

# Estimation of Time to Maximum Rate Under Adiabatic Conditions ( $TMR_{ad}$ ) Using Kinetic Parameters Derived From DSC-Investigation of Thermal Behavior of 3-Methyl-4-Nitrophenol

Bertrand Roduit<sup>1</sup>, Patrick Folly<sup>2</sup>, Alexandre Sarbach<sup>2</sup>, Beat Berger<sup>2</sup>, Franz Brogli<sup>3</sup>, Francesco Mascarello<sup>4</sup>, Mischa Schwaninger<sup>4</sup>, Thomas Glarner<sup>5</sup>, Eberhard Irle<sup>6</sup>, Fritz Tobler<sup>6</sup>, Jacques Wiss<sup>7</sup>, Markus Luginbühl<sup>8</sup>, Craig Williams<sup>8</sup>, Pierre Reuse<sup>9</sup>, Francis Stoessel<sup>9</sup>

(1. AKTS AG, TechnoArk 1, 3960 Siders, Switzerland, <http://www.akts.com>, [b.rodut@akts.com](mailto:b.rodut@akts.com); 2. Armasuisse, Science and Technology Centre, 3602 Thun, Switzerland; 3. Ciba Schweizerhalle AG, P.O. Box, 4002 Basel, Switzerland; 4. DSM Nutritional Products Ltd., Safety laboratory, 4334 Sisseln, Switzerland; 5. F. Hoffmann-La Roche Ltd, Safety laboratories, 4070 Basel, Switzerland; 6. Lonza AG, Safety Laboratory Visp, Rottenstr. 6, 3930 Visp, Switzerland; 7. Novartis Pharma AG, Novartis Campus, WSJ-145.8.54, 4002 Basel, Switzerland; 8. Syngenta Crop Protection Munchwilen AG, WMU 3120.1.54, 4333 Munchwilen, Switzerland; 9. Swiss Safety Institute, Schwarzwaldallee 215, WRO-1055.5.02, 4002 Basel, Switzerland)

**Abstract:** Kinetic parameters of the decomposition of hazardous chemicals can be applied for the estimation of their thermal behavior under any temperature profile. Presented paper describes the application of the advanced kinetic approach for the determination of the thermal behavior also under adiabatic conditions occurring e.g. in batch reactors in case of cooling failure.

The kinetics of the decomposition of different samples (different manufacturers and batches) of 3-methyl-4-nitrophenol were investigated by conventional DSC in non-isothermal (few heating rates varying from 0.25 to 8.0 K/min) and isothermal (range of 200–260 °C) modes. The kinetic parameters obtained with AKTS-Thermokinetics Software were applied for calculating reaction rate and progress under different heating rates and temperatures and verified by comparing simulated and experimental signals. After application of the heat balance to compare the amount of heat generated during reaction and its removal from the system, the knowledge of reaction rate at any temperature profiles allowed the determination of the temperature increase due to the self-heating in adiabatic and pseudo-adiabatic conditions.

Applied advanced kinetic approach allowed simulation the course of the Heat-Wait-Search (HWS) mode of operation of adiabatic calorimeters. The thermal safety diagram depicting dependence of Time to Maximum Rate (TMR) on the initial temperature was calculated and compared with the results of HWS experiments carried out in the system with  $\Phi$ -factor amounting to 3.2. The influence of the  $\Phi$ -factor and reaction progress reached at the end of the HWS monitoring on the TMR is discussed. Presented calculations clearly indicate that even very minor reaction progress reduces the  $TMR_{ad}$  of 24 h characteristic for a sample with initial reaction progress amounting to zero.

Described estimation method can be verified by just one HWS-ARC, or by one correctly chosen ISO-ARC run of reasonable duration by knowing in advance the dependence of the TMR on the initial temperature for any  $\Phi$ -factor. Proposed procedure results in significant shortening of the measuring time compared to a safety hazard approach based on series of ARC experiments carried out at the beginning of a process safety evaluation.

**Key words:** adiabatic condition; methyl; nitrophenol; DSC;  $\Phi$ -factor; kinetics; thermal runaway, TMR  
中图分类号: O642.1 文献标识码: A 文章编号: 1672-2191(2011)01-0084-13

## Introduction

Differential Scanning Calorimetry (DSC)<sup>[1-3]</sup> and Accelerating Rate Calorimetry (ARC)<sup>[4-9]</sup> are often used for the precise determination of the heat flow generated (or consumed) by a sample during experiments carried out in non-isothermal or isothermal (DSC), adiabatic or pseudo-adiabatic conditions (ARC). In the DSC technique the heating rate, being the very important experimental parameter, is arbitrarily chosen by the user, in contrary, in ARC, the temperature increase during exothermic reactions results from the self-heating of the material.

The runaway reactions are generally investigated by the time-consuming ARC experiments or in isothermal (ISO-ARC) or Heat-Wait-Search (HWS) modes. In the present paper we discuss the application of the DSC traces after advanced kinetic analysis for the determination of the Time to Maximum Rate under adiabatic conditions ( $TMR_{ad}$ ) and simulation of the course of ARC experiments performed in both modes. We propose an advanced kinetic elaboration of the DSC data which allows constructing link between the results collected in different experimental conditions:

(i) DSC signals recorded in non-isothermal conditions (constant temperature rise) using heating rates in the range generally between 0.25~10 K/min;

(ii) Isothermal DSC data obtained at different temperatures (heating rate amounts to 0 K/min);

(iii) ARC data obtained from adiabatic ( $\Phi=1$ ) or pseudo-adiabatic conditions ( $\Phi>1$ ) in which the temperature rise changes progressively from zero to several K/min due to the sample self-heating. This process depends mainly on the kinetics of the decomposition, adiabatic temperature rise,  $c_p$  of the sample and  $\Phi$ -factor.

The key factor allowing the simulation of the reactions course under any temperature mode is the knowledge of the kinetic parameters depicting the dependence of the rate of heat evolution on different heating rates. These kinetic parameters are calculated from the non-iso or isothermal signals using advanced kinetic analysis based on the differential isoconversional approach<sup>[10-13]</sup>. Isoconversional

methods of the kinetic determination are based on the assumptions that the reaction rate  $d\alpha/dt$  for a given reaction progress  $\alpha$  is only a function of the temperature. This assumption is valid for most of the decomposition reactions but as it is not an axiom it needs to be verified in each analysis. If the isoconversional assumption is valid, the calculated kinetic parameters can be applied for simulating the reaction rate at any temperature change mode such as:

(i) 'non-isothermal' (constant heating rate);

(ii) 'isothermal' (constant temperature);

(iii) 'adiabatic' (progressive temperature rise due to 'self-heating' of the sample)

Depending on the type of technique and experimental set-up e.g. non-isothermal or isothermal DSC, HWS or ISO-ARC, the process of data collection can be more or less time consuming.

