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Thermochimica Acta 284 (1996) 299–308

thermochimica
acta

Kinetic data of low-temperature thermal decomposition of *N*,2,4,6-tetranitro-*N*-methylaniline

A. Książczak *, T. Książczak

Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

Received 11 January 1995; accepted 7 May 1995

Abstract

Differential scanning calorimetry has been used to determine kinetic parameters for the thermal decomposition of *N*,2,4,6-tetranitro-*N*-methylaniline (tetryl) in the decay phases. The mean value of the thermal decomposition enthalpy is $\Delta H_D = -404 \text{ kJ mol}^{-1}$. The influences of several factors on the kinetic parameters and compensation effects are presented. The kinetic parameters are used to predict critical temperature and mole fraction of the thermal decomposition products during the induction phase.

Keywords: Compensation effect; Critical temperature; DSC; Kinetic data; Thermal decomposition

1. Introduction

The properties of high energy materials are determined by the kinetic parameters of the thermal decomposition process. The Arrhenius equation is widely accepted in reaction kinetics as a useful tool for predicting a change in reaction rate constant as a function of temperature:

$$k = A \exp(-E_a/RT) \quad (1)$$

where k is the reaction rate constant, A is the pre-exponential (frequency) factor, E_a is the activation energy, R is the gas constant and T is the absolute reaction temperature. The overall decomposition of explosives is quite a very complex process involving

* Corresponding author.

numerous sequential and parallel chemical reactions. Frequently the thermal decomposition of explosives is best described by assuming a pseudo first order reaction [1–4]:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n; \quad n = 1 \quad (2)$$

where α is the degree of conversion, t is the time, n is the reaction order. The kinetic parameters can be used to predict the lowest temperature (T_C) at which any specific size and shape of explosive can self heat to explosion, as follows [5]:

$$\frac{E_a}{T_C} = R \ln \left[\frac{a^2 d Q A E_a}{T^2 \lambda \delta R} \right] \quad (3)$$

where a is the radius of a sphere or cylinder or the half-thickness of a slab, d is the density, Q is the heat of reaction during the self-heating process, A is the pre-exponential factor, E_a is the activation energy from the Arrhenius expression, λ is the thermal conductivity and δ is the shape factor (0.88 for infinite slabs, 2.00 for infinite cylinders and 3.32 for spheres).

The second important application of the kinetic parameters is to predict the concentration of the thermal decomposition products Σx_i during the thermal degradation or storage process. Good agreement between measured and predicted T_C and Σx_i values confirms the correctness of the assumed decomposition model and estimated kinetic parameters. The values obtained for these parameters using different methods such as gas evolution [1, 6], calorimetry [2, 7], manometry [8, 9], high temperature infrared spectroscopy [3] and thermogravimetry [3, 4] are in poor agreement. The main reason for the variation in the values obtained for the kinetic parameters of the same explosive are the different conditions used for thermal decomposition in the different devices used. For example, the influence of gaseous decomposition products on the decomposition of an explosive depends on the pressure in the device or the ratio of the mass of explosive to the device volume. The purity of the materials used also has an influence on the mechanism of thermal decomposition determined by cryometric method [10, 11].

The aim of this work is to determine the kinetic parameters of the thermal decomposition of *N*-2,4,6-tetranitro-*N*-methylaniline (tetryl) as a model of a high energy material prepared with different purities and to predict the critical temperature and the concentration of the decomposition products. DSC was used for investigation of the exothermic low-temperature thermal decomposition.

2. Experimental

2.1. Apparatus

DSC 605M UNIPAN was used. Samples (about 1 mg) of tetryl were sealed in an aluminium cell under a reduced pressure of about 1.3 kPa. The calibration procedure was described in our previous paper [11].

2.2. Samples

The tetryl was prepared and purified in the Department of Analytical Chemistry of the Institute of Organic Industrial Chemistry (Warsaw). Purity was determined by the cryometric method and was 99.8 mol%. This sample was purified by additional crystallisation until the purity obtained was 99.9 mol%. Samples containing 3.7 and 7 mol% of thermal decomposition products were taken to study the kinetic parameters.

