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Kinetics of exothermal decomposition of some ketone-2,4-dinitrophenylhydrazones

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Abstract In this study, the thermal stability and exothermal decomposition of some ketone-2,4-dinitrophenylhydrazones have investigated using the DSC technique. The synthesized and purified crystalline solids are thermally stable and start to decompose after melting. Non-isothermal DSC curves, recorded at several heating rates, were used to evaluate the melting properties and the kinetics of thermal decomposition. The isoconversional and model-fitting methods were applied to determine the activation parameters from the common analysis of multiple curves measured at different heating rates. Based on the results of the model—free method, a kinetic model was derived, and the kinetic parameters were obtained by means of a multivariate nonlinear regression. The results are discussed in relation to the effect of the ketone structure.

Keywords Differential scanning calorimetry · Exothermal decomposition · Isoconversional methods · Ketone-2,4-dinitrophenylhydrazones · Multivariate nonlinear regression

Introduction

Detection and measurement of the explosive properties of low- and high-energetic compounds is a subject of important interest for both practical applications and hazard analysis and prevention [1–3]. Among the available techniques, the differential scanning calorimetry (DSC) proved to be one of the most efficient methods for both screening and fundamental analyses of exothermic chemical reactions. Many organic compounds can decompose releasing a large amount of heat because of their thermodynamic instability. A frequently utilized reagent in analytical chemistry, 2,4-dinitrophenylhydrazine (DNPH), is known as a hazardous compound leading to explosive decomposition when heated [4, 5]. The important structural changes of DNPH, through derivatization of carbonyl compounds (aldehydes and ketones) with the formation of hydrazones, are expected to result in significant variations of their thermal stabilities. The characteristic features of these compounds are primarily of interest for risk assessment and also for structure–property relationship analysis. The study of the thermal stabilities of several hydrazones derived from the condensation of DNPH with different aldehydes [6, 7] have shown that small structural changes of aldehyde moiety can modify substantially the thermal behavior: some compounds decompose exothermically in the solid state, while others only after melting. These features cannot be safely predicted on the basis of structural considerations, and consequently, only the experimental study is able to give the right answer. The aim of this article is to study the thermal behavior of some ketone-2,4-dinitrophenylhydrazones in isothermal and non-isothermal regime. The derivatives are obtained from the condensation of DNPH with the corresponding ketone (acetone, methyl-ethyl-ketone, acetophenone, cyclopentanone, and cyclohexanone) as follows (Fig. 1):

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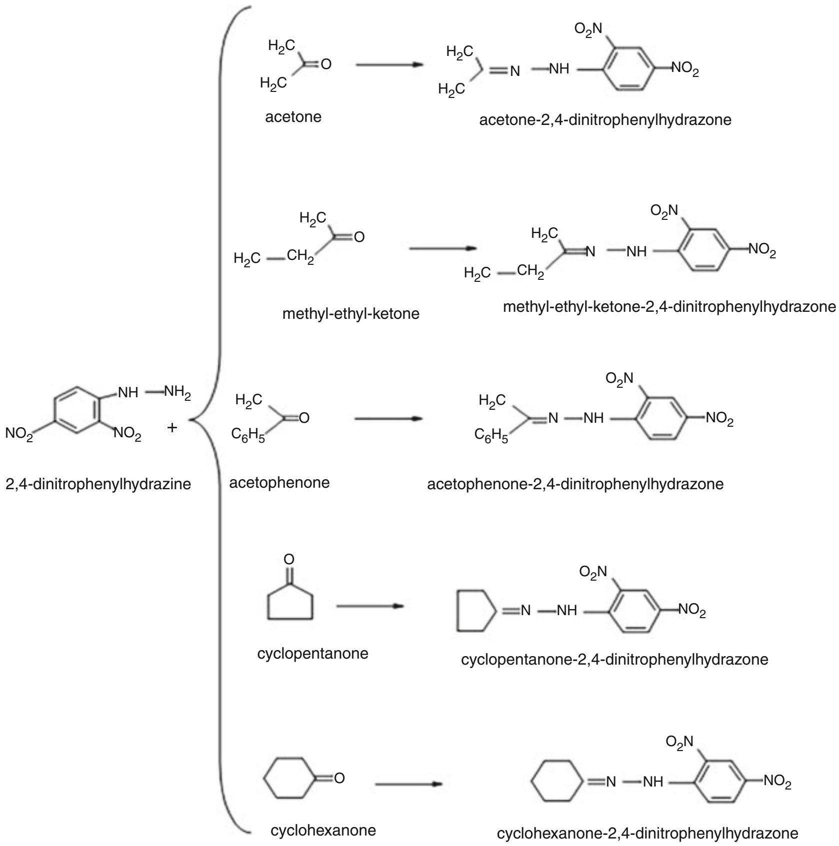
Fig. 1 DNPH and its condensation products with ketones



