

Model-Based Prediction of the Adiabatic Induction Period and SADT of Dicumyl Peroxide Solution and Comparison to Large-Scale Experiments Performed Using 216.5-Liter Steel Drums in the UN-Test H.1

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The thermal decomposition of dicumyl peroxide dissolved in ethylbenzene has been studied in our laboratories using differential scanning calorimetry (DSC), calvet calorimetry (C80), adiabatic calorimetry, reaction calorimetry and micro calorimetry.

Based on the DSC and C80 experiments a formal kinetics model has been derived, which was compared to the other applied techniques. Finally we used our model to predict the thermal response of 216.5 L steel drums to exposure to constant elevated temperatures, both using the stationary Semenov approach as well as time-resolved CFD simulations. The prediction was compared to one-to-one testing using the UN-Test H.1. The observed level of consistency between model and experiments is remarkably good. The comparison with the 216.5 L testing clearly demonstrates that reliable and conservative predictions for technically relevant scales are possible as long as a validated model is used.

1. Introduction

A common challenge in industrial practice is to assess the storage stability (e. g. determination of the self-accelerating decomposition temperature, SADT) or the adiabatic induction period (AIP) for pure substances or mixtures in large-scale apparatuses (e. g. tank containers, storage tanks or reactors). However one-to-one experiments are prohibitive both due to safety and economy considerations. This situation creates an urgent need for methods allowing an assessment of large scale devices based on small scale experiments. A promising approach to predict both SADT and adiabatic induction periods is the use of formal kinetics as the basis for simulations.

Because the hazard potential of industrial-scale storage tanks, reactors or tank containers can be significant it is crucial to precisely understand the uncertainties associated with predictions of SADT or AIP over many orders of magnitude in volume - only this way reasonable safety margins can be defined.

In our contribution we will show that the creation of highly reliable formal kinetics models is possible with methods which are routinely used in chemical hazard laboratories. To do so we have chosen the thermal decomposition of dicumyl peroxide (DCP) dissolved in ethylbenzene (EB), for which we created a model based on dynamic measurements using dynamic scanning calorimetry (DSC) and calvet calorimetry (C80), respectively.

Based on this model we predicted various quantities such as isothermal heat flows or adiabatic temperature profiles. By comparison of the model predictions to direct measurements of these quantities we were able to demonstrate the reliability of the model. We furthermore compared a prediction of the SADT for a 216.5 L steel drum to direct measurements using the H.1 test.

For all investigations described here a mixture of 40 wt.-% DCP (Akzo Nobel, purity > 99 %) dissolved in 60

wt.-% EB (BASF, purity > 99 %) was used. The mixture for the large-scale steel drum (1A1) experiments was prepared in a single batch using a technical scale stirred reactor. The concentration of DCP was checked after mixing using DSC measurements.

2. Experimental Investigation of DCP Decomposition by DSC and C80

10 different DSC instruments have been used in the BASF safety laboratory to assess DCP decomposition. On each instrument two runs were done using heating rates of 2.5 K/min and 5 K/min, respectively. Furthermore the reaction has been observed 8 times in one calvet calorimeter in the BASF safety laboratory. These runs have been done with a heating rate of 0.3 K/min.

Table 1 shows the mean values of the relevant quantities obtained in the DSC and C80 measurements. It becomes evident that the observed reaction enthalpies are very consistent (see figure 1 for a comparison of the detected DSC and C80 signals). As discussed below in the modelling part, the shift in the observed onset- and peak temperatures, respectively, can be explained by the change in the used heating rates.

Table 1: Results of DSC Measurements

	T _{onset} [°C]	T _{max} [°C]	H [J/g]
DSC: Mean Values (2.5 K/min)	110	166.5	361.8
C80: Mean Values (0.3 K/min)	90	144.3	365.4

3. Formal Kinetics Model

For the development of a formal kinetics model, dynamic calorimetric measurements at different heating rates were conducted and kinetically evaluated using the NETZSCH Thermokinetics 3 program. The heat flow curves of four DSC (0.3 K/min – 5.0 K/min) and three C80 (0.1 K/min – 0.5 K/min) measurements were used here. The best fit to the experimental results is achieved with a single-step *n*-th order reaction according to the following differential equation.

$$\frac{d[A]}{dt} = -k_0 \cdot \exp\left(\frac{E_A}{RT}\right) \cdot [A]^n$$

The corresponding kinetic parameters are listed in table 2. These results are in quite good accordance to published data from Marco et al. (2000). The good agreement between modelled and experimental data is depicted in figure 1.

