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139. **Yoshishige Sato**: Studies on Organic Compounds containing Water or Solvent of Crystallization. X.[*1] Hydrate of Calcium 5-Ethyl-5-pentylbarbiturate.

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Amount of crystal water of calcium 5-ethyl-5-pentylbarbiturate (Pental-Ca) has not yet been determined except in J.N.F. II[*3] and N.N.R.,[*4] where the weight loss on drying is given as 7% when heated at 105° for 2 hours.

The preceding paper[*1] described the method of determination of crystal water contained in compounds which were submitted to isothermal reaction or absorption of water vapor. Studies on the amount of crystal water in Pental-Ca were made in accordance with this method.

Experimental

Thermo-balance used was the same as that described in detail in Part II of this series.[1] The apparatus has a quartz spring which shows the amount of weight loss of the sample caused by heating in its shrinkage.

Water vapor absorption apparatus consists of a water vapor source, a mercury manometer, and an absorption glass tube suspended at the end of the quartz spiral. The sample was kept in a constant temperature bath or electric furnace heated from outside the absorption glass tube. Water vapor was introduced into the absorption tube from its source and the spiral elongation resulting from weight gain and equilibrium pressure on a mercury manometer were measured by means of a cathetometer. The relationship between the increasing fraction $\Delta w/w$ and specific pressure P_e/P_t was thus obtained. The apparatus and experimental procedure were described in detail in Parts I[2] and VIII[3] of this series.

Results and Discussion

I) Dehydration

The dehydration curves obtained from thermobalance are shown in Fig. 1 (I~IV), from which it was recoginized that the amount of water in the sample showed different value individually and experimental values from 7.8% to 6.5% did not agree with any theoretical values of 6.84% for 2 moles, 8.41% for 2.5 moles, and 9.93% for 3 moles of crystal water.

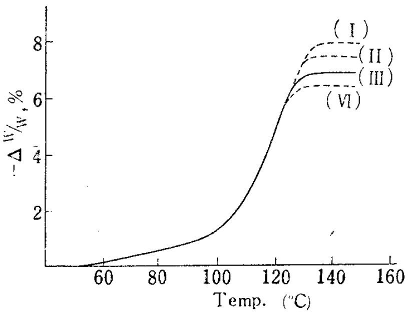

Fig. 1. Dehydration Curves of Pental-Ca Hydrate

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*1 Part IX: Yakugaku Kenkyu, **31**, 231(1959).
*2 Kashima-cho, Higashiyodogawa-ku, Osaka (佐藤善重).
*3 "The National Formulary of Japan," Second Ed., (English Edition), 315(1957).
*4 "Test and Standards for New and Nonofficial Remedies," 208(1953). J.B. Lippincott Company, New York.

1) T. Noto, H. Sawada, Y. Sato, N. Fukuda: Yakugaku Kenkyu, **29**, 71(1957).
2) Y. Sato: Nippon Kagaku Zasshi, **78**, 917(1957).
3) Y. Sato, N. Fukuda, K. Kotera: *Ibid.*, **80**, 209(1959).

II) Isothermal Sorption of Water Vapor on Various Samples

A sample containing 6.99% of water was submitted to isothermal adsorption with water vapor at 16.5° in the evacuated apparatus and the relationship of the amount adsorbed or desorbed to equillibrium pressure is shown in Fig. 2.

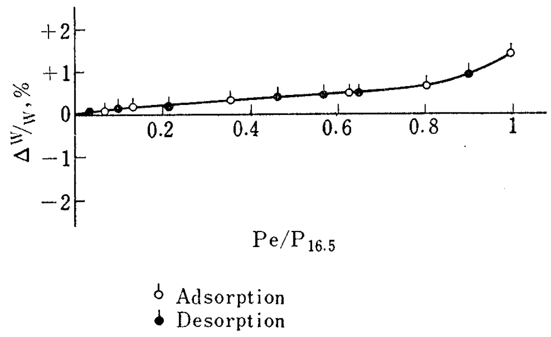

Fig. 2. Isothermal Adsorption and Desorption of Water Vapor on Pental-Ca containing 6.99% of Water

Since these curves were identical, reversible, and the time required for reaching the equilibrium was so short that it was assumed that the curves are of a physical desorption or adsorption, and the level portion of 6.99% of water was therefore considered as crystal water.[2,4] After the above experiments, the sample was dehydrated by heating in vacuum. The amount of weight loss showing 6.99% was again obtained, corresponding to the value of curve III in Fig. 1.

