THERMAL DECOMPOSITION OF MAGNESIUM PEROXOBORATE

T. Nagaishi, M. Inoue, M. Matsumoto and *S. Yoshinaga*

DEPARTMENT OF INDUSTRIAL CHEMISTRY, FACULTY OF ENGINEERING,
KYUSHU SANGYOU UNIVERSITY, 2–327, MATSUKA-DAI, HIGASI-KU,
FUKUOKA 813, JAPAN

The thermal decomposition of magnesium peroxoborate was studied by means of a derivatograph. It was found that the decomposition involves a sequence of reactions: dehydration and O_2 evolution. The kinetic parameters were obtained in each step of the reaction. The thermal stabilities of three kinds of metal peroxoborates are discussed.

It is well known that there exist various kinds of metal per(oxo)borates and addition compounds of borate with hydrogen peroxide. Especially, sodium perborate has been widely used for detergent, disinfectant and cosmetic manufacture.

Magnesium peroxoborate is also important in the pharmaceutical industry for its stability, very weak basic nature, high content of O_2, and lack of flavour.

The structures and physico-chemical properties of per(oxo)borates and addition compounds of borate with hydrogen peroxide are surveyed by Gmelin [1] and Mellor [2]. Machu described the properties and manufacture of magnesium peroxoborate [3].

As concerns the addition compound of sodium borate with hydrogen peroxide and potassium peroxoborate, the decomposition steps and their rates have been described [4, 5].
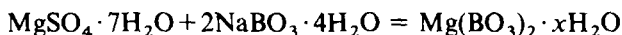
Our search of the literature revealed that, despite its wide industrial use, the thermal decomposition of magnesium peroxoborate has not been studied so far.

The present investigation was designed to clarify the thermal decomposition of magnesium peroxoborate and to obtained the kinetic data. The thermal properties of magnesium peroxoborate were also compared with those of the sodium and potassium salts.

Experimental

Materials used

Magnesium peroxoborate was prepared [6] by heating a mixture of magnesium sulfate heptahydrate (0.1 mol) and sodium peroxoborate (0.2 mol) at 65–70° in a water-bath for about an hour. Magnesium peroxoborate or the addition compound of magnesium borate were formed, together with sodium sulfate:

$$MgSO_4 \cdot 7H_2O + 2NaBO_3 \cdot 4H_2O = Mg(BO_3)_2 \cdot xH_2O$$

or

$$Mg(BO_2)_2 \cdot 2H_2O_2 \cdot yH_2O + Na_2SO_4 + zH_2O$$

where $z = 15 - x$ or $13 - y$.

The products on a glass filter were washed with water to dissolve out sodium sulfate. The peroxide of the addition compound remained on the filter as a solid residue. The yield was 85%. The product was dried in vacuum at room temperature for 24 hours. From thermal analysis, mass spectometry (mass peak 34, that of hydrogen peroxide, was not detected) and chemical analysis of peroxide by the standard volumetric method [7], the formula was found to be $Mg(BO_3)_2 \cdot 2H_2O$.

Thermal analysis and kinetic measurements

Thermal analysis was carried out by the method described earlier [4, 5]. For the kinetic measurements, 70–110° was chosen for dehydration and 170–210° for O_2 evolution. The TG method was used for dehydration, and the method of O_2 evolution with gas chromatography for decomposition [8].

Results and discussion

The DTA, TG and O_2 evolution curves are shown in Fig. 1. The DTA curve has two peaks, one of which is endothermic at 100°, while the other is exothermic at 175°. Corresponding to the DTA curve, there are two weight loss regions (50–110° and 140–210°) in the TG curve.

The solid residue of the thermal decomposition of the sample was identified as magnesium borate, $Mg(BO_2)_2$, by X-ray diffraction.

The observed weight loss at 210° is 38%, which is in agreement with the calculated value of 38.2% based on the following reaction:
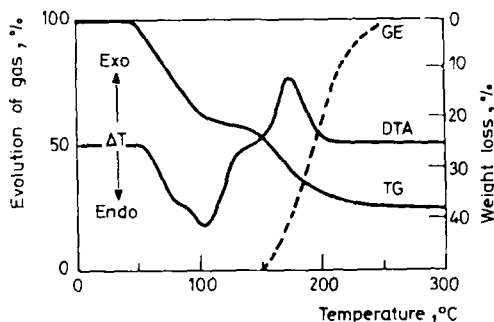
$$Mg(BO_3)_2 \cdot 2H_2O \text{ or } Mg(BO_2)_2 \cdot 2H_2O_2 \rightarrow Mg(BO_2)_2 + 2H_2O + O_2 \quad (1)$$
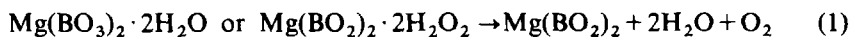
Fig. 1 DTA, TG and EGA curves of $Mg(BO_3)_2 \cdot 2H_2O$ in air (heating rate = 10 deg/min)

