

# REEXAMINATION OF THE KINETICS OF THE THERMAL DESORPTION OF DIMETHYLSULFOXIDE AND N-METHYL FORMAMIDE FROM A GREENSPLETT KAOLIN

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**Abstract**—The kinetics of the thermal decomposition of the kaolin: dimethylsulfoxide (kaolin: DMSO) and the kaolin: N-methylformamide (kaolin: NMF) intercalates have been reexamined. Two different sample sizes (2 mg and 8 mg) and grain-size distributions (<45  $\mu\text{m}$  and 45–63  $\mu\text{m}$ ) were investigated using isothermal and dynamic gravimetry in the temperature range 100°–200°C. All sample configurations for the kaolin: DMSO intercalate (2 mg, <45  $\mu\text{m}$ ; 2 mg, 45–63  $\mu\text{m}$ ; 8 mg, <45  $\mu\text{m}$ ; 8 mg, 45–63  $\mu\text{m}$ ) followed the rate law  $-\ln(1 - \alpha) = kt$  to a value for  $\alpha$ , the reaction fraction complete, of .6, yielding activation energies and standard deviations at the 99% confidence level of  $85.5 \pm 3.79$  and  $71.75 \pm 8.75$  kJ/mole for the isothermal and dynamic runs, respectively. The kaolin: NMF intercalate (2 mg, <45  $\mu\text{m}$ ) also followed the same rate law for  $\alpha < .8$ , with activation energies and standard deviations at the 99% confidence level of  $89 \pm 5.05$  and  $79.25 \pm 6.47$  kJ/mole for the isothermal and dynamic studies, respectively. In solution the rate law  $-\ln(1 - \alpha) = kt$  is known as first-order kinetics, but here it appears to represent the non-instantaneous nucleation of uniformly sized particles, followed by the inward movement of a reaction interface.

**Key Words**—Activation energy, Desorption, Dimethylsulfoxide, Kaolinite, N-methyl formamide, Thermal treatment.

## INTRODUCTION

The kaolin: dimethylsulfoxide (kaolin: DMSO) intercalate has received considerable attention recently in part due to its use as an intermediate in the formation of hydrated kaolins (Costanzo *et al.*, 1984a, 1984b). Thompson (1985) used the <sup>13</sup>C and <sup>29</sup>Si nuclear magnetic resonance spectra of this system to derive input data for the crystal structure determination of the kaolin: DMSO intercalate (Thompson and Cuff, 1985). This structural determination was carried out by constraining the hydrogen bond length between three of the inner-surface hydroxyls and the sulfonyl oxygen at 2.94 Å, a value in close agreement with that determined by Adams (1979) for the three OH...O hydrogen bonds in the kaolin: N-methylformamide (kaolin: NMF) intercalate. Despite the similarity of the host: guest bonding mechanism in both the kaolin: DMSO and kaolin: NMF intercalates, Adams and Waihl (1980) found that the activation energy for the thermal decomposition of the former exceeded that determined by Adams (1978) for the latter by a factor of three. Unfortunately, although several kinetic formulations were evaluated for the thermal decomposition of the kaolin: DMSO intercalate by Adams and Waihl (1980), Adams (1978), apparently assumed the Avrami-Erofeev kinetic law with  $n = 2$  for the decomposition of the kaolin: NMF system simply because solid-state re-

actions commonly follow this formulation (Hach-Ali and Weiss, 1969; Riekel and Schöllhorn, 1976).

More recently, the same criterion was applied to describe the kinetics of dehydration of a 10-Å kaolin hydrate (Costanzo *et al.*, 1984). Furthermore, Criado *et al.* (1984) reexamined the kinetics of the thermal dehydroxylation of kaolinite, paying particular attention to the effects of grain-size distribution and sample size, and cleared up the difficulties concerning the choice of mechanism for the process. In their detailed investigation of the thermal decomposition of the kaolin: DMSO intercalate Adams and Waihl (1980) did not rule out the possibility that the grain-size distribution they employed masked the fact that the reaction was diffusion controlled.

