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KINETICS OF EXOTHERMAL DECOMPOSITION OF 2-NITROPHENYLHYDRAZINE AND 4-NITROPHENYLHYDRAZINE USING DSC NON-ISOTHERMAL DATA

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Kinetics of exothermal decomposition of 2-nitrophenylhydrazine (2-NPH) and 4-nitrophenylhydrazine (4-NPH) was investigated by differential scanning calorimetry. The isoconversional methods, Friedman and Flynn–Wall–Ozawa, were applied to determine the activation parameters from the common analysis of multiple curves measured at different heating rates. For the processes involving two-step reactions the multivariate non-linear regression was used. A good agreement between the experimental and the fitted data was found.

Keywords: *DSC, model-free analysis, nitrophenylhydrazines, non-isothermal kinetics, non-linear regression*

Introduction

The characterization of decomposition reactions of condensed compounds is essential for developing safe chemical manufacturing processes and assessing the stability of chemicals under various conditions: chemical processing, storage and transportation [1–3]. For many exothermal decomposition reactions, experiments have shown that the acceleration of the reaction has both thermal and autocatalytic origin [4–7]. The mechanisms of these reactions have been analyzed and the kinetic equations have been derived [1, 8–10]. Chemical compounds able to decompose autocatalytically are considered more hazardous because the decomposition reactions can accelerate even under isothermal conditions during prolonged storage. Therefore, for assessing thermal hazards and determining the necessary safety recommendations, it is important to identify the decomposition mechanism. Among organic compounds, the nitro derivatives decompose when heated exhibiting large decomposition heat. In most cases the decomposition is explosive [11–13]. Many accidents induced by nitro derivative decompositions have been reported [4].

Differential scanning calorimetry (DSC) is widely used to provide information on initial decomposition temperature of energetic compounds, their decomposition enthalpy and other thermodynamic and kinetic properties without explosion risk because it operates with very small samples [14–16].

The aim of this paper is to study the thermal decomposition of 2-NPH and 4-NPH in non-isothermal regime. The nitrophenylhydrazines are frequently used in analytical chemistry for identification of carbonyl compounds through derivatization to nitrophenylhydrazones. From DSC curves, recorded at several heating rates, several properties such as the melting point, the melting heat, the temperature and heat of decomposition were evaluated. Isoconversional methods, Friedman and Flynn–Wall–Ozawa (FWO) [17–19] were applied to non-isothermal data measured at different heating rates yielding a dependence of the activation energy on conversion. From this dependence the multi-step nature of the processes was detected. The component steps were identified from the deconvolution of the DSC curves and their kinetic parameters were evaluated using linear and/or non-linear regression methods.

Experimental

2-NPH and 4-NPH were of reagent grade (Aldrich).

The thermal decomposition experiments were carried out using a CAHN DSC 550 instrument, at constant heating rates, and the range of temperature from 25 to 300°C. The heating rates were β=3, 5, 10 and 15 K min^{-1}. The samples with masses between 0.9–1.5 mg were contained in aluminum crucibles closed by a lid with a small hole to prevent pressure build up in the crucible during the decomposition due to the gaseous products. The experiments were carried out under argon atmosphere with a flow rate of 10 mL min^{-1}.

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When heated with constant rates both compounds decompose exothermally after melting. The experimental curves were used to investigate the decomposition kinetics using both isoconversional (the differential Friedman and integral FWO methods) and multivariate non-linear regression methods (‘Netzsch Thermokinetics’ program).

The thermal behavior of 2-NPH and 4-NPH in isothermal mode was followed at several temperatures lower than the onset decomposition temperatures. No decomposition was identified after one hour when more than 50% of sample was vaporized.

Results and discussion

Under linear heating rates, 2-NPH and 4-NPH show endothermal processes associated with melting, followed by exothermal decompositions. Figure 1 shows the curve of 2-NPH for a heating rate of 10 K min^{-1}. After the endothermal process with the peak temperature T_{min}=79°C, two separate exothermal processes appear with peak temperatures T_1^{max}=177°C (exotherm 1) and T_2^{max}=203°C (exotherm 2). The evaluation of peak areas gives 58 J g^{-1} for the endothermal process and for each exothermal process ΔH_1=–571 J g^{-1} and ΔH_2=–415 J g^{-1}.

