

Thermolysis of Calcium Iodate: Kinetic Parameters¹

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Abstract—Thermal transformations in calcium iodate were studied by differential scanning calorimetry in the temperature range of 300–973 K. The process was found to proceed by the scheme: $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O} \rightarrow \text{Ca}(\text{IO}_3)_2 \rightarrow \text{Ca}_5(\text{IO}_6)_2 + \text{I}_2 + 9\text{O}_2$. Calculated kinetic parameters adequately described experiment. X-ray diffraction patterns of the intermediate products formed at 523, 723, and 873 K well agreed with the available literature data.

Keywords: thermolysis, calcium iodate, kinetic parameters

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1. INTRODUCTION

Oxygen compounds of iodine, iodic acids, metal iodates are strong oxidizers, which release iodine and oxygen during thermal decomposition. In view of this, these compounds find application in energetic thermite mixtures whose combustion products produce a biocidal effect on dangerous bacteria and their spores [1, 2]. To date, numerous studies have been focused on the behavior and combustion characteristics of such compounds [3–8]. Another urgent problem is the withdrawal from usage of perchlorate-containing pyrotechnic compositions because of their ecological incompatibility, in particular, it was proposed to use periodates instead of perchlorates in pyrotechnic compositions [9].

Calcium iodate $\text{Ca}(\text{IO}_3)_2$ is of especial interest since this salt is present in nature as lautarite mineral and hence is environment-friendly. Calcium iodate is fed to animals as food supplement E916. It is also added to cosmetic ointments and lotions as an antiseptic and deodorant. The advantages of $\text{Ca}(\text{IO}_3)_2$ over KClO_4 as an oxidizing agent are as follows: (a) $\text{Ca}(\text{IO}_3)_2$ contains more oxygen than KClO_4 and (b) the melting (decomposition) temperature of $\text{Ca}(\text{IO}_3)_2$ (813 K) is lower than that of KClO_4 (855 K) only slightly.

As is known, decomposition of KClO_4 in thermite reactions yields KCl that is rather stable at elevated temperatures. Products of $\text{Ca}(\text{IO}_3)_2$ decomposition contain CaI_2 which must partially dissociate into iodine and CaI in the vapor phase at high tempera-

tures. The latter ones are highly reactive and hence are capable of (a) deactivating dangerous bacteria and (b) accelerating chemical reactions due to more efficient gas-phase transfer of intermediates.

In this context, basic knowledge about the chemical transformations taking place during thermolysis of calcium iodate becomes of key importance. To date, thermal decomposition of KClO_4 has been studied in detail [10, 11] while that of calcium iodate, inadequately, largely because of its complexity as is evidenced by the reactions of potassium iodate in aqueous solutions [12]. Synthesis and thermolysis of $\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$ was reported in [13, 14]. It was found to involve the stages of dehydration and formation of a non-aqueous product, followed by decomposition with evolution of gaseous iodine and oxygen. Thermodynamic parameters of the process were calculated. The reaction rate was found to affect a type of product modification: α - $\text{Ca}(\text{IO}_3)_2$ or β - $\text{Ca}(\text{IO}_3)_2$; while ambient pressure, a kind of product: calcium oxide or calcium iodide.

Freshly prepared calcium iodate monohydrate was studied in [13, 14]. In this work, we explored the behavior of commercially available reagent that contained smaller (and unknown) amount of crystallization water (compared to $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ monohydrate). In addition, the commercial calcium iodate could undergo aging during its storage. To our knowledge, the thermolysis of aged calcium iodate has not been explored so far.

Here we report on (i) determining the amount of crystallization water in commercial calcium iodate and (ii) the processes occurring during thermal

¹ The text was submitted by the authors in English.

Table 1. Relationship between reaction order n and extent of conversion α_{\max} at T_{\max} (according to [15])

α_{\max}	0.750	0.632	0.556	0.500	0.457	0.423
n	0.5	1.0	1.5	2.0	2.5	3.0

decomposition of the above calcium iodate and relevant kinetic parameters.

