Journal of Thermal Analysis, Vol. 5 (1973) 5—17

THERMAL REACTIONS OF INORGANIC HYDROXY-COMPOUNDS UNDER APPLIED ELECTRIC FIELDS, I

DEHYDROXYLATION OF KAOLINITE

K. J. D. MacKenzie*

Department of Ceramics, University of Sheffield, Sheffield, England

(Received March 18, 1971; in revised form November 9, 1971)

A method which has been developed for thermogravimetric study of solids in the presence of applied electric fields has been used in a study of kaolinite dehydroxylation in a controlled inert atmosphere. Electric fields of $\sim 10^5$ V/m lower the initiation temperature for dehydroxylation by as much as 60° in some cases; the activation energy for dehydroxylation is reduced by 3—12 kcal/mole. The rate constants for electrolysed samples (based arbitrarily on a first-order law) are increased by electrolysis but this effect falls off at higher temperatures as the normal thermal processes begin to predominate. The effect of the field on the various processes of ionic migration in the lattice is discussed.

In previous papers [1, 2] it has been shown qualitatively that the application of an a.c. or d.c. electric field to hydroxyl-containing solids such as kaolinite [$Al_2Si_2O_5(OH)_4$] above the dehydroxylation temperature results in an enhancement of the high-temperature reactions and a significant improvement in the physical and crystallochemical properties of the product at a given temperature. In the case of the applied d.c. field these results have been attributed to the removal of residual protons present in kaolinite even after dehydroxylation is substantially complete [1]. The operation of such a proton-elimination mechanism during the high temperature reactions suggests that electrolysis of inorganic hydroxyl-containing solids at lower temperatures might also influence the course of their dehydroxylation reactions.

The purpose of this work was to investigate the manner in which d.c. electric fields interact with solids during their thermal dehydroxylation. The course of the dehydroxylation reaction was followed directly by weight-loss measurements made during the electrolysis. Although this was not primarily a kinetic study, a kinetic analysis was made of the resulting weight-loss curves since this was the most convenient means of comparing the behaviour of the electrolysed solid hydroxides with the unelectrolysed control samples.

Previous TG kinetic investigations of kaolinite dehydroxylation have often resulted in differing conclusions; earlier workers generally interpreted their weight-loss data in terms of first-order kinetics [3, 4] which were taken to indicate a random nucleation process. More recent work in vacuo [5, 6] and controlled

---

* Present address: Chemistry Division, D.S.I.R., Gracefield, Wellington, New Zealand.

water vapour atmospheres [6] has established that the kinetic results correspond more closely to a diffusion controlled equation although the fitting of kinetic data to any one model is hampered by particle size distribution in the sample, which in one case has led to a suggested pseudo-phase-boundary controlled mechanism [7]. The apparent activation energy for kaolinite dehydroxylation is also known to depend on the reaction conditions, increasing with an increase in water vapour partial pressure [6]. Another difficulty in making meaningful kinetic measurements on kaolinite arises from the observation by Garn and Anthony [8] that traces of CO and CO_2 are evolved from kaolinite during the early stages of dehydroxylation in a self-generated atmosphere; mass spectrometry has shown however that these gases are not evolved during decomposition in vacuo (MacKenzie, unpublished results), suggesting that they result from oxidation of trace organic impurities. These impurity gases should therefore not interfere with reactions carried out in carefully controlled non-oxidising atmospheres such as those used in the present study.

No attempt has been made in this work to extract mechanistic information from the kinetic analyses, in view of the well known unreliability of the procedure. The present activation energies and pre-exponential factors were derived solely as a means of comparing the progress of the reaction when performed under standard conditions of sample geometry, reaction atmosphere and heating rate but differing electrolysis procedures. Additional information about the electrolysis mechanisms was obtained from X-ray and i.r. examination of the solid reaction products.