In Fig. 2 mass spectrometer runs at various temperatures are shown. While the intensity of the water molecule peak ($m/e = 18$) is strong at low temperature and gradually becomes weak as the temperature increases, that of the O_2 molecule peak ($m/e = 32$) becomes strong with temperature rise, and that of the mass 34 peak, that of hydrogen peroxide, is not detected. These results suggest that the chemical formula of the sample is not $Mg(BO_2)_2 \cdot 2H_2O_2$, but $Mg(BO_3)_2 \cdot 2H_2O$, and that
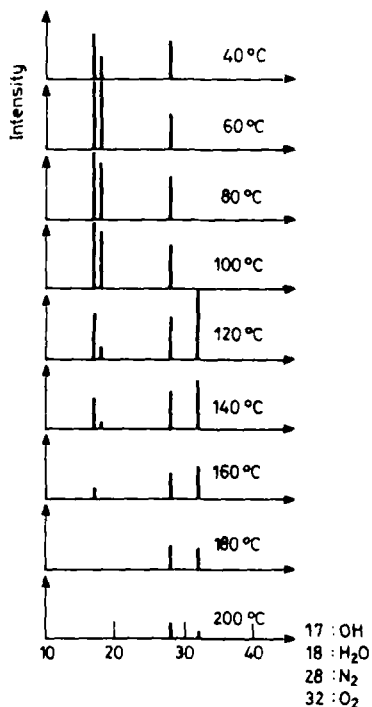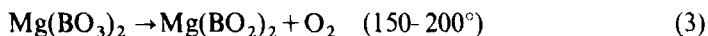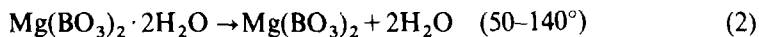

Fig. 2 Mass spectra records at various temperatures

the overall decomposition scheme (1) can be replaced by the following sequence of reactions:

$$Mg(BO_3)_2 \cdot 2H_2O \rightarrow Mg(BO_3)_2 + 2H_2O \quad (50-140°) \qquad (2)$$

$$Mg(BO_3)_2 \rightarrow Mg(BO_2)_2 + O_2 \quad (150-200°) \qquad (3)$$

The observed weight loss at 140° is 22%, which is consistent with the calculated value of 20.2%, based on Eq. (2).

The extent of dehydration reaction (2) as a function of time by isothermal TG measurement is shown in Fig. 3a. The kinetic data are analyzed with a first-order rate law in Fig. 3b. There is fairly good linearity. This suggests that the kinetics of the dehydration follows a first-order rate equation based upon random nucleation and fast growth of nucleation.

The activation energy for dehydration, calculated from the slope of the Arrhenius plot in Fig. 3c, was 44.3 kJ/mol.

It is also shown in Fig. 4a that the rate for decomposition reaction (3), measured from O_2 evolution, obeys a first-order rate equation in the whole range, which is the same as in the case of the dehydration reaction.
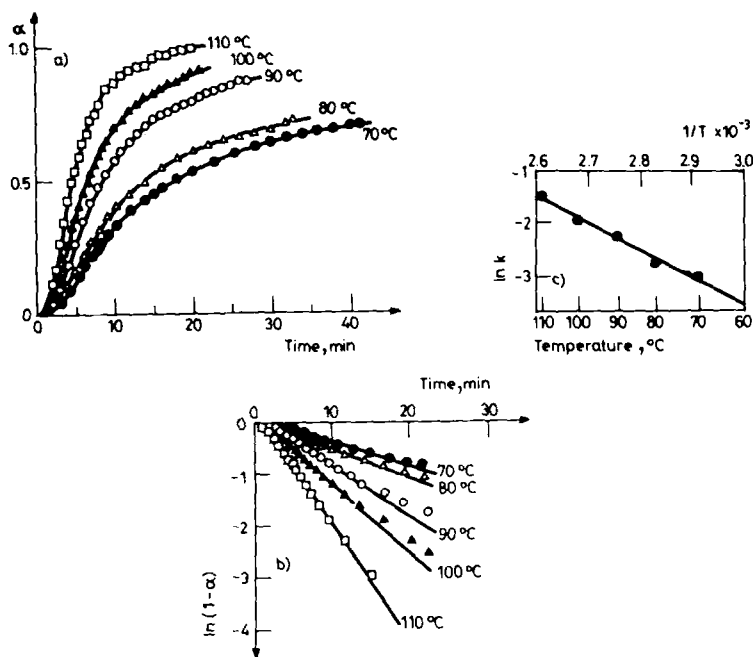

