the following equation is obtained

$$\int_0^1 g(\alpha) = \int_{T_0}^{T_1} k(T)\,dt \tag{4}$$

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–Brounshtein function)
$\ln[\alpha/(1-\alpha)]$	A_u	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

TABLE 2

The correlation coefficient *r* and standard deviation *s* for the least-squares fitting of $g(\alpha)$ vs. *t* for various kinetic models for the isothermal dehydration and decomposition of γ-irradiated and unirradiated $Na_2[Co(C_3H_2O_4)_2]\cdot 2H_2O$

T (K)	Dose (Mrad)		D_1	D_2	D_3	D_4	R_1	R_2	R_3	F_1	A_2	A_3	A_u
480	Dehydration												
	Unirradiated	*r*	0.9691	0.9532	0.9691	0.9623	0.9876	0.9976	0.9999	0.9892	0.9990	0.9911	0.9781
		s	1.0	3.4	2.2	1.0	3.5	1.4	0.3	1.2	0.9	0.7	21
	1.1	*r*	0.9712	0.9645	0.9694	0.9783	0.9900	0.9991	0.9961	0.9916	0.9864	0.9986	0.9641
		s	5.1	2.8	6.3	7.1	2.8	0.6	0.7	0.9	1.1	0.8	18
	10.3	*r*	0.9810	0.9645	0.9712	0.9726	0.9899	0.9989	0.9972	0.9876	0.9812	0.9917	0.9641
		s	1.2	2.8	3.1	4.2	6.1	0.4	0.5	1.6	0.9	0.9	13
	20.0	*r*	0.9790	0.9617	0.9813	0.9814	0.9865	0.9976	0.9981	0.9881	0.9713	0.9918	0.9643
		s	3.4	2.5	1.7	2.1	4.5	0.7	0.5	0.8	0.7	0.6	32
610	Decomposition												
	Unirradiated	*r*	0.9651	0.9812	0.9757	0.9799	0.9849	0.9813	0.9841	0.9994	0.9645	0.9820	0.9651
		s	4.2	2.1	3.1	1.9	1.7	1.0	0.9	0.8	0.9	0.7	21
	1.1	*r*	0.9713	0.9725	0.9773	0.9643	0.9943	0.9861	0.9871	0.9981	0.9618	0.9861	0.9661
		s	4.2	2.3	1.9	2.5	2.5	0.6	0.3	2.5	0.8	0.8	16
	10.3	*r*	0.9720	0.9864	0.9810	0.9721	0.9889	0.9813	0.9841	0.9989	0.9823	0.9843	0.9721
		s	1.7	0.6	0.3	1.4	0.8	1.2	0.4	3.7	0.9	0.6	9
	20.0	*r*	0.9790	0.9813	0.9888	0.9846	0.9876	0.9871	0.9861	0.9990	0.9710	0.9857	0.9774
		s	2.3	1.8	2.4	3.1	1.9	1.1	0.5	5.0	1.0	0.6	7.2

TABLE 3

Effect of γ-irradiation on the kinetic parameters of the isothermal decomposition of $Na_2[Co(C_3H_2O_4)_2]\cdot 2H_2O$

Dose (Mrad)	R_2 function		R_3 function		A_3 function		F_1 function	
	log *A* (s^{-1})	*E* (kJ mol^{-1})	log *A* (s^{-1})	*E* (kJ mol^{-1})	log *A* (s^{-1})	*E* (kJ mol^{-1})	log *A* (s^{-1})	*E* (kJ mol^{-1})
Dehydration								
Unirradiated	8.9	110.1	8.3	105.2	9.9	119.0	–	–
1.1	8.5	105.1	7.8	100.4	9.2	112.1	–	–
10.3	8.1	99.8	7.5	95.3	8.6	105.6	–	–
20.0	7.8	95.4	7.3	92.1	8.2	98.1	–	–
Decomposition								
Unirradiated	–	–	–	–	–	–	18.7	250.4
1.1	–	–	–	–	–	–	18.6	250.2
10.3	–	–	–	–	–	–	18.8	250.6
20.0	–	–	–	–	–	–	18.6	249.9

For isothermal analysis eqn. (4) is simply

$$g(\alpha) = kt \tag{5}$$

The different kinetic model functions $g(\alpha)$ listed in Table 1 were examined for the dehydration and decomposition stages by conventional isothermal analysis. An appropriate $g(\alpha)$ for the isothermal reaction could be selected by plotting various $g(\alpha)$ against time *t*. Correlation coefficients *r* and standard deviations *s* were used as a measure of the linearity for the least-squares fitting in various $g(\alpha)$ versus *t* plots. The comparison of fits given in Table 2 shows that the best fit of data for the dehydration reaction is obtained by phase-boundary mechanisms (R_2 and R_3 functions) but that the random nucleation model (A_3) is also very close. On the other hand, the fitting data of the decomposition reaction shows that the decomposition is controlled by a first-order mechanism (F_1). This is attributed to melting the complex before its decomposition (homogeneous dissociation). The kinetic parameters E_a and log *A* for each step are given in Table 3.

γ-irradiation lowers the peak temperatures (*T*) at which both the dehydration and the melting of the complex occurs. More reduction in *T* is observed with increasing the radiation dose. For a sample irradiated with 20 Mrad the dehydration step was found to be lowered by 12 K, while the melting temperature was lowered by only 5 K. The kinetic parameters of the dehydration and decomposition of the irradiated complex are given in Table 3, from which it can be seen that the irradiation affects only the kinetic data of the dehydration step. The activation energy values of the dehydration decrease to a small extent with an increase in the radiation dose. This indicates that the same chemical processes govern the dissociation of both the unirradiated and irradiated complexes. The irradiation produces an ionization of Co^{2+} to Co^{3+} [11]. This ionization of Co^{2+} ions produces chemical damage and crystal defects in the matrix of the complex. The presence of these damaged species in the crystal will result in a steady accumulation of strain. Accordingly, the nuclei formed by irradiation grow by heating and the rate of the thermal dehydration is enhanced. Because the complex melts before it decomposes, the kinetic data of its homogeneous decomposition is not affected by irradiation damage.

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