NON-ISOTHERMAL KINETIC ANALYSIS OF THERMAL DECOMPOSITION OF 2, 4-DINITROPHENYLHYDRAZINE

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The thermal decomposition of 2, 4 - dinitrophenylhydrazine (DNPH) occurring after melting has been studied using TG/DTA and DSC techniques. Non-isothermal TG/DTA and DSC curves, recorded at several heating rates, were used to evaluate the kinetics of thermal decomposition. Both isoconversional and model fitting methods were used for the evaluation of kinetic parameters. From the model-free method it was found that the thermal decomposition of DNPH is a three - step consecutive reaction. Based on the results of the model - free method, the kinetic model was derived and the kinetic parameters were obtained by means of a multivariate non-linear regression.

INTRODUCTION

The knowledge of thermal behavior of condensed compounds is vital for assessing the stability of such compounds under various conditions. The nitro - derivatives constitute a very important class frequently encountered in chemical industry and in different laboratories. Thermal runaway incidents caused by nitro compounds are due to –NO$_2$ group, which is intrinsically unstable.[1, 2] Nitro compounds are also used as explosives because of their characteristic exothermal decomposition with sudden gas evolution and shock wave. Many accidents caused by nitro compounds have been reported.[3, 4] Several studies on thermal behavior of nitro compounds have been made in order to provide thermal stability information such as initial decomposition temperature and decomposition enthalpy.[1] Chemical reactivity of such compounds can lead to significant hazards under certain conditions, and uncontrolled reactions can develop under reactive chemical incidents.[5, 6] Without a proper control of hazards and risk, chemical incidents can cause numerous losses in the process industries. Not only thermodynamic properties of reactants, intermediates and products, but also the kinetics of possible reactions represents the possible requirements for identifying and assessing risks. Various techniques of thermal analysis have been applied to determine the thermal behavior of nitro compounds.

DNPH, a common example of this group of compounds, is a reagent frequently used in analytical chemistry for derivatization of carbonyl compounds, [7] as shown in Fig. 1:
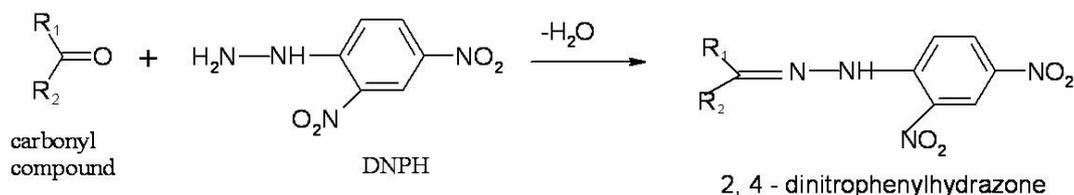

Fig. 1 – DNPH and its condensation product with a carbonyl compound.

In this paper the thermal decomposition of DNPH was investigated by TG/DTA and DSC methods, under non-isothermal conditions. The kinetic parameters of DNPH decomposition were

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obtained by differential isoconversional Friedman method and the reaction model was validated by means of a multivariate non-linear regression analysis. Investigation of the kinetics and mechanism of thermal decomposition of DNPH can provide valuable information on the behavior of its hazardous nature.

A preliminary DSC analysis of thermal behavior of DNPH indicated its instability at temperatures higher than $180^{\circ}C$ (for samples of 1-2 mg) in both solid and molten states.[8] The kinetics of its isothermal decomposition in solid state was recently reported.[9]

EXPERIMENTAL PART

DNPH was Aldrich reagent grade (reported m.p. = $197 – 200^{\circ}C$).

The thermal decomposition experiments were performed on a Mettler – Toledo STAR SW 7.01 thermal analyzer TG/DTA and a CAHN DSC 550 differential scanning calorimeter, within the temperature range $25 – 300^{\circ}C$.

The samples were held in aluminum crucibles with a pinhole in the lid to prevent pressure build up due to gaseous products. The TG curves were recorded in nitrogen atmosphere with a flow rate of 10 mL min^{-1} and at heating rates of 2, 5 and 10 K min^{-1}. The DTA curves were calculated from the sample thermocouple signal and were subsequently designated as c-DTA. The DSC curves were obtained under argon atmosphere, with heating rates of 2, 2.5, 5 and 10 K min^{-1}. The extrapolation to zero heating rate of the melting peak gave the melting point of $197.9^{\circ}C$. Sample mass was between 1 and 1.5 mg for both methods. At the end of the heating process the remaining sample mass represents approximately 30% from its initial value.