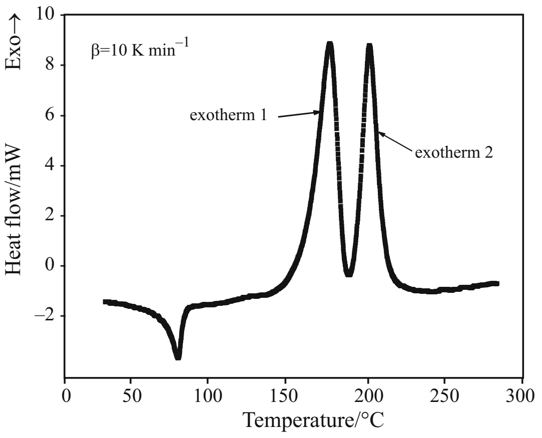

Fig. 1 DSC curve of 2-NPH

The DSC curve of 4-NPH for a heating rate of 10 K min^{-1} is represented in Fig. 2. The curve indicates an endothermal peak, associated with the melting process at peak temperature T_{min}=156°C and ΔH=111 J g^{-1}, which is immediately followed by an exothermal decomposition with peak temperature T_{max}=202°C and ΔH=–802 J g^{-1}.

It can be observed that the melting and beginning of decomposition are partially superposed. The corresponding melting and decomposition heats were initially evaluated neglecting this superposition.

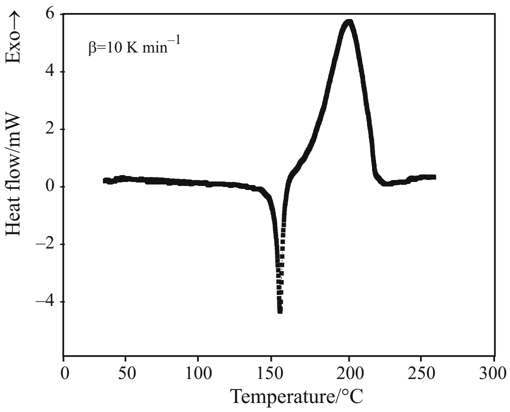

Fig. 2 DSC curve of 4-NPH

According to a less accessible mechanistic study [20] the first exothermal peak of 2-NPH can be attributed to intermolecular dehydration forming 1-hydroxybenzotriazole (HOBT) and the second one to the decomposition of HOBT formed in the first step of decomposition. The exothermal peak of 4-NPH was also attributed to dissociation of hydrazino and nitro groups.

The recorded curves were used to calculate the conversion *vs.* temperature data subsequently used for kinetic analysis.

The apparent values of the activation energy for the decomposition process of the two nitrophenylhydrazines were initially estimated using the isoconversional Friedman and FWO methods. Using the differential method according to Friedman, the regression of ln(dα/d*t*) *vs.* 1/*T* for a given conversion, for measurements with different heating rates, gives the activation parameters according to Eq. (1) [21]:

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_\alpha = \mathrm{cons}\tan t - \frac{E_\alpha}{RT} \qquad (1)$$

where α is the conversion, dα/d*t* is the rate of conversion, E_α the activation energy, *R* the molar gas constant and the subscript α indicates the values related to a given conversion.

For the integral method according to FWO lnβ is analyzed as a function of 1/*T*, for a given conversion according to Eq. (2) [21]:

$$\ln\beta = \mathrm{cons}\tan t - 1.0518\frac{E_\alpha}{RT_\alpha} \qquad (2)$$

For both methods 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 for a first-order reaction with differential conversion function *f*(α)=(1–α) for Friedman method. According to FWO method the frequency factor can be obtained assum-

Table 1 Kinetic parameters for the thermal decomposition of 2-NPH (exotherm 1)

Conversion (α)	Friedman analysis		FWO analysis	
	E/kJ mol^{-1}	lg$A$/s^{-1}	E/kJ mol^{-1}	lg$A$/s^{-1}
0.05	79.4±11.1	6.8	83.0±8.2	6.8
0.10	88.4±7.9	8.1	84.4±7.8	7.1
0.20	98.4±5.8	9.5	84.1±7.1	7.7
0.30	100.8±5.8	9.9	88.8±6.9	8.0
0.40	104.7±0.9	10.4	90.2±5.9	8.3
0.50	104.8±1.8	10.5	91.5±5.4	8.5
0.60	104.2±1.0	10.6	92.5±5.0	8.7
0.70	104.5±0.4	10.7	93.8±4.6	9.0
0.80	108.3±1.3	11.2	95.6±4.2	9.3
0.90	111.5±2.1	11.7	97.7±3.9	9.6
0.95	115.1±0.7	12.1	99.1±3.5	9.9

Table 2 Kinetic parameters for the thermal decomposition of 2-NPH (exotherm 2)

