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THERMAL DECOMPOSITION OF N-2,4,6-TETRANITRO-N-METHYLANILINE

Kinetic parameters determined by differential scanning calorimetry technique

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Abstract

Purity determination by calorimetry has been used to determine the rate constant of thermal decomposition of N-2,4,6-tetranitro-N-methylaniline in liquid and solid states. The ratios of the initial rates of decomposition in solid and liquid decrease when temperature increases in the region not far below the melting point. The predicted rate constants in solid state are about 10 times greater than the one estimated by Wiseman. The thermal decomposition process at lower temperatures has been used to determine the rate constant in the decay phase. Activation energy and pre-exponential factor are also presented.

Keywords: DSC, kinetics, purity determination, N-2,4,6-tetranitro-N-methylaniline

Introduction

N-2,4,6-tetranitro-N-methylaniline (tetryl) decomposition proceeds through intermediate formation of picric acid, 2,4,6-trinitroanisol and N-methyl-2,4,6-trinitroaniline. Since the products of initial thermal decomposition decompose simultaneously with tetryl, determined kinetic parameter gives an average value for all the decomposition reactions. The overall decomposition of tetryl is quite a very complex process. Pyrolysis gas chromatography of tetryl shows about 16 products which have not been yet identified completely. This complicated thermal decomposition process has been investigated using different methods such as gas evolution [1, 2], calorimetry [3–6], manometric method [7, 8], high temperature infrared spectroscopy [9] and thermogravimetry [9, 10]. Values of so obtained kinetic parameters are scattered.

In our previous paper [11] we have presented application of cryometric method to determination of the velocity of thermal decomposition at melting temperature. The investigated compounds can be distributed on two different groups. In the first group determined eutectic purity is independent from the

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heating rates and in the second one depends on the heating rates. This discussed relationship relates to the decomposition mechanism at the induction period.

The aim of this work is to determine the kinetic parameters of thermal decomposition of tetryl using several methods performed on DSC. To estimate kinetic parameters the solid–liquid equilibrium and thermal decomposition at lower temperatures were taken into consideration. The cryometric method was used to determine the amount of impurities in liquid and solid phases.

Experimental

Tetryl was synthesized and purified in the Department of Analytical Chemistry of the Institute of Organic Industry Chemistry. The purity determined by cryometric method was 99.8% mole.

The measurements were performed on the heat-flux DSC 605M UNIPAN calorimeter cooperating with the IBM AT computer. The calibration was made using the following substances: gallium, indium, cadmium, lead, tin, zinc, naphthalene, benzoic acid. The metals used possessed the purity greater than 99.999% and the organic compounds greater than 99.95%. For the thermal decomposition process the temperature calibrations were made using the melting temperature determined by cryometric analysis and separately taking onset melting temperatures of the calibrants.

Results and discussion

A typical thermoanalytical curve of tetryl is presented in Fig. 1. The first endothermic peak relates to the melting process and the second one represents thermal decomposition at lower temperatures. The both processes are taken into consideration to estimate kinetic parameters of thermal decomposition in the induction period and the decay phase. The amount of impurities increases during the thermal decomposition of tetryl. Figure 2 shows the eight consecutive melting curves for the same sample of tetryl at a heating rate $\varphi = 2$ deg·min^{-1} with the same final temperature ($T_f = 417.6$ K) of each measurement. The melting curve for the eight consecutive melting processes is shifted in the direction of lower temperatures. The heights of the first three consecutive thermoanalytical curves slightly increase. The thermoanalytical curves were interpreted according to the manner presented in papers [11, 12]. The melting enthalpy (ΔH_m) and eutectic purity (mole percent, $x\cdot100$) for consecutive melting processes are collected in Table 1, column 2 and 3, respectively. The eutectic purity for consecutive melting processes decreases roughly by the same value. The increases of the amounts of thermal decomposition products ($\Sigma x_i\cdot100$) are listed in column 4. This is a difference between two consecutive purity determinations.

