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STUDY OF THERMAL DECOMPOSITION KINETICS OF LOW-TEMPERATURE REACTION OF AMMONIUM PERCHLORATE BY ISOTHERMAL TG

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Abstract

The kinetics of the thermal decomposition of ammonium perchlorate at temperatures between 215 and 260°C is studied, in this work, by measuring the sample mass loss as a function of time applying the isothermal thermogravimetric method.

From the maximum decomposition rate – temperature dependence two different decomposition stages, corresponding to two different structural phases of ammonium perchlorate, are identified. For the first region (215–235°C), corresponding to the orthorhombic phase, the mean value of the activation energy of 146.3 kJ mol^{-1}, and the pre-exponential factor of $3.43\cdot10^{14}$ min^{-1} are obtained, whereas for the second region (240–260°C), corresponding to the cubic phase, the mean value of the activation energy of 153.3 kJ mol^{-1}, and the pre-exponential factor of $4.11\cdot10^{14}$ min^{-1} are obtained.

Keywords: activation energy, ammonium perchlorate, decompositon, isothermal, kinetics, thermogravimetry

Introduction

Because of ammonium perchlorate (NH_4ClO_4) enjoys widespread use as an oxidiser in composite solid propellants, and pyrotechnics in general, its decomposition has been studied more frequently than that of any other oxygen rich salt [1–8]. It has been found that the thermal decomposition of ammonium perchlorate is rather complex and exhibits several unusual characteristics. Bircumshaw and Newman [3] have shown, in the first comprehensive study of the thermal decomposition of ammonium perchlorate, that at temperatures below about 300°C ammonium perchlorate undergoes an autocatalytic reaction which ceases after about 30% decomposition, leaving a residue which is ammonium perchlorate itself, apparently chemically identical with the starting material but having a larger specific surface area [3, 4]. Galwey and Mohamad [7] have also reported that the residual solid has a composition and crystal structure very similar to those of original ammonium perchlorate. This is usually called the low-temperature reaction. At temperatures above 300°C, the so-called

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high-temperature decomposition occurs. This reaction, which is not autocatalytic, goes up to complete decomposition. Parallel with the decomposition of ammonium perchlorate, sublimation takes place, making kinetic interpretation of thermal decomposition of ammonium perchlorate more complex [9, 10].

Dodé [11, 12] and later Bircumshaw and Newman [3], have shown that the chemical analysis of the decomposition products is rather complex, showing a temperature-sensitive distribution of decomposition products.

It has been proved by numerous investigations [3, 5, 7, 9] that the low-temperature decomposition of ammonium perchlorate, like many other solid-state decomposition processes, exhibits an induction period, the duration of which depends mostly on the applied temperature. The induction period is followed by a rapidly accelerating reaction which attains a maximum rate, and then it gradually decelerates [5]. The extent of decomposition is commonly about 30%, but may depend on the testing conditions and sample history [5].

The induction period and acceleratory stage are associated with the nucleus formation and growth [13]. The analysis of numerous investigations shows that different kinetic equations and different kinetic approaches were applied to derive kinetic parameters and to describe the decomposition mechanism. It seems that the Avrami–Erofeev, and Prout–Tompkins equations are most frequently applied to analyse kinetic data [5, 14].

However, there is still a considerable variation of values of the activation energy of the low-temperature decomposition of ammonium perchlorate in literature. The values reported in the literature are in the range of 71–172 kJ mol^{-1} [5]. Some of these variations are undoubtedly due to the widely different kinetic analyses employed in the derivation of kinetic parameters.

Thermal analysis techniques have been widely used today to characterise energetic materials [15]. Differential scanning calorimetry (DSC), and thermogravimetry (TG) provide information about the thermal stability, heat of decomposition, ignition temperatures and reaction kinetics of these materials [16–19]. In particular, thermogravimetric analysis, which can follow a sample mass loss over a long period of time at a specified temperature, is a technique which rapidly provides data for understanding decomposition processes. The results of thermogravimetric analysis, concerning the rate and mass loss, have been extensively used for the evaluation of the kinetic parameters of thermal decomposition [20].