The TG/c-DTA and DSC curves were used to characterize the accompanying mass and heat changes during the linear heating and to perform the kinetic analysis of DNPH decomposition. The kinetic parameters were calculated using the "Netzsch Thermokinetics" software program.[10]

RESULTS AND DISCUSSION

TG and DTG curves of the thermal decomposition of DNPH for three heating rates are shown in Figs. 2 and 3.
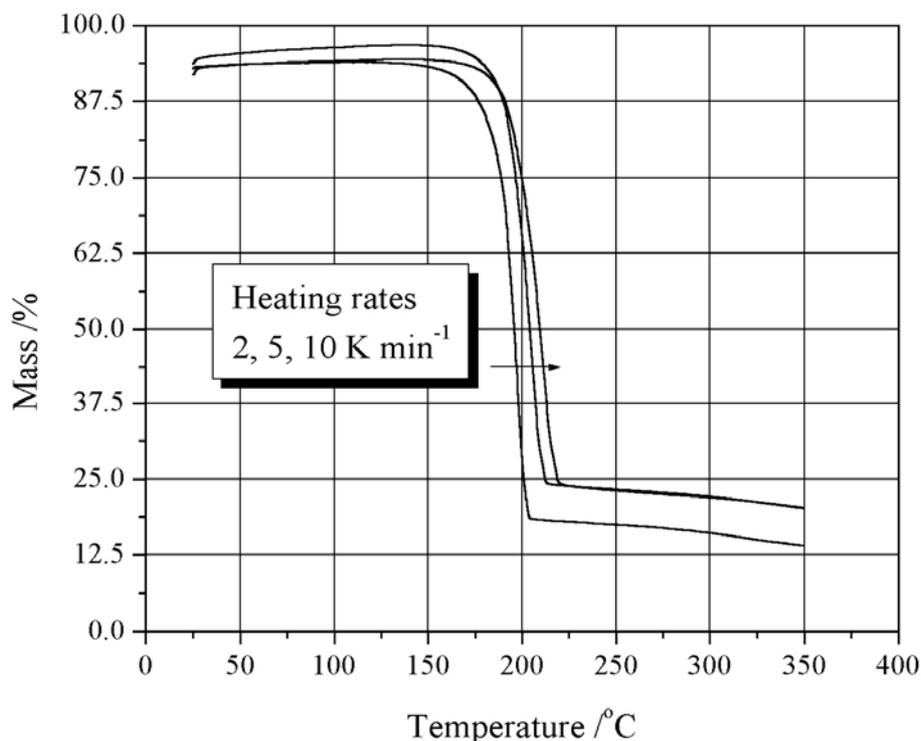

Fig. 2 – TG curves of DNPH at different heating rates.

The DTG curves given in Fig. 3 show two consecutive peaks at $211.4^{\circ}C$ and $217.6^{\circ}C$. A weak shoulder is observed at $194.9^{\circ}C$, which becomes more distinct when the curve is recorded at 2 K min^{-1}.
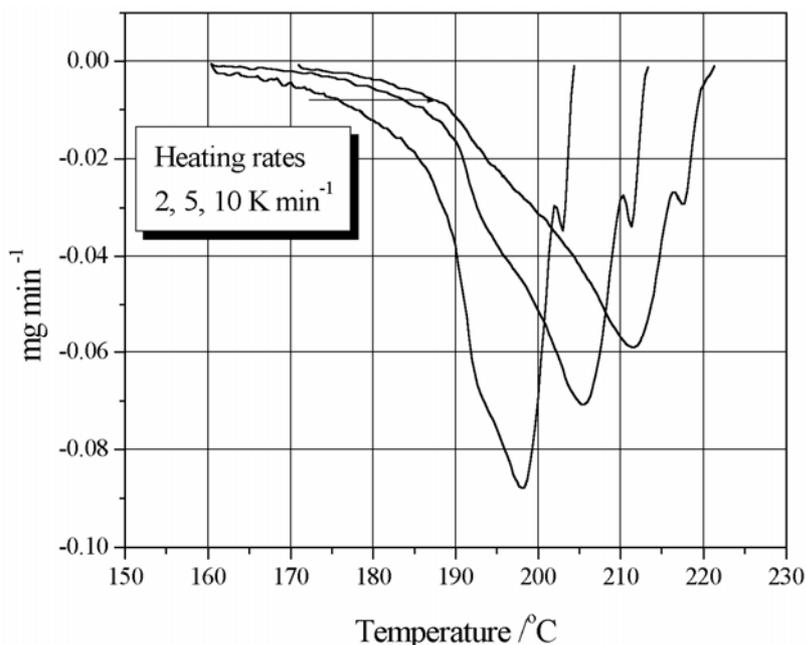
Fig. 3 – DTG curves of DNPH at different heating rates.

