

# Estimation of Time to Maximum Rate under Adiabatic Conditions (TMR<sub>ad</sub>) using Kinetic Parameters derived from DSC

## Investigation of Thermal Behavior of 3-METHYL-4-NITROPHENOL

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### Introduction

The runaway reactions are generally investigated by the time-consuming Accelerating Rate Calorimetry (ARC) or in isothermal (ISO-ARC) or heat-wait-search (HWS) modes. In present poster we discuss the application of the Differential Scanning Calorimetry (DSC) for the determination of the Time to Maximum Rate under adiabatic conditions (TMR<sub>ad</sub>). Additionally we present the method of simulation of the course of ARC experiments performed in both modes. We propose an advanced elaboration of the DSC data leading to the determination of the kinetic parameters of investigated reactions which, in turn, allows the simulation of the reaction course under any temperature mode. These kinetic parameters obtained in mg-scale considered simultaneously with a heat balance gave a powerful tool for the prediction of the thermal behaviour of the substance in kg-scale (pseudo-adiabatic conditions: SADT, cook-off) or in ton-scale (adiabatic conditions: TMR<sub>ad</sub>).

### Experimental

The applied procedure is illustrated by the prediction of the TMR<sub>ad</sub> value for the 3-methyl-4-nitrophenol (MN) using the results collected in a round robin test done by participants with different batches of MN on different calorimeters using company specific setups. Decomposition of MN was investigated in non-isothermal experiments in the range 20-350°C at heating rates between 0.25-8 K/min and isothermally between 200-260°C. Kinetic parameters were calculated using AKTS-Thermokinetics Software based on differential isoconversional approach [1-3].

### Results

#### Determination of kinetic parameters from DSC data followed by simulation of the reaction course in mg-scale at any temperature

The DSC signals of MN, recorded in non-isothermal conditions, after baseline subtraction are presented in Figure 1. In order to present the results of all participants in one diagram they are normalized and the reaction course is displayed as the dependence of the reaction rate and reaction progress  $\alpha$  on the temperature. The kinetic parameters: pre-exponential factor  $A$  and activation energy  $E$  determined by isoconversional method allowed simulating the DSC traces at any temperature profiles. The comparison of the simulated and experimental results for the heating rate 4 K/min is depicted in the insets.

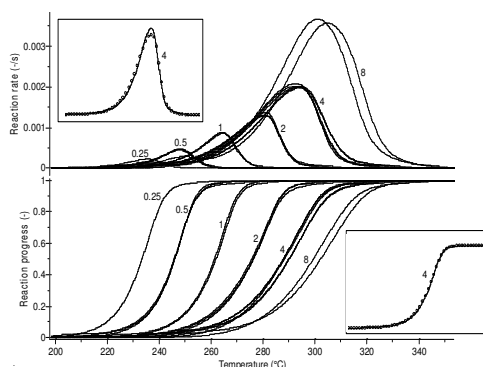


Fig. 1. Reaction rates  $dx/dt$  (top) and progresses  $\alpha$  (bottom) corresponding to the normalized DSC-signals for the decomposition of all 3-methyl-4-nitrophenol samples under non-isothermal conditions. The values of the heating rates are marked on the curves. The comparison of the experimental and simulated signals at 4 K/min is shown in the respective insets.

#### Simulation of thermal behaviour at adiabatic and pseudo-adiabatic conditions

Kinetic parameters calculated from DSC measurements can be used for describing thermal behaviour of energetic material also at the self-heating rate (not programmed by the user) which corresponds to thermal runaway reaction in adiabatic or semi-adiabatic conditions. Contrary to DSC experiments, where all heat created is exchanged with surrounding, in adiabatic measurements the generated heat stays in the system therefore for the simulation of the reaction course not only their kinetics but also the heat balance of the system has to be considered. In the current study for a MN mass of 1.5975g and the ARC bomb with  $\Phi=3.2$ , taking  $C_p=2$  J/(g·K) (determined with C80-calorimeter) and an average heat release  $\Delta H_r = -2001.7 \pm 216.5$  J/g obtained from the DSC data, we can write:

$$\frac{dT}{dt} = \frac{1}{\Phi} \frac{(-\Delta H_r)}{c_p} \frac{d\alpha}{dt} = \frac{1}{3.2} \frac{2001.7 \pm 216.5 \text{ J/g}}{2 \text{ J/(g·K)}} \frac{d\alpha}{dt} = 312.8 \pm 33.8 \text{ K} \frac{d\alpha}{dt}$$

The safety diagram based on these calculations is shown in Figure 2. Presented dependence illustrates how the kinetic parameters obtained from DSC data enable to estimate precisely the initial temperature of an ISO-ARC which results in reasonable duration of the data collection without necessity of carrying out some preliminary HWS testing. Moreover, the ARC test carried out in a HWS mode can be simulated as well. As presented in Figure 3 (symbols) the temperature at the detection limit which corresponds usually to a self-heating rate of 0.02 K/min amounts to ca. 183.8°C with  $\Phi$ -factor = 3.2 and was reached after 11.29h.