Table 2: Formal kinetic parameters for decomposition of DCP in EB

Activation energy, <i>E_a</i> [kJ/mol]	149.2084
Pre-exponential factor, <i>k₀</i> [log (s ⁻¹)]	15.3548
Reaction order, <i>n</i>	0.9868

4. Prediction of the Heat Flow and Comparison to Direct Measurements

In the following subsections the model is used to estimate the thermal behaviour of the mixture under isothermal conditions and to validate the quality of model predictions by comparison with corresponding experimental data from different calorimetric techniques.

4.1 Isothermal Measurements by Reaction Calorimetry

The thermal decomposition of DCP dissolved in EB was measured in a reaction calorimeter (RC) (ChemiSens CPA202) at 120 and 130 °C. The good agreement with the results of the DSC and C80 experiments can be seen in table 3. Especially the reaction enthalpy which was obtained from the experiment at 120 °C fits very well to the DSC and C80 values (see table 1). A reason for the slightly smaller reaction enthalpy in the 130 °C experiment might be that decomposition is taking place to some extent already during the heating phase. For this reason the heat flow could not be detected completely.

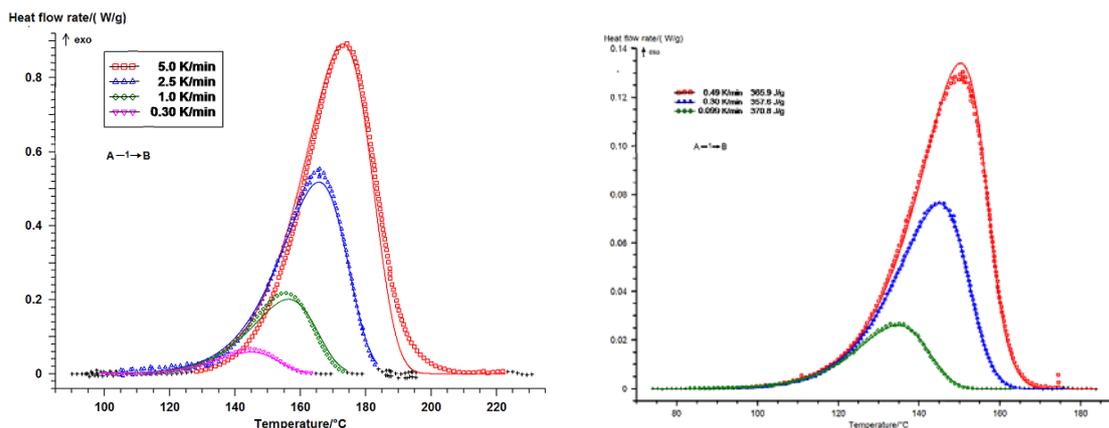


Figure 1: Fit of the kinetic model (solid lines) to the DSC and C80 measurements at different heating rates. Left: DSC data. Red squares 5 K/min, blue triangles: 2.5 K/min, dark green diamonds: 1 K/min, pink triangles top down: 0.3 K/min. Right: C80 data. Red squares: 0.5 K/min, blue triangles: 0.3 K/min, green diamonds: 0.1 K/min.

Additionally, we determined the rate constants for the DCP decomposition in EB. As shown in table 3, our results agree well with ARSST data from Marco et al. (2000).

Table 3: Reaction enthalpy H and rate constants k from RC measurements and comparison with DSC and C80 enthalpies as well as rate constants from literature.

