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Thermal decomposition of 2,4,6-trinitrotoluene during the induction period

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Abstract

The influence of the thermal decomposition products on the solid–liquid equilibrium of 2,4,6-trinitrotoluene was investigated. The cryometric method was used to determine the thermal decomposition products and the kinetic parameters during the induction period. The oscillation changes of the thermal decomposition rate have been observed.

Keywords: Kinetic parameter; Solid–liquid equilibria; Thermal decomposition

1. Introduction

The thermal decomposition of 2,4,6-trinitrotoluene (TNT) has been the subject of recurring interest for over 70 years. Studies have been carried out in different ways to determine the thermal decomposition kinetic models and to separate the decomposition products. Dacon et al. [1] indicate that the thermal decomposition product mixtures contain at least 25 discrete species as well as large amounts of telomeric or polymeric materials. According to Rogers' results [2], the following products appear in the mixtures: 2,4,6-trinitrobenzyl alcohol, 4,6-dinitroanthranil, 1,3,5-trinitrobenzene, 2,4,6-trinitrobenzoic acid and traces of unidentified compounds. The thermal decomposition activation energy varies from 58.6 to 192.5 kJ mol^{-1} [3–10] demonstrating that the process is far from well understood.

The thermal decomposition of TNT is controlled by a homolytic, covalent C–H bond cleavage to its methyl moiety. An intermolecular transfer of a hydrogen atom to the ortho-nitro group, followed by the elimination of H_2O, would provide the isolated

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4,6-dinitroanthranil product. An intermolecular hydrogen atom transfer from one TNT molecule provides a 2,4,6-trinitrobenzyl radical and a protonated TNT radical where the para-nitro group picks up the hydrogen atom [11].

The thermal decomposition as an autocatalytic reaction can be described by Eqs. (1) and (2)

$$A \rightarrow B \quad k_1 \tag{1}$$

$$A + B \rightarrow 2B \quad k_2 \tag{2}$$

where A represents the initial reactant and B represents the thermal decomposition products. The rate expression that corresponds to this scheme is

$$\frac{\mathrm{d}(\alpha)}{\mathrm{d}t} = k_1(1-\alpha) + k_2\alpha(1-\alpha) \tag{3}$$

where α is the degree of conversion. Dividing through by $(1-\alpha)$ gives

$$\frac{-\mathrm{d}\ln(1-\alpha)}{\mathrm{d}t} = k_1 + k_2\alpha \tag{4}$$

The experimental results concerning the thermal decomposition of tetryl [12] show that the concentration of catalyst achieves some stationary state

$$\alpha_{\mathrm{cat}} \approx \text{const.} \tag{5}$$

Substituting Eq. (5) into Eq. (4) gives

$$\frac{-\mathrm{d}\ln(1-\alpha)}{\mathrm{d}t} = k_1 + k_2\alpha_{\mathrm{cat}} = k \tag{6}$$

for $\alpha << 1$, the last equation can be written as

$$\frac{-\mathrm{d}\ln(1-\alpha)}{\mathrm{d}t} = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = \bar{V} = k_1 + k_2\alpha_{\mathrm{cat}} = k \tag{7}$$

Eqs. (4)–(6) explain why a catalytic thermal decomposition reaction can be described by a first-order reaction. In this paper we will demonstrate the utility of the cryometric method in obtaining kinetic parameters for the thermal decomposition of 2,4,6-trinitrotoluene. It is anticipated that the cryometric method will lead to a better understanding of the kinetics and mechanisms for the decomposition reactions of energetic materials.

2. Experimental

2.1. Samples

TNT was synthesised and purified in the Department of Analytical Chemistry of the Institute of Organic Industrial Chemistry (Warsaw). The purity of the TNT used as determined by the cryometric method was 99.6 mol%.

2.2. *Apparatus*

A 605M UNIPAN differential scanning calorimeter was used. Samples of about 20 mg of tetryl were sealed in aluminium cells under reduced pressure. The calibration procedure was described in our previous paper [12].