Conversion (α)	Friedman analysis		FWO analysis	
	E/kJ mol^{-1}	lg$A$/s^{-1}	E/kJ mol^{-1}	lg$A$/s^{-1}
0.05	164.5±1.3	16.0	123.3±3.9	10.5
0.10	163.4±0.2	16.0	127.6±4.0	11.3
0.20	170.0±4.4	16.9	132.8±4.1	12.1
0.30	175.0±5.7	17.6	136.3±4.4	12.7
0.40	175.8±6.9	17.7	138.9±4.7	13.1
0.50	178.7±5.4	18.1	143.3±4.9	13.7
0.60	178.8±3.7	18.1	147.5±5.2	14.2
0.70	178.5±4.9	18.1	151.2±4.9	14.7
0.80	185.0±11.6	18.8	156.3±5.0	15.4
0.90	211.1±22.6	21.5	167.4±6.2	16.7
0.95	220.3±32.1	22.5	176.9±11.5	17.7

ing a first-order reaction with integral conversion function $g(\alpha)=-\ln(1-\alpha)$.

The results from the above model-free analysis of 2-NPH decomposition are given in Tables 1 and 2 for each exothermal peak.

A significant variation of the activation energy with conversion, within the significant range 5–95%, resulted from differential Friedman method of analysis was observed. This result clearly shows that at least two-steps must be considered for each exothermal peak.

To discriminate between different kinetic models, a multivariate non-linear regression was applied. A two-step consecutive reaction model was found as a first approximation for both first and second exothermal peaks of 2-NPH, when the overlap was neglected. The evaluated kinetic parameters are given in Table 3.

It can be seen that the main contribution to each exotherm is given by the first step.

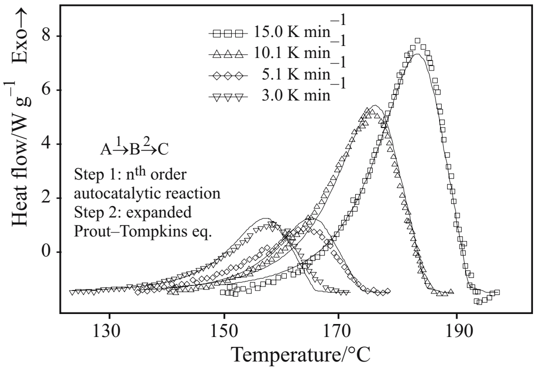

Fig. 3 Experimental and fitted data of DSC curves for 2-NPH (exotherm 1)

The good agreement between experimental DSC curves and the fitted data are shown in Figs 3 and 4.

The next step in the analysis of exotherm 1 and exotherm 2 was to take into account their partial over-

Table 3 Results of non-linear regressions for separate exotherms of 2-NPH

	Exotherm 1		Exotherm 2	
	$A\xrightarrow{1a}B\xrightarrow{2a}C$		$A\xrightarrow{1b}B\xrightarrow{2b}C$	
E/kJ mol^{-1}	93.0	112.0	164.0	180.0
lg$A$/s^{-1}	8.2	9.5	16.7	15.9
n	0.8	0.5	1.2	0.8
	lgK_{cat}=1.2	a=0.6	a=0.5	lgK_{cat}=0.9
Contribution	90%		92%	
Correlation coefficient	0.994		0.998	

1a, 2b – $f(\alpha)=(1-\alpha)^n(1+K_{cat}\alpha)$, n^{th}-order reaction with autocatalysis [19]

1b, 2a – $f(\alpha)=\alpha^a(1-\alpha)^n$, a^{th}-degree autocatalytic reaction with a n^{th}-order reaction (expanded Prout–Tompkins equation) [19]

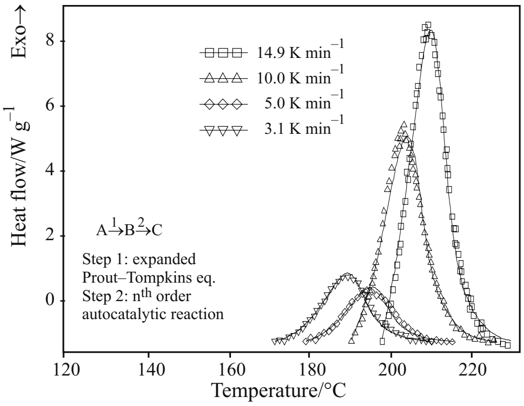

Fig. 4 Experimental and fitted data of DSC curves for 2-NPH (exotherm 2)

