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Initial stage of thermal decomposition of *N*,2,4,6-tetranitro-*N*-methylaniline

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Abstract

The solid–liquid equilibria (cryometry) formed during the thermal ageing of *N*,2,4,6-tetranitro-*N*-methylaniline (tetryl) with purities of 99.8 and 99.9 mol% were investigated using DSC. The mean rates and rate constants were determined for the temperature range from the start of melting to the chosen final temperature. For small degrees of tetryl conversion, $\alpha < 0.02$, small changes in purity introduced considerable influences on the thermal decomposition rate. For tetryl (99.9 mol%), a strong catalytic effect on the thermal decomposition was observed for this degree of conversion. The calculated ratio of the unimolecular reaction rate constant and the catalytic reaction rate is $k_1/k_2 = 187$. Oscillations of the mean rate values were obtained for the whole investigated range of conversion degrees below 0.06. The mechanism of the thermal decomposition of the initial stage is proposed.

Keywords: Kinetic model; Phase transition; Thermal decomposition

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1. Introduction

The thermal decomposition of *N*,2,4,6-tetranitro-*N*-methylaniline (tetryl) proceeds through intermediate formation of picric acid, 2,4,6-trinitroanisol and *N*-methyl-2,4,6-trinitroaniline in the condensed state, and NO_2, NO, CO_2, CO, and N_2 in the gaseous state [1–4]. The listed decomposition products in the condensed state are thermally unstable and decompose simultaneously with tetryl. Pyrolysis gas chromatography of tetryl shows about 16 products. Decomposition does not occur in simple consecutive stages but rather runs along parallel pathways, of which only one takes place at the

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beginning of the reaction and is then inhibited by the decomposition products. At the same time, volatile catalytically-active products accumulate and considerably accelerate the decomposition [1,2]. It has been shown that picric acid quantitatively determines the self-acceleration of the reaction. High-temperature IR spectroscopic study and product analysis by IR and HPLC show that the primary step in the decomposition of tetryl is cleavage of the $N{-}NO_2$ bond. The bond energy of $N{-}NO_2$ is around 168 kJ mol^{-1} and is the weakest linkage in tetryl. The kinetic parameters determined by several methods give an average value for all the decomposition reactions.

The thermal decomposition reaction can be written as

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

It was assumed that the products (B) are soluble in liquid (A) but completely insoluble in solid (A). In kinetics, the change in reactants is frequently expressed by the so-called degree of conversion (α) which is dependent on the change in purity P (mol%)

$$\alpha_t = (P_0 - P_t)/100 = \sum x_i \tag{2}$$

where P_0 and P_t are the purities of tetryl at the initial time ($t = 0$) and the final time (t), respectively, and Σx_i is the mole fraction of the decomposition condensed products. The time dependence of α is expressed in the form of a differential equation

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

where k is the rate constant and $f(\alpha)$ is a kinetic model. It is assumed that the decomposition of tetryl is best described by the pseudo-first-order reaction

$$\mathrm{d}\alpha/\mathrm{d}T = k(1-\alpha) \tag{4}$$

For a small change in purity, the rate of thermal decomposition can be written as

$$\mathrm{d}\alpha/\mathrm{d}t \approx \sum x_i/t = \bar{V} = k \tag{5}$$

because $(1-\alpha) \approx 1$, where $\bar{V}$ is the mean thermal decomposition rate.

An autocatalytic reaction can be described by Eqs. (6) and (7)

$$A \rightarrow B \quad k_1 \tag{6}$$

$$A + B \rightarrow 2B \quad k_2 \tag{7}$$

where A represents the initial reactant and B represents products. The rate expression that corresponds to this kinetic scheme is given by

$$\mathrm{d}(\alpha)/\mathrm{d}t = k_1(1-\alpha) + k_2\alpha(1-\alpha) \tag{8}$$

Dividing throughout by $(1-\alpha)$ gives

$$-\frac{\mathrm{d}\ln(1-\alpha)}{\mathrm{d}t} = k_1 + k_2\alpha \tag{9}$$

Eqs. (5) and (9) were used for calculation of the decomposition rate and rate constants.

