

# Scale-up Based on Advanced Kinetics. Influence of DTBP/Toluene Ratio on the Thermal Behavior of Samples in mg, kg and ton-Scales

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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>) of various concentrations of Di-tert-butyl peroxide (DTBP) in toluene. Additionally we present the method of simulation of the course of ARC experiments. 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 give 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 concentrations of DTBP in toluene ranging from 5 to 25%. Decomposition was investigated in non-isothermal experiments in the range 20-300° C at heating rates between 0.5-8 K/min but also some isothermal measurements between 150-175° C were performed. Kinetic parameters were calculated using AKTS-Thermokinetics Software [1] based on differential isoconversional approach [2, 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 DTBP together with the simulations, recorded in non-isothermal conditions, after baseline subtraction are presented in Figure 1 at heating rates between 0.25-8 K/min and for concentrations of DTBP ranging from 5 to 25%. 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 isothermal conditions at 150 and 170° C is depicted in the inset.

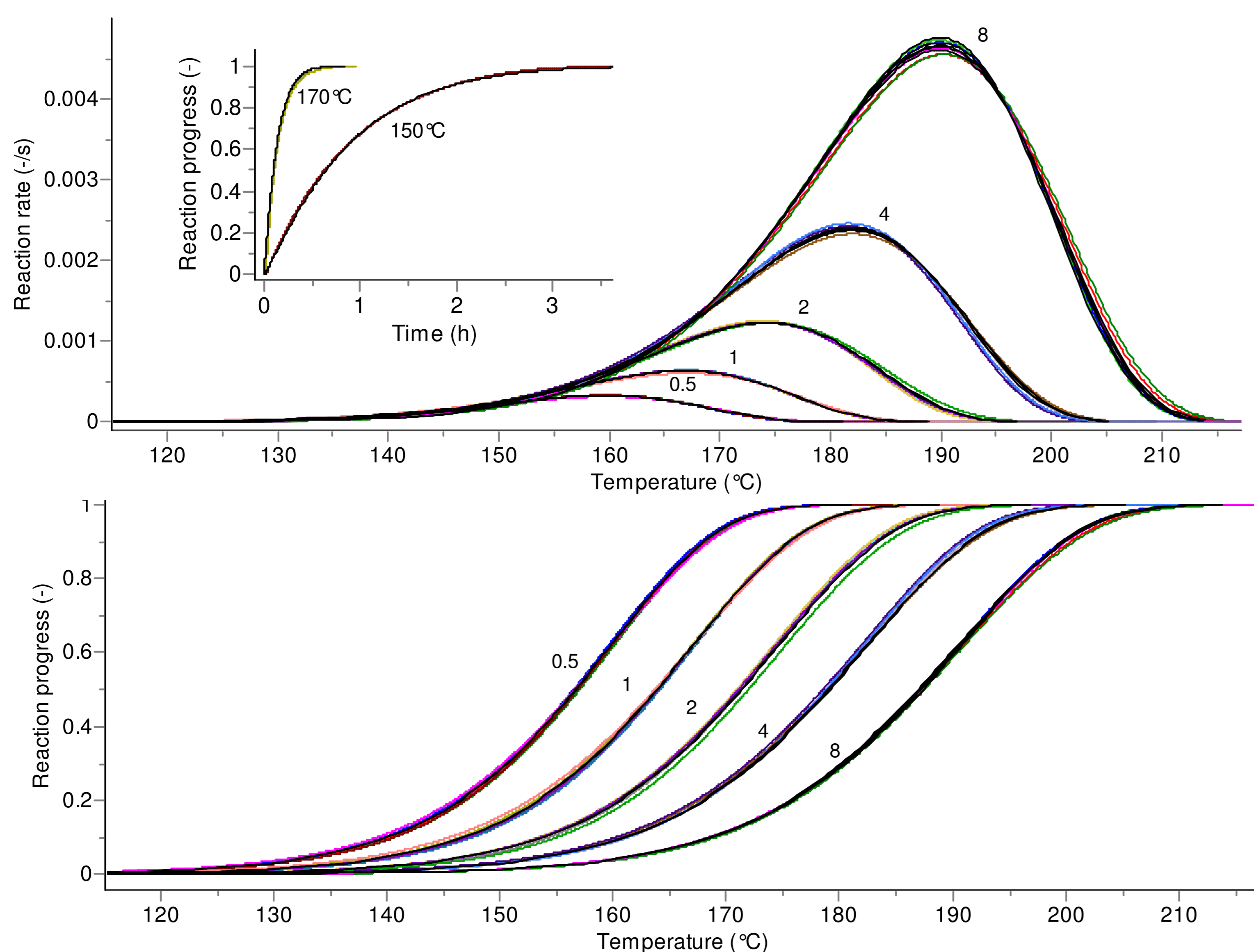


Fig. 1. Reaction rates  $da/dt$  (top) and progresses  $\alpha$  (bottom) corresponding to the normalized DSC-signals for the decomposition of all DTPB samples under non-isothermal conditions. Experimental and simulated curves are presented in color and black, respectively. The values of the heating rates are marked on the curves. The comparison of the experimental and simulated reaction progress under isothermal conditions at 150 and 170° C for a concentration of DTBP of 10% is shown in the inset.