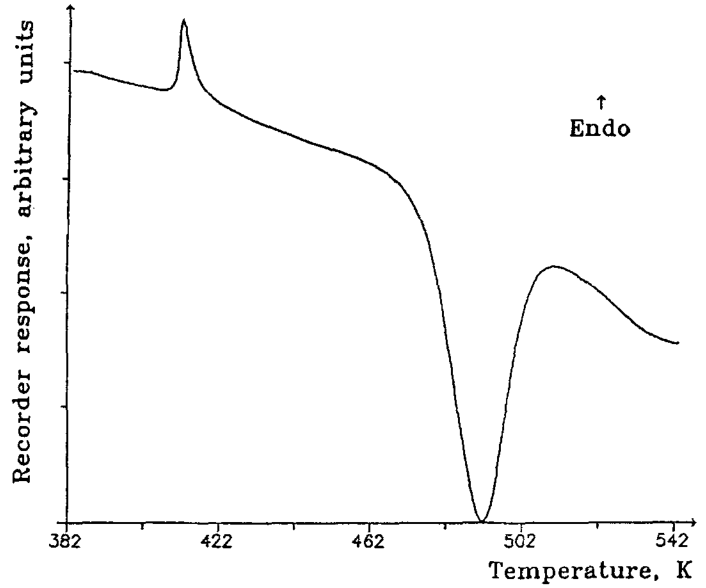

Fig. 1 DSC trace of tetryl at heating rate φ = 2 deg·min^{-1}. The first peak is due to melting process and second one is the thermal decomposition at lower temperature

Table 1 Eutectic purity of tetryl for consecutive scans performed on the same sample

No. of scans	ΔH_m/kJ·mol^{-1}	x·100	Σx_i 100	T_i / K	T_f / K	W / %	$\Delta H_{m(cor)}$/kJ·mol^{-1}
1	22.76	99.81	0.71	401.3	416.7	2.7	23.49
2	23.72	99.10	0.52	398.9	416.7	9.6	25.99
3	23.15	98.58	0.51	397.7	416.7	12.1	25.92
4	22.17	98.07	0.67	396.7	417.6	15.7	25.66
5	20.48	97.40	0.60	395.5	416.7	19.7	24.88
6	19.37	96.80	1.15	394.8	416.6	24.8	24.18
7	20.94	95.65	0.69	393.1	416.7	23.9	25.87
8	20.45	94.96		391.2	417.2	25.7	25.67

Formation of impurities is more or less constant during this simple measurement. The melting enthalpy of the second melting process is greater than the others one. This result may indicate that the reaction of thermal decomposition is an endothermic process for small amounts of thermal decomposition products and exothermic process for the greater amount of decomposition products. The values of initial melting temperatures (T_i) and final temperature (T_f) are collected in Table 1, column 5 and 6, respectively. The cryometric correction values (*W*) are listed in column 7. This correction value assures the linear relationship between the equilibrium temperature and the fraction of sample melted for the first melting temperature and the same melting temperature of pure tetryl for the next melting processes. The correction value *W* relates to the existence of some amount of liquid at the initial melting temperature (T_i). The correction (*W*) increases with the number of consecutive melting processes performed on the same sample. The melting enthalpies with correction ($\Delta H_{m(cor)}$) for liquid existing at T_i are placed in the last column. This parameter is more or less constant.