Experimental

a) Materials

The kaolinite used in this work was a Cornish China clay, described in detail elsewhere [1]. Pellet samples 7.5 mm dia. by 4.0 mm thick were prepared from a stiff paste mixed with distilled water. The pellets were dried at 50° and the faces trued up with a scalpel before being clamped in the electrolysis cell.

b) Electrolysis experiments

Weight-loss measurements were made in the presence of an electric field in a cell designed specifically for use with thermobalances such as the Stanton TR – 1 which employs a loading platform. The sample is clamped securely between platinum foil electrodes in a stainless steel jig (Fig. 1). The platinum lead-out wires are brought out of the furnace through an alumina thermocouple sheath to prevent shorting. Outside the hot zone, the platinum leads are connected to copper wires which are heavy enough to carry the required current (about 8 mA) but fine enough to minimise the damping effect on the balance mechanism. This cell can also be used to make simultaneous conductance and weight-change measurements.

All the TG runs were made in a flowing atmosphere of dried argon (300 ml/min.) to protect the cell from corrosion at higher temperatures and establish a reproducible non-oxidising atmosphere of controlled composition.

Although kinetic weight-loss measurements of this type should ideally be made under isothermal conditions in vacuo, difficulties associated with the electrolysis experiment made this impracticable. However, since previous kinetic studies on kaolinite in vacuo [5] and in dry inert (helium) flowing atmospheres [7] have yielded activation energies in excellent agreement, the use of a dried argon flowing atmosphere in the present study is considered to provide reaction conditions comparable to those of reaction in vacuo. Moreover, since all the samples were reacted under identical atmospheric conditions, any observed differences in activation energy should be due solely to differences in the electrolysis procedures.

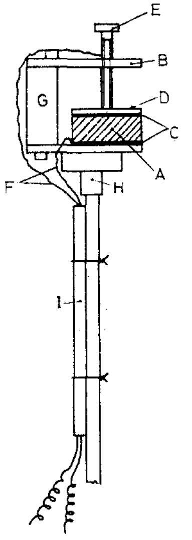


Fig. 1. Electrolysis cell for use with platform-loading thermobalances. A. Pellet sample, B. Stainless steel jig, C. Platinum foil electrodes, D. Stainless steel tension block, E. Stainless steel tension screw, F. Platinum lead-out wires, G. Alumina spacer, H. Thermobalance platform, I. Insulating sheath for lead-out wires

The samples were heated at a constant linear temperature rise of 2°/min.; although isothermal kinetic measurements are usually preferred since they eliminate the temperature gradient which is always present in a sample under dynamic heating conditions, it has been shown that for other oxide systems [9] kinetic parameters obtained under dynamic conditions are in good agreement with isothermal results, provided the heating rate is sufficiently slow. In this work the difficulty of reproducing exactly the electrical contact in a given set of isothermally heated kinetic samples was considered to outweigh any advantages inherent in the isothermal method.

The electrolysing potential (400 V d.c.) was obtained from a Labgear type D4019/8 stabilized E.H.T. unit delivering up to 2 kV. Experiments were made in which the electrical polarity was applied both in the direction of the gas flow and in the opposite direction. In other experiments the effect of starting the electrolysis at various temperatures was studied. Control experiments were also made in which pellet and powder samples were heated without electrolysis both in the cell and in crucibles.

c) X-ray and i.r. examination of the solid product

After reaction, both faces of each pellet were X-rayed in a Philips diffractometer using Cu Kα radiation. Small scrapings were taken from each pellet face, ground under isopropyl alcohol, suspended in KBr discs and analysed by an i.r. frequency shift method [10] using a Perkin – Elmer 337 spectrophotometer.

Results

Plots of the fraction of kaolinite reacted (α) as a function of temperature are shown in Fig. 2, from which it is seen that although the electrolysed samples begin to dehydroxylate at slightly lower temperatures than the unelectrolysed samples, all the curve shapes are broadly similar, suggesting that the reaction mechanism is probably unchanged by electrolysis.

