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Kinetics of Thermal Decomposition of
Nickel Dimethylglyoxime

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ABSTRACT. The thermal decomposition of nickel dimethylglyoxime has been studied in air using DTA-TG measurements. The kinetics of the thermal decomposition were studied using isothermal and nonisothermal thermogravimetric techniques. The results were discussed using various reaction interface models and different techniques of computational analysis of nonisothermal data. The activation parameters, calculated using a composite method of integral analysis of nonisothermal data, showed in addition to their independence on the heating rate and fractional reaction, better correlation and agreement with the results obtained under isothermal conditions.

KEYWORDS: Decomposition; DTA; TG; nickel dimethylglyoxime.

Introduction

Thermal analysis methods have been used extensively for studying the kinetics of solid powder thermal decomposition reactions. The kinetics of the thermal decomposition of solids are affected by experimental factor[1-2], such as heating rates, particle size, sample mass, holder design, the enthalphy of reaction upon the sample temperature and the atmosphere. In the kinetic analysis of data it is true that the conventional isothermal method is more precise for estimating the kinetic model and activation parameters, but dynamic methods have advantages over it in several respects[2-4].

Although several studies have been published on the thermal properties of metal glyoximes[5-6], no studies were performed on the kinetics of the decomposition of these compounds. In the present study, nickel dimethylglyoxime was chosen as a typical representative of these compounds to study the kinetics of the thermal decomposition using isothermal and dynamic thermogravimetric techniques. Kinetic analysis of dynamic data were made using integral methods due to Ozawa[7], Coats-Redfern[8], Mad-

husudanan *et al.*[9] and Diefallah composite method[4] and the results were compared with those obtained under isothermal conditions.

Experimental

The solid complex of nickel dimethylglyoxime was prepared by mixing a hot saturated alcoholic solution of dimethylglyoxime (0.025 M) with an ammonia solution of nickel sulphate (1.0 M ammonia and 0.010 M nickel sulphate). The mixture was stirred on a water bath for 1 hour. The complex separated out on cooling the mixture, was filtered off, washed with dry ethanol and dried in vacuo. The product was sieved and samples with particle size less than 117 μm were used for experiments.

The thermal behaviour of nickel dimethylglyoxime was investigated in air flow using Shimadzu model DT 40 Thermal Analyzer. The kinetics of the thermal decomposition of nickel dimethylglyoxime were studied using isothermal and dynamic TG techniques. In the isothermal studies the reaction temperature was varied between 250-280ºC, whereas the dynamic experiments were carried out at heating rates of 5, 10, 15 and 20 K min^{-1}. The sample weights were about 6-8 mg to ensure linear heating rates and accurate temperature measurements.

Results and Discussion

Figure (1) shows the DTA and TG curves in flowing air obtained for nickel dimethylglyoxime. The DTA curve shows an endothermic peak at about 185ºC, which corresponds to the removal of water of hydration, and an exothermic peak at about 295ºC which is attributed to the decomposition and oxidation of the anhydrous complex to form NiO. The TG curve shows two steps, the first step corresponds to the dehydration with a weight loss of about 34% (calculated 33.3%) and the second step corresponds to the decomposition of the anhydrous salt with a weight loss of 50% (49.6% calculated).