The solid–liquid equilibrium (cryometry) of high-purity tetryl was used to study its thermal decomposition during the induction period.

2. Experimental

2.1. Samples

Tetryl was synthesised and purified in the Department of Analytical Chemistry of the Institute of Organic Industrial Chemistry (Warsaw). The purity of sample I determined by the cryometric method was 99.8 mol%. The purity of sample II obtained by additional crystallisations of sample I from benzene was 99.9 mol%.

2.2. Apparatus

The measurements were performed on the heat-flux DSC 605M UNIPAN calorimeter combined with an IBM-AT computer. Calorimetric measurements of the melting processes were performed using hermetic aluminium pans. The calibration was made using the following substances: gallium, indium, cadmium, lead, tin, zinc, naphthalene, and benzoic acid. The metals used were of purity higher than 99.999%, and the organic compounds were more than 99.95% pure. The temperature calibration was made using the melting temperature of the substances determined by cryometric analysis.

2.3. Procedure

Samples of tetryl were sealed in hermetic pans under a reduced pressure of about 1.3 kPa. The thermal decomposition products were produced during linear heating at rate β, from the melting temperature (T_m) to the arbitrarily chosen final temperature (T_f). The thermal decomposition products were characterised by the cryometric method. The melting temperature of absolute pure tetryl determined for high-purity tetryl (T_m^0) was taken as a reference for the purity determinations of thermally aged samples. The beginning of the investigated sample melting was assumed to be the beginning of the thermal decomposition.

3. Results and discussion

The mole fractions of the thermal decomposition products Σx_i and the initial thermal decomposition rate $\bar{V}$ of tetryl having 99.8 mol% purity taken for consecutive runs using the same sample are listed in Table 1. The mean degrees of conversion are listed in column 3. Assuming that the thermal decomposition proceeds according to Eqs. (4) and (5), the mean initial rate is equal to the mean rate constant k for the temperature range from the beginning of melting to the final temperature. Calculated mean thermal decomposition rates are presented in Fig. 1. The large and irregular character of the mean rate spreading is due to the change in catalyst concentration during the consecutive run. The ratio of the maximum rate to the minimum one is 1.95. The great change in mean thermal decomposition rate is probably caused by the freezing of super-cooled liquid tetryl. Frozen catalyst in solid tetryl is not active.

Table 1
Mole fraction of thermal decomposition products and thermal decomposition rate of tetryl of purity 99.8 mol% for consecutive runs at a heating rate of $\beta = 2\,\mathrm{K\,min^{-1}}$

Scan	$\Sigma x_i \times 10^2$	$\bar{\alpha} \times 10^2$	$\bar{V} \times 10^6/\mathrm{s}^{-1}$
	Sample I, $T_f = 416.7\,\mathrm{K}$		
1	0.71	0.35	15.4
2	0.52	0.97	9.7
3	0.51	1.48	9.0
4	0.67	2.08	10.7
5	0.60	2.71	9.4
6	1.15	3.59	17.6
7	0.69	4.51	9.7
	Sample II, $T_f = 417.6\,\mathrm{K}$		
1	0.51	0.25	10.4
2	0.64	0.84	11.2
3	0.63	1.48	10.2
4	0.97	2.28	14.9

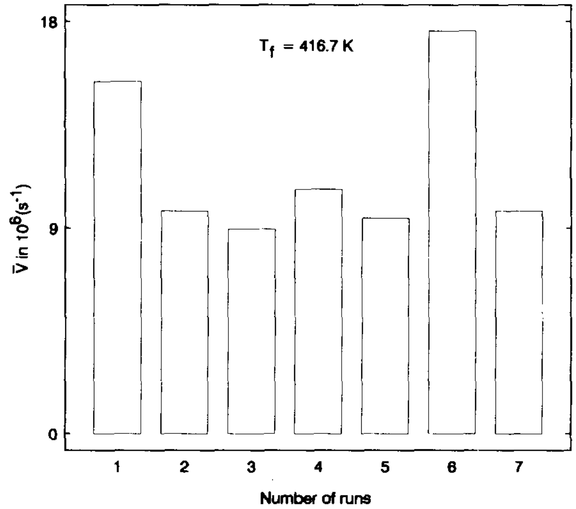

Fig. 1. Mean thermal decomposition rate of tetryl of purity 99.8 mol% for the final temperature $T_f = 416.7$ K for consecutive runs using the same sample.