2. EXPERIMENTAL

Calcium iodate (from Almerdale Assets) was used as the object of our study. Its thermal decomposition was studied by differential scanning calorimetry (NETZSCH STA 409 PC/PG analyzer, under Ar). After holding samples at 523, 723, and 873 K for 1 h, their phase composition was determined with a RIKOR portable X-ray diffractometer (Cu- K_{α} radiation).

3. CALCULATING KINETIC PARAMETERS

Kinetic parameters for decomposition of calcium iodate were calculated using the algorithm described in [15]. The calculation procedure involved the following steps.

(1) Extent of conversion α is calculated for each temperature T_i using the values of initial sample mass m_0 , end sample mass m_e , and running sample mass m_i at the i th point on a TG curve:

$$\alpha_i = (m_0 - m_i)/(m_0 - m_e).$$

(2) Derivatives $(d\alpha/dT)_i$ are numerically calculated for each T_i using the method of rectangles.

(3) Maximum values— T_{\max} , $(d\alpha/dT)_{\max}$, and α_{\max} —are obtained from the curve plotted at Step 2 or from the DTG, DTA, DSC curves. Reaction order n , used as an initial approximation, is obtained by interpolating the values presented in Table 1.

(4) The values of Y_i and X_i (expressions (2) and (3), respectively) are calculated using Eq. (1) (taken from [15]):

$$\ln\left(\frac{d\alpha}{dT}\right)_i - n\ln(1 - \alpha_i) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT_i}, \quad (1)$$

where A is pre-exponential factor, β heating rate, E activation energy, and R universal gas constant.

$$Y_i = \ln\left(\frac{d\alpha}{dT}\right)_i - n\ln(1 - \alpha_i), \quad (2)$$

$$X_i = \frac{1}{T_i}. \quad (3)$$

For each temperature T_i within the temperature range of a given step, coefficients a and b in the equation $Y_i = aX_i + b$ are obtained using the linear LS method to calculate parameters $E = -aR$ and $A = \beta \exp b$.

Correlation coefficient r for Y_i and X_i is calculated as follows: (a) when $r \neq 1$, n is changed and Step 4 is repeated until the absolute value of r approaches to unity as close as possible and (b) the values of n , E , and A obtained at the last iteration are taken as final.

All calculations were performed using MS Office Excel 365, Windows 10.

4. RESULTS AND DISCUSSION

The thermograms of calcium iodate decomposition are shown in Fig. 1. The process is seen to have three endothermic stages. The first one (413–493 K) is a decrease in sample mass; the second one peaked at 683 K proceeds without mass change; and the third one is a two-step process accompanied by significant mass loss.

As follows from Fig. 2a, starting calcium iodate represented a mixture of two phases, $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Ca}(\text{IO}_3)_2$. Our calculations based on the TG curve have shown (see Table 2) that these are present in the amounts of 44 and 56 wt %, respectively. After holding at 523 K for 1 h, the sample contained only the $\text{Ca}(\text{IO}_3)_2$ phase (see Fig. 2b), which is indicative of complete water removal.

Figure 3 shows processed TG data for the first stage of calcium iodate decomposition. Figure 4 presents these data linearized according to Eq. (2) while Table 3, respective kinetic parameters. Curve 3 in Fig. 3 shows the derivative $d\alpha/dT$ plotted using Eq. (4) and calculated kinetic parameters.

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)(1 - \alpha)^n. \quad (4)$$

Table 2. Results of calculations based on the parameters of TG curve

$T_0 - T_e$, K	T_{\max} , K	M_{meas} , g	M_{cltd} , g	Process
298		0.04927	0.492	$0.44\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O} + 0.56\text{Ca}(\text{IO}_3)_2$
413–513	448	0.048	0.048	$\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O} \rightarrow \text{Ca}(\text{IO}_3)_2 + \text{H}_2\text{O}$
773–973	883	0.0175	0.0159	$\text{Ca}(\text{IO}_3)_2 \rightarrow 1/5\text{Ca}_5(\text{IO}_6)_2 + 0.2\text{I}_2 + 1.8\text{O}_2$

Notes: M_{meas} is the sample mass derived from the TG curve, M_{cltd} is that defined by reaction scheme or product composition.