In this work, differential scanning calorimetry, and thermogravimetric analyses are applied for the thermal characterisation of ammonium perchlorate, and for the determination of the kinetic parameters of thermal decomposition at temperatures between 215 and 260°C.

Experimental

Ammonium perchlorate, 80 μm of average particle size, being of commercial grade of quality (purity above 98.8%), was used in the study.

The measurements were performed by using a differential scanning calorimeter, (TA Instruments, DSC Model 2910), and a thermogravimetric analyser, (TA Instruments, SDT Model 2960), coupled with a mass spectrometer (Thermolab Model MS). The samples were placed in aluminium sample pans (TA Instruments, Part Number 900786.901).

The DSC curves were obtained by placing sample of ≈5 mg, in open aluminium sample pan, with heating rate of 5°C min^{-1}, and under nitrogen atmosphere (purity above 99.996%) with flow rate of 50 ml min^{-1}. The DSC cell was calibrated by indium. The thermogravimetric curves were obtained by placing sample of ≈5 mg, in open aluminium sample pan, with heating rate of 5°C min^{-1} and under nitrogen pouring with flow rate of 50 ml min^{-1}.

The isothermal thermogravimetric curves were obtained for several temperatures in the temperature range 215–260°C, in the following way. The apparatus furnace was preheated to the temperature of interest, and then heated isothermally about ten minutes before the sample was introduced. After that, when the temperature equilibrated, the pan with the sample was placed on the sample platform.

Results and discussion

The DSC curve of ammonium perchlorate (Fig. 1), obtained under non-isothermal conditions and placing sample in an open sample pan, shows two endothermic peaks with the maximums at about 246 and 400°C respectively, and one exothermic peak with the maximum at about 302°C. The first endothermic DSC peak, not accompanied by any visible stepwise in mass loss, corresponds to the transition from the orthorhombic to the cubic phase, the second DSC peak (exothermic) corresponds to the low-temperature decomposition, whereas the third DSC peak (endothermic), with

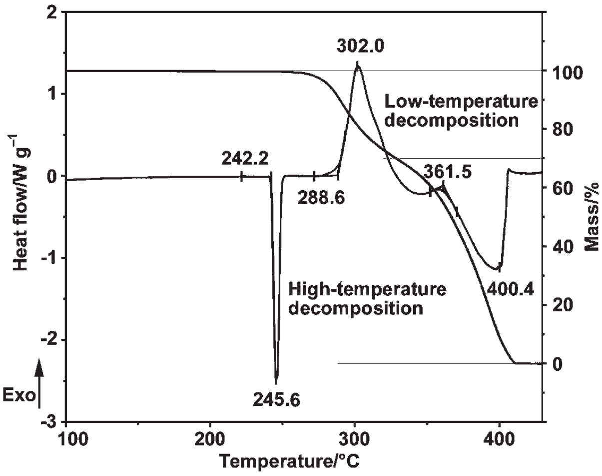

Fig. 1 DSC and TG curves of ammonium perchlorate obtained with heating rate of 5°C min^{-1} and under nitrogen flow rate of 100 ml min^{-1}

the heat of reaction of ≈21 kJ mol^{-1}, is connected with the high-temperature decomposition of ammonium perchlorate. It should be noted that the shape of the DSC curves of ammonium perchlorate depends strongly on the testing conditions (if experiment is run in a closed sample pan, then instead of third endothermic peak an exothermic peak occurs).

The TG curve shows that ammonium perchlorate decomposes in two rapid stages. The first stage corresponds to the low-temperature decomposition reaction (215–330°C), while the second stage (330–420°C) corresponds to the high-temperature decomposition reaction [16, 17]. However, the first deviation from the baseline (first mass loss) is visible at about 200°C. Parallel with this decomposition sublimation takes place, but its extent depends on the testing conditions.

There is no endothermic peak attributable to the melting of ammonium perchlorate, showing thus that it decomposes without melting.