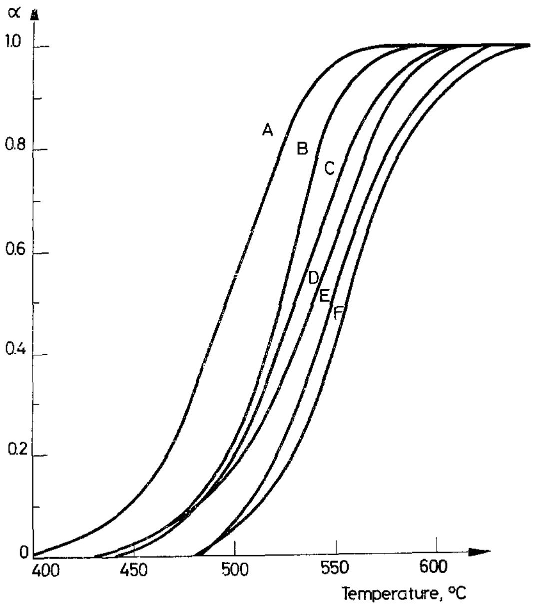


Fig. 2. Graphs of fraction of kaolinite reacted (α) as a function of temperature. Description of samples A to F as given in Table 1

The data of Fig. 2 were analysed by the method of Coats and Redfern [11] using a computer programme to solve the equation for orders of reaction (*n*) of 0.5, 0.67, 1.0 and 2.0, corresponding to various solid state reaction models. Data were also computed according to a parabolic (diffusion-controlled) law.

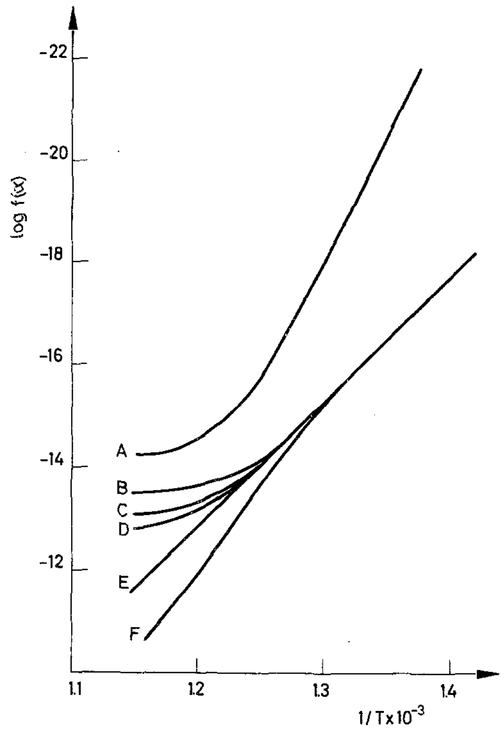


Fig. 3. Plots of $f(\alpha)$ vs. reciprocal temperature for kaolinite kinetic data, computed by the Coats and Redfern equation for various values of n. A. Diffusion-controlled equation, B. Zero-order reaction ($n = 0$), C. Two-dimensional interface model ($n = 0.5$), D. Three-dimensional interface model ($n = 0.66$), E. First-order reaction ($n = 1$), F. Second-order reaction, no physical significance ($n = 2$)

The best straight line for all the data is given by $n = 1$ although none of the equations is valid over the whole reaction (Fig. 3). The fit of the data to first-order kinetics, at least up to $\alpha = 0.85$, cannot be taken as confirmation of a random nucleation mechanism however, since almost as good a straight line is given by $n = 2$, an equation which has no physical meaning in solid state reactions.

The first-order kinetic law was arbitrarily assumed for the purpose of calculating activation energies and pre-exponential factors, shown in Table 1.

The reproducibility of the activation energies under given conditions was within 0.3 kcal/mole. Although activation energies for kaolinite dehydroxylation

Table 1

Kinetic parameters derived from a first-order model and i.r. analyses for electrolysed and unelectrolysed kaolinite samples

Sample geometry	Reaction conditions	Direction of gas flow	Activation energy ΔH, (kcal/mole)	Pre-exponential factor, A	Degree of high-temperature reaction (i.r.), %.	
					+ve face	−ve face,
Pellet (A)*	400 V applied at 20°C	−ve to +ve	39.8	1.26×10^5	9.5	0
Pellet (C)	400 V applied at 400°C	−ve to +ve	44.8	3.98×10^5	11.0	1.5
Pellet (B)	400 V applied at 20°C	+ve to −ve	47.0	8.71×10^6	8.5	0
Pellet (D)	400 V applied at 400°C	+ve to −ve	38.0	1.78×10^4	8.5	8.0
Pellet	Unelectrolysed, in cell	—	50.3	1.99×10^7	11.5	
Pellet (E)	Unelectrolysed, in crucible	—	50.0	1.70×10^7	8.0	
Powder (F)	Unelectrolysed, in crucible	—	50.0	1.99×10^7	11.0	

* Letters refer to the kinetic curves of Fig. 2.