Catalysts in super-cooled liquid tetryl undergo further chemical transformations to form inactive products or inhibitors. The catalyst concentration depends on the time of tetryl solidification which is not under control. The DSC curve of super-cooled tetryl is presented in Fig. 2. The first exothermic peak is due to the crystallisation of super-cooled tetryl and the second endothermic peak is caused by its melting. Rapid

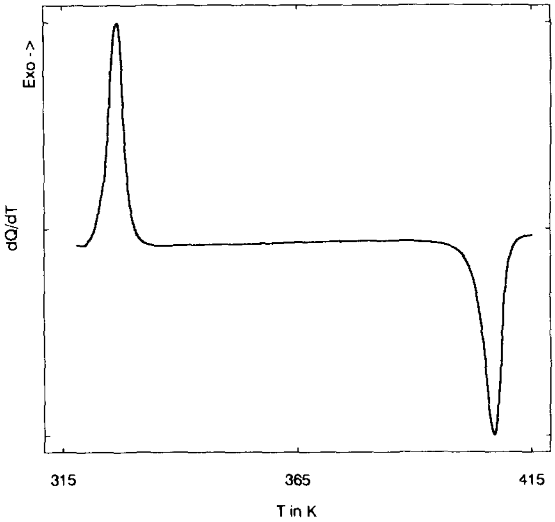

Fig. 2. DSC curve of super-cooled liquid tetryl.

solidification of the sample freezes the catalysts. For this reason the mean thermal decomposition rate of a subsequent thermal ageing process is greater than the previous one. Oscillations of the mean thermal decomposition rate indicate that the thermal decomposition reaction is a pseudo-first-order reaction and the catalyst concentration reaches the quasi-stationary state.

$$\alpha_{\mathrm{cat}} \approx \mathrm{const.} \tag{10}$$

Substituting Eq. (10) into Eq. (9) gives

$$\frac{-\mathrm{d}\ln(1-\alpha)}{\mathrm{d}t} = k_1 + k_2\alpha_{\mathrm{cat}} = k \tag{11}$$

For $\alpha \ll 1$, the last equation can be written

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{-\mathrm{d}\ln(1-\alpha)}{\mathrm{d}t} = k_1 + k_2\alpha_{\mathrm{cat}} = k = \bar{V} \tag{12}$$

Autocatalytic reactions (6) and (7) can be described by Eq. (4) only when the catalyst concentration is constant (stationary state). The mole fractions of the thermal product Σx_i and the mean thermal decomposition rates of tetryl with purity 99.9 mol% for different final temperatures are given in Table 2. The mean rates $\bar{V}$ for consecutive thermal ageing processes are presented in Fig. 3. On the basis of Eq. (11), the mean rates $\bar{V}$ presented by the shaded bars were taken for the estimation of the rate constants and of the catalytic reaction. The thermal decomposition rate increases in the initial period and then oscillates in the stationary state period. Calculated k_1 and k_2 values are shown in Fig. 4 and collected in Table 3. It is important to stress that the calculated rate

Table 2
Mole fraction of thermal decomposition products and thermal decomposition rate of tetryl of purity 99.9 mol% for consecutive runs at a heating rate of $\beta = 2$ K min^{-1}

