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KINETICS AND MECHANISM OF DEHYDROXYLATION PROCESSES: II. TEMPERATURE AND VAPOR PRESSURE DEPENDENCE OF DEHYDROXYLATION OF SERPENTINE

G. W. Brindley, B. N. Narahari Achar and J. H. Sharp,[1] *Materials Research Laboratory, and Department of Geochemistry and Mineralogy, The Pennsylvania State University, University Park, Pennsylvania.*

Abstract

Measurements of the dehydroxylation of a nearly pure serpentine from Cardiff, Md., at constant temperature in the range 630–770°C, and constant water vapor pressure in the range $<10^{-3}$ to 47 mm Hg, agree well with a single curve when the fraction α of material reacted is plotted against t/t_{50}, where t is reaction time, and $t_{50}$is the time for 50% of complete reaction. The form of the curve α *vs* t/t_{50} is consistent with a diffusion-controlled mechanism for the reaction. Under isobaric conditions, the *apparent* activation energy of the reaction ranges from 68 kcals/mole at $<10^{-3}$ mm Hg to about 120 kcals/mole at 47 mm Hg. This large variation reflects the retardation of the reaction even in quite low pressures of water vapor. The vapor pressure dependence of the reaction at constant temperature is interpreted in terms of a fractional coverage, θ, of the reacting surface by chemisorbed water, given by $\theta = mP^n$ where m and n are temperature dependent parameters. Values of θ range from near zero at $P=10^{-3}$ mm Hg and $T=630$–700°C, to 0.95 at $P=47$ mm Hg and $T=636$°C.

Introduction

In Part I of this study (Brindley, Sharp, Patterson and Achar, 1967), the dehydroxylation of a fine-grained Florida kaolinite, with surface area 30 m^2/g, determined by the Brunauer, Emmett and Teller nitrogen adsorption method, was shown to follow a diffusion-controlled reaction mechanism throughout the ranges of temperature (400–500°C) and water vapor pressure ($<10^{-3}$-175 mm Hg) employed. The very sensitive dependence of the reaction on water vapor pressure was interpreted in terms of a fractional coverage of the surface by chemisorbed water. Subsequent experiments (Brindley and Millhollen, 1966) have shown directly that when the surface of a kaolinite powder, dehydroxylating in vacuo at a suitable constant temperature, is effectively covered by approximately a monolayer of chemisorbed water by introducing water vapor of controlled pressure into the reaction vessel, the dehydroxylation is completely halted; when the chemisorbed layer is removed by re-evacuation, the dehydroxylation continues normally along the same kinetic curve from the stage where it had previously been halted.

The present study provides kinetic data for the dehydroxylation of serpentine in relation to temperature and water vapor pressure. Al-

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[1] Present address: Dept. of Ceramics, University of Sheffield, Sheffield, England.

though the dehydroxylation and recrystallization of several forms of serpentine have been studied from a structural (crystallographic) standpoint (Brindley and Zussman, 1957; Ball and Taylor, 1963; Brindley, 1963; Brindley and Hayami, 1964, 1965) little attention has been given to the kinetics of the process. Weber and Greer (1965) studied the dehydroxylation of thirty-three serpentine samples in water vapor atmospheres of about 1 atm. pressure by differential thermal analysis and derived values for a kinetic parameter n in the empirical kinetic equation, $-dc/dt = kc^n$, where c = 'concentration' of reactant at time t and k = rate constant. They found values of n ranging 0.2–1.6 for fibrous varieties of serpentine (chrysotiles), and 0.4–2.2 for materials described as antigorite and/or lizardite. No theoretical significance can be attached to these widely ranging values of n and the validity of using this type of equation for solid state reactions is open to serious criticism (Brindley, Sharp and Achar, 1965), although certain values of n ($n=0$, 1/2, 2/3, 1) may be given a theoretical justification (Coats and Redfern, 1963, 1964). A particular disadvantage is that diffusion-controlled reactions cannot be expressed in the form $-dc/dt = kc^n$.

The present experiments are similar to those described in Part I and readers interested in further details should consult Part I.