The thermal stabilities of the synthesized and purified hydrazones were investigated by differential scanning calorimetry (DSC) under isothermal and non-isothermal conditions. From the DSC curves, recorded at various initial temperatures and heating rates, the stability of the crystalline compounds was established and several physical properties, such as the melting point, the melting heat and the melting entropy, the average overall heat of the decomposition, and the maximum peak temperatures, were evaluated. The kinetic analysis started with the isoconversional differential Friedman [8] and integral Flynn–Wall–Ozawa (FWO) methods [9, 10], and the reaction model was validated by means of a multivariate nonlinear regression analysis. The activation energy was also determined using two equations based on the variable heating rate method, by differential Kissinger [11] and integral Ozawa [12] isoconversional methods. Investigation of the kinetics and mechanism of thermal decomposition of studied compounds can provide valuable information on the behavior of their hazardous nature.

Experimental

Synthesis of compounds

To the clear solution, obtained by warming of DNPH (25 mmol) in 10 mL concentrated hydrochloric acid and 250 mL ethanol, the carbonyl compound (25 mmol) was added and heated just to boiling. The reaction mixture was cooled to room temperature and was filtered and recrystallized from ethanol or glacial acetic acid. The compounds were purified by double recrystallization.

The thermal stability experiments were performed using a CAHN DSC 550 differential scanning calorimeter, within the temperature range 300–800 K. The samples of approximately 1 mg were held in aluminum crucibles with a pinhole in the lid to prevent pressure build up due to gaseous products. All the experiments were made in argon atmosphere with a 10 mL min^{-1} flow rate. Heating rates of 2, 4, 6, 8, 10, 15, 20, and 30 K min^{-1} were used. At the end of the heating process, the mass of the remaining sample represents approximately 30% from its initial values.

The melting temperatures were determined both in open capillary tubes using an electric STUART SMP3 Melting Point Apparatus and also from DSC curves. The calibration of DSC was made using the melting curves of two pure substances (indium and tin) in the same conditions as the experiments (onset temperature of the melting peak: 156.6 °C for indium and 419.6 °C for tin, heat of fusion: 28.6 J g^{-1} for indium and 107.5 J g^{-1} for tin).

The thermal behaviors of compounds in isothermal mode were followed at several temperatures at 5, 10, and 15 °C lower than the onset melting temperatures. Heating rate of 30 K min^{-1} ensured a fast heating between initial and working temperatures. The time necessary to reach the isothermal regime is negligible as compared to the isothermal one. No decomposition was identified after 2 h and less than 50% of sample was vaporized. For acetophenone-2,4-dinitrophenylhydrazone, the isothermal temperatures were of 517, 513, and 508 K. At 517 K, in isothermal mode, after 2 h, 30% of sample was vaporized, and for 508 K, the mass of vaporized sample was about 15%, respectively. These results show that, during an experiment, this mass loss significantly affects kinetic and thermodynamic parameters of melting and decomposition. All the compounds are accompanied by the vaporization process that begins to be significant at temperatures lower than the melting ones and increases for lower heating rates.

The experimental DSC curves were used to determine the characteristic melting and decomposition properties and to investigate the decomposition kinetics using the ''Netzsch Thermokinetics: A Software Module for the Kinetic Analysis of Thermal Measurements'' program [13, 14], which includes initially a model-free analysis according to isoconversional Friedman and FWO methods, followed by nonlinear regression analysis to determinate the multistep nature and kinetics of decomposition. For calculation, the raw DSC data were imported as ASCII files and corrected by the software using device-specific correction parameters. After loading the DSC curves, the measurements are desmeared and smoothed. The system function for the deconvolution of the original curves is obtained for the tail of a melting peak, using a pure sample with comparable heat conductivity and heat capacity. The Netzsch Thermokinetics software has several possibilities (linear, sigmoidal, left-starting, right-starting, etc) of constructing the baseline between the chosen limits of peak integration. A "zero"-baseline is the best alternative because the DSC scans have already been corrected with an independently measured base line. The "Netzsch Thermokinetics" software was subsequently used to predict the stability of the investigated compounds in molten state using the kinetic parameters and kinetic models obtained by nonlinear regression as starting values. Recently, this program was used for kinetic analysis of non-isothermal and isothermal data [15–18].