Figure (2) shows typical α-t curves for the isothermal decomposition of nickel dimethylglyoxime. The kinetic analysis of the decomposition were studied with reference to different models of heterogeneous solid state reactions[10,11]. Under isothermal conditions, the rate constant, k, is independent of reaction time and so $g(\alpha) = kt$. A plot of $g(\alpha)$ versus time t should give a straight line if the correct form of $g(\alpha)$ is used. Table (1) lists some of the important kinetic equations given in the literature[10,11]. The function $g(\alpha)$ depends on the mechanism controlling the reaction and on the size and shape of the reacting particles. The isothermal data of the fraction decomposed versus time were analyzed by linear regression analysis according to various kinetic equation using a computer program. The composition of fit to the various models was made for α values in the range of $0.05 < \alpha < 0.95$ and the results showed that the best fit of data is obtained for random nucleation (A_3) and first order reaction (F_1) models, which gave lowest standard deviation and highest correlation coefficient. The phase boundary and diffusion models gave a less satisfactory fit. The activation parameters were calculated on the basis of the random nucleation, Eroffeev equation (A_3 model) and the results are shown in Table (2).
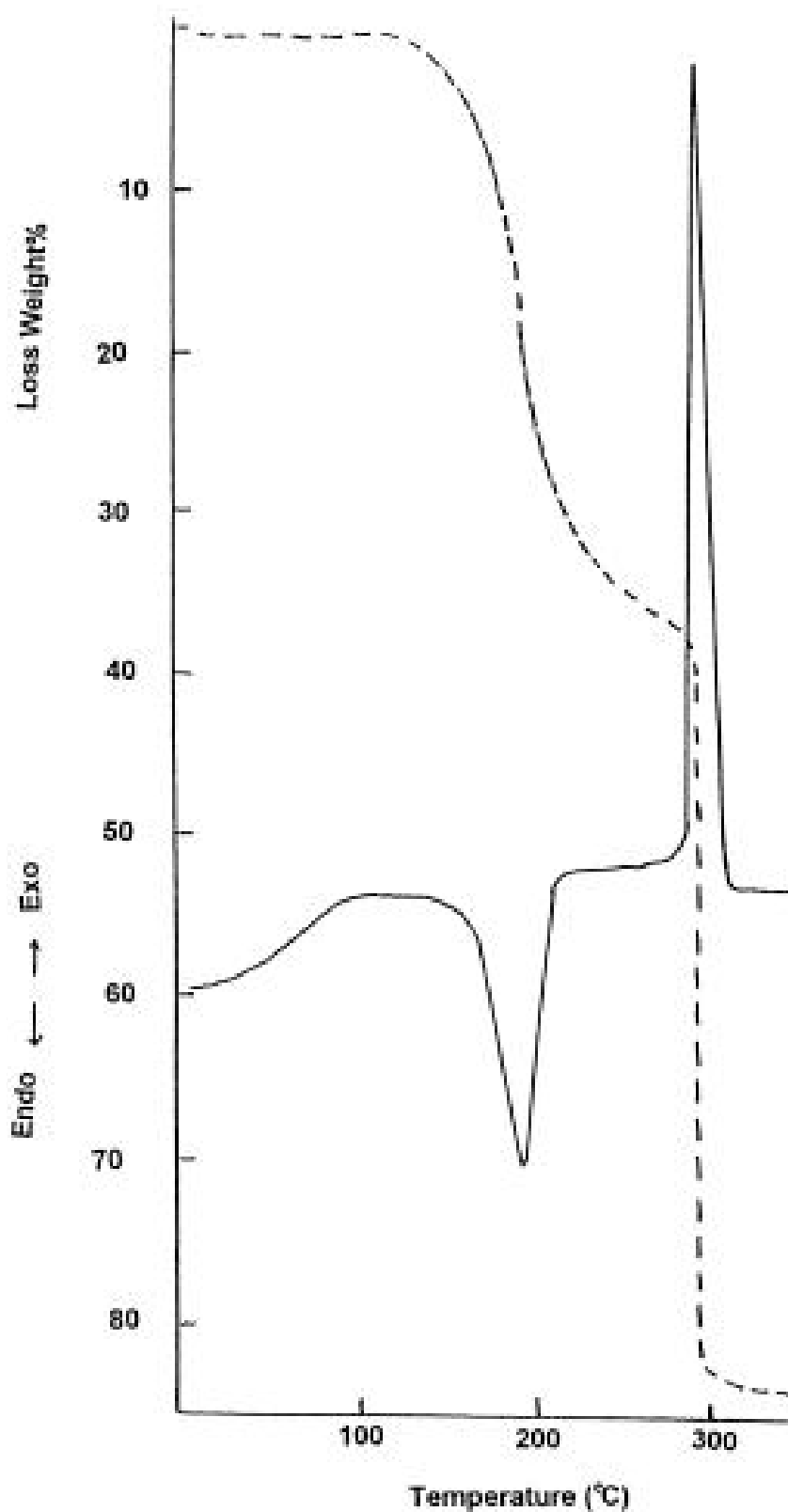
FIG. 1. DTA (––––––) and TG (- - - - -) curves of nickel dimethylglyoxime in air heating rate 10 deg/min.
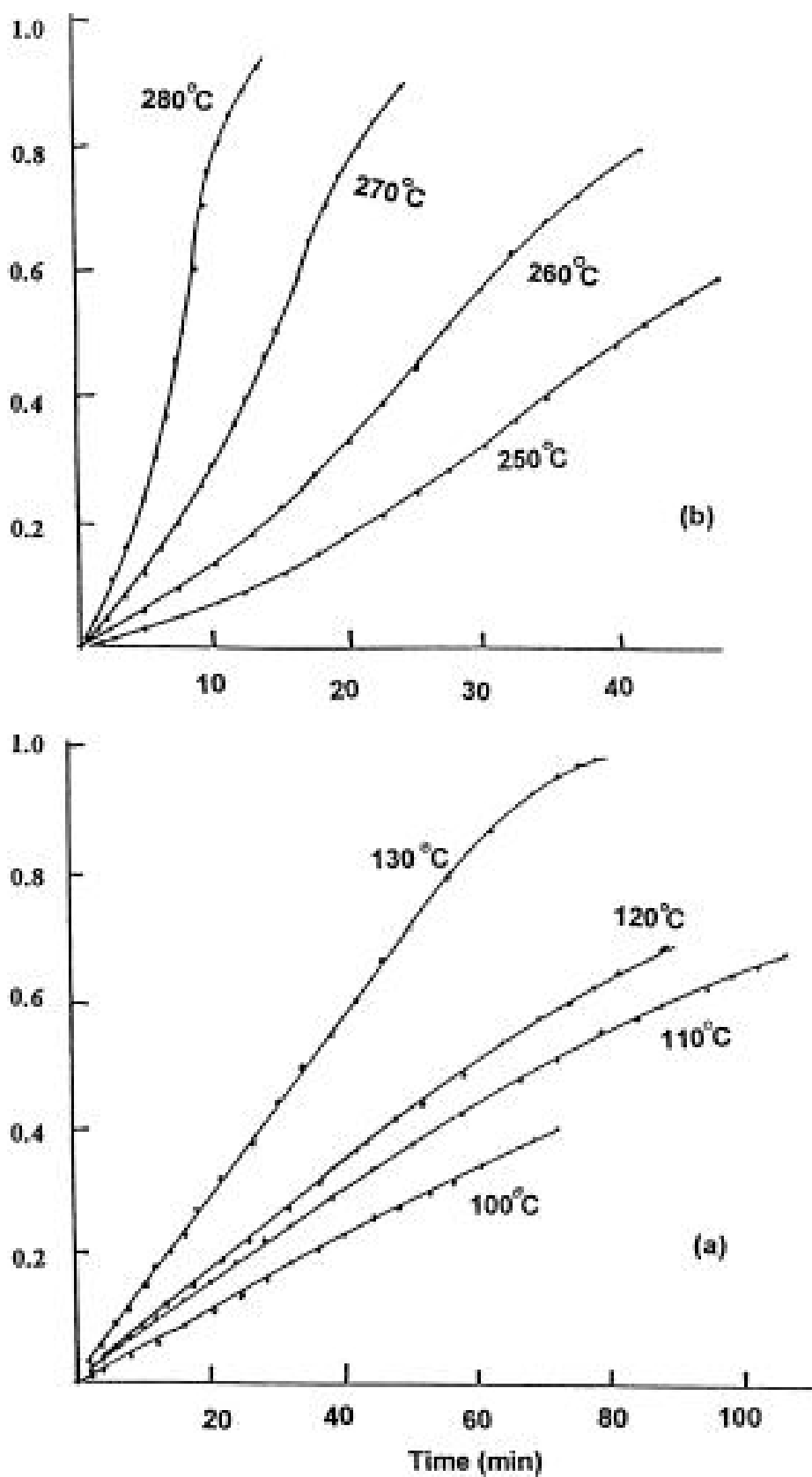
FIG. 2. α/t curves for isothermal decomposition of nickel dimethylglyoxime (a) dehydration and (b) decomposition.