The present investigation of the thermal decomposition of the kaolin: DMSO and kaolin: NMF intercalates was therefore initiated to establish whether the rates and mechanisms of the decomposition process for the two intercalates are indeed different and to determine the role played by grain and sample size on the interpretation of the reaction process.

## EXPERIMENTAL

The kaolin: DMSO intercalate was prepared, following Adams and Waihl (1980), by immersing a kaolin sample (from the Greensplatt Pit, St. Austell, Cornwall) in excess DMSO for 72 hr and then drying it at 60°C for 48 hr. The kaolin: NMF intercalate was prepared in the same manner and dried at 60°C for the optimum 72 hr determined by Adams (1978).

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Table 1. Algebraic expressions of  $g(\alpha)$ <sup>1</sup> functions and the slopes of the plots of  $\ln(\ln(1 - \alpha))$  against  $\ln t$ .<sup>1</sup>

Model	$g(\alpha)$	Slope
D <sub>3</sub>	$[1 - (1 - \alpha)^{1/2}]^2$	0.54
D <sub>4</sub>	$1 - 2\alpha/3 - (1 - \alpha)^{3/2}$	0.57
D <sub>2</sub>	$(1 - \alpha)\ln(1 - \alpha) + \alpha$	0.57
D <sub>1</sub>	$\alpha^2$	0.62
F <sub>1</sub>	$-\ln(1 - \alpha)$	1.00
R <sub>3</sub>	$1 - (1 - \alpha)^{1/2}$	1.07
R <sub>2</sub>	$1 - (1 - \alpha)^{3/2}$	1.11
A <sub>2</sub>	$[-\ln(1 - \alpha)]^{1/2}$	2.00
A <sub>3</sub>	$[-\ln(1 - \alpha)]^{3/2}$	3.00

<sup>1</sup>  $\alpha$  = reaction fraction completed at time  $t$  after the start of the reaction.  $g(\alpha)$  is an expression which depends upon the reaction mechanism. See Equation 1.

Thermogravimetric analyses were made using a Stanton Redcroft TG750 thermobalance and a nitrogen purge gas that had been dried by passing it through a 4-Å molecular sieve and phosphorus pentoxide. The thermobalance was calibrated in the temperature range 100–200°C using the known melting points of the standard substances 2,2'-bipyridine (70°C), tetrabutylammonium bromide (101°C), and p-aminobenzoic acid (186°C).

The intercalates were ground until they passed through stainless steel sieves of the appropriate mesh sizes to give grain-size fractions of <45 μm, 63–45 μm, 125–63 μm, 250–125 μm, and >250 μm. The effects of altering the heating rate, sample mass, grain size, and nitrogen flow rate on the dynamic decomposition of the kaolin : DMSO intercalate were studied with a view to minimizing the temperature at which 50% decomposition was achieved. The optimum conditions for dynamic thermal analysis were found to be 2 mg of <45-μm sample heated at 5°C/min under a nitrogen gas flow rate of 25 cm<sup>3</sup>/min. Under these optimized conditions the kaolin : DMSO intercalate exhibited a weight loss of ~19% by 175°C, after a weight loss of ~1% due to the evolution of surface species. The kaolin : NMF intercalate lost ~14%. These weight losses are in excellent agreement with those reported by Adams (1978) and Adams and Waihl (1980). X-ray powder diffraction (XRD) patterns of the kaolin : DMSO intercalate exhibited two peaks. One strong peak corresponding to the expanded intercalate at 11.21 Å and the second, which was much weaker, commensurate with the 7.16-Å unexpanded, parent kaolin. The XRD pattern of the kaolin : NMF intercalate showed no evidence of the 7.16-Å peak, only an intense peak corresponding to the 10.8-Å intercalate.

Isothermal studies were conducted under a nitrogen flow rate of 25 cm<sup>3</sup>/min in the temperature range 120–165°C. All kinetic equations reported in the literature for performing the kinetic analysis of solid-state reactions assume a single particle size. Delmon (1969) and Lahiri (1980) showed theoretically that a marked

Table 2. Results of the  $\ln(\ln(1 - \alpha))$  vs. time analysis for the isothermal decomposition of kaolin : dimethylsulfoxide.