Table 2

Average values of first-order rate constants for electrolysed and unelectrolysed kaolinite pellets

Temperature, °C	k_1 (electrolysed), min^{-1}	k_1 (unelectrolysed), min^{-1}
462	1.06×10^{-7}	2.57×10^{-8}
484	2.34×10^{-7}	6.92×10^{-8}
508	5.63×10^{-7}	1.95×10^{-7}
533	1.26×10^{-6}	5.37×10^{-7}
567	3.79×10^{-6}	1.95×10^{-6}

are extremely dependent on the water vapour concentration of the surrounding atmosphere, the values of Table 1 are all of the order of activation energies determined at low water vapour pressures by previous workers [5–7]. The activation energies and pre-exponential factors for the electrolysed samples are, however, consistently lower than for unelectrolysed samples, reflecting the tendency of the reaction to proceed over a wider temperature range in the presence of an electric field. The difference in activation energy between the electrolysed and unelectrolysed sample ranges between 3.0–12.0 kcal/mole with an average value of 7.5 kcal/mole.

The first-order reaction rate constants derived from the weight-loss measurements are shown in Table 2, from which it is seen that at all temperatures the application of a field increases the rate of reaction. The average increase in rate falls off at higher temperatures however, as shown by a plot of k_1 (electrolysed)/k_1 (unelectrolysed) vs. temperature (Fig. 4).

X-ray examination of each pellet face showed that complete dehydroxylation had occurred in every case. No trace of the high temperature product mullite ($3Al_2O_3 \cdot 2SiO_2$) was apparent in any of the samples although the i.r. results of Table 1 show that in some cases the aluminium–oxygen and silicon–oxygen structure has progressed towards the atomic configuration of the high-temperature phase. Marked differences were recorded in the i.r. results at the opposite ends of those pellets which had been electrolysed while being heated to the reaction temperature. The prolonged electrolysis time apparently promotes a polarization effect similar to that observed in electrolysed kaolinite at higher temperatures [1] but in the present case the direction of the asymmetry seems to depend as much on the direction of the gas stream as on the polarity of the electric field, as might be expected for a reaction in which a gaseous product is evolved.

Discussion

Two alternative types of process have been postulated for the removal of hydroxyl water from kaolinite. The essential feature of the first, known as the homogeneous mechanism, is a loss of water more or less uniformly from all parts of the crystal [12]. The alternative process (the inhomogeneous mechanism) involves an initial migration of protons to regions of the crystal from which water is later lost, concomitant with a counter-migration of aluminium and silicon ions to "acceptor regions" which later segregate into aluminium-rich and silicon-rich areas, becoming Al–Si spinel and cristobalite respectively [13]. More recently, Rouxhet et al. [14] have suggested that a clear-cut distinction between the two mechanisms might not be meaningful since the preservation of a topotactic relationship between reactant and product (usually taken as evidence for the inhomogeneous mechanism) may not reflect the fundamental processes of dehydroxylation. Likewise, kinetic studies, which are often used to interpret dehydroxylation processes do not provide precise mechanistic information because of their inability to distinguish between different models [15]. Little significance should therefore be placed on the fact that the reaction apparently obeys first-order kinetics in the present study, not only because of the inherent uncertainty of the mechanistic interpretation but also because the pellet-like geometry imposed on the sample by the requirements of the electrolysis experiment is non-ideal from the point of view of kinetic measurements.

In view of the foregoing, the more significant results are the activation energies calculated arbitrarily from the first order law; in the unelectrolysed samples these energies are independent of sample geometry (Table 1). The average reduction o 7.5 kcal/mole in the activation energies of the electrolysed samples suggests that whatever the rate-determining process, the migrating species involved must be charged. The nature of the various possible diffusing species and their interaction with an electric field should therefore be considered.