Below we propose the optimization of the experimental procedure which will be illustrated by the prediction of the TMR value for the 3-methyl-4-nitrophenol (MN), CAS N°: 2581-34-2, using the results collected in a round robin test in which few participants have investigated the different batches of MN in different calorimeters using company specific experimental set-ups. In the procedure proposed by us all non-iso and isothermal data delivered by the participants of the test were used for the determination of the kinetic parameters of the reaction of the MN decomposition and the heat of the reaction  $\Delta H_r$ . The correctness of the procedure of the determination of kinetic parameters was verified by the comparison of the experimental and simulated signals. The DSC derived kinetic parameters were applied for the simulation of the adiabatic experiments.

## Experimental

For the determination of the kinetic parameters of the decomposition of MN originating from different suppliers and different batches, the DSC technique was applied. Different DSC apparatus from various manufacturers were used. The measured data were subsequently exported in ASCII format and

elaborated with AKTS-Thermokinetics Software. The decomposition of the MN was investigated in non-iso experiments in the range of 20 °C to 350 °C at different heating rates of 0.25, 0.5, 1, 2, 4 and 8 K/min and, isothermally, at temperatures 200, 210, 220, 230, 240, 250 and 260 °C. All experiments were performed in gold plated high pressure sealed crucibles<sup>[14]</sup> with a sample mass varying between

4.8 and 12.22 mg.

## Results and Discussion

### DSC Data-Elaboration and Simulation

The typical DSC signal of MN recorded in non-isothermal conditions is presented in Figure 1 (top). After endothermic melting (maximum of endo-peak centred at 128.2 °C, the sample starts to decompose.

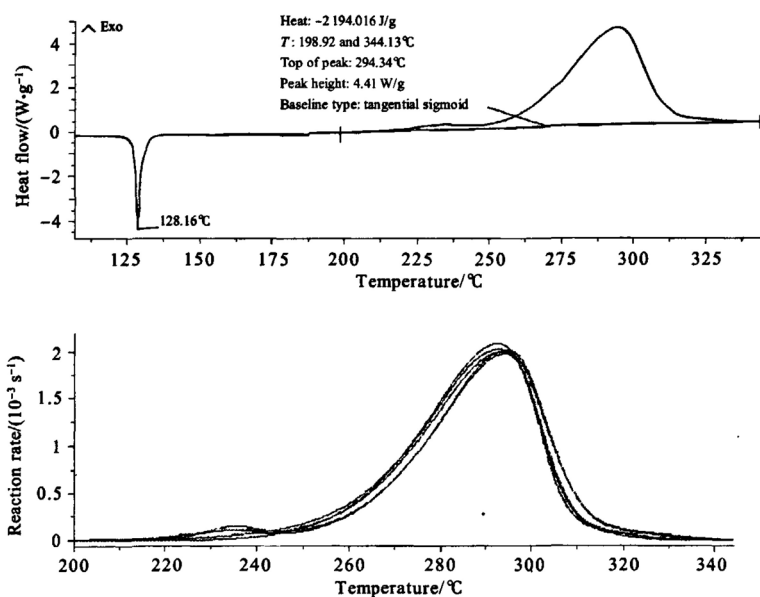


Fig.1 (Top) Typical DSC trace of 3-methyl-4-nitrophenol recorded at 4 K/min and sigmoid baseline construction. (Bottom) The reaction rates for all samples at 4 K/min. Despite of the different experimental setups and sample origins the reproducibility of the DSC traces is acceptable.

For the depicted sample, analysed with the heating rate of 4 K/min, the maximum of the exo-peak is centred at 294.3 °C. With the applied sigmoid-type baseline the determined reaction heat and temperatures of the beginning and the end of the decomposition amount to about -2 194 J/g; 199 °C and 344 °C, respectively. In order to present the results for all samples in one diagram (Figure 1, bottom) they are normalized and the reaction course is displayed as the dependence of the reaction rate (rate of the change of the reaction progress  $\alpha$  varying between 0 and 1 at the beginning and the reaction end, respectively) on the temperature.

The comparison of the DSC traces recorded for different samples on different calorimeters at the same heating rate of 4 K/min (Figure 1, bottom) shows

quite high reproducibility of the results. Experimental discrepancy between the curves concerns mainly the occurrence of a small thermal event in the region of the detected decomposition onset as well as the temperature of the exothermal event. All data collected in non-isothermal and isothermal experiments are displayed in Figure 2.

The simulation of the experimental data (see insets in Figure 2) requires the determination of the kinetic parameters of the decomposition reaction. It was done applying a differential isoconversional method based on Friedman approach<sup>[15]</sup>.

The reaction rate can be expressed as

$$\frac{d\alpha}{dt} = (A(\alpha) \cdot f(\alpha) \exp(-\frac{E(\alpha)}{R} \frac{1}{T(t)})) \quad (1)$$

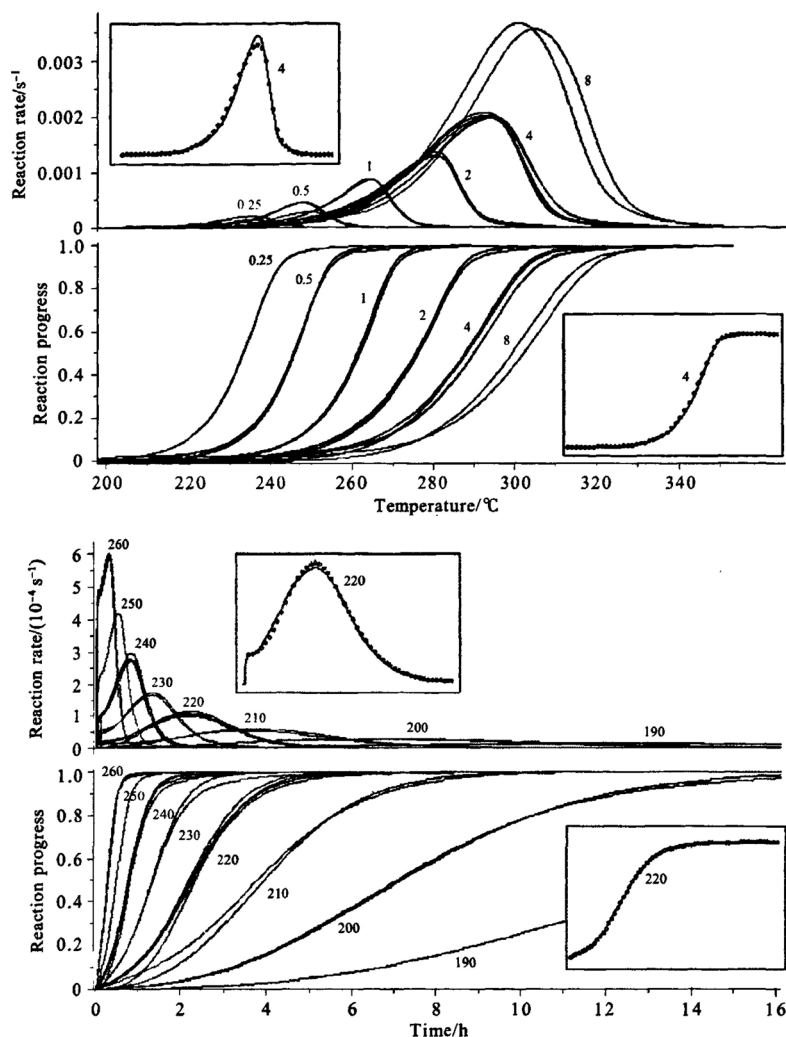


Fig.2 Reaction rates  $d\alpha/dt$  and progresses  $\alpha$  corresponding to the normalized DSC-signals for the decomposition of all 3-methyl-4-nitrophenol samples under non-isothermal (top) and isothermal (bottom) conditions. The values of the heating rates and temperatures are marked on the curves. The comparison of the experimental and simulated signals at chosen experimental conditions is shown in the respective insets.

