

THERMAL DECOMPOSITION OF A KAOLINITE:DIMETHYL SULFOXIDE INTERCALATE

J. M. ADAMS AND G. WALTJ

Edward Davies Chemical Laboratories, University College of Wales
Aberystwyth, SY23 1NE, Dyfed, United Kingdom

Abstract—The thermal decomposition of a kaolinite:dimethyl sulfoxide intercalate has been studied by thermogravimetry. The decomposition is complete by 175°C and has a ΔH of 58 ± 5 kJ/mole of dimethyl sulfoxide. For the first 70–80% of the reaction a plot of $\log(1 - \alpha)$ vs. time is linear, where α is the reaction fraction complete. A two-dimensional, contracting-circle type of mechanism is consistent with this linearity, provided that the nucleation process is considered to be exponential rather than instantaneous. An activation energy of 105 ± 8 kJ/mole of dimethyl sulfoxide has been derived. This value is inconsistent with the simple assumption that the rate-determining step is the freeing of single organic molecules from their bonding to the clay layers. The mechanism of this decomposition is different from that found for kaolinite: N-methyl formamide, and the activation energy is considerably greater than that found for that material (30 ± 3 kJ/mole).

Key Words—Dimethyl sulfoxide, Intercalation, Kaolinite, Kinetics, Thermal decomposition.

INTRODUCTION

Sheet silicates have recently received considerable attention as very selective catalysts for organic synthesis (e.g., Thomas *et al.*, 1977) of molecules which are difficult to synthesize by conventional means (Adams *et al.*, 1978). While it is true that most of the catalysts studied have been smectites, it is important to obtain knowledge about the rate and mechanism of insertion and release of organic molecules in layered silicates in general. Such knowledge does not appear to exist at present, and work on relatively simple kaolin intercalates may lay the groundwork for the study of more complicated systems in the future. In particular, there is merit in knowing whether diffusion control is important or whether the nucleation process is rate determining in such processes.

The thermal decomposition of a kaolinite:N-methyl formamide (K:NMF) intercalate was studied by Adams (1978a). However, the dimethyl sulfoxide (DMSO) molecule is sufficiently unlike NMF that any assumption of a similar decomposition mechanism would be unsound. In addition, the rationale of bonding between the organic molecules and kaolin layers suggested by Adams (1978b) would make the number of strong hydrogen bonds in the K:DMSO and K:NMF intercalates the same, i.e., three bonds from clay hydroxyls to the oxygen atom of the DMSO or NMF. Thus, a determination of the activation energy of the decomposition is of interest since similar values of the correct magnitude would suggest that the energy barrier to be overcome was the breaking of H-bonds, whereas if the values are significantly different, some other process must determine the rate.

EXPERIMENTAL

The intercalate was prepared by immersing a kaolinite sample obtained from the Greensplatt Pit, St. Aus-

tell, England, in an excess of DMSO for 72 hr. The liquid was decanted, and the sample was dried at 60°C for 48 hr. The intercalate was then ground until it passed through a 300-mesh sieve, i.e., until the particle size was $< 53 \mu\text{m}$. A preliminary thermogravimetric analysis (TGA) run in static air at 5°C/min gave weight losses of ~1% of loosely bound surface material (below 100°C) and ~19% DMSO removed by 220°C. The weight loss data suggest a formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{DMSO})_{0.74}$.

The ratio of DMSO to clay is lower than was reported by Sanchez Camazano and Gonzalez Garcia (1966) and Weiss *et al.* (1966), although Olejnik *et al.* (1968) also reported relatively minor intercalation by DMSO. The ratio is also lower than would be expected for the type of bonding between DMSO and clay hydroxyl groups suggested by Adams (1978b). X-ray powder diffractometry (XRD) showed that a small proportion of the kaolin layers had not expanded. The area of the 001 peak of the intercalate at 11.18 Å was, however, considerably greater than that of the 001 clay peak at 7.16 Å. When corrections to the peak areas had been made for structure-factor and Lorentz-polarization effects it was evident that approximately one quarter of the layers still had the kaolin spacing. The TGA results are therefore consistent with the XRD measurement. It is possible that in addition to the fraction of clay layers which are not expanded by DMSO, incomplete filling of some of the intercalate layers could exist. TGA under flowing dry nitrogen gas showed a marked reduction in the temperature below which all the DMSO was removed from the clay compared with TGA under static conditions. At a nitrogen flow of 20 cm³/min there was no further effect, i.e., the minimum temperature of complete DMSO removal was 175°C. All experimental runs were therefore made at 20 cm³/min nitrogen flow so that the reaction was not impeded. A series of isothermal runs from 133° to 157°C was made on a Stanton Redcroft

