ELSEVIER

Thermochimica Acta 274 (1996) 165–172

thermochimica
acta

Gamma irradiation effects on the kinetics of the non-isothermal decomposition of manganese acetate tetrahydrate

El-H.M. Diefallah[a,*], A.Y. Obaid[a], A.H. Qusti[a], A.A. El-Bellihi[b], M. Abdel Wahab[b], M.M. Moustafa[b]

[a] *Faculty of Science, King Abdulaziz University, P.O. Box 9028, Jeddah, Saudi Arabia*
[b] *Faculty of Science, Zagazig University, Benha-Branch, Benha, Egypt*

Received 28 March 1995; accepted 5 August 1995

Abstract

The thermal dehydration and decomposition of ^{60}Co-gamma-irradiated and non-irradiated crystals of manganese acetate tetrahydrate were studied using dynamic thermogravimetric techniques. The effects of radiation on the kinetics of the thermal decomposition reactions were studied up to a total dose of about 700 kGy. A computer program has been used for kinetic evaluation of non-isothermal thermogravimetric data according to a composite integral method. Kinetic analyses of dynamic TG curves were discussed in view of the composite method in comparison with the methods due to Coats and Redfern and to Ozawa. The activation parameters of the decomposition reactions for non-irradiated and gamma-irradiated crystals were calculated and the results of the different methods of data analysis were compared and discussed.

Keywords: Decomposition; DTA-TG; Gamma irradiation; Kinetics; Manganese acetate tetrahydrate; Non-isothermal

1. Introduction

High-energy radiation has been used to introduce changes into solids and these defects may influence various manifestations of reactivity [1]. The influence of radiation on the reactivity of solids has been examined by several investigators. In the

---

[*] Corresponding author.

SSDI 0040-6031(95)02695-9

reduction of hematite to iron, gamma-irradiation of samples causes a decrease in activation energy, frequency factor and half-life time of the reaction which is remarkable at higher temperatures and higher doses [2]. ESR studies of radiation effects on silver oxalate [3] showed that radiation caused an increased delocalization of electrons and increased electron concentrations at structural defects.

Several heterogeneous solid-state reaction models and computational techniques were used to discuss the kinetics of isothermal and non-isothermal data [4]. The composite method of the integral analysis of dynamic data was discussed, and the method has been used for comparing results obtained on samples studied under similar experimental processing parameters [2, 5]. In a previous paper [5], we studied the thermal decomposition of manganese acetate tetrahydrate and made a critical comparison of the isothermal and various dynamic results of analysis. In the present investigation, we studied the effects of ^{60}Co-gamma radiation on the kinetic and activation parameters of the non-isothermal dehydration and decomposition of manganese acetate tetrahydrate using different integral methods of kinetic analysis of data.

2. Experimental

The manganese acetate tetrahydrate samples were BDH, reagent grade, used without further purification. The starting material was sieved and samples of particle size less than 117 μm were used for simultaneous DTA-TG experiments using a Shimadzu DT 30 thermal analyser. The experiments were performed at heating rates of 2, 5, 10, 15, 20 and 30°C min^{-1} under nitrogen atmosphere at a flow rate of 3.0 l h^{-1}.

For irradiation, samples were placed in glass-stoppered pyrex tubes and irradiated in air using a ^{60}Co-Gamma cell 220 (Atomic Energy of Canada, Ltd., Commercial Products Div., Ottawa, Canada). Samples were exposed to successive increasing doses at a dosimeter rate of 1.2 ± 0.04 kGy h^{-1}.

3. Results and discussion

The thermal behaviour of manganese acetate tetrahydrate and the kinetics of the non-irradiated samples were previously described [5]. The kinetics of the non-isothermal decomposition of the gamma-irradiated samples of manganese acetate tetrahydrate is considered here in view of three integral methods: the Ozawa method [6], the Coats–Redfern method [7] and the Diefallah composite method [5], based either on the modified Coats–Redfern equation [8] (composite method I) or on Doyle's equation [9] (composite method II). Integral methods of kinetic analysis are generally preferred because they are more reliable and convenient than the differential methods [4]. In composite method I, the modified Coats–Redfern equation was rewritten in the form

$$\ln[\beta g(\alpha)/T^2] = \ln(AR/E) - E/RT$$

where $g(\alpha)$ is the kinetic model function calculated for the fraction reacted α at temperature T and heating rate β, and is given by the equation

$$g(\alpha) = (A/R)\int_0^T \exp(-E/RT)\,\mathrm{d}T$$

A is the frequency factor, and E is the energy of activation. The dependence of $\ln[\beta g(\alpha)/T^2]$, calculated for different α-values at their respective β-values, on $1/T$ must give rise to a single master straight line for the correct form of $g(\alpha)$, and hence a single activation energy and frequency factor can be readily calculated.