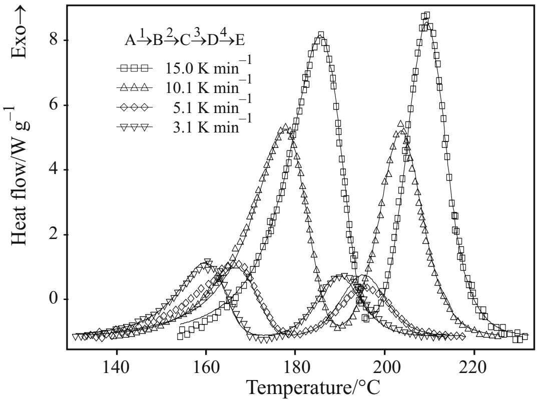

Fig. 5 Experimental and fitted data for thermal decomposition of 2-NPH

lap. The results of the non-linear regression analysis for the best kinetic model (highest F-test) $A\xrightarrow{1}B\xrightarrow{2}C\xrightarrow{3}D\xrightarrow{4}E$ are given in Fig. 5 and Table 4. Steps 1 and 4 are n^{th}-order reactions with autocatalysis and steps 2 and 3 are a^{th}-degree autocatalytic reactions with an n^{th}-order reaction (expanded Prout–Tompkins equation).

A better fit was obtained for the overall analysis of DSC curve when the overlap of the two exotherms was also taken into account. The kinetic parameters of the first three steps, according to the assumed mechanism, agree well with those obtained from the analysis of separate exotherms. Important differences were however obtained for the fourth step. The existence of this step was proved by the statistical analysis of either separate or overlapped exotherms (worse fits were obtained when this step was neglected). The found differences can be attributed either to overlap omission or to its low contribution to the overall reaction.

The same procedure was applied to determine the kinetic parameters for the thermal decomposition of 4-NPH. The results of model-free analysis according to Friedman and FWO methods are given in Table 5.

It can be seen that the activation energy has a high value at the beginning of decomposition due to the influence of the melting process. Since the activation energy is approximately the same for various conversions within the significant range 5–95%, it

Table 4 Results of non-linear regression for four-step decomposition mechanism of 2-NPH

Kinetic parameters			
Step 1	Step 2	Step 3	Step 4
E_1/kJ mol^{-1}=92.9	E_2/kJ mol^{-1}=84.2	E_3/kJ mol^{-1}=156.4	E_4/kJ mol^{-1}=120.0
lgA_1/s^{-1}=8.3	lgA_2/s^{-1}=8.6	lgA_3/s^{-1}=15.9	lgA_4/s^{-1}=8.8
n_1=0.6	n_2=1	n_3=1.3	n_4=0.4
lgK_{1cat}=1.0	a_2=0.7	a_3=0.6	lgK_{4cat}=1.3
contribution=48%	contribution=8%	contribution=42%	
Correlation coefficient=0.998			

Table 5 Kinetic parameters for the thermal decomposition of 4-NPH

Conversion (α)	Friedman analysis		FWO analysis	
	E/kJ mol^{-1}	lg$A$/s^{-1}	E/kJ mol^{-1}	lg$A$/s^{-1}
0.05	102.2±8.2	9.0	133.1±5.7	12.3
0.10	97.9±5.1	8.6	123.0±4.9	11.2
0.20	98.4±6.6	8.8	115.4±4.4	10.5
0.30	96.5±4.5	8.6	110.3±4.2	9.9
0.40	98.3±4.9	8.9	108.0±4.2	9.8
0.50	95.0±5.6	8.6	106.5±4.1	9.6
0.60	95.1±5.7	8.6	104.7±4.4	9.5
0.70	92.5±4.4	8.4	103.0±4.4	9.3
0.80	91.8±5.0	8.4	101.3±4.5	9.2
0.90	99.2±5.3	9.3	99.9±4.4	9.1
0.95	98.6±8.2	9.3	100.1±4.3	9.2

Table 6 Results of linear regression for exothermal decomposition of 4-NPH

Kinetic parameters	Statistics
E/kJ mol^{-1}=95.2	Correlation coefficient=0.995
lg$A$/s^{-1}=8.6	
n=0.74	
a=0.30	

Table 7 Results of non-linear regression for 4-NPH

Kinetic parameters	
Step 1	Step 2
$f(\alpha)=(1-\alpha)^n$ (n^{th}-order)	$f(\alpha)=\alpha^a(1-\alpha)^n$ (expanded Prout–Tompkins equation)
E_1/kJ mol^{-1}=839.3	E_2/kJ mol^{-1}=94.9
lgA_1/s^{-1}=101.2	lgA_2/s^{-1}=8.5
n=0.35	n=0.73
	a=0.26
Correlation coefficient=0.995	

can be assumed that the thermal decomposition of 4-NPH is likely to occur as a single-step reaction.