Jacobs and Whitehead, in their systematic review of the literature data, have proposed a unified reaction scheme for the low-temperature and high-temperature decomposition of ammonium perchlorate [5, 21]. The fundamental and rate controlling step of decomposition is proton transfer, which results in adsorbed ammonia and perchloric acid on the surface of the ammonium perchlorate ($NH_4ClO_{4(s)} \rightarrow NH_{3(g)} + HOClO_{3(g)}$). It is generally believed that the key early step is rupture of the $HO–ClO_3$ bond ($HOClO_3 \rightarrow HO + ClO_3$) [8].

Several papers have drown attention to the importance of some intermediate, such as HNO and NO_2ClO_4 [7, 8]. Galwey and Mohamed [7] have proposed reaction mechanism in which NO_2ClO_4 is an essential intermediate in the thermal decomposition of ammonium perchlorate. The authors identified nitryl perchlorate as the reaction intermediate as it is unstable at the reaction temperature and its presence can be maintained by dynamic equilibrium through ammonia oxidation by the active oxygen species resulting from ClO_4^- breakdown. NH_3 and/or NH_4^+ reacts with the products of

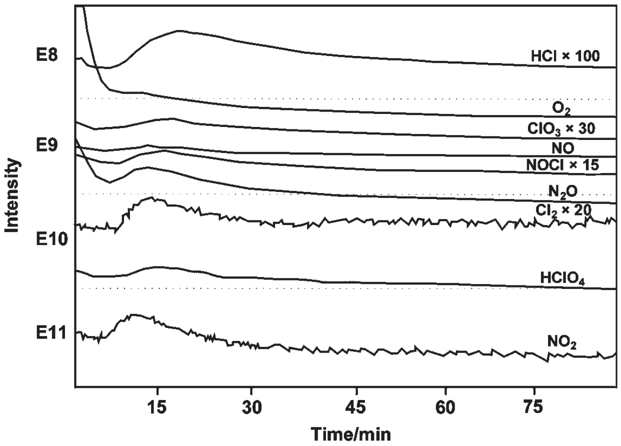

Fig. 2 Mass chromatogram of volatile products of ammonium perchlorate decomposition obtained isothermally at 250°C

ClO_4^- disintegration to yield NO_2^+ which combines with a reaction anion and, on decomposition, the cycle continues.

Among the final products that have been observed under various conditions, in evidently rather a complex decomposition process, are HCl, H_2O, N_2, O_2, NO, NO_2, N_2O, Cl, ClO and $HClO_3$ [8].

The results of analysis of volatile products of ammonium perchlorate decomposition, carried out in this work by isothermal thermogravimetry coupled with mass spectrometry techniques, are in good agreement with the above statement (Fig. 2).

It follows from the DSC curve given in Fig. 1, that at about 246°C ammonium perchlorate undergoes a transformation from the orthorhombic to the cubic phase. This has been found to have marked effect on the maximum rate of decomposition above and below this temperature. This transformation has been reported by Bircumshaw and Newman [3] to occur at 240°C, while Maycock and Pai Verneker [14], on the basis of conductance measurements have found out a corresponding transformation occurring at 255°C. They also stated that there are three regions into which the temperatures ranging from 200 to 440°C can be classified: 200–250, 270–340 and 380–440°C, each region being characterised by its own activation energy.

Results of our isothermal thermogravimetry measurements confirm that there is a break in the maximum decomposition rate with temperature. This break occurs at about 235°C (Fig. 3).