TG/c-DTA curves of DNPH at a heating rate of 5 K min^{-1} are shown in Fig. 4. The endothermal DTA peak starts after a significant mass loss, which could be associated with sample vaporization and solid state decomposition. The exothermal DTA peak closely corresponds to the weight loss from TG curve associated with the DNPH decomposition.
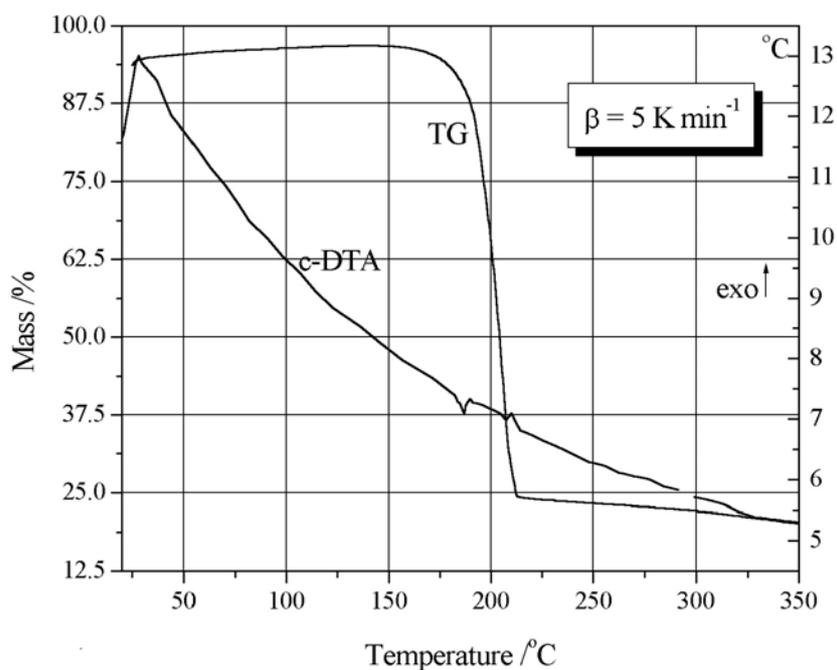

Fig. 4 – TG/c-DTA curves of DNPH at heating rate of 5 K min^{-1}.

The TG curves of DNPH measured with several heating rates were used to evaluate the activation energy by differential isoconversional method.[11]

The Friedman differential analysis[11] is based on the Eq. (1):

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha} = \text{constant} - \frac{E_{\alpha}}{RT} \qquad (1)$$

where α is the conversion, $d\alpha/dt$ is the rate of conversion, E the activation energy, R the molar

gas constant and the subscript α indicates the values related to a given conversion.

The regressions of $\ln(d\alpha/dt)$ versus $1/T$ should give a straight line with the slope directly proportional to the activation energy. The estimated