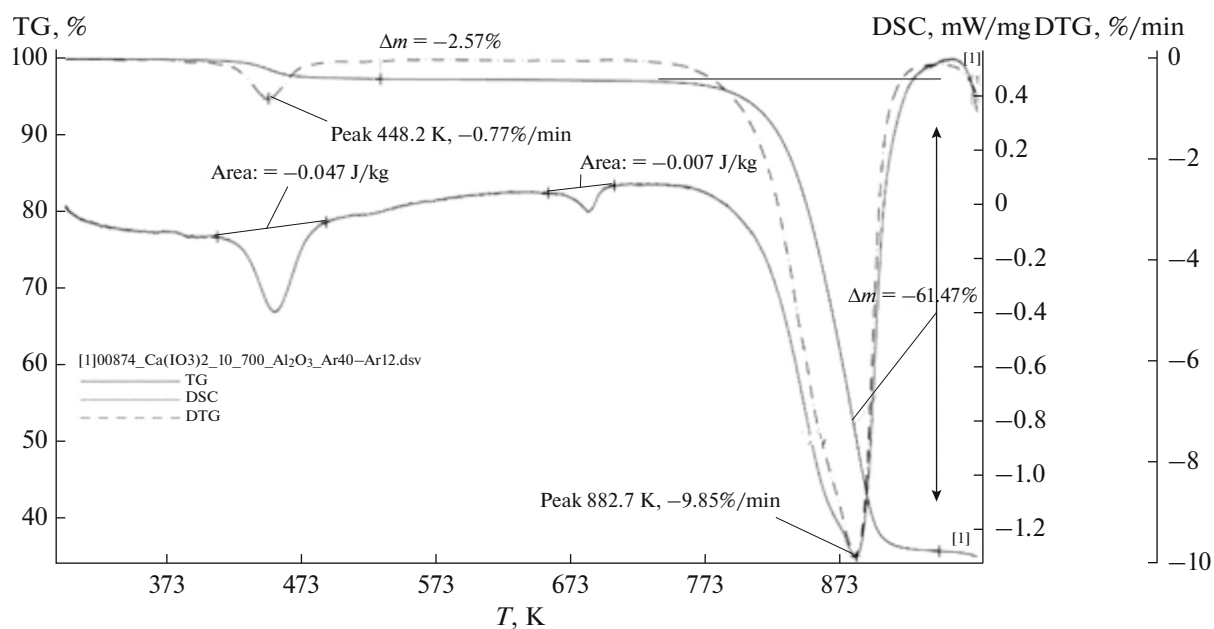


Fig. 1. DSC results for commercial calcium iodate.

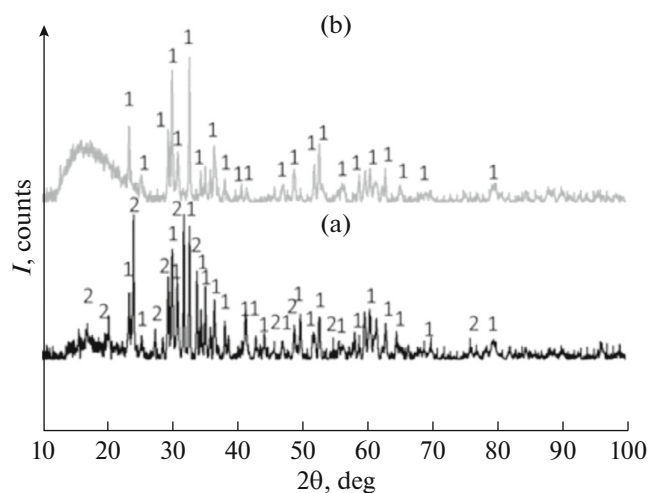


Fig. 2. Diffraction pattern of (a) starting calcium iodate and (b) calcium iodate held at 523 K for 1 h (b). Phases: (1) $\text{Ca}(\text{IO}_3)_2$, (2) $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$.

