

Kinetic analysis of thermal decomposition reactions. Part 8. Radiation effects on the thermal decomposition of ammonium oxalate monohydrate

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(Received 11 March 1993; accepted 5 April 1993)

Abstract

The effects of gamma radiations on the kinetic parameters of the dynamic thermal decomposition–gasification reactions of ammonium oxalate monohydrate have been investigated using differential thermal analysis and thermogravimetry techniques. Kinetic analysis of the dynamic TG results are discussed in view of a composite integral method in comparison with the integral methods due to Coats and Redfern and to Ozawa. The activation parameters for the non-irradiated and irradiated samples are calculated and the results of the different methods of data analysis are compared and discussed.

INTRODUCTION

Thermal analyses methods have been used extensively for studying the kinetics of solid powder decomposition reactions. In the kinetic analysis of data it is true that the conventional isothermal method is more precise for estimating the kinetic model and parameters, but dynamic methods have advantages over it in several respects [1, 2]. Comparisons of thermal stabilities and reactivity parameters among a series of solids by means of dynamic thermal analyses should be meaningful, if the experiments and the data analysis were carried out under identical conditions.

Several studies were reported on the pyrolysis of ammonium salts of halogeno acids [3]. Kinetic, analytic, microscopic, electrical conduction of the solid and other experimental approaches gave evidence that proton transfer is the first step in both decomposition and sublimation reactions [3, 4]. Although the reaction rate could be independent of the method of measurement, it may be significantly influenced by surface impurities and

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imperfections. Ammonium oxalate monohydrate decomposes endothermically, and in a similar manner both in nitrogen and oxygen [5]. Two endothermic peaks due to dehydration and decomposition were observed. The decomposition remains endothermic in oxygen because the material is entirely gaseous and there is no active solid product surface to serve as a catalyst for oxidation reactions [5]. Studies of the decomposition of ammonium chlorate showed that the reaction is autocatalytic, accelerated by chloric acid and inhibited by ammonia [3, 6].

A large number of studies of radiation effects on decomposition reaction has been reported in the literature. The objectives of these experiments were to find out how the physicochemical properties of the substance and the kinetic and activation parameters of decomposition are affected by irradiation. Herley and Levy [7] studied the influence of radiation on the decomposition of ammonium perchlorate crystals and concluded that decomposition commenced at points of dislocations at crystal surfaces. Irradiation reduced the induction period to reaction by generation of dislocations which function as decomposition nuclei.

The present study deals with the investigation of radiation effects on the kinetics of thermal decomposition of ammonium oxalate monohydrate using dynamic thermogravimetric techniques. Kinetic analysis of the constant heating rate TG curves were made using three integral methods: the Ozawa [8] method, the Coats–Redfern method [9] and Diefallah's composite method [10, 11], which was based either on Doyle's equation [12] or on the modified Coats–Redfern equation [13]. The effect of ^{60}Co -gamma radiation on the dynamic thermal decomposition reactions is discussed in view of the three integral methods of analysis.

EXPERIMENTAL

Ammonium oxalate monohydrate (BDH, reagent grade), was used without further purification. The starting material was sieved and samples of particle size 125–150 μm were used for simultaneous DTA–TG experiments using a Shimadzu DT30 thermal analyser. Samples were placed in aluminium crucibles, 0.1 cm^3 in volume, which were loosely covered. The sample mass in the aluminium cell was kept at about 6 mg in all experiments, in order to ensure linear heating rate and accurate temperature measurements. The experiments were performed at different specified heating rates under nitrogen at a flow rate of 3.01 h^{-1} .