2.3. *Procedure*

TNT samples were closed in hermetic pans under a reduced pressure of about 1.3 kPa. The thermal decomposition products were produced during linear heating rate (β) from the melting temperature (T_m) to the arbitrarily chosen final temperature (T_f), or during isothermal pyrolysis. In the case of the isothermal process, production of the decomposition products formed from T_m to the chosen temperature T_f was determined in separate measurements. The melting temperature of pure TNT determined for high-purity TNT (T_m^0) was taken for the purity determination of thermally aged samples. The start of melting of the investigated sample was taken as the beginning of the thermal decomposition. The thermal decomposition reactions were stopped by rapid temperature decrease by placing samples on the surface of ice. The change in TNT during thermal decomposition is frequently expressed by the degree of conversion (α) which depends on the change in purity (P mol%)

$$\alpha_t = (P_0 - P_t)/100 = \Sigma x_i \tag{8}$$

Table 1
Mole fraction of thermal decomposition products, mean degree of conversion and thermal decomposition rate of TNT for the consecutive scan; $T_f = 514.8$ K, $\beta = 10$ K min^{-1}

No. scan	$\Sigma x_i \times 10^2$	$\bar{x} \times 10^2$	$\bar{V} \times 10^6/\mathrm{s}^{-1}$
1	0.43	0.21	4.41
2	0.31	0.59	3.18
3	0.23	0.85	2.36
4	0.45	1.19	4.62
5	0.36	1.60	3.69
6	0.14	1.85	1.44
7	0.53	2.22	5.44
8	0.23	2.60	2.36
9	0.27	2.85	2.77
10	0.56	3.26	5.75
11	0.11	3.60	1.13
12	0.11	3.70	1.13
13	0.52	4.02	5.34
14	0.31	4.43	3.18
15	0.24	4.71	2.46
16	0.49	5.07	5.03
17	0.35	5.50	3.59
18	0.37	5.86	3.80

where P_0 and P_t are the purities of TNT at the initial time ($t = 0$) and the final time (t), respectively and Σx_i is the total mole fraction of the thermal decomposition products in the liquid phase.

3. Results and discussion

Thermal decomposition reactions in energetic materials proceed at every temperature but only at higher temperatures is the rate of this process measurable. The range of temperatures was chosen to obtain a measurable amount of thermal decomposition products determined by the cryometric method (Σx_i). The upper limit of the total mole fractions was assumed to be lower than 0.06. Decomposition products were formed using isothermal or non-isothermal decomposition processes. Mole fractions of TNT thermal decomposition products for non-isothermal decomposition processes depend on the final temperature (T_f) and heating rate (β). For the same sample, this process was performed several times with the same final temperature and heating rate. The number