3. Results and discussion

Tetryl is unstable at its melting temperature [10]. A typical DSC curve with the heating rate $\beta = 10 \text{ K min}^{-1}$ is presented in Fig. 1. The first endothermic peak is due to the melting process and the second exothermic peak relates to the low-temperature thermal decomposition. The complex baseline after the second peak is due to further thermal pyrolysis of thermal decomposition products. The complex baseline complicates calculation of the degree of conversion of tetryl (α) and estimation of the heat of decomposition. It was assumed that the thermal decomposition proceeds according to Eq. (2). The kinetic parameters were determined on the basis of a single DSC curve, using the method developed by Borchardt and Daniels [12]. The region analysed was that in which the degree of conversion, α , varied from 0.1 to 0.8. The range of $\Delta\alpha$ for which the parameter $n = 1$ was used for the prediction of the kinetic parameters. The maximum limit of the degree of conversion was always the same value ($\alpha = 0.8$). The minimum limit of the degree of conversion was changed. This range of $\Delta\alpha$, and also the range of temperatures for which $n = 1$, decreases when the heating rate (β) decreases.

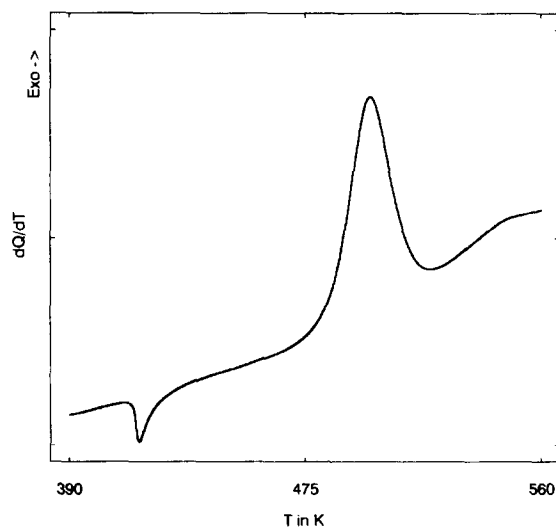


Fig. 1. DSC curve for thermal decomposition of tetryl.

Table 1
Tetryl thermal decomposition enthalpy and kinetic parameters for different masses with a heating rate of $\beta = 10 \text{ K min}^{-1}$

Mass/mg	$-\Delta H_D/\text{kJ mol}^{-1}$	$\log(A/\text{s}^{-1})$	$E_a/\text{kJ mol}^{-1}$
0.37	421	6.14	75.23
		6.97	83.09
		8.07	93.19
		5.97	73.71
0.49	428	18.69	194.05
		14.64	155.64
0.71	401	13.97	149.12
		16.46	172.66
0.76	381	9.55	106.58
		11.67	126.40
		9.52	106.36
0.95	399	10.31	114.76
		13.75	147.26
1.04 ^a	398	7.47	87.8
		9.53	107.2
		10.56	116.83

^a Sample contained 7 mol% thermal decomposition products.

The uncertainty of the estimated kinetic parameters (A and E_a) is higher when the range of temperatures used decreases [13]. The results of calculations for tetryl of purity 99.8 mol% at the heating rate $\beta = 10 \text{ K min}^{-1}$ for different sample masses are summarised in Table 1. The mean value of the thermal decomposition enthalpy is $\Delta H_D = -404 \text{ kJ mol}^{-1}$ and is consistent with the value obtained by Hall [14], $\Delta H_D = -393.0 \text{ kJ mol}^{-1}$. The kinetic parameters A and E_a are collected in columns 3 and 4, respectively. For analysis different ranges of the baseline both before and after the peak for the same sample were taken. These parameters ($\log A$ and E_a) show a linear relationship:

$$\log A = 0.10564(\pm 0.0003)E_a - 1.78064(\pm 0.04) \quad (4)$$

with a correlation coefficient (r) of 0.9994. The numbers in the brackets represent the standard error for these parameters.

The linear relationship may be obtained from the Arrhenius equation and is expressed as:

$$\ln A = \ln k_{\text{iso}} + E_a/RT_{\text{iso}} \quad (5)$$

where k_{iso} is the isokinetic rate constant and T_{iso} is the isokinetic temperature. The isokinetic temperature estimated from Eqs. (4) and (5) is $T_i = 494.4 \text{ K}$.