RESULTS AND DISCUSSION

The DTA–TG curves of ammonium oxalate monohydrate are shown in Fig. 1. The TG curve showed two steps due to dehydration and

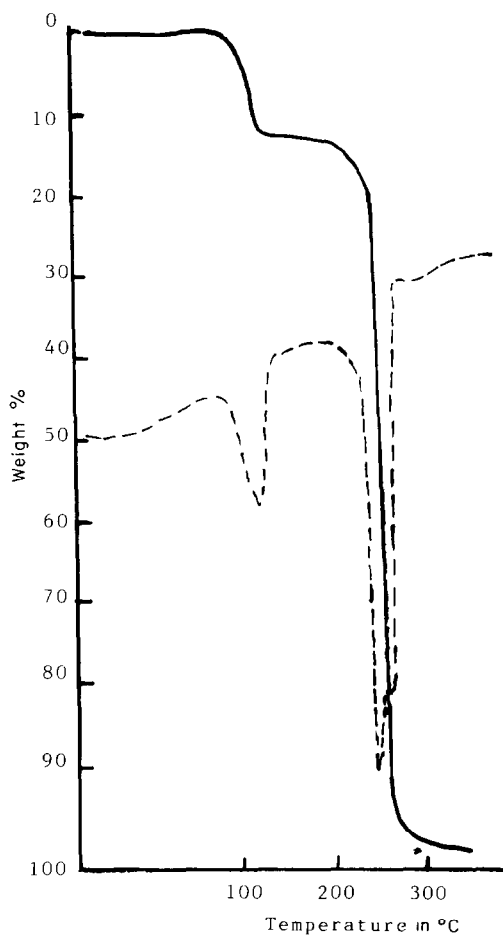


Fig. 1. DTA (---) and TG (—) curves of ammonium oxalate in nitrogen; heating rate = $15^{\circ}\text{C min}^{-1}$.

decomposition of the anhydrous salt to gaseous products. The peaks in the DTA closely correspond to the weight changes observed on the TG trace. The first relatively broad endothermic peak due to dehydration showed a minimum at about 110°C . The decomposition of the anhydrous salt starts at about 190°C and is complete at 280°C , and the DTA showed a peak temperature at about 240°C . In general, the results agree with those reported in the literature [5]. However, the DTA curve showed that the main decomposition peak has a shoulder indicating that the decomposition of the anhydrous salt proceeds in at least two stages. This two-stage decomposition indicates the presence of the carbonate intermediate. The TG curve, however, showed that the decomposition of the anhydrous salt proceeds in one step with total loss in weight and sublimation of the products.

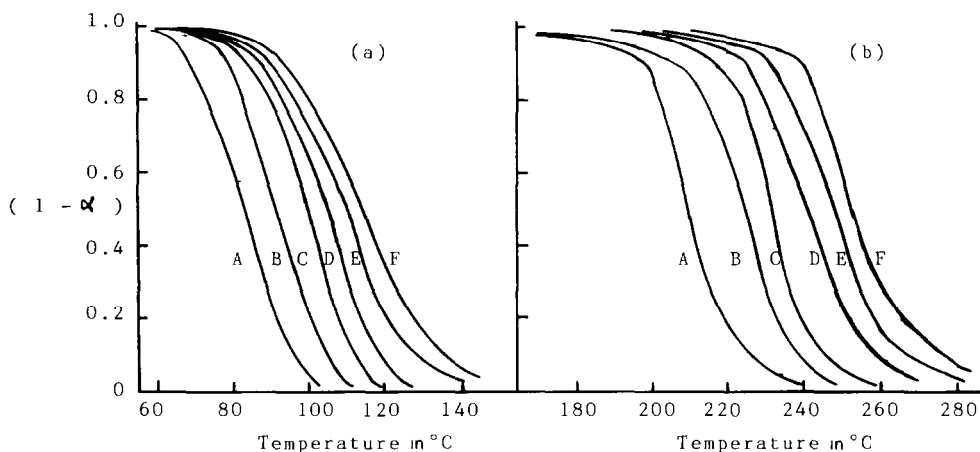


Fig. 2. Dynamic measurements for ammonium oxalate monohydrate thermal decomposition in nitrogen. Heating rate in $^{\circ}\text{C min}^{-1}$: curve A, 2; curve B, 5; curve C, 10; curve D, 15; curve E, 20 and curve F, 30. (a) Dehydration; (b) decomposition.