TABLE 1. Some kinetic equations examined in this work.

Reaction model	$g(\alpha)$	Function symbol
One-dimensional diffusion	α^2	D_1
Two-dimensional diffusion	$\alpha + (1 - \alpha) \ln (1 - \alpha)$	D_2
Jander equation, three-dimensional diffusion	$\{1 - (1 - \alpha)^{1/3}\}^2$	D_3
Ginstling-Broundshtein equation, three-dimensional diffusion	$(1 - 2/3 \alpha) - (1 - \alpha)^{2/3}$	D_4
Two-dimensional phase boundary reaction	$\{1 - (1 - \alpha)^{1/2}\}$	R_2
Three-dimensional phase boundary reaction	$\{1 - (1 - \alpha)^{1/3}\}$	R_3
First-order kinetics	$\{- \ln (1 - \alpha)\}$	F_1
Random nucleation: Avrami equation	$\{- \ln (1 - \alpha)\}^{1/2}$	A_2
Random nucleation: Erofeev equation	$\{- \ln (1 - \alpha)\}^{1/3}$	A_3

TABLE 2. The activation parameters of the thermal decomposition of nickel dimethylglycoxime according to random nucleation (A_3 model).

Step of decomposition kinetic method of analysis			Decomposition step A_3	
			E kJ. $_{mol}^{-1}$	log A min^{-1}
Isothermal			295 ± 30	28.1 ± 5.1
Nonisothermal (a) Coats-Redfern				
	$\beta =$			
	5		311	28.8
	10		311	28.8
	15		282	26.1
	20		268	24.7
	average		293 ± 18	27.1 ± 1.7
(b) Madhusudanan	$\beta =$			
	5		312	28.9
	10		308	28.5
	15		285	26.3
	20		267	24.5
	average		293 ± 18	27.1 ± 1.7
(c) Ozawa		$(1 - \alpha) =$		
		0.1	264	24.6
		0.2	267	24.9
		0.3	274	25.5
		0.4	280	26.0
		0.5	290	27.0
		0.6	292	27.1
		0.7	298	27.7
		0.8	303	28.1
		0.9	339	31.6
	average		290 ± 16	26.9 ± 1.5
(d) Composite method			288 ± 25	26.7 ± 3.5

Figure (3) shows the results of the typical weight changes of the thermal decomposition under nonisothermal measurements for samples studied in air atmosphere at different heating rates of 5, 10, 15 and 20 deg/min. The kinetic analysis of the nonisothermal decomposition is considered here in view of four integral methods: the Ozawa method[7], the Coats-Redfern method[8], the Madhusudanan *et al.* method[9] and the Diefallah composite method[4]. In the composite method of analysis, the results obtained not only at different heating rates but also with different α values, are superimposed on one master curve. This has been achieved by rewriting the different approximate integral equation due to different workers for the integral kinetic analysis of nonisothermal data in a form such that the kinetic function $g(\alpha)$ and the linear heating rate β lie on one side of the equation and (1/T) on the other side. When use is made of the modified Coats-Redfern equation[12], then in order to do the composite analysis the equation is written in the form:

$$\ln [\beta g (\alpha) / T^2] = \ln (AR/E) - E/RT \tag{1}$$

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:

$$g(\alpha) = A / R \int_0^T \exp(-E / RT) \ dt \tag{2}$$

A is the frequency factors and E is the energy of activation. Equation (1) shows 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 $g(\alpha)$.