Results and discussion

An examination of the DSC curves shows that the decomposition occurs after melting and exhibits an exothermal peak.

For 10 K min^{-1} heating rate, acetone-2,4-dinitrophenylhydrazone shows an exothermal peak located at 568 K, after the melting process located at 400 K (Fig. 2).

The substitution of a methyl group with an ethyl group on the molecule of dinitrophenylhydrazone engenders no important changes of the thermal stability. The DSC curve, at 10 K min^{-1} heating rate, of methyl-ethyl-ketone-2,4-dinitrophenylhydrazone (Fig. 3) shows a melting process, located at 389 K (peak temperature) followed by exothermal decomposition with maximum at 560 K.

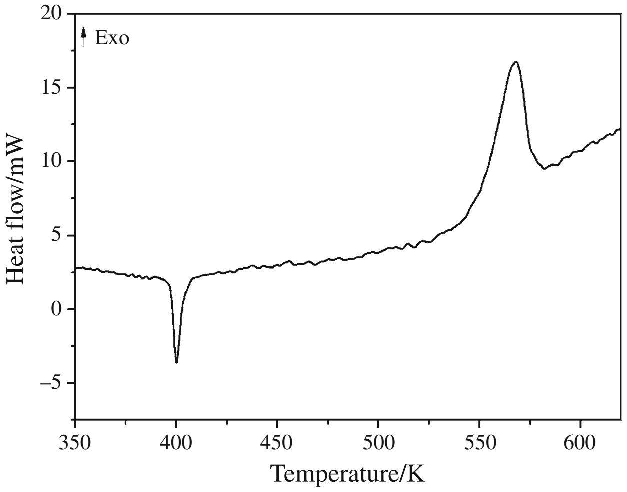


Fig. 2 The DSC curve of acetone-2,4-dinitrophenylhydrazone at 10 K min^{-1} heating rate

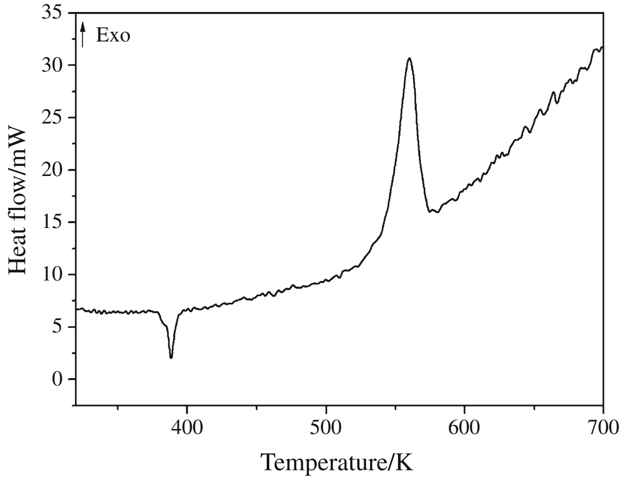


Fig. 3 The DSC curve of methyl-ethyl-ketone-2,4-dinitrophenylhydrazone at 10 K min^{-1} heating rate

For linear heating, acetophenone-2,4-dinitrophenylhydrazone decomposes exothermally after its melting. The exothermal process with the maximum temperature at 580 K (peak temperature) follows the endothermal process with the peak temperature located at 524 K, for a heating rate of 10 K min^{-1} (Fig. 4).

The DSC curve of cyclopentanone-2,4-dinitrophenylhydrazone given in Fig. 5 (for 10 K min^{-1} heating rate) shows an endothermal process located at 421 K followed by an exothermal one with maximum at 533 K.