	H [J/g]	k / s ⁻¹
RC @120 °C	368.7	3.2×10^{-5}
RC @130 °C	348.4	1.1×10^{-4}
DSC: Mean Values (2.5 K/min)	361.8	
C80: Mean Values (0.3 K/min)	365.4	
Marco et al. (2000) @120 °C		5.3×10^{-5}
Marco et al. (2000) @130 °C		1.6×10^{-4}

4.2 Comparison

The model presented in chapter 3 has been used to predict the isothermal heat flow at various temperatures. From each modelled signal the maximum heat flow has been extracted. The dependence of the maximum heat flow on temperature could be represented by an exponential fit, as presented in figure 2 (left). The prediction was compared to many isothermal measurements of the maximum heat flow. As can be seen in figure 2 the agreement between modelled and measured maximum heat flow is remarkably good over several orders of magnitude. For the RC experiments one can also compare the time-resolved heat flow signal with the simulated curve. The agreement between experiment and model is very good as can be seen in figure 2 (right).

5. Prediction of Adiabatic Temperature Signals and Comparison to Direct Measurements

5.1 Adiabatic Calorimetry

In addition to the above mentioned experiments the DCP decomposition in EB was also investigated in an adiabatic calorimeter (DWS, in-house method of BASF). The starting temperature in the experiment was 90 °C with an adiabatic induction time of 16 h (after correction with a phi-factor of 1.2). From this experiment the activation energy was determined to be 141 kJ/mol. With this activation energy the adiabatic induction time was extrapolated according to the approach described by Townsend (1981). With the model described in section 3 the adiabatic induction time for different temperatures is simulated with Netzsch Thermal Simulation 2. A comparison between the simulated values and the ones obtained by extrapolated experimental data is shown in figure 3.

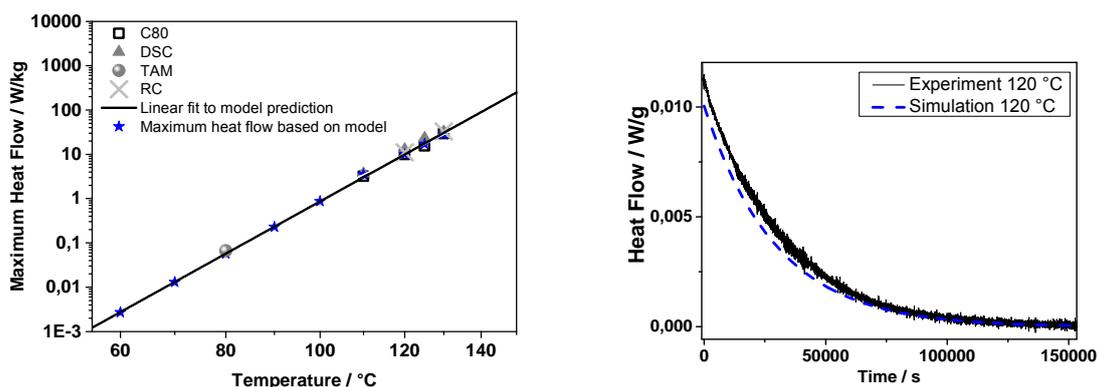


Figure 2: Comparison of modelled and measured quantities. Left: maximum heat flow for a 40 wt.-% DCP solution in EB. Blue stars: maximum heat flow based on isothermal modelling. Black line: linear fit to modelling results. Hollow black squares: isothermal C80 experiments. Grey triangles: isothermal DSC experiments. Grey sphere: isothermal TAM experiment. Light grey crosses: isothermal RC experiments. Right: time-resolved heat flow. Blue dashed line: heat flow simulated by using the model described in section 3. Black straight line: experimental data from RC experiments at 120 °C.

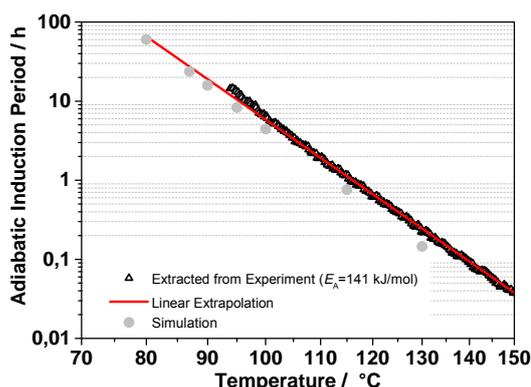


Figure 3: Comparison of modelled and extrapolated adiabatic induction times. For simulation of the adiabatic induction time the following values are used: $C_p = 2$ J/(g K) and $H = 364$ J/g. For the extrapolation according Townsend (1981) an activation energy of 141 kJ/mol was used.

