Specification of the Limit Temperature T_{exo} for a Peroxide Synthesis Using Different Estimation Methods

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A major item of thermal process safety, concerning the industrial realisation of exothermic reactions, is the determination of a temperature, where a reaction can be carried out without risk for humans, environment, and of economic loss. The so-called limit temperature T_{exo} is a safety parameter for the reaction process and should not be mixed up with the Self Accelerating Decomposition Temperature (SADT). The last one refers to a temperature value for safe transportation including specific conditions like transport time and type of containment.

In Germany a technical guide (Identification and Control of Exothermic Chemical Reactions, TRAS 410, 2012) specifies three approaches for determining T_{exo}. In this work, all these approaches were applied to specify T_{exo} for the synthesis of three tert-Butyl peroxycarboxylic esters. Peroxycarboxylic esters are a subdivision of organic peroxides, known for their high hazardous potential.

Results differed partly significant. Anyhow, all of the used techniques and evaluation methods led to T_{exo} values, which were on the safe side – taken the T_{exo} value estimated by the heat release criterion as reference. This method is considered by the authors as a very accurate one.

1. Introduction

One main parameter for a safe process design is the setting of the so-called limit temperature T_{exo}. According to TRAS 410 it is defined as follows (citation from the English version of TRAS 410): "The limit temperature ("T_{exo}") is the maximum permitted temperature at which a substance or reaction mixture can just be handled without risk". T_{exo} depends not only on specific substance properties, but also on the specific plant conditions, especially on the ratio of heat production and heat removal, and on individual process parameters like hold-up time at a defined temperature. The approaches given in TRAS 410 are:

a)   Estimation of temperature, where an exothermic reaction is detected by a thermal screening method, e.g. Differential Thermoanalysis (DTA) or Differential Scanning Calorimetry (DSC), reduced by 100 K (100 K rule).

b)   Estimation of temperature for an adiabatic induction period of 24 hours ($TMR_{ad}24$), reduced by 10 K.

c)   Estimation of temperature where the specific heat release rate is 0.1 W/kg, reduced by 10 K (heat release criterion).

All the methods were applied to a tert-Butyl peroxycarboxylic ester synthesis. The synthesis is often carried out as a 2 step reaction. In the first step tert-Butyl hydroperoxide is converted with an alkaline hydroxide to form an intermediate in an aqueous solution. In the second step it reacts with a monocarboxylic acid halide to form the peroxycarboxylic ester (DP, 1972). The intermediate solution is monophase, whereas final reaction mixture is bi-phasic. The organic phase of the final product consists mainly of the peroxyester. Several aspects in thermal safety assessment of peroxycarboxylic ester production had been already discussed by the authors (Fritzsche and Knorr, 2009). As far as educts, intermediate and produced reaction mixture are concerned, the organic phase of the reaction mixture possesses the lowest decomposition temperature and the highest decomposition energy. In addition the

heat production during the second step is up to six times higher than during the formation of the intermediate. Therefore, the focus was set on the second step of the reaction and on the organic phase of reaction mixture for further investigation of thermal stability and the estimation of T_{exo}.

2. Approaches

2.1 Estimation of T_{onset} by DSC and application of 100 K rule

In using this rule, the onset temperature, where a self-heating is detected, is reduced by 100 K to estimate T_{exo}. Thermal screening methods like Differential Scanning Calorimetry (DSC) are common tools to estimate thermal stability of substances and mixtures right in the beginning of safety assessment (Grewer et al., 1989). By a dynamic DSC run both onset temperature ($T_{Onset\ DSC}$) and decomposition energy (ΔH_d) are identified.

2.2 Estimation of $TMR_{ad}24$ and subtraction of 10 K

Three ways to estimate $TMR_{ad}24$ for the decomposition of the tert-Butyl peroxycarboxylic esters were chosen and will be explained in the following.