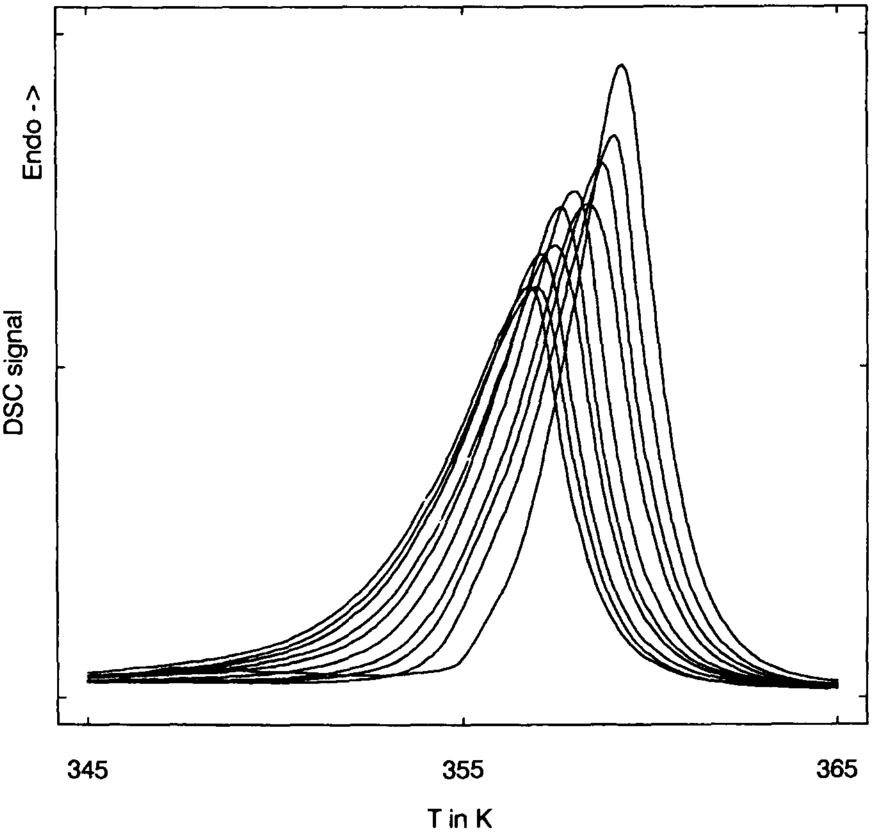

Fig. 1. Comparison of the consecutive DSC curves for TNT melting ($\beta = 2$ K min^{-1}) performed with the same sample heated to the final temperature $T_f = 520$ K with a heating rate of $\beta = 10$ K min^{-1}.

of decomposition processes performed with the same sample is collected in the first column of Table 1. The amount of impurities increases during the thermal decomposition process. Fig. 1 shows consecutive melting in DSC traces at heating rate $\beta = 2$ K min^{-1} performed on the same sample heated to a final temperature $T_f = 520$ K with a heating rate $\beta = 10$ K min^{-1}. The melting curves for consecutive melting processes are shifted in the direction of lower temperatures. The formation of thermal decomposition products (Σx_i) and the average degree of conversion ($\bar{\alpha}$) were calculated using Eq. (8) and

$$\bar{\alpha} = \sum_{j-1} \sum_{i} x_i^{j-1} + \sum x_i^j/2 \tag{9}$$

where j is the number of decomposition processes performed with the same sample. The mean decomposition rates, calculated according to the relation

$$\bar{V}_j = \frac{\Delta\bar{\alpha}}{\Delta t} = \beta \frac{\Sigma x_i^j}{T_f - T_m} \tag{10}$$

