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Thermosonimetry and microscopic observation of the thermal decomposition of potassium chlorate

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Abstract

The thermal decomposition of potassium chlorate has been followed by simultaneous TS–DTA measurements and high-temperature microscopic observations. After melting, TS curves were found to consist of four broad peaks a to d. The origin of these peaks is assumed to result from bubbling, formation and movement of films on the melt surface, formation of viscous gelatinous melt and its movement, and formation of precipitated islands. The onset temperature of KClO_3 decomposition was determined to be around 360°C .

Keywords: Decomposition; DTA; Microscopy; Potassium chlorate; TS

1. Introduction

Acoustic emission (AE) in a solid results from various internal processes involving release of elastic energy, such as the generation and propagation of cracks or movement of dislocations. Recently, the analysis of acoustic emission resulting from chemical reaction has been a subject of increasing interest in analytical and thermoanalytical chemistry. The author has constructed a unique apparatus for the simultaneous measurement of AE and differential thermal analysis (DTA) [1] and has applied this technique to dehydration, phase transition and decomposition of several inorganic salts including several perchlorates [2–7]. The AE technique, which was first used as a thermoanalytical tool by Lonvik [8], is called thermosonimetry (TS); the notation TS will be used below instead of AE.

Compared with the many reports on the decomposition of KClO_4 , KClO_3 has not been so intensively studied, nor has the decomposition behavior been fully

explained [9,10], probably because decomposition in the molten state is difficult to follow by different analytical techniques except for thermogravimetry (TG). The present paper describes the decomposition behavior of KClO_3 followed by the TS–DTA technique and high temperature microscopic observation.

2. Experimental

As-received powdered samples of KClO_3 (Kanto Chem. Co. Ltd., Japan) were used for TS–DTA experiments. $\alpha\text{-Al}_2\text{O}_3$ powder was used as the reference material. The sample and reference materials were placed in two fused silica holders covered with a cap. Alumel–chromel thermocouples were used for recording the heating temperature and DTA signals. The heating rate was 5°C min^{-1} . A fused silica rod, fixed at the bottom of the sample holder, acted as a waveguide. A piezo-electric sensor resonating at a nominal frequency of 140 kHz, 500 kHz or 1 MHz was used for detecting AE signals, which then were transformed to electric signals in the form of voltage amplitude–time traces. The traces were discriminated by a threshold voltage in the range 50 to 200 mV. This apparatus has been reported in more detail elsewhere [1].

During heating the sample was observed by a high temperature optical microscope, comprising an optical microscope (Nikon Optical Co., XP type) equipped with a hot stage (ULVAC, MS-E1S type). An infra-red image lamp was used as a heating element. A Pt–Pt13Rh thermocouple was used for measurement of the temperature and control of heating at a rate of 5°C min^{-1} . During heating the sample was viewed on a color television screen and the pictures were simultaneously stored on a video cassette tape using a video recorder from which selected micrographs were later reproduced by a color video printer.

3. Results and discussion

Fig. 1 shows the simultaneous TS–DTA results on heating KClO_3 samples in air, using three types of sensor (140 kHz, 500 kHz and 1MHz). The DTA curve shows an endothermic peak due to the melting at $340\text{--}380^\circ\text{C}$ and two successive exothermic peaks due to the decomposition of molten KClO_3 over the range $540\text{--}610^\circ\text{C}$. Markowitz et al. [9] reported a similar DTA result due to the decomposition of KClO_3 , from which it is assumed that the first exotherm is due to the combined reactions of Eqs. (1) and (2), and the second to the reaction of Eq. (3)



The TS curve, measured at a threshold value of 200 mV using a 140 kHz sensor, shows four main broad peaks a to d (Fig. 1B); peak a appears in the range

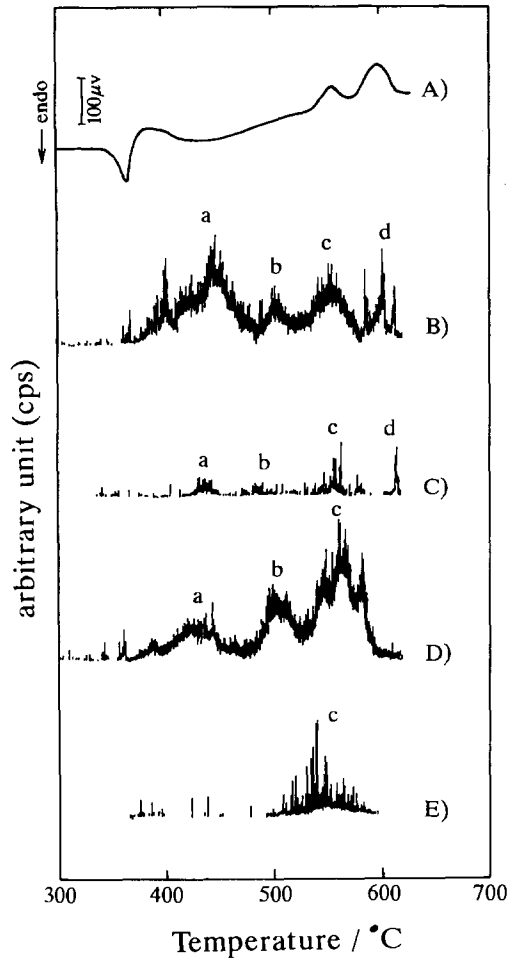
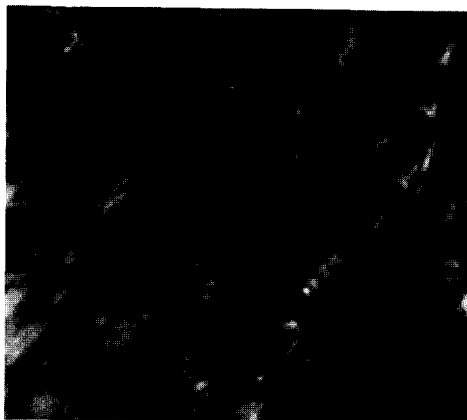


