Thermochimica Acta, 241 (1994) 43–49
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(94)01721-R

The thermal behaviour of caesium periodate and the kinetics of the decomposition reaction

C.A. Strydom * and L.C. Prinsloo

Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

(Received 30 September 1993; accepted 22 January 1994)

Abstract

Using a heating rate of 5°C $\mathrm{min^{-1}}$, $CsIO_4$ decomposes between 300 and 350°C according to the reaction $2CsIO_4(s) \rightarrow 2CsIO_3(s) + O_2(g)$, with an enthalpy change of $-57\ \mathrm{kJ\ mol^{-1}}$ $CsIO_4$. The reaction occurs in two distinct parts. First a maximum number of nuclei (approx. 14 per μm^2) forms at a constant rate according to the power law. Then these nuclei grow according to the contracting area equation. Using isothermal decomposition data, an activation energy value of $226\ \mathrm{kJ\ mol^{-1}}$ and ln *A* of 40.9 were calculated for the first part of the reaction where nuclei are formed, while the activation energy value for the growth of the nuclei is $138\ \mathrm{kJ\ mol^{-1}}$ and ln *A* is 21.7. Secondary electron micrographs were used to determine the most parsimonious kinetic equation for the decomposition data.

INTRODUCTION

The possible use of periodate crystals of alkali elements in laser frequency doubling has been discussed in the literature [1, 2]. The thermal behaviour and decomposition of caesium periodate are therefore of great interest to this field of study.

The decomposition of some solids can be described by the general reaction

$$A(s) \rightarrow B(s) + \text{gases}$$

The decomposition reaction is initiated at regions on the crystals as nuclei of the solid product are formed. These nuclei then grow until only the solid product remains. The gaseous products escape into the atmosphere. Kinetic models based on the different mechanistic possibilities of these processes have been derived [3]. Kinetic analysis involves the relation of experimental α,t (fraction reaction, time) values at constant temperature to the models, and the determination of the equation and, thus, the mechanism that best describes the decomposition reaction.

---

* Corresponding author.

0040-6031/94/$07.00 © 1994 – Elsevier Science B.V. All rights reserved

When using this method, it is, however, essential to make sure that the process under investigation is a single-step reaction, involving no intermediates [4]. As a criterion for a single-step process, the method described by Vyanzovkin and Lesnikovich can be used [5]. Activation energy values at different conversion values are determined from dynamic thermogravimetric data using different heating rates. This isoconversion method represents the results of several non-isothermal runs as

$$\ln[(\mathrm{d}\alpha/\mathrm{d}t)\beta] = \ln Af(\alpha) - (E/RT)$$

where β is the heating rate and T the temperature at the degree of decomposition, α [6, 7]. This can be used to determine the activation energy E without identification of the reaction model of $f(\alpha)$, by plotting $\ln\beta$ against $1/T$ at constant α. The existence of a dependence indicates a complex process. If activation energy does not change with α, then the decomposition occurs in a single step.

EXPERIMENTAL

Sample preparation

HIO_4 was added to $CsCO_3$, dissolved in distilled water. A fine white powder immediately precipitated. The precipitate was washed with distilled water and dried. Infrared spectroscopy and X-ray diffraction analysis identified the powder as $CsIO_4$.

Thermogravimetric analysis

A Stanton Redcroft STA 780 simultaneous thermal analyser was used to collect thermogravimetric data. Nitrogen was used as a dynamic atmosphere (flow rate approx. 20 $\mathrm{cm}^3\,\mathrm{min}^{-1}$). Platinum sample pans were used and temperature calibration was achieved using the ICTAC recommended DTA standards. Sample masses varied between 5.0 and 10.0 mg.

Infrared spectroscopic analysis

Infrared spectra were recorded on a Bruker IFS 113V spectrometer between 400 and 4000 cm^{-1}. Samples were prepared in the form of KBr discs.

Electron microscopic analysis

Secondary electron micrographs were obtained on a JEOL 840 scanning electron microscope.

Calorimetric analysis

Enthalpy measurements were made on a Du Pont 910 differential scanning calorimeter, controlled by a 1090 thermal analyser. ICTAC recommended standards were used for calibration. Aluminium sample pans in a nitrogen atmosphere were used.