Figure 2 shows the results obtained from dynamic measurements for the dehydration and decomposition reactions, for samples studied in nitrogen at different heating rates of 2, 5, 10, 15, 20 and $30^{\circ}\text{C min}^{-1}$. In the kinetic analysis of the dynamic TG curves, we made a comparison of three integral methods: the Ozawa [8] method, the Coats–Redfern method [9] and Diefallah's composite method [10, 11] which was based either on Doyle's equation [12] (composite method I) or on the modified Coats–Redfern equation [13] (composite method II).

Different solid state reaction models were used to describe the kinetics of the reaction [14, 15]. Under constant heating rate conditions, the kinetic model function $g(\alpha)$ is related to the heating rate β and the activation energy E , as Doyle's equation

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp(-E/RT) dT = \frac{AE}{R\beta} P(E/RT)$$

The function $P(E/RT)$ has been approximated by the equation [12]

$$\log P(E/RT) = -2.315 - 0.4567(E/RT)$$

Using this approximation, the equation for $g(\alpha)$ (in composite method I) may be written in the form

$$\log g(\alpha)\beta = \left(\log \frac{AE}{R} - 2.315 \right) - \frac{0.4567E}{RT}$$

Assuming that the same kinetic model $g(\alpha)$ is the same at different

fractional reaction (α) and heating rate (β), then linear regression analysis between the left side of this equation for the different values of α at their respective β -values (for a specified kinetic model $g(\infty)$), and $1/T$ gives the activation energy E and the frequency factor A of the reaction. Although, it is sometimes difficult to select a single model in view of such linearity, the statistical analysis of data determines the reaction model $g(\alpha)$ which gives the best fit to the results. All kinetic computations were done using a computer with a plotter. Figures 3(a) and 4(a) show that for the three-dimensional phase boundary, the R3 model gives the best fit for both the dehydration and the decomposition of the anhydrous salt. Diffusion and other models gave less satisfactory fit of data as shown in Figs. 3(b) and 4(b) for the D4 model. This would probably indicate that the rate controlling