The results of the calculation for tetryl of purity 99.8 and 99.9 mol% for different heating rates β are presented in Table 2. Eq. (6) represents the results from linear

Table 2
Kinetic parameters for tetryl decomposition at different heating rates

$\beta/\text{K min}^{-1}$	$\log(A/\text{s}^{-1})$	$E_a/\text{kJ mol}^{-1}$
<i>Tetryl 99.8 mol%</i>		
20	10.40	118.99
10	11.34	124.90
7	15.99	167.79
5	11.20	121.54
2	20.41	203.69
<i>Tetryl 99.9 mol%</i>		
20	11.78	132.83
15	11.96	132.80
10	13.61	146.59
7	18.28	188.80
5	17.16	177.21
2	21.06	209.76
1	15.05	154.72

squares analysis between $\log A$ and E_a for tetryl with a purity of 99.8 mol%:

$$\log A = 0.11424(\pm 0.0036)E_a - 3.0(\pm 0.5) \quad (6)$$

with a correlation coefficient (r) of 0.9987. The estimated isokinetic temperature is $T_i = 457.1$ K. The correlation between $\log A$ and E_a for tetryl with a purity of 99.9 mol% is:

$$\log A = 0.1168(\pm 0.004)E_a - 3.5(\pm 0.6) \quad (7)$$

with a correlation coefficient (r) of 0.997. The isokinetic temperature is $T_i = 447.1$ K. The parameters in Eqs. (6) and (7) for tetryl with a small change of purity are the same within the scope of the standard error of the estimated parameters. The maximum temperature of the peak for $\beta = 5 \text{ K min}^{-1}$ is 477.2 K for tetryl with 3.7% thermal decomposition products. The same temperatures for tetryl of 99.8 and 99.9 mol% purity are 477.0 and 476.9 K, respectively. The maximum temperature is not sensitive to the purity of the tetryl used. Relationships (6) and (7) are presented in Figs. 2 and 3, respectively. The numbers near the experimental points are the heating rates used in the DSC measurements. The sequence of the heating rates on the estimated line indicates that there is not a simple relationship between E_a and β .

Table 3 summarises the kinetic parameters taken from the literature for the evaluation of the pseudo first order reaction. Fitting the data according to Eq. (5) results in the following expression:

$$\log A = 0.131082(\pm 0.0004)E_a - 5.58611(\pm 0.8) \quad (8)$$

with a correlation coefficient (r) of 0.995. The estimated isokinetic temperature is $T_i = 398.4$ K. Relationship (8) has the lowest correlation coefficient because of the

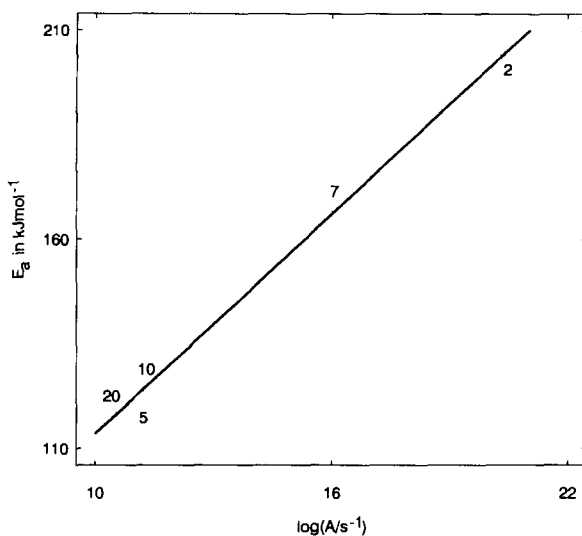


Fig. 2. Plot of $\log A$ versus E_a for tetryl with a purity of 99.8 mol% for different heating rates (the number near a point indicates heating rate in K min^{-1}).