Scan	$\Sigma x_i \times 10^2$	$\bar{\alpha} \times 10^2$	$\bar{V} \times 10^6/\mathrm{s}^{-1}$
$T_f = 415.8$ K			
1	0.04	0.02	0.99
2	0.10	0.09	2.32
3	0.10	0.19	2.25
4	0.12	0.30	2.63
5	0.24	0.54	5.12
6	0.26	0.73	5.38
7	0.32	1.02	6.35
8	0.44	1.40	8.19
9	0.39	1.82	6.88
10	0.58	2.31	10.3
$T_f = 418.2$ K			
1	0.10	0.05	2.06
2	0.25	0.30	4.89
3	0.31	0.51	5.68
4	0.46	0.88	8.18
5	0.61	1.42	10.0
6	0.69	2.08	9.80
7	0.55	2.69	7.82
8	1.32	2.85	18.7
9	0.54	4.55	6.80
10	1.00	5.32	12.4
$T_f = 419.6$ K			
1	0.10	0.05	1.91
2	0.29	0.24	5.31
3	0.49	0.66	8.42
4	0.31	1.06	4.83
5	0.57	1.50	9.05
6	0.86	2.21	13.0
7	1.27	3.20	17.9
1	0.24	0.12	4.03
2	0.39	0.48	6.03
3	0.95	1.11	14.03
4	10.8	2.12	14.09
5	1.02	3.64	12.72
6	1.27	4.37	13.35
7	1.18	5.60	11.81
$T_f = 422.2$ K			
1	0.17	0.08	2.86
2	0.42	0.38	6.46
3	1.18	1.18	17.2
4	1.02	2.28	13.0
5	1.46	3.52	18.1
6	1.08	5.54	12.4
$T_f = 433.3$ K			
1	1.32	0.66	13.7
2	4.15	3.39	39.2