Sample mass (mg)	Grain size (μm)	Temperature (°C)	Slope (m)
2		120	0.85
2		130	0.86
2	<45	140	0.80
2		150	0.69
2		161	0.74
8		127	0.89
8	<45	142	0.86
8		155	1.00
8		165	1.14
2		130	1.04
2	63–45	140	1.04
2		158	1.20
8		130	0.90
8	63–45	140	0.90
8		158	0.99

deviation in behavior from that predicted for a discrete particle size can occur if the ratio between the largest and the smallest sizes >6. Adams and Waihl (1980) were aware of this limitation and chose to use a grain size of <53 μm. Unfortunately, they did not report their sample weight; consequently direct comparison is not possible. In the present study the kinetic analysis of the decomposition of kaolin : DMSO was performed on two different grain-size fractions (<45 μm and 63–45 μm) and sample masses of 2 and 8 mg. Kinetic analysis of kaolin : NMF was made using the optimized values for kaolin : DMSO (i.e., 2 mg sample of <45-μm size particles).

Kinetic analysis of the isothermal data was conducted using the general equation:

$$g(\alpha) = kt, \quad (1)$$

where  $\alpha$  is the reaction fraction completed at time  $t$ ,  $k$  is the rate constant, and  $g(\alpha)$  is an expression which depends upon the mechanism assumed for the reaction. Table 1 lists various expressions taken from the literature: homogeneous (F<sub>1</sub>), diffusion controlled (D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub>, D<sub>4</sub>), phase-boundary controlled (R<sub>2</sub>, R<sub>3</sub>), and random nucleation (A<sub>2</sub>, A<sub>3</sub>) mechanisms. Using these expressions in Eq. (1) and plotting the left-hand side against time  $t$  results in a straight line having a slope related to  $k$  for the correct equation. To determine the correct formulation the isothermal decompositions were evaluated using the generalized Avrami-Erofeev plot of the form  $\ln(\ln(1 - \alpha))$  vs.  $\ln t$  (Hancock and Sharp, 1972). Plots of this form are linear over a wide range of  $\alpha$  (0.05–0.65), and the slope,  $m$ , can facilitate the selection of an appropriate kinetic model, as indicated in Table 1.

Kinetic analysis of the dynamic decompositions was performed by plotting  $\log(g(\alpha)/T^2)$  vs.  $1/T$  (Coats and Redfern, 1964) inasmuch as the linearity of these plots