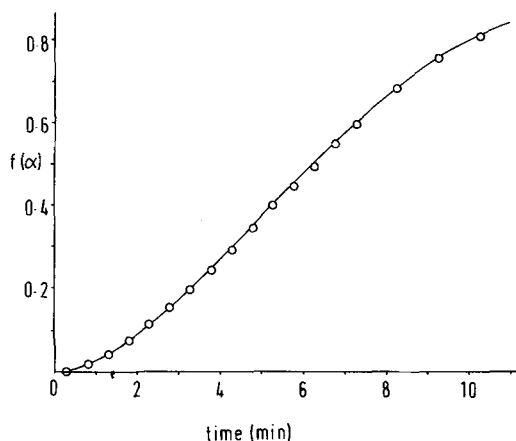


Figure 1. Graph of $(1 - \alpha)\ln(1 - \alpha) + \alpha$ vs. time for the thermal decomposition at 150°C . For lamellar particles, of equal radius, such a plot should be linear for a diffusion controlled reaction.

TG770 thermobalance with aluminum sample pans. XRD measurements made on small portions of sample during the decomposition showed that there was a continuous smooth reduction in the area of the 11.2 \AA intercalate peak and a concomitant increase in the area of the 7.16 \AA kaolinite peak.

The ΔH for the loss of the organic species was measured using a Perkin-Elmer DSC1b differential scanning calorimeter with aluminum sample holders, calibrated with tin (ΔH for fusion = 60.7 J/g) and was found to be $58 \pm 5 \text{ kJ/mole DMSO}$.

RESULTS AND DISCUSSION

Where *exchange* of chemically identical organic molecules in the interlamellar regions of layered systems has been studied, e.g., ammonia exchanged with deuterio-ammonia in tantalum disulfide (Riekell, 1978),

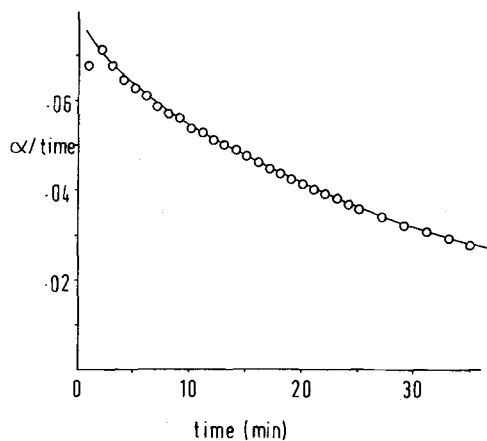


Figure 2. Graph of α/t vs. time for the decomposition of kaolinite:DMSO at 138°C . The negative slope implies a decelerating reaction.

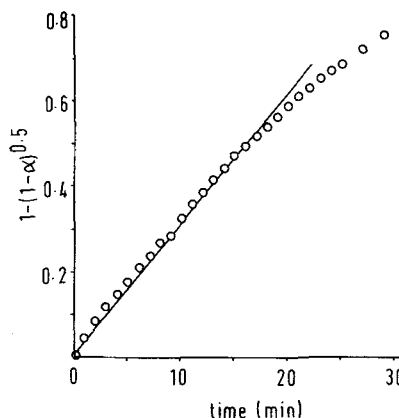


Figure 3. Plot of $1 - (1 - \alpha)^{1/2}$ vs. time for the decomposition at 138°C . The deviation from linearity shows that the standard contracting-circle formulation is not a good description of the process.