The most mobile of the possible diffusing species is the proton, which has already been suggested as the principal charge transfer agent in the high temperature electrolysis of kaolinite [1]. The mobility of this species has been ascribed to its ability to tunnel through potential energy barriers in the lattice; the jump frequency ν of protons between two P.E. wells has been estimated from i.r. measurements on micas as about $10^{9}-10^{11}$ sec^{-1} [14]. Under the influence of a uniform field E the mean drift velocity Ω of the proton is given by:

$$\Omega = \frac{E e \nu a^2 c}{kT} \exp\left(-Uo/kT\right) \tag{1}$$

where a is the jump distance, Uo the barrier height and c is a constant, taken as ≈ 10 for ionic crystals. To evaluate this expression it is necessary to estimate values for the inter-proton distance a and the barrier height Uo. The latter can be calculated if the mobility V of the protons in the lattice is known, since this is related by the equation:

$$V = \frac{e \nu a^2 c}{kT} \exp\left(-Uo/kT\right) \tag{2}$$

An approximate value of $V = 10^{-12}$ cm^2/volt·sec has been obtained by Vedder and Wilkins [16] from deuteration experiments with talc. Setting the inter-proton distance as 3Å, the height of the energy barrier from Eq. (2) is 27.6 kcal. It is interesting to note that this value compares well with the barrier height in the related aluminium oxyhydroxide boehmite, calculated as 26 kcal by Fripiat, Bosmans and Rouxhet [17] from quantum-mechanical considerations by assuming an equilibrium value for the inter-oxygen distance.

Substituting in Eq. (1) for a field of 1000 V/cm shows that at 735°K the mean drift velocity of the proton is approximately 10^{-10} cm·sec^{-1}, i.e. the rate of proton drift has been increased by a factor of 10^2. Thus, proton migration cannot in itself be the rate-determining step since the observed effect of the field on the rate of dehydroxylation is much smaller, and falls off with temperature (Fig. 4). The rate-determining migrating species is therefore apparently heavier and less mobile.

A dehydroxylation species with these characteristics has been postulated by Rouxhet et al. [14] on the basis of the observed isotopic exchange energies in micas, which have a value of about 47 kcal/mole and are therefore much too high for a proton transfer reaction. The diffusing species is thought to be a complex containing oxygen; N.M.R. studies of related aluminium hydroxides have suggested that these species are H_2O^+ intrinsic or extrinsic defects [18]. Further support for the concept of proton transfer by a "proton-bearing vehicle" or "transport complex" is provided by dielectric measurements on aluminium hydroxides [19]. The jump frequency ν of the complex is $10^{8}-10^{10}$ sec^{-1} lower

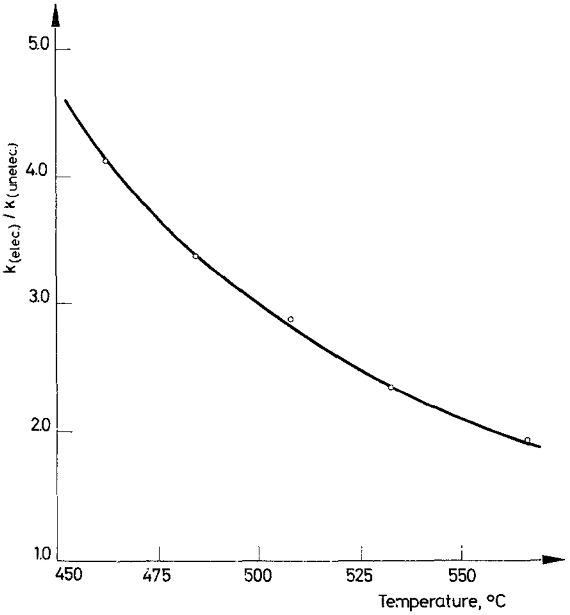
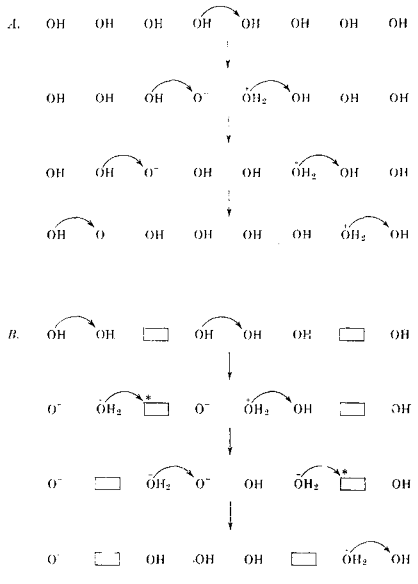


Fig. 4. Graph of ratio of first order rate constants for electrolysed and unelectrolysed kaolinite pellets as a function of temperature



*Slow jumps — proton-bearing vehicle with high energy barrier.