where  $t$ ,  $T(t)$ ,  $E(\alpha)$  and  $A(\alpha)$  are the time, temperature, apparent activation energy and preexponential factor at conversion  $\alpha$ , respectively. In logarithmic form one can write:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(A(\alpha) \cdot f(\alpha)) - \frac{E(\alpha)}{R} \cdot \frac{1}{T(t)} \quad (2)$$

where  $-E(\alpha)/R$  and  $\ln(A(\alpha) \cdot f(\alpha))$  are the slope and the intercept with the vertical axis of the plot of  $\ln(d\alpha/dt)$  vs.  $1/T(t)$  (Figure 3, top),  $f(\alpha)$  depicts the differential form of the function of the reaction progress  $\alpha$  depending on the reaction mechanism.

The logarithm of the reaction rates is presented as a function of the reciprocal temperature for the different temperatures and heating rates (Figure 3, top). The differential isoconversional analysis allows finding the Arrhenius dependence for any, arbitrarily chosen decomposition progress  $\alpha$ . The slope of this dependence gives the apparent activation energy and preexponential factor at each stage of the decomposition progress  $\alpha$  (Figure 3, bottom). For example we see that for a reaction progress  $\alpha$  of 0.5 the apparent activation energy amounts to about 102



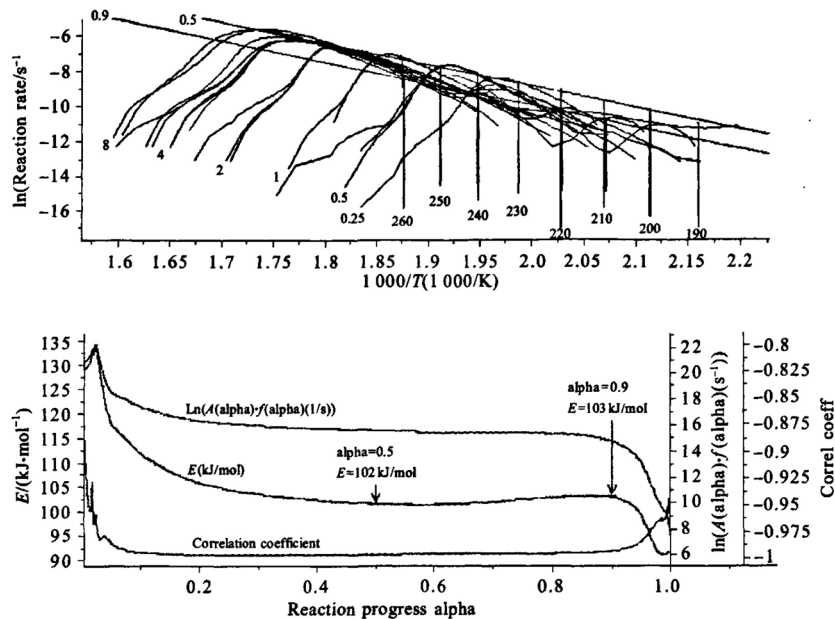


Fig.3 (Top) Differential isoconversional analysis of the decomposition of 3-methyl-4-nitrophenol based on the non-isothermal and isothermal data. The values of the heating rates and temperatures are marked on the curves. (Bottom) Apparent activation energy, pre-exponential factor and a correlation coefficient as a function of the reaction progress  $\alpha$ .

kJ/mol and for  $\alpha=0.9$  the apparent activation energy is only slightly larger (different slope) and amounts to ca. 103 kJ/mol.

The construction of the baseline of the DSC signal (Figure 1, top) plays an important role in the correct determination of the reaction progress which is based on the integration of the DSC signals area. Incorrect baseline construction influences the integral intensity of the signal what leads to the incorrect determination of the reaction progress what, in turn, influences the values of the kinetic parameters. In order to optimize the determination of the kinetic parameters from DSC traces in AKTS-Thermokinetics Software Version 3 the reaction range is divided into numerous intervals and the evaluation of the apparent activation energy  $E(\alpha)$  and preexponential factor  $A(\alpha) \cdot f(\alpha)$  is carried out for each differential reaction progress  $\alpha$ . In an ideal situation, i.e. without experimental noise and with the isoconversional assumption holding in 100%, the average value of all correlation coefficients of all straight lines obtained in the coordinates expressed in the eq.2 and depicted in Figure 3 (top) should reach the best value of '-1'. AKTS-Thermokinetics Software applies

non-linear numerical analysis for baseline optimization to reach that best value by adjusting the tangents used for the constructions of all sigmoid baselines. The average value of all regression coefficients is a measure of the quality of the experimental data (level of experimental noise, correctness of baseline construction, correct choice of the temperature in the isothermal experiments, etc.) and the correctness of the assumption concerning the isoconversional principle stating that the reaction rate depends only on the temperature. The optimized adjustment of the baseline changes additionally the standard deviation of the value of the reaction heat  $\Delta H_r$ . The mean value of the  $\Delta H_r$  was measured from the DSC traces by calculating the average of the values measured at different heating rates (non-isothermally) and temperatures (isothermally). The standard deviation is calculated using the following formula:

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (\Delta H_{r,i} - \overline{\Delta H_r})^2}{n-1}} \quad (3)$$

where  $\overline{\Delta H_r}$  is the mean value of the heat of reaction obtained from the various DSC traces,  $\Delta H_{r,i}$  is the heat of reaction determined from each DSC trace and  $n$  is the number of applied heating rates and

temperatures. Since, generally, we don't know the value of the heat of reaction we are measuring, its standard deviation may help in estimation how reliable our measurements and baseline construction are. If the isoconversional principle applies to the examined reaction, the heat of reaction should be independent of the heating rate and therefore the same for all considered thermoanalytical curves. Depending on the quality of the measured data, the additional adjustment of the baseline construction enables a better estimation of the average heat of reaction for all curves. As a rule of thumb the values of the reaction heat used later for the kinetic evaluation should have the maximal standard deviation lower than 10%. In addition, a kinetically dependent relationship should be retrieved when plotting the reaction progress as a function of the temperature. Consequently, when increasing heating rate one should observe a consistent shift of  $\alpha$ - $T$  dependences into the direction of the higher temperatures. An improper baseline construction leads however to a low value of the average correlation coefficient and confirms an inconsistent relationship  $\alpha$ - $T$ . Generally, our average correlations coefficients amounting to at least to '-0.99' will lead to reliable kinetic analysis.