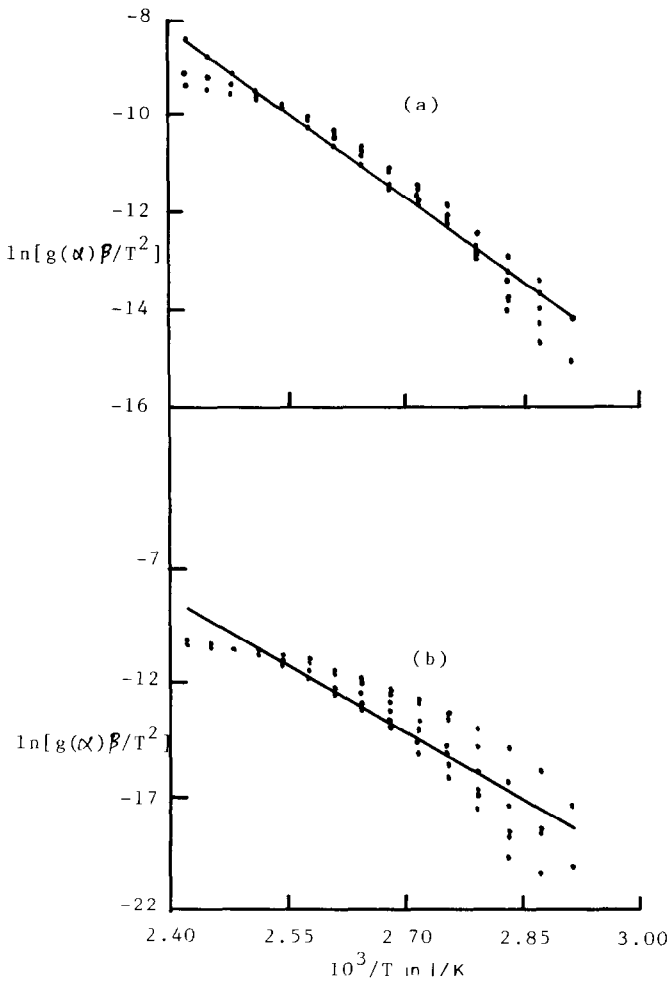


Fig. 3. Composite analysis of dynamic TG data of the dehydration of ammonium oxalate monohydrate based on Coats-Redfern equation: (a) R3, (b) D4.

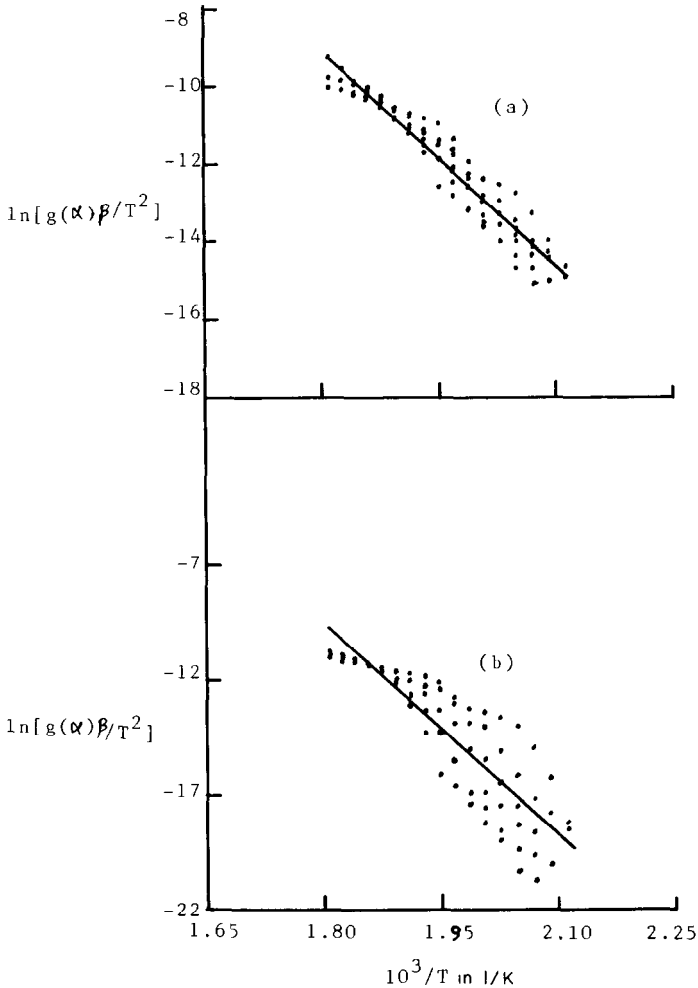


Fig. 4. Composite analysis of dynamic TG data of the decomposition of ammonium oxalate based on Coats–Redfern equation: (a) R3, (b) D4.

step is bond rupture at the reaction interface and not diffusion of the product gas.

In composite method II, use has been made of the modified Coats–Redfern equation [13]

$$\frac{g(\alpha)}{T^2} = \frac{AR}{E} e^{-(E/RT)}$$

The equation was rewritten in the form

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

Again, linear regression of $\ln[\beta g(\alpha)/T^2]$ and $1/T$ must give rise to the

