Thermosonimetry and thermomicroscopy of the phase transition and decomposition of $CsClO_4$

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(Received 16 January 1992)

Abstract

The phase transition and decomposition of $CsClO_4$ was investigated by simultaneous TS–DTA measurement and high-temperature optical microscopy observation. The powdered $CsClO_4$ samples yield a low-temperature TS peak (peaks **a** and **b**) at 110–230°C and a high-temperature TS peak (peaks **c**–**e**) at 560–630°C. The visual microscopic observation indicated that peak **a** arises from vigorous shaking of the particles in a pre-transition event. Peak **b** corresponds to the endothermic DTA peak due to the transition, during which movement of the bright lines indicative of a phase boundary was observed on the surface of the particles. Peak **c** corresponds to the endothermic/exothermic peaks due to the melting/decomposition of $CsClO_4$. Peaks **d** and **e** appear at the corresponding endothermic peak temperatures of 615 and 628°C. It is suggested that peak **c** results both from the bubbling caused by oxygen generation and from the precipitation of product CsCl. Peaks **d** and **e** are associated with the change in form of the precipitates and their melting, respectively.

INTRODUCTION

Acoustic emission (AE) is emitted in a solid by various internal processes involving release of elastic energy, such as the generation and propagation of cracks or the movement of dislocations. Recently, the analysis of acoustic emissions resulting from chemical reactions has been a subject of increasing interest in analytical and thermoanalytical chemistry [1–4]. Lønvik has used the AE technique to follow the thermal behavior of several minerals, and has named the technique thermosonimetry (TS) [5]. The author has constructed a new apparatus for the simultaneous measurement of AE and differential thermal analysis (DTA), and has described its application to the dehydration, phase transition and decomposition of several inorganic salts [6–10]; the TS notation will be used below in place

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of AE. The phase transition and thermal decomposition of $KClO_4$ and $NaClO_4$ have been followed using the TS–DTA apparatus. In the case of $KClO_4$, it was shown that the low-temperature TS signals result from break-up of particles, liquid release from the surface of the particles and the phase transition, the first two changes not being detected by DTA [9]. The high-temperature TS peaks were shown to arise from the subsequent melting/decomposition processes [8,9]. The influences on the TS peaks were investigated with respect to the different sample amounts and sizes and the different sample sources, and the sensors resonated at different frequencies [8]. The TS peaks and their power spectra in the decomposition of $NaClO_4$ were also examined [10].

Of the alkali perchlorates, the decompositions of $KClO_4$ and $NaClO_4$ have received much attention from a thermoanalytical viewpoint, including our TS studies. By contrast, the decomposition of $CsClO_4$ has not been extensively investigated, the DTA or TG curve due to the decomposition being shown only for comparison with $KClO_4$ [11]. It is of interest to follow the thermal behavior of $CsClO_4$ by TS–DTA measurement, and to compare its TS results with those of $KClO_4$ and $NaClO_4$.

It is desirable to determine which mechanical events are actually taking place in the thermal process and give rise to acoustic emission. High-temperature optical microscopic observation (thermomicroscopy, designated TM) can provide in situ information about the events occurring during the thermal process. In fact, TM was found to be very useful in explaining the origins of the six TS peaks appearing during the decomposition of $NaClO_4$ [12]. The present paper describes the characteristic TS peaks resulting from the phase transition and decomposition of $CsClO_4$, and the origin of the TS signals based on TM observation.

EXPERIMENTAL

As-received, powdered $CsClO_4$ samples were used as a starting material (Soekawa Chem. Co. Inc.). α-Al_2O_3 powder was used as the reference material. The sample and reference powders were placed in two fused silica holders covered with a cap. A fused silica rod, fixed at the bottom of the sample holder, acts as a waveguide. An AE sensor resonating at a nominal frequency of 140 kHz, 500 kHz, 1 MHz or 1.5 MHz, was attached at 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 an AE tester. A threshold value of 250 μV was used unless otherwise noted. The TS measurement has been reported in more detail elsewhere [7].