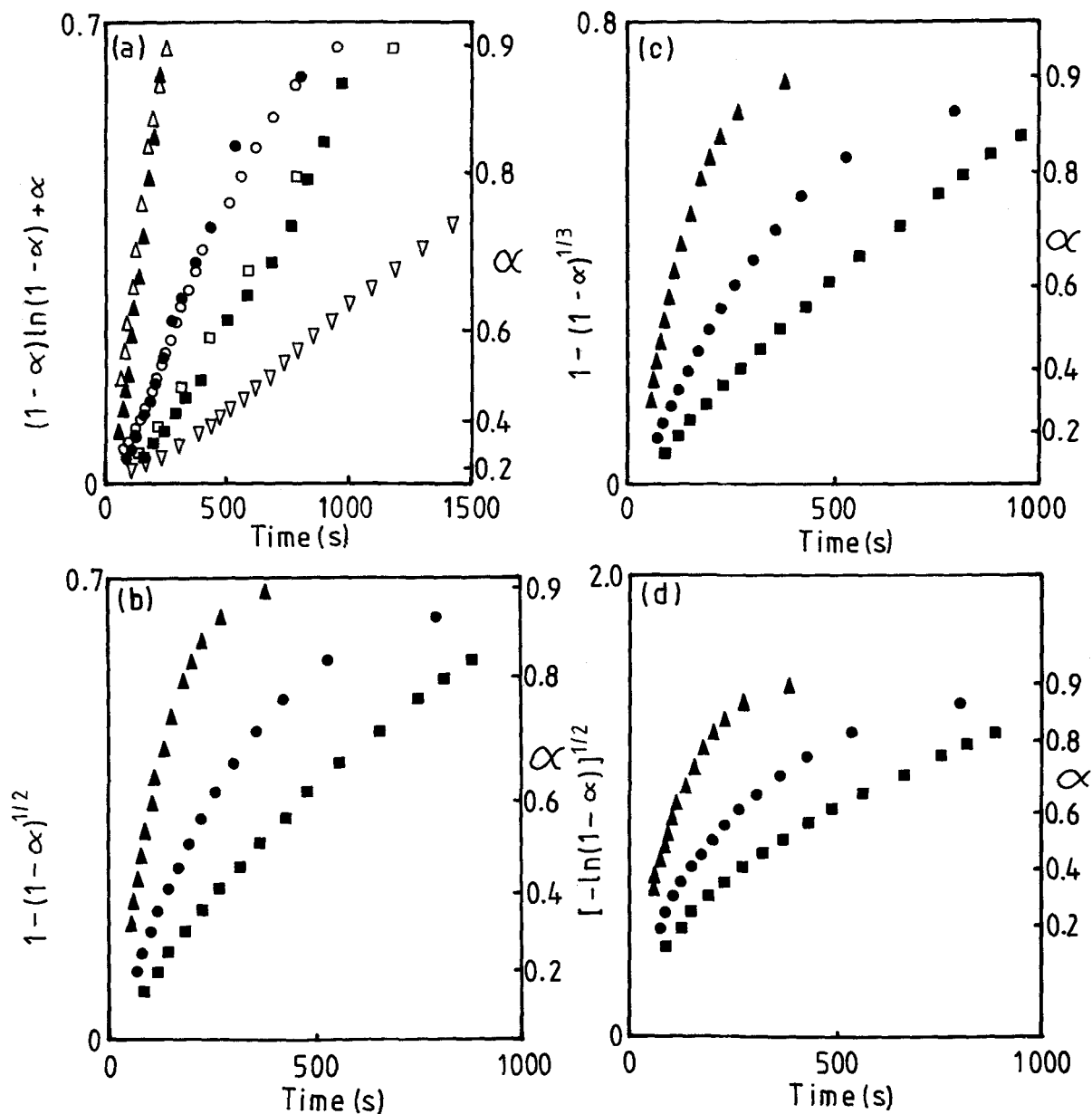


Figure 1. Isothermal decomposition of kaolin:dimethylsulfoxide intercalate plotted as kinetic expressions (a)  $D_2$ , (b)  $R_2$ , (c)  $R_3$ , and (d)  $A_2$ , as defined in Table 1.

provides an indication of the quality of the fit for a particular kinetic model.

## RESULTS AND DISCUSSION

### *Kaolin: DMSO intercalate*

The values of  $m$  (i.e., the slope) obtained by linear regression of the  $\ln(\ln(1 - \alpha))$  vs.  $\ln t$  plots for the isothermal decomposition of the kaolin: DMSO intercalate as a function of temperature, sample weight, and grain-size interval are listed in Table 2. The values of the slope were such that diffusion and random nuclea-

tion could be ruled out as rate limiting; the models that best describe the process were  $F_1$ ,  $R_2$ , and  $R_3$ . Adams and Wautl (1980) found that model  $F_1$  gave the best fit to their experimental data for the kaolin: DMSO system, whereas model  $A_2$  was chosen to describe the decomposition of the kaolin: NMF intercalate (Adams, 1978). Furthermore, Adams and Wautl (1980) observed a marked lack of linearity when plotting their kaolin: DMSO isothermal decomposition data to model  $D_2$ , but were unable to exclude the possible detrimental effect of their large grain-size distribution. Consequently, to verify the choice of model,  $g(\alpha)$  was plotted against