For linear heating, cyclohexanone-2,4-dinitrophenylhydrazone decomposes exothermally after its melting. The

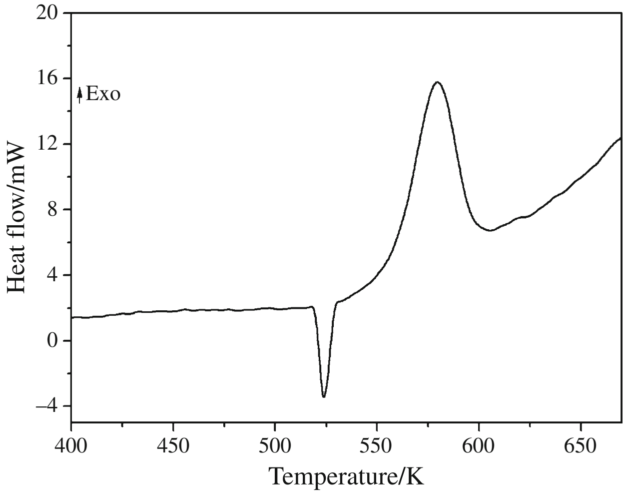


Fig. 4 The DSC curve of acetophenone-2,4-dinitrophenylhydrazone at 10 K min^{-1} heating rate

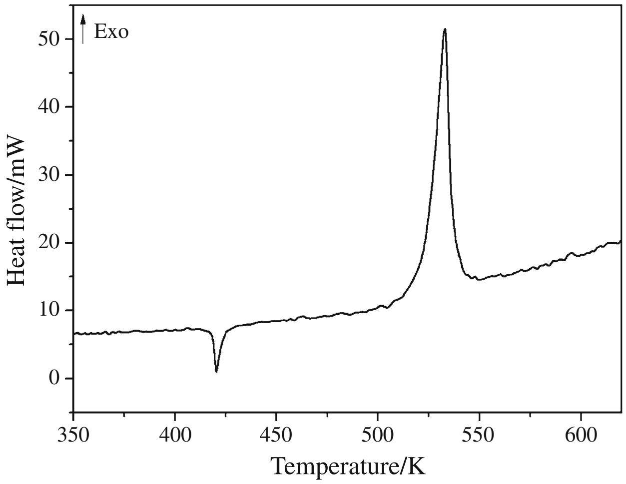


Fig. 5 The DSC curve of cyclopentanone-2,4-dinitrophenylhydrazone at 10 K min^{-1} heating rate

exothermal peak with maximum at 528 K follows the endothermal process located at 434 K (peak temperature), for a heating rate of 10 K min^{-1} (Fig. 6).

The melting properties and the decomposition heats, ΔH_d (determined from CAHN and "Netzsch Thermokinetic" programs), of the investigated compounds are given in Tables 1 and 2. The melting temperatures, determined from extrapolation to zero of the heating rates, are listed in Table 1 together with the literature data. The observed melting endotherms of the studied compounds are very sharp indicating the purity of the synthesized compounds. The melting temperatures, T_m, and the heats of melting, ΔH_m were used to calculate the melting entropies, as $\Delta S_m = \Delta H_m / T_m$.

The results indicate that ΔH_m and ΔS_m tend to increase with addition of a C_6H_5- group on the molecule in the ketone aliphatic compounds. The melting entropies are smaller for the cyclic compounds. The values of melting entropy are higher as compared with those determined for aldehyde-2,4-dinitrophenylhydrazones in our previous studies [6, 7]. In addition, the values of melting entropy are in the agreement with those reported in literature for similar compounds [2, 20, 21].

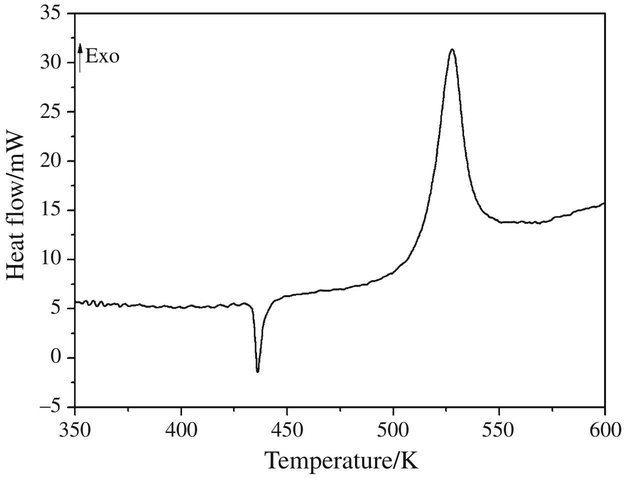


Fig. 6 The DSC curve of cyclohexanone-2,4-dinitrophenylhydrazone at 10 K min^{-1} heating rate

