KINETICS AND MECHANISM OF DEHYDROXYLATION PROCESSES, I. TEMPERATURE AND VAPOR PRESSURE DEPENDENCE OF DEHYDROX-YLATION OF KAOLINITE[1]

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Abstract

Isothermal measurements of the dehydroxylation of kaolinite at temperatures from 400–540°C and with controlled water vapor pressures from $<10^{-3}$ mm Hg to 175 mm Hg are shown to conform with a single curve of α (fraction reacted) versus t/t_{50}, where t_{50} is the time for 50 percent reaction. The curve agrees well with the supposition that the reaction is diffusion controlled rather than obeys first-order kinetics. The reaction rate constant depends on both the temperature and the ambient water vapor pressure. The activation energy, 51 kcal/mole at $<10^{-3}$ mm Hg, increases with vapor pressure, becoming 112 kcal/mole at 47 mm Hg. The rate constant diminishes with vapor pressure according to an equation of the type $\log (1 - k_p/k_0) = m + n \log P$, where m and n are temperature-dependent parameters, which is interpreted in terms of a partial coverage of the dehydroxylating surface by chemisorbed water molecules. The criteria for distinguishing first order kinetics from diffusion controlled reactions are reviewed critically.

Introduction

Although the kinetics of dehydroxylation of kaolinite, $Al_2Si_2O_5(OH)_4$, have been studied extensively, both by isothermal and by dynamic methods (*i.e.*, with progressively rising temperature), many basic problems remain, and particularly the role of the ambient vapor pressure. Many experiments have indicated that the water vapor generated by the reaction itself exercises a considerable influence on the reaction rate (Murray and White, 1949, 1955; Brindley and Nakahira, 1957a, b, 1958; Evans and White, 1958), so that loosely compacted samples and low reaction rates (the latter emphasized by Toussaint *et al.*, 1963) are important conditions for detailed work particularly with vapor pressures below about one atm. At higher vapor pressures, the dehydroxylation reaction rate is greatly reduced, the reaction temperatures are increased, and the activation energies increased (Stone and Rowland, 1955; Evans and White, 1958; Weber and Roy, 1965).

Even at low vapor pressures, less than 100 mm Hg, the effect on the

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dehydroxylation reaction is considerable. Holt, Cutler and Wadsworth (1962) appear to have been the first to vary the ambient vapor pressure in a controlled way and they concluded that at low pressures, < about 1 mm Hg, the reaction was diffusion controlled, but appeared to follow first-order kinetics above 4.5 mm Hg pressure. Toussaint, Fripiat and Gastuche (1963) also found first-order kinetics at vapor pressures in the range 0.8–11.2 mm. Hg and their studies were made at low reaction rates to avoid any vapor pressure build-up within the powder samples.

Much attention has been given to the kinetics of the reaction which most investigators have interpreted in terms of first-order kinetics (Murray and White 1949, 1955; Brindley and Nakahira, 1957, 1958; Kissinger, 1957; Toussaint et al., 1963). In most dynamic studies of the reaction, an equation of the type $-dc/dt = kc^n$, where $c =$ concentration of reactant at time t, $n =$ order of reaction, has been assumed and the results (either differential thermal analysis data or thermogravimetric data) analyzed to obtain n. Values of n ranging from < 1 to 3 have been obtained (Tsuzuki and Nagasawa, 1957; Weber and Roy, 1965). The validity of applying this equation to heterogeneous systems is dubious, although certain values of n (0, $\frac{1}{2}$, $\frac{2}{3}$, 1) have physical significance (Coats and Redfern, 1964). An equation of this type, however, is not applicable to diffusion-controlled, solid state reactions, except as a very poor approximation.

The present study was undertaken to reexamine the evidence for a diffusion-controlled mechanism at low vapor pressures and the first-order kinetics generally accepted at higher pressures. It was considered important also to explore more fully the vapor pressure dependence of the reaction at pressures below one atm and to elucidate the role played by water vapor in determining the reaction rate.

EXPERIMENTAL

The present experiments have been carried out mainly with a Florida kaolinite in which the only X-ray detectable impurity was a trace of quartz. Samples dried in vacuo at 100°C and then heated to 800°C showed a weight loss of 13.77 percent which agrees closely with the value 13.95 percent calculated for the ideal composition. The material has a surface area of 30 m²/g as determined by BET nitrogen adsorption. A few measurements have been made also with other kaolinites, from Georgia, British Guiana, and Yangambi (Congo).