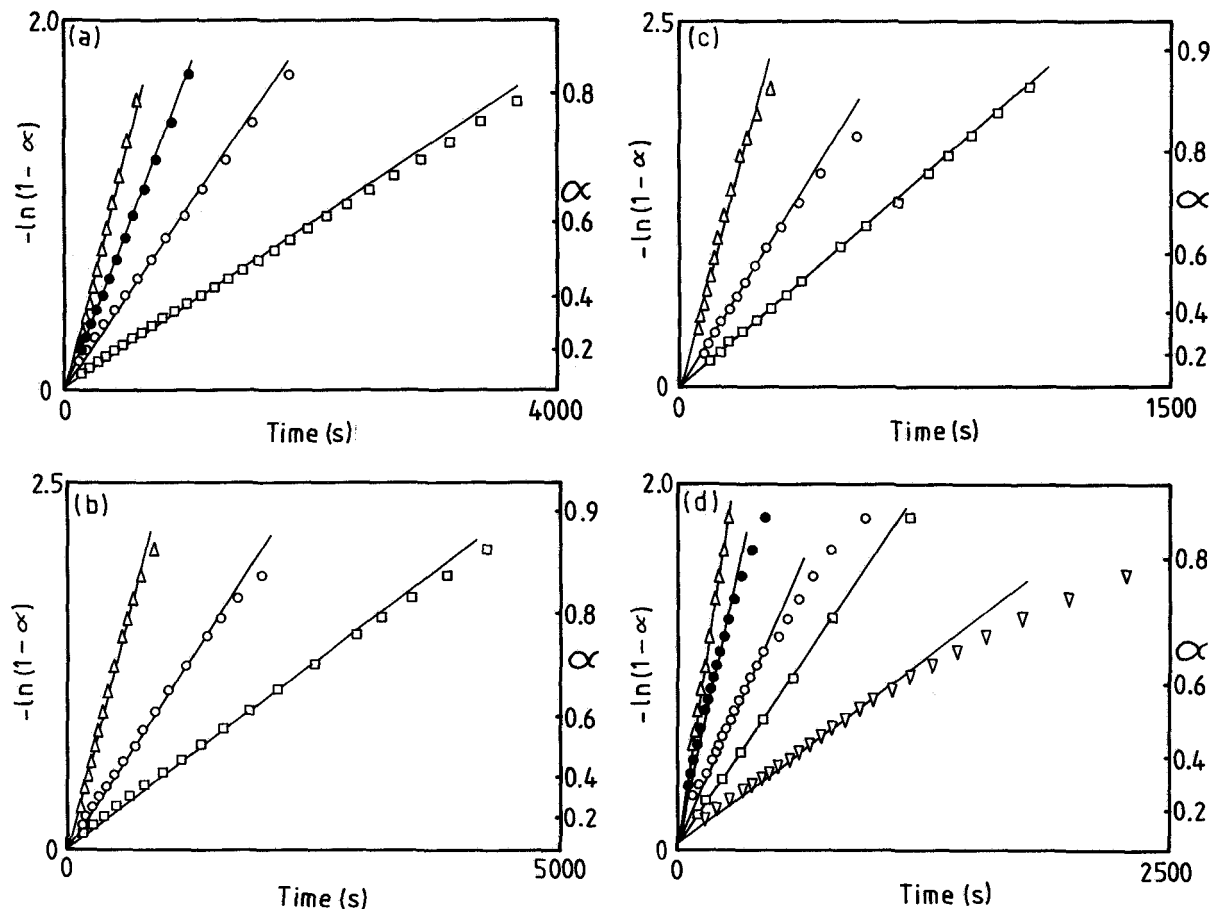


Figure 2. Effect of sample size and grain-size interval on the fit of the kaolin:dimethylsulfoxide isothermal decomposition to the  $F_1$  kinetic expression. (a) 8 mg,  $<45 \mu\text{m}$ ; (b) 8 mg, 63–45  $\mu\text{m}$ ; (c) 2 mg, 63–45  $\mu\text{m}$ ; and (d) 2 mg,  $<45 \mu\text{m}$ .

time to assess the quality of the fit for models  $D_2$ ,  $R_2$ ,  $R_3$ , and  $A_2$  for the kaolin:DMSO intercalate. This plot is reproduced here for the 2-mg sample of the 63–45- $\mu\text{m}$  size fraction in Figure 1, but it is representative of the other three sample configurations listed in Table 2. The obvious lack of linearity exhibited by the experimental data not only precludes these models, but also shows that the grain-size distribution does not affect the model.

