

Note

A study on the thermal decomposition of KClO_4 by acoustic emission thermal analysis: influences of particle and sample sizes on acoustic emission curve ^a

Shiro Shimada ^a, Yuji Katsuda ^a and Ryusaburo Furuichi ^b

^a *Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060 (Japan)*

^b *Analytical Chemistry Laboratory, Faculty of Engineering, Hokkaido University, Sapporo 060 (Japan)*

(Received 10 September 1990)

In previous papers [1,2] the authors described a new apparatus for the simultaneous measurement of acoustic emission (AE) and differential thermal analysis (DTA) and its successful application to the decomposition, dehydration and phase transition of several inorganic salts. In the case of KClO_4 , it was shown that on the AE count-rate curve, one broad peak appears at 200–340 °C and three sharp peaks appear at 560–660 °C [1]. Further experiments showed that the low temperature AE peak is greatly reduced by grinding the sample, while two of the high temperature peaks partially overlap as the sample mass decreases. This work reports the influence of the particle and sample sizes on the low and high temperature AE peaks associated with the phase transition and decomposition of KClO_4 .

EXPERIMENTAL

The samples were as-received powders of KClO_4 (Wako Chemical Co. Ltd., Japan). These powders were sieved to four fractions of 63–75, 75–106, 106–150 and 150–300 μm . Some powders were ground for 10 min with a mortar and pestle. $\alpha\text{-Al}_2\text{O}_3$ powder was used as the reference material. The sample and reference materials were placed in two fused silica holders (15 mm in diameter and 15 mm in length) fitted with caps, and were heated at a rate of 5 K min^{-1} in air. Alumel–chromel thermocouples were used for recording the heating temperature and DTA signal. A fused silica rod for the waveguide was fixed at the bottom of the sample holder. A 140 kHz

^a Paper presented at the Second Japan–China Joint Symposium on Calorimetry and Thermal Analysis, 30 May–1 June 1990, Osaka, Japan.

resonance frequency piezoelectric sensor was attached at the end of the rod. The acoustic waves generated in the sample are transmitted through the rod to its end where they are converted by the sensor to electrical signals in the form of voltage-amplitude-time traces. The traces are discriminated at preselected levels of voltage (designated threshold value) with an AE tester. The discriminated waves are finally converted to two output parameters: the event count-rate and the cumulative event count. The details of this apparatus are reported elsewhere [2].

RESULTS AND DISCUSSION

Figure 1 shows the variation of the AE event count-rate with sample weights in the range 500–1.0 mg, the size fraction being 106–150 μm . EXP 1-A and EXP 1-B correspond to the DTA curve and the cumulative AE count curve, respectively, for the 500 mg sample of KClO_4 . The DTA curve shows an endothermic peak at 298–330 $^\circ\text{C}$, which is due to the orthorhombic to cubic phase transition, and endothermic/exothermic peaks at

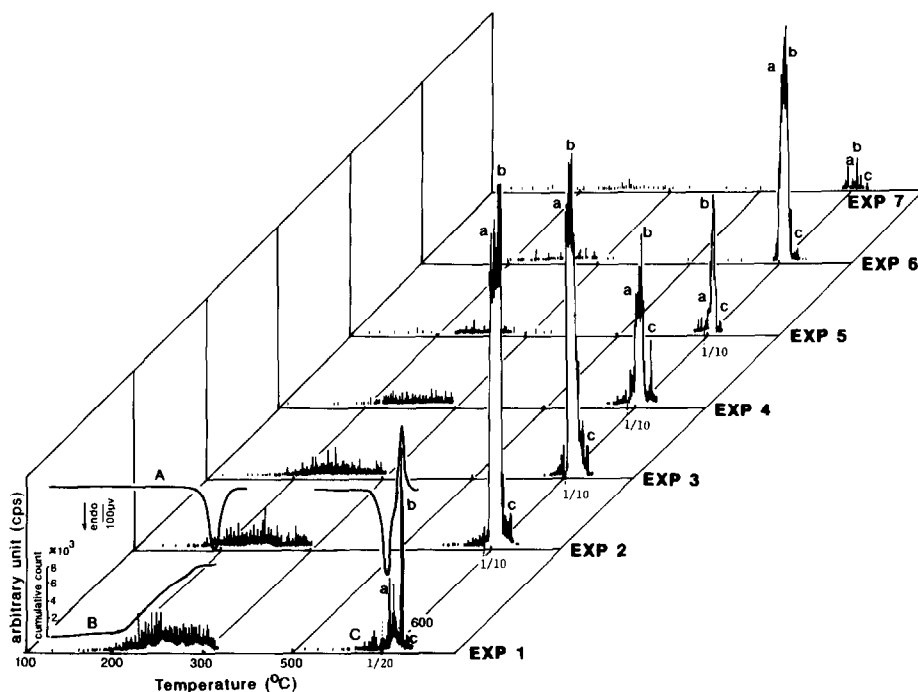


Fig. 1. Influence of the sample amount on the AE peak (particle size, 106–150 μm). EXP 1, 500 mg; EXP 2, 200 mg; EXP 3, 100 mg; EXP 4, 50 mg; EXP 5, 10 mg; EXP 6, 5 mg; EXP 7, 1 mg. The intensity of each AE count-rate curve is reduced by 1/20 or 1/10 above 600 $^\circ\text{C}$ by raising the threshold voltage from 250 to 500 or 400 μV (EXP 1–5).