The samples were observed during heating by a high-temperature optical microscope, comprising an optical microscope (Nikon Optical Co., XP
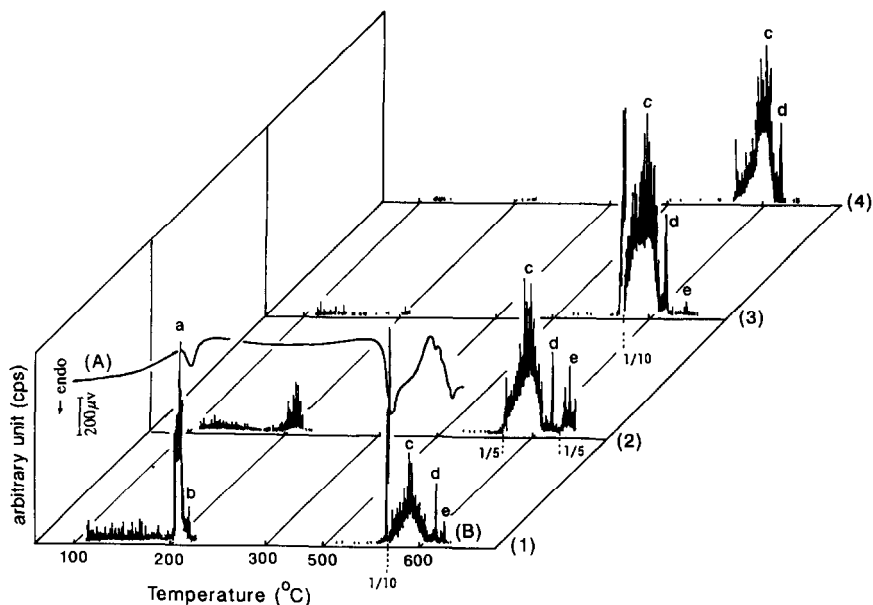
Fig. 1. Simultaneous TS–DTA curves of the phase transition and decomposition of $CsClO_4$. (A), DTA curve; (B), TS curve: (1), 140 kHz; (2), 500 kHz; (3), 1 MHz; (4), 1.5 MHz. Sample amount, 400 mg; air atmosphere; heating rate, 5°C min^{-1}. The intensity in the AE count-rate curves (1)(B) and (2) is reduced by 1/10 to 1/5 above 565°C by raising the threshold voltage from 250 to 450 or 500 μV. The intensity in the curve (3) is reduced by 1/10 above 568°C by raising the threshold voltage from 50 to 250 μV.

type) equipped with a hot stage (ULVAC, MS-E1S type). The hot stage is composed of sample and heating chambers, which are separated from each other by a fused silica window. 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 and cooling. A few milligrams of $CsClO_4$ were placed in a Pt crucible in the sample chamber and heated or cooled in air at a rate of 5°C min^{-1}. During heating, the samples were viewed microscopically on a color television screen and simultaneously stored on a video cassette tape using a video recorder (Sony, SVO-160), from which selected micrographs were later reproduced by a color video printer (Mitsubishi, CP-11). The morphologies of the samples obtained from the TS–DTA experiment were also observed by scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Figure 1 shows the simultaneous TS–DTA curves of $CsClO_4$ samples heated to 660°C in air, using four kinds of sensor. The DTA curve shows an endothermic peak due to the transition from orthorhombic to cubic phase

at 210–230°C and the endothermic/exothermic peaks due to the melting of $CsClO_4$ and its subsequent decomposition at 550–630°C (Fig. 1(1)(A)). A reproducible endothermic peak, overlapping with the exothermic peak, appears at around 615°C. No explanation for this peak can be given. An additional endothermic peak observed in the range 630–640°C is probably due to the melting of solid CsCl product, because the temperature range is near the reported melting point of CsCl (645°C).