Figure 2 shows the quality of fit of the experimental data to model  $F_1$  for the various combinations of sample weight and grain size. For all combinations the linearity of the fits is acceptable up to  $\alpha$  values of 0.6, although the best overall fit at all temperatures investigated is for the 8-mg sample of the  $<45\text{-}\mu\text{m}$  grain size (Figure 2a). The rate constants calculated from the slopes of these plots were used to derive activation energies and pre-exponential factors from the Arrhenius equation (Table 3). These values are in excellent agreement with each other at  $85 \pm 2 \text{ kJ/mole}$ .

Four dynamic decompositions were carried out under the optimized conditions of a sample mass of 2 mg

and a grain size of  $<45 \mu\text{m}$ . Plots of  $\log(g(\alpha)/T^2)$  vs.  $1/T$  were drawn for various models inasmuch as the linearity of these plots gives an indication of the quality of fit for a particular kinetic model (Figure 3). Although the correlation coefficients are all close to 1, Figure 3 shows that only models  $F_1$  and  $A_2$  are sufficiently linear to warrant consideration. Those two models yield activation energies of  $72 \pm 4$  and  $32 \text{ kJ/mole}$ , respectively, and represent the mean of the four replicates. The value of  $72 \pm 4 \text{ kJ/mole}$  is in reasonable agreement with the value derived above from the isothermal stud-

Table 3. Activation energies,  $E$ , and pre-exponential factors,  $A$ , for the thermal decomposition of the kaolin:dimethylsulfoxide intercalate, derived from isothermal data using the model,  $-\ln(1-\alpha)$  vs. time.

Sample mass (mg)	Grain size ( $\mu\text{m}$ )	$E$ (kJ/mole)	$A$ ( $\text{s}^{-1}$ )
2	$<45$	84	$6.8 \times 10^6$
8	$<45$	87	$5.1 \times 10^7$
2	63–45	86	$6.9 \times 10^7$
8	63–45	85	$2.7 \times 10^8$

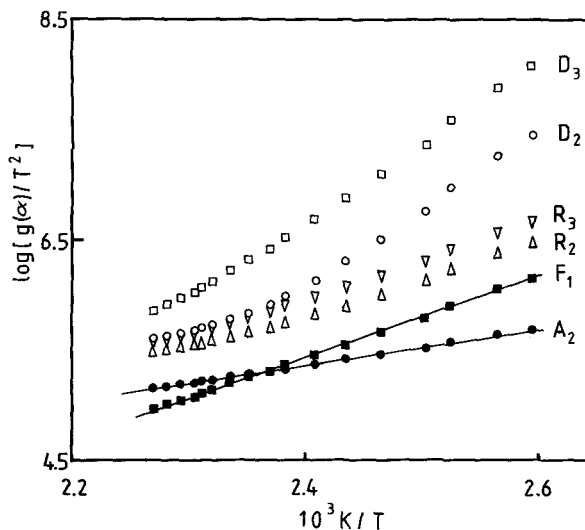


Figure 3. Fit of the dynamic thermal decomposition of kaolin:dimethylsulfoxide to several of the kinetic expressions defined in Table 1.

ies and that determined by Adams and Watl (1980) of 78 kJ/mole for an unspecified sample weight and a grain size of  $<53 \mu\text{m}$ .

Statistical analysis of the isothermal and dynamic replicates at the 99% confidence limit indicate that there was no significant difference between the standard deviations for the results from the two models. The values of the activation energies and standard deviations for the isothermal and dynamic studies were  $85.5 \pm 3.79$  and  $71.75 \pm 8.7$ , respectively. Thus, at the 99% confidence level the values for the activation energies are the same.

#### Kaolin:NMF intercalate

The same approach as that described for the kaolin:DMSO system was applied to the kaolin:NMF intercalate. The values of the slope,  $m$ , for the plot of  $\ln(\ln(1 - \alpha))$  vs.  $t$  were uninformative, increasing from 1.05 at  $95^\circ$  to 1.51 at  $135^\circ\text{C}$ . Plots of  $g(\alpha)$  vs.  $t$  for the models listed in Table 1, however, showed unequivocally that the data fitted the formulation  $F_1$ , as shown in Figure 4. The activation energy for the desorption process was 89 kJ/mole, a value similar to that noted above for kaolin:DMSO, which is expected because the bonding mechanism of the guest molecule to the kaolin is identical.