### 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 materials 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 fully 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 taking different values of  $C_p$  and  $\Delta H_r$  measured by DSC for various DTBP concentrations, we can write:

$$\frac{dT}{dt} = \frac{1}{\Phi} \frac{(-\Delta H_r)}{c_p} \frac{d\alpha}{dt} = \Delta T_{ad} \frac{d\alpha}{dt}$$

The safety diagram based on these calculations is shown in Fig. 2 and Tab.1 together with the results for the other concentrations. Presented dependence illustrates how the kinetic parameters obtained from DSC data enable the construction of a thermal safety diagram, i.e. starting temperature and corresponding adiabatic induction time TMR<sub>ad</sub> relationship for the various DTBP concentrations. Moreover, the ARC test carried out e.g. in a HWS mode can be simulated too. 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. 114.7°C was reached after 3.77 h. The time remaining from this point to the measured TMR<sub>ad</sub> (see Fig. 3) amounts to 12.14 – 3.77h = 8.37 h.

In addition, having the kinetic description of the reaction rate derived from the DSC data, one can estimate that the reaction progress  $\alpha$  after 3.77 h of HWS testing (Fig.3) amounts to about 0.0114 (ca. 1.14%). The simulation of the adiabatic temperature rise from that temperature of 114.7°C can be further calculated for an experimental adiabatic temperature rise of  $\Delta T_{ad,exp}=57.5^\circ\text{C}$  as measured by ARC for a sample mass of 5g with at DTBP concentration of 10%. (Fig.3, red line). The calculations are consistent with the measured values (Fig.3, in green) confirming TMR<sub>ad</sub> results presented in Figure 2.