RESULTS AND DISCUSSION

Non-isothermal measurements

Using a heating rate of 5°C min^{-1}, $CsIO_4$ decomposes between 300 and 350°C with a mass loss of 5%, as shown in Fig. 1. This percentage corresponds to the mass loss observed in the reaction

$$2CsIO_4(s) \rightarrow 2CsIO_3(s) + O_2(g)$$

$CsIO_3$ was identified as the decomposition product using infrared spectroscopy and X-ray diffraction analysis.

The decomposition of caesium periodate to caesium meta-iodate and oxygen was then studied using heating rates of between 0.5 and 5°C min^{-1} to obtain the activation energy values E at different transformation degree values α, as described in the Introduction. Using this method, it was

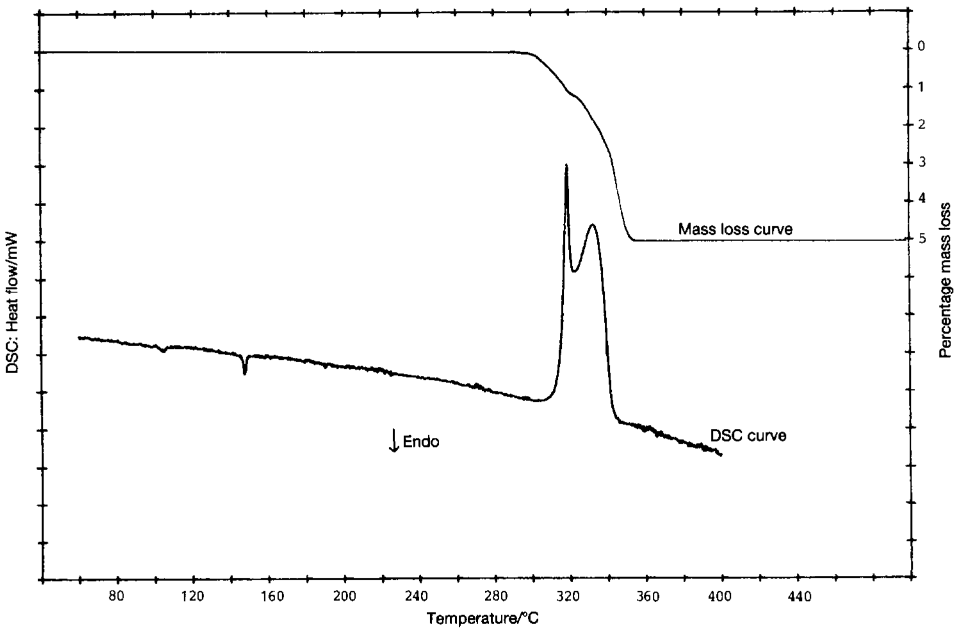

Fig. 1. The mass loss and DSC curves of the decomposition of $CsIO_4$ using a heating rate of 5°C min^{-1}.

observed that the $E-\alpha$ dependence of the decomposition reaction can be divided into two parts. Between α values of 0 and 0.2, the activation energy is constant at a value of 187 kJ mol^{-1}, and between 0.2 and 1, the activation energy is calculated as 158 kJ mol^{-1}. This result indicates that the rate of the reaction is controlled by different factors in the two regions. The two regions can also be seen in Fig. 1 after mass losses of 1% and 5% of $CsIO_4$.

Isothermal measurements

$CsIO_4$ was heated at constant temperatures between 280 and 325°C. The α–time data were analysed separately for the two regions, i.e. between α values of 0 and 0.2 and between 0.2 and 1.

It proved difficult to distinguish between the contracting area equation ($f(\alpha) = 1 - (1 - \alpha)^{1/2}$), the power law equation with $n = 1(f(\alpha) = \alpha)$, and the second-order equation ($f(\alpha) = [1/(1 - \alpha)] - 1$) for the reaction between α values of 0 and 0.2, because all three fit with correlation coefficient values of 0.96 and higher. The kinetic parameters, however, do not differ for the three different equations and are: for the contracting area equation, $E = 226$ kJ mol^{-1} and $\ln A = 40.3$; for the power law, $E = 226$ kJ mol^{-1} and $\ln A = 40.9$; and for the second-order equation, $E = 227$ kJ mol^{-1} and $\ln A = 41.3$. To choose between the three mechanisms, electron micrographs were obtained as described below.