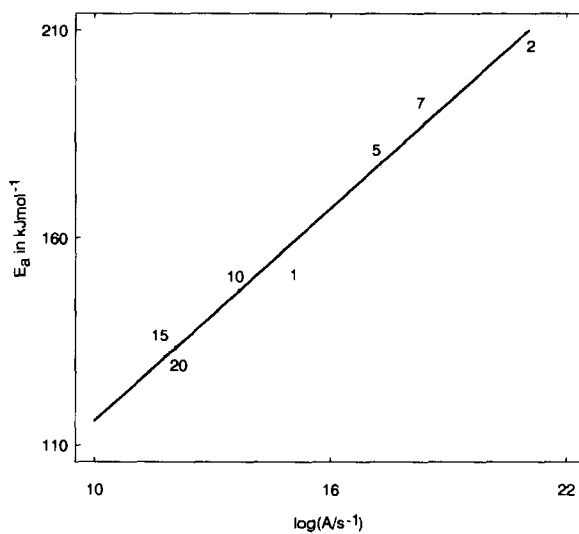


Fig. 3. Plot of $\log A$ versus E_a for tetryl with a purity of 99.9 mol% for different heating rates (the number near a point indicates heating rate in K min^{-1}).

experimental errors obtained in the different laboratories. Eqs. (4) and (6)–(8) represent so-called “kinetic composition effect” [13] as a result of different factors such as: mass of sample, heating rate, baseline character, experimental method used. These factors change the error of estimation of the kinetic parameters (A , E_a). The influence of the

Table 3
Comparison of tetryl thermal decomposition kinetic parameters reported by various researchers

$\log(A/s^{-1})$	$E_a/kJ\ mol^{-1}$	Ref.
15.40	160.7	[1]
12.90	146.0	[4]
13.80	150.6	[15]
15.50	147.3	[8]
16.00	167.0 ^a	[9]
18.84	177.0	[3]
12.96	144.0	[3]
27.50	251.0	[6]
24.50	232.2	[16]
11.20	125.8	[10]
11.40	125.1	[10]

^a Unimolecular rate constants only were used.

factors mentioned on the kinetic parameters indicates that the thermal decomposition is a complex process. The factors may change a stationary state. Evidence for this is presented in a previous paper [11].

Kinetic parameters are necessary for prediction of the critical temperature of tetryl using Eq. (3). This prediction was made for the same size and shape as specified in Ref. [17] but with the shape interpretation proposed by Rogers [18]. The pressed sample was approximated as a slab, therefore factor 0.88 was used for δ . The critical temperatures, T_c , predicted using Eqs. (4) and (8) are shown in Fig. 4. The solid line indicates the experimental critical temperature $T_c = 473\ K$ [17]. The observed change of E_a from 70 to 200 $kJ\ mol^{-1}$ introduced the estimated change of critical temperature from 477.5 to 478.2 K with minimum $T_c = 475.5\ K$ for Eq. (4). Predicted critical temperatures are consistent with the experimental temperatures. The small influence of the big change of the E value is because of the small difference between isokinetic temperature and the predicted critical temperature. For Eq. (8) the observed changes of E_a from 125 to 251 $kJ\ mol^{-1}$ caused the critical temperature to change from 506 to 439 K. Better agreement is obtained for Eqs. (6) and (7). The observed changes of E_a from 120 to 210 $kJ\ mol^{-1}$ caused the change of predicted critical temperature from 482 to 466 K.

The mole fractions of the thermal decomposition products obtained with the heating rate $\beta = 2\ K\ min^{-1}$ to the final temperature T_f are collected in Table 4. Mole fractions Σx_i were determined by the cryometric method [10] ($\log(A/s^{-1}) = 11.2$, $E_a = 125.8\ kJ\ mol^{-1}$). The mean decomposition rates for the range of temperatures from melting temperature to the final temperature are listed in the last column of Table 4. Fig. 5 shows results of the prediction of mole fraction of thermal decomposition products Σx_i using Eqs. (1) and (2) that is equal to the degree of thermal conversion of tetryl of α . This prediction is made using the kinetic parameters listed in Table 3. The best agreement is obtained only for the kinetic parameters obtained by the cryometric method [10] using

Table 4

Mole fraction of thermal decomposition products with a heating rate of $\beta = 2 \text{ K min}^{-1}$ for different final temperatures

$\Sigma x_i \times 100$	T_f/K	$\bar{V} \times 10^6/\text{s}^{-1}$
0.27	412.6	7.9
0.36	413.6	9.6
0.55	416.2	12.1
0.51	417.6	10.4
0.70	417.6	12.2
1.99	427.6	25.0
2.26	427.6	28.3