EXPERIMENTAL RESULTS

Material used. The mineral studied is a dark green, massive sample from Cardiff, Md., containing no impurities detectable by X-ray diffraction but with a small proportion, probably $\ll 1\%$, of a fibrous material, probably chrysotile, seen in electron micrographs. The bulk of the material appears to be lizardite rather than antigorite or any other modification. The weight loss on ignition in air was 12.65% which is slightly less than the 'water' content derived from the ideal formula, $Mg_3Si_2O_5(OH)_4$ or $3MgO \cdot 2SiO_2 \cdot 2H_2O$, namely 13.04%. Chemical analysis (R. T. Greer, analyst) gave 3.30% FeO, 2.73% Fe_2O_2 in the serpentine used. The substitution of Fe for Mg in the serpentine formula could lead to an expected weight loss of 12.70%, in agreement with the observed value.[1]

Sample preparation. Experiments were carried out with powders of −60, +80 mesh particle size; photomicrographs showed well-sized an-

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[1] The oxidation of hydrous silicates containing ferrous iron may proceed by two mechanisms, namely, (1) $2Fe^{2+} + (1/2)O_2 \rightarrow 2Fe^{3+} + O^{2-}$, with *gain* of weight by addition of oxygen to the structure, and (2) $2\ Fe^{2+} + 2(OH)^- + (1/2)O_2 \rightarrow 2Fe^{3+} + 2O^{2-} + H_2O$, with slight *loss* of weight by removal of 2H. In both cases, the change in formula weight by the presence of Fe in place of Mg must be considered. The value 12.70% is based on reaction (2) with the assumption that *all* the iron is present in the structure as Fe^{2+} replacing Mg^{2+}. More complex replacements are possible, giving different calculated values for the ignition loss.

gular particles of about 0.18–0.20 mm size. Measurements were made initially on powders which subsequently were suspected to contain a much finer component and this was verified by electron micrographs; much of this fine material was removed by water elutriation.

Kinetic data. Using the silica spiral microbalance described in Part I, and with samples of 50–100 mg loosely distributed on the sample pan, data were recorded for the fraction of material reacted, α, as a function of time t, for various isothermal and isobaric conditions. The observed data for all experimental conditions fit closely to a single curve of α versus t/t_{50}, (t_{50} = time for 50% of complete reaction), as shown in Figure 1. The curves marked $D_3(\alpha)$ and $F(\alpha)$ in Figure 1 correspond to the equations

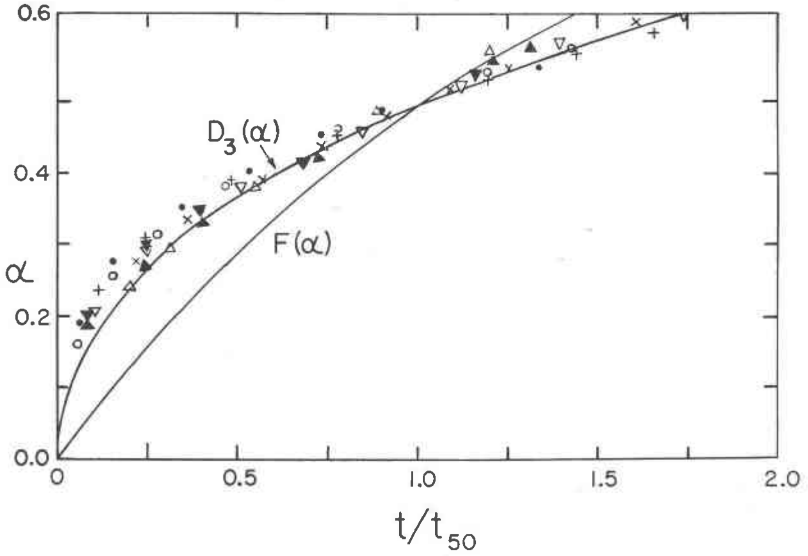

FIG. 1. Experimentally determined values of α, fraction of material reacted, versus t/t_{50} where t = reaction time and t_{50} = time for 50% reaction. Only a small fraction of experimentally determined values are shown in order to avoid confusion. Curves $D_3(\alpha)$ and $F(\alpha)$ are calculated (see text). The various symbols used correspond to different constant values of T and P (see Fig. 2).

$$D_3(\alpha) = 1 - 2\alpha/3 - (1 - \alpha)^{2/3} = k(P, T)\cdot t$$

and

$$F(\alpha) = -\ln(1 - \alpha) = k(P, T)\cdot t$$

and relate respectively to reactions controlled by three-dimensional diffusion in spherical particles, and reactions following first-order kinetics (see Part I).