Fig. 5. Schematic representation of proton transfer in solid hydroxide lattices. A. Non-defect lattice, fast proton transfer by tunnelling. B. Defect lattice, proton transfer by tunnelling (fast) and by proton-bearing vehicle (slow)

than for the proton [14] and its energy barrier much higher since the transfer of oxygen is involved. The transport of protons in conjunction with oxygen atoms may be necessitated by the presence of discontinuities in the lattice; in a regular lattice proton transfer can proceed directly but in a lattice containing an increasing number of holes, these may have to be bridged by an oxygen-bearing species. A schematic representation of proton transfer in both regular and defect lattices is shown in Fig. 5 but it must be emphasized that this picture of the transfer mechanism is strictly qualitative and over-simplified.

Despite its crudity, however, the mechanism for proton transport in the defect lattice (Fig. 5B) is compatible with the concept of Rouxhet et al. [14] of fast proton transfer through crystal areas bounded by high energy barriers over which transport can only occur via an oxygen complex. In Fig. 5B these high energy barriers are represented as lattice holes, the concentration of which limits the rate of dehydroxylation particularly at higher temperatures where the increased degree of dehydroxylation gives rise to a high lattice defect concentration. The suggested bridging of lattice holes by an oxygen complex is also not unlike a dehydroxylation mechanism suggested by Freund [20] in which a transient bond similar to a hydrogen bond is formed between adjacent hydroxyl groups.

Although the assumption of a transport complex explains qualitatively why the rate of reaction is influenced by the electric field less than is the proton, and why the effects falls off as dehydroxylation proceeds, little has yet been said about the process by which the charged species surmounts its energy barrier. In the case of the proton this has been explained in terms of the quantum-mechanical tunnelling probability P_i [21], which depends on the height and width of the barrier above the tunnelling level i (U_i and l_i) and the mass m of the tunnelling species:

$$P_i \approx \exp - [4\pi l_i/h (2mU_i)^{\frac{1}{2}}] \qquad (3)$$

The tunnelling probability for a proton in boehmite, AlOOH has been shown in a calculation by Fripiat, Bosmans and Rouxhet [17] to approach unity at an energy level 11 kcal above the fundamental; in other words all protons which have been excited to an energy level approximately half-way up the barrier will penetrate the barrier by tunnelling. At lower energy levels the probability of penetration by tunnelling falls off exponentially. Although the application of an electric field will undoubtedly influence the proton tunnelling probability by distorting the energy barrier and altering the distribution of the higher-energy levels, proton migration has already been shown to be too fast to be the rate-determining step.

The transport of the "proton-bearing vehicle" also involves the overcoming of an energy barrier but the greater mass of this complex and its higher energy barrier severely limit its tunnelling ability according to Eq. (3) and render such a transfer mechanism highly unlikely; this is reflected in the decreased jump frequency of the complex ($\sim 10^2$ sec^{-1}) [14]. As in the case of the proton, however, the mobility of the charged "transport complex" will be increased by the lowering of the potential energy barrier by the electric field. The amount by which the energy barrier is shown to be decreased in the presence of a field (~7 kcal) is of the order of the potential barrier to the low-temperature conductance process in kaolinite, variously reported as 4 kcal [22] and 10 kcal [2]. This energy has been associated with proton "delocalization" or tunnelling [17], which however are probably best considered as separate descriptions of the same process [23]. The present electrolysis results are therefore open to two alternative interpretations:

(1) The barrier height of 11 kcal refers to the movement of the charged complex and not as previously supposed to protons, which should therefore have a much smaller barrier height.

