

# Kinetic analysis of isothermal decomposition of 2,4-dinitrophenylhydrazine using differential scanning calorimetry

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## Abstract

Differential scanning calorimetry was used to study the thermal decomposition of 2,4-dinitrophenylhydrazine (DNPH) in isothermal regime. The DSC curves were carried out at several constant temperatures lower than the melting temperature. The standard isoconversional analysis of the obtained curves suggests an autocatalytic decomposition mechanism. This mechanism is also supported by the temperature dependence of the observed induction periods.

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## 1. Introduction

The thermal stability of condensed compounds can be studied under both isothermal and non-isothermal conditions. The experimental techniques such as thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC) generate the necessary experimental data [1,2].

DNPH, currently used for derivatization of carbonyl compounds for their quantitative analysis [3], decomposes exothermally after melting [4]. Its thermal stability under various conditions is of interest for risk evaluation.

Solid nitro derivatives decompose usually after melting following an autocatalytic complex mechanism [5,6]. Exothermal decomposition in solid state is also of practical interest for hazard evaluation before melting. The DSC curves offer useful physical and thermodynamic decomposition parameters. They can be also used for the kinetic analysis of the process.

In this study the thermal behavior of DNPH was followed using differential scanning calorimetry in isothermal regime.

## 2. Experimental

2,4-Dinitrophenylhydrazine was Aldrich reagent grade

The thermal decomposition experiments were carried out under argon atmosphere with a flow rate of 10 mL min<sup>-1</sup>, using a CAHN DSC 550 differential scanning calorimeter. Instrument calibration was performed with standard indium samples of known temperatures and enthalpies of melting. The samples with mass between 1 and 1.5 mg were enclosed in aluminum crucibles with a pinhole in the lid. To evaluate the thermal behavior of DNPH within a wide temperature range, a non-isothermal experiment was performed with a heating rate of 10 K min<sup>-1</sup>. The results were used to set out the solid-state temperature range. The isothermal decomposition reaction was followed up to a temperature lower than the melting point. The temperatures of 182, 185, 187, 190, 192, 195 and 197 °C were selected for the experiments. A heating rate of 20 K min<sup>-1</sup> ensured a fast heating between initial and working temperature. Isothermal DSC run was stopped when no further process was observed.

## 3. Results and discussion

Under linear heating DNPH shows a melting peak at 202 °C (peak temperature) which is immediately followed by the exothermal decomposition between 205 and 230 °C with a mul-

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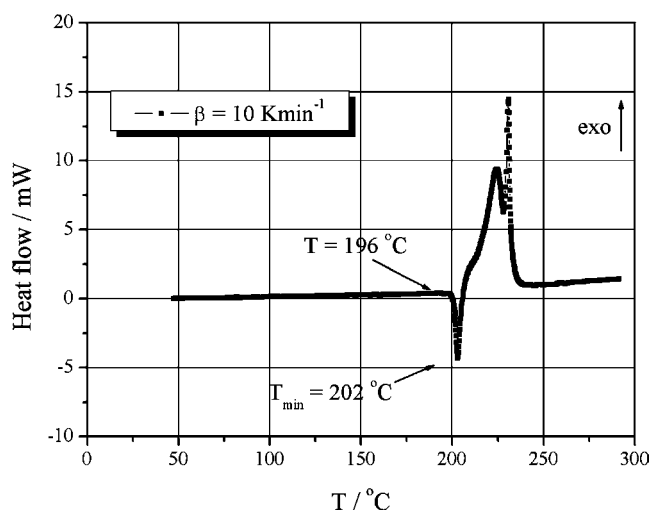


Fig. 1. The DSC curves in non-isothermal regime.

tistep exothermal pattern. A typical curve is shown in Fig. 1 for a heating rate of  $10 \text{ K min}^{-1}$ . It can be seen that the melting and decomposition processes are partially overlapped. The decomposition process occurs in this case in liquid phase.

For solid-state stability study, several experiments in isothermal regime were performed. Fig. 2 shows the DSC curves for thermal decomposition of DNPH reached at three fixed temperatures.