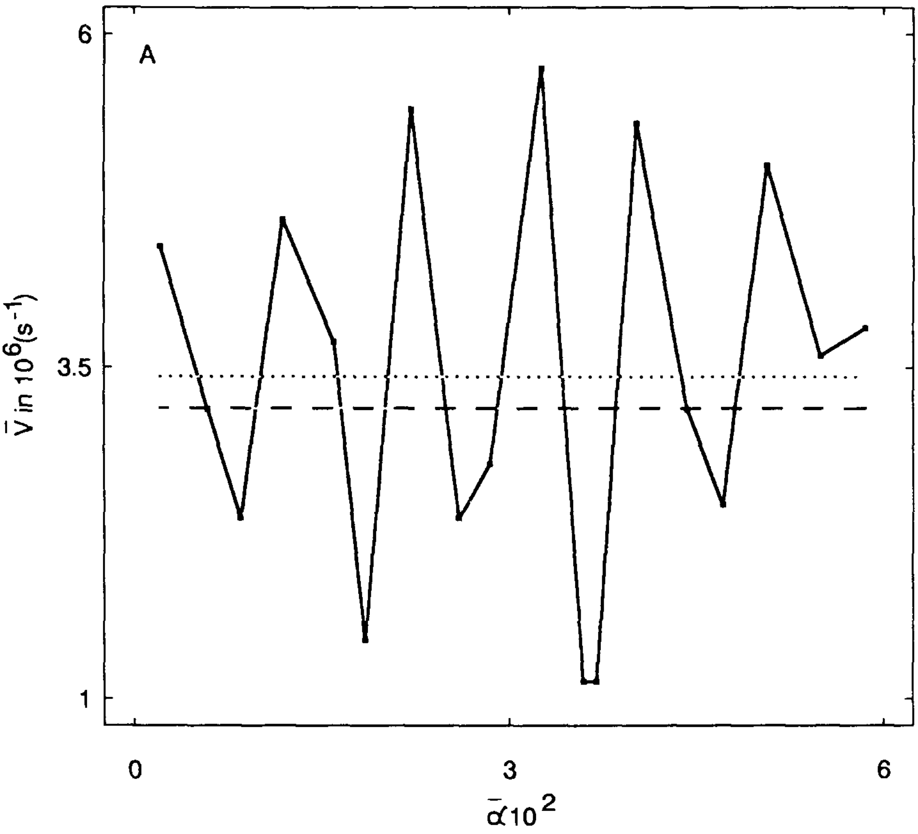

Fig. 2. TNT decomposition rate determined from consecutive measurements using the same sample for the final temperature $T_f = 514.8$ K and heating rate $\beta = 10$ K min^{-1}: A, as a function of degree of conversion; B, for consecutive runs.

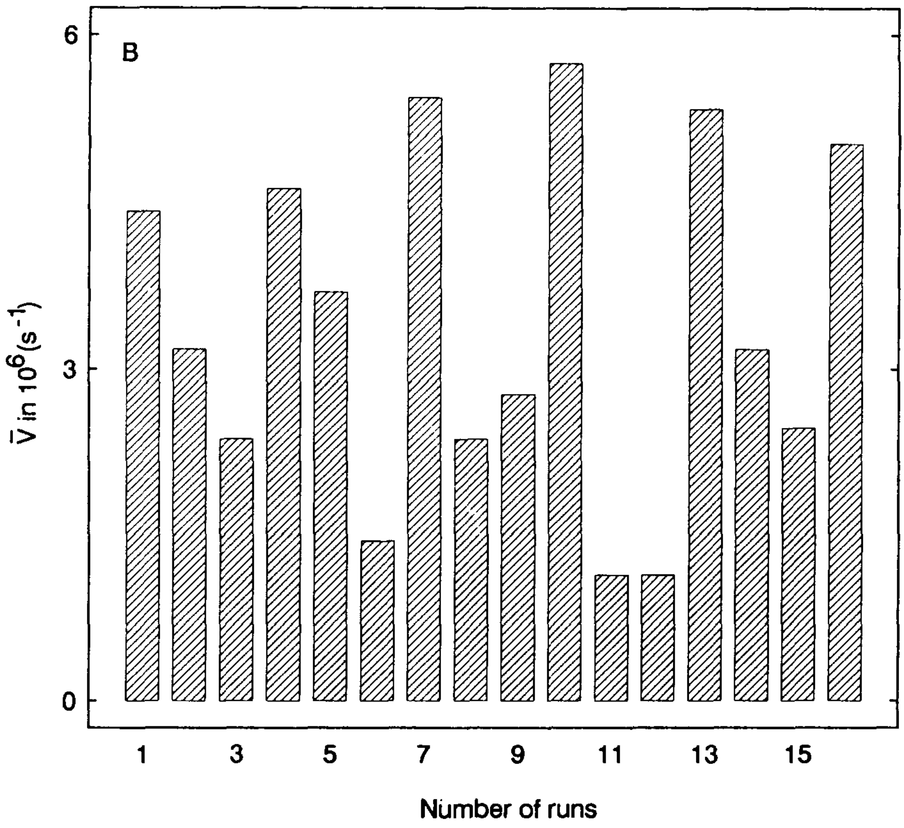

Fig. 2. (*Continued*)

are listed in the last column of Table 1. It is assumed that the TNT decomposition begins at the TNT melting temperature $T_m = 353.5$ K. The mean decomposition rate is equal to the mean decomposition constant (k) for the first-order reaction and $\bar{\alpha} << 1$.