In composite method II, Doyle's equation has been rewritten in the form

$$\log[\beta g(\alpha)] = [\log(AE/R) - 2.315] - 0.4567\,E/RT$$

Hence, the dependence of $\log g(\alpha)\beta$, calculated for the different α-values at their respective β-values on $1/T$ must again give rise to a single master straight line for the correct form of $g(\alpha)$. Fig. 1 shows the flow-chart for a computer program used for the kinetic analysis of non-isothermal thermogravimetric data according to the two composite methods using the available kinetic model $g(\alpha)$ functions [4, 5]. The data can be fed by hand or from a data file and the results can be printed out, plotted and saved. The results of the calculation allow us to choose the kinetic mechanism which best fits the data and gives the highest correlation coefficient and the lowest standard deviation. The program also calculates the activation energy E and the frequency factor A from the slope and intercept of the linear fit line.

Analyses of dynamic data for the dehydration and decomposition of the irradiated samples of manganese acetate tetrahydrate have shown that the kinetics of the reactions are best described by the two- and three-dimensional phase boundary and random nucleation models. This conclusion agrees with the results obtained for the isothermal analysis of the kinetic data of decomposition of non-irradiated samples [5]. Figs. 2 and 3 show the results of the kinetic data analysis for the decomposition reaction calculated using the two-dimensional phase-boundary R_2 model according to composite methods I and II, respectively. Analysis of the dynamic data was also carried out using the Ozawa and Coats–Redfern methods, and the results were compared with those obtained using the composite method of analysis. The results of the different methods are shown in Table 1 for samples irradiated up to a dose of 690 kGy. The two composite methods of data analysis gave identical results for the activation parameters which are in good agreement with the values calculated by the Coats–Redfern method. However, these results do not show agreement with values calculated by the Ozawa method which is possibly due to the neglect in the Ozawa method of the reaction mechanism in calculating energies of activation. The composite method allows the choice of the reaction model and a complete analysis of all non-isothermal curves obtained at the different fractions reacted and heating rates into a single curve, so that the kinetic results obtained on samples having different doses of radiation are conveniently compared.

In the present study, analysis of data according to the various heterogeneous reaction models showed that radiation did not introduce a change in reaction model or