Therefore, to avoid improper baseline construction and achieve reliable analyses three procedures can be applied:

(i) slight modification of the tangents at the beginning or at the end of the signals;

(ii) minor change of the temperature range of the selected of thermal analysis curves;

(iii) new measurements when necessary.

In the current study, the average value of all correlation coefficients amounts to  $-0.9928$  and the mean reaction heat  $\Delta H_r$  to  $(-2001.7 \pm 216.5)$  J/g. Deviation of the average regression coefficient from its maximal value and relatively large standard deviation of the  $\Delta H_r$  value result mainly from the experimental error i.e. the not optimal choice of temperatures in isothermal mode of the investigations. At too high isothermal temperatures (as 250 and 260 °C) the significant part of the data collected at the beginning of the decomposition is not fully applicable in kinetic analysis. Due to the time required for the temperature settling in the sample, some part of the decomposition (as larger as temperature is higher) occurs at temperatures lower than set. Also, if the reactions rate are high, the problem of the time constant of the measuring sensors — see e.g. in<sup>[16-17]</sup> — starts to play an important role in the correct evaluation of the thermograms. These remarks are illustrated by the results of the isothermal thermal decomposition of the MN at 260 °C depicted in Figure 4. Due to the very fast reaction at the beginning, the significant part of the decomposition occurs in not well defined experimental conditions what leads to the decreasing of the accuracy of the kinetic analysis. This issue will be discussed in details in a forthcoming paper.

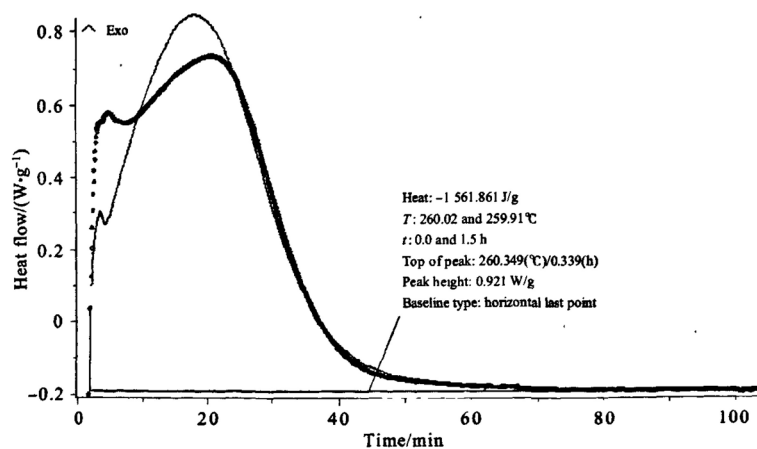


Fig.4 Experimental (symbols) and simulated (solid line) DSC signals of MN decomposed isothermally at 260 °C. Note that the significant part of the reaction occurs in very narrow time range and in not well defined temperature.

The optimal procedure of the recording of DSC data which are later used for kinetic calculations consists in carrying out 4~5 non-isothermal experiments in the range of heating rates of 0.25~10 K/min and one or two isothermal experiments rather in lower limit of the applicable temperature range. The verification of the correctness of the kinetic parameters can be achieved by comparing the course of the experimental and simulated signals.

### Adiabatic and Pseudo-Adiabatic Conditions

Kinetic parameters calculated from DSC measurements can be used for describing thermal behavior at any heating rate therefore also for progressive heating rate (self-heating rate) which corresponds to thermal runaway reactions in adiabatic or pseudo-adiabatic conditions as in ARC experiments or in a batch reactors containing a larger amount of substance (in case of cooling failure). However, when considering the problem of modelling of the adiabatic reactions two important factors have to be taken into account:

(i) the application of advanced kinetics, which properly describes the complicated, multistage course of the decomposition process,

(ii) the effect of heat balance in the adiabatic system when all (fully adiabatic) or majority (pseudo-adiabatic) of the generated reaction heat stays in the system in contrary to the DSC experiments where it is assumed that all generated heat is fully transferred to the environment.

### Heat Balance

In heat transfer problems it is convenient to write a heat balance and to treat the conversion of chemical energy into thermal energy as heat generation. The energy balance in that case can be expressed as

$$\underbrace{Q_{in} - Q_{out}}_{\text{Net heat transfer}} + \underbrace{Q_r}_{\text{Heat generation}} = \underbrace{\frac{\Delta Q}{\Delta t}}_{\text{Energy storage}} \quad (4)$$

The energy balance of an exothermic reaction taking place in semi-adiabatic conditions (ARC calorimeter or batch reactor) can read as follow

$$\underbrace{UA(T_{env} - T_s)}_{\text{Net heat transfer}} + \underbrace{m_s(-\Delta H_r)}_{\text{Heat generation}} \frac{d\alpha}{dt} = \underbrace{m_s c_{p,s}}_{\text{Energy storage}} \frac{dT_s}{dt} + m_c c_{p,c} \frac{dT_c}{dt} \quad (5)$$

with  $m$ : mass,  $c_p$ : specific heat,  $T$ : temperature,  $U$ : overall heat transfer coefficient,  $A$ : contact surface between the sample and the calorimetric cell or container,  $\Delta H_r$ : heat of reaction, indices c, s and env: calorimetric cell or container, sample and environment, respectively. In a fully adiabatic environment ( $U=0$ ) all the heat released is used to heat the sample and the calorimetric cell or container. If there is thermal equilibrium within the sample and the cell then

$$T_c(t) = T_s(t) \Rightarrow \frac{dT_c}{dt} = \frac{dT_s}{dt} = \frac{dT}{dt} \quad (6)$$

and the whole system will have the same temperature rise rate, therefore we can simplify the above equation to:

$$\frac{dT}{dt} = \frac{m_s c_{p,s}}{m_c c_{p,c} + m_s c_{p,s}} \frac{(-\Delta H_r)}{c_{p,s}} \frac{d\alpha}{dt} \quad (7)$$

that can be rewritten as

$$\frac{dT}{dt} = \frac{1}{\Phi} \Delta T_{ad,true} \frac{d\alpha}{dt} \quad (8)$$

with:

(i) the adiabatic temperature rise:

$$\Delta T_{ad,true} = \frac{(-\Delta H_r)}{c_{p,s}} \quad (9)$$

(ii) the phi factor:

$$\Phi = \frac{m_c c_{p,c} + m_s c_{p,s}}{m_s c_{p,s}} \quad (10)$$

(iii) the reaction rate  $d\alpha/dt$  calculated from the kinetic parameters (eqs. 1 and 2) derived from the DSC traces using isoconversional analysis.

For the adiabatic process as e.g. in batch reactor with large sizes ( $>1 \text{ m}^3$ ), it can be assumed that  $m_s \gg m_{c(\text{jacket})}$  so that we obtain

$$\frac{dT}{dt} = \Delta T_{ad,true} \frac{d\alpha}{dt} \quad (\text{with } \Phi \approx 1) \quad (11)$$

and finally  $T = f(t, \text{kinetics}, \Delta H_r, c_{p,s})$  (12)

The graphical presentation of the main parameters of the process running in the adiabatic conditions is presented in Figure 5.

