

KINETICS AND MECHANISM OF THE REACTION OF $\text{Ba}(\text{NO}_3)_2$ WITH TiO_2 (ANATASE)
IN THE SOLID-SOLID STATE AND THE LIQUID-SOLID STATE

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ABSTRACT

The reaction of $\text{Ba}(\text{NO}_3)_2$ with TiO_2 (anatase) was studied by TG and DTA. According to simultaneous TG and DTA, the reaction occurred sharply around the melting temperature of $\text{Ba}(\text{NO}_3)_2$, $\sim 577^\circ\text{C}$, at low heating rates, and the reaction followed after melting of $\text{Ba}(\text{NO}_3)_2$ as the rate was raised. For the isothermal reactions the conversion α vs time relationship was given by the equation: $kt = 1 - (1-\alpha)^{1/3}$. The relationship was shown by one straight line below 577°C , and by two lines with a bend above 577°C . The reaction rates at the earlier period above 577°C were about 1/5 smaller than those at the later period, which were nearly on the extrapolated $\log k$ vs $1/T$ line obtained below 577°C . The activation energy was 212 kJ mol^{-1} for the solid-solid reaction and 231 kJ mol^{-1} for the earlier period in the liquid-solid reaction.

INTRODUCTION

In the study on the formation of BaTiO_3 with emphasis on chemical reactivity of raw materials, it was found that the reaction of $\text{Ba}(\text{NO}_3)_2$ with TiO_2 (anatase) yielded the single phase BaTiO_3 at much lower temperatures, around 600°C , than other reactions between BaCO_3 , $\text{Ba}(\text{OH})_2$ or $\text{Ba}(\text{COO})_2$ and hydrate or rutile of TiO_2 (ref.1). As the melting temperature of $\text{Ba}(\text{NO}_3)_2$ is known to be 575°C (ref.2), it is deduced that the reaction occurs in the solid-solid state below the melting temperature and in the liquid-solid state above the temperature. In the present work, kinetics and mechanism of the reaction accompanied with the phase change were examined by isothermal and non-isothermal TG and DTA. The reaction was studied by Kubo and Shinriki (ref.3), but the kinetics was not known in details.

EXPERIMENTAL

$\text{Ba}(\text{NO}_3)_2$ (GR grade, Kanto Chemical Co.) and anatase (Extra Pure grade, Wako Chemical Co.) were used as raw materials. The particle sizes of the anatase, measured by scanning electron microscopy, were $0.14 \mu\text{m}$. Both compounds were thoroughly mixed at an equimolar ratio in an agate mortar, and compacted at 3 t cm^{-2} into the cylindrical pellets, 7 mm in diameter and about 5 mm in height. The weight of a pellet was about 300 mg.

Experiments for studying reaction kinetics were carried out by use of the

apparatus, which consisted of an electrobalance (Cahn Co., USA, Model 1000) as a thermobalance, a Kanthal resistance furnace, a gas supply system and vacuum pumps. The sample pellet in a Pt bucket, 10 mm in diameter and 5 mm in height, was heated at $30^{\circ}\text{C min}^{-1}$ in a $100\text{ cm}^3\text{ min}^{-1}$ flow of air and kept at the desired temperatures. The temperature of the sample was measured with a Pt/Pt-13%Rh thermocouple placed close to the bucket inside the quartz reaction tube.

The reaction behavior was examined by using a TG-DTA apparatus (Shinku Riko Co., type TGD-5000). A powder mixture of about 100 mg in a Pt sample holder, 8 mm in diameter and 10 mm in height, was heated at different heating rates in flowing air for simultaneous TG and DTA. The same apparatus was also used for isothermal TG and DTA to determine the change in the sample temperature during the reaction. The powder sample was heated at $200^{\circ}\text{C min}^{-1}$ in flowing air of $100\text{ cm}^3\text{ min}^{-1}$ and kept at the desired temperatures.

X-ray diffraction for powder specimens was performed by a diffractometer (Rigaku Denki Co., type Rad-1A) with $\text{CuK}\alpha$ radiation monochromatized with a bent graphite crystal.

RESULTS AND DISCUSSION

Simultaneous TG and DTA of $\text{Ba}(\text{NO}_3)_2$ and a mixture of $\text{Ba}(\text{NO}_3)_2$ and TiO_2 (anatase)

Figure 1 (A) and (B) show TG and DTA curves of $\text{Ba}(\text{NO}_3)_2$ and an equimolar mixture of $\text{Ba}(\text{NO}_3)_2$ and TiO_2 , respectively, where the theoretical weight loss is taken as 100% in (A), and $10\ \mu\text{V}$ corresponds to about 1°C in (B). The TG curve of $\text{Ba}(\text{NO}_3)_2$ at $5^{\circ}\text{C min}^{-1}$ shows that the thermal decomposition occurs at 570°C . The initial temperatures at 10 and $20^{\circ}\text{C min}^{-1}$ were 570 and 575°C , respectively.