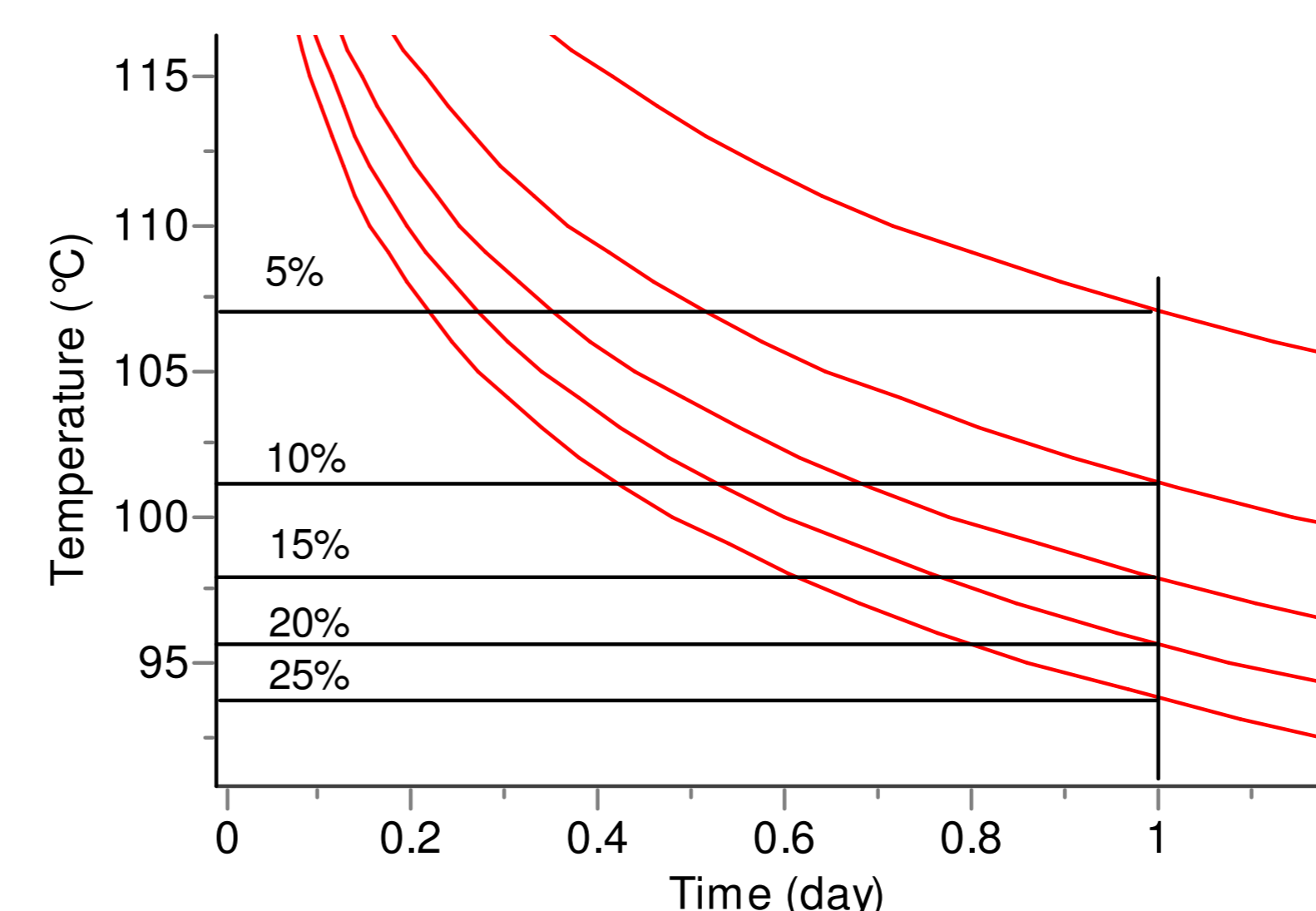


Fig. 2. Thermal safety diagram for DTBP in toluene. The simulation parameters are given in text. The initial temperatures leading to TMR<sub>ad</sub> = 24 h for concentrations of DTBP ranging from 5% to 25% in toluene are presented in Tab. 1.