The reaction has been followed gravimetrically under isothermal and isobaric conditions by using a silica spiral balance. The spiral was maintained at constant temperature in a thermostatically controlled, double-walled vessel independently of the temperature of the sample. The whole system could be evacuated to better than 10^{-5} mm Hg by means of a

two-stage mechanical pump, mercury diffusion pump and liquid nitrogen trap. Various pressures of water vapor were maintained in the reaction system by means of a water reservoir kept at various temperatures to produce saturated vapor pressures of 4.6, 14, 47, or 175 mm Hg. The lowest vapor pressure adjacent to the powder during a reaction cannot be as low as the best vacuum given by the pumps, but must be considerably less than 1 mm Hg as shown by the measured reaction rates; it is described as $<10^{-3}$ mm Hg. The furnace temperature was controlled and measured to $\pm 1°C$. A steady temperature was developed in the furnace before it was raised around the sample, which had previously been dried in vacuo overnight and then equilibrated for two hours with the desired water vapor pressure. Weight losses were measured with respect to the vacuum-dried sample. Samples of ap-
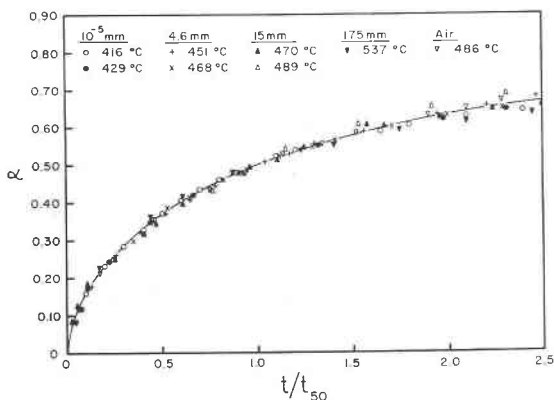

Fig. 1. Fraction reacted, α, versus t/t_{50}, reaction time with respect to the time for 50% reaction, for Florida kaolinite dehydroxylated at temperatures and vapor pressures indicated.

proximately 100 mg weight were used, mainly as thin layers of uncompacted powder in a hemispherical boat, or as a thin layer on a Pt foil deposited from a slurry.

RESULTS AND DISCUSSION

Standard representation of experimental data. The experimental results are presented by plotting α, the fraction of material reacted, versus a reduced time scale t/t_x, where t_x is the time to attain some convenient fraction x of total reaction; Holt *et al.* (1962) used $x=30\%$, Toussaint *et al.* (1963) used $x=70\%$; in the present work, t/t_{50} has been chosen for the time scale. Since the sample does not (and cannot) take up instantaneously the furnace temperature, the effective starting time has been obtained by plotting α^2 versus t, which is practically linear at the commencement of the reaction, and extrapolating back to $\alpha=0$. The correction to the time scale is practically negligible for slow reactions, $t_{50}>100$ min., but becomes appreciable for fast reactions, $t_{50}<30$ min.

Experimental data for a Florida kaolinite are shown in Figure 1 for temperatures ranging from 416 to 537°C, and water vapor pressures

from about 10^{-5} mm Hg to 175 mm Hg, and also normal atmospheric conditions. Similar results have been obtained for kaolinites from three other localities, and all the data conform to the same curve of α versus t/t_{50}.

It is concluded that, within the range of experimental conditions employed, *the same reaction mechanism is operative in all cases*; the differences noted by Holt *et al.* (1962) between reactions at higher and lower water vapor pressures are not confirmed.

The reaction mechanism. Holt *et al.* (1962) showed that the initial part of the α versus t curve at low vapor pressures was of the form

$$D_1(\alpha) = \alpha^2 = k_1 t, \tag{1}$$

a simple parabolic relation consistent with a diffusion process through an increasingly developing product layer. It follows directly from Fick's first law, that the rate of reaction $d\alpha/dt$ is inversely proportional to the thickness of the product layer and therefore proportional to $1/\alpha$. It may be applicable to the dehydroxylation of kaolinite if the reaction procedes mainly in a direction normal to (001). The crystal structure of kaolinite, however, suggests that diffusion may take place more readily parallel to the layers of the structure and in this case a cylindrical model with radial diffusion and constant flux of the diffusing species may be more appropriate. Holt *et al.* (1962) derived the equation

$$D_2(\alpha) = (1 - \alpha) \ln (1 - \alpha) + \alpha = k_2 t \tag{2}$$

The corresponding equation for a reacting sphere has been given by Valensi (1936), Ginstling-Brounshtein (1950), Moriya and Sakaino (1955), Carter (1961), and can be written,

$$D_3(\alpha) = (1 - 2\alpha/3) - (1 - \alpha)^{2/3} = k_3 t \tag{3}$$

In these equations, k_1, k_2 and k_3 are constants involving a diffusion coefficient which is treated as a material constant which does not change as the reaction proceeds. Although very different in analytical form, equations (1), (2) and (3) give similar variations of α with t/t_{50}. Figure 2 compares the calculated curves with representative experimental data taken from Figure 1.