(2) The process most greatly affected by the field at lower temperatures is proton migration; whereas at higher temperatures the charged complex becomes increasingly rate-determining.

Although (1) cannot be definitely ruled out since the information about the relevant activation energies in kaolinite and related minerals comes from studies which might all involve the charged complex rather than the proton (i.e. diffusion and conductance measurements), it is less likely than (2) since activation energies of 4 – 10 kcal have been recorded for processes known to involve the proton [22].

Possibility (2) is also supported by the observed decrease in the effect of the field on the rate at higher temperatures (Fig. 4). As the concentration of lattice defects increases with temperature at the expense of protons, the defect-controlled mechanism begins to predominate. Absolute Rate Theory [24] shows that the rate of a process depends both on the frequency of crossing the energy barrier (ν) and the concentration of "activated complexes" (C^*), according to the equation:

$$\frac{d\alpha}{dt} = C^* \frac{(2\,\pi\, m^* kT)^{\frac{1}{2}}\, \delta\nu}{h} \tag{4}$$

where m^* is the mass of the activated complex and δ is the effective width at the top of the barrier. Although this treatment of rate theory is only strictly correct for reaction in gases and some liquids, in the case of a solid, C^* is proportional to the total number of rate-determining energy barriers in the lattice, i.e. the defect concentration in this case. Thus, when the hydroxy-solid is at temperatures which are ordinarily too low for significant reaction because of insufficient proton mobility, the application of a field reduces the energy barrier by an amount equivalent to the energy at which proton tunnelling probability approaches unity. The protons then migrate under the influence of the field and dehydroxylation is initiated. As the reaction proceeds, the defect concentration increases, with a resulting decrease in the effect of the field, offset to some extent by the rising temperature which increases the mobility of all the species irrespective of the field. Thus, the greatest divergence in the shape of the dehydroxylation curves occurs at lower temperatures; at higher temperatures all the curves tend to become parallel (Fig. 2).

The migration of charged species implies a mechanism similar to the inhomogeneous mechanism, in which however a counter-migration of silicon and aluminium ions is also predicted [13]. Because of their relatively low mobility at dehydroxylation temperatures, the polarizing effect of a field on these ions is expected to become evident only at long electrolysis times. Evidence of this polarization is found in the i.r. analyses of those samples in which the electrolysis was started at room temperature and continued throughout dehydroxylation (Table 1). The degree to which the silicon and aluminium ions have progressed towards their final configurations is in each case greatest at the positive electrode but is probably influenced by other factors such as the water vapour concentration gradient across the sample, depending in turn on the direction of flow of the inert gas atmosphere and the presence in the sample of trace impurity ions, which would also be expected to polarize in the field.

Conclusion

The application of an electric field to kaolinite during its dehydroxylation lowers the initiation temperature of the reaction and increases the rate, probably by increasing the tunnelling probability and mobility of the protons. As the reaction proceeds the effect of the field on the rate is diminished because of the increased importance in the rate-determining process of defects. The activation energy for dehydroxylation is reduced by the electric field by an amount similar to the electrical conductance energy of the protonic species. The electrolytically-induced changes in activation energy are sensitive to the flow direction of the gas atmosphere, which influences the water vapour concentration gradient across the sample.

*

This work was supported by an S.R.C. Research Grant. The author is indebted to Dr W.T. Raines and Dr G.M. Fryer for helpful discussion.

References

1. K. J. D. MacKenzie, J. Appl. Chem., 20 (1970) 80.
2. K. J. D. MacKenzie, Proc. Brit. Ceram. Soc., 19 (1971) 207.
3. P. Murray and J. White, Trans. Brit. Ceram. Soc., 54 (1955) 137.
4. G. W. Brindley and M. Nakahira, J. Amer. Ceram. Soc., 40 (1957) 346.
5. J. B. Holt, I. B. Cutler and M. E. Wadsworth, J. Amer. Ceram. Soc., 45 (1962) 133.
6. G. W. Brindley, J. H. Sharp, J. H. Patterson and B. N. N. Achar, Amer. Min., 52 (1967) 201.
7. H. B. Johnson and F. Kessler, J. Amer. Ceram. Soc., 52 (1969) 199.
8. P. D. Garn and G. D. Anthony, J. Thermal Anal., 1 (1969) 29.
9. D M. Tinsley, Personal Communication.
10. K. J. D. MacKenzie, J. Appl. Chem., 19 (1969) 65.
11. A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
12. G. W. Brindley and M. Nakahira, J. Amer. Ceram. Soc., 52 (1969) 311.