It can be observed that, for acetone-2,4-dinitrophenylhydrazone and cyclohexanone-2,4-dinitrophenylhydrazone, there is a significant increase of the enthalpy of decomposition with the increase of the heating rate. This can be attributed to the more important mass losses through vaporization occurring for lower heating rates.

The recorded curves were used to calculate the conversion versus temperature data subsequently used for kinetic analysis of the decomposition process using the "Netzsch Thermokinetic" program. The apparent values of the activation energy of the decomposition processes of the investigated ketone-2,4-dinitrophenylhydrazones were initially estimated using the isoconversional Friedman [8] and FWO analyses [9, 10], as a first approximation. Using the differential method according to Friedman, the regression of ln (dα/dt) versus 1/T for a given conversion, α, for measurements with different heating rates, gives the activation parameters according to Eq. 1:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha} = \ln[Af(\alpha)] - \frac{E_a}{RT}. \quad (1)$$

where α is the conversion, t the time, T the temperature, E_a the activation energy, and R the ideal gas constant. The activation energy was determined from the slope of isoconversional line, and the frequency factor A was determined from the intercept. The frequency factor is calculated for a first-order reaction with differential conversion function $f(\alpha) = (1 - \alpha)$.

Table 1 The properties of investigated ketone-2,4-dinitrophenylhydrazones

Compound	T_m(exp)/K (from DSC curves)	T_m(exp)/K (from open capillary tubes)	T_m (literature)/K [19]	ΔH_m(exp)/J g^{-1}/kJ mol^{-1}	ΔS_m(exp)/J mol^{-1} K^{-1}
Acetone-2,4-dinitrophenylhydrazone	398	399	399	141/33.5	84.2
Methyl-ethyl-ketone-2,4-dinitrophenylhydrazone	386	390	390	129/32.4	84.1
Acetophenone-2,4-dinitrophenylhydrazone	521	521	521	172/51.6	98.9
Cyclopentanone-2,4-dinitrophenylhydrazone	419	419	419	118/31.3	74.7
Cyclohexanone-2,4-dinitrophenylhydrazone	436	435	435	144/40.2	92.3

Table 2 The decomposition heats of ketone-2,4-dinitrophenylhydrazones

Compound	ΔH_{desc}/J g^{-1}	4 K min^{-1}	6 K min^{-1}	8 K min^{-1}	10 K min^{-1}	15 K min^{-1}
Acetone-2,4-dinitrophenylhydrazone	Netzsch Thermokinetics	793.8	778.2	867.2	797.9	1044.5
	CAHN DSC software	754.3	832.9	931.6	812.6	1164.1
Methyl-ethyl-ketone-2,4-dinitrophenylhydrazone	Netzsch Thermokinetics	1402.1	1337.2	1503.6	1416.3	1138.7
	CAHN DSC software	1282.4	1355.02	1357.9	1433.7	1125.3
Acetophenone-2,4-dinitrophenylhydrazone	Netzsch Thermokinetics	1205.6	1265.1	1089.8	1359.4	1229.4
	CAHN DSC software	1313.1	1376.6	1272.9	1381.2	1325.3
Cyclopentanone-2,4-dinitrophenylhydrazone	Netzsch Thermokinetics	1650.4	1959.8	1969.8	2091.1	2202.9
	CAHN DSC software	1524.2	1884.1	1961.9	1874.4	2028.4
Cyclohexanone-2,4-dinitrophenylhydrazone	Netzsch Thermokinetics	1579.5	1695.6	1867.2	1737.7	1871.7
	CAHN DSC software	1530.6	1595.8	1722.6	1636.9	1840.2

Table 3 Kinetic parameters for the thermal decomposition of acetone-2,4-dinitrophenylhydrazone

