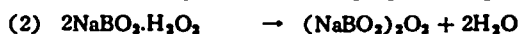
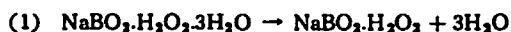


Thermal decomposition of sodium perborate

by Toshiyuki NAGAISHI*, Masato TOHBO*, Junichi YOSHIMURA*,
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The thermal decomposition of sodium perborate was studied by thermal analysis and kinetic measurements. The decomposition process consisted of three steps: first of dihydration, second of decomposition of hydrogen peroxide and third of O₂ evolution. These steps are expressed by following reactions.



The kinetics of the reactions (2) and (3) obey a contracting-area Eq. (1),

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

Each of the activation energy and pre-exponential factor for the reactions (2) and (3) is 17.9 kcal/mol, 1.4×10^{10} , 18.9 kcal/mol and 2.0×10^9 respectively.

1. Introduction

It is well known that sodium perborate is widely used for detergent, cosmetic and a raw material manufacturing hydrogen peroxide.

For the nature of sodium perborate, F. Foerester¹⁾ concluded that the chemical formula of sodium perborate is not NaBO₃·4H₂O, but NaBO₃·H₂O₂—

3H₂O, addition compound of sodium borate with hydrogen peroxide from the experimental observations. The dehydration and thermal decomposition processes were reported in Gmelin²⁾ that three molecules of water are removed from perborate by dehydration to give O-B(H₂O₂)-ONa, from which the fourth water molecule is removed at higher temperature to produce (NaBO₃)₂O₂, and then the decomposition occurs evolving O₂ gas.

However, it seems that much experimental facts are needed to understand the process of

thermal decomposition of sodium perborate.

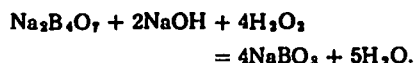
A search of the available literatures showed that thermal decomposition of sodium perborate has not been studied so far.

The purpose of this report is to discuss the decomposition process and to get the kinetic data.

2. Experiment

2.1 Material used in the experiment

Sodium borate was prepared from "Special" grade reagents and synthesized at room temperature³⁾. It was crystalized from a saturated solution of sodium metaborate mixed with 40 ml of 20 wt % sodium hydroxide and 45 ml of 30 wt % hydrogen peroxide, formed as follows:



The precipitate was washed with methanol and dried in vacuum at room temperature for 24 hours.

The chemical analysis of sodium perborate was done by the standard volumetric method described in elsewhere⁴⁾. The purity was 99.4 % for peroxide content.

2.2 Thermal analysis

The major part of the studies of thermal a-

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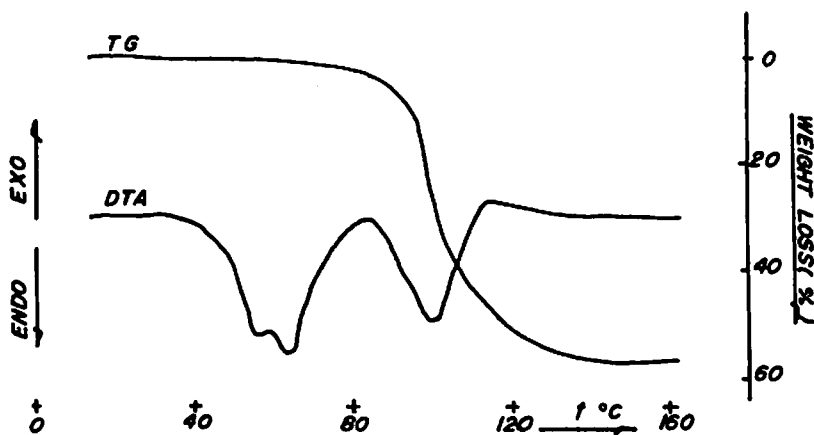


Fig. 1 DTA and TG curves of sodium perborate in air (heating rate = 10°C/min)

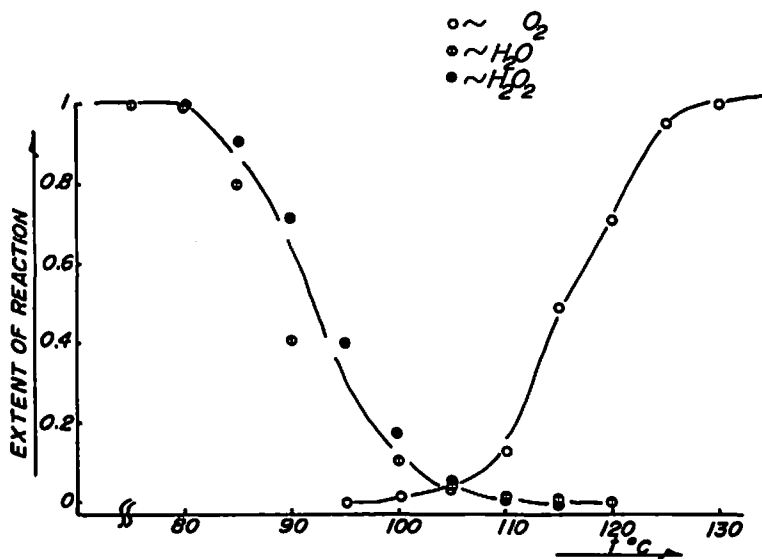


Fig. 2 Dehydration, chemical analysis of hydrogen peroxide and evolution of O₂ gas at various temperatures.

analysis are described in the earlier paper³. For the kinetic study, a known amount of the powdered sample was taken and the reaction was carried out in an electric furnace.