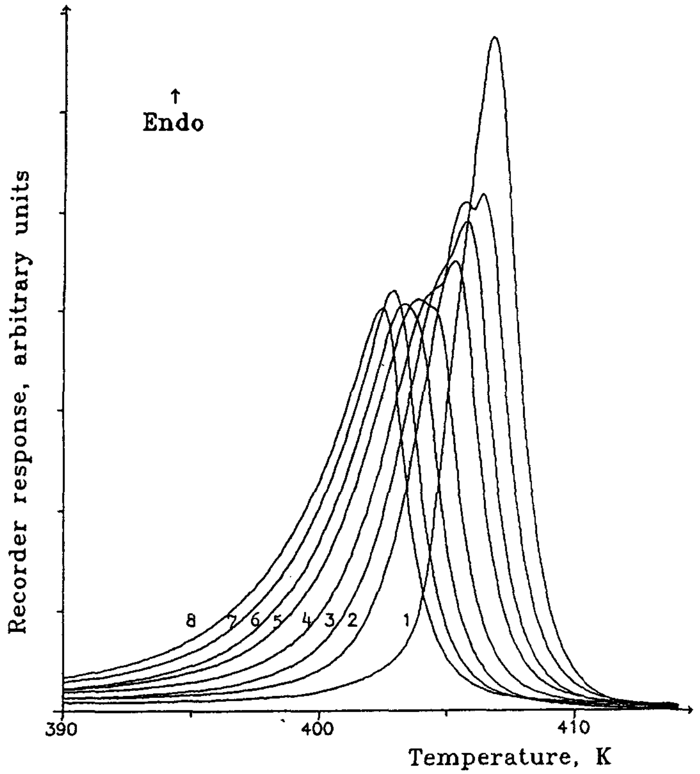

Fig. 2 Comparison of the consecutive melting curves performed for the same sample of tetryl. The number above the thermoanalytical curve indicates the numbers of melting processes run on the sample

The cryometric method was used for determination of the mole fraction of thermal decomposition products. It is assumed that one molecule of tetryl gives one molecule of the thermal decomposition product in liquid phase which can be determined by cryometric method. The molecules such as NO_2, NO, N_2,

CO_2 CO are only in gaseous phase not to be determined by cryometric method. The thermal decomposition reaction can be written as

$$A \rightarrow B + \text{gaseous products} \tag{1}$$

and the products (B) are soluble in liquid (A) but completely insoluble in the solid (A).

In kinetics the change of reactants is frequently expressed by so-called degree of conversion (α) which is depended on the change of purity (x)

$$\alpha_t = x_o - x_t = \Sigma x_i \tag{2}$$

The subscripts in Eq. (2) correspond to the value at initial time and time (t), respectively. The time dependence of α is expressed in the form of differential equation

$$d\alpha/dt = kf(\alpha) \tag{3}$$

where k is the rate constant and f(α) is a kinetic model. It is assumed that the decomposition of tetryl is in the best way described by Avrami–Erofe'ev equation for the 1st order decay:

$$d\alpha/dt = k(1-\alpha)^n; \qquad n = 1 \tag{4}$$

For small change of purity the velocity of thermal decomposition can be written as

$$d\alpha/dt \approx \Sigma x_i/t \approx k \tag{5}$$

because $(1-\alpha)\approx 1$.

Table 2 Initial rates of the thermal decomposition determined by cryometric method for liquid tetryl

T/K	k/sec$^{-1}\cdot 10^5$
427.6	7.68
416.2	2.42
412.6	2.08
410.2	1.75

The values of thermal decomposition rate constants for liquid tetryl are listed in Table 2. The change of purity during the thermal decomposition varied from

0.5 to 2% mole. The initial rate of decomposition can be described applying Arrhenius equation

$$k_l\ (\mathrm{sec}^{-1}) = 10^{12.1}\cdot e^{-133\ \mathrm{kJ/RT}} \tag{6}$$

Table 3 First-order rate constants of the thermal decomposition determined by cryometric method for solid tetryl and the ratio for both phases

T/K	k_s/sec$^{-1}\cdot 10^7$	k_l / k_s
394	1.9	16.2
397	3.4	12.3
399	22.2	2.3

The same measurements were preformed for solid tetryl below melting temperature. The results are summarised in Table 3. The ratios of rate constants (k_l/k_s) are listed in column 3. The ratio decreases when the difference between the temperature measurement and melting temperature of tetryl decreases. Wiseman (quoted by Bawn) [13] had re-analysed Farmer's data [21] and deduced that the ratio of decomposition of solid tetryl obeys the following relationship

$$k_s = 10^{12.7}\cdot e^{-153\ \mathrm{kJ/RT}}\ \mathrm{sec}^{-1} \tag{7}$$

The initial rate of decomposition predicted from Eq. (7) is about 10 times lower than rate constant based on our results presented in Table 3. Bawn [13] used Robertson's data for liquid tetryl and Eq. (7) to calculate the same ratio (k_l/k_s). He has obtained contradictory results. The ratio increases when the difference between the measurement temperature and melting temperature decreases. In our opinion this relation is not expected. The partial liquefaction of the system [13] increases the initial rate of decomposition for solid. The partial liquefaction effects occurring during the decomposition of solid should increase when the difference between the measurement temperature and melting temperature decreases. For this reason the ratio (k_l/k_s) can decrease when the measurement temperature increases.