Figure 2 includes also a curve based on first-order kinetics, represented by the equation:

$$F(\alpha) = - \ln (1 - \alpha) = kt \tag{4}$$

Numerical evaluations of these and other reaction equations have been given by Sharp *et al.* (1966).

The experimental data fall close to the curves given by equations (2) and (3), being nearer to curve $D_3(\alpha)$ for $t/t_{50} > 1$ and nearer to curve $D_2(\alpha)$ for $t/t_{50} < 1$, and obviously do not agree with the curve $F(\alpha)$ based on first-order kinetics.

It is concluded that the reaction does not follow first-order kinetics, but is controlled by a diffusion process. It is not possible to affirm whether the process is mainly two-dimensional or three-dimensional in character, since the curves given by equations (2) and (3) fall close together up to values of α of the order of 60–70 percent. The observed reaction rates fall well below both curves at higher values of α so that it is very doubtful
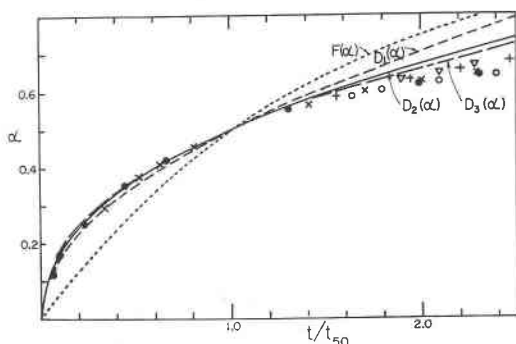

Fig. 2. Comparison of experimental data for dehydroxylation of Florida kaolinite (selected data taken from Fig. 1) with calculated curves given by equations (1)−(4) in the text.

if the material constants involved can remain unchanged as α tends to 100 percent.

In the subsequent discussion, rate constants will be calculated by utilizing equation (2) since the crystal structure and morphology of kaolinite suggest that the two-dimensional model is most appropriate.

Determination of rate constants and activation energies at different water vapor pressures. Experimental values of the function $D_2(\alpha)$, plotted against the time t, (Fig. 3), give straight lines from which the rate constants k_2 are obtained. These values vary with the absolute temperature T, at constant pressure p, and accordingly can be written $k_p(T)$. From the Arrhenius equation

$$k_p(T) = A_p \exp\left(-\Delta E_p/RT\right)$$

the plots shown in Figure 4 are obtained, the slopes of which give the activation energies ΔE_p listed in Table 1.
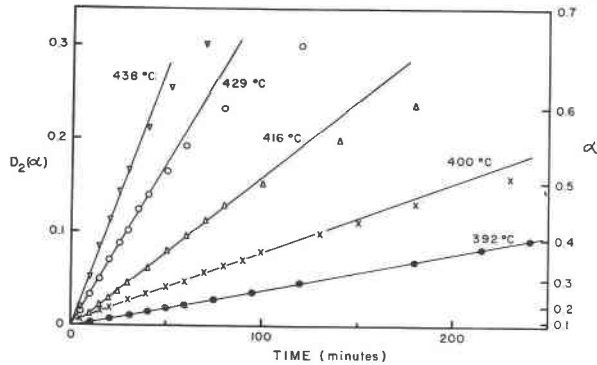
FIG. 3. Plots of $D_2(\alpha)$, (see equation 2), versus time t for dehydroxylation of Florida kaolinite at a pressure of $<10^{-3}$ mm Hg. Scale of α, fraction reacted, is given on the right.

When the function $D_1(\alpha)$, (see equation 1), is plotted against t, linear plots are again obtained, and lead to an activation energy of 50 kcal/mole for dehydroxylation in vacuo. This value is essentially the same as 51 kcal/mole shown in Table 1 and it agrees reasonably well with the value 43.5 kcal/mole determined by Holt *et al.* (1962), for a Georgia kaolinite heated in vacuo. This illustrates that the activation energies are insensitive to the particular diffusion model used.
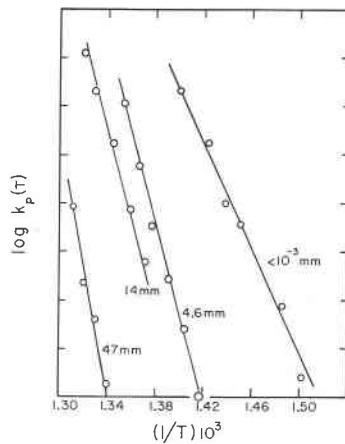

FIG. 4. Plots of log $k_p(T)$ versus $1/T$, $T=$ absolute temperature, for kaolinite dehydroxylated at water vapor pressures $<10^{-3}$ mm Hg, 4.6 mm Hg, 14 mm Hg, and 47 mm Hg.

