

## **THERMOSONIMETRY AND THERMOMICROSCOPY OF THE DECOMPOSITION OF NaClO<sub>4</sub> AND KClO<sub>4</sub>**

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Thermal decompositions of NaClO<sub>4</sub> and KClO<sub>4</sub> were followed by simultaneous TS-DTA and thermomicroscopy. For NaClO<sub>4</sub> TS curves corresponding to melting/decomposition and solidification of molten NaCl were found to consist of six peaks. During decomposition of KClO<sub>4</sub>, three TS peaks appeared. The origin of these TS peaks is discussed on the basis of thermomicroscopic observations during which melting of the particles, evolution of bubbles of different sizes, formation of solid products of varied morphologies, vigorous vibration of these solids, and precipitation of NaCl or KCl were observed.

**Keywords:** DTA, KClO<sub>4</sub>, NaClO<sub>4</sub>, thermomicroscopy, thermosonimetry

### **Introduction**

Thermal decompositions of the perchlorate salts, NaClO<sub>4</sub>, KClO<sub>4</sub>, CsClO<sub>4</sub>, have received much attention but have not been fully understood because of the difficulty of following by conventional thermoanalytical or spectroscopic techniques the rapid decompositions occurring concurrently with fusion of the salts.

In a previous paper, [1], the author described new apparatus for simultaneous measurement of acoustic emission (AE) and DTA, and its successful application to the decomposition, dehydration and phase transition of several salts. The AE method was found to be an useful and sensitive technique for detecting some mechanical events caused by rapid decomposition of the salts during heating which cannot be monitored by conventional thermal techniques such as DTA or TG [2-5].

Decompositions of NaClO<sub>4</sub>, and KClO<sub>4</sub> have previously been studied using the AE-DTA technique by the author, who observed several peaks on the AE curve during decomposition, but could not explain their origin. This paper describes a comparative TS\* study on the decompositions of NaClO<sub>4</sub> and KClO<sub>4</sub>

## Experimental

As-received powdered  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  and  $\text{KClO}_4$  samples were used as starting materials.  $\alpha\text{-Al}_2\text{O}_3$  powder was used as reference material. Sample and reference powders were placed in two fused silica holders covered with a cap, and heated at  $5 \text{ deg} \cdot \text{min}^{-1}$  in air. A fused silica rod, fixed at the bottom of the sample holder, acted as a waveguide. An AE sensor resonating at a nominal frequency of 140 kHz was attached to the end of the rod. The acoustic waves generated in the sample were transmitted through the rod to the end where they were converted by the sensor to voltage–amplitude–time signals. The signals were discriminated at a pre-set level of voltage, designated the threshold, by a TSE tester. TS measurement has been reported in more detail elsewhere [1].

The samples were observed during heating by an optical microscope, equipped with a hot stage. An infra-red image was used as a heating element. A few milligrams of the samples were placed in a Pt crucible, and were heated at a rate of  $5 \text{ deg} \cdot \text{min}^{-1}$  in air. During heating, the samples were viewed on a colour television screen and simultaneously stored on a video cassette tape using a video recorder from which selected micrographs were later reproduced by a colour video printer.

## Results

### *Decomposition of $\text{NaClO}_4$*

Figure 1 (A) and (B) shows the simultaneous TS–DTA curves of  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  samples heated to  $560^\circ\text{C}$  in air. On heating, four endothermic peaks and one exothermic peak were observed on the DTA curve (A). Referring to a previous paper, [4], three low-temperature endothermic peaks are due to loss  $0.2 \text{ H}_2\text{O}$  at  $50^\circ\text{--}125^\circ\text{C}$  and of  $0.8 \text{ H}_2\text{O}$  at  $155^\circ\text{--}200^\circ\text{C}$ , and a phase transition (orthorhombic to cubic) at  $295^\circ\text{--}315^\circ\text{C}$ . Further heating results in an endothermic peak followed by an exothermic one above  $450^\circ\text{C}$ .