Figure 3 shows the changes of the base line before the melting peak. The changes appears about 10 K before onset melting temperature and are due to some highly exothermic reaction of the decomposition as a result of partial liquefaction. Probably, this reaction is catalysed by impurities existing in the investigated sample. For this reason the purity determination depends on heating rate. Purity of tetryl at $\varphi = 0.5$ deg·min^{-1} was 99.6% mole to be about 0.2% lower than at $\varphi = 2$ deg·min^{-1}.

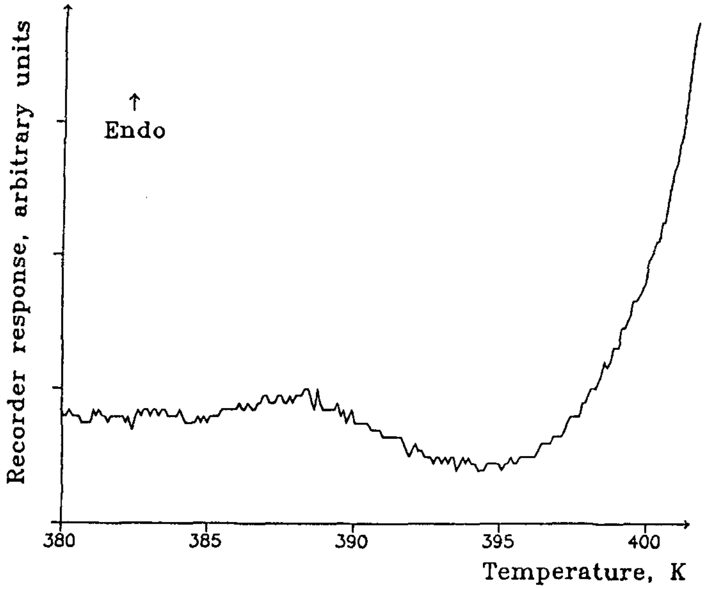

Fig. 3 Enlargement of the base line of tetryl before the melting peak. The minimum before the melting peak results from the exothermic reaction of decomposition

Table 4 The effect of heating rate on peak temperature for thermal decomposition of tetryl

Heating rate / deg·min^{-1}	Peak temperature, T_p / K
20	499.2
10	486.8
7	482.9
5	477.0
2	465.0
1	456.2

The effects of heating rate on peak temperature for thermal decomposition of tetryl are summarized in Table 4. The kinetic parameters of thermal decomposition were determined from Kissinger's treatment of DSC data [14]. It has been found that the peak temperature is a function of the rate of heating of the sample and a relationship exists between peak temperature and heating rate for a (pseudo) first-order reaction. This relationship can be expressed by the equation

$$\ln (\Phi/T_p^2) = \ln \left(\frac{R}{E} A\right) - \frac{E}{R} \cdot \frac{1}{T_p} \qquad (8)$$

where R is the gas constant, T_p is the peak temperature, E is the activation energy, A is the preexponential factor and $\varphi = dT/dt$ is the heating rate. The plot of $\ln(\varphi/T_p^2)$ *vs.* $1/T_p$ is shown in Fig. 4. The rate of thermal decomposition of liquid tetryl obeys the relationship:

