ELSEVIER

Thermochimica Acta 367–368 (2001) 381–385

thermochimica acta

www.elsevier.com/locate/tca

The thermal properties of $KClO_4$ with different particle size

Jinn-Shing Lee[a,b,c,*], Chung-King Hsu[a], Kuen-Shan Jaw[d]

[a]*Department of Material and Mineral Resources Engineering, National Taipei University of Technology, Taipei, Taiwan, ROC*
[b]*Department of Chemistry, Chung Yuan Christian University, Chung Li, Taiwan 32023, ROC*
[c]*P.O. Box 90008-15-9, Chung Shan Institute of Science and Technology, Lung Tan, Taiwan 32526, ROC*
[d]*Department of Chemical Engineering, Kuang Wu Junior College of Technology and Commerce, Peito, Taipei, Taiwan, ROC*

Received 5 August 1999; accepted 22 June 2000

Abstract

The focus of this work is on the use of thermal analysis to understand the influence of the particle size on the decomposition of $KClO_4$. DSC curves of $KClO_4$, with different particle sizes, show an endothermic peak from a phase transition close to 308°C and a melting point at 608°C. DTA curves gave similar results. Also observed is the fusion of KCl at about 770°C. The corresponding TG curves of decomposition for the reaction of $KClO_4 \rightarrow KCl + 2O_2$ were recorded and the percentage of mass loss is close to the theoretical value (46.18%). The initial decomposition temperature of $KClO_4$ with smaller particle sizes is shifted to lower temperatures, and the decomposition activation energies of $KClO_4$ range from 231 to 269 kJ mol^{-1}.

Keywords: Thermal analysis; $KClO_4$; Particle size

1. Introduction

Potassium perchlorate is a powerful oxidizing agent and decomposes at elevated temperature to produce oxygen as one of its major products. Previous studies on the thermal properties of potassium perchlorate by differential thermal analysis (DTA) showed an exothermic peak at about 300°C, that is a phase change of potassium perchlorate from rhombic structure to cubic structure [1]. Potassium perchlorate subsequently melts at about 588°C, and then decomposes rapidly above 600°C [2]. In general, particle size, purity of material and heating rate of instrument are the factors that can affect the resulting experimental curves. Since DTA is a dynamic temperature technique, the experimental curves would be different owing to the experimental conditions. At higher temperature, the lattices of cubic structure are expanded sufficiently to allow O_2 to escape easily. In this work, the thermal behaviors of potassium perchlorate with different particle sizes were studied using DSC, DTA, and TG. And the activation energies for thermal decomposition of potassium chlorate with different particle sizes were evaluated by dynamic TG techniques.

2. Experimental

$KClO_4$ (Ferak Berlin, purity 99.5%) was first carefully ground for 10 min in an aluminum oxide mortar and pestle, and the fractions of particles passing

* Corresponding author. Present address: Department of Material and Mineral Resources Engineering, National Taipei University of Technology, Taipei, Taiwan, ROC.

0040-6031/01/$ – see front matter
PII: S0040-6031(00)00691-2

Table 1
Weight percentage of potassium perchlorate with a particle size region

Particle size	Mass percentage (%)
≥100 mesh (≤150 μm)	3.25
100–150 mesh (106–150 μm)	9.14
150–200 mesh (75–106 μm)	48.78
200–325 mesh (45–75 μm)	33.84
−325 mesh (≤44 μm)	4.98

through a series of sieves (NBS) were taken. The mass percentage of each particle size range is shown in Table 1. Five categories of potassium perchlorate powder with different particle sizes were the samples used for the DSC, DTA and TG investigation. A Du Pont TA 2000 with 951 TG and 910 DSC cell base and a Rigaku Denki thermoanalyzer (model 8121) DTA were used under static air and flowing 50 ml/min N_2 atmospheres, with heating rates from 5 to 50°C min^{-1}. The reference material for DSC and DTA was powdered α-Al_2O_3, and the sample weight of experiment is approximating 6.5 mg.

