

KINETICS OF ISOTHERMAL DECOMPOSITION OF γ -IRRADIATED AND UNIRRADIATED Co(II) SUCCINATO COMPLEX

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A kinetic study of the dehydration and decomposition of γ -irradiated and unirradiated $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_4)_2] \cdot 7\text{H}_2\text{O}$ has been studied using isothermal and dynamic thermogravimetric methods. The thermal dehydration occurs in one step regulated by a random nucleation model (A_3), while the decomposition of anhydrous salt is controlled by a phase boundary controlled model (R_3). The kinetic parameters obtained at three heating rates are in good agreement; however, the values of the kinetic parameters estimated isothermally are slightly different from those estimated dynamically. Irradiation enhanced both the dehydration and the decomposition reactions but did not modify their mechanisms. The activation energy decreases as the irradiation dose increases.

Keywords: Co(II) succinate complex, isothermal decomposition, kinetics

Introduction

Progress in an increasing number of areas of technology and hence industry is being recognized as directly related to understanding the factors influencing reactivity of solids and how they react. The thermal dissociation of solids can be considered as a separate group. In such reactions, solids are transformed and gaseous and solid substances result from them.

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The thermal dissociation depends on many internal and external factors [1, 2]. The most important internal factors are reaction products, lattice defects, mobility of crystal lattice elements, and others. However, the most important external factors are: temperature, pressure, doping, reaction time, and others. The defects, which may be produced in such type of complexes by the use of high radiation dose, may change the rate of thermal decomposition and the physical properties of the product formed during the dissociation process.

Literature references concerning the thermal stability of transition metal succinato complexes are very scanty [3, 4]. Previous study [3] on the thermal stability of $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_4)_2] \cdot 7\text{H}_2\text{O}$ has been reported, but no details on the kinetics or mechanism of its thermal decomposition were included. It was also our aim, therefore, to examine the effect of defects induced by γ -irradiation on the decomposition mechanism and on the kinetic parameters of $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_4)_2] \cdot 7\text{H}_2\text{O}$ calculated by isothermal and dynamic thermogravimetric techniques.

Experimental

The synthesis of cobalt succinato complex, $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_4)_2] \cdot 7\text{H}_2\text{O}$ was prepared in aqueous solution by the reaction between $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, succinic acid ($\text{H}_2\text{C}_4\text{H}_4\text{O}_4$) and disodium succinate $\text{Na}_2\text{C}_2\text{H}_4\text{O}_4 \cdot 6\text{H}_2\text{O}$. The solution obtained was concentrated, filtered off and allowed to crystallize at room temperature. The product was purified by successive recrystallization. The complex obtained was characterized by elemental analysis and IR spectroscopy. The percentage of cobalt ion was confirmed by atomic absorption spectrophotometry.

Thermogravimetric (TG) and differential thermal analysis (DTA) were recorded simultaneously by a DT-30 thermal analyser (Shimadzu, Japan) using samples of Ca of 7 mg to ensure linear heating.

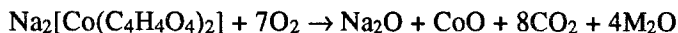
Samples sealed in glass ampoules were irradiated at room temperature with ^{60}Co -cell. The exposure rate of $10 \text{ rad} \cdot \text{s}^{-1}$ was applied at room temperature. The irradiation dose were 103, 300 and 601 KGy.

Results and discussion

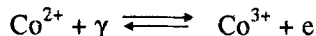
The DTA and TG curves for the unirradiated cobalt succinato complex $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_4)_2] \cdot 7\text{H}_2\text{O}$ are presented in Fig. 1. The DTA curve shows one endothermic peak at 405 K followed by two exothermic peaks at 560 and 640 K.

The TG curve shows mass losses at 405 and 640 K amount to about 27.2% and 70.4% corresponding to the dehydration process of $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_4)_2] \cdot 7\text{H}_2\text{O}$ and

decomposition of unhydrated complex according to the following reaction, respectively.