It can be observed that two separated exothermal peaks appeared after a characteristic temperature dependent induction period. At  $195^\circ\text{C}$ , close to the melting temperature, the DSC curve presents also an endothermic peak associated with partial melting and the last exothermal peak better separated than for linear heating.

The recorded curves were used to calculate the conversion versus time data subsequently used for kinetic analysis.

The isothermal conversions versus time curves at different temperatures are given in Figs. 3 and 4 for the two exothermal peaks.

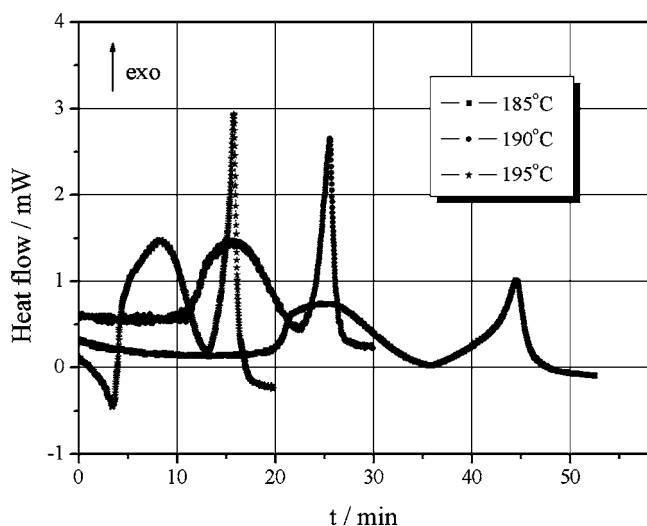


Fig. 2. The DSC curves for different isothermal decomposition experiments.

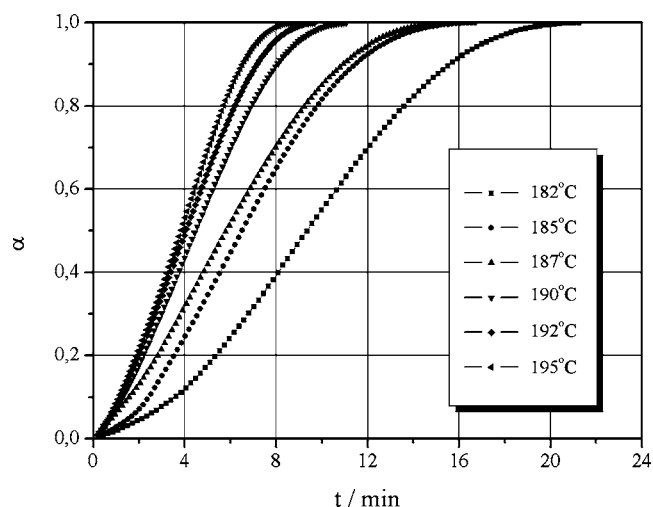


Fig. 3. Conversion vs. time curves at different temperatures for the first exothermal peak.

As can be seen from Figs. 3 and 4, the conversion–time curves have a characteristic sigmoid shape.

For the kinetic analysis of the thermal decomposition, the reduced time plots were constructed. Generalized reduced time plots [7,8], in which  $\alpha$  values for each curve are plotted as a function of the ratio  $t/t_{0.5}$  ( $t_{0.5}$  being the experimental time corresponding to  $\alpha = 0.5$ ) are given in Figs. 5 and 6.

It can be seen that the conversion–reduced time plots have also a sigmoid form. The comparison of experimental  $\alpha(t/t_{0.5})$  plots with those reported in literature [7,8] suggests that either a process controlling mechanism of nucleus production and growth or the existence of an autocatalytic mechanism is expected for this thermal decomposition. Additional arguments necessary to discriminate between these mechanisms can be obtained from the shape of reaction rate against time dependence. From the conversion–time data, the conversion rate  $(d\alpha/dt)$ –time curves were obtained using a local polynomial regression according to Savitzky–Golay method [9]. The con-