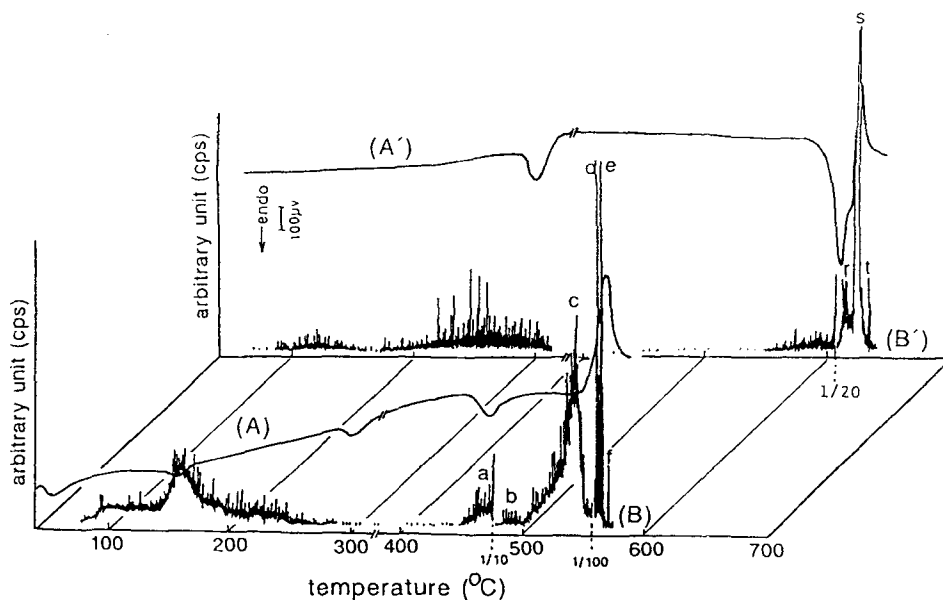
Two main TS features, the low-temperature peak at  $80^\circ\text{--}310^\circ\text{C}$  and the high-temperature peak at  $450^\circ\text{--}580^\circ\text{C}$ , were observed on the TS curve (B). The low-temperature TS peak is associated with loss of  $0.8 \text{ H}_2\text{O}$  or liquid release from the surface of the particle [4]. The high-temperature TS peak gives six peaks (*a–f*) above  $450^\circ\text{C}$ , which correspond to thermal processes including melting and decomposition. Peak *a* is apparently due to the melting of  $\text{NaClO}_4$ . Peak *b* begins near the minimum temperature of the endothermic peak due to melting, and con-

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\* TS is used in place of AE in the present paper

tinues over the temperature range 480°–500°C during which no distinct DTA signal is seen. Peak *c* appears intensely at 500°–560°C, its later part overlapping with the earliest part of the exothermic DTA peak. Subsequently, two sharp well-resolved peaks *d* and *e* occur at temperatures corresponding to the exothermic peak (peaks *d* and *e* sometimes overlap). Peak *f* appears at 570°C, corresponding to the later part of the exothermic peak.

Thermal microscopic examination showed that the particles melt gradually from 460°C and vibrate slightly owing to flowing of the melt on their surface. It was observed that bubbles about 30  $\mu\text{m}$  in size evolve slowly from the bottom of the crucible at 465°C, followed by generation and movement of many small bubbles several micrometers in size from grooves or scratches in the crucible. Interference colours, suggesting formation of a thin film, appeared on the surface of the melt at temperatures of 520°–540°C, and appearance/disappearance of the colours was repeated over a short period. Above 540°C a skeletal cubic crystal was observed to roll over slowly in the melt (Fig. 2(A), arrow). In addition, a glove-shaped solid formed (Fig. 2(B)), from the surface of which continuous bubbling occurred, causing vigorous vibration of the solids. Ellipsoid and spherical solids were deposited at the bottom of the crucible (Fig. 2(C)) after evolution of gases ceased.



**Fig. 1** Simultaneous TS-DTA curves of decompositions of  $\text{NaClO}_4$  and  $\text{KClO}_4$ . (A) and (B), DTA and TS curve of  $\text{NaClO}_4$ ; (A') and (B'), DTA and TS curve of  $\text{KClO}_4$ . Sensor, 140 kHz; sample mass, 600 mg ( $\text{NaClO}_4$ ) and 400 mg ( $\text{KClO}_4$ ); air atmosphere; heating rate,  $5 \text{ deg. min}^{-1}$ . The intensity in the TS count rate curves is reduced by 1/10 – 1/100, as shown in the figure, by raising the threshold

### *Decomposition of KClO<sub>4</sub>*

A simultaneous TS–DTA curve of KClO<sub>4</sub> powder heated to 640°C is shown in Fig. 1(A') and (B'). The endothermic peak at 280°–330°C is due to transition from orthorhombic to cubic form. The endothermic/exothermic peaks at 585°–630°C are due to melting of KClO<sub>4</sub> and its subsequent decomposition to KCl (curve (A')). The TS curve (B') displays two main features: one broad peak at 80°–310°C (low-temperature TS peak) and three sharp peaks, *r*, *s* and *t*, at 560°–630°C (high-temperature TS peak). The low-temperature TS peak results from formation of large grooves or angulation of the particles, emergence of small particles hidden under the skin of mother particles because of release of fluids, and cracking on the surface of some particles due to the structural transition [2, 3].