The two main low- and high-temperature TS peaks appear at 110–225°C and 560–630°C, respectively, on the TS curve when the 140 kHz sensor was used (Fig. 1(1)(B)). The low-temperature TS peak contains an intense peak (peak a) and a weak peak (peak b). The high-temperature peak is seen to consist of three peaks: c, d and e. It should be noted that the high-temperature TS peak is observed with samples as small as 1.4 mg. Because the
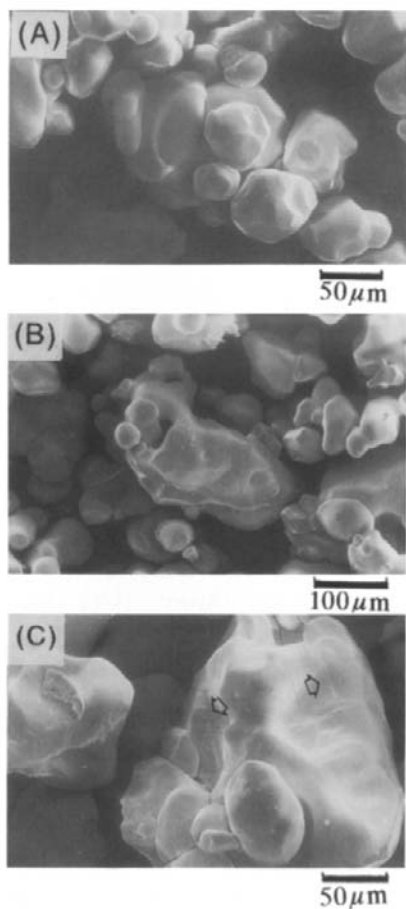

Fig. 2. SEM micrographs of the as-received sample of $CsClO_4$ (A), the sample heated to 185°C (B) and the sample heated to 230°C (C).

initiation temperature of the low-temperature TS peak (110°C) is much lower than that of the phase transition, it would seem that the TS signals are emitted prior to the transition. The SEM photograph of the samples heated to 185°C showed that the surface of the particles becomes uneven and pitted, with small particles emerging from the parent particles (Fig. 2(B)), as compared with the starting particles (Fig. 2(A)). These changes must be caused by loss of the surface skin of the parent particles, in a manner similar to that seen in $KClO_4$ [9]. The loss of the surface skin is confirmed by the TG result of the as-received samples, which show a weight loss of 0.1–0.2 wt.% at 110–200°C. Thus, the low-temperature TS signals at 110–200°C prior to the transition can be attributed to the mechanical changes on the surface of the particles.

It is interesting that peak **a** is strongest at temperatures of 200–210°C, just before the transition. Peak **b** corresponds to the endothermic DTA peak due to the transition. During heating, it was observed that the aggregate particles did not greatly change up to a temperature of 185°C (Fig. 3(A)). On heating to 200°C, they began to shake vigorously, some seeming to almost detach themselves from the parent particles. It is clear that peak **a** can be attributed to the shaking of the particles prior to the transition.

Immediately after the particles cease to shake (216°C), distinct bright lines were observed moving on the surface of the particles (see arrows in Fig. 3(B)). The lines, which are indicative of a phase boundary, were probably formed by shear imposed by the volume difference between the new and old phases. The line movement indicates the dynamic progress of the transition. After the particles have gone through the transition, they become deformed or rearranged (Fig. 3(C)) and crack (see arrows in Fig. 2(C)). It is thus concluded that peak **b** is strongly associated with the deformation/rearrangement and cracking of the particles, caused by the phase boundary movement due to the transition. It could be seen that, during the cubic to orthorhombic transition induced by cooling, the bright lines on the surface of the particles move in the opposite direction to that observed in the forward orthorhombic to cubic phase transition.

