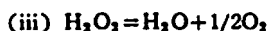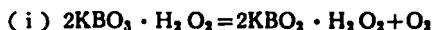# Thermal Decomposition of Potassium Perborate

by Toshiyuki NAGAISHI*, Yoshifumi TANISAWA*
Masaru MATSUMOTO* and Shunichi YOSHINAGA*

The thermal decomposition of potassium perborate was carried out by means of thermal analysis and kinetic measurements. The decomposition process consists of three steps described as follows:

(i) $2KBO_3 \cdot H_2O_2 = 2KBO_2 \cdot H_2O_2 + O_2$

(ii) $2KBO_2 \cdot H_2O_2 = 2KBO_2 + H_2O_2$

(iii) $H_2O_2 = H_2O + 1/2O_2$

The overall kinetics obeys the first-order reaction, $\ln(1-a) = kt$.

The activation energy and pre-exponential factor were determined to be 33. 0 kcal/mol and 1.37×10^{14}, respectively.

1. Introduction

It is well known that there exist many metal perborates and addition compounds of metal borates with hydrogen peroxide. Their structures and physico-chemical properties are presented in Gmeline[1] or Mellor's book[2]. W. Machu described the manufacturing and applications of metal perborates in his book[3]. Sodium and magnesium perborates are used industrially for bleaching purpose.

However, the thermal analysis for metal perborates has been little studied, though the thermal decomposition of sodium perborate was reported by this author[4]. Potassium perborate was prepared by a method similar to that employed for sodium salts, but the chemical constitution was different. C. von Girsewald[5] obtained $2KBO_3 \cdot H_2O$ and $2KBO_3 \cdot H_2O_2$. The latter compound deflagrated at 150℃ to 160℃, when rapidly heated, but if heated slowly, the active oxygen is quantitatively evolved. It was felt from our search of the literatures that little attension was paid to the thermal decomposition of potassium perborate. The aim of this paper is to study the thermal decomposition of potassium per-

borate as well as to obtain the kinetic data.

2. Experimentals

2. 1 Materials used and preparation of the perborate

Potassium meta borate and hydrogen peroxide obtained from Nakai Chemicals were chemical reagent grade. Potassium perborate was prepared by mixing 100ml of the saturated potassium meta borate solution with 50ml of 35wt% hydrogen peroxide solution. Under cooling by ice, 150ml of methanol was added to the mixture solution to precipitate potassium perborate crystals. The precisitate was filtrated, washed with methanol and dried in vacuum at room temperature for 24 hours. The chemical analysis of potassium perborate was done by the standard volumetric method. The purity was above 97.3% as for the peroxide content.

2. 2 Thermal analysis

Thermal analysis for the decomposition of potassium perborate is the same method as described earlier[4]. O_2 gas was measured by a gaschromatography at elevated temperatures in He flow.

2. 3 Kinetic measurement

Three kinds of the method were used to obtain the kinetic data as well as to observe the catalytic effect of the reactant, the solid or gaseous products. The first one is to measure the extent of reaction from the chemical analysis of the reactant. The

second one is to measure the weight loss on TG under isothermal condition. The last one is to use gas burette method[6] by which the volume of gas evolved is measured.

3. Result

3.1 Thermal analysis

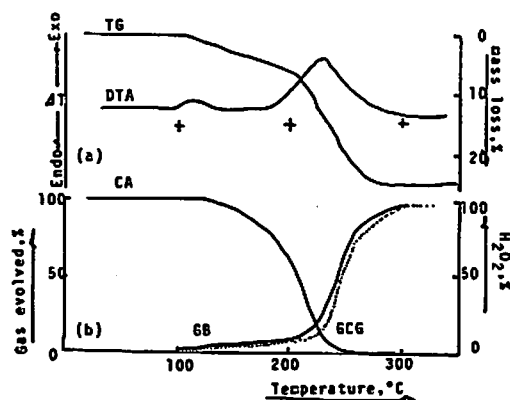The DTA and TG traces of potassium perborate

Fig. 1 DTA and TG curves, and three curves of evolved gas analysis (GB), O_2 gas evolved (GCG) and the perborate decomposed (CA) at elevated temperaters.
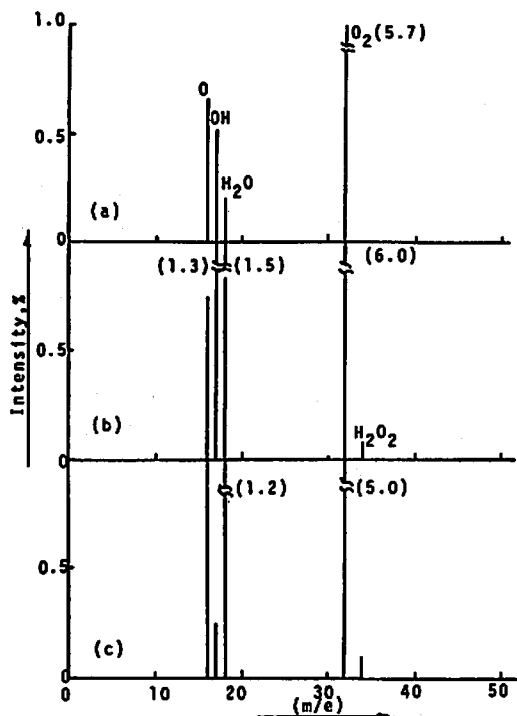