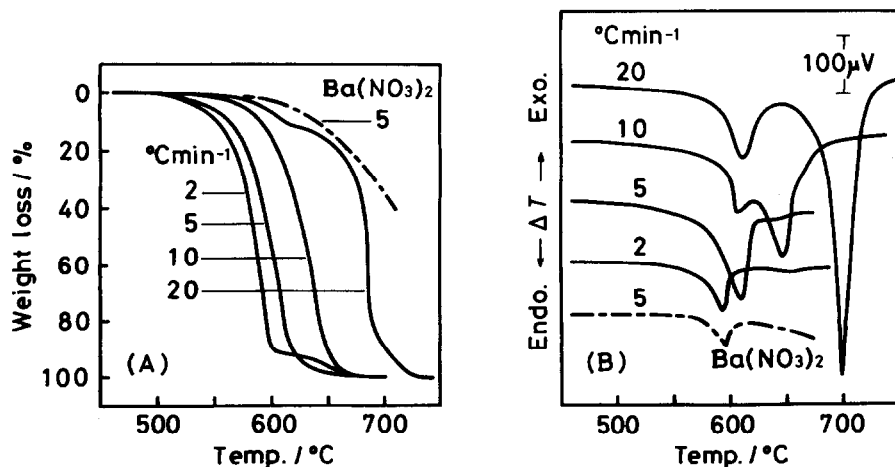


Fig. 1, (A) TG and (B) DTA curves simultaneously obtained for the reaction of $\text{Ba}(\text{NO}_3)_2$ with TiO_2 and the thermal decomposition of $\text{Ba}(\text{NO}_3)_2$ in a $100\text{ cm}^3\text{ min}^{-1}$ flow of air at different heating rates.

The DTA curve of $\text{Ba}(\text{NO}_3)_2$ shows the departure from the base line at about 567°C . The intersection of the extrapolated base line with the tangent of the peak was 575°C . From the results, it is deduced that the decomposition of $\text{Ba}(\text{NO}_3)_2$ occurs after the phase change into liquid.

The reaction of $\text{Ba}(\text{NO}_3)_2$ with TiO_2 began at 457 , 476 , 497 and 508°C for the heating rates of 2 , 5 , 10 and $20^\circ\text{C min}^{-1}$, respectively. These initial temperatures were much lower than the decomposition temperature of $\text{Ba}(\text{NO}_3)_2$. The final temperatures were around 680°C except at $20^\circ\text{C min}^{-1}$. DTA curves of the reaction showed an endothermic peak at the heating rates below 5°C min^{-1} . When the heating rate was raised, it was splitted into two endothermic peaks: The peak at the lower temperature was due to the melting of $\text{Ba}(\text{NO}_3)_2$ and the other at the higher temperature was due to the reaction. This means that the reaction occurs in the liquid-solid state after melting of $\text{Ba}(\text{NO}_3)_2$ at the higher heating rates.

Kinetics of the isothermal reaction

Figure 2 shows the conversion α vs time curves for the reaction of $\text{Ba}(\text{NO}_3)_2$ with TiO_2 at various temperatures. The reaction gave the product of the single phase BaTiO_3 at any temperature. The conversion calculated on the basis of weight loss was in good agreement with that obtained from X-ray diffraction. The figure shows that the shape of curves below 580°C are different from those above 580°C . The temperature, at which the shape of the curves were changed, was obtained to be $\sim 577^\circ\text{C}$ from TG experiments. Here, the temperature is regarded as the melting temperature of $\text{Ba}(\text{NO}_3)_2$. The curves below 577°C were turned downward with time, but the curves above 577°C were changed upward.

After the reaction finished, the cylindrical pellet was not geometrically changed in the reactions below $\sim 577^\circ\text{C}$. At temperatures exceeding 577°C the top and bottom surfaces of the pellet were expanded around the center. The product heated above $\sim 588^\circ\text{C}$ sometimes was fixed on the inner wall of the bucket.