Figure 4 shows the repeated TS–DTA experiments, during which the heating/cooling cycle of the samples was carried out at a rate of 5°C min^{-1} between 175 and 250°C. The first heating run gives almost the same result as that shown in Fig. 1(1)(B). On first cooling, weak TS signals can be seen prior to the transition, followed by a relatively intense TS peak (Fig. 4(1)(A′)) corresponding to the exothermic DTA peak (Fig. 4 (1)(B′)) due to the transition. In this cooling run, the particles did not shake as much before the transition as during the first heating run, the weak TS signals appearing as a pre-transition event. The second heating run (Fig. 4(2)(A) and (2)(B)) did not produce any pre-transition TS peak, whereas a reduced TS peak due to the transition is observed. In the second cooling run (Fig.
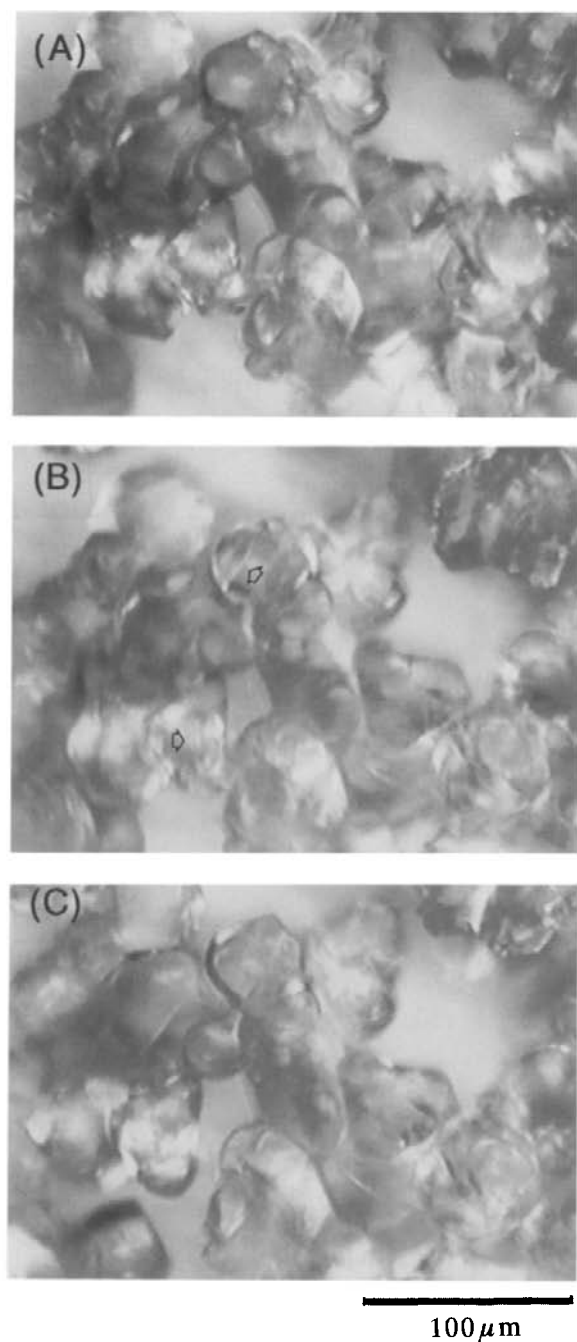
$100 \mu m$

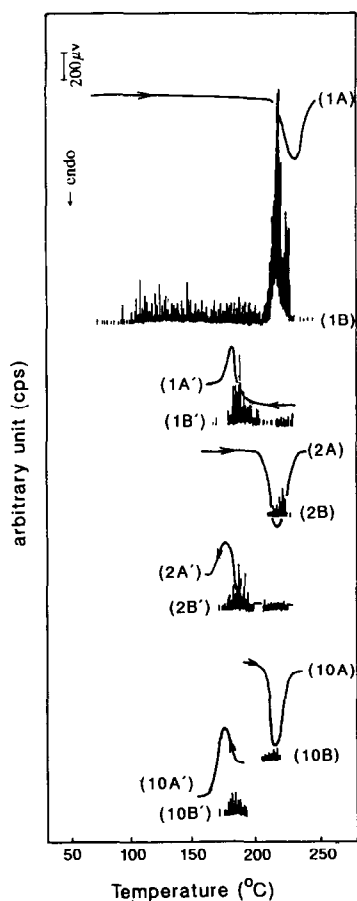Fig. 3. Thermomicrographs of the transition in the $CsClO_4$ samples. Temperature (°C): (A), 185; (B), 216; (C), 227.

