Thermochimica Acta, 13 (1975) 7–14

KINETICS OF TALC DEHYDROXYLATION

J. RICHARD WARD
Ballistic Research Laboratories, Aberdeen Proving Ground, Md. 21005 (U.S.A.)
(Received 28 April 1975)

ABSTRACT

The kinetics of the dehydroxylation of talc have been measured in the temperature interval 1100–1160 K by means of isothermal weight-change determinations. The reaction follows first-order kinetics. Over the indicated temperature range the enthalpy of activation was found to be 101 ± 4 kcal mol^{-1}, and the entropy of activation was found to be 16 ± 4 cal mol^{-1} K^{-1}. The error estimates correspond to one standard deviation. The enthalpy necessary to break the Mg–OH bond was estimated from the heat of reaction for $MgOH(g) \rightarrow Mg(g) + OH(g)$. This turns out to be 97 kcal mol^{-1} in reasonable agreement with the measured enthalpy of activation.

These activation parameters are consistent with the mechanism proposed for dehydroxylation of talc consisting of Mg–OH bond scission and subsequent migration of magnesium. These results contradict a previous report on the kinetics of talc dehydroxylation in which a diffusion-controlled expression was claimed to represent the rate of talc weight loss. It is suggested that the presence of adsorbed water on the talc used in the previous investigation is responsible for the discrepancy.

INTRODUCTION

Talc, a hydrated magnesium silicate, is added to gun propelling charges to reduce the rate of gun barrel erosion[1]. The mechanism by which talc reduces barrel wear is still open to question[2]. Two sets of investigators found a direct correlation between the specific heat of metal oxides tested as wear-reducing additives and their erosion-reducing capability[3,4]. This suggests that an analytical model to predict how these additives reduce erosion will require terms for the endothermic dehydroxylation of talc including the rate ofreaction.

Talc has a double-layer structure (Fig. 1) with an octahedrally-coordinated magnesium layer sandwiched between two tetrahedrally coordinated silicon layers[5]. The empirical formula is $3MgO \cdot 4SiO_2 \cdot H_2O$. Gruner[6] and Hendricks[7] discovered the general structure shown in Fig. 1, and showed the unit cell to be 6Mg, 8Si, 20O, and 4OH. Reyner and Brown[8] only recently reported a detailed structure for the talc crystal.

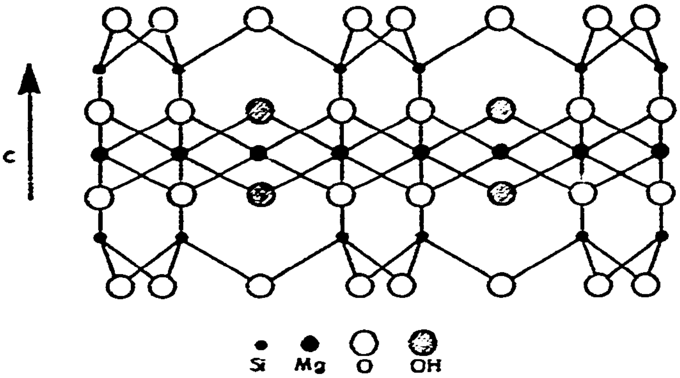

Fig. 1. Structure of talc.

The dehydroxylation of talc takes place near 1120K by the following reaction

$$Mg_3(Si_2O_5)_2(OH)_2 \rightarrow 3MgSiO_3 + SiO_2 + H_2O \qquad (1)$$

The three products of reaction are enstatite, an amorphous form of silica, and water. The reaction itself has also been the subject of repeated studies[9–15]. These studies, however, tried to deduce the mechanism of the reaction by comparing the crystal structure of the products with talc. Daw and co-workers[15] claim their results conclusively support the Nakahira-Kato model of dehydroxylation[13]. They postulate that the oxygen ions preserve the quasi-rigid, close-packed structure of talc with dehydroxylation proceeding by cation migration. This so-called "inhomogeneous" mechanism is similar to a current model for kaolinite dehydroxylation[16].

Despite the similarity in mechanism, the published kinetic data on talc dehydroxylation[17] differs substantially from the more extensively studied kaolinite dehydroxylation (reviewed in ref. 18). Kaolinite dehydroxylation follows first-order kinetics; Boskovic[17] claims talc dehydroxylates as a diffusion-controlled reaction expressed as either equation (2) or (3)

$$[1-(1-\alpha)^{1/3}]^2 = kt, \qquad (2)$$

$$1-(2\alpha/3)-(1-\alpha)^{2/3} = kt, \qquad (3)$$

where

α = weight fraction reacted,
k = rate coefficient,
t = time.