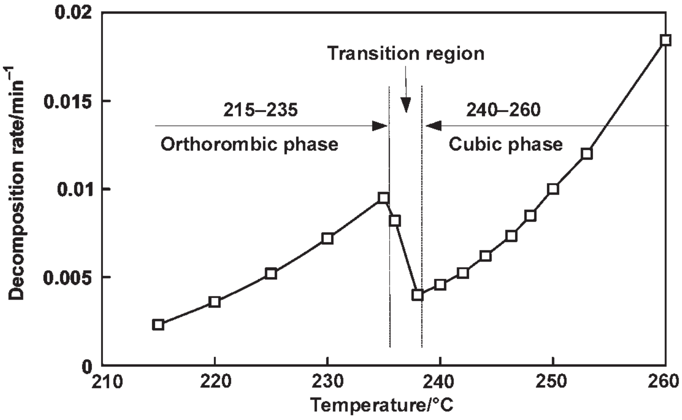

Fig. 3 Maximum decomposition rate of ammonium perchlorate *vs*. temperature

It is also found from isothermal measurements, that the maximum decomposition rate $[(dm/dt)_{max}]$ for temperatures below 235°C attains at about 14–15% decomposition, while for temperatures between 240 and 260°C, the maximum decomposition rate is attained at 9–10% decomposition of the sample (Fig. 5).

In accordance with the results presented in Fig. 1, the temperature range from 215 to 260°C is divided into two regions: the region between 215 and 235°C (corresponding to the orthorhombic phase), and the region between 240 and 260°C (corresponding to the cubic phase). The kinetic parameters for these two phases are evaluated (separately) in the paper.

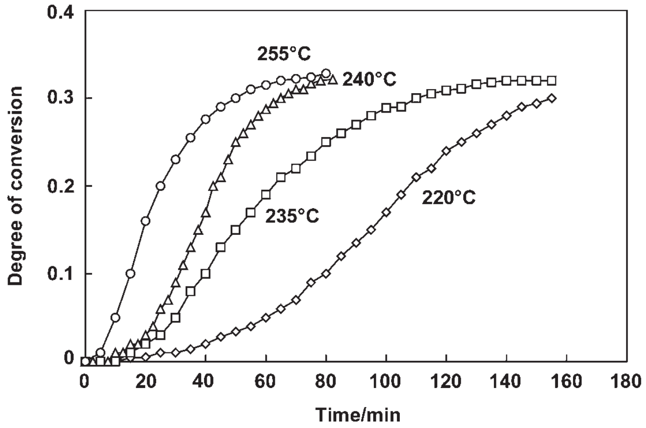

Fig. 4 Degree of conversion of ammonium perchlorate *vs*. time for several temperature durations between 215–260°C

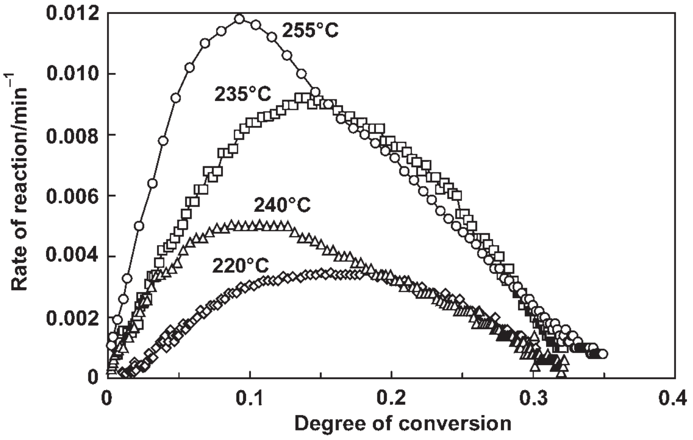

Fig. 5 Reaction rate *vs*. degree of conversion for several temperatures between 215–260°C

To obtain the information about the kinetic parameters and the associated mechanism of ammonium perchlorate decomposition, we have started from the relation $(d\alpha/dt)=f(\alpha)$, in accordance with the requirements given by the basic kinetic equation in differential form (Eq. (1)).

$$\frac{d\alpha}{dt}=k(T)f(\alpha) \tag{1}$$

where α is the degree of conversion, $(\mathrm{d}\alpha/\mathrm{d}t)$ is the reaction rate, $k(T)$ is a temperature dependent rate constant, and $f(\alpha)$ is a function representing the hypothetical model of the reaction mechanism.

The experimentally obtained thermogravimetric data are treated in the following way. The sample mass loss as a function of time is converted into the degree of conversion as a function of time (Fig. 4), according to the following equation:

$$\alpha=\frac{m_\mathrm{i}-m_\mathrm{t}}{m_\mathrm{i}-m_\mathrm{f}} \tag{2}$$

where m_i is the initial sample mass, m_f is the final sample mass, and m_t the sample mass at particular time.