Fig. 3 (a) Extent of reaction corresponding to (2) by isothermal TG method in air, (b) first order plot, (c) Arrhenius plot
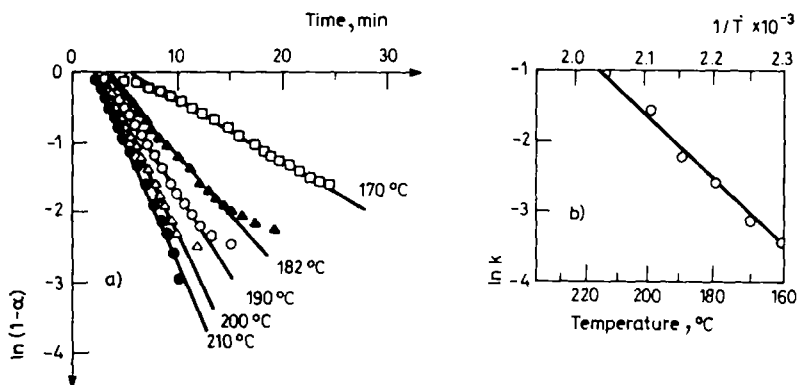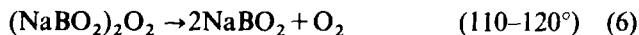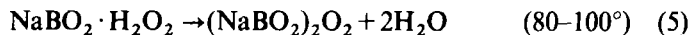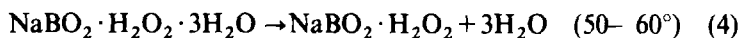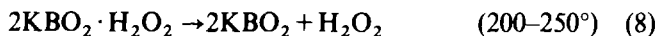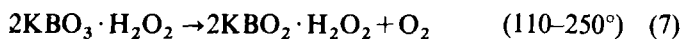
Fig. 4 (a) First order plot corresponding to the reaction (3), (b) Arrhenius plot

The kinetic parameters derived from the Arrhenius plot are shown in Fig. 4b. The activation energy and the frequency factor were obtained as 75.7 kJ/mol and 2.1×10^9 s^{-1}, respectively.

The thermal decompositions of peroxoborates of sodium and potassium have been reported [4, 5]. The decomposition scheme for the sodium salt is expressed as follows:

$$NaBO_2 \cdot H_2O_2 \cdot 3H_2O \rightarrow NaBO_2 \cdot H_2O_2 + 3H_2O \quad (50-60°) \quad (4)$$

$$NaBO_2 \cdot H_2O_2 \rightarrow (NaBO_2)_2O_2 + 2H_2O \quad (80-100°) \quad (5)$$

$$(NaBO_2)_2O_2 \rightarrow 2NaBO_2 + O_2 \quad (110-120°) \quad (6)$$

For the potassium salt, the following equations are given:

$$2KBO_3 \cdot H_2O_2 \rightarrow 2KBO_2 \cdot H_2O_2 + O_2 \quad (110-250°) \quad (7)$$

$$2KBO_2 \cdot H_2O_2 \rightarrow 2KBO_2 + H_2O_2 \quad (200-250°) \quad (8)$$

$$H_2O_2 \rightarrow H_2O + 1/2O_2 \quad (200-250°) \quad (9)$$

The kinetic parameters are listed in Table 1. The amount of O_2 evolution per 1 g sample increases in the sequence Na salt $<$ Mg salt $<$ K salt, as calculated on the basis of the overall decomposition reaction such as reaction (1). The temperature at which O_2 evolves is the lowest for the Na salt. For the potassium salt, the temperature is lower than for the Mg salt, but the DTA peak temperature is lower for the Mg salt than for the K salt.