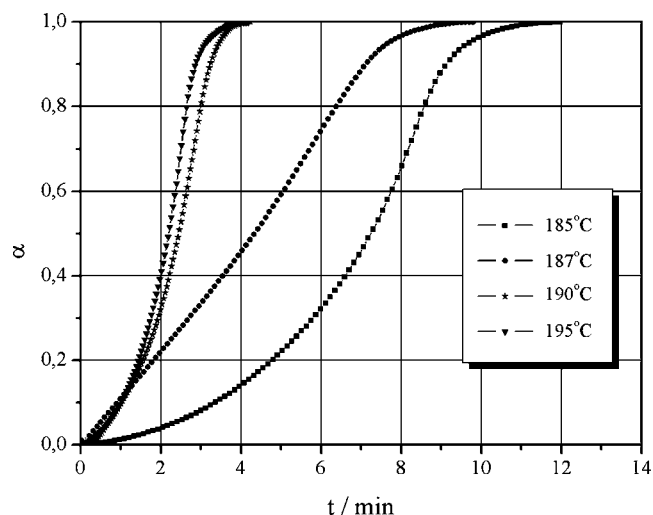


Fig. 4. Conversion vs. time curves at different temperatures for the second exothermal peak.

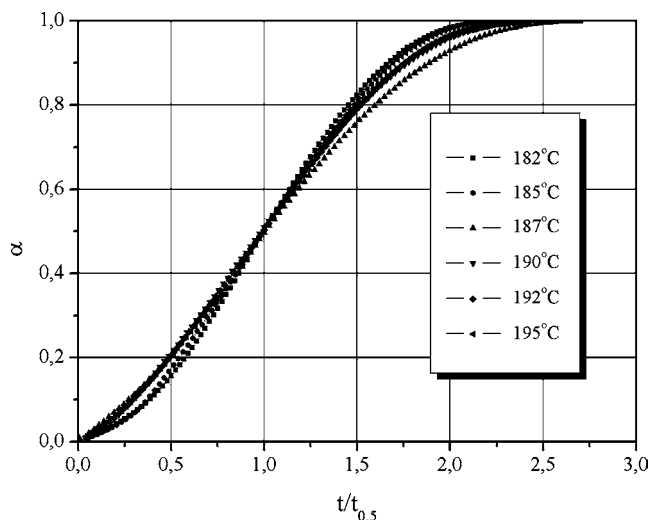


Fig. 5. Conversion vs. reduced time plots carried out at fixed temperatures for the first exothermal peak.

version rates versus time for the various temperatures are given in Figs. 7 and 8.

As shown in Figs. 7 and 8 the conversion rate peak becomes higher and shifts to shorter times when the temperature increases. This pattern confirms the existence of an autocatalytic mechanism for this thermal decomposition [8].

Similar isothermal data reported in literature were analyzed using either integral or differential isoconversional methods. The qualities and drawbacks of these methods were critically discussed by Vyazovkin [10]. Although the integral method introduces systematic errors in the evaluated activation energies, it is less sensitive to experimental noise. A comparative study of these methods is expected to discriminate between their prediction powers of measured data.

The kinetic parameters of decomposition were estimated using the both isothermal isoconversional methods. Using the

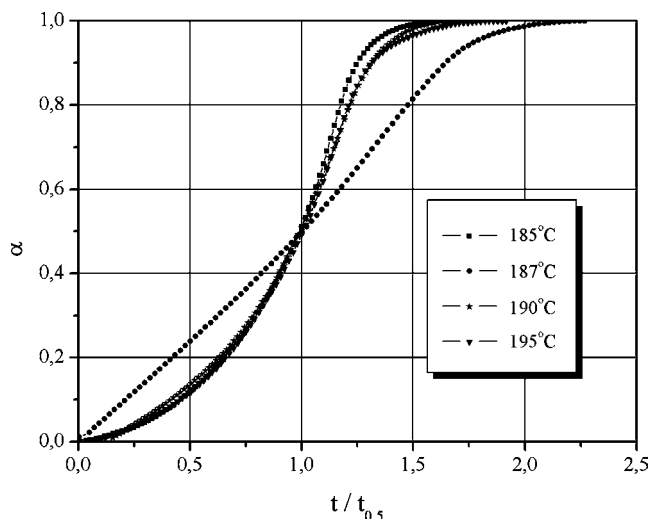


Fig. 6. Conversion vs. reduced time plots carried out at fixed temperatures for the second exothermal peak.