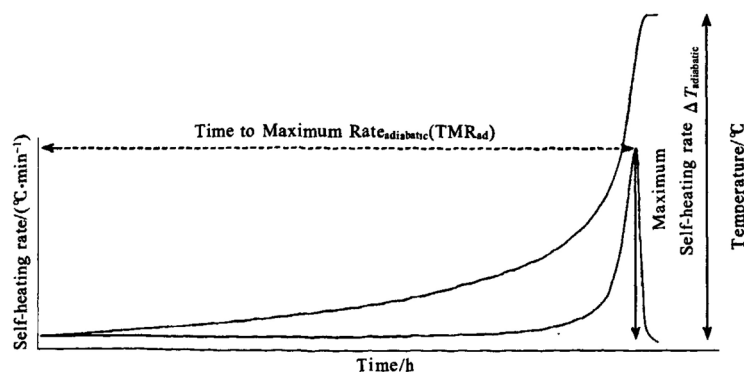


Fig.5 Graphical presentation of key parameters of the process in the adiabatic conditions. Self-heating rate and  $\Delta T_{ad}$  are expressed by the eqs. 8 and 9, respectively.

It comes from the above equations that using the kinetic based approach for predicting the reaction progress  $\alpha(t)$  and rate  $d\alpha/dt$  one can, in turn, predict the development of the temperatures  $T(t)$  and  $dT/dt$  and Time to Maximum Rate  $(dT/dt)_{max}$  for several initial temperatures after integration of  $dT/dt$ . This allows constructing a thermal stability diagram. The simulation of an ARC curve and its TMR can be obtained similarly for any initial temperatures. However, one has to additionally consider the effect of the vessel's inertia and take into account the value of the  $\Phi$ -factor which influences:

(i) the  $\Delta T_{ad,measured}$  because it comes from above that  $\Delta T_{ad,measured} = \frac{1}{\Phi} \Delta T_{ad,true}$ ;

(ii) and the TMR<sub>ad</sub> in different ways, depending on the decomposition kinetics.

Determination of TMR may be also influenced by some uncertainties in the values of various parameters such as the adiabatic temperature rise  $\Delta T_{ad} \pm \sigma$  resulting from deviations in heat  $\Delta H_r \pm \sigma$ :

$$\frac{dT}{dt} \pm \sigma = \frac{\Delta T_{ad} \pm \sigma}{\Phi} \frac{d\alpha}{dt} \quad (13)$$

After all, the numerical integration of  $dT/dt$  enables to predict TMR in ISO-ARC tests for several initial temperatures  $T_0$  and  $\Phi$ -factors within some confidence interval.

### Simulation of Iso-ARC and HWS Adiabatic Experiments

In time-consuming adiabatic experiments it seems to be advantageous to use the kinetic

parameters for the prediction of the adiabatic temperature at which the process can be investigated in a reasonable time scale. Such prediction leads to the optimization of the experimental work because if an ISO-ARC test is performed at an initial temperature that is too low, then the duration of the experiment can last over hours or even days. In the current study for a MN mass of 1.5975 g and the ARC bomb with  $\Phi=3.2$ , taking  $c_p=2 \text{ J/(g}\cdot\text{K)}$  and an average heat release  $\Delta H_r=(-2001.7 \pm 216.5) \text{ J/g}$  we obtained

$$\frac{dT}{dt} = \frac{1}{\Phi} \frac{(-\Delta H_r)}{c_p} \frac{d\alpha}{dt} = \frac{1}{3.2} \times \frac{(2001.7 \pm 216.5) \text{ J/g}}{2 \text{ J/(g}\cdot\text{K)}} \cdot \frac{d\alpha}{dt} = (312.8 \pm 33.8) \text{ K} \cdot \frac{d\alpha}{dt} \quad (14)$$

The initial temperatures may contain some uncertainties. For an initial temperature  $T=184^\circ\text{C}$  assuming a deviation  $\Delta T = \pm 1^\circ\text{C}$ , after integration one obtains

(i) a conservative TMR of 4.22 h for  $T=(184+1)^\circ\text{C}=185^\circ\text{C}$  and  $\Delta T_{ad}=(312.8+33.8)^\circ\text{C}=346.6^\circ\text{C}$

(ii) a best TMR prediction of c.a. 4.86 hours for  $T_0=184^\circ\text{C}$  and  $\Delta T_{ad}=312.8^\circ\text{C}$ ;

(iii) a non-conservative TMR of 5.63 h for  $T=(184-1)^\circ\text{C}=183^\circ\text{C}$  and  $\Delta T_{ad}=(312.8-33.8)^\circ\text{C}=279^\circ\text{C}$ .

The safety diagram based on these calculations is presented in Figure 6.

Results shown in Figure 6 illustrate 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

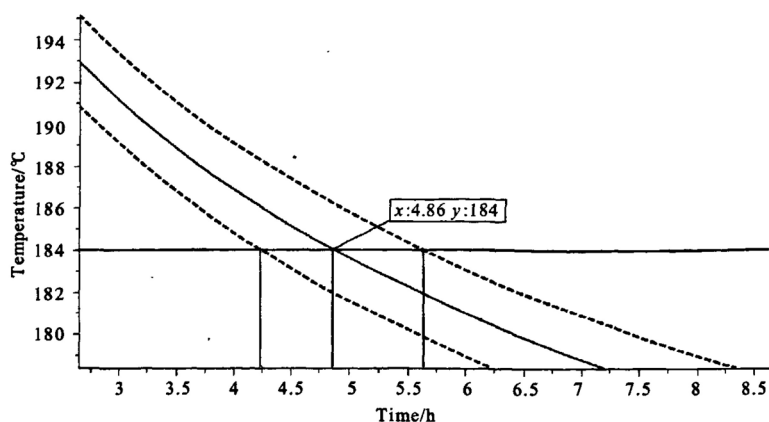


Fig.6 Thermal safety diagram for 3-methyl-4-nitrophenol simulated for the following parameters:  $\Delta H_r = (-2001.7 \pm 216.5) \text{ J/g}$ ,  $\Delta T_{ad} = (-\Delta H_r)/(c_p \cdot \Phi) = (312.8 \pm 33.8)^\circ\text{C}$ ,  $\Phi = 3.2$  and  $c_p = 2 \text{ J/(g}\cdot^\circ\text{C)}$ . For an initial ISO-ARC temperature of  $184^\circ\text{C}$ , TMR amounts to ca. 4.86 h with the confidence interval (range 4.22~5.63 h) calculated for the adiabatic temperatures lower by 1 K (top curve) and higher by 1 K (bottom curve).

collection without necessity of carrying out some preliminary HWS testing. However, the ARC test carried out in a HWS mode can be simulated as well. As presented in Figure 7 (symbols) the temperature at the detection limit which corresponds usually to a self-heating rate of  $0.02 \text{ K/min}$  amounts to ca.  $183.8^\circ\text{C}$  with  $\Phi$ -factor = 3.2 and was reached after 11.29 h. The time remaining from this point to the measured TMR (see Figure 7) amounts to  $(15.67 - 11.29) \text{ h} = 4.38 \text{ h}$ . The measured TMR value is consistent with the calculated results presented in Figure 6 confirming that an initial ISO-ARC temperature of  $184^\circ\text{C}$  leads to a TMR of about 4.86 h. However, some minor reaction progress  $\alpha$  occurs during the initial period of a HWS-ARC test when the sample is still in the heat-wait-search mode. When the detection limit of the ARC apparatus is reached, the reaction progress  $\alpha$  is no longer = 0, but  $\alpha > 0$ . Having the kinetic description of the reaction rate derived from the DSC data, one can estimate that the reaction progress  $\alpha$  after the 11.29 h of HWS testing (Figure 7) amounts to about 0.009 5 (ca. 1%). The simulation of the adiabatic temperature rise from that temperature of  $183.8^\circ\text{C}$  can be further calculated and is presented in Figure 7 as a solid line. The numerical results are in accordance with the experimental data and indicate that the calculated remaining TMR is ca. 4.4 h.

