

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

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Critical process safety and thermal stability parameters (e.g. TMR_{ad} , SADT, etc.) can be determined quickly and reliably from a modest amount of calorimetry data by using AKTS Thermokinetics Software (Thermal Safety Version). This advanced software utilizes differential isoconversional kinetic techniques for the precise modeling of runaway chemical reactions. From just a few DSC data sets, recorded at different heating rates and/or at different constant temperatures, a fully scalable model of the reaction can be generated which is then used to predict stability in different thermal environments. Verification of the model can be completed by a comparison of the measured and calculated reaction profiles, either rates or conversion, under both non-isothermal and isothermal conditions. As numerical methods are available to use any combination of arbitrary temperature programs, further validation can be performed using a single adiabatic calorimetry experiment. This process is illustrated here based on a recent round-robin investigation by seven of the top Swiss chemical companies [1].

Introduction

Decomposition of 3-methyl-4-nitrophenol (MN) was studied using Differential Scanning Calorimetry

(DSC) and Accelerating Rate Calorimetry (ARC). The results of DSC experiments carried out with different heating rates (non-isothermal mode) and at different temperatures (isothermal mode) were used for the precise determination of the kinetic parameters by AKTS software. These kinetic data allowed calculation of the variation of the runaway time under true adiabatic conditions (with a thermal inertia factor $\phi=1$) for any process temperature; the determined critical value $TMR_{ad} = 24h$ (24 hour time-to-maximum-rate) amounted to ca. 151°C. Both isothermal DSC and pseudo-adiabatic (ARC) experiments ($\phi>1$) were performed for final validation.

Experimental

Analysis of MN samples of various origins was done using DSC systems from various manufacturers. The decomposition was investigated in non-isothermal experiments in the range from 20°C to 350°C at heating rates from 0.25 to 8 K/min, and isothermally at temperatures from 200°C to 260°C. All DSC experiments were performed in gold plated high pressure sealed crucibles with a sample mass varying between 4.8 and 12.2 mg (see Fauske PSN Fall 2010 or <http://www.fauske.com/swissidsc.html> for details on these special SWISSI crucibles).

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Results

The temperature dependences of the reaction rate $d\alpha/dt$ and reaction progress α for all samples were normalized. Typical DSC signals recorded under non-isothermal conditions are presented in Fig. 1. Data were exported in ASCII format and processed with AKTS-Thermokinetics Software to determine the kinetic parameters (pre-exponential factor and activation energy) by the differential isoconversional technique [2] wherein the reaction rate $d\alpha/dt$ at a given reaction progress α is only a function of temperature. The knowledge of the kinetic parameters allows the simulation of the DSC experimental data. Comparison of experimental and simulated results at 4 K/min is shown in the Fig. 1 insets. Isothermal results are published elsewhere [1].