Once again four dynamic decompositions were performed. The data gave excellent fits to models  $F_1$  and  $A_2$  (Figure 5), yielding activation energies of  $79 \pm 3$  and 36 kJ/mole, respectively. The value of 79 kJ/mole is in reasonable agreement with that derived from the isothermal studies reported here, whereas the value of 36 kJ/mole is similar to that reported by Adams (1978) for the dynamic decomposition followed by differential

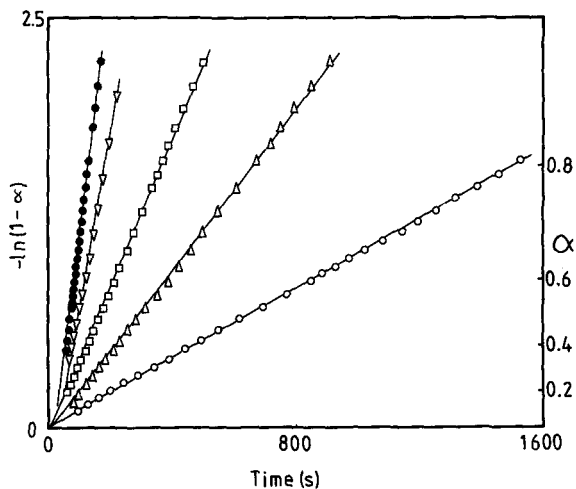


Figure 4. Isothermal decomposition of kaolin:N-methylformamide plotted as expression  $F_1$ . Sample weight = 2 mg; grain size =  $<45 \mu\text{m}$ .

scanning calorimetry and fitted to the Avrami-Erofeev model with  $n = 2$ , i.e., model  $A_2$  in Table 1. Values of the activation energies for the isothermal and dynamic runs calculated at 99% confidence limits give values of  $89 \pm 5.05$  and  $79.25 \pm 6.47$ , respectively.

## CONCLUSIONS

The kinetic model followed by the thermal decomposition of kaolin:DMSO and kaolin:NMF is  $F_1$  (Table 1), which is known as the first-order decay law and is usually observed in the final 10% of many solid-state reactions. As Adams and Watl (1980) pointed out, however, rarely does the law apply over the large range of  $\alpha$  observed here. Consequently, the chosen interpretation of this algebraic expression is that suggested by Adams and Watl (1980), based on the work of

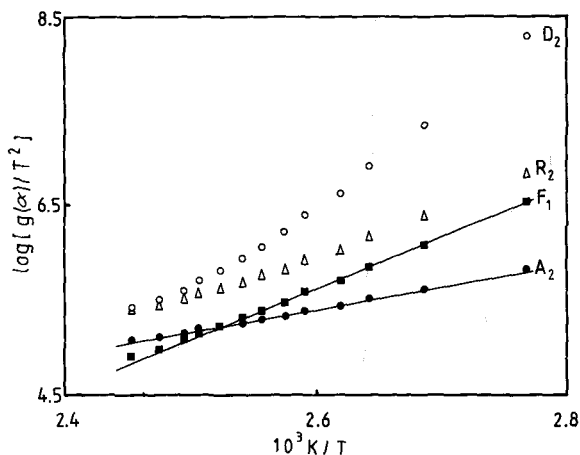


Figure 5. Fit of the dynamic thermal decomposition of kaolin:N-methylformamide to several of the kinetic expressions defined in Table 1.

Bradley *et al.* (1932) in which non-instantaneous nucleation of uniform-size particles takes place followed by the inward movement of a reaction interface. The activation energies thus determined represent the energy required to form a nucleus of the product kaolin intercalate.

It remains only to stress that kinetic models for the thermal desorption of intercalated moieties should be chosen with care, and that information based on data derived from a dynamic model should be viewed with caution unless corroborated by at least one isothermal study.

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