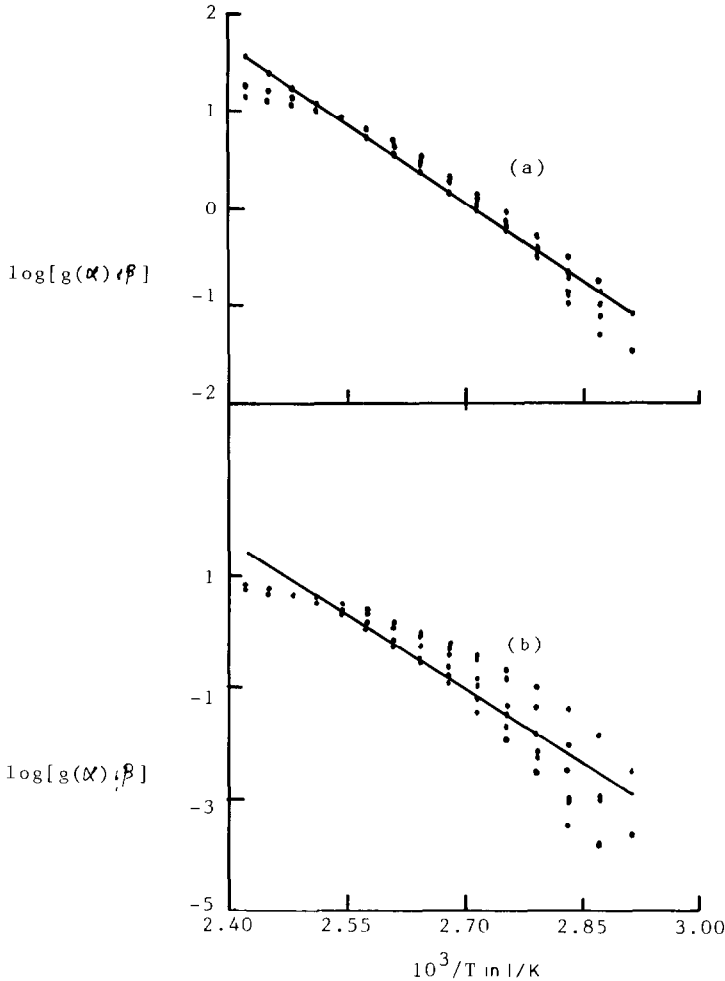


Fig. 5. Composite analysis of dynamic TG data of the dehydration of ammonium oxalate monohydrate based on Doyle's equation: (a) R3, (b) D4.

activation energy, the frequency factor and the correct form of $g(\alpha)$ for the best fit of the results. Kinetic analysis of the dehydration and decomposition stages showed that the best fit is obtained with the R3 model, as shown in Figs. 5 and 6.

The advantage of the composite analysis of dynamic thermal data is that the method involves a complete analysis of all non-isothermal curves into a single curve and allows the results obtained not only at different heating rates but also with different α values to be superimposed on this one master curve. Tables 1 and 2 show the values of the activation parameters of the dynamic dehydration and decomposition of ammonium oxalate in nitrogen assuming the contracting volume, R3 model, calculated for