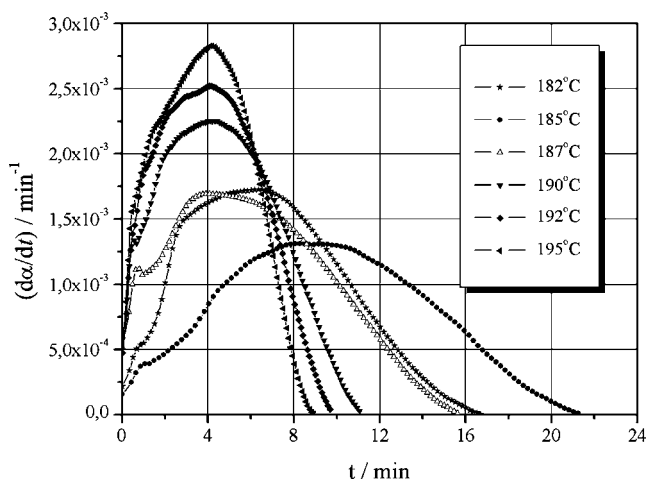


Fig. 7. Conversion rate vs. time for the first exothermal peak.

integral isoconversional method, according to Eq. (1) [11,12]:

$$-\ln t = \ln \left( \frac{A}{g(\alpha)} \right) - \frac{E_a}{RT} \quad (1)$$

a plot of  $-\ln t$  versus  $1/T$  yields  $E_a$  for selected conversions, where  $t$  is the isoconversional time,  $A$  is the pre-exponential factor,  $E_a$  is the activation energy,  $T$  is the absolute temperature,  $R$  is the molar gas constant and  $g(\alpha)$  is the integral conversion function. The basic assumption of this method is that  $g(\alpha)$  at constant conversion does not vary with temperature [13]. The intercept  $\ln[A/g(\alpha)]$  is used to evaluate the pre-exponential factor when a certain form of  $g(\alpha)$  is assumed.

Using the isoconversional differential Friedman's [14] method, according to Eq. (2):

$$\ln \left( \frac{d\alpha}{dt} \right) = \ln [A f(\alpha)] - \frac{E_a}{RT} \quad (2)$$

a plot of  $\ln(d\alpha/dt)$  versus  $1/T$  at each  $\alpha$  yields  $E_a$  for  $\alpha = \text{constant}$ . The pre-exponential factor was also calculated from the intercept, assuming a certain form of the corresponding differential conversion function,  $f(\alpha)$ .

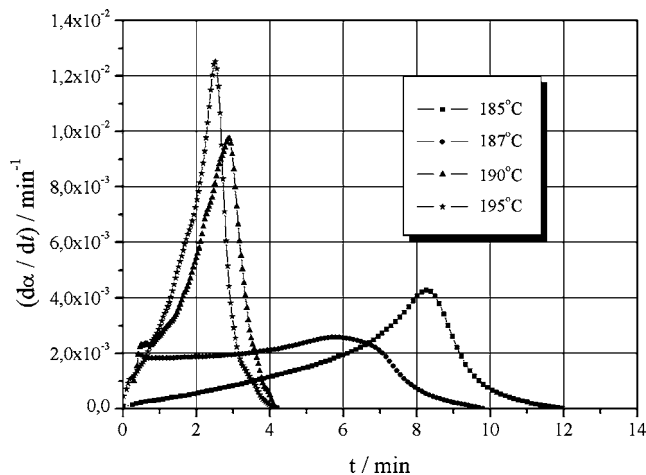


Fig. 8. Conversion rate vs. time for the second exothermal peak.