590–630 °C, due to the melting of KClO_4 and its subsequent decomposition to KCl . Although the DTA curve for another sample mass is not shown, the deviation of peak temperatures for the three peaks is within $\pm 5^\circ\text{C}$. Two main AE features can be recognized at 190–320 °C and 570–630 °C on the AE count-rate curve (EXP 1-C). Since the initiation temperature of the low temperature AE peak (190 °C) is much lower than that of the transition (298 °C), some mechanical change occurs in the particles prior to the transition; the AE signals due to the transition are recognized as a slight rise on the cumulative count curve from about 300 °C, the temperature at which the transition begins. It is seen that the high temperature group of AE signals consists of three peaks (a, b and c). Peak a begins at 570 °C, below the initiation of the endothermic peak (590 °C) and increases suddenly at its peak temperature of 615 °C. The high intensity peak b occurs in a temperature range from the DTA inflexion of the endothermic/exothermic peak to the highest exothermic peak. Thus the two peaks a and b suggest a two-step decomposition [2]. The small peak c corresponds to the solidification of the molten product, KCl , which is not detected from the DTA curve.

From EXP 1–7, it is apparent that the low temperature AE signals decrease with decreasing sample weight. The cumulative counts covering this peak were measured as 4200, 1690, 790, 320, 80, 40 and 25 for sample weights of 500, 200, 100, 50, 10, 5.0 and 1.0 mg respectively; almost constant event counts of about eight per sample content (mg) are emitted. This indicates that the AE peak is the result of the emission not only from those particles in contact with the inner surface of the sample holder, but from the whole sample. Because the three high temperature peaks for the sample weights of 500–10 mg are of high intensity (EXP 1–5), the preselected threshold value (250 μV) had to be raised to 500 or 400 μV from around 600 °C, the resulting reduction in intensity being 1/20 or 1/10 (see broken lines); the three peaks for the 1 and 5 mg samples were measured at 250 μV . With decreasing sample weight, the initiation temperature of peak a approaches that of the endothermic peak of melting (590 °C). Peaks a and b tend to overlap partially as the sample weight decreases. This overlap is explained by assuming that the mixed high and low voltage-amplitude–time traces occur at the same time; the high amplitude traces have two peaks in the intensity corresponding to peaks a and b, in contrast with the low amplitude traces which occur more frequently. When a high threshold of 500 μV is used to cut off most of the low amplitude waves, separate peaks appear as a result of the survival of the high amplitude components among the mixed waves (EXP 1). However, the mixed waves discriminated above 250 or 400 μV produce the partially overlapping peaks (EXP 2–7), since the low amplitude traces occur more frequently compared with those of high amplitude. Peak c, due to the solidification of molten KCl , is observed irrespective of sample size. It should be noted that this technique can follow the decomposition process of KClO_4 using samples as small as 1.0 mg.

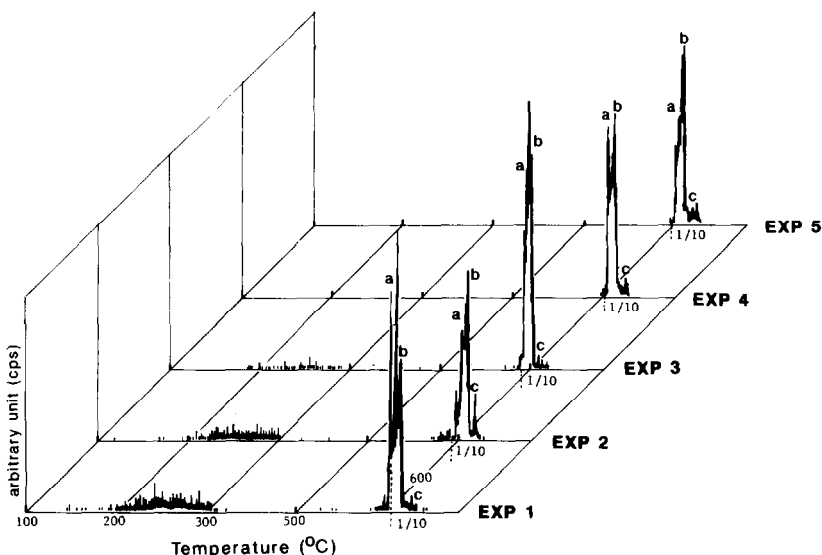


Fig. 2. Influence of the particle size on the AE peak (sample amount, 50 mg). EXP 1, 150–300 μm ; EXP 2, 106–150 μm ; EXP 3, 75–106 μm ; EXP 4, 63–75 μm ; EXP 5, ground sample. The intensity in each AE count rate-curve is reduced by 1/10 above 600 $^{\circ}\text{C}$ by raising the threshold voltage from 250 to 400 μV .

Figure 2 shows the variation of the AE peaks with particle size, the sample weight being 50 mg. The low temperature AE peak is sensitive to particle size, decreasing rapidly with decreasing size, and is undetected in the 63–75 μm size range and in the ground sample. It seems unlikely that peaks a–c are affected by the particle size of the sample.

REFERENCES

- 1 S. Shimada and R. Furuichi, *Thermochim. Acta*, 163 (1990) 313.
- 2 S. Shimada and R. Furuichi, *Bull. Chem. Soc. Jpn.*, 63 (1990) 2526.