Curve 3 satisfactorily describes experiment only up to 470 K. The deviation can be explained by the involvement of water vapor diffusion through the intergranular space.

Note that our values of activation energy E , reaction order n , and pre-exponential factor A are much higher than those for the dehydration of related compounds such as $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ [16]. Nevertheless, the fact that absolute correlation coefficient r is close to unity allows us to consider our results close to true ones. According to the theory of topochemical reactions, $n = 1.4$ means that a given reaction proceeds in a kinetic mode [17].

Table 3. Kinetic parameters for the first stage of calcium iodate decomposition

T_{\max} , K	448
α_{\max}	0.51
$d\alpha_{\max}/dT_{\max}$	0.033
r	-0.9976
n	1.4
E , kJ/mol	159
A , min^{-1}	2.78×10^{18}

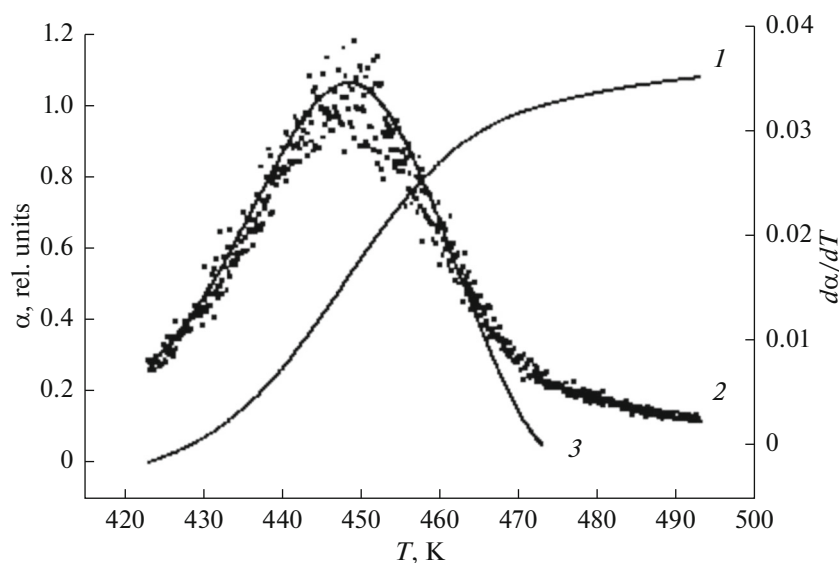


Fig. 3. (1) Extent of conversion α and its derivative $d\alpha/dT$ for the first stage of calcium iodate decomposition: measured (data points 2) and calculated (solid line 3).

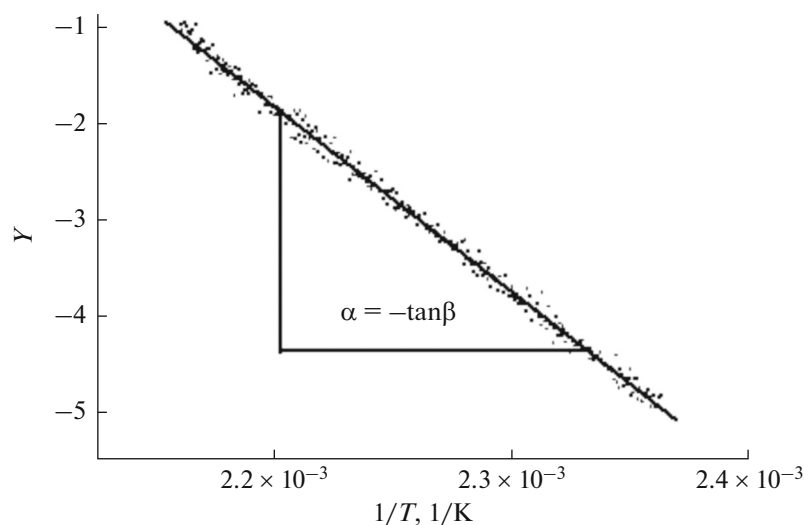


Fig. 4. Linearized Eq. (1) for the first stage of calcium iodate decomposition; Y is given by formula (2).