Boskovic and his co-workers heated 4 to 5 g samples for 1/2, 1, 2, and 3 h each at temperatures ranging from 665 to 1373 K. The loss in weight was recorded at each time and plotted as fraction reacted *versus* time as shown in Fig. 2. At either end of the temperature scale they recorded only one or two points for a given temperature. Their talc sample also had physically-absorbed water that was lost near 770 K, but no attempt was made to distinguish the dehydration of this water from the dehydroxylation. Instead the fraction reacted is calculated using the sum of the weight lost by dehydroxylation and dehydration. It was decided to repeat the kinetics of the dehydroxylation of talc using a talc sample with no hydroscopic water to resolve this seeming discrepancy between the kinetics and mechanism of talc and kaolinite decomposition.

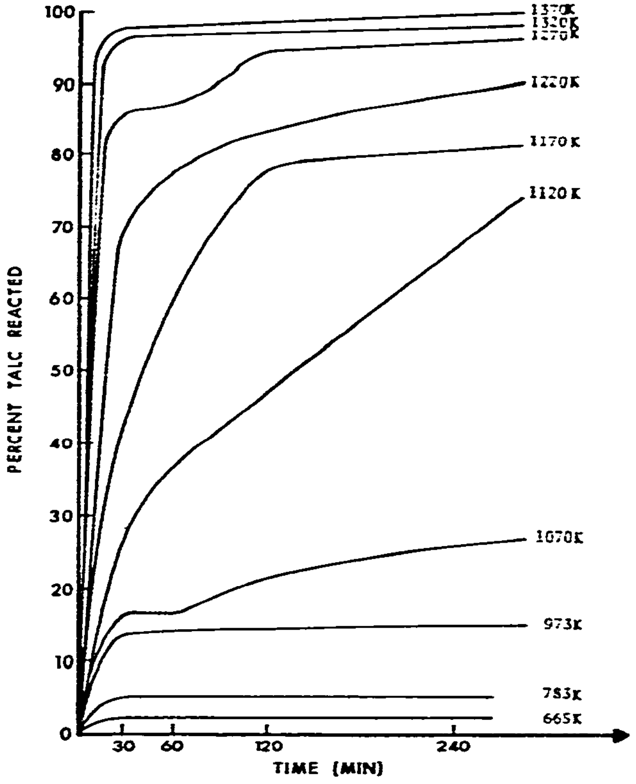

Fig. 2. Dehydroxylation of talc from ref. 17.

EXPERIMENTAL

Finely-ground "pure-grade" talc from the Will Scientific Co., Inc. of Baltimore, Md. was used without further treatment. A commercial thermogravimetric analyzer (DuPont Model 951) was used in this investigation with a quartz furnace tube and a platinum sample pan. All experiments were carried out in an atmosphere of flowing argon (zero-grade, Matheson Co., Inc.).

The talc obtained from Will Scientific is free of adsorbed water as shown on the thermogravimetric curve in Fig. 3. Full-scale deflections were obtained by electronically suppressing 95% of the original sample weight.

The stoichiometry of the dehydroxylation reaction was determined by comparing the experimental weight loss with that expected from eqn (1). Two talc samples weighing about 60 mg were heated isothermally at 1220 K until no further weight loss was recorded. The talc sample was then cooled and reweighed. The average percent weight loss was 4.73 compared to a theoretical weight loss of 4.75%.