Fig. 2A shows the relation between the mean decomposition rate ($\bar{V}$) and the mean degree of conversion during several thermal decomposition processes performed with the same sample. The dotted line represents the mean decomposition rates for all decomposition processes. This relation proves that the concentration of catalyst achieves some stationary state in an oscillatory manner. Changes in the mean decomposition rate ($\bar{V}$) for consecutive melting processes are collected in Fig. 2B. The number of experimental data points having a decomposition rate lower than the calculated mean value (dotted line) is about twice the number of experimental points above the mean value. This result shows that the investigated system reaches the lower state of the decomposition rate more easily than the higher state.

Table 2 collects results similar to those in Table 1 but these were obtained for the isothermal decomposition process at the chosen temperature. The temperature transition of the investigated system from a temperature below the TNT melting temperature

Table 2
Mean degree of conversion and TNT thermal decomposition rate constant for consecutive isothermal decompositions performed for the same sample

$\bar{\alpha} \times 10^2$	$\bar{k} \times 10^5/\mathrm{s}^{-1}$
$T = 499.0$ K; $t = 20$ min	
0.54	1.09
1.88	1.32
3.52	1.24
5.09	1.13
$T = 500.0$ K, $t = 3.5$ min	
0.35	1.04
1.17	1.58
2.40	2.70
3.05	0.89
3.65	2.19
4.35	1.85

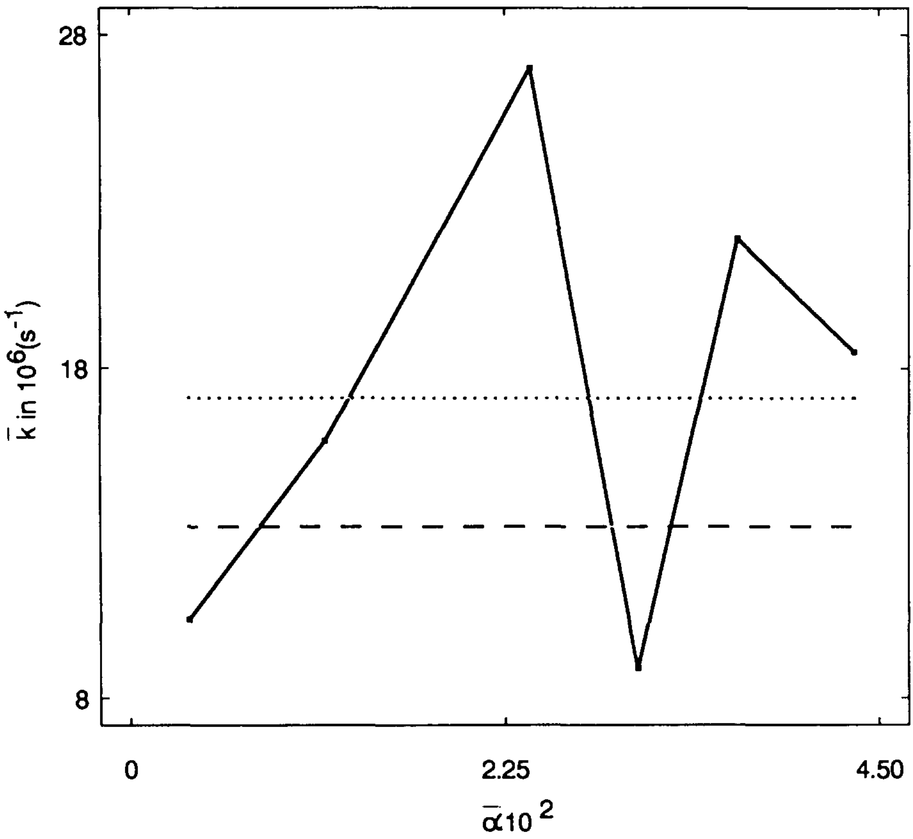

Fig. 3. TNT thermal decomposition rate constant for consecutive measurements using the same sample at $T = 500.0$ K for 3.5 min.

to the chosen temperature was made using a heating rate $\beta = 10$ K min^{-1}. The concentration of thermal decomposition products for this heating run was determined in a separate experiment and was used for calculation of the concentration of the thermal products obtained during the isothermal process. Two different isothermal periods were used (3.5 and 20 min). Consecutive isothermal processes performed with the same sample are collected in the first column of Table 2. The mean degree of conversion ($\bar{\alpha}$) and the decomposition rate constant were calculated for the simple isothermal process.