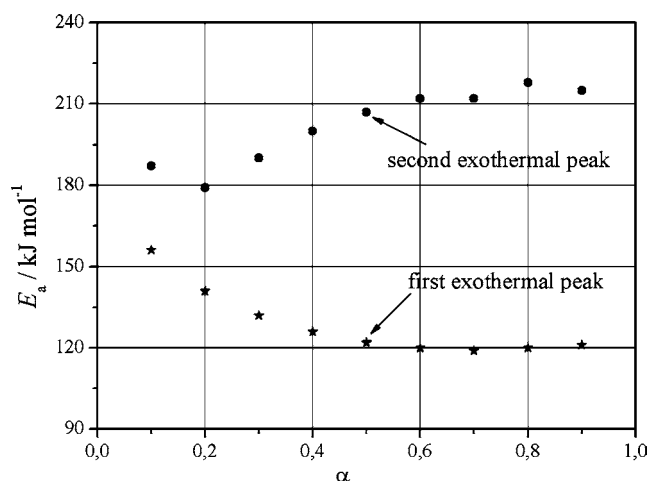


Fig. 9. The variation of activation energy with conversion determined from isoconversional integral method with error 20%.

Using the integral isoconversional method the activation energy at each conversion was evaluated from the slope of isoconversional lines with a good regression coefficient (0.983–0.941); the results are presented in Fig. 9. A significant variation of the activation energy with conversion within the significant range 10–90% can be observed.

Using the differential isoconversional method, the apparent values of activation energy for each conversion was obtained with a regression coefficients within 0.843–0.951 and an error of 15%. The results are given in Fig. 10. A variation of activation energy with conversion, within the significant range 10–90%, was also observed.

There are some significant differences between the activation energies evaluated according to isoconversional integral and differential methods. As seen from Figs. 9 and 10, the activation energy obtained with integral method has higher values than those obtained with differential method for the first exothermal peak. For the second peak the activation energy shows a different trend. The results suggest the existence of a more complex decomposition mechanism.

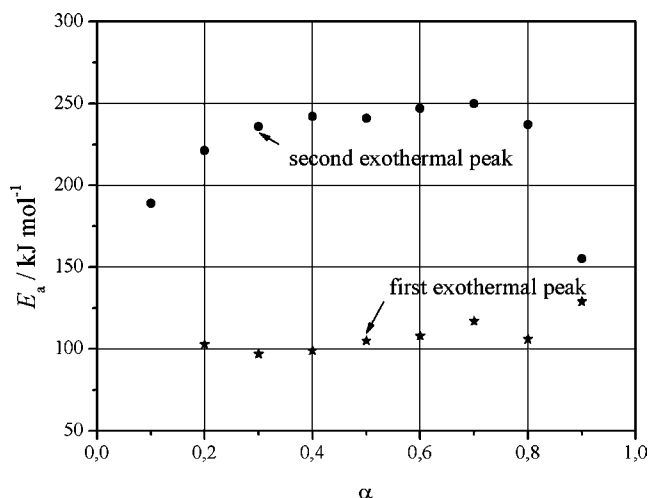


Fig. 10. The variation of activation energy with conversion determined from isoconversional differential method.

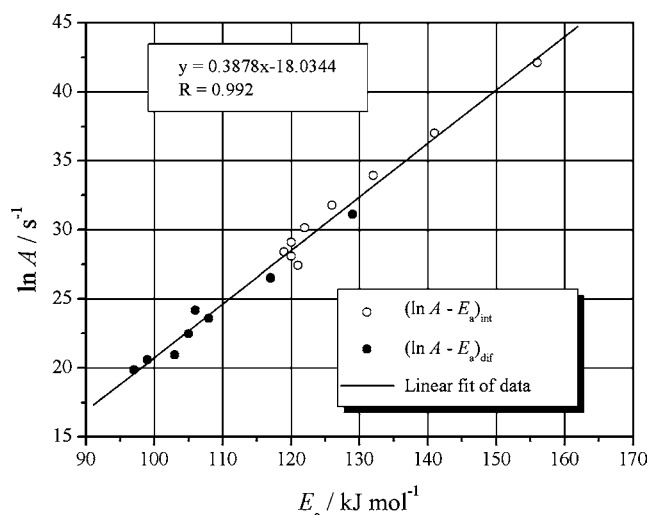


Fig. 11. Compensation plot of kinetic parameters from integral and differential isoconversional methods for the first peak.