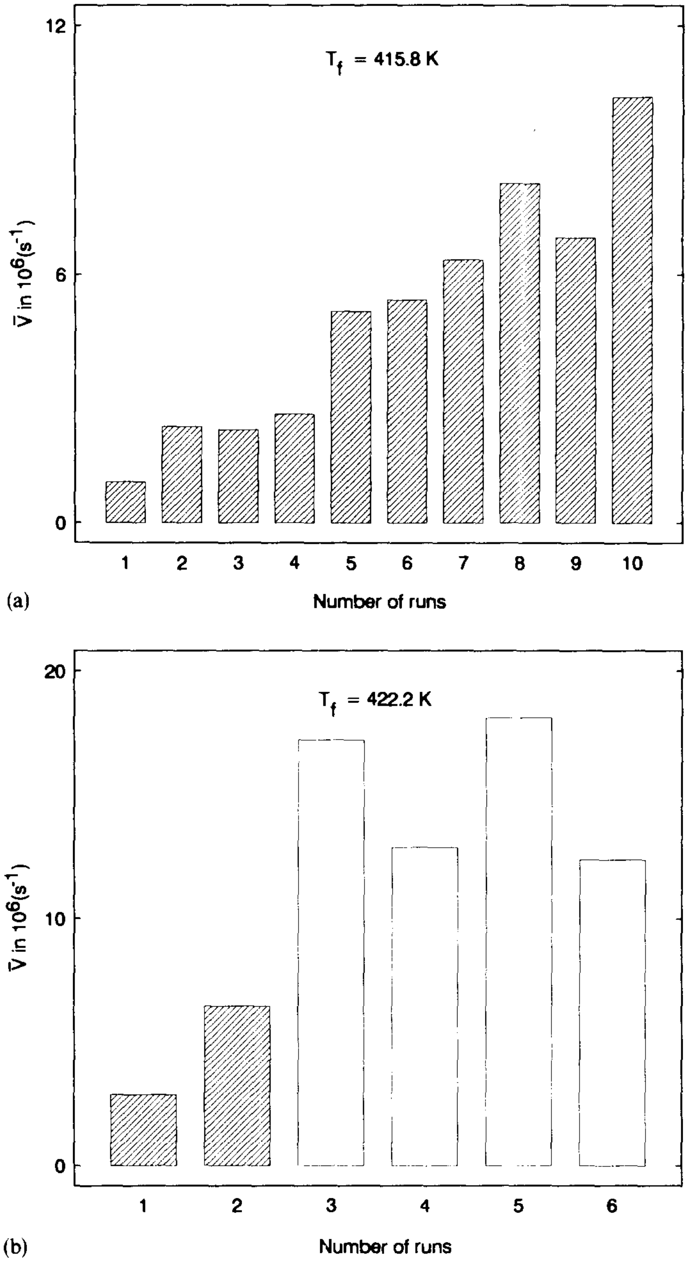

Fig. 3. Mean thermal decomposition rate of tetryl of purity 99.9 mol% for different final temperatures. (a) $T_f = 415.8$ K. (b) $T_f = 422.2$ K. Solid bars are data taken for estimation of the autocatalytic reaction rate constant. The same sample was used for consecutive runs.

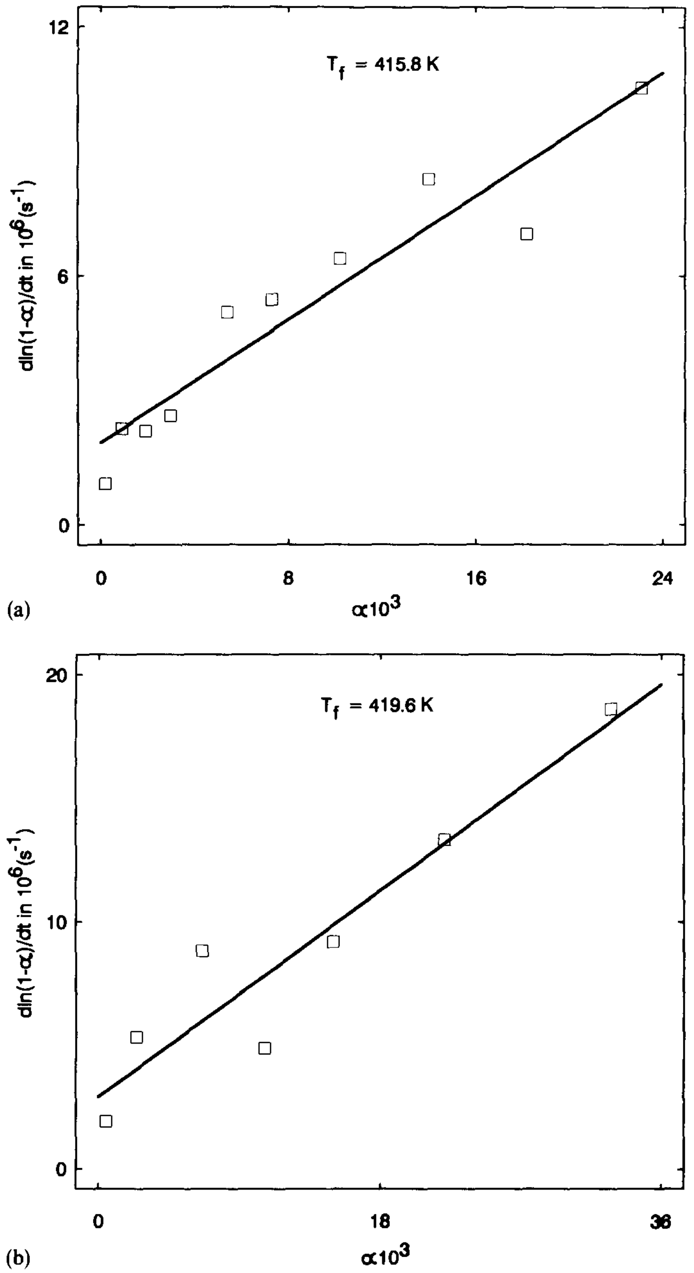

Fig. 4. The relationship for approximation of the unimolecular and autocatalytic reaction rate constants. (a) T_f = 415.8 K. (b) T_f = 419.6 K.