The residual weight corresponding to Na_2O and CoO lines is confirmed by X-ray diffraction. The TG curve shows no changes in the weight at the exothermic peak appearing at 560 K. Therefore, this peak can be attributed to a phase change of $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_4)_2]$ [3]. Both dehydration and decomposition steps of irradiated samples started at lower temperatures than did that of unirradiated one, and further reduction in decomposition temperature was observed with increasing radiation dose. At a heating rate of $5 \text{ deg}\cdot\text{min}^{-1}$ the inception temperatures of each of the dehydration and decomposition steps was found to be lowered by 2 K and 25 K respectively for samples irradiated with 602 KGy. This behaviour was also observed for other metal organic compounds [5–7]. The ionizing radiation creates chemical damages and crystal defects in the crystal lattice. Severe disruption of the lattice is possible with the formation of a large number of vacancies due to a formation of Co^{3+} as a result of the following interaction:



The vacancy migration and aggregation in a solid are known to lead to the formation of dislocation loops. These dislocations produce a strain in the crystal lattice of the complex which causes an acceleration of the decomposition reaction.

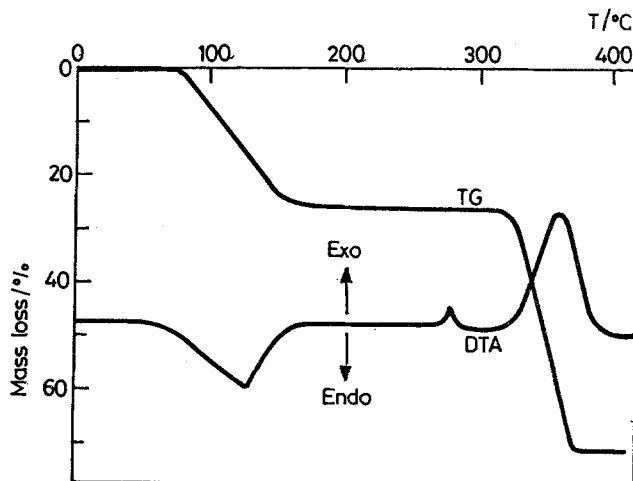


Fig. 1 DTA and TG curves for $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_4)_2]\cdot 7\text{H}_2\text{O}$

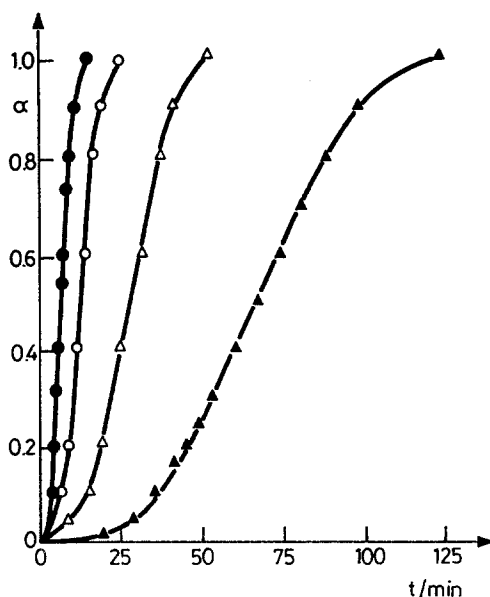


Fig. 2 Plot of α vs. t at 410 K for the isothermal dehydration of unirradiated and irradiated $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_4)_2] \cdot 7\text{H}_2\text{O}$;
 \blacktriangle — \blacktriangle : unirradiated, \triangle — \triangle : 103 KGy, \circ — \circ : 300 KGy and \bullet — \bullet : 601 KGy

The kinetics for the dehydration and decomposition reactions were studied by thermogravimetric analysis using both the isothermal and dynamic methods. The $\alpha - t$ curves for both isothermal dehydration and decomposition at temperatures within the dissociation steps are shown in Figs 2 and 3. Under isothermal conditions, the rate constant, K is independent of reaction time and so $g(\alpha) = Kt$, where

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)
$\ln[\alpha/(1 - \alpha)]$	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

α is the decomposition fraction of the complex at time t . The isothermal α/t data were analysed by linear regression analysis according to various kinetic model functions $g(\alpha)$ [8] listed in Table 1. The results showed that the random nucleation model (A_3) is the model which best coincides with our dehydration data. On the other hand, the phase boundary controlled (R_3) reaction is the model which best coincides with the decomposition data.