Presented results show that the good fit of simulated and experimental results in HWS-ARC test can be additionally applied for the verification of the calculated kinetic parameters.

The next important advantage of the use of the kinetic parameters derived from DSC data consists 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 very difficult to achieve from the experimental point of view. Such a simulation is presented in Figure 8 depicting the safety diagram for 3-methyl-4-nitrophenol calculated for few initial temperatures by the procedure applied for the simulation of TMR in ISO-ARC shown in Figure 6. Depending on the decomposition kinetics and  $\Delta T_{ad}$ , the initial temperatures differently influence the  $\text{TMR}_{ad}$  values and the rate of the temperature evolution under adiabatic conditions. For  $\Phi=1$  the determined  $\text{TMR}_{ad}$  is about 8 hours at an initial temperature of about  $164.9^\circ\text{C}$  (for that temperature a more conservative value for  $\text{TMR}_{ad}$  is 6.76 h). The critical value  $\text{TMR}_{ad} = 24$  hours, commonly accepted as the safety limit in the industrial scale, is obtained at about  $151^\circ\text{C}$  (for that temperature a more conservative value for  $\text{TMR}_{ad}$  is 20.22 h). The confidence interval is determined similarly as explained in Figure 6.

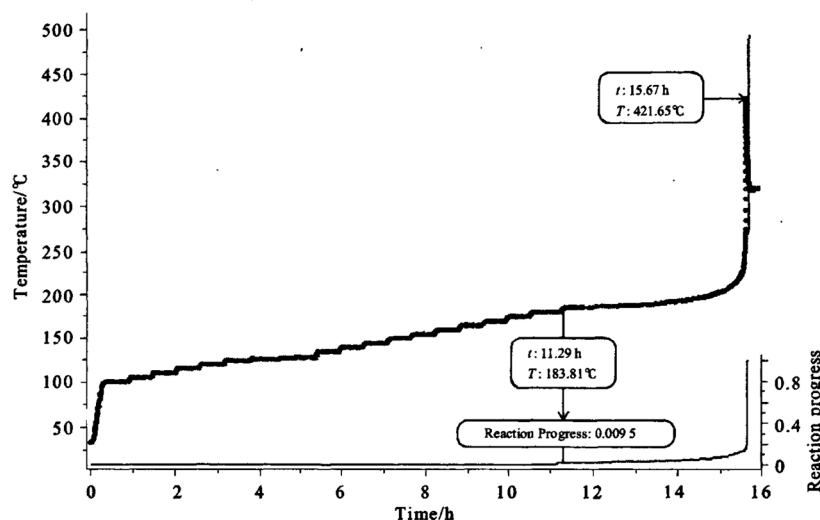


Fig.7 Typical ARC test for 3-methyl-4-nitrophenol carried out in HWS mode. Having the kinetic description of the reaction rate from the DSC data, one can estimate that the reaction progress  $\alpha$  after ca. 11.3 h of HWS testing amounts to about 0.009 5 (ca. 1%). From the time at which the temperature of the detection limit (183.81 °C) was reached the value of TMR amounts to ca. 4.4 h (15.67~11.29 h). Solid line depicts the simulation being in a good agreement with the experimental HWS-ARC data presented as symbols.

The Table 1 contains the results of the calculations of the TMR<sub>ad</sub> for all experimental data delivered by the participants of the round robin test. Despite the variety of the experimental set-ups and different origins of the samples the mean value of the initial temperature at which TMR<sub>ad</sub> = 24 h amounts to (151.27 ± 3.01) °C which is in accordance with the temperature displayed in the Figure 8.

The TMR<sub>ad</sub> values calculated by the presented method are less conservative as those derived by using the estimation of Keller et al<sup>[18]</sup>. He presented the estimation method for TMR<sub>ad</sub> from non-isothermal DSC measurements based on the model of zeroth

order reaction. Similar approach was presented in the paper of Pastre et al<sup>[19]</sup> which verified his model by Dewar vessel experiments. They proposed the linear regression procedure to find out a conservative value of the initial temperature that leads to TMR<sub>ad</sub> = 24 h as a function of  $T_{\text{Onset}}$ :

$$\text{TMR}_{\text{ad}, 24\text{h}}(\text{K}) = 0.65 \cdot T_{\text{Onset}}(\text{K}) + 50\text{K} \quad (15)$$

If one estimates roughly from Figure 1 that the possible detected onset lays between 220 and 250 °C, then according the Keller's approximation TMR<sub>ad</sub> = 24 h will be reached for initial temperatures between 97 and 117 °C. These values are 30~50 °C more conservative compared to presented by us value of

Tab.1 Summary of the results of determination of the initial temperatures leading to TMR<sub>ad</sub> = 24h with AKTS-Thermokinetics Software by using all DSC data collected in round robin test. (\*) Two HWS-ARCs with  $\Phi$ -factor = 3.2 and DSC with 2.5 K/min were applied. Determination of the initial temperature leading to TMR<sub>ad</sub> = 24h was done by combining the non-isothermal DSC data of 2.5 K/min with the ARC data using AKTS-Thermokinetics Software.

Participant of round robin test	Heating rates applied (non-isothermal)	Temperatures applied (isothermal)	$\Delta H_r \pm \sigma$	Initial temperature for TMR <sub>ad</sub> = 24 h	Sum of all correl coeff
CibaSC	0.25, 0.5, 1, 2, 4	200, 210, 220, 240	-1 961.2 ± 151.8	156.4	-0.996 0
DSM	0.5, 1, 2, 4, 8		-2 070.5 ± 166.7	153.6	-0.989 4
Lonza	4, 4	220, 240, 260	-2 143.2 ± 115.1	148.9	-0.993 2
Novartis	0.5, 2, 4, 8	210, 220, 230, 240	-2 133.8 ± 144.7	149.4	-0.993 4
Roche(*)	2.5, 2.5			148.0	
Swissi		190, 200, 210, 220	-2 112.1 ± 76.5	152.5	-0.997 8
Syngenta	5	220, 230, 240, 250, 260	-1 655.8 ± 141.9	150.1	-0.997 2