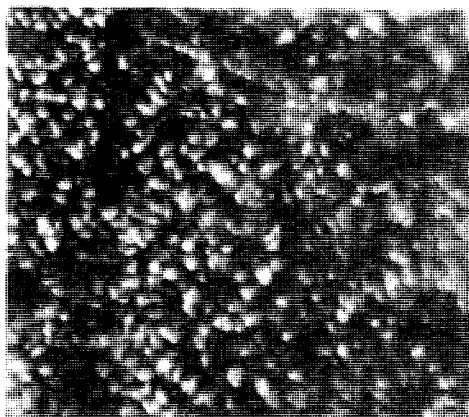
Fig. 1. Simultaneous TS-DTA curves of the decomposition of KClO_3 . (A) DTA curve; (B) to (E), TS curves: (B) 140 kHz and threshold voltage 200 mV; (C) 500 kHz and 200 mV; (D) 500 kHz and 50 mV; (E) 1 MHz and 50 mV.

360–480°C, peak b in the range 485–520°C, peak c in the range 530–570°C and peak d in the range 570–620°C. Although no apparent thermal change is observed in the temperature range 380–530°C between the melting and decomposition, peaks a and b are found to arise by some events occurring successively after the melting. Peaks c and d correspond to the two exothermic peaks due to the decomposition of KClO_3 and KClO_4 , respectively. The TS curves C–E of Fig. 1 were obtained by measurement at the threshold values of 200 or 50 mV using 500 kHz and 1.0 MHz sensors. The four peaks a to d decay greatly with increase of resonance frequency from 140 to 500 kHz. Peaks b and c become larger at 500 kHz relative to peaks a and d, and peak c survives at 1 MHz in spite of the disappearance of the other three peaks. These results suggest that peaks b and c have relatively higher

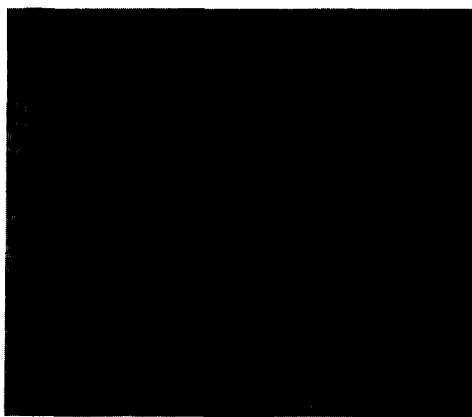
(A)



(B)



(C)



200 μm

Fig. 2. High temperature micrographs of the decomposition of KClO_3 : (A) 380°C; (B) 530°C; (C) 570°C

frequency components around 500 kHz, the latter peak also containing events around 1.0 MHz.

High temperature microscopic (HTM) observation showed that the particles of KClO_3 gradually melt around 340°C; this is followed by the occurrence of many bubbles due to gas evolution, probably because of oxygen release (Fig. 2(A)). Increasing temperature increased the number of bubbles which moved around vigorously in the melt. The events associated with bubbling gave rise to peak a, which has low frequency components mainly around 140 kHz. Interference colors, suggesting the presence of a thin film, appeared around 420°C on the surface of the melt during bubbling. The films continuously moved back and forth on the melt surface, during which the bubbles were produced without intermission, and moved more vigorously at temperatures between 480 and 520°C. It is thought that peak b corresponds to the sequence of these events of vigorous movement of films and bubbles.

Around 530°C, the melt became viscous and then gelatinous like curds (see Fig. 2(B)) in which bubbles formed with difficulty. The gelatinous melt moved and vibrated with the escape of inflated bubbles from the viscous melt. This movement and vibration became more intense with increasing temperature. A part of the melt solidified to produce islands of precipitate on the base of the crucible (Fig. 2(C)). These subsequent events are probably associated with peak c containing higher frequency components around 1.0 MHz, and correspond to the first exothermic peak. Around 570°C, the remaining fluid flew between the islands, with their accompanying vibration and bubble formation. Eventually solidification on the base occurred. These changes produce peak d, mainly corresponding to the second exothermic peak. It is concluded that although the DTA result gave no thermal change at temperatures between the melting and decomposition, the TS technique could detect mechanical changes related to oxygen release leading to bubbling and formation of interference colors at lower temperatures just after the melting is completed, which were supported by high temperature microscopic observation. Therefore, the TS results indicate that the onset temperature of KClO_3 decomposition is around 380°C, in contrast to values of about 530°C given by the present DTA curve or of 500°C by TG.

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