When use is made of the original Coats-Redfern equation[8], then the equation for composite analysis has the forms:

$$\ln [\beta g (\alpha) / T^2] = \ln [(AR/E) (1-2RT/E)] - (E/RT) \tag{3}$$

When using Doyle's approximate equation[13], we have to use the equation written as:

$$\log [\beta g (\alpha)] = [\log (AE/R) - 2.315] - 0.4567 (E/RT) \tag{4}$$

Again, use may also be made of MacCallum and Tanner[14] approximate equation, rewritten as:

$$\log [\beta g (\alpha)] = \log (AE/R) - 0.483E^{0.435} - (0.449 + 0.217E) \times 10^3/T \tag{5}$$

We have also performed composite calculation making use of Madusudanan *et al.* approximate equation[9], rewritten in the form:

$$\ln [\beta g (\alpha) / T^{1.921503}] = \ln (AE/R) + 3.77205 - 1.921503 \ln E - (E/RT) \tag{6}$$

Equations (4), (5) and (6) show that the dependence of the left side of the equation, calculated for different α- values at their respective β-values, on (1/T), should give rise to a single master straight line for the correct form of $g(\alpha)$ and hence the activation energy and the frequency factor can be readily calculated. In general, analysis of nonisothermal kinetic data according to the composite method showed that the different approximate integral equations gave rise within experimental error, to identical values of activation parameters using the same model for the reaction interface[4,15-17].
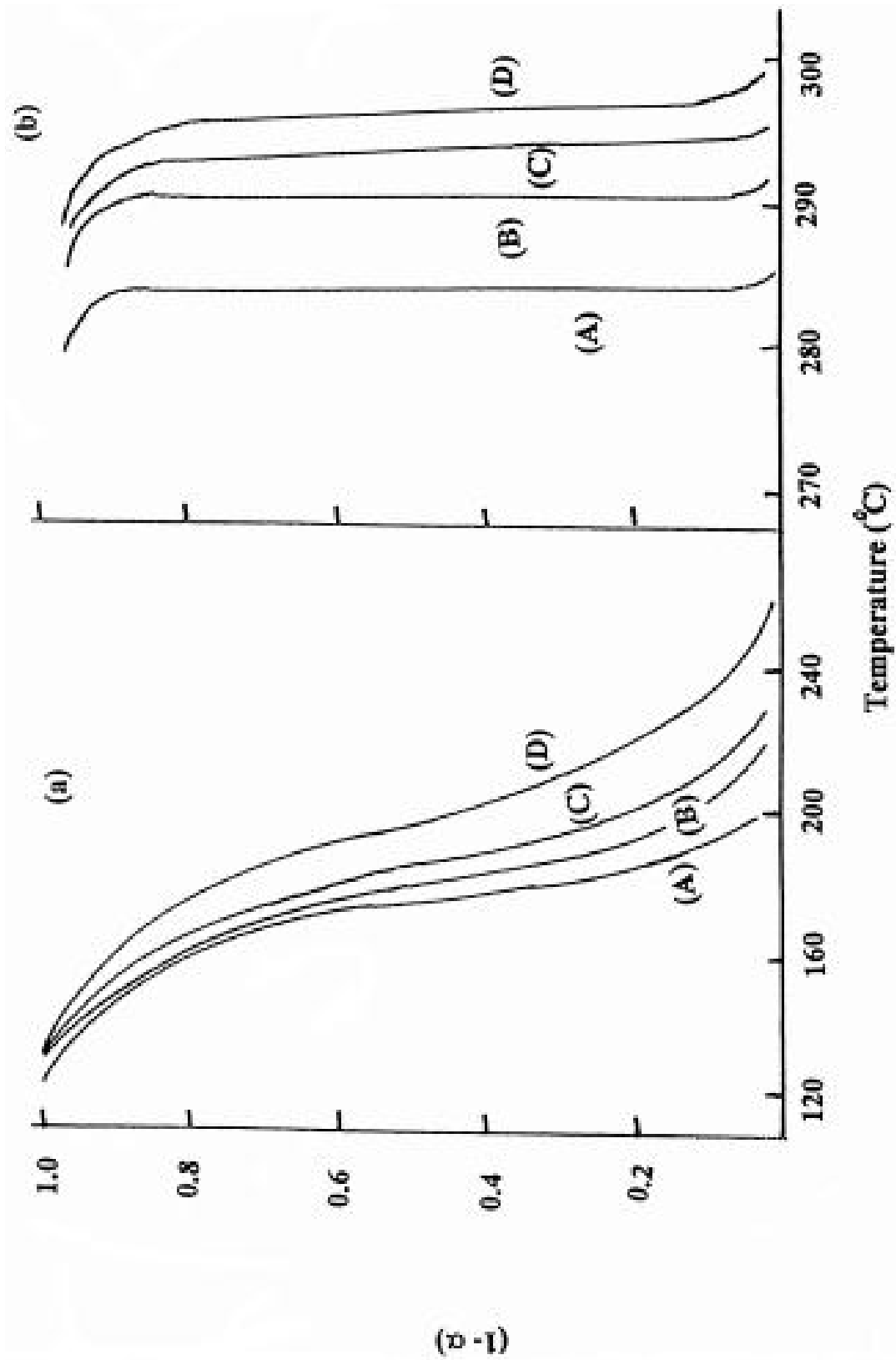
FIG. 3. Dynamic measurements for nickel dimethylglyoxime thermal decomposition heating rate (A) 5, (B) 10, (C) 15 and (D) 20 deg/ming; (a) dehydration and (b) decomposition.