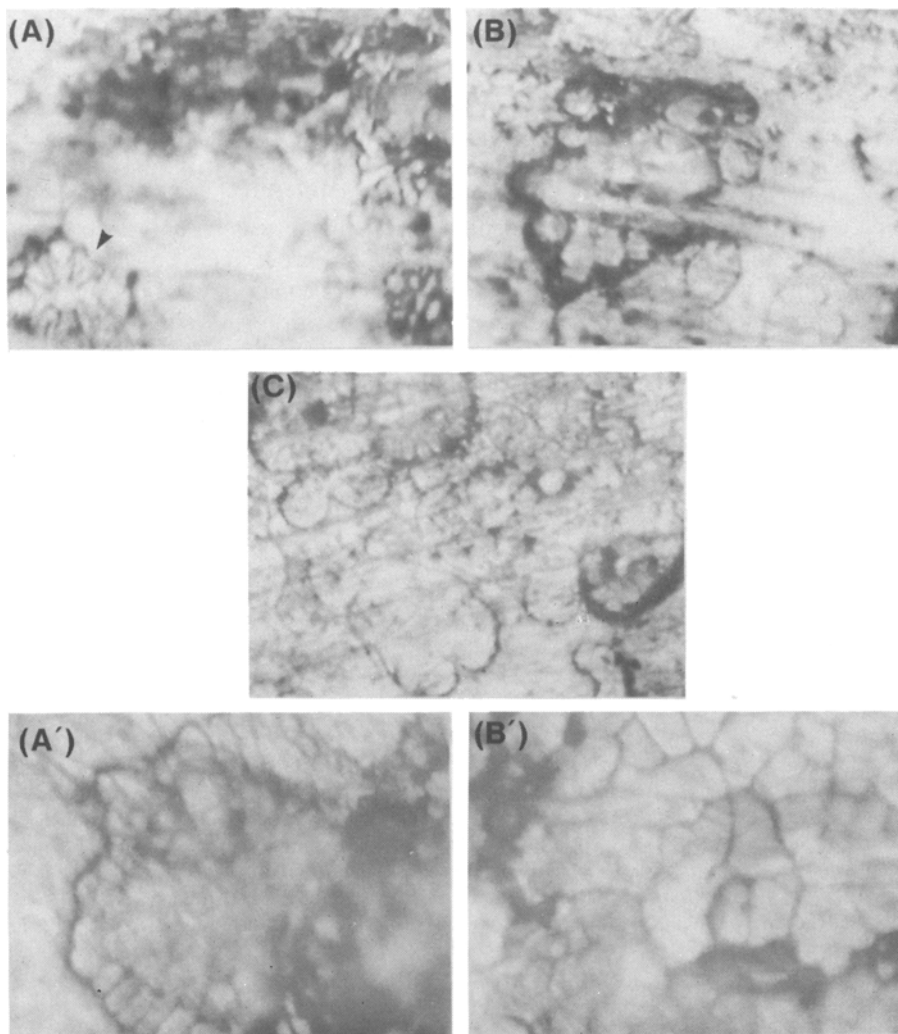
The high-temperature TS peak starts at 540°C, much lower than the initiation temperature of melting (around 590°C). TS signals gradually increase in intensity, become more intense at the endothermic peak, and continue to the inflexion temperature of the endothermic/exothermic peak (peak *r*). Peak *s* of the high intensity begins at the inflexion temperature and terminates around the exothermic peak temperature. Peak *t* appears near the shallower slope on the later part of the exothermic peak at 630°C.