$$k = 10^{11.4} \cdot e^{-125.1 kJ/RT} \tag{9}$$

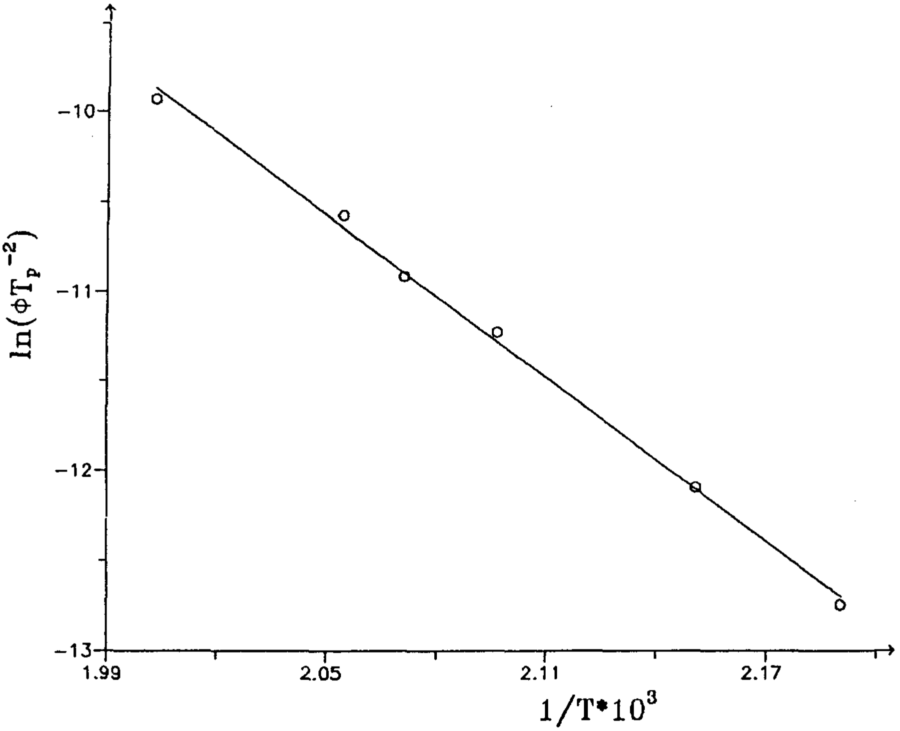

Fig. 4 The effect of heating rate on peak temperature for thermal decomposition of tetryl (Kissinger's method)

Table 5 Thermal decomposition kinetic parameters of tetryl from a single non-isothermal run

Heating rate / deg·min^{-1}	ΔT	$\Delta\alpha$	E/kJ·mol^{-1}	log$A$/sec^{-1}	k/sec^{-1}·10^{-5}
20	522–529	0.55–0.8	119.0	10.4	4.0
10	501–505	0.63–0.8	124.9	11.3	7.6
7	494–497	0.68–0.8	133.9	12.4	5.6
5	487–489	0.70–0.8	121.5	11.2	12.3
average			124.8±5.6	11.3±0.7	7.4±3.1

Table 6 Comparison of tetryl thermal decomposition kinetic parameters reported by various investigators

Method	ΔT/K	Uncatalytic reaction		Catalytic reaction		k/sec$^{-1}\cdot 10^{-5}$ 420 K	Ref.
		E/kJ·mol^{-1}	log$A$/sec^{-1}	E/kJ·mol^{-1}	log$A$/sec^{-1}		
manometry	484–533	160.7	15.4			2.6	1
thermogravimetry	405–437	146.0	12.9			0.6	10
calorimetry	403–428	150.6	13.8	159.0	15.6	1.2(6.7)	5
manometry	413–433	147.3	13.5	154		1.5	7
manometry	413–438	167	16	148.5	14.5	1.7(10.7)	8
IR spectrometry	404–418	177	18.84			67	9
thermogravimetry	424–446	144	12.96			1.1	9
	non-specify the reaction						
gas analysis	403–412	251.0	27.5			19.2	2
gas analysis	413–423	232.2	24.5			4.2	16
gas analysis	423–448	146.4					17
DSC		229.7					6
DSC	443–447	242.7					4
	this study (DSC)						
cryometry	410–428	125.8	11.2			3.8	
Kissinger	456–499	125.1	11.4			7.0	
single non-isotherm.	487–529	124.8±5.6	11.3±0.7			7.4±3.1	

The kinetic parameters were determined also on the basis on a single linear heating scan rate, using the method developed by Borchardt and Daniels [15]. The region of fractional convertion α from 0.1 to 0.8 was taken to analyse. The results of calculation are summarized in Table 5. The region of fractional convertion ($\Delta\alpha$) for which the reaction order is equal to one ($n = 1$) was taken to estimate the kinetic parameters (E) and (A). This region decreases when the heating rate decreases. It was impossible to find that region for heating rate $\varphi = 2$ deg·min^{-1} and 1 deg·min^{-1}. The rates of decomposition at 420 K are collected in the last column of Table 5. The mean value of the rate constant ($k_{420} = 7.4\cdot10^{-5}$sec^{-1}) is consistent with the same rate constant calculated from Kissinger's method ($k_{420} = 7\cdot10^{-5}$sec^{-1}).