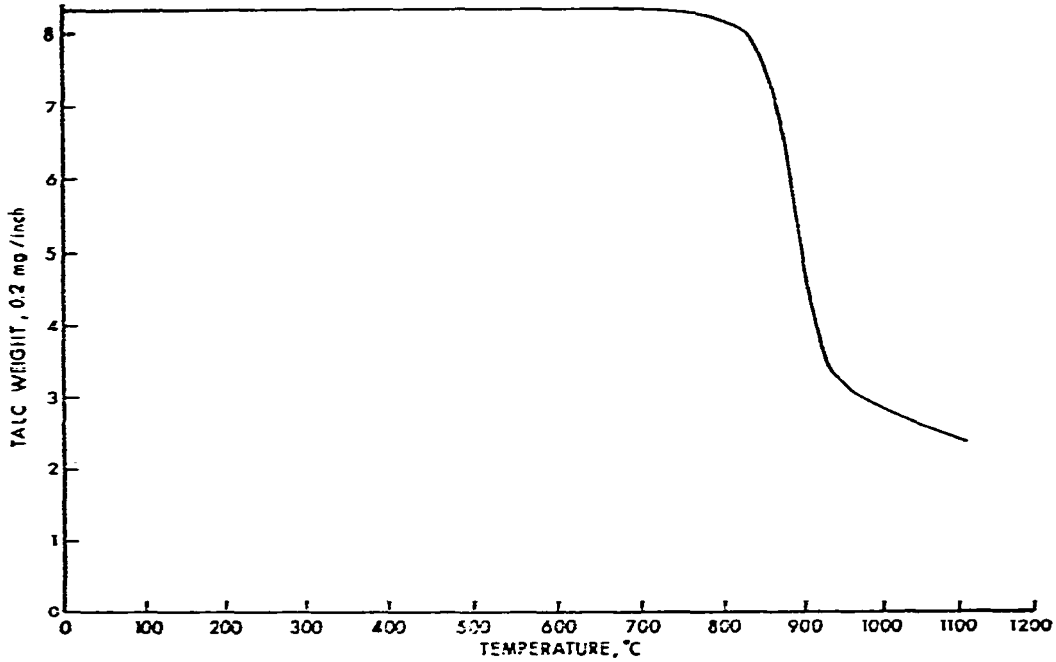

Fig. 3. Thermogravimetry of talc, 10°C min^{-1}, argon atmosphere.

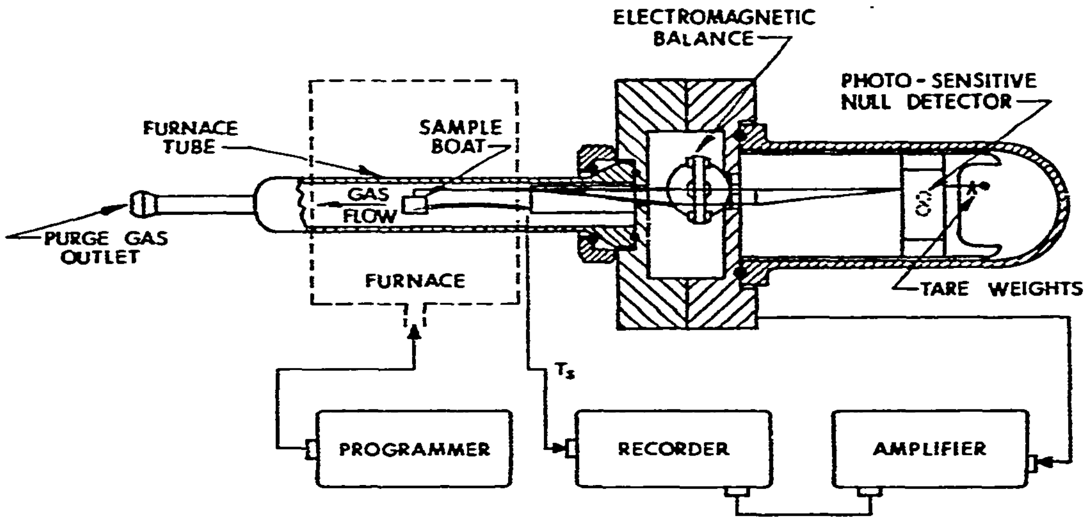

Fig. 4. Thermogravimetric analyzer used in these experiments.

The isothermal weight-change measurements were performed in the following manner which resulted in the talc sample reaching the desired reaction temperature in 60 sec. Referring to Fig. 4, one may notice that the commercial unit used in these investigations has two parts, the furnace which is fixed and the balance assembly which can be moved. For the kinetic runs, the quartz furnace tube was left in the furnace in order to keep the furnace tube at the reaction temperature. The talc samples were loosely loaded onto the platinum sample pan with the spatula provided with the TG accessory kit and weighed. The sample thermocouple was adjusted so it would be within a few millimeters of the talc sample. After electronically suppressing sufficient sample weight to achieve as close to full-scale display as possible, the talc sample was moved into the furnace and the furnace tube was reconnected to the balance assembly. Both the weight and the sample temperature were monitored continuously with this particular commercial unit. A typical isothermal determination is depicted in Fig. 5.