The apparent pre-exponential factors can be also obtained from the intercepts, for each conversion, using Eqs. (1) and (2) and assuming an autocatalytic reaction with integral conversion function  $g(\alpha) = [(1 - \alpha)\alpha^{-1}]^{0.9} \times 0.9^{-1}$ , for integral method [7,13]. According to the differential method the pre-exponential factor can be obtained assuming also an autocatalytic reaction with differential conversion function  $f(\alpha) = \alpha^{0.1}(1 - \alpha)^{1.9}$  [7,13].

The results given in Figs. 11 and 12 indicate the existence of a linear correlation between  $\ln A$  and  $E$  (compensation effect), very frequently reported in literature [15,16]:

$$\ln A = a + bE \quad (3)$$

where  $a$  and  $b$  are constants.

For the first exothermal peak the two sets  $(E_a, A)$ , for both integral and differential isoconversional methods, satisfy the same isokinetic relationship. A straight line fits data with a good regression coefficient (Fig. 11). This linear relation suggests that the rate constant can be expressed only by a single activation parameter.

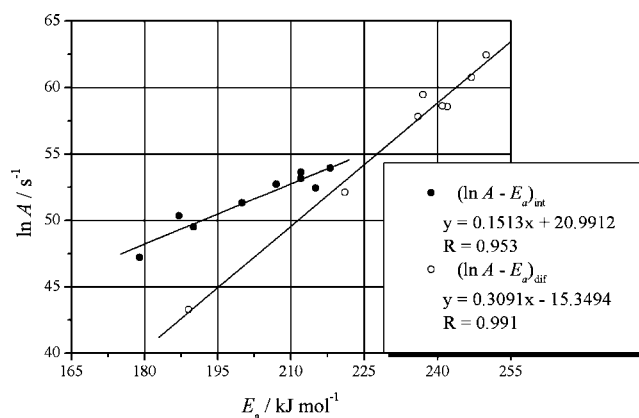


Fig. 12. Compensation plot of kinetic parameters from integral and differential isoconversional methods for the second peak.

For the second exothermal peak the two parameter sets ( $E_a$ , A) satisfy two different relationships (Fig. 12). In this case the simplification of rate constant is not longer possible.

The differential method gives constant activation energy for the first decomposition process, while a significant increase (higher than average error of 15%) with conversion was found for the second process, a characteristic feature of multistep reactions.

The integral method gives higher activation energies with an apparent decrease at the beginning of the first process (within the experimental errors of 20%). A different trend was found for the second process where the activation energy is lower and exhibits also an increase at the beginning. The differences between differential and integral methods are however within the experimental errors (20%).

There are several additional factors like sublimation and sample dispersion which follow the first process, able to increase the uncertainty in the kinetic parameters of the second process.

A better criterion to discriminate between two methods is to evaluate the rate constant for a certain conversion  $\alpha$ , both directly as:

$$k_{\text{calc}} = \frac{(d\alpha/dt)_\alpha}{f(\alpha)} \quad (4)$$

and from the kinetic parameters obtained with differential and integral methods, at the same conversion:

$$k_{\text{dif}} = A_{\text{dif}} e^{-E_{a,\text{dif}}/RT} \quad (5)$$

or

$$k_{\text{int}} = A_{\text{int}} e^{-E_{a,\text{int}}/RT} \quad (6)$$

For  $\alpha = 0.5$  the following results (in  $\text{min}^{-1}$ ) were obtained:  $k_{\text{calc}} = 0.0101$ ;  $k_{\text{dif}} = 0.0092$ ;  $k_{\text{int}} = 0.2386$  for the first process and  $k_{\text{calc}} = 0.0314$ ;  $k_{\text{dif}} = 0.0185$ ;  $k_{\text{int}} = 0.3513$  for the second process. Similar results were obtained for  $0.2 \leq \alpha \leq 0.8$ . An acceptable agreement was obtained only for the differential method.

