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INFLUENCE OF DSC MEASUREMENT CONDITIONS ON KINETIC PARAMETERS OF THERMAL DECOMPOSITION OF 2,4,6-TRINITROTOLUENE

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Abstract

An autocatalytic model involving the limited solubility of volatile catalytic products was applied to the thermal decomposition of 2,4,6-trinitrotoluene. The critical supersaturation of the thermal decomposition products with the catalytic properties was higher at a low heating rate. Decrease of the sample mass led to an increased critical supersaturation of the decomposition products. This is probably a result of the greater contribution of products adsorption on the aluminium pan surface. It is presumed that the differences observed in the rate constant are connected with the uncontrolled critical supersaturation of the volatile thermal decomposition products.

Keywords: DSC, kinetics, thermal decomposition, 2,4,6-trinitrotoluene

Introduction

The kinetic parameters of thermal decomposition of energetic materials (EMs) are of great significance as concerns safety and changes in properties as a function of time. Thermally induced changes in composition are accompanied by the liberation of large quantities of heat, which permits the application of DSC for investigation of the kinetics. In spite of the wide-ranging interest in the determination of these kinetic parameters, consistent results have not been obtained [1, 2]. The thermal decompositions of EMs are very complicated processes. The conditions of DSC measurement can exert a large influence on the estimated kinetic parameters, i.e. the activation energy (E_a) and the preexponential factor (A).

The aim of this paper is to investigate the influence of the heating rate (β) and the mass of the sample (m) on the values of the kinetic parameters determined from a single DSC run, 2,4,6-trinitrotoluene (TNT) being used as a model EM. The thermal decomposition of TNT is controlled by a homolytic C–H bond cleavage involving the methyl moiety. The intramolecular transfer of a hydrogen atom to an *ortho*-nitro group would provide the isolated product 4,6-dinitroanthranil. An intermolecular hydrogen atom transfer from a TNT molecule furnishes a 2,4,6-trinitrobenzyl radical and a protonated TNT radical, the *para*-nitro group accepting the hydrogen atom [3]. Dacons *et al.* [4] reported that the thermal decomposition product mixtures contain at

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least 25 discrete species, and also large amounts of telomeric or polymeric materials. Rogers [5] found the following products 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 rate constant of the thermal decomposition of TNT in the liquid state is about 10 times greater than that in the gas phase. This indicates the predominant influence of intermolecular hydrogen transfer.

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

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \tag{1}$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_2} 2\mathrm{B} \tag{2}$$

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

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

The experimental results relating to the thermal decomposition of TNT [1, 2] reveal that the catalyst concentration achieves a stationary state:

$$\alpha_{\mathrm{cat.}} \approx \mathrm{const.} \tag{4}$$

Substitution of Eq. (4) into Eq. (3) gives

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (k_1 + k_2\alpha^*)(1-\alpha) \equiv k(1-\alpha) \tag{5}$$

Equations (3)–(5) explain why such a catalytic thermal decomposition can be described by a first-order reaction. The reaction rate k depends on the temperature and on the thermodynamic properties of the reaction phase determining the solubility of the volatile catalytic products (α^*):

$$k = k_1 + k_2\alpha^* \tag{6}$$

The classical Arrhenius equation with two adjustable parameters (E_a and A) is widely accepted as describing the relationship between rate constant and temperature. Equation (6) may be written in the following form:

$$k \equiv k_1 + k_2\alpha^* = A_1 e^{-E_{a1}/RT} + \alpha^* A_2 e^{-E_{a2}/RT} \equiv A e^{-E_a/RT} \tag{7}$$

where A_1, A_2 and A are pre-exponential factors, and E_{a1}, E_{a2} and E_a are the activation energies for the first-order, autocatalytic and overall reactions, respectively. The value of E_a depends not only on the kinetics, but also on thermodynamic factors such as the relation between the stability of volatile catalyst (α^*) and temperature.

Experimental

TNT was synthesized and purified in the Department of Analytical Chemistry of the Institute of Organic Industry Chemistry. The purity, determined cryometrically, was 99.6 mol%.

Measurements were made on a heat-flux DSC 605 UNIPAN calorimeter. The calibration was performed with gallium, indium, cadmium, lead, tin, zinc, naphthalene and benzoic acid. The metals used had purities greater than 99.999%, and the organic compound had purities greater than 99.95%.

The measurements were made with hermetic aluminium pans. The samples were sealed under a reduced pressure of about 1.3 kPa. Samples of from 0.4 to 0.6 mg were subjected to total thermal decomposition at a heating rate of from 1 to 20 K min^{-1}. In partial thermal decomposition processes, the mass of samples was varied from 1 to 46 mg, with a heating rate of 2 K min^{-1}.