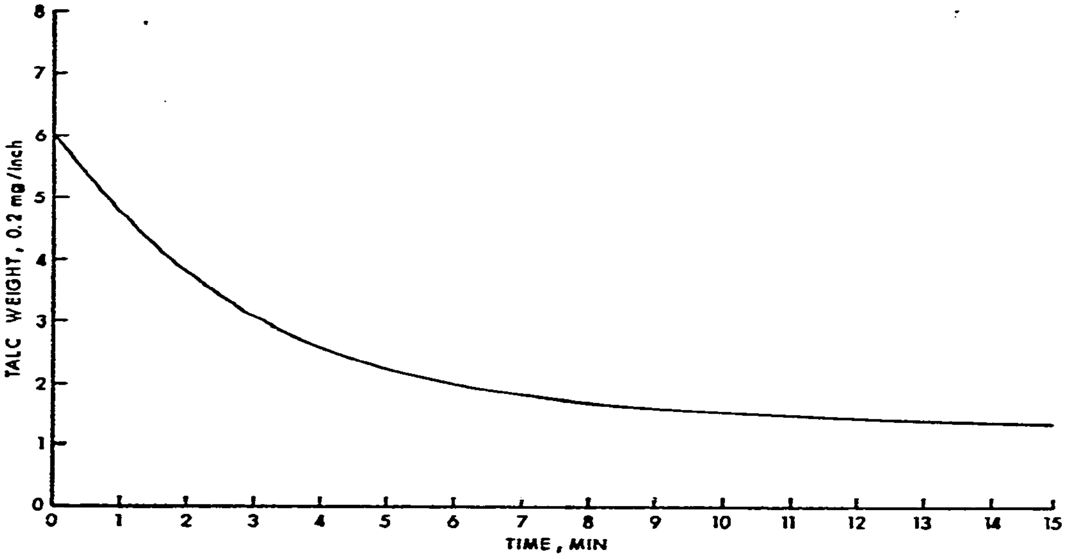

Fig. 5. Isothermal weight-change determination of talc at 1160K, argon atmosphere.

RESULTS AND DISCUSSION

Isothermal weight-change determinates were made in the temperature range 1000 to 1160 K. The weight loss vs. time appeared to follow first-order kinetics. To test this quantitatively, the weight of talc at a given time was fitted to eqn (4):

$$W_t = W_\infty + (W_0 - W_\infty)e^{-kt} \tag{4}$$

where

W_t = weight of talc at time t,

W_0 = weight of talc at time zero,
W_∞ = final weight,
k = rate coefficient,
t = time.

The weight, W_0, is taken at a time after the temperature of the talc sample reaches steady-state. A non-linear least-squares program from the Los Alamos Scientific Laboratories[19] was used to see how well the experimental weight of talc vs. time agreed with eqn (4). Time became the independent variable, the weight of talc at time t was the dependent variable. The remaining three quantities, W_0, W_∞, and k, were parameters to be fit. The results of this calculation for the kinetic run in Fig. 5 are listed in Table 1. The data fit the expression for first-order kinetics. The best-fit value of the final weight, W_∞, was slightly higher than the experimental final weight. This was judged to be that the very end of the reaction was not first-order; the estimate of the fraction reacted following first-order kinetics was made from the ratio of the best-fit to experimental $W_0 - W_\infty$. Results for all of the kinetic runs are given in Table 2.

The activation parameters were determined from a linear least-squares fit of the ln (k/T) vs. $(1/T)$. The enthalpy of activation was found to be 101 ±4 kcal mol^{-1}

TABLE 1

FIRST-ORDER KINETIC FIT OF TALC DEHYDROXYLATION[a]

W_t *exp.* (*in.*)[b,c]	t (*min.*)	W_t *calc.*, (*in.*)	W_t *exp.*$-W_t$ *calc.*, ($\times 10^2$ *in.*)
5.42	0	5.43	1
5.29	0.10	5.30	−1
5.17	0.20	5.17	0
5.03	0.30	5.04	−1
4.93	0.40	4.92	1
4.80	0.50	4.81	−1
4.59	0.50	4.58	1
4.38	0.90	4.37	1
4.18	1.10	4.17	1
3.99	1.30	3.99	0
3.82	1.50	3.82	0
3.44	2.00	3.44	0
3.11	2.50	3.12	−1
2.83	3.00	2.85	−2
2.61	3.50	2.62	−1
2.25	4.50	2.26	−1
2.01	5.50	2.00	1
1.82	6.50	1.82	0
1.70	7.50	1.67	3
1.53	9.50	1.52	1
1.40	12.5	1.42	−2

[a] 1159 K, argon flow-rate = 0.1 l min^{-1}, mass = 27.6 mg. [b] W_∞ expt = 1.25 mg, W_∞ calc = 1.35 mg.
[c] $k = 0.34$ min^{-1}.