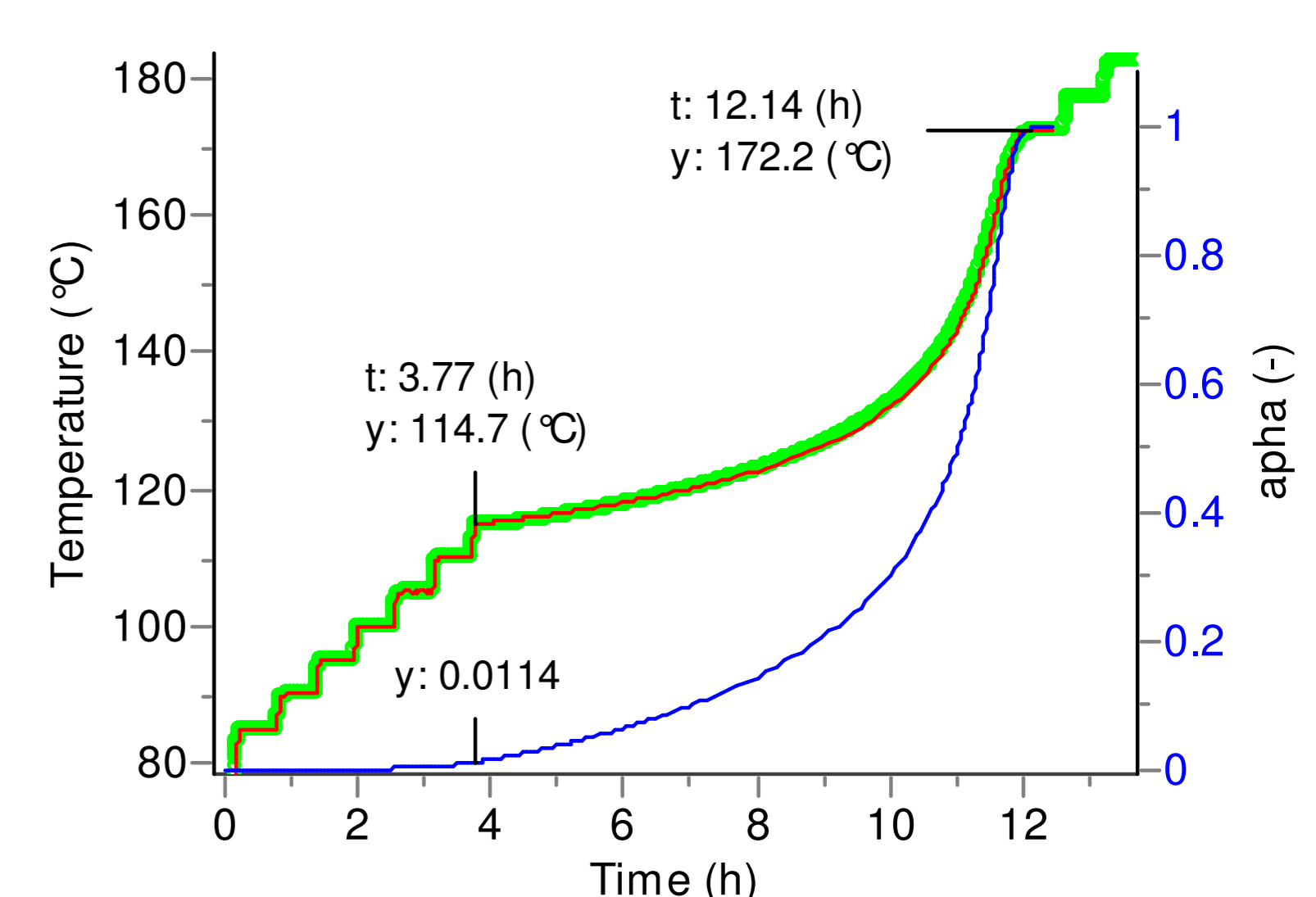


Fig. 3. ARC test for a DTBP concentration of 10% in toluene carried out in HWS mode. The reaction progress  $\alpha$  after ca. 3.77 h of HWS testing amounts to about 0.0114 (ca. 1.14%). From the time at which the detection limit (114.7°C) was reached the value of TMR<sub>ad</sub> amounts to ca. 8.37 h (12.14 - 3.77 h). Solid line (in red) depicts the simulation being in a good agreement with the experimental HWS-ARC data (in green).

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 undecomposed sample ( $\alpha=0$ ) what is difficult to achieve from the experimental point of view. Such a simulation is presented in Fig. 4 depicting the adiabatic runaway and self-heating rate curves of DTBP for the same initial temperature by the same procedure applied for the simulation of TMR<sub>ad</sub> and for concentrations of DTBP ranging from 5 to 25%. The critical value TMR<sub>ad</sub>=24 hours, commonly accepted as the safety limit in the industrial scale, is obtained at about 93.7°C for a concentration of DTBP of 25% (for that temperature TMR<sub>ad</sub> is c.a. 4.8 days for a concentration of 5%) (see Fig. 4, left).