Fig. 2 Mass spectra at three different temperatures, (a) at 140°C, (b) at 150°C, (c) at 180°C.

are shown in Fig. 1 (a). The DTA trace has two exothermic peaks at around 140°C and 250°C, respectively. The TG trace has also two weight loss regions corresponding to the DTA trace. The observed weight loss at 300°C was 27.3% which is agreed with the calculated value of 28.7% based on the follwing overall scheme:

$$2KBO_3 \cdot H_2O_2 = 2KBO_2 + H_2O + 3/2O_2$$

The final product was KBO_2 identified by X-ray diffraction. Fig. 1 (b) shows the three curves corresponding to O_2 gas evolution, the decomposition of peroxide and the evolved gas analysis. The initial temperature at which either the CA curve is falling or both GCG and GB curves are rising, is the same as that of DTA and TG. However, these curves have not two distinct regions unlike DTA and TG. It is suggested from this fact that two step reactions may occur consecutively and may partly overlap each other.

In Fig. 2, mass spectra are shown under various temperatures. It should be noted that (1) the evolution of O_2 is the largest, (2) the mass peak 34, that of hydrogen peroxide was detected, and (3) the evolution of H_2O increased with the evolution of hydrogen peroxide.

3.2 Kinetic measurement

The kinetics of the decomposition of potassium perborate were measured under three different methods as stated in Experimentals.

It is revealed that the kinetic law obeys the first-order reaction, $\ln(1-\alpha) = kt$ (I), regardless of the different methods used. Fig. 3 shows the applicability of the equation (I), from which the linearity is proved to be good. The Arrhenius plots are shown in Fig. 4. All of the observed points were fitted on the same line. The activation energy and logarithm of preexponential factor were determined to be 33.0kcal/mol and 32.55, respectively.

4. Discussion

4.1 The decomposition mechanism

The decomposition scheme of potassium perborate was deduced on the basis of the results obtained from the thermal analysis, X-ray diffraction, mass spectrometry, the evolved gas analysis and chemical analysis of peroxide as follows:
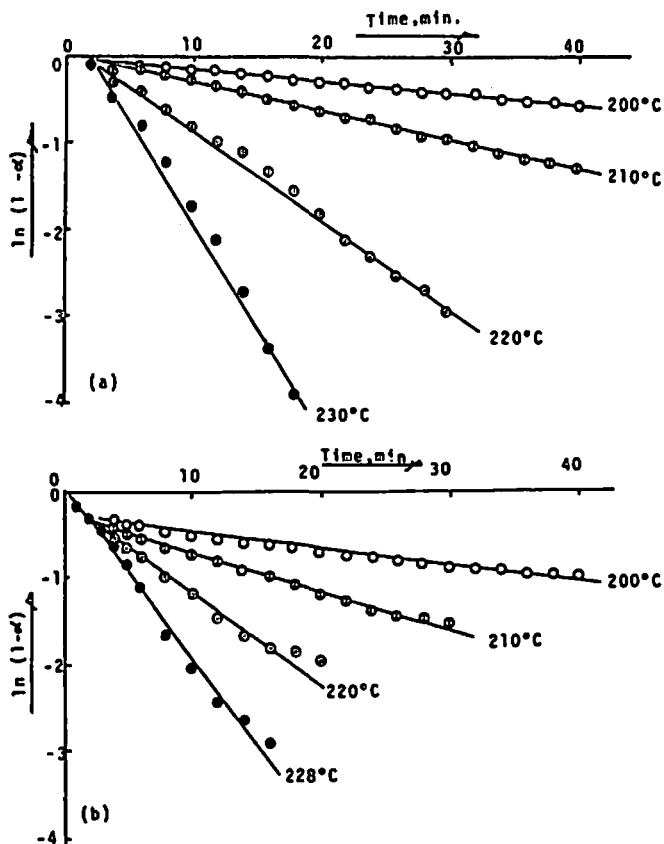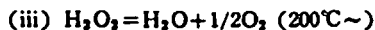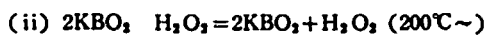
(i) $2KBO_3 \cdot H_2O_2 = 2KBO_2 \cdot H_2O_2 + O_2$
   (100°C~)
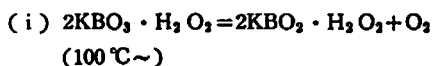
Fig. 3 The first-order plot.
(a) Measured from the perborate decomposed by the method of chemical analysis and (b) Measured from weight loss on TG.

