A Study of the Hydration of Calcium Orthoplumbate. IV. The Behavior of Dehydration

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In the previous papers[1] it was demonstrated that Kissinger's method[2] of differential thermal analysis could be used to analyze the reaction kinetics of the dehydration of calcium orthoplumbate hydrates. That is, the reaction order and the activation energy of dehydration were determined, and the information thus obtained was used to analyze the behavior of the dehydration.

In the present paper, the authors will attempt to confirm the previous conclusion by thermogravimetric analysis. The reaction order and the activation energy of the dehydration will also be examined by Freeman's method[3] of thermogravimetric analysis.

The results of present experiments will support the conclusions of the previous papers.

Experimental Procedure

Material.—*Calcium Orthoplumbate Hydrate-Calcium Hydroxide Mixtures.*—The mixture used in this experiment was prepared by hydrating calcium orthoplumbate. The process of hydration was carried out with the apparatus and procedure previously described.[1] Hydrated mixtures were identified by X-ray diffraction patterns, differential thermal and thermogravimetric curves, and chemical analysis.

Calcium Orthoplumbate Hydrate.—Franke's method[4] was used to remove calcium hydroxide from hydrated mixtures, as has been described before.[1]

The samples employed for thermal analysis are the same as those used in the previous work.

Apparatus and Procedure.—The DTA-TGA unit (Automatic Differential Thermobalance, made by the Rigaku Denki Company, Tokyo), designed for simultaneous differential thermal and thermogravimetric analyses, was used in this work. Specimen holders made of platinum and beryllium oxide were employed. A platinum-rhodium thermocouple was used. The reference material was α-alumina. Each of the eight samples was run in analysis at the rate of 2.5 and 10°C per min. in order to determine the activation energy and the reaction order. The samples were ground enongh to pass them through a 250-mesh sieve. Specimen holders were filled loosely with 400—600 mg. of the sample. The differential temperature variation and the weight change as a function of the time and the temperature were recorded continuously.

Results and Discussion

The continuous tracings of the weight change accompanying the heat treatment of calcium orthoplumbate hydrate and calcium orthoplumbate hydrate - calcium hydroxide mixtures are given in Figs. 1 and 2 respectively. A typical comparison of simultaneously-recorded curves of thermogravimetric and differential thermal analyses is then given in Fig. 3.

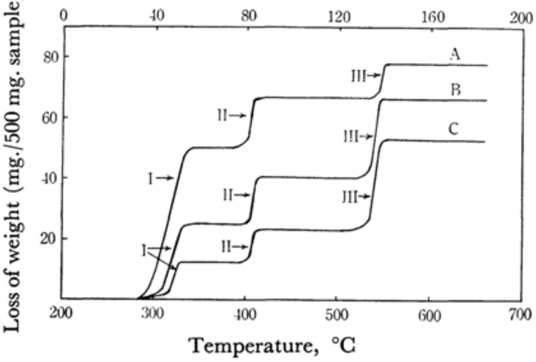

Fig. 1. Thermogravimetric analysis curves for calcium orthoplumbate hydrate - calcium hydroxide mixtures.

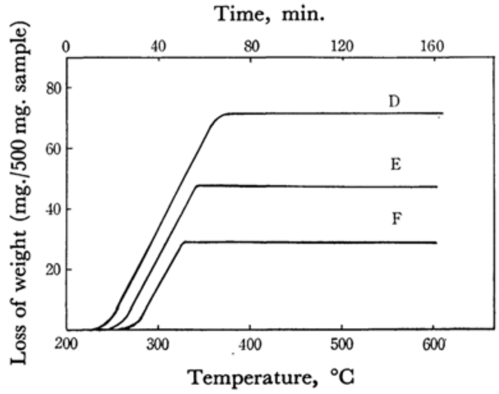

Fig. 2. Thermogravimetric analysis curves for calcium orthoplumbate hydrate.