13. H. F. W. Taylor, Clay Min. Bull., 5 (1962) 45.
14. P. G. Rouxhet, R. Touilleaux, M. Mesdagh and J. J. Fripiat, Proc. Int. Clay Conf. Tokyo 1 (1969) 109.
15. J. H. Sharp, G. W. Brindley and B. N. N. Achar, J. Amer. Ceram. Soc., 49 (1966) 379.
16. W. Vedder and R. W. T. Wilkins, Amer. Min., 54 (1969) 482.
17. J. J. Fripiat, H. Bosmans and P. G. Rouxhet, J. Phys. Chem., 71 (1967) 1097.
18. J. J. Fripiat and R. Touilleaux, Trans. Farad. Soc., 65 (1969) 1236.
19. A. Mata Arjona and J. J. Fripiat, Trans. Farad. Soc., 63 (1967) 2936.
20. F. Freund, Personal Communication.
21. F. Freund and H. Nagerl, Proc. 2nd Int. Conf. Thermal Analysis, Worcester, Mass, 2 (1968) 1207.
22. J. J. Fripiat and F. Toussaint, J. Phys. Chem., 67 (1963) 30.
23. J. J. Fripiat, P. G. Rouxhet and H. Jacobs, Amer. Min., 50 (1965) 1937.
24. S. Glasstone, K. J. Laidler and H. Eyring, The Theory of Rate Processes. 1st ed. McGraw-Hill, New York, 1941.

Résumé. — On a mis au point une méthode pour l'étude thermogravimétrique des solides sous l'action d'un champ électrique et on l'a utilisée pour suivre la déshydroxylation de la kaolinite en atmosphère inerte contrôlée. L'application de champs électriques d'environ 10^5 V/m abaisse la température initiale de la déshydroxylation de 60 °C dans certains cas et l'énergie d'activation est réduite de 3 à 12 kcal/mol. On observe l'augmentation des constantes de vitesse des échantillons soumis à l'action du champ électrique (par rapport à une loi choisie arbitrairement du 1^{er} ordre) mais cet effet cesse aux températures élevées où les processus thermiques normaux deviennent prédominants.

On discute l'influence du champ électrique sur les processus de migration d'ions dans la grille.

Zusammenfassung — Eine zur thermogravimetrischen Analyse von Festkörpern unter Anwendung elektrischer Felder entwickelte Methode wurde zum Studium der Dehydroxylierung von Kaolinit in einer geregelten inerten Atmosphäre herangezogen. Elektrische Feldstärken von etwa 10^5 V/m setzten die Anfangstemperatur der Dehydroxylierung in einigen Fällen sogar um 60 °C herab; die Aktivierungsenergie der Dehydroxylierung wird um 3 bis 12 kcal/mol herabgesetzt. Die — willkürlich aufgrund einer Gesetzmäßigkeit erster Ordnung berechneten — Geschwindigkeitskonstanten der elektrolysierten Proben werden durch die Elektrolyse erhöht, doch fällt dieser Effekt bei höheren Temperaturen, wo er von den normalen thermischen Vorgängen überlagert wird, weg.

Die Wirkung des elektrischen Feldes auf die verschiedenen Vorgänge der Ionenwanderung im Gitter wird erörtert.

Резюме. — Метод разработан для термогравиметрического изучения твердых веществ в присутствии электрических полей и использован для изучения дегидроксилирования каолина в инертной атмосфере. В некоторых случаях электрическое поле, составляющее 10^5 V/м, снижает начальную температуру дегидроксилирования не больше, чем на 60°C; энергия активации этого процесса уменьшается на 3—12 Ккал/моль. Постоянная скорости для электризованных образцов (определена при допущении закона первого порядка) увеличивается, но этот эффект отпадает при высоких температурах, когда начинают преобладатр нормальные термические процессы.