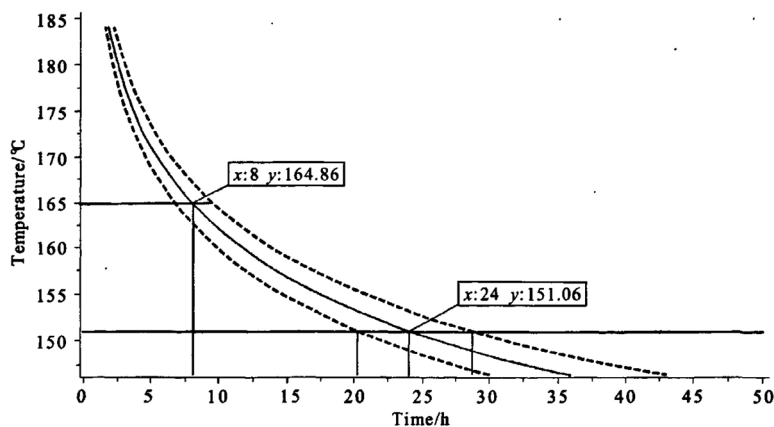


Fig.8 Thermal safety diagram for 3-methyl-4-nitrophenol in fully adiabatic conditions with  $\Phi = 1$ . The choice of the initial temperatures strongly influences the adiabatic induction time. With  $\Delta H_r = (-2001.7 \pm 216.5) \text{ J/g}$ ,  $\Delta T_{ad} = (-\Delta H_r)/(c_p \cdot \Phi) = 1000.9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

151°C. Nevertheless, this of Keller's rule of thumb can be considered as an interesting preliminary step in a thermal hazard assessment for determining  $\text{TMR}_{ad} = 24 \text{ h}$ .

**Influence of  $\Phi$ -factor on the reaction course**

The interesting feature of the simulation method presented in this paper is the possibility of the comparison of the predicted signals in isothermal, pseudo-adiabatic and fully adiabatic conditions.

At a constant temperature of 151°C one can see (Figure 9) that the reaction progress  $\alpha$  after 3 days amounts to about 0.038 (ca. 3.8%) only. The decrease of the  $\Phi$  value significantly changes the time required for the total decomposition. As presented in this figure the total decomposition under fully adiabatic conditions occurs after 1 day (24 h) however, with  $\Phi = 3.2$  (value applied with ARC calorimeter Figure 6) the reaction ends after ca. 2.4 days.

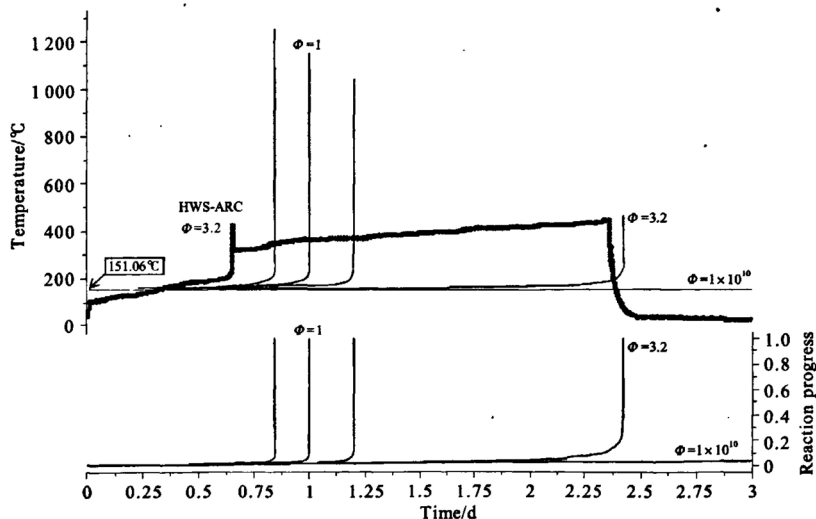


Fig.9 Comparison between the  $T$ - $t$  relationship (top) and reaction progress (bottom) in isothermal ( $T = 151.06^\circ\text{C}$ ) and adiabatic conditions.  $\text{TMR}_{ad}$  were calculated for a starting temperature of 151.06°C with  $\Phi = 3.2$  and 1, respectively using the values of  $\Delta H_r = (-2001.7 \pm 216.5) \text{ J/g}$  and  $C_p = 2 \text{ J/g} \cdot ^\circ\text{C}$ . Under isothermal conditions the reaction progress  $\alpha$  after ca. 2.4 days amounts to only ca. 0.038 (3.8%). The decrease of the  $\Phi$ -factor results in significant shortening of the time required for the total decomposition which occurs after 2.5 and 1 day for  $\Phi$ -factors 3.2 and 1.0, respectively.

Note that isothermal conditions can be numerically retrieved by setting an exceptionally large value of the thermal inertia factor such as  $\Phi=10^{10}$  to achieve an insignificant adiabatic temperature rise  $\Delta T_{ad} \approx 0$ . If the  $\Phi$  is very high all heat released by the reaction is dissipated to the surrounding. As a consequence, the sample temperature remains constant because with

$$\frac{dT}{dt} = \frac{1}{\Phi} \Delta T_{ad, true} \frac{d\alpha}{dt} \quad (16)$$

for very large values of  $\Phi$  we have

$$\frac{dT_s}{dt} \approx 0 \text{ and } T_s(\alpha=0) \approx T_s(\alpha=1) \approx T_{isothermal} \quad (17)$$

Simulated can be not only the temperature but the rate of the heat evolution during self-heating process as well. The simulated reaction rate in fully adiabatic conditions ( $\Phi=1$ ) as a function of temperature (top) and time (bottom) is presented in Figure 10.

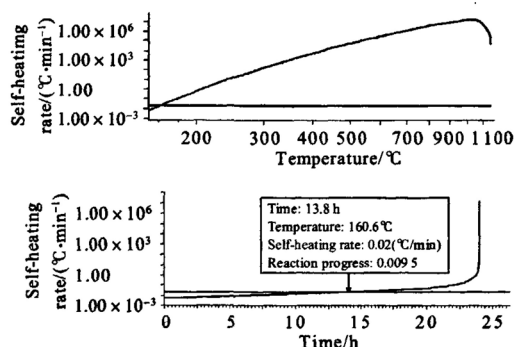


Fig.10 Simulated self-heating rate curves for 3-methyl-4-nitrophenol under adiabatic conditions ( $\Phi=1$ ) as a function of temperature (top) and time (bottom) calculated for an initial temperature of 151 °C. Typical detection limit of adiabatic calorimeters (0.02 K/min) is reached after 13.56 h i.e. 10.44 h before  $TMR_{ad}=24$  h. Reaction progress at 13.56 h amounts to about 0.009 5 (ca. 1%).

The simulation indicates that the typical detection limit of the heat evolution rate 0.02 K/min is reached after 13.8 h i.e. 10.2 h before  $TMR_{ad}$  value of 24 h. During this initial period of the adiabatic reaction the sample starts to decompose, the reaction progress at the point of the detection limit amounts to 0.009 5 (ca. 1%). Even such a small reaction progress can influence the value of the time remaining to 24 h, this issue is discussed in the following paragraph.