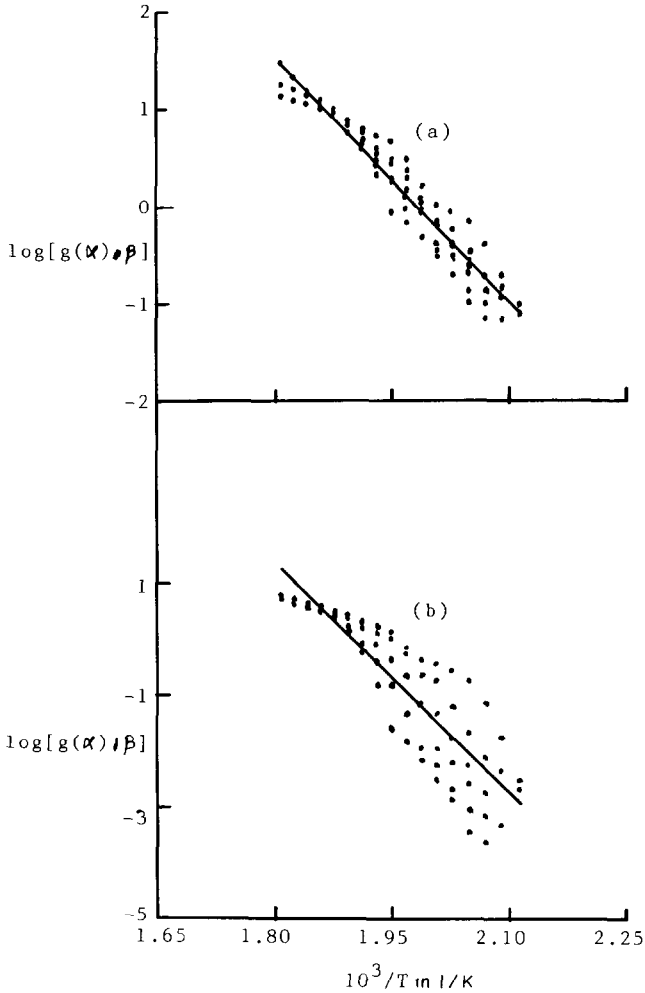


Fig. 6. Composite analysis of dynamic TG data of the decomposition of ammonium oxalate based on Doyle's equation: (a) R3 (b) D4.

non-irradiated and gamma irradiated samples, according to the integral composite methods in comparison with the values calculated according to the Coats–Redfern and Ozawa methods.

It is obvious that both composite methods of analysis give equivalent curves and identical values for the activation parameters, but the results are different from those obtained using the other methods. The values listed in Table 2 for E and $\log A$ calculated by the Coats–Redfern method reflect the well known compensation effect, in which $\log A$ increases in line with E as the experimental variables (in this case the heating rate) are changed. The values obtained from the Ozawa method demonstrate that E and $\log A$ vary with α , which is possibly due to the variation of reaction mechanism with

TABLE 1

Activation parameters of dynamic dehydration of ammonium oxalate monohydrate in nitrogen assuming the contracting volume (R3) model

Method of analysis		$E/\text{kJ mol}^{-1}$	$\log(A/\text{min}^{-1})$
Composite method I		97 ± 3	12.7 ± 0.4
Composite method II		96 ± 3	12.5 ± 1.0
Coats-Redfern method	$\beta = 2$	92.2	12.1
	$\beta = 5$	132.5	18.0
	$\beta = 10$	113.1	15.1
	$\beta = 15$	115.1	15.3
	$\beta = 20$	97.6	12.8
	$\beta = 30$	99.4	13.0
	Average	108 ± 12	14.4 ± 1.8
Ozawa method	$\alpha = 0.1$	102.4	13.7
	$\alpha = 0.2$	99.8	13.2
	$\alpha = 0.3$	93.0	12.2
	$\alpha = 0.4$	91.7	12.0
	$\alpha = 0.5$	90.8	11.9
	$\alpha = 0.6$	87.5	11.5
	$\alpha = 0.7$	86.3	11.2
	$\alpha = 0.8$	84.0	10.9
	$\alpha = 0.9$	82.9	10.7
Average	91 ± 8	11.9 ± 0.7	

TABLE 2

Activation parameters of dynamic decomposition of ammonium oxalate in nitrogen assuming the contracting volume (R3) model

Method of analysis		$E/\text{kJ mol}^{-1}$	$\log(A/\text{min}^{-1})$
Composite method I		153 ± 6	14.7 ± 0.6
Composite method II		153 ± 6	14.7 ± 1.4
Coats-Redfern method	$\beta = 2$	149.0	14.5
	$\beta = 5$	165.5	16.2
	$\beta = 10$	199.5	19.8
	$\beta = 15$	169.1	16.4
	$\beta = 20$	170.0	16.3
	$\beta = 30$	183.2	17.7
	Average	173 ± 13	16.8 ± 1.3
Ozawa method	$\alpha = 0.1$	121.1	11.2
	$\alpha = 0.2$	125.8	11.8
	$\alpha = 0.3$	126.9	12.0
	$\alpha = 0.4$	125.8	12.0
	$\alpha = 0.5$	124.3	11.9
	$\alpha = 0.6$	121.9	11.6
	$\alpha = 0.7$	117.6	11.2
	$\alpha = 0.8$	118.2	11.3
	$\alpha = 0.9$	117.9	11.1
Average	122 ± 3	11.6 ± 0.3	