TABLE 1. ACTIVATION ENERGIES FOR FLORIDA KAOLINITE DEHYDROXYLATED
AT VARIOUS WATER VAPOR PRESSURES

p_{H2O} (mm Hg)	Range of temperature (°C)	Activation energy (kcal/mole)
<10^{-3}	390–450	51
4.6	435–475	84
14	450–480	90
47	470–495	112

Dependence of reaction rate on water vapor pressure. The marked dependence of the reaction rate on vapor pressure is illustrated by calculating t_{50}, the time for 50 percent reaction, for various temperatures and pressures. For these calculations, the linear relations shown in Figure 4 are extrapolated where necessary. The results (Table 2) show, for example, that at a fixed temperature of 425°C, t_{50} increases by a factor of almost 3000 when the vapor pressure increases from <10^{-3} mm Hg to 47 mm Hg.

Following the work of Toussaint *et al.* (1963), plots of log $(1 - k_p/k_0)$ versus log P are shown in Figure 5 for two temperatures, 473°C and 496°C, where k_p and k_0 are reaction rates at pressures P and zero respectively. The observed values are represented approximately by linear relations of the type

$$\log(1 - k_p/k_0) = m + n \log P \qquad (5)$$

where the parameters m and n are temperature dependent. A simple interpretation of this equation can be given. If, at any temperature T and vapor pressure P, a fraction θ of the mineral surface is effectively blocked for the dehydroxylation process by a chemisorption of water

TABLE 2. TIME, IN MINUTES, TO PRODUCE 50 PERCENT DEHYDROXYLATION OF
FLORIDA KAOLINITE AT THE TEMPERATURES AND WATER
VAPOR PRESSURES SHOWN

p \\ T	400°C	425°C	450°C	475°C
<10^{-3} mm Hg	200	55	16	5
4.6 mm Hg	1.3×10^4	1,370	161	22
14 mm Hg	7.9×10^4	5,000	380	44
47 mm Hg	—	1.3×10^5	5,300	315

molecules such that $\theta = mP^n$, then the free surface is proportional to $(1-\theta)$. If the reaction rate at pressure P, k_p, is proportional to $(1-\theta)$, then it follows that

$$k_p = k_0(1 - mP^n) \tag{6}$$

from which equation (5) is immediately obtained.

The plots shown in Figure 5 extrapolate to $\log(1-k_p/k_0)=0$, or $k_p=0$, when $\log P \simeq 1.65$ or $P \simeq 45$ mm Hg. The experiments have shown that at temperatures of the order 470–500°C and vapor pressure of this order, the reaction rates are indeed very slow. Toussaint *et al.* (1963), obtained a similar plot for reactions at 431°C, which extrapolates to
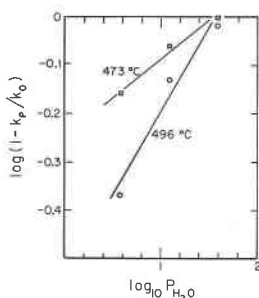

FIG. 5. log $(1-k_p/k_0)$, where k_p and k_0 are reaction rates at pressures p and zero, plotted against log p_{H_2O} in mm Hg for dehydroxylation of Florida kaolinite at 473 and 496°C.

$k_p=0$ at $P \simeq 17$ mm Hg though their rate constants were determined on the basis of first-order kinetics.

From the results it appears that the ambient vapor pressure controls the dehydroxylation reaction as a result of some kind of chemisorption reaction which restricts the effective dehydroxylation surface. Toussaint, Fripiat and Gastuche (1963) came to a somewhat similar conclusion, namely that "a water film probably operates as a diffusion barrier." At an earlier date Evans and White (1958), studying the dehydration and rehydration of bentonite and kaolinite, but mainly bentonite, in an atmosphere of steam, concluded that the retardation of the dehydration arose from a surface reaction, but the data then available were less quantitative than those now presented.

Attempts to extend the data beyond the limits shown in Figure 5 were not possible without considerable extrapolations of the linear plots in Figure 4. Some doubt remains, therefore, as to the linearity of the relation between $\log(1-k_p/k_0)$ and $\log P$. Current studies on the dehydroxylation of serpentine indicate that a corresponding diagram to Figure 5 can be

obtained with a wider range of the parameters involved. Further consideration of the pressure dependence of the dehydroxylation reaction will be deferred until the serpentine data become available.