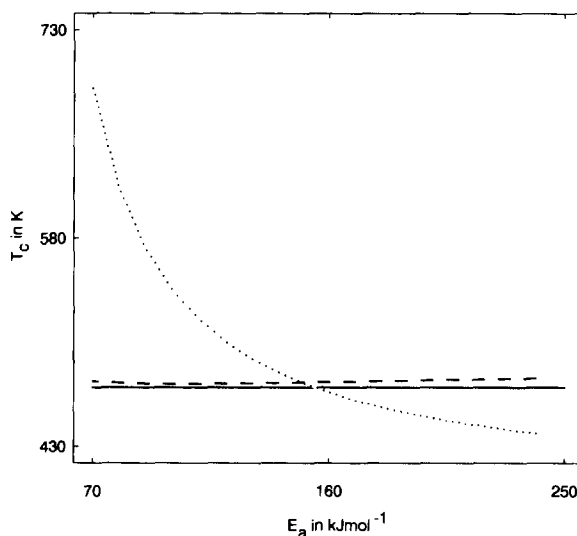


Fig. 4. Comparison of the predicted critical temperature on the basis of our own data presented in Table 1 (---) and the literature data presented in Table 3 (.....). The parallel solid line (—) represents the experimental data.

isothermal conditions for the thermal decomposition process. The kinetic parameters obtained by Robertson [1] give results consistent with those presented in Table 4. Lower agreement is obtained for our kinetic parameters [10] obtained from the Kissinger treatment ($\log(A/\text{s}^{-1}) = 11.4$, $E_a = 125.1 \text{ kJ mol}^{-1}$). All the other kinetic parameters from Table 3 give poor agreement.

4. Conclusions

The gaseous and condensed products from thermal decomposition possess catalytic or inhibiting properties related to the tetryl decomposition reaction. The obtained

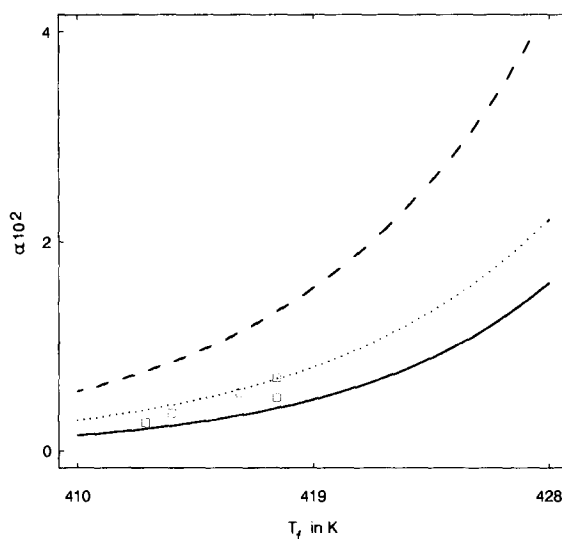


Fig. 5. Comparison of the mole fraction of thermal decomposition products obtained using Robertson's kinetic parameters (—) [1], obtained by the authors using the cryometric method (····) and from Kissinger's method (---) [10]. The points indicate the experimental results.

kinetic parameters depend on such factors as: mass of sample, baseline character, heating rate, used experimental method. Changes in the factors listed give the set of kinetic parameter values (A and E_a) with a good linear correlation between the terms $\log A$ and E_a . The correlation coefficient of "kinetic compensation effects" depends on the changing factors. Increasing the number of changing factors decreases the correlation coefficient r . The decrease of the correlation coefficient decreases the "isokinetic temperature". The observed different "kinetic compensation effect" is caused by the experimental errors and the complex thermal decomposition processes. In this kind of reaction existing stationary states depend strongly on the initial conditions such as: temperature, pressure, volume of the reaction vessel, purity. Impurities may possess catalytic properties. The linear correlation used for the prediction of critical temperature gives a range of critical temperatures; the minimum corresponds well with the experimental critical temperature.

Prediction of the mole fraction of thermal decomposition products is very sensitive to the values of the kinetic parameters. Only kinetic parameters obtained using similar values of the listed factors as were used for evaluation of thermal products give the best agreement.

Acknowledgement

This work was supported by the Committee for Scientific Research—grant No. 20571 91 01.

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