In Table 6 are summarized the kinetic parameters obtained by various investigators using different methods [8]. The initial rate constants and catalytic rate constants (in parenthesis) at arbitrary chosen temperature $T = 420$ K are given in column 7. The mean initial rate constant (without one the extremely high rate constant, $k = 67\cdot10^{-5}$sec^{-1}) is $k = 4\cdot10^{-5}$ and is consistent with our result from cryometric method. The mean rate constant for the catalytic reaction is consistent with our values of the rate of decomposition using single runs (Table 5) and Kissinger's method. Our values of the activation energy and pre-exponential factor are lower than the values taken from the literature data. Good agreement of our results obtained by using different methods (Kissinger's, cryometry and single non-isothermal run) suggests that the mentioned difference of the kinetic parameters may result from different purity of used tetryl. Impurities are able to catalyse or inhibit the thermal decomposition reaction.

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References

1 A. J. B. Robertson, Trans. Faraday Soc., 44 (1948) 677.
2 R. C. Farmer, J. Chem. Soc., 117 (1920) 1603.
3 R. N. Rogers and E. D. Morris, Anal. Chem., 38 (1966) 412.
4 P. G. Hall, Trans. Faraday Soc., 67 (1971) 556.
5 F. I. Dubowitskii, I. Rubsow and G. B. Manelis, Izw. Dokl. Akad. Nauk S.S.S.R., (1960) 1763.
6 R. N. Rogers and L. S. Smith, Analyt. Chem., 38 (1966) 412.
7 F. I. Dubowitskii, G. B. Manelis and L. P. Smirnow, Zh. Fiz. Khim., 35 (1961) 521.
8 F. I. Dubowitskii and B. L. Korsonskii, Usp. Khim., 50 (1981) 1828.
9 K. Raha, P. S. Makashir and E. M. Kurian, J. Thermal Anal., 35 (1989) 1173.
10 M. A. Cook and M. T. Abegg, Ind. Eng. Chem., 48 (1956) 1090.
11 A. Książczak and T. Książczak, J. Thermal Anal., in press.
12 E. E. Marti, Thermochim. Acta, 5 (1972) 173.

13 C. E. H. Bawn, Chemistry of the Solid State, ed. W. E. Garner (Butterworths, London), 1955, p. 261, 265.
14 M. E. Kissinger, Anal. Chem., 29 (1957) 1702.
15 H. J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957).
16 C. N. Hinshelwood, J. Chem. Soc., (1921) 721.
17 C. L. I. Knowles, Ind. Eng. Chem., 12 (1920) 246.

Zusammenfassung — Mittels der Reinheitsbestimmung durch Kalorimetrie wurde die Geschwindigkeitskonstante der thermischen Zersetzung von N-2,4,6-Tetranitro-N-methylanilin im flüssigen und festen Aggregatzustand bestimmt. Das Verhältnis der Anfangsgeschwindigkeit der Zersetzung zwischen fester und flüssiger Phase nimmt ab, wenn die Temperatur in dem Bereich unweit unter dem Schmelzpunkt ansteigt. Die vorausgesagten Geschwindigkeitskonstanten im festen Aggregatzustand sind um etwa eine Größenordnung größer als die von Wiseman vorausgesagten Werte. Der thermische Zersetzungsprozess bei niedrigeren Temperaturen wurde zur Bestimmung der Geschwindigkeitskonstante in der Zersetzungsphase benutzt. Aktivierungsenergie und präexponentieller Faktor werden ebenfalls angegeben.