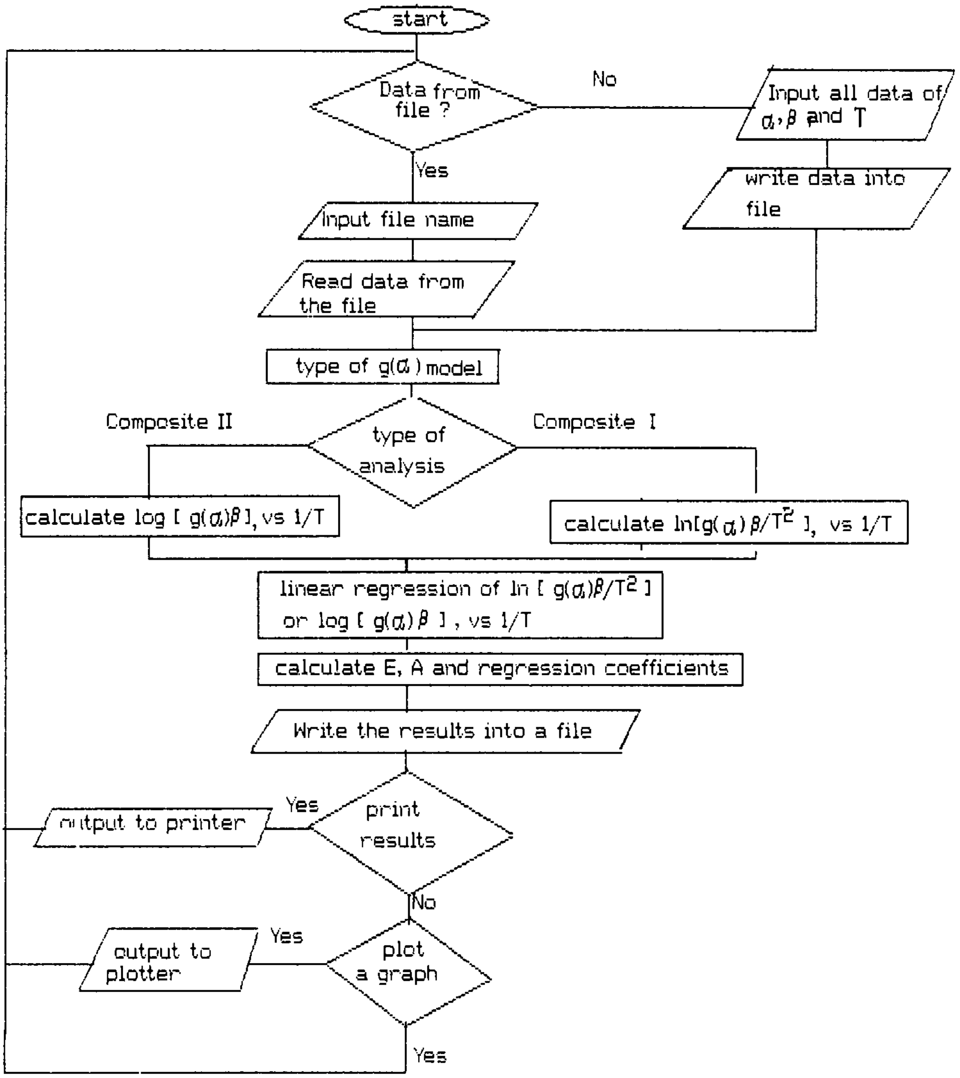

Fig. 1. Flow-chart of the computer program for the kinetic analysis of non-isothermal thermogravimetric data according to the composite method.

mechanism and the applicability of the phase-boundary-controlled models would imply that, in the dehydration step, the increase in the concentration of the decomposition nuclei and surface etch pits [10] tends to be more important than the increase in the porous character of the solid [11]. Irradiation of hydrated manganous salts produces Mn^{4+} and H_2; the hydrogen produced rapidly diffused out of the lattice [12]. In radiolysis of acetates, methane, carbon dioxide and carbon monoxide could also be formed. Moreover, radiation creates a high concentration of electron-hole pairs which