### Influence of Reaction Progress Occurring During Initial Period of HWS Adiabatic Experiment on Determination of $TMR_{ad}$

The correct interpretation and simulation of the adiabatic experiments requires introducing into considerations the problem of the certain, unknown degree of the decomposition of the investigated material which starts to decompose before the temperature of the detection limit is reached. This, even being relatively small, reaction progress leads to the shortening  $TMR_{ad}$  value comparing to the value characteristic for the absolutely not decomposed material having the reaction progress  $\alpha=0$ .

The simulation of the  $TMR_{ad}$  for the samples with different initial decomposition degree  $\alpha$  (in the range 0~5%) is depicted in Figure 11. The value of  $TMR_{ad}=24$  h for the initial temperature of about 151 °C and the sample with  $\alpha=0$  decreases to 23.03; 21.49; 17.59 and 9.75 h for the samples with the reaction progress of 0.001, 0.01; 0.025, and 0.05, respectively.

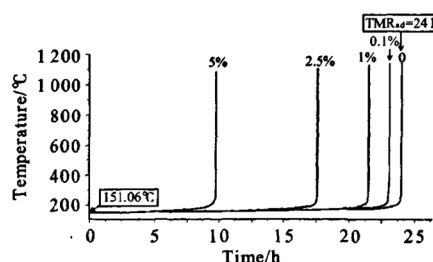


Fig.11 Influence of preliminary reaction progress  $\alpha$  on  $TMR_{ad}$  values. Note that the reaction progress  $\alpha$  is displayed in percent.

Presented results of the simulations clearly show that a special care has to be taken when interpreting results of  $TMR_{ad}$  obtained experimentally for the sample with unknown decomposition degree (like in HWS-ARC). This uncontrolled reaction progress depends not only on the experimental settings (the choice of the initial temperature in adiabatic experiments) but also on the kinetics of the decomposition. Depending on the kind of the rate-controlling step in the decomposition process this influence of the preliminary  $\alpha$  value on the  $TMR_{ad}$  can be different and this issue will be discussed in our next paper.



## Conclusion

The decomposition of 3-methyl-4-nitrophenol samples of different origins was studied using DSC and ARC. The DSC results delivered by the participants of a round robin test and 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 (with a thermal inertia factor  $\Phi = 1$ ) 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  $TMR_{ad} = 24$  h 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.

The precise kinetic description of the process allowed simulation of the influence of the  $\Phi$ -factor value on the reaction course. Due to the possibility of the simulation of ISO- and HWS modes of the ARC experiments the 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 knowledge of the kinetic parameters of the reaction allowed determining reaction progress occurring in the initial period of the adiabatic experiment before reaching by the system the detection limit of the heat evolution. Presented simulations showed that the influence of this initial reaction progress on the  $TMR_{ad}$  value has to be carefully considered because even not significant reaction progress as e.g. 0.025 can decrease by ca.

6.4 h the value of  $TMR_{ad}$  (24 h for  $\alpha=0$  and ca. 17.6 h for  $\alpha=0.025$ ).

## References

- [1] Zogg A, Stoessel F, Fischer U, et al. *Thermochim Acta*, 2004, 419: 1.
- [2] am Ende D J, Ripin D B H, Weston N P. *Thermochim Acta*, 2004, 419: 83.
- [3] Liu S Y, Tseng J M, Lee M K, et al. *Therm Anal Cal*, 2009, 95: 559.
- [4] Bhattacharya A. *Chem Eng J*, 2005, 110: 67.
- [5] Townsend D I, Tou J C. *Thermochim Acta*, 1980, 37: 1.
- [6] Iizuka Y, Surianarayanan M. *Ind Eng Chem Res*, 2003, 42: 2987.
- [7] Bodman G T, Chevrin S, Hazard J. *Materials*, 1994, 115: 101.
- [8] Bunyan P F, Griffiths T T, Norris V J. *Thermochim Acta*, 2003, 401: 17.
- [9] Kersten R J A, Boers M N, Stork M M, et al. *J Loss Prev Process Ind*, 2005, 18: 145.
- [10] Roduit B, Dermaut W, Lunghi A. et al. *J Therm Anal Cal*, 2008, 93: 163.
- [11] Roduit B, Folly P, Berger B, et al. *J Therm Anal Cal*, 2008, 93: 153.
- [12] Roduit B, Xia L, Folly P, et al. *J Therm Anal Cal*, 2008, 93: 143.
- [13] AKTS-Thermokinetics and AKTS-Thermal Safety software, AKTS AG, Advanced Kinetics and Technology Solutions[2010-10-06]. <http://www.akts.com>.
- [14] Swiss Institute of Safety and Security. Offer for sale-High pressure crucibles for differential scanning calorimeters [EB/OL][2010-10-08]. <http://www.swissi.ch/index.cfm?rub=1010>.
- [15] Friedman H L. *J Polym Sci(Part C): Polymer Symposium (6PC)*, 1964, 183.
- [16] Schoenborn K H. *Thermochim Acta*, 1993, 69: 103.
- [17] Patt M E, White B E, Stein B, et al. *Thermochim Acta*, 1992, 197: 413.
- [18] Keller A, Stark D, Fierz H. *J Loss Prev Ind*, 1997, 10: 31.
- [19] Pastre J, Wörsdörfer U, Keller A, et al. *J Loss Prev Ind*, 2000, 13: 7.

\*\*\*\*\*

### 三菱瓦斯拟扩能超纯过氧化氢

占全球超纯过氧化氢市场近60%市场份额的日本三菱瓦斯化学公司(MGC)近日表示,将在2011年大幅提高超纯过氧化氢生产能力,计划投资数十亿日元对美国、韩国、新加坡以及中国台湾省的相关设施进行扩能改造。

超纯过氧化氢广泛应用于半导体材料生产的晶片清洗工序,美国和亚洲市场增长迅速。据预测,这方面需求

正以超过10%的年均速度增长。为确保市场供应, MGC计划将美国亚利桑那州生产厂装置产能从3.5万t/a提高至7万t/a,将新加坡厂产能提高至1万t/a。在韩国市场,为满足三星电子业务扩张的需要,将把目前的4万t/a产能提高到6.5万t/a。对于中国台湾省生产厂,将通过脱瓶颈改造和生产使产能增至2万t/a。

(于剑昆提供)

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236632029>

# Estimation of time to maximum rate under adiabatic conditions (TMRad) using kinetic parameters derived from DSC-investigation of thermal behavior of 3-methyl-4-nitrophenol.

Article · January 2011

CITATIONS

9

READS

626

15 authors, including:



**Patrick Folly**

Armasuisse

31 PUBLICATIONS 730 CITATIONS

[SEE PROFILE](#)



**Francesco Mascarello**

DSM Nutritional Products

13 PUBLICATIONS 145 CITATIONS

[SEE PROFILE](#)



**Mischa Schwaninger**

Novartis

7 PUBLICATIONS 41 CITATIONS

[SEE PROFILE](#)



**Thomas Glarner**

Roche

5 PUBLICATIONS 49 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Daring the Challenge and Thinking Big: The Value of Early Process R&D [View project](#)



On-line monitoring of a chemical reaction using Mid-IR [View project](#)