values of the apparent activation energy of thermal decomposition of DNPH from TG curves are presented in Fig. 5.
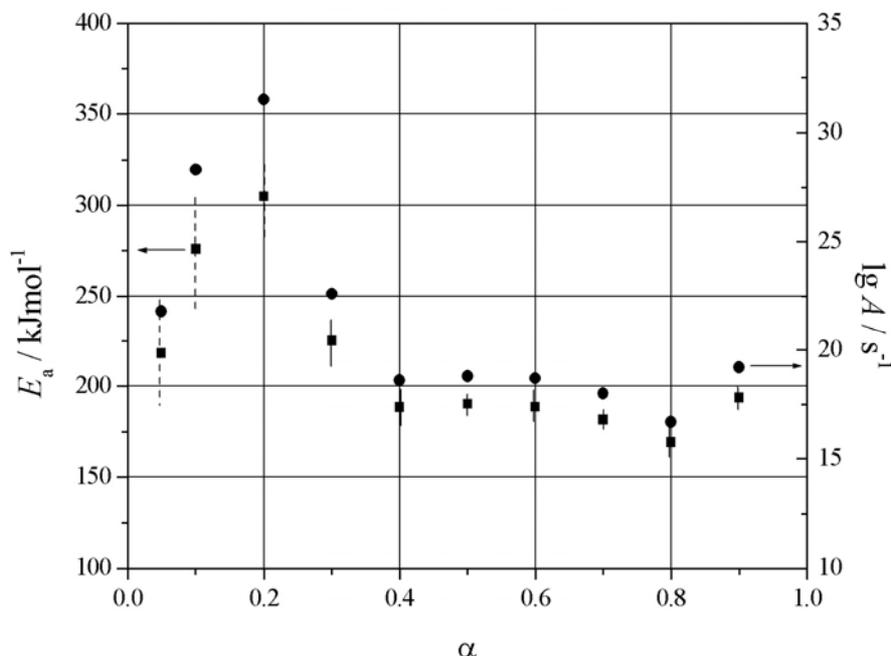

Fig. 5 – E_a and lg A – dependencies on conversion from Friedman analysis.

The significant variation of the activation energy with conversion, within the range 5% - 90% confirms the existence of a multi - step mechanism suggested also by DTG curves. Accordingly, the possible steps through which the decomposition process can occur were investigated. A multivariate non-linear regression on the dynamic TG measurement runs at different heating rates was performed to determine the most probable kinetic model.[12 - 14] Considering the fitting quality (highest F – test), the following three - step mechanism $A \xrightarrow{\ 1\ } B \xrightarrow{\ 2\ } C \xrightarrow{\ 3\ } D$ was accepted as the most probable for the thermal decomposition

of DNPH, each step of n-th order with autocatalysis (Prout – Tompkins equation):

$$f(\alpha) = (1 - \alpha)^n (1 + K_{cat}\alpha) \qquad (2)$$

where K_{cat} is the catalytic constant.

Several other kinetic models available in the "Netzsch Thermokinetics" package were analyzed and rejected according to the corresponding lower F - tests. The results of the non - linear regression analysis are listed in Table 1, and the curves fitted to the experimental ones are shown in Fig. 6.

Table 1

Results of non - linear regression for the three step – mechanism

Kinetic parameters		
Step 1	Step 2	Step 3
E / kJmol⁻¹: 255.9	E / kJmol⁻¹: 175.0	E / kJmol⁻¹: 150.0
lg A/s⁻¹: 26.3	lg A/s⁻¹: 18.4	lg A/s⁻¹: 13.9
n: 1.20	n: 1.26	n: 1.17
lg K_{cat}: 0.50	lg K_{cat}: 0.87	lg K_{cat}: 1.26
contribution: 26%	contribution: 30%	contribution: 44%
Correlation coefficient: 0.999		

It can be seen that the largest contribution to the overall decomposition reaction is given by the third step. A three – step mechanism for DNPH thermal decomposition could imply the following chemical transformations:
Step 1: the intermolecular dehydration forming 4 – nitro – 1 - hydroxybenzotriazole;
Step 2: the break of N-N-N triazole bond;

Step 3: the decomposition of compound formed in step 2 to gaseous and solids products.