TABLE 3

Gamma irradiation effects on the activation parameters of the thermal dehydration of ammonium oxalate monohydrate in nitrogen calculated according to different integral methods

Radiation dose (MGy)	Composite method I		Composite method II		Coats-Redfern method		Ozawa method	
	$E/$ 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)
Non-irradiated	97 ± 3	12.7 ± 0.4	96 ± 3	12.5 ± 1.0	108 ± 12	14.4 ± 1.8	91 ± 8	11.9 ± 0.7
0.16 ± 0.01	134 ± 3	18.2 ± 0.4	135 ± 3	18.3 ± 1.0	150 ± 19	20.5 ± 2.9	107 ± 10	14.4 ± 1.4
0.39 ± 0.02	136 ± 4	18.3 ± 0.5	137 ± 4	18.4 ± 1.2	143 ± 2	19.4 ± 0.2	128 ± 5	17.2 ± 0.8
0.82 ± 0.04	139 ± 5	18.6 ± 0.8	140 ± 6	18.7 ± 1.8	156 ± 13	20.9 ± 1.8	121 ± 4	16.2 ± 0.7

TABLE 4

Gamma irradiation effects on the activation parameters of the thermal decomposition of ammonium oxalate in nitrogen calculated according to different integral methods

Radiation dose (MGy)	Composite method I		Composite method II		Coats-Redfern method		Ozawa method	
	$E/$ 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)
Non-irradiated	153 ± 6	14.7 ± 0.6	153 ± 6	14.7 ± 1.4	173 ± 13	16.8 ± 1.3	122 ± 3	11.6 ± 0.3
0.16 ± 0.01	157 ± 3	15.2 ± 0.4	157 ± 3	15.2 ± 0.8	164 ± 27	16.0 ± 2.9	201 ± 9	19.8 ± 1.1
0.39 ± 0.02	166 ± 3	16.1 ± 0.4	166 ± 3	16.0 ± 0.8	166 ± 15	16.0 ± 1.6	209 ± 8	20.8 ± 0.9
0.82 ± 0.04	160 ± 4	15.7 ± 0.4	161 ± 4	15.7 ± 1.0	171 ± 29	16.7 ± 3.2	207 ± 14	20.6 ± 1.5

fraction reacted [10]. The composite method, however, would allow a better choice of the reaction model since it treats all the experimental data obtained at different fractions reacted (α) and heating rates (β) at one time.

For the irradiated samples, the best fit of data is again obtained with the R3 model and the composite method affords a proper way of comparison between these samples. Tables 3 and 4 list the effects of dose on the activation parameters up to a dose of about 0.8 MGy. The activation energy of dehydration, calculated for the non-irradiated sample by the different methods, indicates that the water molecules are present in the crystal as lattice water. There is a remarkable increase in the activation parameters of the dehydration reaction for the small radiation dose, but there are no variations, within experimental error, in the activation parameters of the decomposition reaction with increasing radiation dose. The increase in activation energy of dehydration must be due to the effect of ammonia, a major radiolysis product, on the reaction. Table 4 shows that for the decomposition reaction, there is agreement between the two composite methods and the Coats–Redfern method, but the Ozawa method gives much less satisfactory results. In general, the composite analysis of dynamic data allow a better method of comparison between the series of samples giving correlation between the results with less standard deviations in the calculated experimental parameters.

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