6. SADT determination in a 200 L steel drum

The experimental setup for the determination of the SADT is described in detail elsewhere, see Malow et al. (2015). For the large scale SADT tests standard steel drums (UN 1A1) with a volume of 216.5 L (diameter 58.5 cm, height 88.2 cm) were used. Tests with the DCP/EB mixture were performed at 85, 95 and 100 °C. For the 85 and 100 °C experiment 166.6 kg substance was used, respectively. For the 95 °C experiment 160.1 kg was used. The correct storage temperature for each experiment was adjusted in a preliminary experiment utilizing a 216.5 L steel drum filled with 200 L pure EB. For practicality reasons the double jacket vessel was heated up empty to the preset storage temperature before inserting the steel drum to be tested. The temperature in the center, at half radius/half height and at half radius/three-quarter height (top section) of the steel drum was measured with type K thermocouples. In Fig. 4 the center temperatures for all tests are shown. The runaway reaction after the start of the experiment occurred after ~ 30 h at 100 °C storage temperature and after ~ 36 h at 95 °C storage temperature. At 85 °C storage temperature no runaway reaction was recorded up to 332 h after the start of the experiment. Table 4 summarizes the test results.

Due to the lack of data point at 90 °C the SADT for a 200 L steel drum as determined according to the UN Test H.1 in real scale tests is reported here to be either 90 °C or 95 °C.

Table 4: UN-Test H.1 test results at different storage temperatures.

UN-Test H.1 storage temperature [°C]	85	95	100
Heat loss due to cooling ¹ [mW/(kg K)]	47	68	51
$\Delta T \geq 6$ K during 7 days ²	no	yes	yes
Induction time [h]	-	7.1	3.9

¹determined by the semi-log plot according to 28.3.6 (UN TDG) ² $\Delta T = (T_{\text{substance, center}} - T_{\text{ambient, storage}})$

7. Prediction of the SADT and Comparison to Direct Measurements

We employed our model to predict the thermal response of a 216.5 L steel drum to exposure to constant elevated temperatures, both using the stationary approach by Semenov (1928) and time-resolved CFD simulations. For these simulations the CISP software package “thermal safety” was employed. For all simulations in this section a heat release of 360 J/g has been used, based on the DSC results summarized in table 1.

7.1 Semenov Approach to Determine the SADT

For the 1A1 steel drums we estimated a heat exchange surface of 1.84 m² and a heat loss per unit mass of 44.22 mW / (kg K). Assuming that the steel drum is completely filled the Semenov plot (see figure 4, left) shows a critical ambient temperature (directly corresponding to the SADT) of 83 °C. The heat flow data which were used to generate the Semenov plot were obtained by an isothermal prediction with the NETZSCH Thermokinetics 3 software package.

7.2 Time-resolved Simulation of SADT

To simulate the SADT for the 216.5 L steel drum we used the ConvEx FK routine of the CISP software package. We assumed a pseudo one-component liquid and used the formal kinetics described above to determine the SADT. The simulation predicts a value of 86 °C for the SADT. In addition the isoperibolic experiments with the 1A1 steel drum were modelled with ConvEx FK taking convection into account. In this simulation the environment temperature was set to 85, 95 and 100 °C, respectively, and the starting temperature of the DCP solution was set to the starting temperature of the DCP solution in the experiments. Table 5 lists the parameters used in the simulation. We note that aside from the use of the proper starting temperature of the DCP solution no further adjustment of the simulation to the experiment was made. We found good agreement with the experiments, as shown in figure 4 (right). The slight difference in the temperature dependence of the induction time between experiment and simulation might be due to increasing non-ideal heat transport and non-constant temperature conditions in the experiments as the temperature increases.

Table 5: Parameters used in the CFD simulation.