The time remaining from this point to the measured TMR<sub>ad</sub> (see Fig. 3) amounts to 15.67 – 11.29h = 4.38 h. The measured TMR<sub>ad</sub> value is consistent with the calculated results presented in Figure 2 confirming that an initial ISO-ARC temperature of 184°C leads to a TMR<sub>ad</sub> of about 4.86h. Having the kinetic description of the reaction rate derived from the DSC data, one can estimate that the reaction progress  $\alpha$  after 11.29h of HWS testing (Fig.3) amounts to about 0.0095 (ca. 1%). The simulation of the adiabatic temperature rise from that temperature of 183.8°C can be further calculated and is presented in Figure 3 as a solid line.

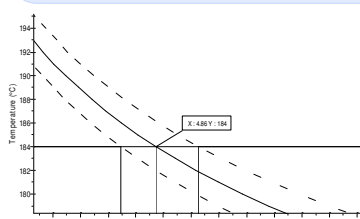


Fig. 2. Thermal safety diagram for 3-methyl-4-nitrophenol simulated for the parameters given in text. For an initial ISO-ARC temperature of 184°C, TMR<sub>ad</sub> amounts to ca. 4.86h with the confidence interval (range 4.22-5.63hrs) calculated for the adiabatic temperatures lower by 1K (top curve) and higher by 1K (bottom curve).

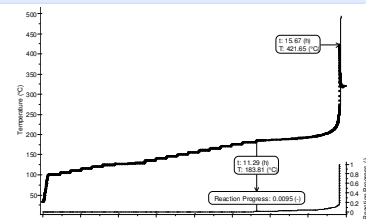


Fig. 3. ARC test for MN carried out in HWS mode. The reaction progress  $\alpha$  after ca. 11.3 h of HWS testing amounts to about 0.0095 (ca. 1%). From the time at which the detection limit (183.81°C) was reached the value of TMR<sub>ad</sub> amounts to ca. 4.4h (15.67-11.29h). Solid line depicts the simulation being in a good agreement with the experimental HWS-ARC data (symbols).

The important advantage of the use of the kinetic parameters derived from DSC data consists also in the possibility of the simulation of the reaction course in fully adiabatic conditions ( $\Phi=1$ ) for the totally not decomposed sample ( $\alpha=0$ ) what is difficult to achieve from the experimental point of view. Such a simulation is presented in Fig. 4 depicting the safety diagram of MN for few initial temperatures by the same procedure applied for the simulation of TMR<sub>ad</sub> as in ISO-ARC shown in Figure 2. For  $\Phi=1$ , TMR<sub>ad</sub> is 8 hours at an initial temperature of about 164.9°C (for that temperature a more conservative value for TMR<sub>ad</sub> is 6.76 h). The critical value TMR<sub>ad</sub>=24 hours, commonly accepted as the safety limit in the industrial scale, is obtained at about 151°C (for that temperature a more conservative value for TMR<sub>ad</sub> is 20.22 h).

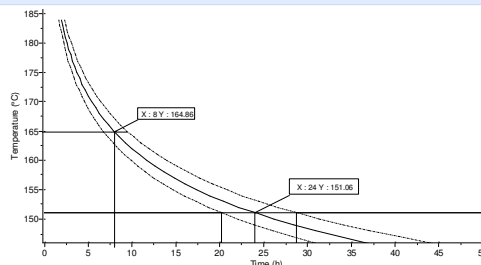


Fig. 4. Thermal safety diagram of 3-methyl-4-nitrophenol in fully adiabatic conditions with  $\Phi = 1$ . The choice of the initial temperatures strongly influences the adiabatic induction time. With  $\Delta H_r = -2001.7 \pm 216.5$  J/g,  $\Delta T_{ad} = (-\Delta H_r)/(C_p \cdot \Phi) = 1000.9 \pm 108.3^\circ\text{C}$  and  $C_p = 2$  J/g°C, TMR<sub>ad</sub> are 8 and 24 h for initial temperatures of 164.86 and 151.06°C, respectively. Dashed lines depict the confidence interval.

The calculated TMR<sub>ad</sub> values from all experimental data delivered by the participants of the round robin test amount to:

156.4; 153.6; 148.9; 149.4; 148.0; 152.5 and 150.1°C

Despite the variety of the experimental setups and different origins of the samples the mean value of the initial temperature at which TMR<sub>ad</sub>=24h amounts to

151.3 ± 3.0°C

which is in accordance with the temperature displayed in the Fig. 4.

### Conclusion

DSC results delivered by the participants of a round robin test obtained with different heating rates (non-isothermal mode) and at different temperatures (isothermal mode) were elaborated by AKTS-Thermokinetics software and applied for the determination of the kinetic parameters of the decomposition reaction. Due to their precise determination, the variation of the runaway time under true adiabatic mode ( $\Phi = 1$ ) was calculated for any initial process temperature. Results were reported in a thermal safety diagram depicting the dependence of Time to Maximum Rate (TMR) on the initial temperature. The critical value TMR<sub>ad</sub>=24 hours was obtained for the initial adiabatic temperature of about 151°C. Both isothermal DSC and adiabatic experiments with  $\Phi$ -factor > 1 were used for the final validation of the kinetic parameters. Applied method can help in the optimal choice of the initial adiabatic temperature what results in shortening of the time required for the adiabatic investigations. The observed influence of the preliminary reaction progress on the TMR<sub>ad</sub> values is described in [3].

### References

- AKTS-Thermokinetics and AKTS-Thermal Safety Software <https://www.aks.com>
- <https://www.aks.com/tk> and <https://www.aks.com/ts>
- <https://www.aks.com/tk/video> and <https://www.aks.com/ts/video>