Results and discussion

A typical DSC curve for TNT, with two peaks, is depicted in Fig. 1. The first peak is due to the melting process, and the second to the thermal decomposition. The heat of thermal decomposition determined is $\Delta H_\text{D}=-462\pm10$ kJ mol^{-1}. The kinetic parameters were estimated from a single DSC run by the method of Borchardt and Daniels [6].

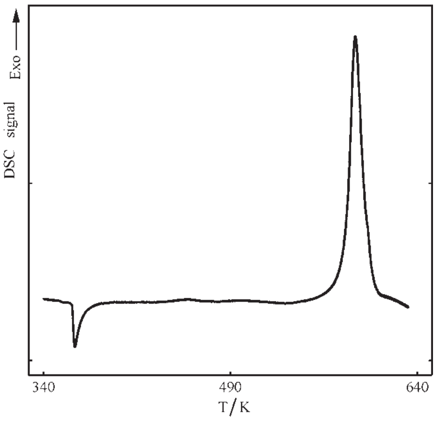

Fig. 1 Thermal DSC curve for TNT melting and decomposition

A and E_a were calculated on the basis of a pseudo-first-order reaction. The range of degree of conversion from α=0.02 to α=0.95 was taken for the kinetic analysis. A distinct change in the kinetic relation was observed near the peak maximum, indicating a change in the decomposition mechanism. This is probably connected with the exhaustion of the TNT. Further processes are then connected with the presence of thermal decomposition products or some reaction between them. It was demonstrated by Rogers [5] that, at the peak maximum, 94% of the TNT had decomposed, but only

64% of the total decomposition heat had been released. This leads to the conclusion that the subsequent significant heat quantity is a result of further decomposition of the products. As our interest related to the kinetic parameters of pure TNT, we decided to extrapolate these parameters to a small degree of conversion, arbitrarily chosen as α_e=0.02. The relation between the kinetic parameters and the range of the conversion degree (between α_e and α) was obtained by changing only the upper limit of the conversion degree (α_{max}) The kinetic parameters (ln*A* and E_a) and the upper limit of the conversion degree (α) extrapolated for a heating rate of 10 K min^{-1} for two samples are collected in Table 1.

Table 1 Kinetic parameters calculated from the range of conversion degree α_e=0.02 to α_{max} at a heating rate of 10 K min^{-1}

Mass/mg	ln$A$/s^{-1}	E_a/kJ mol^{-1}	α_{max}
0.40	80.04	405.02	0.4328
	79.78	406.18	0.1643
	77.62	393.72	0.2791
	71.61	365.75	0.1538
	63.38	327.57	0.0807
	56.85	297.32	0.0504
	53.84	283.44	0.036
	50.06	265.97	0.0287
0.58	74.15	379.86	0.1001
	70.71	363.78	0.0704
	66.61	344.68	0.0449
	64.05	332.76	0.0321
	62.20	324.14	0.0255

A linear relation was observed between ln*A* and E_a:

$$\ln A = B + CE_a \tag{8}$$

Equation (8) reflects a typical kinetic compensation effect [7–10]. Parameter *C* from Eq. (8) was used to estimate the isokinetic temperatures:

$$T_{iso} = \frac{1}{C}R \tag{9}$$

Values of *A* and E_a for different heating rate (β) are listed in Table 2. For easier comparison of the kinetic parameters obtained, the kinetic rate constants k_{530} at *T*=530 K were predicted and are given in the last column of Table 2. The values of the rate constant varied considerably, from k_{530}=0.7·10^{-5} to k_{530}=67.7·10^{-5} s^{-1}. The question arises of why the values of the rate constant of the thermal decomposition differ so considerably in spite of the fact that the DSC measurements were carried out by the same method and on the same substance. It might be supposed that it could be caused by the surface of the aluminium pan and solid particles changing the critical concentration of supersaturation of the catalytic products. The critical concentration is sometimes about 100 times greater than the equilibrium solubility [11]. The high values of the rate constants for low heating rate (β=1 K min^{-1}) indicate that the critical concentration of supersaturation of the volatile catalytic products (α^*) is higher.