3. Results and discussion

Fig. 1 shows the DSC curves of $KClO_4$ with different particle sizes under static air atmosphere with a 10°C min^{-1} heating rate. The endothermic peak of the phase transition is close to 308°C. The result was in agreement with Cordes and Smith [3] and Rudolf and Freeman [4]. Melting point of $KClO_4$ was observed to start at about 608°C. Decomposition was rapidly accomplished following melting at higher temperature. DTA measurements on the solid state reaction in the region 300–800°C were carried out in static air atmosphere with 10°C min^{-1} heating rate, and DTA curves of $KClO_4$ samples with different particle sizes are shown in Fig. 2. DTA curves gave similar results to DSC except that the fusion of KCl at about 770°C could be observed [5,6]. The TG curves of $KClO_4$ with different particle size region under a static air atmosphere with a 10°C min^{-1} heating rate, are also shown in Fig. 3. The average percentage of mass loss for the four particle sizes is 50%. This value is close to the theoretical value (46.18%) for decomposition $KClO_4 \rightarrow KCl + 2O_2$, and we found that the initial

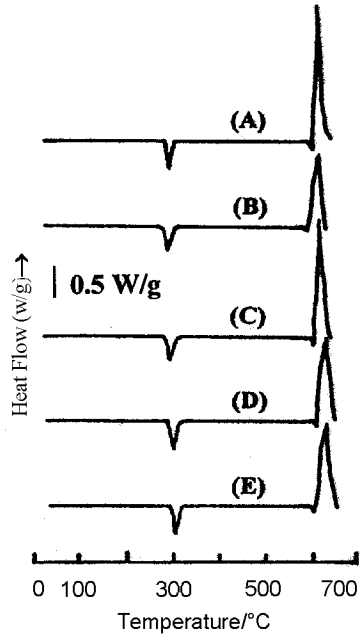

Fig. 1. DSC curves of $KClO_4$ with different particle sizes under static air atmosphere with a 10°C min^{-1} heating rate. (A) ≥100 mesh; (B) 100–150 mesh; (C) 150–200 mesh; (D) 200–325 mesh; (E) ≤325 mesh.

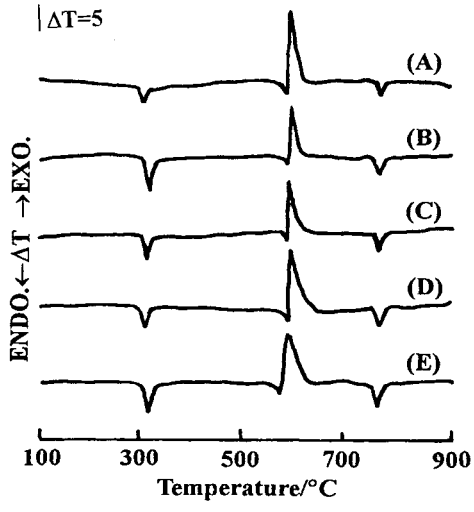

Fig. 2. DTA curves of $KClO_4$ with different particle sizes under static air atmosphere with a 10°C min^{-1} heating rate. (A) ≥100 mesh; (B) 100–150 mesh; (C) 150–200 mesh; (D) 200–325 mesh; (E) <325 mesh.

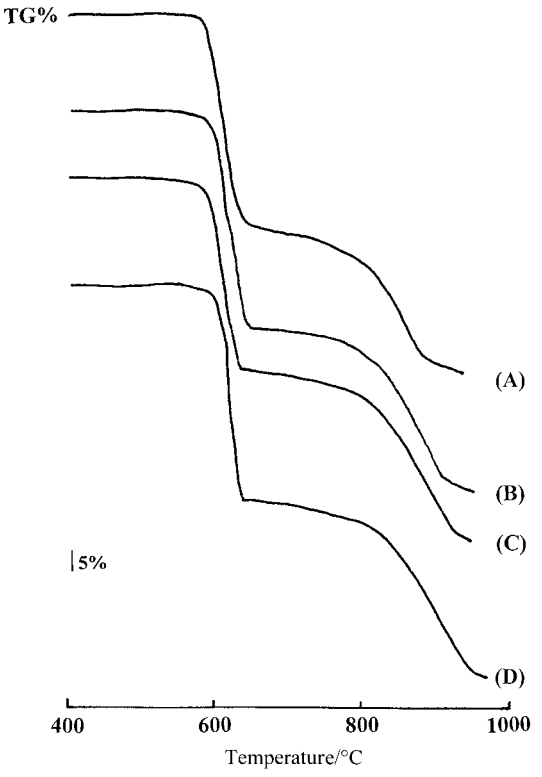

Fig. 3. TG curves of $KClO_4$ with different particle sizes under static air atmosphere with a $10^{\circ}C\,min^{-1}$ heating rate. (A) ≥100 mesh; (B) 100–150 mesh; (C) 200–325 mesh; (D) <325 mesh.

decomposition temperatures of $KClO_4$ powders were shifted to lower temperature in this work, and were lower with decreasing particle size. But this result was discontinued for the powder size smaller than 44 μm.