Fig. 3 shows the relation between k and $\bar{\alpha}$ for a short period of the isothermal decomposition process (3.5 min). Fig. 4 shows the same relationship for a longer isothermal decomposition period (20 min). In this case the changes (oscillations) in the decomposition rate constants are smaller than for the short period.

The thermal decomposition rate constants using long-period isothermal decomposition processes for different temperatures are listed in Table 3. Fig. 5 shows the

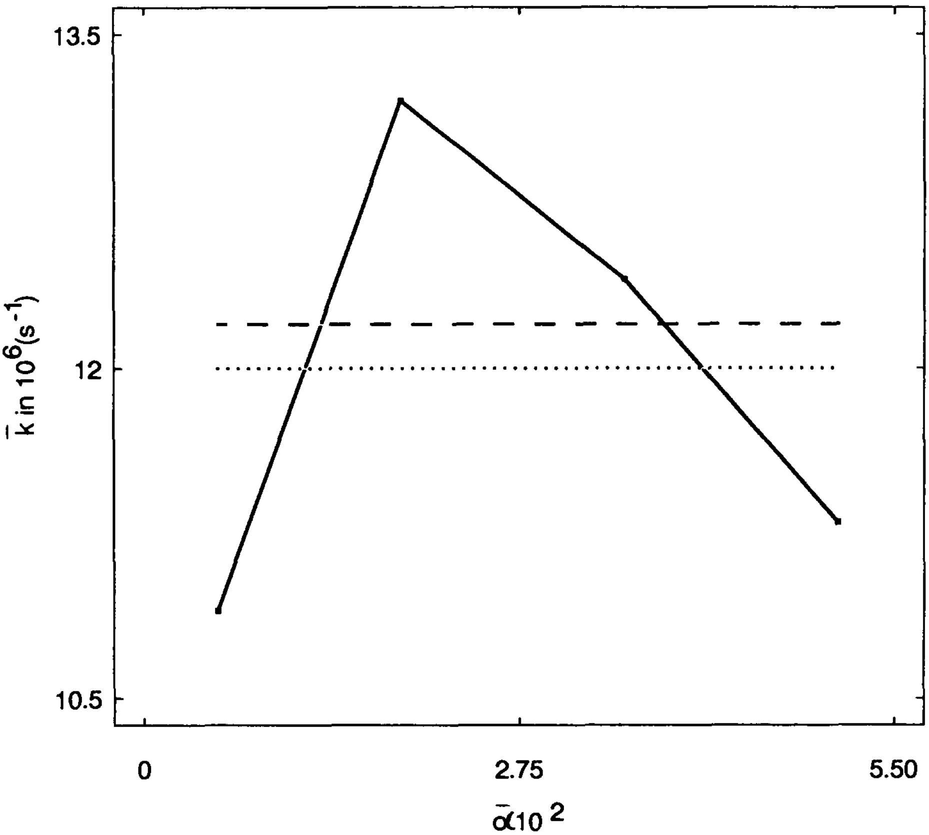

Fig. 4. TNT thermal decomposition rate constant for consecutive measurements using the same sample at $T = 499.0$ K for 20 min.