Conversion α	Friedman analysis		FWO analysis	
	E_a/kJ mol^{-1}	lg(A/s^{-1})	E_a/kJ mol^{-1}	lg(A/s^{-1})
0.10	138 ± 12	10	133.1 ± 6.1	9.6
0.20	135.9 ± 6.7	10	131.9 ± 4.3	9.7
0.30	134.0 ± 5.7	10	131.6 ± 3.6	9.8
0.40	136.2 ± 4.8	10	130.9 ± 3.4	9.8
0.50	139.9 ± 4.6	11	130.1 ± 3.7	9.7
0.60	134.6 ± 6.9	10	129.8 ± 3.7	9.9
0.70	135.1 ± 8.1	10	129.8 ± 3.9	9.9
0.80	135 ± 12	10	129.9 ± 4.3	10
0.90	135 ± 16	10	130.9 ± 4.9	10

Table 4 Kinetic parameters for the thermal decomposition of methyl-ethyl-ketone-2,4-dinitrophenylhydrazone

Conversion α	Friedman analysis		FWO analysis	
	E_a/kJ mol^{-1}	lg(A/s^{-1})	E_a/kJ mol^{-1}	lg(A/s^{-1})
0.10	122 ± 11	9.2	128.1 ± 7.9	9.3
0.20	125.2 ± 9.4	9.7	128.9 ± 4.5	9.6
0.30	137.4 ± 8.3	10	128.6 ± 2.8	9.7
0.40	129.6 ± 9.4	10	128.7 ± 2.2	9.8
0.50	141.3 ± 8.6	11	128.3 ± 1.9	9.8
0.60	143.6 ± 9.1	11	128.7 ± 2.1	9.9
0.70	144 ± 15	11	128.8 ± 2.4	10
0.80	157 ± 14	13	129.7 ± 2.9	10
0.90	157 ± 38	13	133.3 ± 5.0	10

For the integral method according to FWO [9, 10], lnβ is analyzed as a function of 1/T, for a given conversion according to Eq. 2:

$$\ln\beta = ct - 1.0518\frac{E_a}{RT}. \qquad (2)$$

where β is the heating rate. The activation energy E_a was determined from the slope of isoconversional line, and the frequency factor A was determined from the intercept. The frequency factor is calculated assuming a first-order reaction with integral conversion function $g(\alpha) = -\ln(1-\alpha)$.

The result of isoconversional Friedman and FWO analyses for the studied compounds are given in Tables 3, 4, 5, 6 and 7. Both the apparent values of activation energy determined by application of Friedman and FWO, respectively are independent on the conversion degree, and exhibit absolute values of the relative standard deviation lower than 10% for $0.1 \leq \alpha \geq 0.9$.

Since the activation energy is approximately the same for various conversions within the significant range 10–90%, it can be assumed that the thermal decomposition

Table 5 Kinetic parameters for the thermal decomposition of acetophenone-2,4-dinitrophenylhydrazone

Conversion α	Friedman analysis		FWO analysis	
	E_a/kJ mol^{-1}	lg(A/s^{-1})	E_a/kJ mol^{-1}	lg(A/s^{-1})
0.10	155.4 ± 6.1	11	166.1 ± 5.8	12
0.20	152.2 ± 6.8	11	161.7 ± 3.7	12
0.30	147.7 ± 5.0	11	159.3 ± 2.8	12
0.40	149.0 ± 5.4	11	157.2 ± 2.3	11
0.50	142.8 ± 3.6	11	155.6 ± 2.0	11
0.60	146.8 ± 4.0	11	153.9 ± 1.9	11
0.70	140.9 ± 3.8	10	152.7 ± 1.8	11
0.80	138.1 ± 4.5	10	150.5 ± 1.9	11
0.90	136.8 ± 5.6	10	147.4 ± 2.3	11

Table 6 Kinetic parameters for the thermal decomposition of cyclopentanone-2,4-dinitrophenylhydrazone

Conversion α	Friedman analysis		FWO analysis	
	E_a/kJ mol^{-1}	lg(A/s^{-1})	E_a/kJ mol^{-1}	lg(A/s^{-1})
0.10	120 ± 11	9.7	127.8 ± 4.5	9.8
0.20	121.8 ± 3.5	10	124.6 ± 3.5	9.7
0.30	120.1 ± 4.9	10	121.8 ± 2.4	9.6
0.40	124.1 ± 4.5	10	118.9 ± 2.1	9.4
0.50	125.4 ± 4.4	10	116.7 ± 1.6	9.3
0.60	128.8 ± 2.8	11	114.5 ± 1.3	9.1
0.70	136.2 ± 4.0	12	113.1 ± 0.8	9.1
0.80	132.2 ± 9.8	11	111.6 ± 1.1	9.0
0.90	147 ± 36	13	112.4 ± 1.2	9.2

of ketone-2,4-dinitrophenylhydrazones is likely to occur as single-step reactions.