The α-t data are then, by numerical differentiation, transformed into the $\mathrm{d}\alpha/\mathrm{d}t$–$\alpha$ data (Fig. 5), which are required for the further kinetic treatment in accordance with Eq. (1).

Two procedures are applied in the calculation of the degrees of conversion, and consequently in the evaluation of the kinetic parameters. The first procedure starts from the fact that the low-temperature decomposition of ammonium perchlorate stops at about 30%, i.e. it does not go to the completion. Accordingly, the degree of conversion and the conversion rate are calculated taking the final sample mass (m_f) to be the mass corresponding to the mass at the end of low-temperature decomposition. It is found, by the extrapolation of the $\mathrm{d}\alpha/\mathrm{d}t$–$\alpha$ curves obtained for the temperatures between 215 and 235°C, that reaction stops (i.e. reaction rate tends asymptotically to zero value) at 33.7% decomposition (mean value). This means that for 33.7% decomposition the corresponing degree of conversion equals to 1. The same value of the final sample mass is taken in the kinetic analysis for both ammonium perchlorate phases.

The following kinetic equations are used for the estimation of the probable reaction mechanism and for the evaluation of the kinetic parameters [22]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(1-\alpha)(-\ln(1-\alpha))^{(\mathrm{n}-1)/\mathrm{n}} \quad \text{(Avrami–Erofeev equation)} \tag{3}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k\alpha(1-\alpha) \quad \text{(Prout–Tompkins equation)} \tag{4}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k\alpha^\mathrm{n}(1-\alpha)^\mathrm{m} \tag{5}$$

By applying the nonlinear curve fitting procedure, it is found that Eq. (5) fits the best our kinetic data for a very broad range of degrees of conversions: 0.05–0.95 (i.e. 1.7–32% decomposition) for the orthorhombic phase, and 0.05–0.75 (1.7–25% decomposition) for the cubic phase (Fig. 6).

The activation energy and the pre-exponential factor are calculated from the rate constant–temperature dependence, in accordance with the Arrhenius equation (Fig. 7), for two temperature regions separately.

Table 1 Summary of kinetics the results of low-temperature decomposition of ammonium perchlorate obtained in this work, along with some results reported in literature

Authors	Experimental method	Material	Kinetic analysis equation	Phase	$\log A$/ min^{-1}	E/kJ mol^{-1}	Ref.
Bircumshaw and Newman	pressure increase (in vacuum)	2R, powder	$\mathrm{lm}[\alpha/(1-\alpha)]=$ $kt+c$	O C		116.4 79.1	[4]
Galwey and Jacobs	pressure increase (in vacuum)	2R, powder	$-\ln(1-\alpha)=kt^n$	O C		102.9 103.8	[6]
		2R, crystal	(n=4 for O, and n=2 for C phase)	O C		86.2 105.9	
Manelis and Rubtsov	mass loss	2R, powder	$d\alpha/dt=k_1(1-\alpha)^n$ $+k_2\alpha(1-\alpha)^n$	O,C O C	7.75 10.10 4.50	125.6 125.6 76.2	cited in [9]
Gross and Amster	adiabatic			O,C		172.5	cited in [5]
Shidlovskii *et al.*	mass loss	1R, powder	$-\ln(1-\alpha)=(kt)^n$ (n=4.5)	O C		167.9 105.1	cited in [5]
Raevskii and Manelis	direct measurement under microscope	2R, crystal	linear growth	$O^{(L)}$ $O^{(T)}$ C		138.3 129.8 71.2	cited in [5]
Jacobs *et al.* (reanalysed data)	mass loss, pressure increase	pellets	$-\ln(1-\alpha)=(kt)^n$ (n=2)	O C O,C	13.00 9.89 9.78	141.9 112.9 111.5	