These facts, as well as the results of the kinetic measurements in Table 1, show that the thermal stability decreases in the sequence
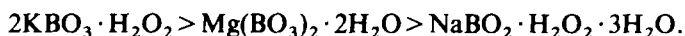
$$2KBO_3 \cdot H_2O_2 > Mg(BO_3)_2 \cdot 2H_2O > NaBO_2 \cdot H_2O_2 \cdot 3H_2O.$$

Table 1 Summary of kinetic data for decomposition of metal peroxoborates

Formula	Temperature range, °C	Method	Kinetic equation	Activation energy, kJ/mol	Frequency factor, s⁻¹
$NaBO_2 \cdot H_2O_2 \cdot 3H_2O$	70–100[1]	CA[5]	$1-(1-\alpha)^{1/2}$	74.9	8.4×10^{11}
	100–175[2]	gaschro.[6]	$1-(1-\alpha)^{1/2}$	79.1	1.2×10^{11}
$2KBO_3 \cdot H_2O_2$	200–230	gaschro.	$\ln(1-\alpha)$	138.1	8.2×10^{15}
$Mg(BO_3)_2 \cdot 2H_2O$	70–110[3]	TG	$\ln(1-\alpha)$	44.3	1.4×10^7
	170–210[4]	gaschro.	$\ln(1-\alpha)$	75.7	2.1×10^9

1), 2), 3), 4) Corresponding to the reactions (5), (6), (2) and (3), respectively. For K salt, corresponding to the reactions (7) + (8) + (9). 5) Extent of reaction determined by chemical analysis of hydrogen peroxide. 6) Extent of reaction determined by O_2 gas evolution with a gaschromatography

Conclusion

Magnesium peroxoborate, $Mg(BO_3)_2 \cdot 2H_2O$, decompose in two steps, given by the equations:

$$Mg(BO_3)_2 \cdot 2H_2O \rightarrow Mg(BO_3)_2 + 2H_2O \qquad (50-140°)$$

$$Mg(BO_3)_2 \rightarrow Mg(BO_2)_2 + O_2 \qquad (150-200°)$$
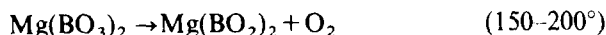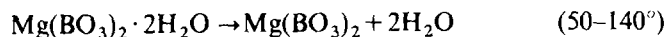
Each step of the decomposition obeys a first-order rate equation. The activation energies and frequency factors for the steps of the decomposition were obtained as 44.3 kJ/mol and 1.4×10^7 s⁻¹ for the dehydration, and 75.7 kJ/mol and 2.1×10^9 s⁻¹ for O_2 evolution, respectively.

The sequence of thermal stability of three kinds of peroxoborates is

$$KBO_3 \cdot H_2O_2 > Mg(BO_3)_2 \cdot 2H_2O > NaBO_2 \cdot H_2O_2 \cdot 3H_2O.$$
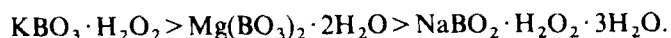
References

1 Gmelin Handbuch der Anorganischen Chemie, Verlag Chemie, 1975, Band 28, Teil 7, p. 221.
2 J. Mellor, Mellor's Treaties on Inorganic and Theoretical Chemistry, Longmans, 1960, Vol. 5, p. 118.
3 W. Machu, Das Wasserstoffperoxyd und die Perverbindungen, Springer Verlag, 1950, p. 13.
4 T. Nagaishi, M. Tohbo, J. Yoshimura, M. Matsumoto and S. Yoshinaga, J. Industrial Explosives Society, Japan, 42 (1981) 304.

5 T. Nagaishi, Y. Tanisawa, M. Matsumoto and S. Yoshinaga, ibid. 45 (1984) 94.
6 Chemical Society of Japan, Experimental Chemistry, Maruzen, 1977, Vol. 8, p. 595.
7 M. Ishibashi, Experimental Quantitative Analysis, Fuzanbo, 1963, p. 452 (in Japanese)
8 H. Nakamura, S. Nakamura and I. Nakamori, J. Industrial Explosives Society, Japan, 36 (1975) 27.

Zusammenfassung — Die thermische Zersetzung von Magnesiumperoxoborat wurde mittels eines Derivatographen untersucht. Es wurde festgestellt, daß an der Zersetzung zwei Reaktionen beteiligt sind: Dehydratisierung und Sauerstoffentwicklung. Die kinetischen Parameter beider Schritte wurden bestimmt. Die thermische Stabilität von drei Arten von Metallperoxoboraten wird erörtert.

Резюме — Посредством дериват ́графа изучено термическое разложение перекиси бората магния. Установлено, что разложение протекает в две последовательные стадии дегидратации и выделении кислорода. Для каждой стадии реакции вычислены кинетические параметры. Обсуждена термоустойчивость трех типов перекиси боратов металлов.