Dehydroxylation kinetics of other kaolinites. As stated previously, the experimental values of α for four different kaolinites fit exactly the same curve of α versus t/t_{50} so that no difference in the basic mechanism is to be expected for different samples. The actual rate constants, however, can be expected to vary because k in equations (2) and (3) depends on $1/r^2$, where r is the radius of a particle. The Yangambi kaolinite used in the present work has a surface area of about 42 m^2/g and reacts faster than the Florida kaolinite with an area about 30 m^2/g, but precise comparisons involve the size and shape of the particles and so far have not been found feasible.

CONCLUSIONS

The dehydroxylation of kaolinite in the temperature range 400–540°C and in water vapor atmospheres from $<10^{-3}$ mm Hg to 175 mm Hg is a diffusion controlled process. The temperature dependence of the reaction under constant vapor pressure follows an Arrhenius type expression, $k_p(T) = A_p \exp(-\Delta E_p/RT)$, in which both A_p and ΔE_p vary with pressure P; ΔE is 51 kcal/mole at $<10^{-3}$ mm Hg, and increases to 112 kcal/mole at 47 mm Hg vapor pressure. The pressure dependence of the reaction at constant temperature is expressed by the equation $\log (1 - k_p/k_0) = m + n \log P$, where m and n are temperature-dependent parameters. The reaction depends not only on processes within the crystalline material, but also on the interaction with the surrounding atmosphere. The behavior of the surface is considered to play an important role in the overall reaction.

ACKNOWLEDGMENTS

APPENDIX

Differentiation of first-order kinetics from diffusion-controlled processes. It is pertinent to enquire why many investigators have concluded that the dehydroxylation reaction follows first-order kinetics if, as the present results indicate, it is mainly a diffusion-controlled

process. The main evidence has consisted in the linear or nearly linear relation found between log $(1-\alpha)$ and the time t. If values of α calculated from the diffusion equation (2) are plotted in the form of log $(1-\alpha)$ versus t (Fig. 6), an approximately linear plot is obtained over a considerable range of the diagram, and this linear approximation extrapolates to a value of $(1-\alpha)$ of about 0.8 when $t=0$. This result was indeed obtained much earlier by Dünwald and Wagner (1934) who showed that the diffusion equations could be expressed approximately in the form

$$-\ln (1 - \alpha) = k_0 + kt$$

for the values of t sufficiently large. The calculations give extrapolated values of $(1-\alpha)$ at $t=0$ equal to 0.80, 0.70, and 0.60 for diffusion processes respectively in one, two, and three dimensions. Later work by Serin and Ellickson (1941) and by Fripiat (1964) has led to similar conclusions. The previous experimental data of Brindley and Nakahira (1957, 1958)
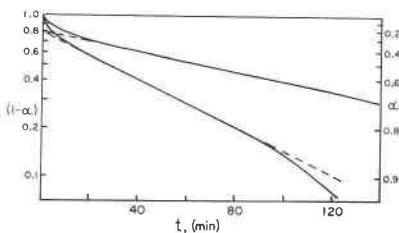

Fig. 6. $(1-\alpha)$ on a logarithmic scale plotted againt t (time for a reaction following the diffusion equation (2). Observe that over the range $\alpha=0.2$ to $\alpha=0.8$, the curves become nearly linear and that the linear portions can be extrapolated back to $(1-\alpha)\simeq0.8$ at $t=0$. The diagram shows how easily a diffusion-controlled reaction may be confused with a first-order reaction, for which log $(1-\alpha)=-kt$.

were exactly of this kind. It is important, then, to observe that the full criterion for first order kinetics is that log $(1-\alpha)$ should vary linearly with t, and should pass through the point $\alpha=0$ at $t=0$. Determining the effective starting time of the reaction is obviously important to check this criterion.

Although much of the earlier work in which first-order kinetics were deduced was carried out with conditions that were not favorable for evaluating the basic mechanism, such as large samples and no vapor pressure control, not all the evidence can be regarded in this way. The work of Toussaint, Fripiat and Gastuche (1963) which gave results consistent with first-order kinetics, was undertaken with a good appreciation of the necessary precautions; they controlled the ambient vapor pressure and used slow reaction rates, but their samples (cylinders about 10.6 mm tall and 7.4 mm diameter, weighing about 400 mg) were considerably larger than those used in the present studies (uncompacted layers about 1–1.5 mm thick and weighing about 100 mg). No satisfactory explanation can be suggested for the differences between their results and those presented here.

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