Additional information on the overall activation energy can be obtained from the temperature dependence of induction periods ( $\tau_{\text{ind}}$ ). Similar dependencies were reported in literature for decomposition of other solid compounds [17–19]. For the autocatalytic decomposition reactions the existence of an induction period is determined by accumulation of a critical quantity of products,  $\Delta c^*$ , and the reaction rate is given by:

$$\frac{d\alpha}{dt} \cong \frac{\Delta c^*}{\tau_{\text{ind}}} \quad (7)$$

Using the general rate equation:

$$\frac{d\alpha}{dt} = A e^{-E_a/RT} f(\alpha) \quad (8)$$

one obtains:

$$\tau_{\text{ind}} = \frac{a}{f(\alpha)} e^{E_a/RT} \quad (9)$$

where  $a$  is constant:

$$a = \frac{\Delta c^*}{A} \quad (10)$$

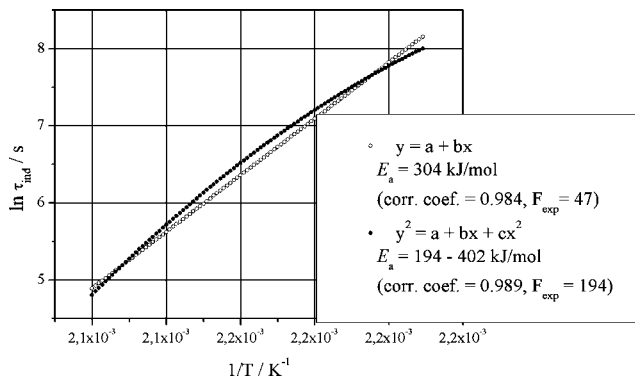


Fig. 13. Determination of activation energy from induction periods.

Assuming that the reaction mechanism  $f(\alpha)$  and  $\Delta c^*$  are temperature independent, the following relationship is finally obtained:

$$\tau_{\text{ind}} = b e^{E_a/RT} \quad (11)$$

where  $b$  is constant. The natural logarithm of Eq. (11) gives:

$$\ln \tau_{\text{ind}} = \ln b + \frac{E_a}{RT} \quad (12)$$

A plot of  $\ln \tau_{\text{ind}}$  versus  $1/T$  (Fig. 13) should give the overall activation energy  $E_a$ .

It can be seen that the best fit ( $F$ -test and correlation coefficient) of experimental data was obtained using a non-linear (parabolic) equation. The activation energy determined at lower temperatures has a value close to that obtained at small conversion using the isoconversional integral method. On the other hand, the data obtained at lower temperatures are more reliable for correlations of the form  $\ln \tau_{\text{ind}}$  versus  $1/T$ , because the time necessary to reach the isothermal regime is negligible as compared to the induction period.

The obtained activation energy is in good agreement with those reported in literature ( $113\text{--}444 \text{ kJ mol}^{-1}$ ) for similar nitro compounds decomposing by an autocatalytic mechanism [20–24].

#### 4. Conclusions

The study of thermal behavior of solid DNPH in isothermal regime at several temperatures lower than the melting point showed that this compound exhibit an exothermal decomposition with two separated exothermal peaks. The decomposition occurs after a temperature dependent induction period. The activation energy was determined using both integral and differential isoconversional methods. The kinetic parameters obtained with the differential method allow a realistic reproduction of experimental results. From the analysis of conversion-reduced time and conversion rates–time curves an autocatalytic reaction model was proposed. Assuming an autocatalytic kinetic model, the apparent pre-exponential factors were also evaluated. The analysis of the compensation effect of the overall activation parameters suggests a single step reaction for the first process and a multistep reaction for the second one. The overall activation energy was also evaluated from the temperature

dependence of induction period. The resulted activation energy at lower temperatures was comparable with that obtained with integral isoconversional method at low conversions. Higher activation energies and an autocatalytic mechanism are frequently encountered for decomposition of nitro compounds proving their hazardous nature.

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