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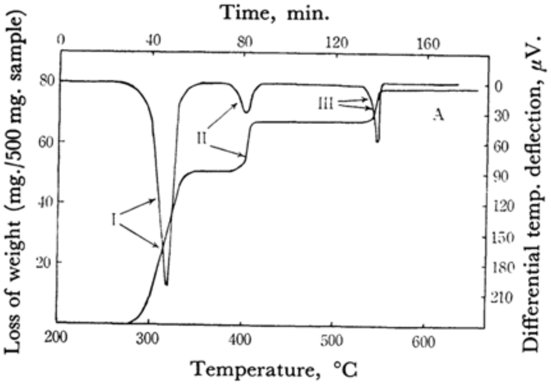

Fig. 3. Comparison of simultaneously recorded thermogravimetric and differential thermal curves.

It is apparent from Figs. 1 and 2 that the dehydration of samples D, E and F proceeds in one stage, while that of samples A, B and C, proceeds in three stages. Stages I and II in Fig. 1 show the first and second stage of the dehydration respectively; Stage III shows the decomposition of calcium hydroxide.

When the thermogravimetric analysis data of Figs. 1 and 2 were plotted according to Freeman's method, straight lines were obtained for each cases, thus enabling us to calculate the activation energy. The results of the thermogravimetric studies in the present work are compared with the values obtained by Kissinger's method based on differential thermal analysis, in Table I.

The value of the reaction order of magnesium hydroxide (1.00) reported in this paper (Table I) differs from those reported by Kissinger and by Gregg and Razouk2) (0.67), but the agreement with the differential thermal analysis value (0.99) is good. The activation energy (25.0 kcal. per mol.) differs slightly from their values (27.2—31.4 kcal. per mol.) in order of magnitude. This discrepancy may be attributed to the difference in the particle size and in the mineral origin of the samples.

The values of the reaction order derived from the thermogravimetric analysis are nearly equal to unity in the cases of samples A, B and C. While the activation energies of the first dehydration were found to be 20.1, 21.0 and 20.1 kcal. per mol., those of the second dehydration were from 41.0 to 45.7 kcal. per mol. The activation energies for samples D, E and F were found to be 11.8, 12.6 and 12.6 kcal. per mol. while their reaction orders were nearly equal to unity.

TABLE I. COMPARISON OF RESULTS WITH THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS METHODS

Material		x		E, kcal./mol.	
		TGA	DTA	TGA	DTA
A	I[*1]	1.10	1.08	20.1	18.2
	II[*2]	0.90	—	41.0	—
	III[*3]	0.70	0.66	32.8	33.0
B	I	1.10	1.10	21.0	18.0
	II	0.90	0.92	43.8	41.0
	III	0.70	0.66	32.8	33.0
C	III	1.00	1.09	20.1	18.0
	II	1.01	0.92	45.7	43.0
	III	0.70	0.66	32.8	33.0
D		0.90	0.88	11.8	11.5
E		1.00	0.96	12.6	11.5
F		1.00	1.05	12.6	12.1
G		0.70	0.66	30.1	30.7
H		1.00	0.99	25.0	25.0
I	a)	0.55 to 0.44		31.4	
	b)	0.69		27.2	

[*1] First dehydration step.

[*2] Second dehydration step.

[*3] Dehydration of liberated calcium hydroxide.

a) Kissinger's data2) by DTA method for Brucite.

b) Kissinger's data2) by isothermal weight-loss measurements for Brucite.

As was concluded in the previous paper, the difference in activation energy between the first and second dehydration processes indicates that the dehydration is influenced by the inhibitive action of the calcium hydroxide liberated; that is, the elevation of the activation energy of the second dehydration seems to result from the fact that small particles of calcium hydroxide liberated in hydrate mixtures are firmly bonded to the hydrate.

The results of the thermogravimetric studies by Freeman's method in the present work agree well with the values obtained by Kissinger's method which based on the differential thermal analysis. It may be concluded from the results of this kinetic investigation that the method of thermogravimetric analysis can be used to obtain information about the kinetics of simple dehydration reactions.

However, several factors which may influence the patterns have not examined, such as pressure, atmosphere and particle size.