the extent of reaction, α , has been found to be approximately proportional to $\sqrt{\text{time}}$, suggesting that the process is diffusion controlled. However, in none of the small number of studies on the kinetics of intercalation, or "deintercalation," has it been observed that the process is controlled by diffusion, with the exception of the dehydroxylation of kaolinite (Brindley *et al.*, 1967). To test this possibility, a graph of $(1 - \alpha)\ln(1 - \alpha) + \alpha$ vs. time was constructed (Figure 1). This function is expected to be linear for diffusion into lamellar particles of constant size (Holt *et al.*, 1962). The observed lack of linearity implies that diffusion is not rate-controlling, unless the effect of having a range of particle sizes is considerable. Scanning electron micrographs taken of the screened intercalate showed a range of sizes, although the distribution peaked between 30 and $50 \mu\text{m}$. The possible influence of the particle size range cannot, therefore, be entirely ruled out.

A different approach has been adopted using solid-state kinetic formulations which have been found useful in many studies of endothermic decomposition (Garner, 1955). Plots of α/time vs. time were made for the isothermal weight loss data (Figure 2) since this plot can give an indication of the type of mechanism of the decomposition (Guarini and Spinicci, 1972). Significantly, the shape of the curve is not consistent with an Avrami-Erofeev expression for the process, which requires a maximum in the α/time vs. time curve, usually at $\alpha \approx 0.6$ or 0.7 . This type of expression assumes a random nucleation of product phase followed by growth of the nuclei and, in the later stages, overlapping of these nuclei. The Avrami-Erofeev law has often been found useful in kinetic studies of intercalates and has, for example, been found to describe quite well the intercalation of ammonia into tantalum disulfide (Riekell and Schollhorn, 1976) and the intercalation of NMF into kaolin (Hach-Ali and Weiss, 1969), as well as the con-

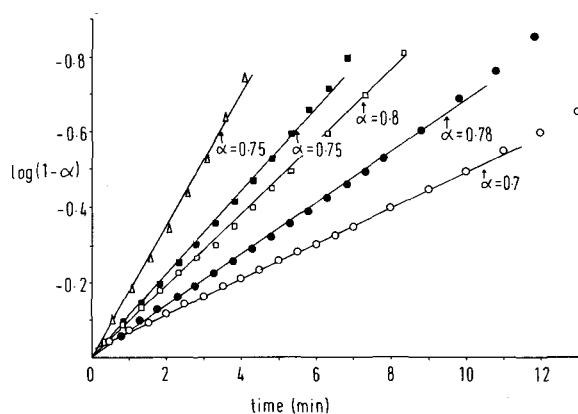


Figure 4. Plots of $\log(1 - \alpha)$ vs. time for a series of temperatures from 133°C to 157°C. In all cases the plots show good linearity until $\alpha = 0.7$ or 0.8. \circ 133°C, \bullet 140°C, \square 144°C, \blacksquare 150°C, \triangle 157°C.

verse, i.e., the thermal decomposition of the K:NMF intercalate (Adams, 1978a).

The negative slope of the curve shows that the reaction is deceleratory. This feature is found for the contracting-solid type of mechanism where instantaneous surface nucleation is followed by movement of an interface into the bulk at a constant propagation rate. The lamellar nature of the clay particles suggests that the contracting-circle model would be more appropriate than the contracting-sphere model. Plots of $1 - (1 - \alpha)^{1/2}$ vs. time are not, however, linear (Figure 3). It is possible that although the basic mechanism may be of contracting-circle type, two reasons may exist for the non-linearity of the curves: (1) the contracting-circle model assumes that all particles have the same radius—this is clearly not true, although all the kaolinite particles used in this study must be $< 53 \mu\text{m}$; and (2) the nucleation of the reaction might not be instantaneous on the surface of all of the particles.