Table 1 Continued

Authors	Experimental method	Material	Kinetic analysis equation	Phase	log$A$/ min^{-1}	E/kJ mol^{-1}	Ref.
This work	mass loss (TG), α calculated taking $m_f=m$ at 33.3% conversion	powder	$d\alpha/dt=k\alpha^n(1-\alpha)^m$ (O phase: $0.05<\alpha<0.95$, $n=1$, $m=1.38$; C phase: $0.05<\alpha<0.75$, $n=0.75$, $m=1.56$)	O C	14.2 14.2	146.1 151.6	
	mass loss (TG)	powder	$d\alpha/dt=k\alpha^n(1-\alpha)^m$ (O phase: $0.05<\alpha<0.75$, $n=1.3$, $m=7.9$; C phase: $0.05<\alpha<0.75$, $n=1.02$, $m=9.35$)	O C	14.7 14.7	146.5 152.7	
	(α calculated taking $m_f=0$)		$d\alpha/dt=k\alpha^m(1-\alpha)^n(-\ln(1-\alpha))^p$ (O phase: $0.05<\alpha<0.75$, $m=0.38$, $n=8.98$, $p = 1.00$; C phase: $0.05<\alpha<0.75$, $m=0.23$, $n=9.60$, $p=0.77$)	O C	14.7 14.9	146.2 155.5	

Abbreviations used: O – orthorhombic phase, C – cubic phase, ^{L} – longitudinal, ^{T} – transverse

The results of calculations, along with some results taken from literature, are summarised in Table 1. It can be seen that our calculations give the same value for the pre-exponential factor for both phases ($1.59\cdot10^{14}$ min^{-1}), while the activation energy is slightly greater for the cubic phase than for the orthorhombic one (151.6 and 146.1 kJ mol^{-1} for orthorhombic and cubic phase respectively).

According to the second procedure, the degree of conversion is calculated taking that the final sample mass is equal to zero (m_f=0), as shown in Fig. 4. The kinetic parameters are evaluated applying Eq. (5), and the Šesták–Berggren equation (Eq. (6)) [21, 22]:

$$\frac{d\alpha}{dt}=k\alpha^{m}(1-\alpha)^{n}(-\ln(1-\alpha))^{p} \tag{6}$$

for which it was found to fit satisfactorily our kinetic data in the range between 1 and 25% decomposition for both phases. The results of the calculation are also summarised in Table 1.

The results presented in the paper have shown that Eq. (5) fits the best our kinetic data in a broad range of the degrees of conversion (0.05–0.95 for the orthorhombic phase, and 0.05–0.75 for the cubic phase). The Avrami–Erofeev (Eq. (3)), and Prout–Tompkins equations (Eq. (4)) cannot satisfactorily describe nonsymmetric ($d\alpha/dt$–α) curves, although in the literature they are most frequently reported to fit well the kinetic data. The generalised Šesták–Berggren equation (Eq.6) fits also very well ($d\alpha/dt$–α) data. However, it cannot give the direct answer in the search for a true reaction mechanism.

From the above statements it follows that the decomposition of ammonium perchlorate in both phases can be described by Eq. (5), i.e. by the nucleation followed by the linear growth of nuclei reaction model. The Eq. (5) describes later stages of two specific mechanisms: (a) the chain growth of nuclei including the possibility of their branching, and (b) the branching nuclei interacting during their growth [22].

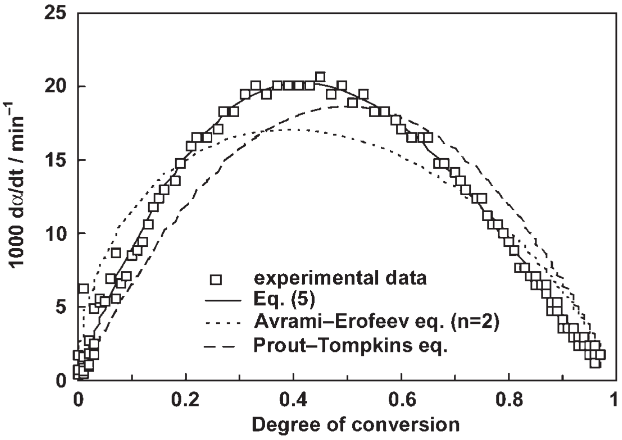

Fig. 6 Test of the applicability of Eqs (3), (4) and (5) to the low-temperature decomposition of ammonium perchlorate

The microscopic study of ammonium perchlorate decomposition performed by Raevskii and Manelis [23] confirmed such reaction model – the formation and linear growth of nuclei in small single crystals of ammonium perchlorate.