Table 4. Kinetic parameters for the second stage of calcium iodate decomposition

T_{\max} , K	883
α_{\max}	0.64
$d\alpha_{\max}/dT_{\max}$	0.0182
r	-0.993
n	0.4
E , kJ/mol	212
A , min^{-1}	1.5×10^{12}

So, the first stage of our process can be described as the decomposition of $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ crystals followed by the diffusion of water vapor over the intergranular space.

The endothermic process around 690 K is not accompanied by mass change. According to [13], this is the $\alpha \rightarrow \beta$ phase transition in calcium iodate. However, after isothermal annealing, no $\beta\text{-Ca}(\text{IO}_3)_2$ was detected by XRD method. Apparently, this can be due to the reversibility of this phase transition. An endothermic process in the range 770–920 K is accompanied by mass loss (cf. Fig. 1). As can be deduced from

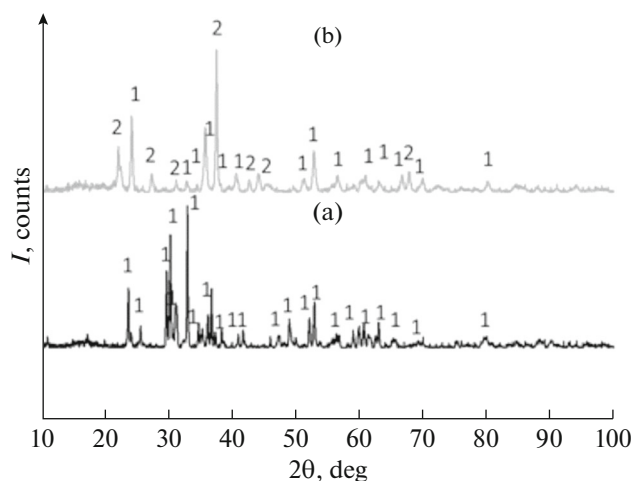


Fig. 5. Diffraction patterns of calcium iodate held at 723 (a) and 873 K (b) for 1 h. Phases: (1) $\text{Ca}(\text{IO}_3)_2$, (2) $\text{Ca}_5(\text{IO}_6)_2$.

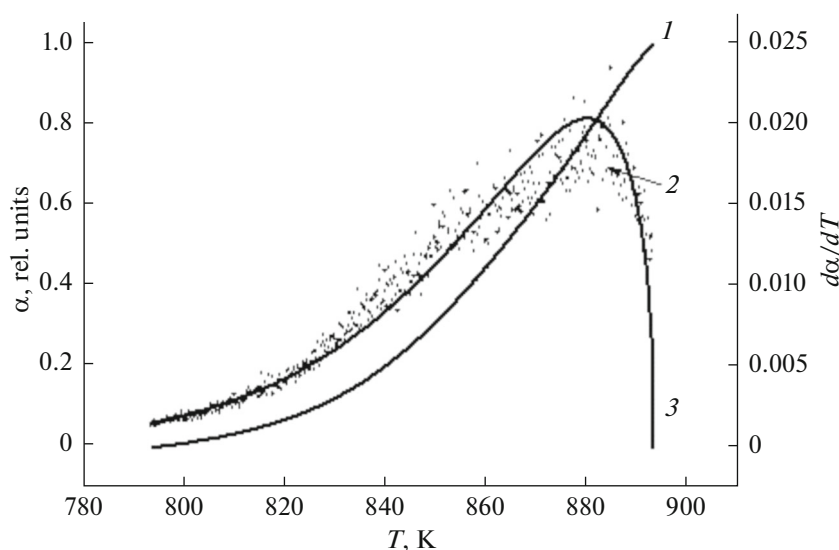
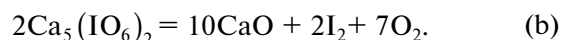
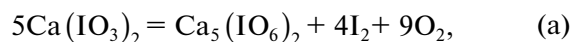


Fig. 6. (1) Extent of conversion α and its derivative $d\alpha/dT$ for the second stage of calcium iodate decomposition: measured (data points 2) and calculated (solid line 3).