For the reaction between α values of 0.2 and 1, two kinetic equations give correlation coefficient values of 0.98 and higher: the contracting area equation and the Avrami–Erofe'ev equation with $n = 4 f(\alpha) = [-\ln(1 - \alpha)]^{1/4}$. As was observed for the first part of the reaction, the kinetic parameters for both these mechanisms are approximately the same: for the contracting area equation, $E = 138$ kJ mol^{-1} and $\ln A = 21.7$; for the Avrami–Erofe'ev equation $E = 136$ kJ mol^{-1} and $\ln A = 21.1$. Electron micrographs were obtained to distinguish between the mechanisms.

Infrared spectroscopic measurements

Figure 2 gives the changes in the infrared absorption bands for the decomposition reaction as the reaction proceeds. The asymmetric stretching vibrations of the IO_4^- ion are observed at 851 and 845 cm^{-1}, and a symmetric stretching vibration lies at 792 cm^{-1} [8]. The new bands at 796, 763 and 747 cm^{-1} are due to symmetric and asymmetric stretching vibrations of the IO_3^- ion [9].

Electron micrographs

To choose between the proposed mechanisms for the reaction, electron micrographs were obtained between α values of 0 and 1 (Fig. 3). From the

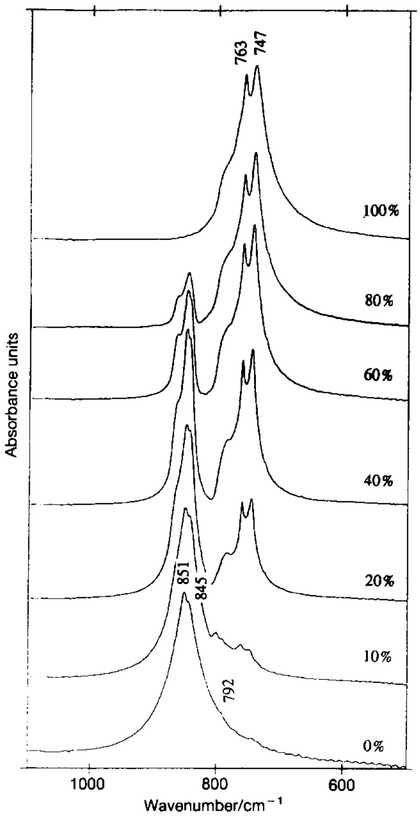

Fig. 2. Infrared spectra of reactant and product at different stages of the decomposition of $CsIO_4$.

figure, it is clear that between the α values of 0 and 0.2, a limited number of nuclei are formed more or less at a constant rate. A very slow growth of the nuclei is also observed. A maximum of approximately 14 nuclei per μm^2 is formed. The micrographs for α values of between 0.2 and 1 indicate a two-dimensional growth of the nuclei. It thus seems that the decomposition of $CsIO_4$ to $CsIO_3$ proceeds via the formation of a limited maximum number of nuclei at a constant rate and growth according to the contracting area equation.

DSC measurements

The phase transition at 146.3°C (Fig. 1) with an enthalpy change of 0.69 kJ mol^{-1} compares very well to the reported phase transition at 146°C with an enthalpy change between 0.628 and 0.795 kJ mol^{-1} as reported by Arend et al. [10].

At least two partially overlapping peaks can be distinguished between 300 and 350°C (Fig. 1). This corresponds to the decomposition of $CsIO_4$ to