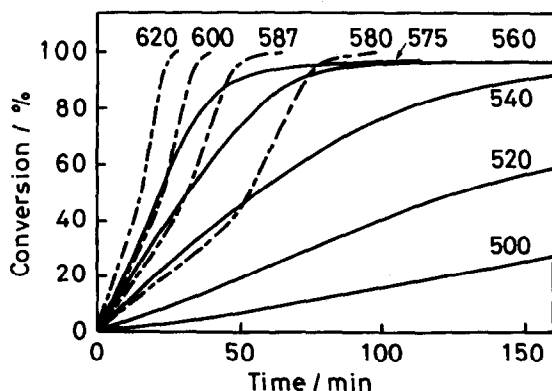


Fig. 2. Isothermal TG curves for the reaction of $\text{Ba}(\text{NO}_3)_2$ with TiO_2 .

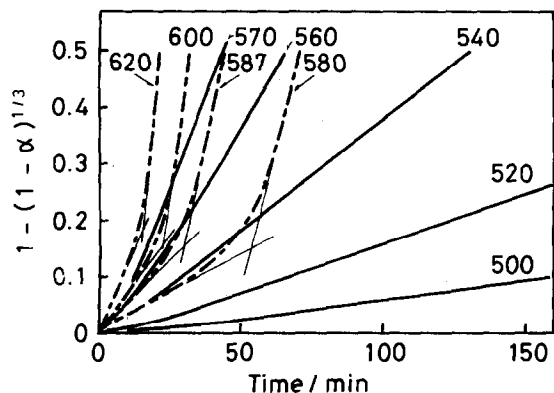


Fig. 3. Relationship between $1 - (1 - \alpha)^{1/3}$ and time for the reaction of $\text{Ba}(\text{NO}_3)_2$ with TiO_2 .

To determine the mechanism of the reaction, the data in Fig. 2 were analysed using equations based on two reaction models: One is the product growth controlled by diffusion of reactant through a product layer, $kt = [1 - (1 - \alpha)^{1/3}]^2$, and the other is product growth controlled by phase boundary reaction,

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

where k is the rate constant and t time. The data for isothermal reactions were fitted to eq. (1). The results re-drawn by using eq. (1) are shown in Fig. 3. The relationship between $1 - (1 - \alpha)^{1/3}$ and time became one straight line in the reactions below the melting temperature of $\text{Ba}(\text{NO}_3)_2$, and two lines with a bend above the temperature. From the slopes the reaction rates were calculated. The decomposition of $\text{Ba}(\text{NO}_3)_2$ also obeyed eq. (1).

Figure 4 shows the temperature dependence on the rate constants for the reaction of $\text{Ba}(\text{NO}_3)_2$ with TiO_2 and the decomposition of $\text{Ba}(\text{NO}_3)_2$. In the figure, \circ shows the rates below 577°C and at the earlier period above 577°C , \bullet the rates at the later period above 577°C , and \triangle the decomposition rates of $\text{Ba}(\text{NO}_3)_2$. The activation energy, Q , of the reaction in each temperature region was calculated according to the Arrhenius equation:

$$k = C \exp(-Q/RT) \quad (2).$$

The values were 212 ± 3 , 231 ± 6 and $184 \pm 8 \text{ kJ mol}^{-1}$ for the solid-solid reaction, and the earlier and later periods in the liquid-solid reaction, respectively. The rates obtained above 577°C , especially those of the later period, were not so accurately because the shape of the sample sometimes was changed. Although scattered, the rates at the later period above 577°C are seen to be on the extrapolated line obtained from the data below 577°C . When calculated from the data, the rate equation was given as $k = 2.38 \times 10^{11} \exp(-215,000/RT)$ in the

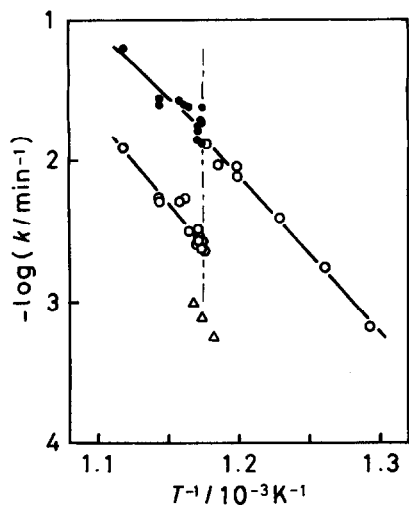


Fig. 4. Temperature dependences of the rate constants for the reaction of $Ba(NO_3)_2$ with TiO_2 and the decomposition of $Ba(NO_3)_2$:

- the solid-solid state and the earlier period in the liquid-solid state;
- the later period in the liquid-solid state; and
- △ the decomposition of $Ba(NO_3)_2$.

overall temperature range instead of $k = 1.60 \times 10^{11} \exp(-212,300/RT)$ below 577 °C. The agreement of both the rate equations will show that the mechanism is not changed even if the phase of $Ba(NO_3)_2$ is changed from solid to liquid. The activation energy for the decomposition of $Ba(NO_3)_2$ was not calculated because the decomposition rate was determined only in a narrow temperature range.