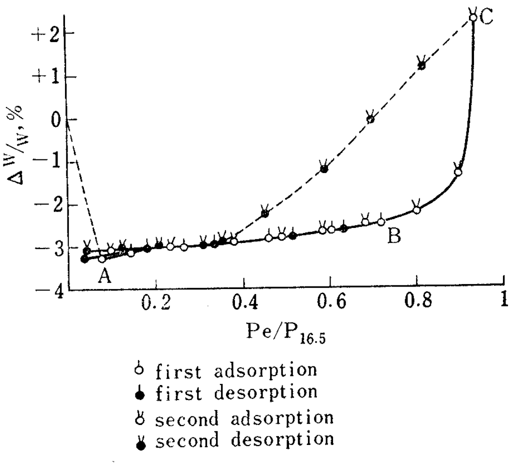

Fig. 3. Isothermal Adsorption and Desorption of Water Vapor on Pental-Ca

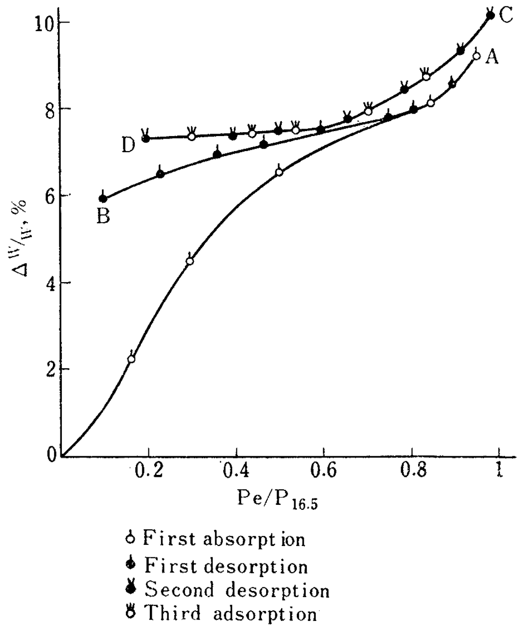

Fig. 4. Isothermal Absorption and Desorption of Water Vapor on Pental-Ca Anhydrate

The sample, obtained by reaction of sodium 5-ethyl-5-pentylbarbiturate solution with calcium chloride solution in a small scale, forms very fine particles because of fast deposition of reaction product. The reaction product was dried in room temperature for 24 hours and the sample, which was placed in a quartz vessel in the evacuated apparatus, showed a decrease in the weight by dehydration up to A point in Fig. 3. The sample in A point was submitted to isothermal reaction with water vapor, and adsorption (I) and

4) R.I. Razouk, R.S. Mikkail: J. Phys. Chem., **59**, 636(1955).

desorption (II) curves are given in Fig. 3. The curves were identical, reversible, and the time required for reaching the equilibrium was so short that it was assumed that the curves were of physical adsorption or desorption. After adsorption proceeded up to C point, the sample was wetted sufficiently. The desorption, which proceeded from C point, is shown by the dotted curve in Fig. 3 which was not in equilibrium state but in irreversible state up to $P_e/P_{16.5} \fallingdotseq 0.35$. The time required for reaching the equilibrium was so slow that water thus increased by adsorption over the flat level portion (AB) interacted with the sample. Each point on the dotted curve was measured every 2 hours. The desorption curve below $P_e/P_{16.5} \fallingdotseq 0.35$ was identical with curve I or II and reversible. When the sample below $P_e/P_{16.5} \fallingdotseq 0.05$ was dehydrated by heating in vacuum, the weight loss was 6.96% calculated on the basis of the weight of the sample in the flat part (curve AB), and this value almost agrees with the theoretical value of 6.84% for 2 moles of water. Decrease in weight shown as curve OA in Fig. 3 was recognized as dehydration of water adsorbed on crystal surface.

The reaction of the anhydrate with water vapor is shown as curve I (OA) in Fig. 4, the time required for reaching the equilibrium being very slow. Therefore, each point on curve I was measured every 24 hours. In the region of low specific pressure of desorption curve AB, the time required for reaching the equilibrium was comparatively long and it was considered that the curve was the result of dehydration of the hydrate produced by the reaction of anhydrate with water vapor. When the crystal lattice of hydrate is not completed, such a phenomenon as above is often observed.[3,5] The sample at B point was allowed to stand for 1 week in a condition of $P_e/P_{16.5} \fallingdotseq 1$ to obtain the hydrate combined completely with water vapor. Desorption experiment was then carried out on the sample in the state at C point. The curve thus obtained was found to be reversible and physical as shown by CD and readsorption from D point was identical with CD. In specific pressure below D point, dehydration was recognized by decrease in the weight. The reversible level portion (CD) of 7.4% of weight agrees approximately with the theoretical value of 7.34% for 2 moles of crystal water calculated on the basis of anhydrate. Judging from these experimental results, amount of crystal water in Pental-Ca should be 2 moles.