Two exothermal steps were identified and reported for the thermal decomposition of a related compound (*ortho*-nitrophenylhydrazine).[15] The presence of a second nitro group, with high oxidation power, is likely to introduce a new step in the overall decomposition process.
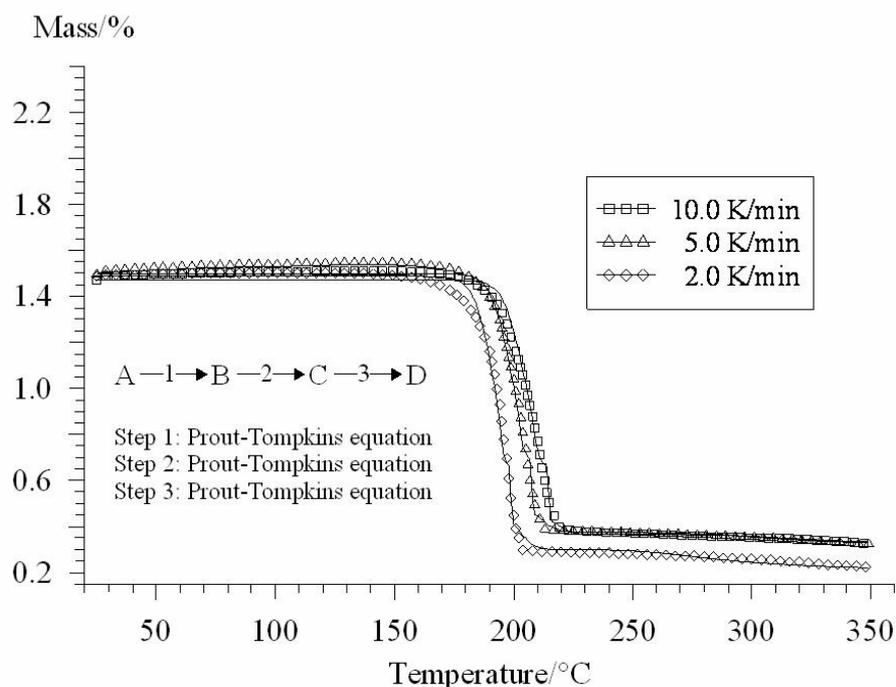

Fig. 6 – Fit of TG measurements for thermal decomposition of DNPH.

Additional information on the thermal decomposition of DNPH can be obtained from DSC curves, associated with the heat effects accompanying the overall process.

A typical DSC curve of DNPH is shown in Fig. 7 at 10 K min^{-1} heating rate. The endothermal peak located at about 198.8°C, with ΔH value of 73.3 Jg^{-1}, is due to the melting process. The thermal decomposition starts at 200.6°C after melting and is apparently the result of superposition of three distinct steps with two maxima. The first exothermal maximum appears at 208.4°C and the second one at 214.9°C. It can be observed that the melting and the beginning of the decomposition process are partially overlapped. The result suggests that the decomposition can be

also modeled as a composite process having at least three steps.

The same procedure described above was applied to evaluate the kinetic parameters for the thermal decomposition of DNPH using DSC data. The results of the non - linear kinetic analysis, neglecting the partial overlap with the melting process, for the best kinetic model, $A \xrightarrow{1} B \xrightarrow{2} C \xrightarrow{3} D$ (highest correlation coefficient and F - test) are given in Table 2 and Fig. 8. A reasonable agreement between the DSC and TG analysis concerning the decomposition mechanism was observed: a three - step consecutive reaction mechanism with an autocatalytic kinetic model for each step (according to Eq. (2)).
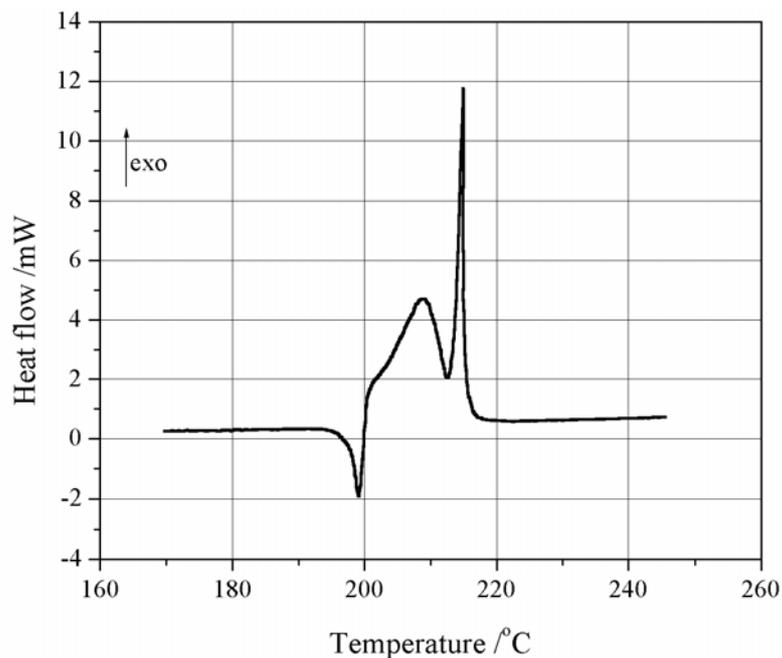
Fig. 7 – DSC curve of DNPH with a heating rate of 10 K min^{-1}.