Table 3
TNT thermal decomposition rate constant

T/K	$\bar{k} \times 10^5/\mathrm{s}^{-1}$
479.0	0.315
489.0	0.538
499.0	1.00
499.0	1.09
508.6	2.37
518.8	5.65
528.2	10.8

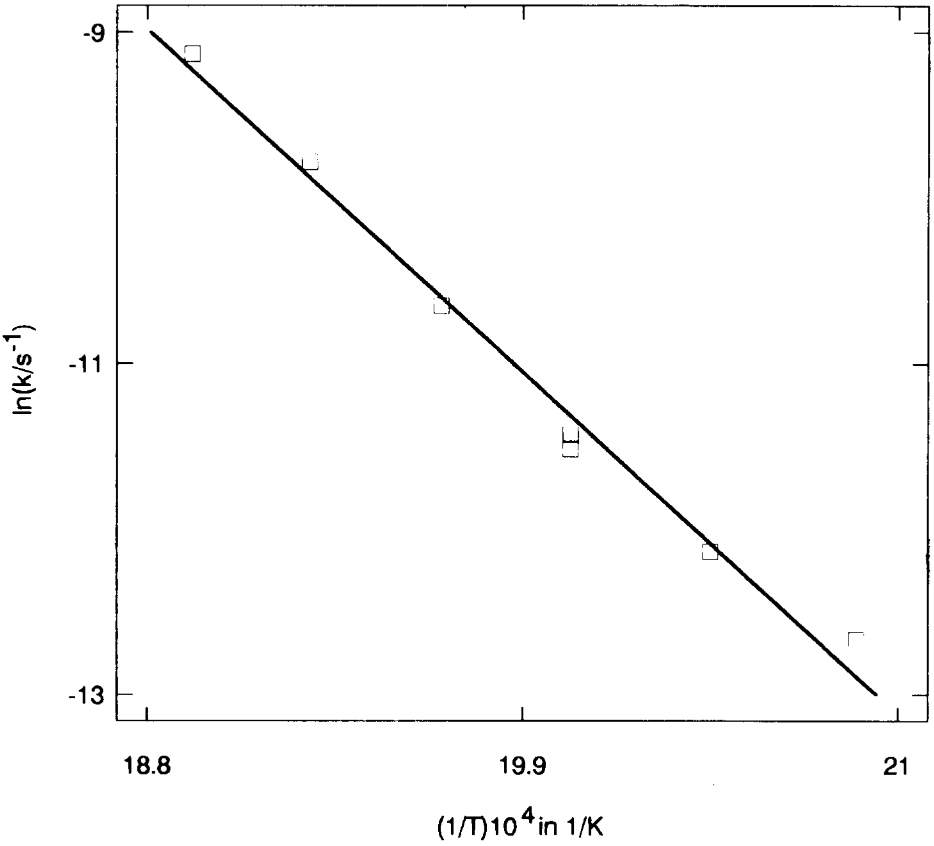

Fig. 5. Arrhenius plot for TNT isothermal decomposition.

Arrhenius plot for these results. The estimated kinetic parameters are: activation energy, $E_a = 156.41$ kJ mol^{-1} and preexponential factor, $A = 11.46$ s^{-1}. These kinetic parameters were used to predict the rate constant (k) for the temperatures 499.0 and 500.0 K and are presented by the dashed lines in Figs. 3 and 4. The mean thermal decomposition rate ($\bar{V}$) was estimated using the kinetic parameters

$$\bar{V} = \left[1 - \exp\left[\frac{A}{\beta}\int_{T_m}^{T_f}\left(\exp\left(\frac{-E_a}{RT}\right)\right)\mathrm{d}T\right]\right]\frac{\beta}{T_f - T_m} \tag{11}$$

The predicted mean decomposition rate ($\bar{V}$) is consistent with the experimental value, as shown in Fig. 2A. The agreements prove that the observed oscillations in the rate constant are due to the oscillation of catalyst concentration around some stationary state. If molecules of a volatile catalyst are created by a reaction in homogeneous solution, the release of gas may take place in repetitive pulses rather than continuously [13,14]. The physical processes of bubble nucleation, growth and escape can explain the oscillation of the catalyst concentration. The processes are strongly dependent on the sample size and the amount of free volume of the confining containers. The parameters mentioned above determine the pressure over the liquid–gas surface.

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