Fig. 4. Simultaneous TS–DTA curves of the transition in the CsClO$_4$ samples in the repeated experiment. A heating run is labelled A and B, a cooling run A' and B'; DTA curve, A; TS curve, B. The numbers 1, 2 and 10 correspond to the first, second and tenth run, respectively. Heating rate, 5°C min^{-1}.

4(2)(A') and (2)(B')), the weak and intense TS signals are similar to those observed in the first cooling run. The 10th heating and cooling runs still show the TS signals due to the transition. It can be observed that the intensity of the TS signals in the forward and backward transition was almost unchanged after the 7th run and that the intensity in the backward transition was greater than in the forward. It seems that an intense, pre-transition TS peak appears only on the first heating of virgin samples. On further heating after the transition, no TS signals are seen, except for noise signals, until the melting of CsClO$_4$ begins (Fig. 1(1)(B)).

TS signals occur again at 555°C with the endothermic effect due to the melting (Fig. 1(A)), and rapidly increase just before the endothermic peak temperature (570°C). Because the signals above 565°C are of high intensity, the pre-selected threshold value (250 μV) had to be raised to above 500

$$40\,\mu\text{m}$$

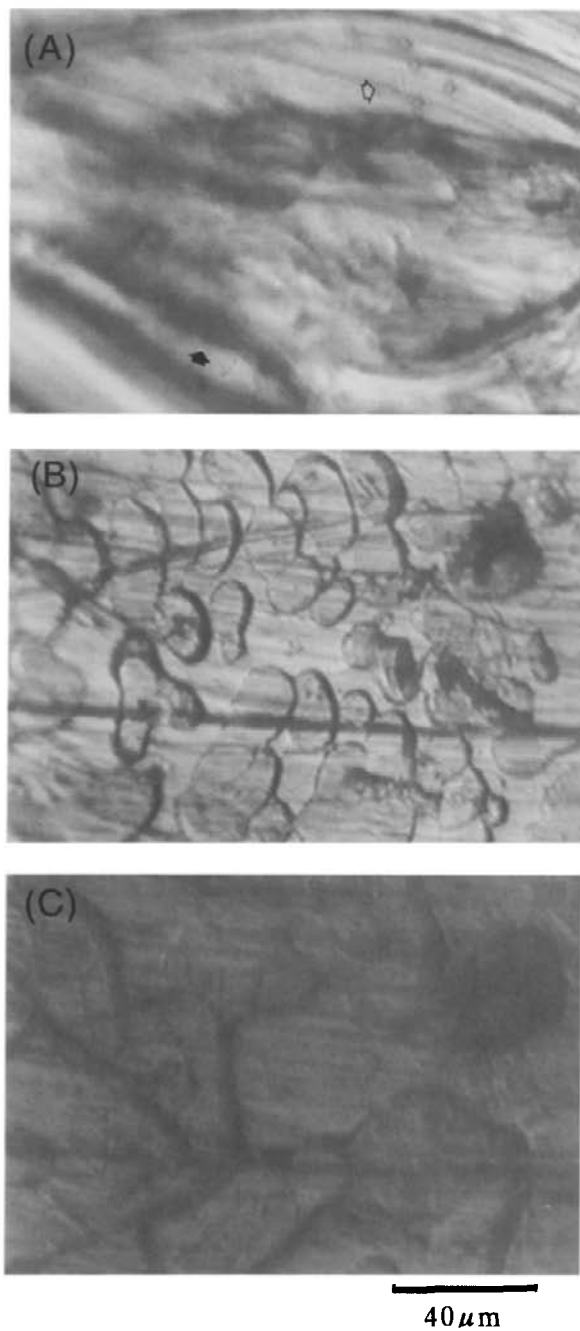Fig. 5. Thermomicrographs of the melting and decomposition of CsClO₄. Temperature (°C): (A), 561; (B), 588; (C), 617.