The activation energy of the ketone-2,4-dinitrophenylhydrazones were also determined form DSC curves using the differential Kissinger method [11] according to equation:

$$\ln\left(\frac{\beta}{T_{\max}^{2}}\right) = \ln\left(\frac{AR}{T}\right) - \frac{E_{a}}{RT_{\max}}. \tag{3}$$

where β is the heating rate, and $T_{\max}$ is the peak temperature of a DSC scan at that rate. In the experiments, $T_{\max}$ value at various heating rates were collected, and values of $\ln\left(\frac{\beta}{T_{\max}^{2}}\right)$ were plotted against $\frac{1}{T_{\max}}$. The activation energy, E_a, was determined from the linear regression, assuming that the term $\ln\left(\frac{AR}{T}\right)$ was constant.

Using the Ozawa method [12], the regression of $\lg \beta$ versus $\frac{1}{T_{\max}}$ at various heating rates, gives the activation energy from the slope according to Eq. 4:

$$\lg \beta = ct - 0.4567\frac{E}{RT_{\max}}. \tag{4}$$

The results are listed in Table 8.

Table 7 Kinetic parameters for the thermal decomposition of cyclohexanone-2,4-dinitrophenylhydrazone

Conversion α	Friedman analysis		FWO analysis	
	E_a/kJ mol^{-1}	lg(A/s^{-1})	E_a/kJ mol^{-1}	lg(A/s^{-1})
0.10	97.2 ± 4.3	7.4	110.9 ± 1.7	8.2
0.20	95.3 ± 3.7	7.4	107.2 ± 1.6	8.0
0.30	106.2 ± 5.1	8.7	105.1 ± 1.7	8.0
0.40	99.3 ± 1.9	8.1	103.2 ± 1.7	7.9
0.50	98.0 ± 1.7	8.0	101.7 ± 1.9	7.8
0.60	93.8 ± 2.4	7.7	100.4 ± 1.9	7.8
0.70	86.5 ± 1.4	7.0	99.6 ± 2.0	7.8
0.80	65.8 ± 5.1	4.9	98.5 ± 1.7	7.7
0.90	49.3 ± 7.9	3.1	92.6 ± 1.6	7.2

To discriminate between different kinetic models, a multivariate nonlinear regression was applied on the dynamic DSC measurements, at different heating rates, to identify the possible number of reaction steps and to evaluate the corresponding kinetic parameters. The most probable kinetic model is chosen for highest F-test on Fit–Quality of the selected mechanisms available in the Netzsch Thermokinetics package and the best correlation coefficient [22, 23]. The calculations were performed for the range of the conversion degree $0.1 \leq \alpha \geq 0.9$.

The activation parameters of exothermal decomposition of the investigated compounds are listed in Table 9. The kinetic models assumed for single-step reaction was of the Prout–Tompkins equation (named as "model a"), Eq. 5, n-th order reaction with autocatalysis, according to Netzsch Thermokinetics nomenclature and Sestak–Berggren model (named as "model b", Eq. 6):

$$f(\alpha) = (1-\alpha)^{n}(1+K_{\mathrm{cat}}\alpha) \tag{5}$$

$$\mathrm{f}(\alpha) = \alpha^{a}(1-\alpha)^{n}. \tag{6}$$

where α is the conversion, K_{cat} is the catalytic constant, n and a are the partial reaction orders [24, 25].

Several other kinetic models available in the Netzsch Thermokinetics pack were analyzed and rejected according to the corresponding lower F-tests. By comparing the activation energies of decomposition with those obtained using model free methods, a good agreement is observed. The obtained activation energies are also in good agreement with those reported in the literature (100–400 kJ mol^{-1}) for similar nitro compounds decomposing by an autocatalytic mechanism [26–29].