Isothermal, simultaneous TG and DTA

The sample temperature, strictly the temperature at the interface between the unreacted matrix and the product layer, is generally lower than the surrounding temperature for endothermic reactions such as the decomposition of metal carbonates. The enthalpy changes of the reaction and the decomposition of $Ba(NO_3)_2$, ΔH°_{r298} and ΔH°_{d298} , are 338.33 and 504.93 kJ mol($Ba(NO_3)_2$)⁻¹, respectively, calculated using NBS Tables(ref.4). The energy required is supplied from the surroundings. When the reaction occurs in the liquid-solid state, the energy for melting of $Ba(NO_3)_2$ is further needed. The enthalpy of the melting of $Ba(NO_3)_2$ is not known. Figure 5 and 6 show simultaneous TG and DTA curves for the isothermal reactions at 570 and 590°C, respectively. Here, experiments were performed by keeping the sample temperature constant. In Fig. 5, after the sample temperature becomes the desired one, the temperature difference due to the reaction is observed. It was -4°C at the minimum of the DTA curve. In Fig. 6, the endothermic peak due to the melting of $Ba(NO_3)_2$ is seen just after the sample temperature reaches 590°C, next the second peak of -8°C at the minimum is observed. As the temperature was measured through the thermocouple attached on the Pt sample holder, the temperature at the reaction interface will be further lower than that measured. The lowering of the sample temperature due to the melting of $Ba(NO_3)_2$ is thought to cause the lowering of the reaction rate at the

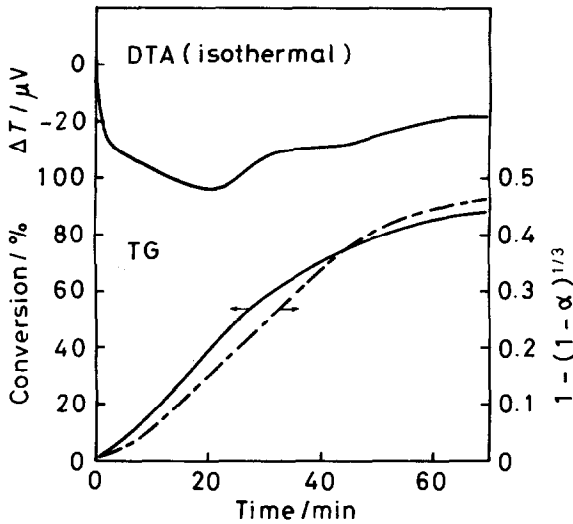


Fig. 5. Isothermal, simultaneous TG and DTA curves for the reaction of $\text{Ba}(\text{NO}_3)_2$ with TiO_2 at 570°C .

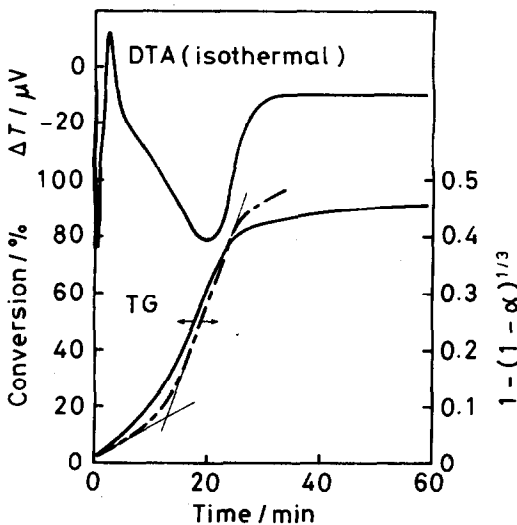


Fig. 6. Isothermal, simultaneous TG and DTA curves for the reaction of $\text{Ba}(\text{NO}_3)_2$ with TiO_2 at 590°C .

earlier period. Thus the difference in the reaction behavior below and above the melting temperature will result from the melting of $\text{Ba}(\text{NO}_3)_2$. It might be thought that the difference in activation energy between 212 and 231 kJ, i.e. 19 kJ, comes from the enthalpy of the melting of $\text{Ba}(\text{NO}_3)_2$.

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