Table 2

Results of non - linear regression for DSC data

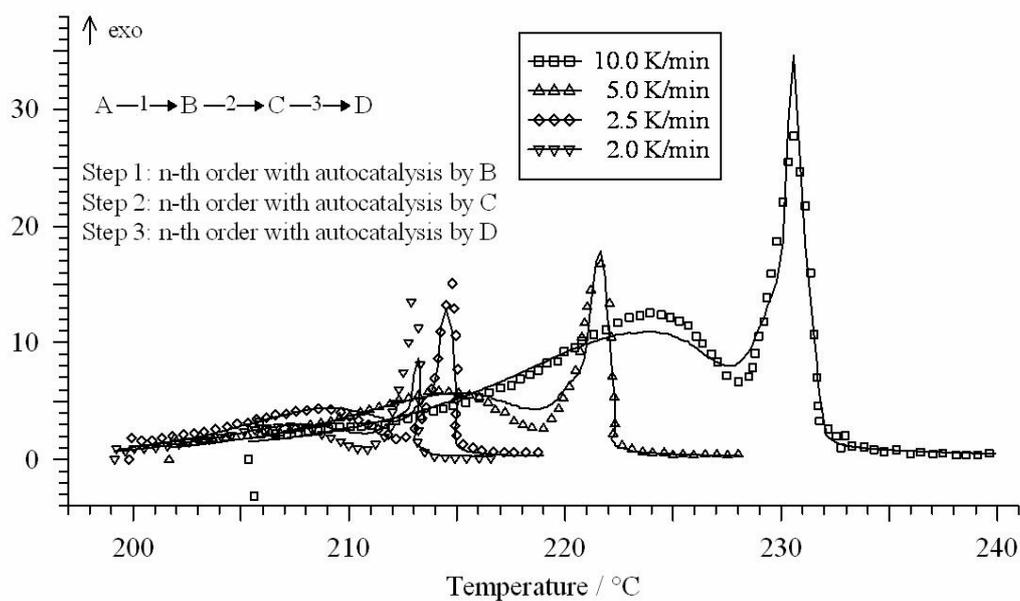| Kinetic parameters		
Step 1	Step 2	Step 3
E (kJ/mol): 129.7	E (kJ/mol): 121.0	E (kJ/mol): 159.0
Lg(A/s^{-1}): 11.4	lg(A/s^{-1}): 5.7	lg(A/s^{-1}): 15.0
n: 0.81	n: 0.50	n: 4.00
lg K_{cat}: 0.80	lg K_{cat}: 6.25	lg K_{cat}: 2.39
contribution: 76%	contribution: 13%	contribution: 11%
Correlation coefficient: 0.965		

Fig. 8 – Fit of DSC measurements of DNPH.

It is worth to notice that the numerical results from DSC curves differ significantly from those calculated from TGA curves, although the overall trend is maintained. The differences can be ascribed to the different weights of the component steps arising from mass losses or from heat effects.[16 - 18] It is also obvious from the values of the correlation coefficients that the DSC data do not fit the analysis as well as the TG data. The lower quality of DSC results is probably due to the influence of delayed heat transfer. Analysis of DSC data, on the other hand, shows an improvement based on the better resolution of the processes. It also offers the possibility to establish the runaway nature of the decomposition process.

It can be concluded that DNPH is thermally unstable and decomposes exothermally in molten state, following a multi - step mechanism. A similar mechanism was also found for its decomposition in solid state.[9] Although the component steps present specific features, in solid and liquid states, both mechanisms imply autocatalytic steps, a characteristic of thermal decomposition of nitro compounds.[19 - 21]

CONCLUSIONS

The thermal decomposition of DNPH was studied by thermal analysis TG/DTA and DSC techniques. The experimental curves recorded at several heating rates were analyzed by Friedman model - free differential method. The strong dependence of the activation energy on the conversion imposed the use of a multi - step kinetic model. Its actual form was established using a multivariate non - linear regression method. The results of kinetic analysis show that DNPH decomposes through three consecutive autocatalytic reactions. The substance first melts and, while in liquid form, dehydration starts as a first step, followed by the break of N-N-N triazole bond and ends by the final degradation of the molecule to gaseous products and a solid residuum.

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