The activation energy E and the frequency factor A of the decomposition reaction of nickel dimethylglyoxime according to the composite methods and using the g(α) functions listed in Table (1) were calculated. A computer program has been used to do the calculation[15] and the results showed that the best fit is obtained for (A$_3$ model) random nucleation model. Typical results are shown in Fig. (4) for composite analysis based on Doyle equation and in Fig. (5) for composite analysis based on Coats-Redfern equation. Figures (4b and 5b) show that the (F$_1$) model gives much less satisfactory fit to the data in comparison with A$_3$ model (Fig. 4a and 5a). Table (2) shows that there is agreement between the results obtained under isothermal condition and the results obtained under dynamic condition calculated according to the composite method using different approximate integral equations[7-14].

In view of the conclusions from isothermal studies and the composite integral method, only random nucleation (A$_3$ model) should be used to analyze the results. However, the results of the present study show large variation in the calculated activation parameters which are more a function of the method of data analysis. In Ozawa method[7], the values of (E) and (log A) varies much with α, which would imply that the reaction mechanism varies with the fraction reacted. The values of (E) and (log A) calculated by the Coats-Redfern method[8] 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[4]. In Madhusudanan method[9] the activation parameters (E) and (log A) decrease as the heating rate increases and the results are similar to those of Coats-Redfern method[8]. However, analysis of data according to the composite methods allow the choice of the reaction model and a complete analysis of all nonisothermal curve obtained at different fractions reacted and heating rates into a single curve, so that a single activation energy and frequency factor for the decomposition reaction is obtained, which is in good agreement with the isothermal results.