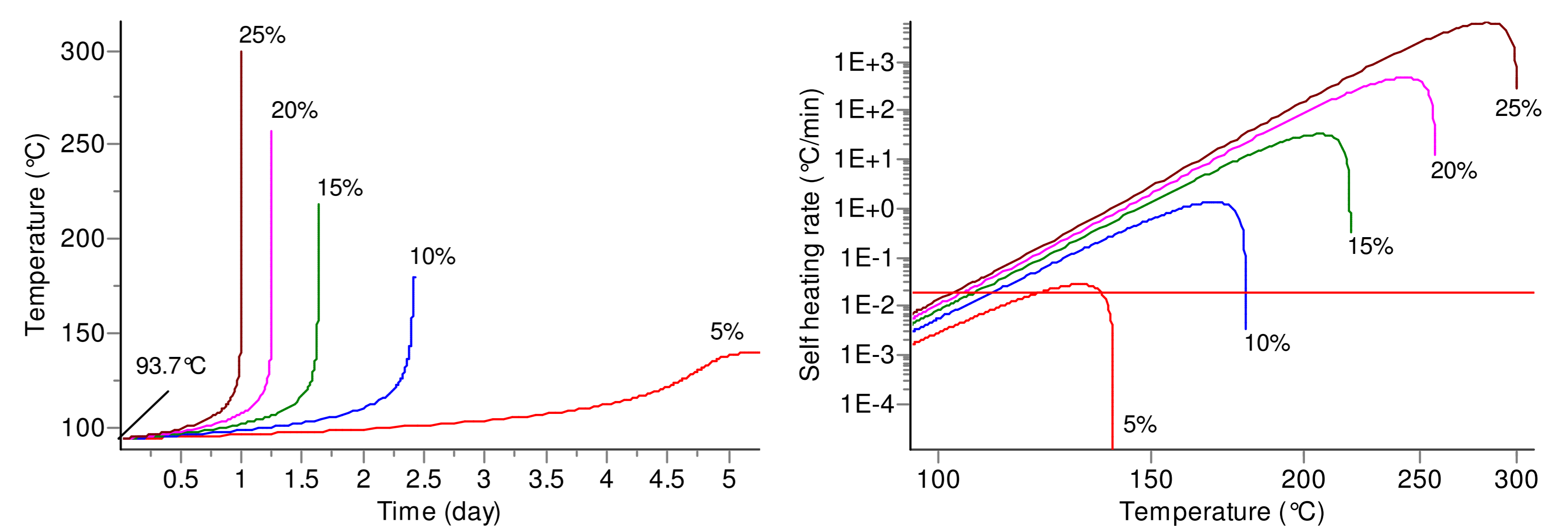


Fig. 4. Adiabatic runaway curves (left) and self-heating rate curves (right) in fully adiabatic conditions for an initial temperature of 93.74° C and concentrations of DTBP ranging from 5 to 25% (indicated on the curves). The different concentrations of DTBP strongly influence the adiabatic induction time. With  $\Delta H_r = -376.9 \pm 16.3$  J/g,  $C_p = 1.82$  J/g/°C,  $\Phi = 1$  and  $\Delta T_{ad} = (-\Delta H_r)/(C_p \cdot \Phi) = 206.5 \pm 8.9$ °C, TMR<sub>ad</sub> is 24h for an initial temperature of 93.7° C. By comparison, TMR<sub>ad</sub> is c.a. 4.8 days for a concentration of 5%, respectively.

The calculated initial temperature values with TMR<sub>ad</sub> = 24h from all experimental data with different concentrations of DTBP in toluene are presented in Tab.1:

DTBP concentration (%)	Heat capacity (J/g/K)	Heat of reaction (J/g)	T (°C) for TMR <sub>ad</sub> =24h
5	1.72	-78.8 ± 5.1	107.1
10	1.75	-150.1 ± 6.4	101.2
15	1.77	-222.2 ± 12.8	97.9
20	1.80	-294 ± 13.8	95.6
25	1.82	-376.9 ± 16.3	93.7

Tab. 1. Comparison between the initial temperatures leading to TMR<sub>ad</sub>=24h for various concentrations of DTBP in toluene. The choice of the different concentrations of DTBP strongly influence the initial temperature with TMR<sub>ad</sub>=24h. For example, TMR<sub>ad</sub> is 24h for initial temperatures of 107.1 and 93.7° C for concentrations of 5 and 25% of DTBP, respectively.

## Conclusion

DSC results 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 of various concentrations of DTBP in toluene. After precise determination of the kinetic parameters, the variation of the runaway time under true adiabatic mode ( $\Phi = 1$ ) was calculated for various initial process temperatures and concentrations. 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 107.1, 101.2, 97.9, 95.6 and 93.7° C for DTBP concentrations of 5, 10, 15, 20 and 25%, respectively. Both non-isothermal and isothermal DSC but also 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 for any investigated concentrations what results in shortening of the time required for the adiabatic investigations.

## References

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