Both of the flow method of a fixed bed flow reactor with a gas chromatography and the static method of chemical analysis of hydrogen peroxide were adopted in isothermal condition.

3. Result

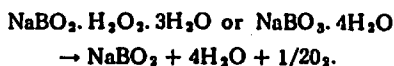
3.1 Thermal and chemical analyses

The DTA and TG curves of the sample are shown in Fig. 1. The DTA trace has three en-

dothermic peaks at 50, 60 and 100°C respectively.

The TG trace shows only one weight loss region in the temperature range of 80 and 140°C.

The observed weight loss of the sample at 150°C is 57%, which is in agreement with the calculated value of 57.2% based on the following reaction:



The decomposition products were NaBO₃·3H₂O

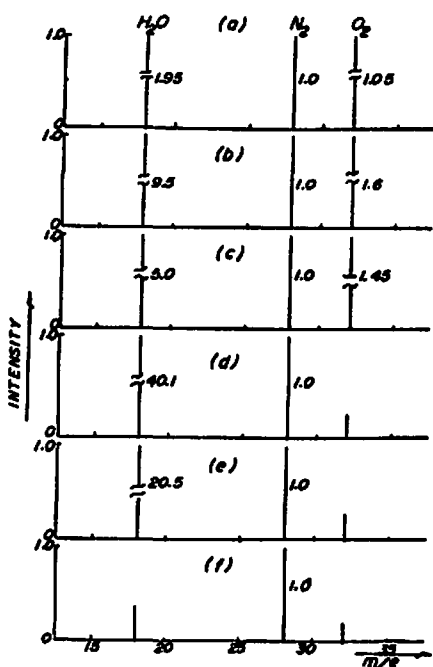


Fig. 3 Mass spectra of sodium perborate at the temperatures of (a) 100°C, (b) 90°C, (c) 80°C, (d) 70°C, (e) 50°C, and (f) 30°C.

or $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ at 70°C and NaBO_2 , the final product at 150°C by X-ray diffraction.

Three curves of O_2 gas evolution, dehydration and decomposition of hydrogen peroxide of the sample are shown in Fig. 2. The DTA trace has two endothermic peaks at 50 and 60°C corresponding to the dehydration, but the TG trace does not show weight loss in this temperature range probably because of low evaporation rate of water. Therefore, dehydration and decomposition of hydrogen peroxide seemed to occur at the same temperature.

After these processes were nearly completed, O_2 gas evolution occurred at the temperature of 95°C. In Fig. 3 mass spectra at various temperatures are indicated. It should be noted that intensity of water molecule increased rapidly at first and then reached maximum followed by the increase in the intensity of O_2 molecule and that the mass peak 34, that of hydrogen peroxide could not be detected at all in contrast with

other addition compounds such as sodium carbonate with hydrogen peroxide¹⁾.

3.2 Kinetic measurement

The thermal decomposition kinetics were measured both in flow and static conditions. It is revealed the kinetics of the reaction follows a contracting-area Eq. (1),

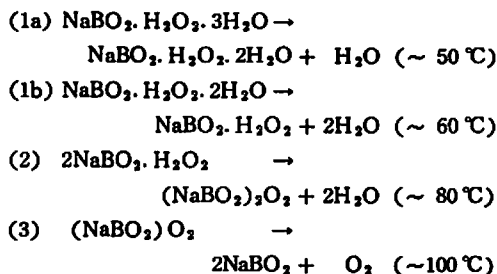
$$1 - (1 - \alpha)^{1/2} = kt \quad (1)$$

The applicability of Eq. (1) is shown in Fig. 4 (a) and (b), where plots of $1 - (1 - \alpha)^{1/2}$ vs. time are linear.

The activation energies were found to be 17.9 and 18.9 kcal/mol for static and flow methods.

4. Discussion

The results obtained from DTA, TG, X-ray diffraction analysis and three measurements of dehydration, decomposition of hydrogen peroxide and O_2 gas evolution suggest the following thermal decomposition mechanism:



The suggested mechanism is consistent with the arguments adopted by F. Foerster¹⁾ the sodium perborate had not a structure of pure perborate but an addition compound with hydrogen peroxide on the following bases:

- (a) The perborate synthesized, could not liberate iodine from a potassium iodate solution, whereas it decomposed evolving O_2 gas.
- (b) $(\text{NaBO}_2)_2\text{O}_2$ was produced by heating the borate in vacuum.