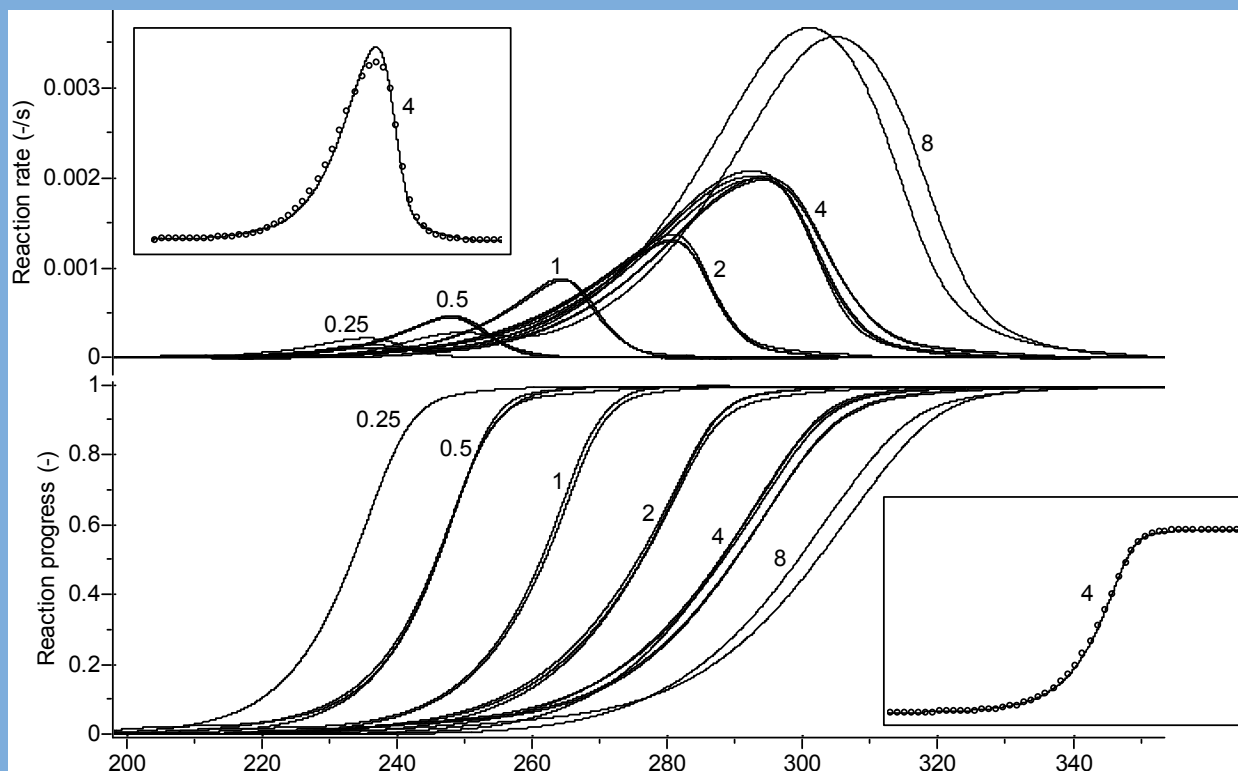


Figure 1: Reaction rates $d\alpha/dt$ (top) and progresses α (bottom) corresponding to normalized DSC signals for the decomposition of all 3-methyl-4-nitrophenol samples under non-isothermal conditions. The values of the heating rates are marked on the curves.

Simulation of Pseudo-Adiabatic Conditions

Kinetic parameters calculated from DSC measurements can be used to describe the thermal behavior of energetic material that is self-heating (i.e. in the absence of external heating) which corresponds to thermal runaway at adiabatic or semi-adiabatic conditions. Under adiabatic conditions the evolved heat stays in the system and simulation must account for the heat balance, including thermal inertia of the vessel or test cell. Considering an ARC experiment with a MN mass of 1.6g and a test cell (bomb) with $\phi = 3.2$, and taking $C_p = 2 \text{ J/(g}\cdot\text{K)}$ and an average heat release $\Delta H_r = -2001.7 \pm 216.5 \text{ J/g}$, one can express the heat balance as

$$\begin{aligned} \frac{dT}{dt} &= \frac{1}{\phi} \frac{(-\Delta H_r)}{c_p} \frac{d\alpha}{dt} = \\ &= \frac{1}{3.2} \frac{2001.7 \pm 216.5 \text{ J/g}}{2 \text{ J/(g}\cdot\text{K)}} \frac{d\alpha}{dt} \\ &= 312.8 \pm 33.8 \text{ K} \frac{d\alpha}{dt} \end{aligned}$$

The safety diagram based on these calculations (Fig. 2) provides a convenient estimate of the initial temperature for a practical isothermal ARC experiment that can be completed in a reasonable amount of time (say 5h) without preliminary HWS (Heat-Wait-Search) testing.

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Moreover, one can also simulate a HWS ARC test. Such a test was performed with an initial temperature of 100°C (Fig. 3). The temperature at the adiabatic self-heating detection limit of 0.02 K/min was about 184°C with $\phi=3.2$ and was reached after 11.3h. The time remaining from this point to the measured TMR was about 4.4h. The measured TMR value is consistent with the calculated results. One can estimate that the reaction progress α after the 11.3h of HWS testing is about 1%. Simulation of the reaction progress is shown in the bottom of Fig. 3.