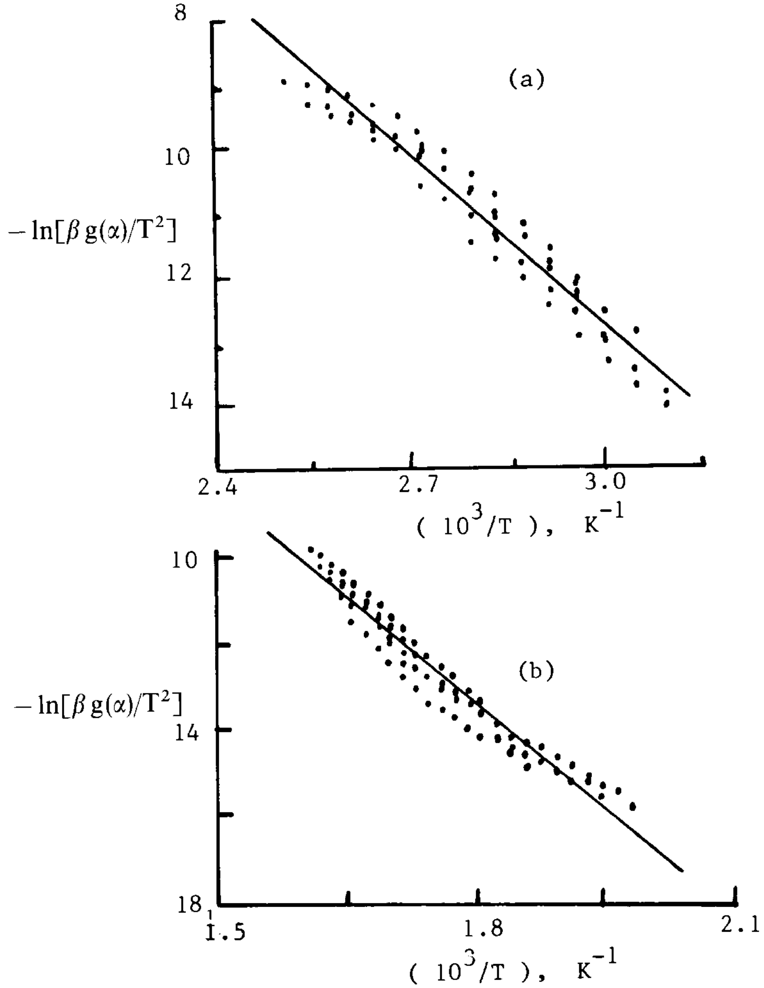

Fig. 2. Composite analysis of dynamic TG data based on the modified Coats–Redfern equation and the R_2 model: (a) dehydration step; (b) decomposition step.

may result in the formation of cationic vacancies according to the Varley mechanism and this could increase the rate of nucleation and decrease the activation energy of the reaction [13]. The calculated activation parameters (Table 1) show a decrease in the activation energy and frequency factor of the dehydration reaction and irregular variations in activation parameters for the decomposition of the anhydrous salt, with increasing radiation dose. The results show large variations which are more a function of the method of data analysis. Although, there are large deviations in the values calculated according to the Coats–Redfern and Ozawa methods, the analysis of data according to the composite method could offer a better method of comparison between a set of data obtained under similar conditions.

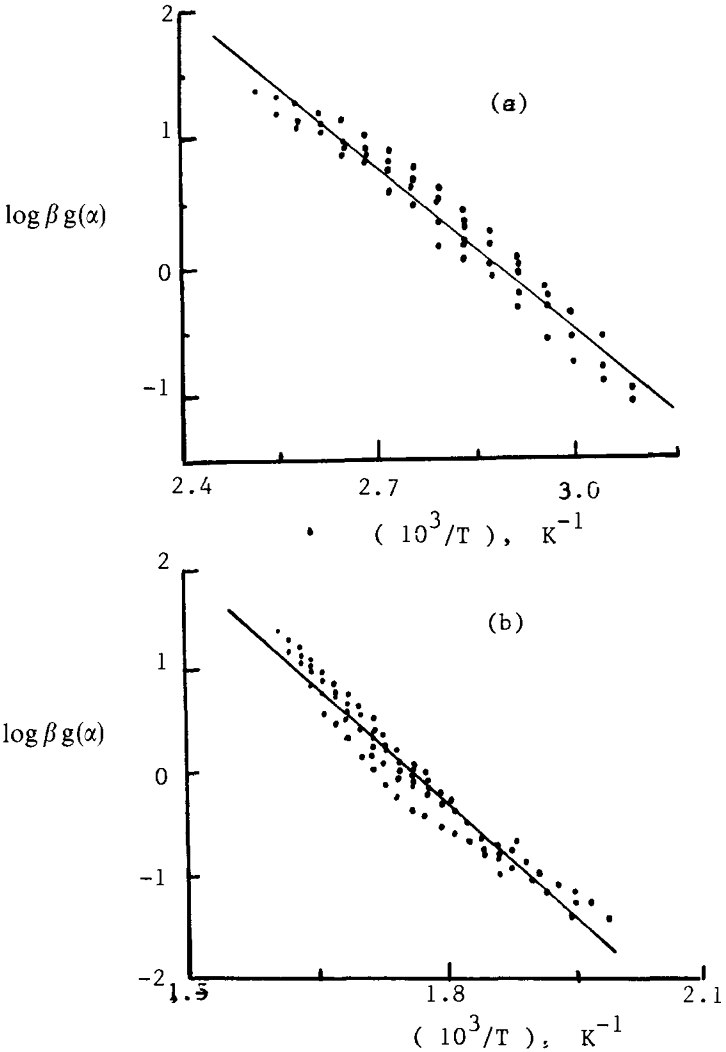

Fig. 3. Composite analysis of dynamic TG data based on Doyle's equation and the R_2 model: (a) dehydration step; (b) decomposition step.