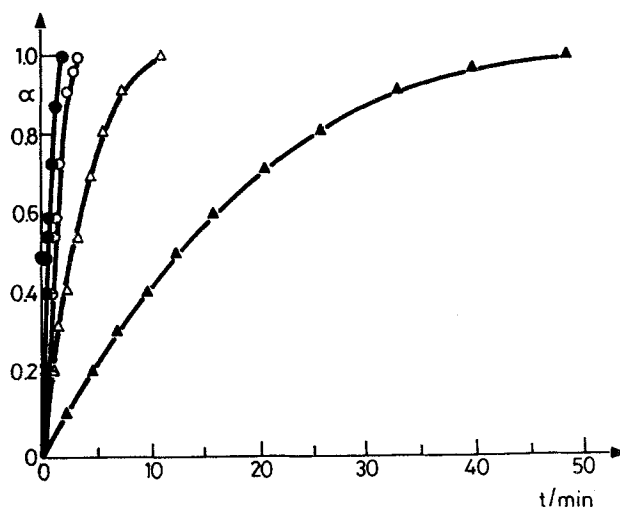


Fig. 3 Plot of α vs. t at 645 K for the isothermal decomposition of unirradiated and irradiated $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_4)_2] \cdot 7\text{H}_2\text{O}$;
 ▲—▲: unirradiated, Δ — Δ : 103 KGy, o—o: 300 KGy and ●—●: 601 KGy

All kinetic parameters of dehydration and decomposition process for irradiated and non-irradiated samples are listed in Table 2. It is shown that the irradiation affects the kinetic data for each of the dehydration and decomposition steps. The activation energy values decrease in each step, with an increase in the radiation dose. However, the lowering in the E -values is not large. It indicates that the irradiation process has not affected the mechanism governing the decomposition reaction.

The kinetics of each of the dehydration and decomposition steps of the irradiated and unirradiated $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_4)_2] \cdot 7\text{H}_2\text{O}$ complex were also studied using a thermogravimetric dynamic method. The kinetic data were evaluated in this method according to Coats and Redfern [9] using the A_3 -model for the dehydration and R_3 -model for the decomposition process. These models showed the best correlation coefficients in the isothermal studies. The kinetic data obtained are also given in Table 2, from which it can be seen a decrease in the activation energy values, E , with the increase in the heating rate. However the results of the two methods showed a slight difference at a lower heating rate.

Table 2 Effect of γ -irradiation on the kinetic parameters of the isothermal and dynamic decomposition of $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_4)_2] \cdot 7\text{H}_2\text{O}$

Process	Method of Analysis	Correlation factor	Irrad. Dose / KGy	Heating rate / deg·min ⁻¹	$E / \text{kJ} \cdot \text{mole}^{-1}$	$\log A / \text{s}^{-1}$		
Dehydration	Isothermal	0.9981	—	—	86.4	7.6		
		0.9976	103		84.5	7.5		
		0.9978	300		81.1	7.4		
		0.9984	601		78.4	7.3		
	Dynamic	—	—	—	5	81.2	7.4	
				103		76.7	7.2	
				300		74.5	7.1	
				601		72.1	7.0	
		—	—	—	—	10	80.5	7.4
					105		75.9	7.2
					300		73.1	7.1
					601		69.6	7.0
		—	—	—	—	20	77.2	7.3
					103		74.7	7.1
					300		72.4	7.1
					601		66.6	6.9
Decomposition	Isothermal	0.9979	—	—	315.2	22.5		
		0.9984	103		304.6	21.8		
		0.9982	300		296.1	21.6		
		0.9983	600		287.9	21.2		
	Dynamic	—	—	—	5	300.6	22.0	
				103		291.4	21.6	
				300		286.0	21.3	
				601		274.0	20.8	
		—	—	—	—	10	290.2	21.7
					100		283.1	21.2
					300		272.4	21.0
					601		272.1	20.7
		—	—	—	—	20	281.4	21.1
					103		271.6	20.6
					300		266.5	20.2
					601		261.3	20.0

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Zusammenfassung — Unter Anwendung von isothermen und dynamischen thermogravimetrischen Methoden wurde eine kinetische Untersuchung der Dehydratation und der Zersetzung von γ -bestrahltem und unbestrahltem $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_4)_2] \cdot 7\text{H}_2\text{O}$ durchgeführt. Die thermische Dehydratation erfolgt in einem Schritt, bestimmt durch ein Random-Keimbildungsmodell (A_3), während die Zersetzung der wasserfreien Salze durch ein phasengrenzenkontrolliertes Modell bestimmt wird (R_3). Die bei drei Aufheizgeschwindigkeiten erhaltenen kinetischen Parameter stehen in guter Übereinstimmung; jedoch weichen die isotherm geschätzten kinetischen Parameter etwas von den dynamisch ermittelten ab. Bestrahlung mehrt sowohl die Dehydratations- als auch die Zersetzungsreaktionen, beläßt deren Mechanismus jedoch unverändert. Die Aktivierungsenergie sinkt mit zunehmender Strahlungsdosis.