Table 2 Extrapolated kinetic parameters of thermal decomposition up to the conversion degree α_e=0.02

β/K min^{-1}	ln$A$/s^{-1}	E_a/kJ mol^{-1}	k_{530}·10^5/s^{-1}
20	39.49	216.26	6.8
15	50.61	270.99	1.9
15	49.87	267.30	2.1
10	28.99	169.70	7.3
10	59.99	313.81	1.3
10	50.54	271.16	1.7
10	61.49	323.55	0.7
10	60.27	311.69	2.8
10	48.45	258.22	3.9
10	32.62	186.06	6.7
10	33.85	189.75	9.9
10	26.91	160.89	6.7
7	25.09	148.92	16.5
5	34.79	194.10	9.5
5	34.42	190.03	16.6
5	61.27	315.99	2.9
3.5	34.79	194.10	9.5
2	58.85	297.63	16.8
1	39.63	209.74	34.7
1	61.18	301.73	67.7

Parameters B and C from Eq. (8), the onset temperatures (T_{onset}) and the isokinetic temperatures (T_{iso}) for different heating rates are compiled in Table 3. The difference between the onset temperatures and the isokinetic temperatures is constant for different heating rates (β):

$$T_{\mathrm{iso}}-T_{\mathrm{onset}}=12.4\ \mathrm{K} \tag{10}$$

The dependence of k_{530} predicted from the kinetic parameters calculated from the minimal range of conversion degree from α_e=0.02 to $\alpha_{\min}$ for $k_{530\ \min}$, and from α_e=0.02 to $\alpha_{\max}$ for $k_{530\ \max}$, at different heating rates, are listed in Table 4. The increase in the range of conversion degree increases the value of the thermal decomposition rate constant. The ratio $k_{\max}/k_{\min}$ can be expressed as follows:

$$\frac{k_{\max}}{k_{\min}}=\frac{k_1+k_2\alpha^*_{\max}}{k_1+k_2\alpha^*_{\min}} \tag{11}$$

Table 3 Isokinetic temperatures, onset temperatures and parameters of Eq. (8) calculated from a single run

β/K min^{-1}	T_{onset}/K	B	C	T_{iso}/K
20	578.1	–6.2911	0.2117	568.2
15	577.3	–7.0227	0.2127	565.5
15	577.2	–6.7282	0.2117	568.1
10	573.2	–7.6792	0.2160	556.8
10	570.6	–7.2576	0.2143	561.3
10	575.0	–7.3579	0.2136	563.2
10	576.3	–7.2931	0.2126	565.8
10	564.4	–7.1871	0.2164	555.8
10	567.6	–7.2067	0.2155	558.1
10	568.1	–7.6123	0.2162	556.3
10	577.3	–7.4579	0.2177	552.6
10	571.1	–7.7910	0.2157	557.8
7	564.6	–7.1241	0.2163	556.1
5	550.6	–8.5157	0.2231	539.1
5	555.0	–8.5565	0.2262	531.8
5	559.4	–7.9995	0.2192	548.7
3.5	554.6	–8.5153	0.2231	539.1
2	538.0	–8.5698	0.2265	531.0
1	533.0	–8.9329	0.2316	519.5
1	528.5	–9.1112	0.2330	516.3

If it is assumed that $k_1 << k_2\alpha$, Eq. (11) can be written in the form

$$\frac{k_{\max}}{k_{\min}}=\frac{\alpha^*_{\max}}{\alpha^*_{\min}} \tag{12}$$

There are larger changes in α^* for higher heating rate (last column of Table 4). The ratio changes from 1 to 5.5.

Together with the increase in the conversion degree, the rate constant also rises, due to the increase in the critical concentration of volatile catalytic products in the reacting liquid phase. The difference in the rate constants is connected with uncontrolled parameters such as the magnitude of the gas–liquid surface in relation to the volume of the investigated sample, the properties of the surface pans used, and the amount of solid particles increasing that rate of evolution of volatile catalytic products from the chemical reaction phase, changing the critical supersaturation (α^*). The changes in the concentrations of the catalytic products lead to uncontrolled changes in the decomposition rate constant. Enlargement of the investigated mass sample diminishes the influence of the above-mentioned factors. With regard to the pan volume, it is possible to perform only partial thermal decomposition of the investigated sample. The upper limit of α depends strongly on the mass of sample used for the measurement. For m=46.8 mg, it is possible to obtain the upper limit of conversion degree α=0.0045. The DSC measurements with a sample mass greater than 1 mg were made at a heating rate β=2 K min^{-1}, because such a rate guaranteed safe interruption of the measurement at the moment of the sudden acceleration of the thermal decomposition processes. In accordance with expectation, the change in the kinetic parameters is very small.