The problem caused by non-instantaneous surface nucleation of lamellar particles was first studied some time ago by Bradley *et al.* (1932) for crystals of $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ which decompose thermally to give the anhydrous product. These authors assumed that the particles were of equal radius and that decomposition was by movement of an interface into the solid. However, they postulated a non-instantaneous nucleation of product. Specifically, the number of crystals nucleated at a time t from the start of the reaction in the time interval dt is $kn_0 \exp(-kt)dt$, where k is the nucleation rate constant and n_0 is the initial number of particles. Bradley *et al.* (1932) derived an expression for such a decomposition as $\log(1 - \alpha) = \text{constant} - kt/2.303$. Suitable plots of $\log(1 - \alpha)$ vs. t were indeed found to be linear up to large values of α (Figure 4) for all temperatures studied. This mechanism is therefore compatible with the present experimental results, al-

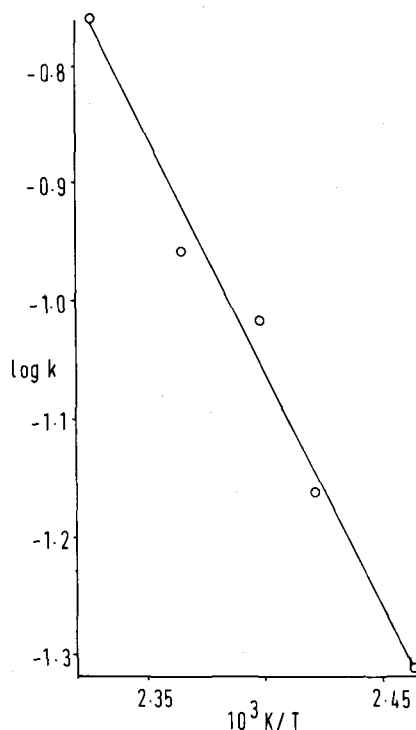


Figure 5. Arrhenius plot of $\log k$ vs. $10^3 T/K$ for the decompositions shown in Figure 4. The activation energy from the decomposition is 78 kJ/mole (i.e., 105 kJ per mole of DMSO).

though the derivation requires equal size particles. It should be noted that the plot of $\log(1 - \alpha)$ vs. t is known in another context as the first-order decay law and is observed in the last 10% or so of many solid-state reactions. It is rare, however, for the law to apply over such a wide range of α .

Evaluation of the slopes of the lines in Figure 4 gave values for the rate constant, k , which were used in an Arrhenius plot (Figure 5) to obtain an activation energy for the decomposition process. The activation energy, E_a , is insensitive to the model used and only depends upon the temperature variation in the rate of reaction. A mechanistic interpretation can initially be disregarded in its derivation. The activation energies found here are considerably different from that found for K:NMF (30 ± 3 kJ/mole), and indeed taking the stoichiometries of the materials into account, E_a values of ~ 30 and ~ 105 kJ per mole of NMF and DMSO, respectively, have been found. Thus, it is inherently unlikely that the rate-determining step is the same in both cases.

The crystal structure of a dickite:NMF intercalate has been determined (Adams, 1979a), and the hydrogen bonding parameters are known. Three O-H \cdots O hydrogen bonds of $\sim 2.95 \text{ \AA}$ exist between the kaolin layers and each NMF molecule. The enthalpy of formation of these bonds can be approximated (Pimentel and McClellan, 1960) as ~ -43 kJ/mole of NMF. This value

contains a large uncertainty, and it could well be in accord with the activation energy derived from the decomposition, i.e., 30 kJ/mole. A crystal structure study of a similar dickite:DMSO intercalate is in progress (Adams, 1979b), but the hydrogen bonding parameters have not been fully defined at present. If a bonding pattern exists that is similar to that found for the NMF intercalate, a similar enthalpy of formation for the triple O—H...O hydrogen bonds would result. In any case, it is unlikely that the hydrogen bonds would be shorter than 2.74 Å, which would increase the enthalpy of formation to ~-56 kJ/mole of DMSO (Pimentel and McClellan, 1960). This value is lower by a factor of two than that found in the present study for the activation energy. It would seem, therefore, that a naive model requiring the rate-determining step to be the freeing of single molecules of the organic species from their bonding to the clay layers is oversimplistic.