The observed data fall close to curve $D_3(\alpha)$, which is consistent with the reaction being diffusion controlled. In the early stages, the reaction proceeds somewhat faster than is indicated by the curve and this could very well arise from the presence of unremoved fine particles and from irregularities (sharp edges and corners) on the particles. This effect was more noticeable before most of the fine particles were removed by elutriation.

Rate constants were obtained from nearly linear plots of $D_3(\alpha)$ versus t (see Figure 2); the linearity is maintained to $\alpha \simeq 60\%$.

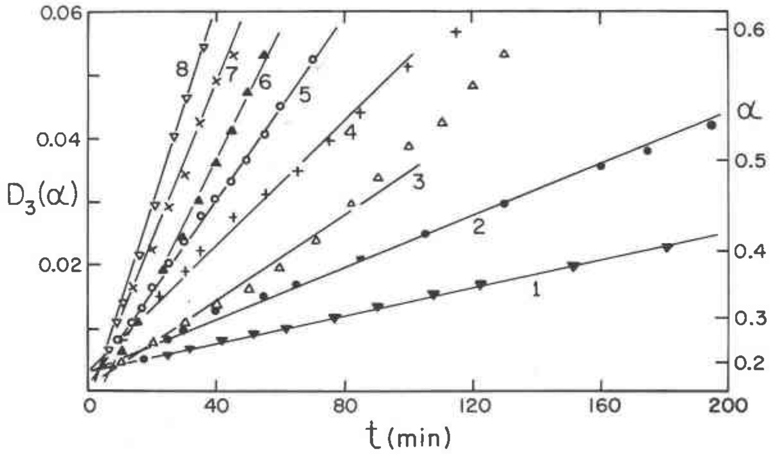

FIG. 2. Experimentally determined values of $D_3(\alpha)$ versus t for the following conditions: (1) 654°C, 30 mm Hg. (2) 632°C, $<10^{-3}$ mm Hg. (3) 675°C, 47 mm Hg. (4) 664°C, 4.6 mm Hg. (5) 667°C, $<10^{-3}$ mm Hg. (6) 693°C, 47 mm Hg. (7) 683°C, 4.6 mm Hg. (8) 694°C, 30 mm Hg. A scale of α values is given on the right of the figure.

Temperature dependence of the reaction at constant vapor pressure. Plots of log $k_P(T)$ versus $1/T$, (T = absolute temperature), are linear (see figure 3) in accordance with an Arrhenius equation,

$$k_P(T) = A_P \exp(-\Delta E_P/RT) \tag{1}$$

where suffix P indicates values relating to a water vapor pressure P. Values of ΔE_P and A_P are listed in Table 1 for various values of T. Preliminary data obtained with non-elutriated powders gave similar values for these parameters so that it is justifiable to consider that the results are not dependent on the presence of residual fine-grained powder. The values of ΔE_P are considered accurate to ± 3–5%, with the lower accuracy at the higher vapor pressure.

TABLE 1. CONSTANTS IN THE FORMULA $k_P(T)=A_P\cdot\exp(-\Delta E_P/RT)$

Vapor Pressure P (mm Hg)	log A_P	ΔE_P (kcal/mole)
$<10^{-3}$	12.7_0	68
1.2		89[a]
4.6	17.9_5	96
12.0		105[a]
30.	24.6	115
47.	23.1	120

[a] Nonelutriated samples.