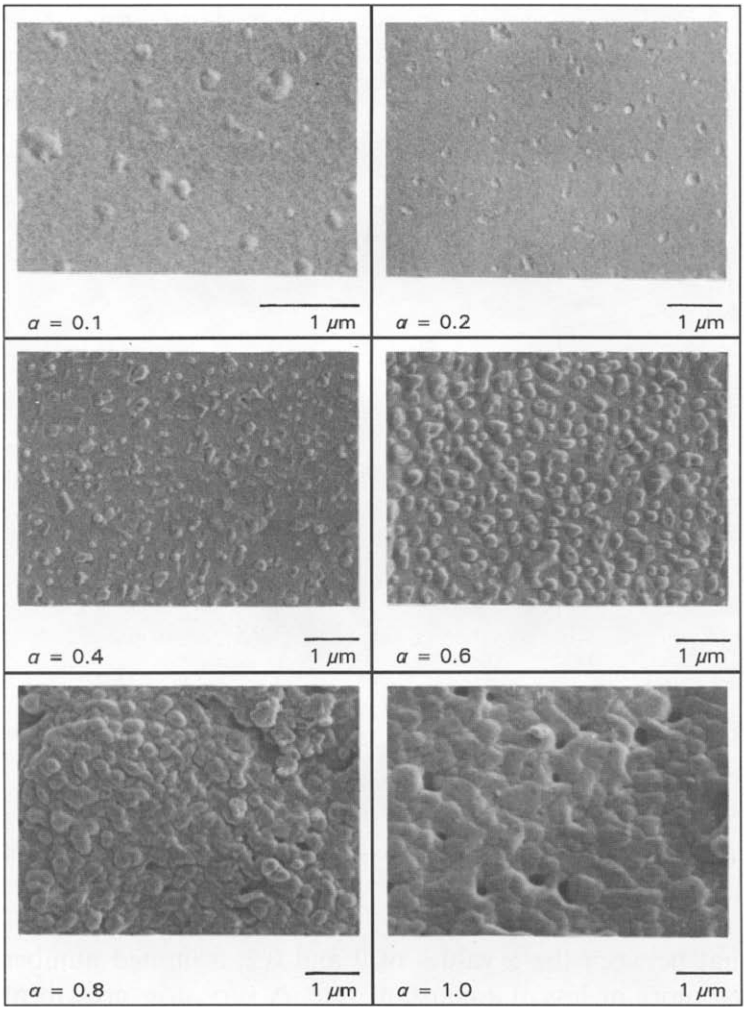

Fig. 3. Secondary electron micrographs of the decomposition of $CsIO_4$ at fraction reaction values (α) between 0 and 1.

$CsIO_3$, and an enthalpy value of $-57\ \mathrm{kJ\ mol^{-1}}$ is calculated for the decomposition reaction.

CONCLUSIONS

Using a heating rate of 5°C $\mathrm{min^{-1}}$ the decomposition occurs between 300 and 350°C according to the scheme

$$2CsIO_4(s) \rightarrow 2CsIO_3(s) + O_2(g)$$

The reaction can clearly be divided into two parts, both exothermic reactions, with a total enthalpy change of $-57\ \mathrm{kJ\ mol^{-1}}$ $CsIO_4$.

Kinetic analysis of the decomposition reaction also indicates that the rate of the reaction is controlled by different factors in the two parts. The activation energy values determined by the non-isothermal method and the isothermal method differ substantially from each other, although the same trend is followed, i.e. a higher constant E value between α values of 0 and 0.2 (non-isothermal method, $E = 187$ kJ mol^{-1}; isothermal method, $E = 226$ kJ mol^{-1}) in comparison to the value between α values of 0.2 and 1 (non-isothermal method, $E = 158$ kJ mol^{-1}; isothermal method, $E = 138$ kJ mol^{-1}). The literature indicates that the values determined by the isothermal methods are more reliable and correct than those determined non-isothermally [3, 4].

Secondary electron micrographs at α values of between 0 and 1 confirmed that the decomposition of $CsIO_4$ to $CsIO_3$ proceeds via the formation of a limited number of nuclei (approx. 14 per μm^2) at constant rate, and that the growth of the nuclei proceeds according to the contracting area equation.

ACKNOWLEDGEMENT

The authors thank the Department of Electron Microscopy of the University of Pretoria for their assistance in obtaining the electron micrographs.

REFERENCES

1 N.G. Golubeva and P.A. Korotkov, Ukr. Fiz. Zh., 29 (1984) 679.
2 J.G. Bergman and G.R. Crane, Inorg. Chem., 17 (1978) 1613.
3 M.E. Brown, D. Dollimore and A.K. Galwey, Reactions in the Solid State, Comprehensive Chemical Analysis, Vol. 22, Elsevier, Amsterdam, 1980.
4 W.W. Wendlandt, Thermal Analysis, John Wiley, New York, 3rd edn., 1985, p. 57.
5 S.V. Vyanzovkin and A.I. Lesnokovich, Thermochim. Acta, 165 (1990) 273.
6 D. Dollimore, Anal. Chem., 62 (1990) 44R.
7 A.R. Salvador, E.G. Calvo and A.I. Gulias, Thermochim. Acta, 73 (1984) 101.
8 R.G. Brown, J. Denning, A. Hallett and S.D. Ross, Spectrochim. Acta Part A, 26 (1970) 969.
9 H.H. Ysel, K.-G. Lipponer, C. Oberle and I. Zahn, Spectrochim. Acta Part A, 48 (1992) 219.
10 H. Arend, H. Gränicher, U. Helg and R. Hofmann, Helv. Phys. Acta, 43 (1970) 484.