In general, it is exceedingly difficult to fit a mechanism to solid state reactions unless the reaction can be monitored by external means such as optical microscopy. Although the linearity of $\log(1 - \alpha)$ vs. t is compatible with a contracting-circle type mechanism (modified for exponential nucleation), the model has not been conclusively proved. Nevertheless, if this mechanism is correct, the values of k , used to determine E_a , are nucleation rate constants, and E_a is the activation energy required to form a nucleus of the product kaolin phase.

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Резюме—Изучалось термическое разложение каолинита:диметил сульфоксидных включений термогравиметрией. Разложение завершается при 175°C и имеет $\Delta H 58 \pm 5$ кдж/моль диметил сульфоксида. Для начальных 70-80% реакции график зависимости $\log(1 - \alpha)$ от времени является линейным, где α —завершенная доля реакции. С этой линейностью согласуется тип механизма двумерного сжимающегося круга при условии, что процесс образования ядер рассматривается как экспоненциальный, а не мгновенный. Была получена активационная энергия равная 105 ± 8 кдж/моль диметил сульфоксида. Эта величина не согласуется с простым предположением, что фаза, определяющая скорость реакции, это разрушение связей одианрных органических молекул со слоями глины. Механизм этого разложения отличается от механизма, найденного для каолинита:N-метил формамида, и активационная энергия значительно больше, чем для этого материала (30 ± 3 кдж/моль). [N. R.]

Resümee—Die thermische Zersetzung einer Kaolinit-Dimethylsulfoxid-Wechsellagerung wurde mittels Thermogravimetrie untersucht. Die Zersetzung ist bei 175°C vollständig und hat ein ΔH von 58 ± 5 kJ pro Mol Dimethylsulfoxid. Für die ersten 70 bis 80% der Reaktion ist die graphische Darstellung von $\log(1 - \alpha)$ gegen die Zeit linear, wobei α die vollständige Reaktion darstellt. Ein zweidimensionaler Mechanismus in der Art eines sich kontrahierenden Ringes geht mit dieser Linearität einher, vorausgesetzt der Keimbildungsprozeß verläuft eher exponential als plötzlich. Eine Aktivierungsenergie von 105 ± 8 kJ pro Mol Dimethylsulfoxid wurde abgeleitet. Dieser Wert stimmt nicht mit der einfachen Annahme überein, daß der geschwindigkeitsbestimmende Schritt die Freisetzung einzelner organischer Moleküle von ihrer Bindung an die Tonschichten ist. Der Mechanismus dieser Zersetzung unterscheidet sich von dem, der bei Kaolinit-N-Methylformamid gefunden wurde. Die Aktivierungsenergie ist beträchtlich größer als die für dieses Material (30 ± 3 kJ/Mol) gefundene. [U. W.]

Résumé—La décomposition thermique d'une kaolinite intercalate sulfoxyde diméthyl a été étudiée par thermogravimétrie. La décomposition est complète à 175°C et a un ΔH de 58 ± 5 kJ/mole de sulfoxyde diméthyl. Pour les premiers 70 à 80% de la réaction, le graphe de $\log(1 - \alpha)$ vis à vis du temps est linéaire, où α est la fraction de réaction complète. Un genre de mécanisme de cercle contractant, en deux dimensions, est consistant avec cette linéarité, à condition que le procédé de nucléation est considéré comme étant exponentiel plutôt qu'instantané. Une énergie d'activation de 105 ± 8 kJ/mole de sulfoxyde diméthyl a été dérivée. Cette valeur est contradictoire l'hypothèse que l'étape déterminant le taux est celle de la libération de molécules organiques simples de leurs liens avec les couches d'argile. Le mécanisme de cette décomposition est différent de celui trouvé pour la kaolinite:formamide N-méthyl, et l'énergie d'activation est considérablement plus élevée que celle trouvée pour cette matière (30 ± 3 kJ/mole). [D. J.]