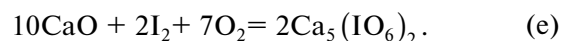
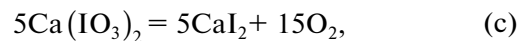
Fig. 5, this is the conversion of $\text{Ca}(\text{IO}_3)_2$ iodate into $\text{Ca}_5(\text{IO}_6)_2$ periodate. The processed data of the TG curve for this stage are given in Fig. 6. Calculated curve 3 (based on kinetic parameters from Table 1) is seen to comply with experiment (data points 2). However, the presence of an inflection point on the DTG and DSC curves (see Fig. 1) suggests that the process is two-stage. Therefore, the kinetic parameters, calculated for this process as a one-stage one, are formal. Nevertheless, since the absolute correlation coefficient of the model is close to unity, it can be recognized that the kinetic constants adequately describe the process (see Fig. 7). The DTG and DSC curves show that temperature ranges in which these two processes proceed are very close and mutually overlapped.

It is difficult to discern these processes in this experiment.

According to [18], the decomposition of $\text{Ca}(\text{IO}_3)_2$ includes two stages:



Reaction (a) starts around 823 K and ends near 1043 K. However, the reaction is reversible and is the sum of reactions (c)–(e):



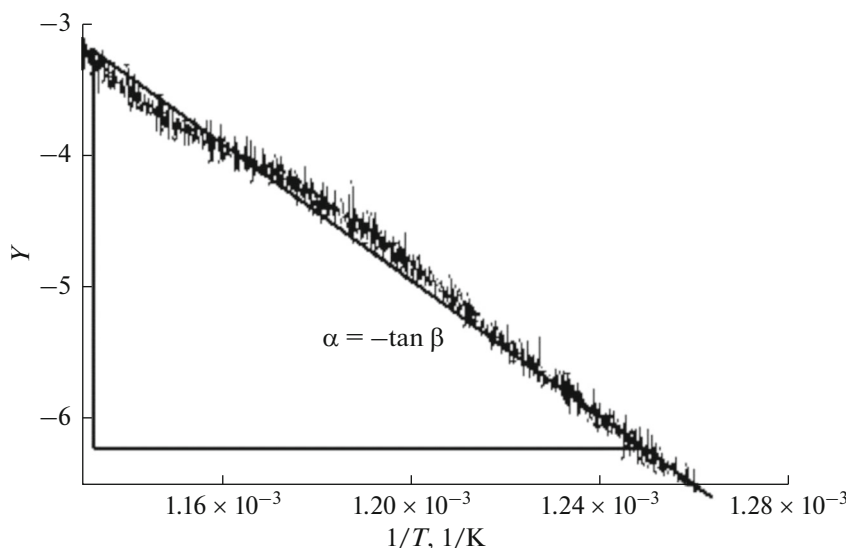


Fig. 7. Linearized kinetic Eq. (1) for the third stage of calcium iodate decomposition; Y is defined by formula (2).

Thus, the two-stage character of our process can be associated with the occurrence of reactions (c)–(e). It is obvious that the process under study must be pressure-dependent.

5. CONCLUSIONS

Thermolysis of commercial calcium iodate—comprising of 44% $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ and 56% $\text{Ca}(\text{IO}_3)_2$ (by weight)—proceeds within the temperature range 300–973 K by the following scheme: (i) dehydration of calcium iodate (413–513 K) and (ii) two-stage decomposition reaction $\text{Ca}(\text{IO}_3)_2 \rightarrow 0.2\text{Ca}_5(\text{IO}_6)_2 + 0.2\text{I}_2 + 1.8\text{O}_2$ (773–973 K). The calculated kinetic parameters adequately describe experiment. The XRD results for thermolysis products formed (in air) at 523, 723, and 873 K are in good agreement with the literature data.

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