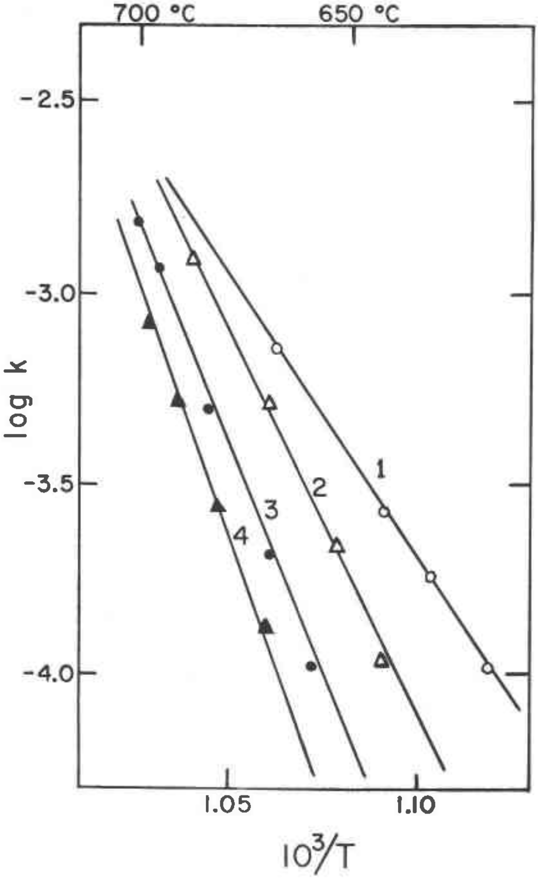

FIG. 3. Values of log k versus reciprocal of absolute temperature for elutriated serpentine, at constant water vapor pressures as follows: (1) $<10^{-3}$ mm Hg. (2) 4.6 mm Hg. (3) 30 mm Hg. (4) 47 mm Hg.

Vapor pressure dependence of the reaction at constant temperature. From the isobaric plots given in Figure 3, the rate constants $k_T(P)$ can be read for various vapor pressures P at particular temperature T. The restricted temperature range over which k can be measured for any given value of P requires extrapolations of the linear plots in Figure 3. In this way, values of $k_T(P)$ have been obtained for $T=636$, 657, 679 and 698°C and $P<10^3$, 4.6, 30, and 47 mm Hg.

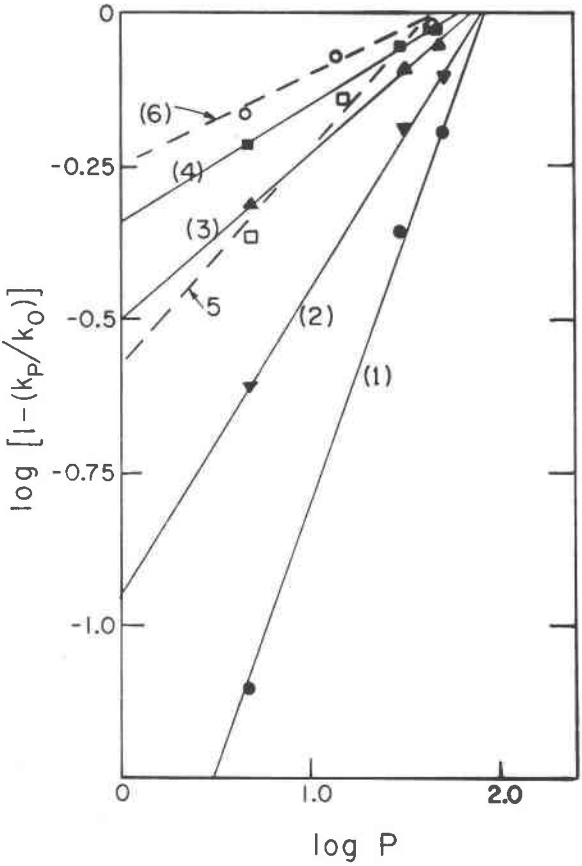

FIG. 4. log $[1\text{-}k_P/k_0]$ versus log P. Solid symbols for serpentine at temperatures (1) 698°C, (2) 679°C, (3) 657°C, (4) 636°C. Open symbols and dashed lines give data for kaolinite at temperatures (5) 496°C, (6) 473°C, (see Part I).