Flynn and Wall [7], Doyle [8], et al., have illustrated that the activation energy of a thermal decomposition process can be determined directly from a series of TG curve, which are carried out at different heating rates. The method that was developed by Flynn and Wall was the rate equation of the form:

$$\frac{d\alpha}{dt} = \left(\frac{A}{h}\right) f(\alpha) \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

where T is the temperature in Kelvin, h the heating rate, A the pre-exponential factor of the Arrhenius equation, E_a the activity energy, R the gas constant, α the degree of conversion and $f(\alpha) = a$ is the function of degree of conversion (mass loss). A, $f(\alpha)$, and E are assumed to be independent of T, and A and E_a are also assumed to be independent of C. By utilizing the successive approximation method and the approximate activation energies as determined, the constant in Eq. (2) may be easily recalculated and the correct activation energies can be obtained. For $20 \leq E_a/RT \leq 60$, the slope with average value of 0.457 is used in Eq. (2) and varies ±3%.

$$\frac{d(\log h)}{d(1/T)} = -\left(\frac{0.457}{R}\right) E_a \quad (2)$$

The TG curves for thermal decomposition of potassium perchlorate with different particle size region, both under N_2 and at static air atmosphere, with heating rates from 5 to $50^{\circ}C\,min^{-1}$ were recorded and analyzed.

Fig. 4 shows the TG curves of $KClO_4$ with different particle sizes with a $10^{\circ}C\,min^{-1}$ heating rate, both under N_2 and at static air atmosphere. In the

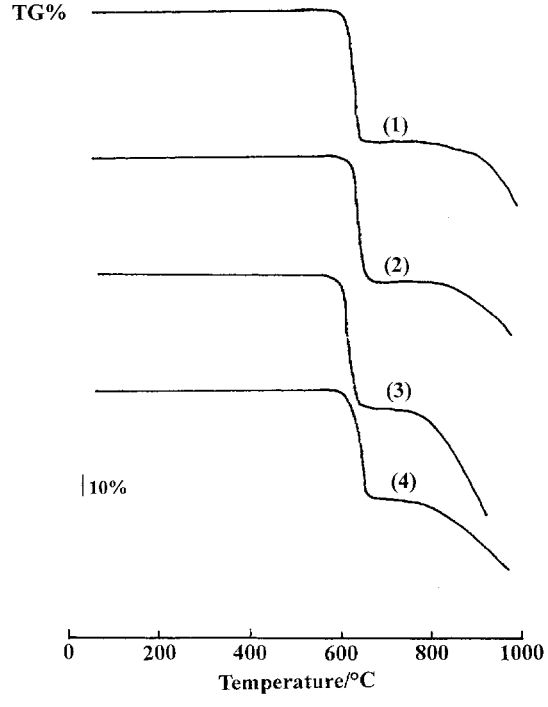

Fig. 4. TG curves of $KClO_4$ with different particle sizes with a $10^{\circ}C\,min^{-1}$ heating rate. (1) <325 mesh, under air atmosphere; (2) <325 mesh, under nitrogen atmosphere; (3) 200–325 mesh, under air atmosphere; (4) 200–325 mesh, under nitrogen atmosphere.