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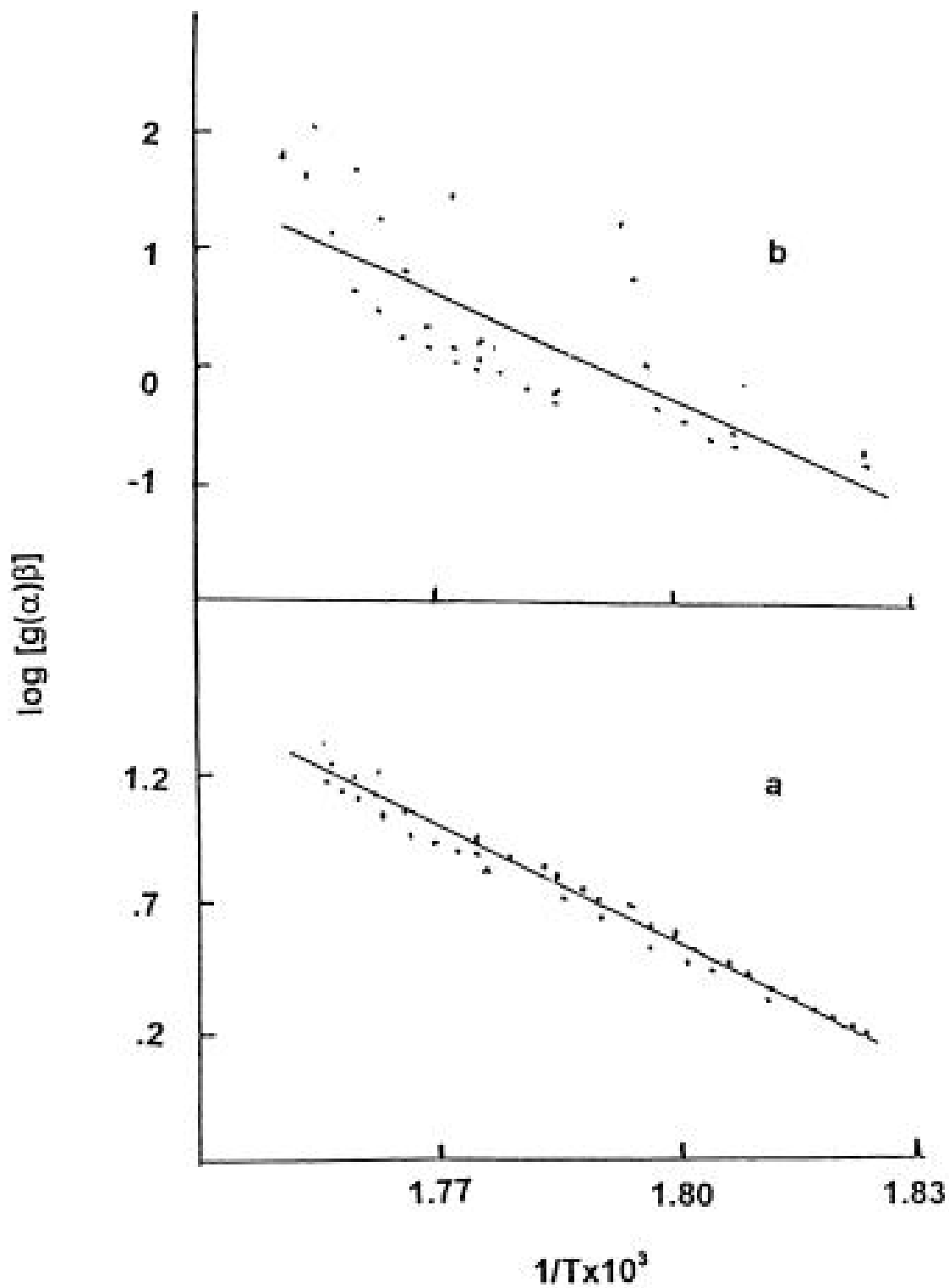