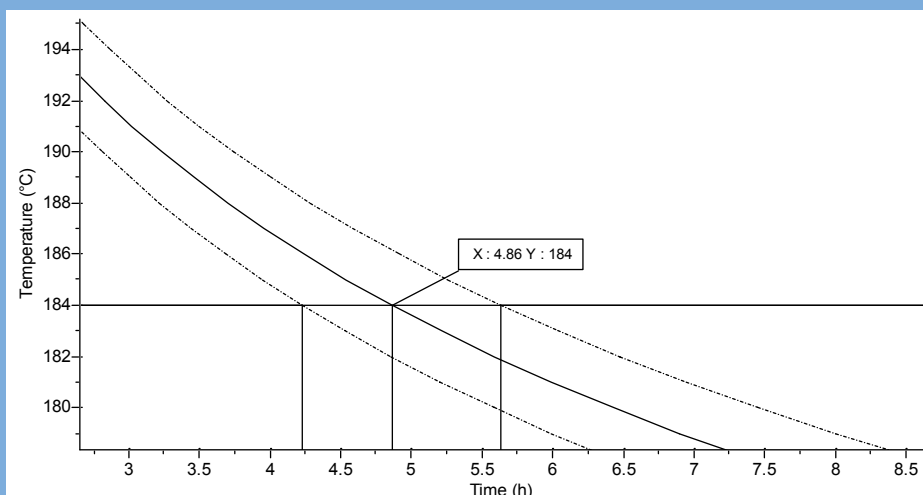


Figure 2: Simulation of thermal safety diagram for 3-methyl-4-nitrophenol. For an initial isothermal ARC temperature of $184 \pm 1^\circ\text{C}$, TMR amounts to about 4.86h with the confidence interval (range 4.2-5.6 hrs) calculated for the adiabatic temperatures lower by 1K (top curve) and higher by 1K (bottom curve).

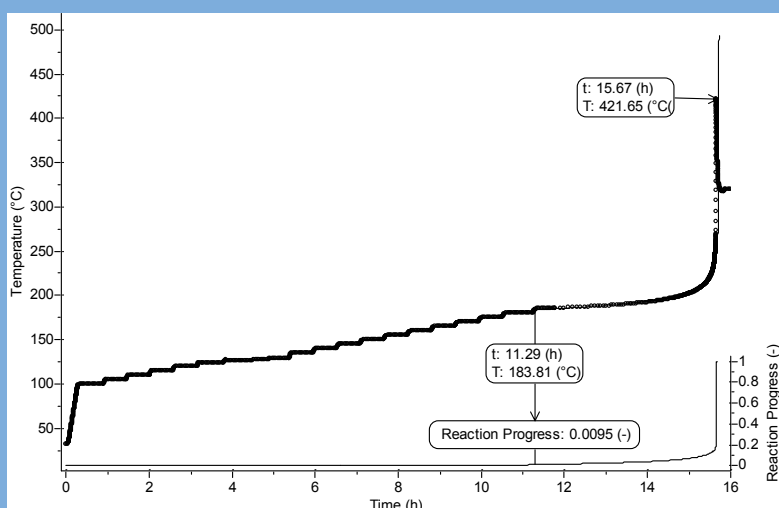


Figure 3: Typical ARC test for 3-methyl-4-nitrophenol carried out in HWS mode. Solid line shows the simulation in good agreement with the experimental ARC data presented as symbols. The measured ΔT_{ad} is lower than predicted since the ARC is not designed to track adiabatically at such high reaction rates. Simulation of the reaction progress is depicted on the bottom.

Simulation of True Adiabatic Conditions

The kinetic parameters derived from DSC data can be applied to full process scale by simulation of true adiabatic conditions ($\phi=1$) in the absence of any initial conversion ($\alpha=0$) which is difficult to achieve experimentally. Such an adiabatic simulation is presented in the safety diagram of Fig. 4. For $\phi=1$ the TMR_{ad} amounts to about 8 hours at an initial temperature of about 165°C (for that temperature a more conservative lower value for TMR_{ad} is 6.8 h). The critical value $\text{TMR}_{ad} = 24\text{h}$, commonly accepted as the safety limit at industrial scale, is obtained at about 151°C (for that temperature a more conservative value for TMR_{ad} is 20.2h).