The linear regression analysis applied as a first approximation to the thermal decomposition of 4-NPH, neglecting the partial overlap with the melting process, for a single-step reaction with $f(\alpha)=\alpha^a(1-\alpha)^n$ reaction type, leads to the kinetic parameters listed in Table 6. The fit between experimental and calculated data is presented in Fig. 6.

The next step in the analysis of thermal decomposition of 4-NPH was also to take into account the possible superposition of melting and decomposition processes. The results of the non-linear kinetic analysis for the best kinetic model A$\xrightarrow{1}$B$\xrightarrow{2}$C are given in Table 7 and Fig. 7.

The melting process is approximated by a n^{th}-order reaction of high activation energy and a small reaction order. It can be seen that melting and decomposition, two well separated processes, do not interfere significantly.

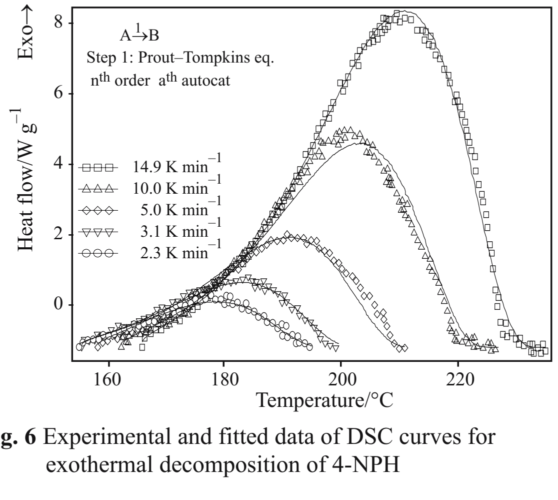

Fig. 6 Experimental and fitted data of DSC curves for exothermal decomposition of 4-NPH

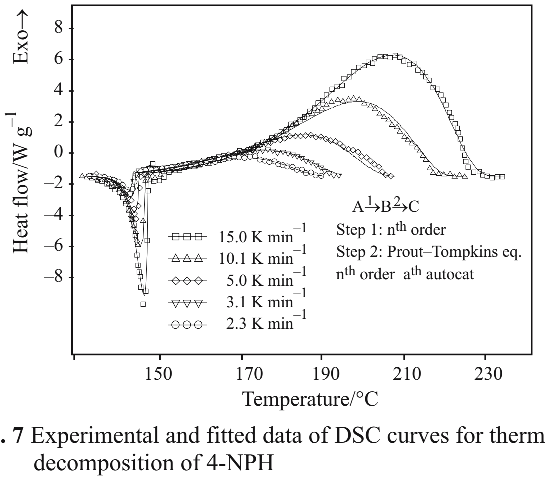

Fig. 7 Experimental and fitted data of DSC curves for thermal decomposition of 4-NPH

Several other kinetic models available in the Netzsch Thermokinetics pack were analyzed and rejected according to the corresponding lower F-tests.

The obtained parameters can be used for prediction of the stability of these compounds in molten state.

Conclusions

The study of thermal behavior of 2-NPH and 4-NPH showed that both compounds exhibit an exothermal decomposition after the melting process proving their hazardous nature. The thermal decomposition of 2-NPH shows two exothermal peaks, whereas 4-NPH shows only one. The evaluation of melting temperature showed that the melting of 2-NPH occurs at a temperature about 77°C lower than for 4-NPH. The corresponding melting heat is also lower for 2-NPH. All these differences revealed a lower stability of 2-NPH as compared to 4-NPH according with literature studies concerning thermal stability of *ortho* and *para* isomers. A similar behavior is also found for these compounds when the onset temperatures and the overall decomposition heats were compared. The decomposition of 2-NPH begins at a temperature about 24°C lower than for 4-NPH. The overall heat of decomposition of 2-NPH is 200 J g^{-1} higher than for 4-NPH.

The results of kinetic analysis indicate the existence of specific reaction mechanisms of thermal decomposition of these two compounds. The thermal decomposition of 2-NPH follows a complex reaction mechanism with at least two significant steps, whereas 4-NPH shows a single-step reaction. The differences observed in the thermal decompositions of 2-NPH and 4-NPH can be attributed to the position of the $-NO_2$ group on the aromatic ring. The decomposition mechanism for both 2-NPH and 4-NPH demonstrated the existence of autocatalytic steps, frequently encountered for the decomposition of nitro derivatives.

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