FIG. 4. Composite analysis of the dynamic TG data of the decomposition of nickel dimethylglyoxime based on Doyle equation (a) A_3, (b) F_1.
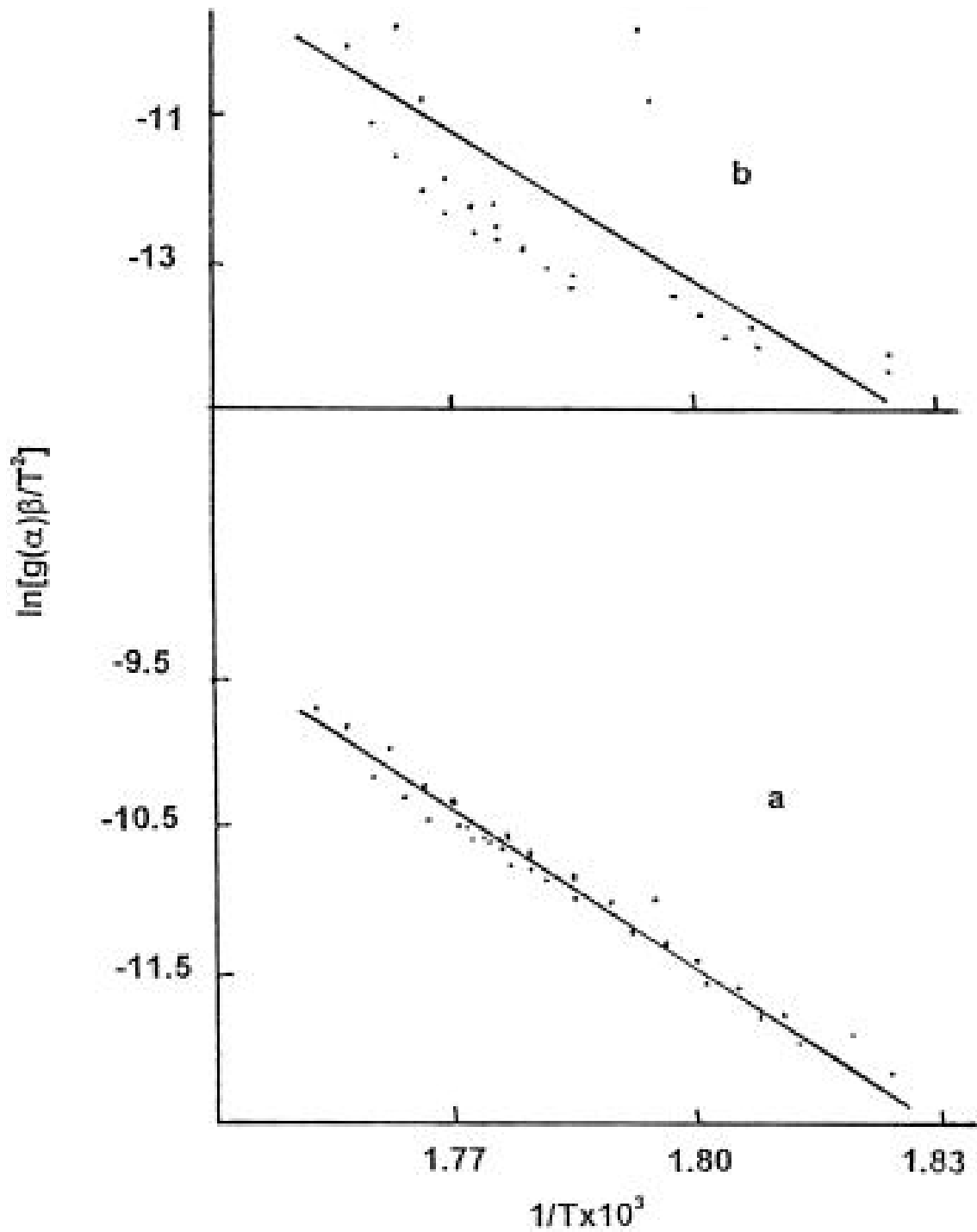
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FIG. 5. Composite analysis of the dynamic TG data of the decomposition of nickel dimethylglyoxime based on Coats-Redfern equation (a) A_3, (b) F_1.

حركية التكسير الحراري لثنائي ميثيل جليوكزيم النيكل

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وقسم الكيمياء ، كلية العلوم ، جامعة بنها ، بنها ، مصـــر

المستخلص .   تم دراسة التكسير الحراري لثنائي ميثيل جليوكزيم النيكل في الهواء باستخدام تقنية التحليل الحراري الوزني والتحليل الحراري التفاضلي . وقد تم دراسة حركية خطوا   التكسيـر الحراري باستخدام طرق التحليل الحراري الوزني الأيزوثرمية وغير الأيزوثرمية . وقد نوقشت النتائج في ضوء نماذج السطوح البينية في التفاعل وباستخدام طرق حسابية مختلفة في تحليل النتائج غيـر الأيزوثرميـة . وأوضـحت نتائـج حسـابا   بارامتـرا   التنشيط باستخدام طرق التحليل التكاملي المشترك للنتائج غير الأيزوثرمية اتفاق وارتباط أفـضل مع النتـائج التي وجـد   عند الظروف الأيزوثرميـة عـلاة على عـدم اعتمادها على معدل التسخين والكسر المتفاعل .