Table 3
Mean decomposition rate for unimolecular and autocatalytic reactions for different final temperatures

T_f/K	$k_1 \times 10^6/\mathrm{s}^{-1}$	$k_2 \times 10^6/\mathrm{s}^{-1}$	k_2/k_1
415.8	1.98	371	187
418.2	2.81	552	196
419.6	2.90	463	160
422.2	2.10	1214	578[a]
433.3	7.31	982	134[a]

[a] These results have a high uncertainty.

constants are characteristic for the range from the beginning of the melting to the final temperature. Three experimental points were taken for estimation of k_1 and k_2 at 422.2 and 433 K. For this reason, the estimated values have a high uncertainty. The last experimental point from the initial period with the greatest value of α may belong to the stationary period.

The mean ratio $\gamma = k_2/k_1$ calculated on the basis of the experimental data for low temperatures (415.8, 418.2, 419.6 K) is 187. The same ratio calculated from calorimetric measurements [5] is 5.6, and by the manometric method [1] is 6.5, at 418 K. The previous authors have investigated tetryl over a greater range of conversion degree than in this study.

The mean thermal decomposition rate for the stationary period is equal to the mean thermal decomposition rate constant k (see Eq. (5)). Eq. (12) allows prediction α_{cat} of the beginning of the stationary period

$$\alpha_{\mathrm{cat}} = (k - k_1)/k_2 \tag{13}$$

Maximum and minimum values of the decomposition rate from the stationary period were used to estimate α_{cat}. For a final temperature of 418.2 K, we have obtained $\alpha_{\mathrm{cat(max)}} = 0.028$ and $\alpha_{\mathrm{cat(min)}} = 0.007$, and $\alpha_{\mathrm{cat(max)}} = 0.012$ and $\alpha_{\mathrm{cat(min)}} = 0.008$ for the first set of data, and $\alpha_{\mathrm{cat(max)}} = 0.011$ and $\alpha_{\mathrm{cat(min)}} = 0.009$ for the second set of data, both for a final temperature of 422.2 K. These parameters were not estimated at 433.3 K because of high mole fractions of decomposition products in this sample. The maximum rates for all data sets are approximately of the same order of magnitude ($\bar{V} = 18.7 \times 10^{-6}$, 17.9×10^{-6}, $18.1 \times 10^{-6}\ \mathrm{s}^{-1}$) and are consistent with the same rate estimated for tetryl with a lower purity (99.8 mol%). Small changes in purity introduce a great influence on the thermal decomposition rate during the initial period. An increase in the decomposition rate during the initial period could be observed only for high-purity tetryl (99.9 mol%). The observed strong catalytic effect for small degrees of conversion α cannot be attributed to the presence of picric acid as the final decomposition product. Picric acid concentration increases continuously during the thermal decomposition process. Frequently, the thermal decomposition reactions are described by Eq. (4) [4,6–9]. The results presented suggest that the observed difference is caused by the different purity of tetryl used for these investigations.

4. Conclusions

This study of the thermal decomposition of tetryl of purity 99.8 and 99.9 mol% demonstrates the great influence of traces of impurities on the thermal decomposition kinetic parameters during the initial period ($\alpha < 0.01$). Tetryl of purity 99.8 mol% is decomposed according to a pseudo-first-order reaction. Tetryl of purity 99.9 mol% possesses an initial decomposition range in which the decomposition is an autocatalytic reaction and then the catalyst concentration achieves the stationary state. For these reasons, the thermal decomposition process becomes a pseudo-first-order reaction. The oscillations of the mean rate during the stationary state for tetryl of purity 99.9 mol% are similar to those for tetryl of purity 99.8 mol%. The oscillations are caused by different times taken for solidification after the thermal ageing process. In the case of rapid sample solidification, the catalysts are frozen in solid tetryl. The mean rate of the next thermal ageing process is greater than for the slow sample solidification process. In the liquid tetryl, the volatile catalysts are transported to the free volume of the hermetically sealed pan and undergo chemical transformations to form uncatalytic products.

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