In the decomposition step, there seems to be no definite trend of radiation effects on the E and log A parameters. At a radiation dose of about 160 kGy, there is a decrease in activation parameters which could be due to the effect of small-dose radiation annealing the defects and nucleation centres present in the original sample [14]. The increase in radiation dose then showed first a decrease in activation parameters, and then an increase for radiation doses above 270 kGy. The decrease in activation energy may be due to forming many potential nucleation centres, rather than compensating for the thermal annealing of defects, and this favours heterogeneous processes. This

Table 1
The activation parameters of irradiated manganese acetate tetrahydrate assuming the contracting area equation R_2 model with respect to different integral methods of kinetic analysis

Dose/kGy	Coats–Redfern		Ozawa method		Composite I		Composite II	
	E/kJ mol^{-1}	log A/min^{-1}	E/kJ mol^{-1}	log A/min^{-1}	E/kJ mol^{-1}	log A/min^{-1}	E/kJ mol^{-1}	log A/min^{-1}
Dehydration step[a,b]								
164	90±8	11.0±2.0	175±6	18.2±2.1	88±2	10.7±0.9	89±2	11.0±0.4
274	87±8	10.5±2.0	170±6	17.8±1.0	83±2	9.9±0.8	84±2	10.3±0.3
454	85±7	10.0±1.7	160±7	17.0±1.2	79±2	9.4±0.9	81±2	9.9±0.4
690	76±6	9.8±1.8	155±7	16.0±0.8	62±2	7.1±0.8	64±2	7.8±0.3
Decomposition step								
Non-irradiated[b]	151±62	12.3±5.8	218±81	18.7±7.1	119±5	9.6±3	114±5	9.0±3
164	234±30	20.0±3.0	300±15	31.1±2.8	228±6	19.7±1.3	226±6	19.5±0.6
274	140±19	12.0±2.2	207±11	21.8±1.4	135±3	11.1±0.7	137±3	11.4±0.3
454	201±27	17.3±2.9	303±14	31.2±1.9	193±9	16.4±1.8	192±8	16.4±0.9
690	213±31	19.9±3.1	306±13	31.6±1.8	208±9	17.8±2.0	207±9	17.7±0.9

[a] For the dehydration step of the non-irradiated sample, the decomposition proceeds in two steps, and under isothermal conditions the first step gave $E = 99 \pm 4$ kJ mol^{-1} and log A min^{-1} = 14.4 ± 0.6.

[b] Ref. [5].

may be followed at the higher doses by retardation effects due to interaction of radicals and accumulation of gaseous radiolysis products, thus resulting in activation energy increase.

References

[1] V.V. Boldyrev, M. Bulens and B. Delmon, The Control of the Reactivity of Solids, Elsevier, Amsterdam, 1979.

[2] S.N. Basahel, A.A. El-Bellihi and El-H.M. Diefallah, J. Therm. Anal., 39 (1993) 87.

[3] H. Jost, J. Jedamzik, U. Proesch and I. Ebert, Z. Chem., 25 (1985) 191.

[4] M.F. Brown, Introduction to Thermal Analysis, Chapman and Hall, London, 1988, Chapt. 13.

[5] El-H.M. Diefallah, Thermochim. Acta, 202 (1992) 1.

[6] T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.

[7] A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.

[8] J.M. Criado, Thermochim. Acta, 24 (1978) 186.

[9] C.D. Doyle, Nature, 207 (1965) 290.

[10] P.J. Herley and P.W. Levy, in J.S. Anderson, M.W. Roberts and F.S. Stone (Eds.), React. Solids, Proc. Int. Symp., 7th. edn., Chapman and Hall, London, 1972, p. 387.

[11] El-H.M. Diefallah, S.N. Basahel and A.Y. Obaid, J. Radioanal. Nucl. Chem., 109 (1987) 177.

[12] S. Huang and E.R. Johnson, ASTM Symposium, Effects of high energy radiations on inorganic substances, Seattle, Washington, October 31–November 5, 1965; ASTM Special Tech, Publ. No. 400, 1965.

[13] El-H.M. Diefallah, A.O. Baghlaf, M.S. El-Meligy and E.A. Abu El-Futooh, Radiat. Phys. Chem., 27 (1986) 123.

[14] S.N. Basahel and El-H.M. Diefallah, Can. J. Chem., 70 (1992) 888.