Both the facts that O_2 gas began to evolve after the decay of hydrogen peroxide was nearly completed, and that the mass spectrum analysis from which hydrogen peroxide could not be detected, support the reactions (2) and (3).

4.2 Kinetic measurement

For both the flow and static methods, kinetic law obeyed a contracting-area Eq. (1).

In the isothermal decomposition reaction, the

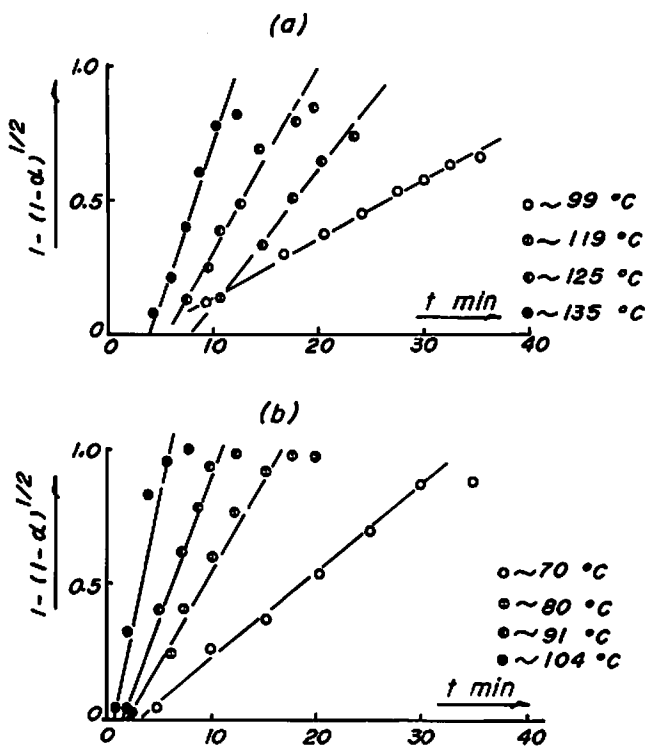


Fig.4 Isothermal decomposition by (a) flow and (b) static methods showing plots of $1 - (1 - \alpha)^{1/2}$ vs. time

temperature range studied by the flow method was different from that by the static one. It is revealed that each of the two methods corresponds to the different reactions. In the flow method by which the amount of O_2 gas evolved from the sample was measured with a gaschromatography, it is understood that kinetic measurement was carried out for the reaction (3).

On the other hand, in the static method by which the concentration of hydrogen peroxide decomposed, was measured, kinetic parameters obtained should be related to the reaction (2).

A theoretical basis for Eq. (1) is provided by a reaction model based on the following assumptions⁶⁾.

- (c) Nucleation is extremely rapid followed by rapid surface growth.
- (d) The shape of a reactant particle is cylindrical.
- (e) A diffuse reaction interface is developed within reactant particles and the rate of advance is constant.

The validity of the model was not confirmed experimentally since the crystal size of sodium perborate was too small to serve for the microscopic examinations.

The activation energies of the reactions (2) and (3) calculated from the temperature coefficient were 19.7 and 18.9 kcal/mol, and the pre-exponential factors were 1.4×10^{10} and 2.0×10^9 respectively.

The rate of the reaction (2) is greater than that of the reaction (3).

These Arrhenius parameters should be identical for the reactions (2) and (3) with any particular bond distribution step in either H_2O_2 breakdown or O_2 evolution. It is however not sure that the values found here have fundamental or mechanistic significance from our results.

5. Conclusion

The solid state decomposition of sodium perborate consisted of three steps, dehydration, decomposition of hydrogen peroxide and O_2 gas

evolution.

Each of second and third steps is a contracting-area rate process.

The mechanism of hydrogen peroxide breakdown and that of O_2 evolution were not characterized, although the activation energies and pre-exponential factors were obtained.

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過ホウサンナトリウムの熱分解

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過ホウ酸ナトリウムの熱分解が研究された。

熱分解は次の三段階に分けられる。

- 第一段 : 過ホウ酸ナトリウムの結晶水の脱水反応
- 第二段 : 過酸化水素の分解反応
- 第三段 : 酸素ガスの発生

上記の三つの過程は脱水曲線や過酸化水素の分解曲線および酸素ガスの発生曲線を求めることにより明確となった。

速度論的測定が第二段と第三段階の反応に対しておこなわれた。反応は面収縮モデルに基づき速度則に適合し、活性化エネルギー、前指数因子としてそれぞれ 17.9 kcal/mol, 18.9 kcal/mol, 1.4×10^{10} , 2.0×10^9 なる値をえた。