The calculated mean value of the pre-exponential factor is almost equal for both phases ($3.43\cdot10^{14}$ min^{-1} and $4.11\cdot10^{14}$ min^{-1} for orthorhombic and for cubic phase respectively), while the mean value of the activation energy is slightly greater for the cubic phase (153.3 kJ mol^{-1}) than that for the orthorhombic one (146.3 kJ mol^{-1}). Galwey and Jacobs [6] have also reported that the activation energy for ammonium perchlorate samples being in crystal and powder form is greater for the cubic than for the orthorhombic one, while for samples being in the pellet form, the activation energy is almost the same for both phases (Table 1). Contrary to this, a number of authors have found that the activation energy is greater for the orthorhombic than for cubic phase. An extensive analysis of the literature data shows that the values of activation energy for both phases differ considerably: for the cubic phase the values are varied between 71 to 126 kJ mol^{-1}, whereas for the orthorhombic phase the values are between 83 and 172 kJ mol^{-1} [5]. Some authors have reported an overall activation energy to be the same for both phases [5].

The evaluation of the activation energy on the basis of isothermal measurements may be accompanied by some experimental difficulties, especially at higher temperatures. Our isothermal therogravimetry measurements have shown that it is hardly to 'catch' the induction and complete accelerating stages of decomposition at temperatures above 260°C. The reason for this lies in the fact that at higher temperatures the induction period is too short, and the decomposition proceeds so rapidly, where a considerable part of the sample decomposes already during its introduction into the apparatus – sample holder. This makes the kinetic treatment of the obtained data more complex, and accordingly the obtained values of kinetic parameters to be less reliable. Due to these reasons, we have limited our experiments up to 260°C.

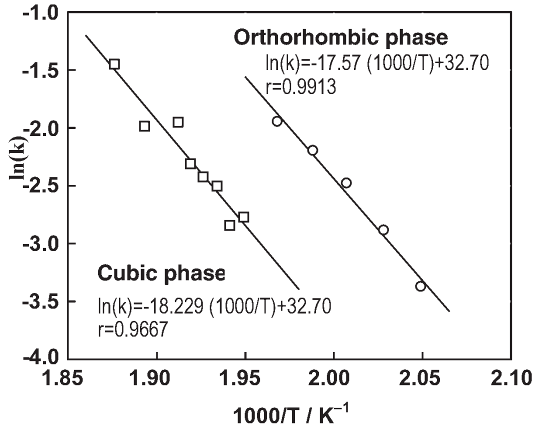

Fig. 7 Arrhenius plots for the decomposition of ammonium perchlorate using rate constant derived from Eq. (5)

Conclusions

The phase transition of ammonium perchlorate from the orthorhombic to cubic form, which takes place in the range of 235–240°C, has a marked effect on the maximum decomposition rate (Fig. 1). Thermal decomposition for both phases can be well described by the following kinetic equation:

$$\frac{d\alpha}{dt}=k\alpha^{n}(1-\alpha)^{m}$$

(where $n\leq 1$, and $m>1$) which describe process controlled by nucleation followed by the linear growth of nuclei.

The activation energy of 153.3 kJ mol^{-1}, and pre-exponential factor of $3.43\cdot 10^{14}$ min^{-1} are obtained for the cubic phase, whereas the activation energy of 146.3 kJ mol^{-1}, and pre-exponential factor of $4.11\cdot 10^{14}$ min^{-1} are calculated for the orthorhombic phase. The obtained value of the activation energy for the orthorhombic phase is very close to the reanalysed Jacobs and Whitehead [5] values of 142 kJ mol^{-1}, whereas the value obtained for the cubic phase of 153.3 kJ mol^{-1} is greater than the values reported in literature (71–126 kJ mol^{-1}).

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