III) The Rate of Dehydration and Activation Energy

The rate of dehydration of the hydrate was examined over the temperature range between 20° and 50° at approximately 10^{-4} mm. Hg pressure. The experimental results are shown in Fig. 5 in which the dehydration degree α is plotted against time t. The rate equation[3,6] of dehydration was derived from assumption and model given below. The crystal would be a spherical particle with initial radius r and the decreased fraction at time t is Δr, $r = r_t + \Delta r$, $\Delta r = kt$.

The fraction decomposed to α at the time t is expressed by the following formula:

$$\alpha = \frac{4/3(\pi r^3) - 4/3\pi(r-kt)^3}{4/3(\pi r^3)} = 1 - \left(\frac{r-kt}{r}\right)^3 \qquad (1)$$

Equation (1) can be given in the form

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

Equation (3) is derived from assumption that the initial radius r is constant

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

The equation (3) was applied to the rate of dehydration of Pental-Ca hydrate (Fig. 6).

5) T. Noto, H. Sawada, Y. Sato, N. Fukuda: Yakugaku Zasshi, **79**, 451(1959).
6) W. E. Garner: "Chemistry of the Solid State," 214(1955). Butterworths Scientific Publications, London.

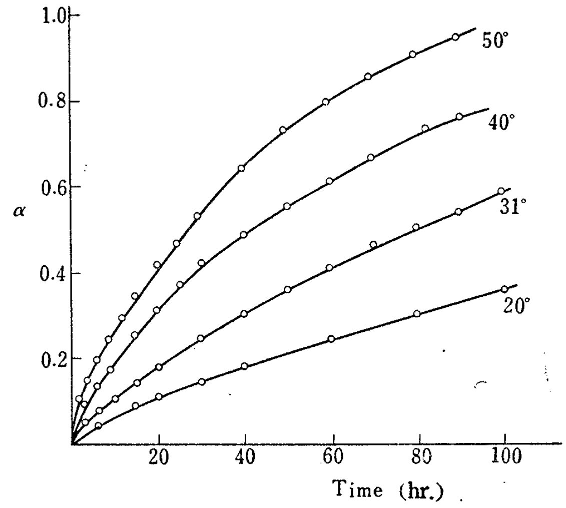

Fig. 5. Relationship between Dehydration Degree (α) and Time

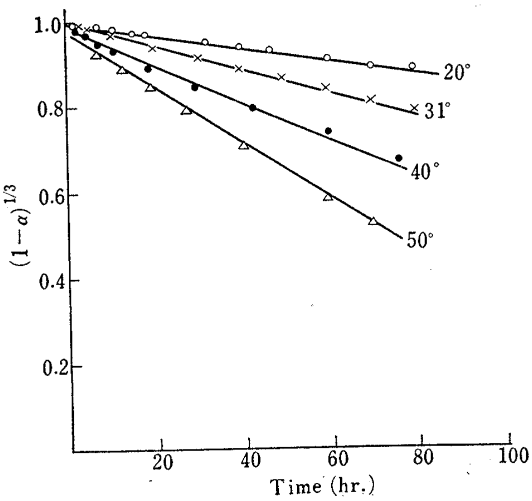

Fig. 6. Relationship between $(1-\alpha)^{1/3}$ and Dehydration Time

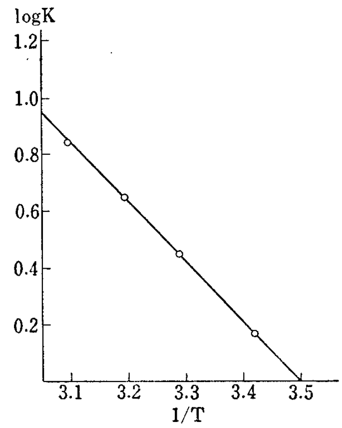

Fig. 7. Relationship between log K and Reciprocal of Absolute Temperature (1/T)

The value of log K was plotted against the reciprocal of absolute temperature ($1/T$) in Fig. 7 and the activation energy was found to be 9.5 kcal./mole.

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Summary

In order to determine the amount of crystal water in calcium 5-ethyl-5-pentylbarbiturate, examinations were made on the action of water vapor on the hydrate and the anhydrate by the use of a quartz spring balance and a mercury manometer which may be able to estimate the reaction amount and equilibrium pressure. The amount of crystal water obtained from the flat part of the desorption curves corresponds to dihydrate. The rate of dehydration was examined over the temperature range of 20° to 50° and the rate of dehydration may be expressed by the formula $(1-\alpha)^{1/3}=1-\frac{kt}{r}$, where k is the rate constant, the fraction dehydrated at time t is α, and r is the initial radius of particle. From the experimental data, it was estimated that the activation energy for dehydration reaction of the hydrate is 9.5 kcal./mole.

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