TABLE 2

FIRST-ORDER RATE COEFFICIENTS FOR TALC DEHYDROXYLATION[a]

T (K)	*mass (mg)*	k *(min· 10)*	*Percent first-order kinetics*[b]
1158	31.6	3.85	95
1155	27.7	4.03	95
1159	30.0	3.51	96
1159	28.6	3.45	96
1159	27.6	3.35	98
1157[c]	30.8	3.61	96
1158[c]	32.8	3.68	96
1157[c]	33.9	3.53	95
1161[c]	31.5	3.39	93
1146	23.1	0.185	96
1143	20.5	0.195	93
1144	21.7	0.225	93
1120	29.7	0.105	98
1126	25.2	0.106	98
1128	25.3	0.128	98
1128	32.5	0.108	96
1126	34.2	0.105	98
1112	23.0	0.0580	96
1116	23.7	0.0485	98
1115	21.6	0.0501	95
1100	23.6	0.0390	97
1101	23.7	0.0304	99

[a] Argon flow-rate 0.1 l min^{-1} unless otherwise specified. [b] $(W_0 - W_\infty)$ best-fit/$(W_0 - W_\infty)$ exp. [c] Argon flow-rate is 0.2 l min^{-1}.

and the entropy of activation 16±4 cal mol^{-1} K^{-1}. The error estimates are for one standard deviation as computed by the least-squares program[19].

The high activation enthalpy and the first-order kinetic behavior point to the rate-determining step as Mg–OH bond-breaking (recall from Fig. 1 that all the hydroxyls are coordinated only to magnesium). To see how the enthalpy of activation compares to the enthalpy needed to rupture an Mg–OH bond, the enthalpy of the following reaction was computed from data available in the *JANNAF Thermochemical Tables*[20]:

$$MgOH(g) \rightarrow Mg(g) + OH(g) \qquad (5)$$

The heats of formation for MgOH(g), Mg(g), and OH(g) are −52, 35.5, and 9.5 kcal mol^{-1}. This turns out to a heat of reaction of 97 kcal mol^{-1} which compares with 101 kcal mol^{-1} for the activation enthalpy. The positive entropy of activation is consistent with cation migration to form the transition state. One also sees that the high dehydroxylation temperature for talc vs. kaolinite and other silicates is the strength of the magnesium–oxygen bond resulting in a higher enthalpy of activation.

The discrepancy between these results and those of Boskovic et al.[17], presumably arises from the presence of the adsorbed water on their sample. The removal of the physically adsorbed water would be a diffusion-controlled process and they made no attempt to separate this process from the chemically-controlled dehydroxylation process.

REFERENCES

1 J. P. Picard, R. G. Wetton and R. L. Trask, *Picatinny Arsenal Technical Memorandum No. 1781*, May 1967.
2 J. R. Ward, *BRL Memorandum Report No. 2172*, April 1972.
3 C. Lenchitz and G. Silvestro, *Picatinny Arsenal Technical Memorandum No. 1869*, December 1968.
4 R. Remaly and T. Stanley, *IIT Research Institute Technical Summary Report*, 6 May 1966–6 August 1968, February 1969.
5 R. C. MacKenzie, in R. C. MacKenzie (Ed.), *Differential Thermal Analysis Vol. 1, Fundamental Aspects*, Academic Press, London and New York, 1970, p. 498.
6 J. W. Gruner, *Z. Kristallogr.*, 88 (1934) 412.
7 S. B. Hendricks, *Z. Kristallogr.*, 99 (1938) 264.
8 J. H. Rayner and G. Brown, *Clays Clay Mineral*, 21 (1973) 103.
9 R. H. Ewell, E. N. Bunting and R. F. Geller, *J. Res. Nat. Bur. Stand.*, 15 (1935) 551.
10 H. Kedesdy, *Ber. Deut. Keram. Ges.*, 24 (1943) 201.
11 A. I. Avgustinik and V. S. Vigdergauz, *Ogneupory*, 13 (1948) 218.
12 M. C. Ball and H. F. W. Taylor, *Mineral. Mag.*, 33 (1963) 467.
13 M. Nakahira and T. Kato, *Clays Clay Mineral.*, 12 (1964) 21.
14 G. Bapst and J. P. Eberhart, *Bull. Groupe Fr. Argiles*, 22 (1970) 17.
15 J. D. Daw, P. S. Nicholson and J. D. Embury, *J. Amer. Ceram. Soc.*, 55 (1972) 55.
16 H. F. W. Taylor, *Clay Mineral. Bull.*, 5 (1962) 45.
17 S. Boskovic, M. Gasic, B. Zwanovic and M. Ristic, *Bull. B Boris Kidric Inst. Nucl. Sci.*, 17 (1966) 381.
18 J. D. Hancock and J. H. Sharp, *J. Amer. Ceram. Soc.*, 55 (1972) 74.
19 R. H. Moore and R. K. Zeigler, *Los Alamos Scientific Laboratory Report LA-2367*, March 1960.
20 *JANNAF Thermochemical Data*, Dow Chemical Co., Inc., Midland, Mich., 1963–1973.