The obtained parameters can be used for prediction of the stability of these compounds in molten state. The kinetic parameters were used to predict the time evolution of thermal decomposition of the studied compounds in molten state using Netzsch Thermokinetics program. The non-isothermal

Table 8 The activation parameters obtained from Kissinger and Ozawa methods

Compound	Kissinger		Ozawa		Temperature range/K
	E_a/kJ mol^{-1}	Correlation coefficient	E_a/kJ mol^{-1}	Correlation coefficient	
Acetone-2,4-dinitrophenylhydrazone	137.1 ± 0.5	0.997	139.1 ± 0.3	0.997	542–590
Methyl-ethyl-ketone-2,4-dinitrophenylhydrazone	122.7 ± 0.3	0.999	125.5 ± 0.1	0.999	530–583
Acetophenone-2,4-dinitrophenylhydrazone	159.2 ± 0.2	0.997	160.5 ± 0.1	0.997	556–599
Cyclopentanone-2,4-dinitrophenylhydrazone	115.2 ± 0.6	0.999	117.9 ± 0.2	0.999	505–556
Cyclohexanone-2,4-dinitrophenylhydrazone	106.3 ± 0.5	0.995	109.4 ± 0.3	0.999	498–551

Table 9 Kinetic parameters of exothermal decomposition

Compound	Kinetic parameters
Acetone-2,4-dinitrophenylhydrazone	E_a/kJ mol^{-1}: 153.8 ± 0.6 lg(A/s^{-1}): 12 n: 1.10 lgK_{cat}: 1.14 $f(\alpha)$–model a Correlation coefficient: 0.991
Methyl-ethyl-ketone-2,4-dinitrophenylhydrazone	E_a/kJ mol^{-1}: 134.7 ± 0.4 lg(A/s^{-1}): 11 n: 0.80 a: 0.62 $f(\alpha)$–model b Correlation coefficient: 0.991
Acetophenone-2,4-dinitrophenylhydrazone	E_a/kJ mol^{-1}: 160.1 ± 1.1 lg(A/s^{-1}): 13 n: 1.03 a: 0.44 $f(\alpha)$–model b Correlation coefficient: 0.995
Cyclopentanone-2,4-dinitrophenylhydrazone	E_a/kJ mol^{-1}:127.3 ± 0.9 lg(A/s^{-1}):9.3 n: 0.69 lgK_{cat}: 1.91 $f(\alpha)$–model a Correlation coefficient: 0.991
Cyclohexanone-2,4-dinitrophenylhydrazone	E_a/kJ mol^{-1}: 106.6 ± 0.7 lg(A/s^{-1}): 7.2 n: 1.44 lgK_{cat}:1 $f(\alpha)$–model a Correlation coefficient: 0.994

simulation of the decomposition reactions of the investigated compounds using the determined kinetic parameters and the chosen kinetic model show that acetone-2,4-dinitrophenylhydrazone totally decompose in final products after 1.2 min, acetophenone-2,4-dinitrophenylhydrazone after 2 min, and the others compounds after a 4 min reaction time.

Conclusions

The thermal stability of five ketone-2,4-dinitrophenylhydrazones was studied by DSC technique. The experimental curves recorded at several heating rates were analyzed by model—free Friedman and FWO methods, and also using two equations based on the variable heating rate method, by differential Kissinger and integral Ozawa methods. From the dependence of the activation energy on the conversion a single-step reaction was assumed. Its actual form was established using a multivariate nonlinear regression method. The results of thermal analysis show that the compounds first melts and, while in liquid form, decomposition starts with the degradation of the molecule to gaseous products and a solid residuum. The activation energies are smaller for the studied ketone-2,4-dinitrophenylhydrazones as compared with those obtained for aldehydes-2,4-dinitrophenylhydrazones in our previous studies. Also, differences appear in the decomposition mechanism: the ketone-2,4-dinitrophenylhydrazones decompose as a single-step reaction, while the thermal decomposition of aldehydes-2,4-dinitrophenylhydrazones occurs in several steps. The differences are attributable primarily to the nature of the substituents on the carbon of C=N group, which affects both the bond strength and steric factors with direct consequences on the packing in the liquid and solid states. The isothermal analysis indicates a good stability of ketone-2,4-dinitrophenylhydrazones in solid state. Their thermal decompositions are associated with the liquid state, a common characteristic of many nitro compounds.

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