As in Part I, the vapor pressure dependence of $k_T(P)$ is attributed to a fractional coverage θ of the surface by chemisorbed water, expressed in

TABLE 2. CONSTANTS IN THE FORMULA $k_T(P)=k_T(vacuo)(1-mP^n)$, WITH P IN MM Hg

T, °C	log m	n	P_{max} (mm Hg) for $mP^n=1$
636	−0.320	0.177	63
657	−0.500	0.272	69
679	−0.930	0.495	76
698	−1.690	0.883	81

the form mP^n. If $k_T(P)$ is proportional to $(1-\theta)$, then the following equation can be written:

$$k_T(P) = k_T(vacuo)(1 - mP^n) \tag{2}$$

or

$$\log [1 - k_T(P)/k_T(vacuo)] = \log m + n \log P \tag{2a}$$

Figure 4 shows that the experimental data agree well with a straight line relation of the type expressed by equation (2a). Values of log m and of n are given in Table 2. Extrapolation of the straight lines shown in Figure 4 to zero value of log $[1-k_T(P)/k_T(vacuo)]$ corresponds to $k_T(P)=0$ and $\theta=1$. The corresponding values of P, called P_{max}, are listed in Table 2 and are the water vapor pressures at which the reaction rate is zero and there is a complete surface coverage by chemisorbed water.

Table 3 lists values of θ calculated for T and P values for which m and n have been determined. One sees that at $P=10^{-3}$ mm, the surface coverage θ is always small, particularly when $T\geq 657$°C. On the other hand, when $P=47$ mm Hg, the surface coverage ranges from about 95–60% over the temperature range covered. The *apparent* activation energy of 120 kcal/mole is greatly increased because of this high coverage, which is variable with temperature.

TABLE 3. VALUES OF SURFACE COVERAGE $\theta=mP^n$, CALCULATED FROM THE EXPERIMENTALLY DETERMINED m AND n VALUES

P, mm Hg / T, °C	10^{-3}	4.6	30	47
636°	0.141	0.627	0.873	0.946
657°	0.048	0.478	0.796	0.902
679°	0.004	0.216	0.547	0.684
698°	0.00005	0.079	0.412	0.617

DISCUSSION

Equations (1) and (2) expressing respectively the reaction rate with respect to temperature at constant vapor pressure, and to vapor pressure at constant temperature, can be combined as follows: In equation (2), the quantity expressed as $k_T(vacuo)$ can be written $A_0 \exp(-\Delta E_0/RT)$ where the zero suffix refers to vacuum conditions, and equation (2) then becomes:

$$k(T, P) = A_0[\exp(-\Delta E_0/RT)](1 - mP^n) \tag{3}$$

In this equation, the independent variables T,P are not separable because m and n are markedly dependent on T. From a comparison of equation (3) with equation (1), which can be written

$$k(P, T) = A_P[\exp(-\Delta E_P/RT)], \tag{4}$$

one might expect to find a relation between ΔE_P, ΔE_0 and the parameters m and n, i.e., to relate the increase in *apparent* activation energy, $(\Delta E_P - \Delta E_0)$, to m and n. So far, no useful relation of this kind has been derived, but nevertheless it is clear that the marked increase of ΔE_P with P shown in Table 1 arises from parameters m and n. An important practical corollary from these results is that activation energies of dehydroxylation reactions measured under the water vapor pressures present in normal open air conditions have very little value. The effect of the ambient water vapor pressure will not become negligible unless it is reduced to values considerably below 0.1 mm Hg.

The achievement of this low vapor pressure within the interstices of a powder producing water vapor by its own dehydroxylation is probably nearly impossible. Small samples loosely compacted and reacted at low rates of reaction in a system with a high rate of evacuation will provide optimum conditions. Figure 4 shows, by dashed lines, the experimental data for kaolinite and it is apparent that the dehydroxylation rate constants for both minerals vary with pressure in a similar manner.

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