Table 4 Rate constants estimated from lower limit range of conversion degree (from α_e=0.02 to α_{min}) and from the upper limit range (from α_e=0.02 to α_{max})

β/K min^{-1}	Mass/mg	α_{min}	α_{max}	$k_{530(min)}\cdot 10^5$/s^{-1}	$\mathrm{k}_{530(max)}\cdot 10^5$/s^{-1}	$\alpha^*_{max}/\alpha^*_{min}$
20	0.32	0.038	0.698	1.5	4.4	2.9
15	0.57	0.028	0.698	1.0	1.6	1.6
10	0.22	0.029	0.133	1.0	5.5	5.5
10	0.25	0.032	0.161	4.5	8.5	1.9
10	0.52	0.032	0.269	0.2	0.6	3.0
10	0.58	0.026	0.164	0.4	1.2	3.0
10	0.60	0.028	0.170	1.0	2.4	2.4
10	0.60	0.039	0.113	2.7	5.6	2.1
10	0.48	0.031	0.123	3.1	5.4	1.7
10	0.56	0.031	0.184	0.4	1.3	3.3
7	0.43	0.043	0.095	2.7	11.6	4.3
5	0.49	0.026	0.149	1.1	3.0	2.7
5	0.55	0.026	0.185	13.2	16.3	1.2
5	0.58	0.031	0.107	15.5	18.7	1.2
3.5	0.53	0.035	0.127	6.4	8.8	1.4
2	0.67	0.036	0.114	1.0	1.5	1.5
2	0.53	0.045	0.698	15.8	16.5	1.0
1	0.89	0.034	0.436	76.0	90.7	1.2
1	0.50	0.034	0.167	38.9	66.0	1.7

For low masses (m<1 mg), the parameters B and C in Eq. (8) were calculated in a similar way as for the samples with masses m>1 mg. They are also given in Table 5. Parameter C is approximately independent of the sample mass used for the measurement. It is worthy of mention that the values of the kinetic parameters change insignificantly. The rate constants predicted for T=530 K are almost independent of the sample mass greater than 15 mg. The kinetic parameters estimated from the whole range of conversion degree for the given sample are presented in Table 6. The predicted rate constants k_{530} are given in the last column; the values increase significantly for masses lower than 5 mg.

Table 5 Extrapolated kinetic parameters up to the conversion degree α_e=0.0045 at β=2 K min^{-1}

Mass/mg	B	C	ln$A$/s^{-1}	E_a/kJ mol^{-1}	$k_{530}\cdot10^5$/s^{-1}
46.80	–11.4206	0.23518	36.66	204.42	5.9
41.90	–11.2922	0.23352	37.52	209.02	4.9
30.35	–10.5677	0.22900	41.94	229.26	4.2
25.15	–10.7769	0.23206	39.03	214.63	6.3
20.55	–10.7671	0.23025	34.26	195.54	4.0
15.30	–8.9639	0.22294	39.70	218.29	5.3
5.35	–10.5770	0.23230	39.70	216.38	8.2
2.05	–9.5817	0.23230	39.59	212.64	17.3
1.32	–9.4097	0.23160	41.31	219.04	22.6

Table 6 Kinetic parameters estimated from full range of conversion degree for different samples

Mass/mg	ln$A$/s^{-1}	E_a/kJ mol^{-1}	α_{min}	α_{max}	$k_{530}\cdot10^5$/s^{-1}
46.80	45.56	242.22	0.0001	0.0053	8.2
41.90	48.45	256.21	0.0001	0.0057	6.1
30.35	45.69	246.06	0.0002	0.0101	3.9
25.15	44.16	237.17	0.0002	0.0109	6.3
20.55	29.29	174.39	0.0037	0.0184	3.4
15.30	41.42	226.22	0.0010	0.0558	4.9
12.32	51.14	268.86	0.0007	0.0367	5.2
10.06	52.42	274.83	0.00013	0.0065	4.8
7.40	60.51	312.86	0.0016	0.0780	2.8
5.35	57.65	297.39	0.0037	0.0184	5.3
2.17	66.14	328.08	0.0070	0.3470	24.5
1.05	79.68	386.13	0.0100	0.5840	35.4
1.05	60.88	304.00	0.0100	0.0990	30.1
1.05	114.18	540.78	0.1000	0.5890	19.3

Conclusions

The rate constants of thermal decomposition of 2,4,6-trinitrotoluene depend on the critical supersaturation of volatile catalytic product evolution from the liquid reaction phase. The critical concentration is connected with uncontrolled parameters. The results presented prove that increase of the sample mass diminishes the influence of these uncontrolled parameters on the rate constant for the thermal decomposition of TNT.

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