Table 2
Activation energy of decomposition for $KClO_4$ with particle size between 44 and 74 μm, and less than 44 μm in static air and in a nitrogen atmosphere

Mass loss (%)	44–74 μm					≤44 μm				
	E (kJ mol^{-1})	$-r_a$	E/RT	b	$E_{corrected}$ (kJ mol^{-1})	E (kJ mol^{-1})	$-r_a$	E/RT	b	$E_{corrected}$ (kJ mol^{-1})
Air										
5	226	0.931	71.6	0.446	231	262	0.945	80.8	0.445	269
10	238	0.968	74.7	0.445	245	257	0.964	80.4	0.445	264
30	241	0.983	74.8	0.445	248	241	0.967	74.8	0.446	247
40	245	0.984	75.7	0.445	252	241	0.942	74.3	0.446	247
50	310	0.953	94.8	0.443	320	263	0.948	78.4	0.445	270
N_2										
5	112	1.00	36.2	0.458	112	134	0.996	43.3	0.454	135
10	117	0.999	37.5	0.457	117	117	0.998	37.5	0.457	117
30	116	0.994	36.2	0.458	116	113	0.980	35.3	0.459	112
40	120	0.986	37.2	0.458	120	109	0.986	33.7	0.460	108
50	113	0.995	34.8	0.459	113	107	0.970	32.9	0.461	106

static air atmosphere case, the initial decomposition temperature of $KClO_4$ for the particle size smaller than 44 μm was shifted from 558 to 606°C, while increasing the linear heating rate of TG, and the initial decomposition temperature of the particle sizes that are between 44 and 74 μm also ranged from 536 to 618°C. Same results were observed in N_2 atmosphere, the initial decomposition temperatures of potassium perchlorate for the particle sizes smaller than 44 μm are from 556 to 625°C, and that for particle size between 44 and 74 μm are from 526 to 621°C, respectively. Experimental results have shown that the initial decomposition temperature of potassium perchlorate with particle sizes smaller than 44 μm are almost higher than that for particle size between 44 and 74 μm no matter in air or at N_2 atmosphere with heating rate of 5–50°C min^{-1}.

The activation energies of potassium perchlorate with different particle sizes are estimated by applying the technique of dynamic TG. The activation energies of the decomposition stage evaluated by dynamic TG method are listed in Table 2. When the percentage of the weight loss is lower than 10%, we found that the $KClO_4$ of particle size smaller than 44 μm has a higher activation energy of decomposition under either static air or at N_2 atmosphere. This result may illustrate that the initial decomposition temperature of potassium perchlorate with particle sizes smaller than 44 μm are almost higher than the particle size between 44 and 74 μm no matter in air or at N_2 atmosphere with heating rate of 5–50°C min^{-1}.

It has to be considered that the initial portion of the TG curves can be fitted with a first-order reaction equation. In this study, we recognized that low weight losses consistently lower than 10% can use the Arrhenius equation to calculate the activation energy, because the TG analysis gave $KClO_4 \rightarrow KCl + 2O_2$ result, and the decomposition activation energies of $KClO_4$ with two kinds of particle size under air atmosphere are 231–269 kJ mol^{-1}, which are close to the results of Cordes (for 210 kJ mol^{-1}) and Harvey (for 295 kJ mol^{-1}).

4. Conclusions

The thermal behaviors of $KClO_4$ with different particle sizes were investigated using DSC, DTA and TG. The corresponding TG curves of decomposition for $KClO_4$ are also recorded and the initial decomposition temperatures of $KClO_4$ with smaller particle size are shifted to lower temperature. The decomposition activation energies of $KClO_4$ with smaller particle size range from 231 to 269 kJ mol^{-1} (mass loss percentage is lower than 10%, calculated by dynamic TG method).

References

[1] A.E. Harvey Jr., M.T. Edmison, E.D. Jones, R.A. Seybert, K.A. Catto, J. Am. Chem. Soc. 76 (1954) 3270.
[2] H. Ellern, Modern Pyrotechnics, Chemical Publish Co., Inc., New York, 1961.
[3] H.F. Cordes, S.R. Smith, J. Phys. Chem. 72 (1968) 2189.
[4] W.K. Rudolf, E.S. Freeman, J. Phys. Chem. 74 (1970) 3317.
[5] B. Beger, E.L. Charsely, J.J. Rooney, S.B. Warrington, Thermochim. Acta 255 (1995) 227.
[6] E.L. Charsley, J. Therm. Anal. 40 (1993) 1399.
[7] J.H. Flynn, L.A. Wall, Polym. Lett. 4 (1966) 323.
[8] C.D. Doyle, J. Appl. Polym. Sci. 6 (1962) 639.