(ii) $2KBO_2$ $H_2O_2 = 2KBO_2 + H_2O_2$ (200°C ~)

(iii) $H_2O_2 = H_2O + 1/2O_2$ (200°C ~)

The suggested mechanism is consistent with the result of mass spectra and other measurements. The reactions (i) and (ii) may occur consecutively and partly overlap. The reaction (ii) was considered because hydrogen peroxide was detected by the mass spectrometer. The reactions (ii) and (iii) may occur simultaneously.
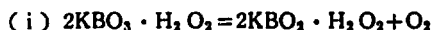
4. 2 Kinetic measurement

It was found that the kinetic law obeyed the same rate law, the first-order reaction, independent of three different methods adopted. The Arrhenius plot was fitted on the same line. It was deduced from these facts that the catalytic effect of the reactant and the products including both gaseous and solid phases on the decomposition, was not recognized. In contrast to the decomposition of sodium perborate, the rate constants of each reaction step (i) and (ii) or (iii) could not be obtained in the decomposition of potassium perborate. It is not sure to which reaction step the rate constant derived from this experiment belongs. This rate constant may be rather called as overall one. The rate determining step may be deduced to be the reaction (ii), taking both the temperature ranges studied and the activation energy into account.

5. Conclusion

The solid state decomposition of potassium perborate occures in three steps, expressed by the following equations:

(i) $2KBO_3 \cdot H_2O_2 = 2KBO_2 \cdot H_2O_2 + O_2$

(ii) $2KBO_2 \cdot H_2O_2 = 2KBO_2 + H_2O_2$

(iii) $H_2O_2 = H_2O + 1/2O_2$

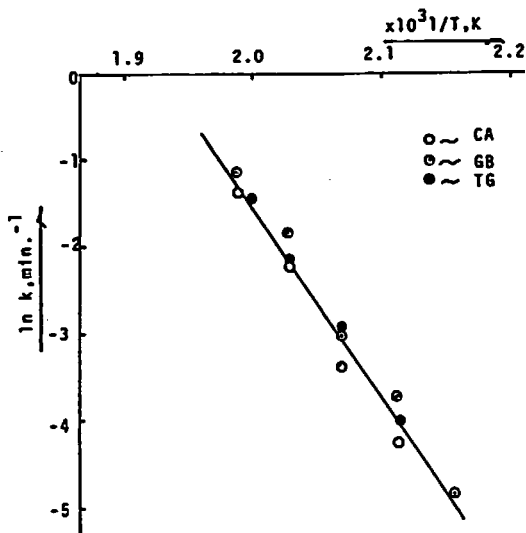The rate law obeys the first-order reaction. The catalytic effect of the reactant, gaseous products and

Fig. 4 Arrhenius plot.
CA is derived from the measurement of the perborate decomposed by chemical analysis; GB from that of volume of gas evolved by gas burette; TG from weight loss measurement.

solid products on the decomposition was not recognized. The rate constant, k was derived as $1.37 \times 10^{14} \exp(-33000, \text{cal/mol/RT})$, min^{-1} The rate determining step was deduced to be the reaction (ii).
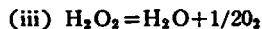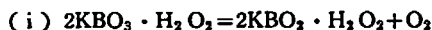
Literatures

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2) J. Mellor, 'MELLOR'S TREAATIES ON INORGANIC AND THEORETICAL CHEMISTRY' 118 (1960) vol. 5, Longmans

3) W. Machu, 'DAS WASSERSTOFFPEROXYD UND DIE PERVERBINDUNGEM' ,13 (1950) SPRINGER-VERLAG

4) T. Nagaishi, M. Tohbo, J. Yoshimura, M. Matsumoto and S. Yoshinaga, J. Industrial Explosives Society, Japan, 42, 304 (1981)

5) C. Girsewald, 'ANORGANISCHE PEROXYDE UND PERSALZE' 54 (1914), Braunschweig

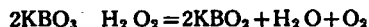6) A. Kodera, 'BUTSURIKAGAKU JIKKENSHO', 188 (1971) ASAKURA SHOTEN

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過ホウ酸カリウムの熱分解

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過ホウ酸カリウムの熱分解を熱分析法と速度測定法により研究した。

熱分解は次の三段階でおこる。

(i) $2KBO_3 \cdot H_2O_2 = 2KBO_2 \cdot H_2O_2 + O_2$

(ii) $2KBO_2 \cdot H_2O_2 = 2KBO_2 + H_2O_2$

(iii) $H_2O_2 = H_2O + 1/2O_2$

速度式は一次反応式に適合した。求めた速度定数は

$2KBO_3 \ H_2O_2 = 2KBO_2 + H_2O + O_2$

なる，(i),(ii),(iii) の反応式をあわせた総括反応の速度定数である。その値として，$k = 1.37 \times 10^{14} \exp(-33000/RT)$ をえた。律速段階の反応として (ii) を推定した。

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