Parameter	Unit	Value	Source
Density (reaction mass)	kg / m ³	919	This work ¹
Specific heat (reaction mass)	J / (kg K)	1500	This work ²
Thermal conductivity (reaction mass)	W / (m K)	0.136	Handbook of Chemistry and Physics
Initial Temperature (reaction mass)	°C	20	Definition
T-expansion coefficient (reaction mass)	1/K	1E-4	Guess ³
Dynamic viscosity	Pa s	1E-4	Guess ³
Density (steel shell)	kg / m ³	7900	Guess ³
Specific heat (steel shell)	J / (kg K)	470	Guess based on Groth and Müller (1995)
Thermal conductivity (steel shell)	W / (m K)	13	Guess based on Groth and Müller (1995)
Wall thickness (steel shell)	m	0.001	Definition
Initial temperature (steel shell)	°C	20	Definition
Initial temperature (ambient)	°C	100	Definition
Heat Transfer coefficient	W / (m ² K)	5	Guess based on UN-TDG

¹determined in BASF laboratory by weighing defined volume; ²determined in BASF laboratory by DSC; ³based on Handbook of Chemistry and Physics

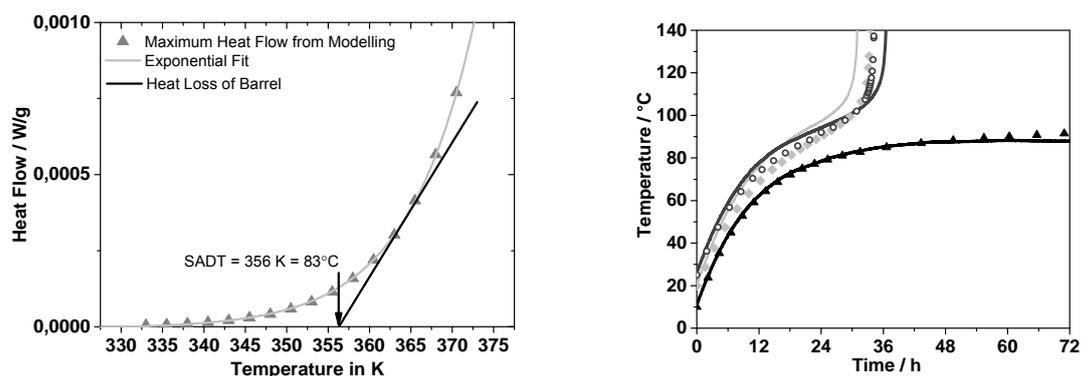


Figure 4: Left: Semenov plot for a 216.5 L steel drum filled with 208 kg of 40wt-% DCP solution in EB. Here we estimated a heat loss per unit mass of 44.22 mW / (kg K) and a heat exchange surface of 1.84 m². Right: Lines: experimental center temperature of 216.5 L steel drum (1A1) SADT tests with DCP/DB mixture at 85 °C (black), 95 °C (dark grey) and 100 °C (light grey). Symbols: corresponding time-resolved CFD simulation using the parameters given in table 5 for 85 °C (black triangles), 95 °C (dark grey circles) and 100 °C (light grey diamonds).

8. Conclusions

In our contribution we have shown that DCP decomposition can be described with a simple first order formal kinetics model. The kinetic data obtained at different temperatures with different experimental methods are very consistent. We have compared the model predictions of various quantities to direct equivalent measurements and observed very good agreement for all considered quantities. We predicted the SADT of a 216.5 L steel drum of 83 °C using the Semenov methodology. An SADT of 86 °C was obtained using CFD simulations. The SADT determined for the 1A1 steel drum with DCP solution according to UN-Test H.1 is between 90 °C and 95 °C. The SADT obtained from modelling for this case hence is conservative. Furthermore we compared the predicted SADT for 216.5 L steel drums to our model-based prediction. It is very notable that the prediction resulted in conservative values compared to the one-to-one experiment when extrapolated over many orders of magnitude. (Note: The model is based on DSC and calvet calorimetry which use sample volumes of several μL or mL, respectively. In contrast the one-to-one experiments have been done in 216.5 L steel drums.) We have demonstrated that a reliable prediction of safety relevant quantities such as SADT or adiabatic induction periods is possible as long as care is taken with respect to model creation and validation. The differences in the SADT for the 216.5 L steel drum between simulation and experiments might be explained by uncertainties in the used substance and heat transfer characteristics.

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