It was observed that at 565°C the particles begin to melt at their angular extremities and the melt flows down inclined surfaces. Above 575°C, bubbles were generated and flowed in the melt. After complete melting, bubbles above 10 μm in size moved around in the melt. Interference colours were observed on the surface of the melt above 586°C. When the colours disappeared, 'hand of banana'-shaped solids, from which bubbles were vigorously evolved, were found in the melt (Fig. 2(A')). Subsequently, the melt began to partly solidify at the bottom of the crucible at 600°C, and the resulting solids increased in size (Fig. 2(B')). Bubbling still occurred from the spaces between the solids. It should be noted that measured temperatures in the TS–DTA experiments were about 30°C higher than those in the microscopic observations.

### **Discussion**

For both NaClO<sub>4</sub> and KClO<sub>4</sub>, TS signals corresponding to the endothermic peak due to melting were observed, these signals probably arising from mechanical events such as slight vibration of particles due to melting and subsequent flow of the melt on their surface; TS signals prior to melting of KClO<sub>4</sub> also appeared. Bubbles occurring almost simultaneously with melting in both salts are oxygen gas formed by decomposition of the melt. In the Na salt, bubbles about 30 μm in size, followed by small ones below 10 μm, were observed, these vigorously moving around in the melt. A characteristic frequency component of 80 and 140 kHz was included in the power spectra of peaks *b* and *c* [4]. Movement of

large and small bubbles could produce a signal with frequencies of 80 and 140 kHz, respectively. In the K-salt, both large and small bubbles were evolved simultaneously, contributing peak *r*. Appearance/disappearance of the interference colours was repeated for a short period in the salts, and this could be associated with peaks *b* and *c*, or peak *r*.



**Fig. 2** Photomicrographs of decompositions of  $\text{NaClO}_4$  and  $\text{KClO}_4$ . (A) to (C),  $\text{NaClO}_4$ ; (A') and (B'),  $\text{KClO}_4$ . Temperature ( $^{\circ}\text{C}$ ): (A) 545; (B) 550; (C) 565; (A') 600; (B') 605

After the interference colours eventually disappeared, a skeletal cubic solid, probably the product (NaCl), was seen to roll over in the melt (Fig. 2(A)). TS signals due to formation and movement of the solid may be contained in peak *c*. Subsequently, 'glove-' or 'hand of banana'-shaped solids appeared in the melt which vibrated vigorously due to continuous evolution of gas (Fig. 2(B) and 2(A')). It is likely that the solids represent the intermediate compounds NaClO<sub>3</sub> or KClO<sub>3</sub> since the gas still continues to be evolved from these. It is probable that the concomitant events of vigorous vibration and gas evolution are contained in peaks *d* and *e*, or peak *s*.

Peak *f* or *t* appeared at temperatures corresponding to the later part or the end of the exothermic peak. When the 'banana'- or 'glove'-shaped solids ceased to vibrate, flat and spherical solids were observed to collect at the bottom of the crucible. It is likely that this deposition brought about TS signals leading to peak *f* or *t*. After completion of decomposition, no TS signal was seen. It is concluded from TS results that the decomposition of NaClO<sub>4</sub> proceeds via four steps corresponding to peaks *b*–*e*, while that of KClO<sub>4</sub> occurs apparently via two steps corresponding to peaks *r* and *s*. Since the decomposition of KClO<sub>4</sub> occurs in a relatively narrow temperature range compared with that of NaClO<sub>4</sub>, peak *r* probably occurred as a result of overlapping of peaks *b* and *c*, and peak *s* as a result of overlapping of peaks *d* and *e*. Solidification of molten NaCl or KCl products was detected as peak *f* or *t*, respectively.

## References

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**Zusammenfassung** Mittels simultaner TS-DTA wurde die thermische Zersetzung von NaClO<sub>4</sub> und KClO<sub>4</sub> verfolgt. Für NaClO<sub>4</sub> fand man, daß die TS-Kurven (entsprechend dem Schmelzen/Zersetzen und des Erstarrens von geschmolzenem NaCl) aus sechs Peaks bestehen. Bei der Zersetzung von KClO<sub>4</sub> treten drei Peaks auf. Der Ursprung dieser Peaks wird auf der Grundlage von thermomikroskopischen Beobachtungen besprochen, bei denen das Schmelzen von Partikeln, die Entwicklung von Blasen unterschiedlicher Größe, die Bildung von Feststoffen verschiedener Morphologie, kräftige Vibrationen dieser Feststoffe und das Ausfallen von NaCl und KCl beobachtet wurde.