Despite variation in test equipment and sample origin used by the round-robin participants, the mean value of the initial temperature at which $\text{TMR}_{ad} = 24\text{h}$ amounts to $151 \pm 3^\circ\text{C}$ which is consistent with the simulation results displayed in Fig. 4.

Finally, correct interpretation and simulation of adiabatic experiments requires careful consideration of the degree of decomposition of the investigated material, which starts to decompose before the temperature of the detection limit is reached. Even relatively small initial reaction progress leads to a lower TMR_{ad} value relative to the completely unreacted material. For example, just a 1% initial conversion reduces the TMR_{ad} at 151°C from 24h to 21.5h.

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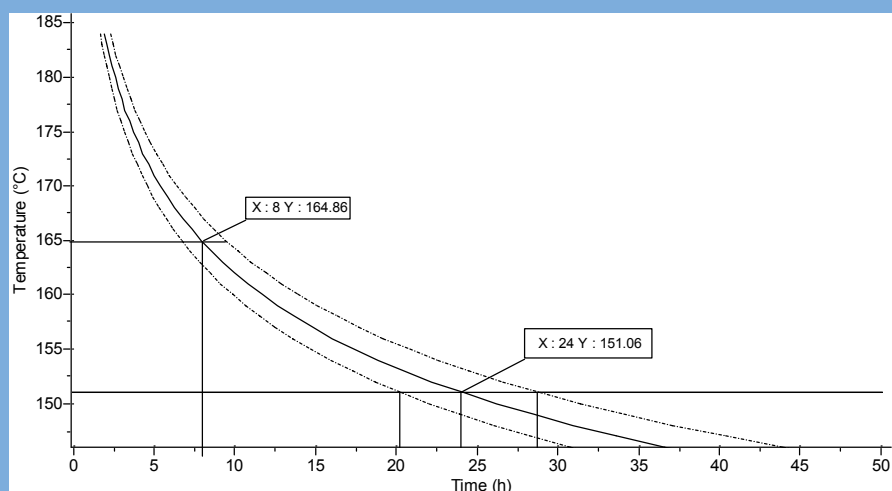


Figure 4: Thermal safety diagram of 3-methyl-4-nitrophenol in true adiabatic conditions with $\phi = 1$. The initial temperature strongly influences the adiabatic induction time. TMR_{ad} are 8 and 24 h for initial temperatures of about 165 and 151°C, respectively. Dashed lines show the confidence interval ($\pm 1K$).

Conclusion

Decomposition kinetics of 3-methyl-4-nitrophenol were precisely determined using DSC data and AKTS-Thermokinetics software and then validated using ARC data. This method can be used to reduce the time required for pseudo-adiabatic experiments by guiding the choice of initial temperature. The variation of the runaway time under true adiabatic mode (with a thermal inertia factor $\phi=1$) can be calculated as a function of the initial process temperature, creating a thermal safety diagram which provides critical safety information for industrial scale operations. Also, it is readily shown that even an insignificant initial reaction progress can considerably decrease the value of TMR_{ad} . This problem is generally underestimated and has to be seriously considered for strong autocatalytic reactions characterized by a long induction period under isothermal conditions. The precise kinetic results can be applied also to non-adiabatic cases to calculate parameters such as the SADT (Self Accelerating Decomposition Temperature).

Further Information

Fauske & Associates, LLC is an authorized distributor of AKTS Thermokinetics Software for Thermal Safety. We are enthusiastic about this collaboration between two well respected and world class companies. For further information about AKTS software or to arrange for a product demonstration please contact Jim Burelbach at burelbach@fauske.com.

References

1. B. Roduit, et al., <http://www.akts.com/thermal-safety-references.html>, 10th European Symposium on Thermal Analysis and Calorimetry (ESTAC), 22 – 27 August 2010, Rotterdam, The Netherlands.
2. H.L. Friedman, J. Polym. Sci., Part C, 6 (1964) 183.

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