μV, the resulting reduction in intensity being 1/10. The TM observation showed that the particles of $CsClO_4$ gradually melt at around 560°C, followed by bubbling due to gas evolution (see the arrows in Fig. 5(A)): the gases are coming from the site marked by the black arrow. Thus, the weak and subsequent increased signals are associated with the melting and bubbling processes, respectively. It is found that the initiation temperature of the increased TS signals corresponds to that of the decomposition leading to gas evolution, although the onset of the decomposition is not clear on the DTA curve.

The TS signals increase with increasing temperature, forming peak c; this peak corresponds to the endothermic/exothermic peaks. Interference colors, suggestive of the formation of a thin film, appeared on the surface of the melt during the course of the bubbling. Immediately after this film moves away, rounded, flat solid particles 10–50 μm in size were precipitated on the base of the crucible (Fig. 5(B)); these must be the product CsCl. A piece of solid was seen floating in the melt, eventually being attached to the precipitated solid. Thus, peak c arises from complex processes including the bubbling due to oxygen generation and the precipitation of the product CsCl; the oxygen generation and precipitation processes contribute to the exothermic peak on the DTA curve. The two TS peaks d and e, which are observed in the range 615–630°C (Fig. 1(1)(B)), correspond to the respective endothermic DTA peaks at 615 and 628°C, the first endothermic peak overlapping with the exothermic peak. It was observed that the precipitates suddenly change their shape at around the temperature of peak d (Fig. 5(C)), and eventually melt. Peak d is probably associated with the change in the form of the precipitates, and peak e is probably due to the melting of CsCl.

The effect of the resonating frequency of the sensor on the TS peaks was also examined (Fig. 1(1)–(4)). The low-temperature TS peak, comprising peaks a and b, decreased with increasing frequency. Peak b and the early part of the low-temperature peak are still present at 1.5 MHz. Peaks c–e in the high-temperature peak also decrease with increasing frequency. The peak position of the intense peak c shifts to higher temperatures with increasing frequency, indicating that TS signals of peak c possess higher frequency components in the higher temperature region. Peak d is observed at all frequencies between 140 kHz and 1.5 MHz, in contrast with the possible detection or disappearance of peak e at 1.0–1.5 MHz. Peak d is found to have higher frequency components.

SUMMARY

The phase transition and decomposition of $CsClO_4$ was followed by simultaneous TS–DTA measurement and high-temperature optical microscopy. The results are as follows.

(1) Low- and high-temperature TS peaks are observed at temperatures of 110–225°C and 560–630°C, respectively, the former containing peaks **a** and **b** at 200–230°C, and the latter consisting of three peaks, **c–e**.

(2) Peak **a**, occurring prior to the phase transition, is attributed to the vigorous shaking of the particles of $CsClO_4$ in a pre-transition event. Peak **b**, corresponding to the endothermic DTA peak due to the transition, is associated with the deformation/rearrangement and cracking of the particles, caused by the boundary movement of the new/old phases on the surface of the particles.

(3) Peak **c** is correlated with the exothermic peak on the DTA curve due to the decomposition, resulting from the oxygen evolution and the precipitation of product CsCl.

(4) Peaks **d** and **e**, corresponding to the respective endothermic peaks at 615 and 628°C, are associated with the change in the form of the precipitates of CsCl and their melting, respectively.

(5) The low- and high-temperature TS peaks have their characteristic frequency components.

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