By one method a single adiabatic run was carried out and induction time for other start temperatures were derived according Eq(1). The symbol t_{ind} stands for the total induction time, which describes the time period from the start temperature to the maximum rate of reaction. The time period $t(T_{0,i})$ describes the time between start temperature and temperature $T_{0,i}$ in the adiabatic run. The value of $T_{0,i}$ is greater than the start temperature. The difference of t_{ind} and $t(T_{0,i})$ is corrected by the Phi factor to eliminate the influence of heat accumulation in the sample container.

$$TMR\big(T_{0,i}\big) = \frac{t_{ind} - t(T_{0,i})}{Phi} \tag{1}$$

Calculated $TMR(T_{0,i})$ values can be mapped in an Arrhenius diagram against inverse absolute temperature $T_{0,i}$. For the initial time of the adiabatic run, where nearly no conversion takes place and the reaction velocity is nearly independent on the reactant concentration a zero order reaction can be assumed. This first part of the TMR $(T_{0,i})$ curve is the linear one in the plot and is used for an extrapolation of $TMR_{ad}24$.

As other method dynamic DCS measurements were used to estimate $TMR_{ad}24$. Keller et al. (1997) employed an approach to derive $TMR_{ad}24$ at a specified temperature (T_0) from a single dynamic DSC run. Eq(2) refers to an approximate solution for reactions of zero order, which is traced back to Townsend and Tou (1980).

$$TMR_{ad} = \frac{c_p \times R \times T_0^2}{q(T_0) \times Ea} \tag{2}$$

The specific heat capacity c_p of sample, the specific heat flow $q(T_0)$ at temperature T_0 and the activation energy Ea have to be known in order to solve Eq(2). The value of $q(T_0)$ is calculated by Eq(3), in which q_{ref} is the reference heat flow in W/kg at a reference temperature (T_{ref}). This reference point (T_{ref}, q_{ref}) is for DSC measurements the onset temperature and the heat flow at this temperature. The onset temperature is obtained when deflection from the baseline is noticeable, so q_{ref} refers to the detection limit of the used DSC apparatus. This value depends on the sensitivity of the specific used DSC apparatus. Taking the threefold value of the signal noise as detection limit is a common practice.

$$q(T_0) = q_{ref} \times exp\left(\frac{Ea}{R} \times \left(\frac{1}{T_{ref}} - \frac{1}{T_0}\right)\right) \tag{3}$$

Finally $TMR_{ad}24$ has to be estimated in an iterative way varying T_0 in Eq(2) and Eq(3).

In addition Keller et al. (1997) proposed another, empiric equation, Eq(4), to calculate $T_{0,24}$. It stands for $TMR_{ad}24$, but derived by DSC. Dimension of temperatures in Eq(4) is Kelvin.

$$T_{0,24} = 0.65 \times T_{Onset\ DSC} + 50 \tag{4}$$

This apparently simple calculation was proved by Pastré et al. (2000), who compared $T_{0,24}$ values, calculated according to Eq(4), with $TMR_{ad}24$ values, which were estimated by adiabatic measurements of 180 samples. Runs at DSC were done with a heating rate of 3 K/min. Pastré et al. confirmed the reliability of the calculation as a useful screening tool for non-autocatalytic reactions.

2.3 Estimation of heat release criterion (0.1 W/kg) and subtraction of 10 K

A heat release of 0.1 W/kg by a decomposition reflects an early stage of conversion. By use of long-term DTA and Setaram C80 calorimeter with low heating rates, e.g. 0.05 K/min, and high signal sensitivity, Goldmann (2002) showed that the temperature, where the heat release of a specific substance is 0.1 W/kg, correlates well with the $TMR_{ad}24$ for this substance. As a proved practice the heat release criterion was taken as one approach to estimate T_{exo} in TRAS 410 (Eberz, 2005).

Beside direct measurement of the temperature also indirect determination is possible. Measurements are carried out in isothermal mode at different temperatures. Based on the assumption of a zero order reaction the maximum heat flow is plotted in dependency on inverse absolute temperature in an Arrhenius diagram. After linearisation, the temperature where the heat release equals 0.1 W/kg could be estimated from the plot.

3. Experimental

3.1 Chemistry

Figure 1 shows the examined peroxycarboxylic esters TBPP, TBPEH and TBPIN. The synthesis and the estimation of several safety parameters are described in a former publication (Fritzsche and Knorr, 2009). The reaction heat was estimated to be for the second reaction step (i. e. of the formation of the peroxycarboxylic ester) in the range from 126 kJ/mol to 135 kJ/mol of the corresponding acid chloride. Adiabatic temperature is in the range from 72 K to 83 K.

To find out if a significant difference can be observed in the behaviour of the organic phase of reaction product and the technical pure, commercially available product, the latter was also studied. These technical products were provided by the former Peroxid Chemie, Pullach (Germany), now United Initiators GmbH & Co KG.
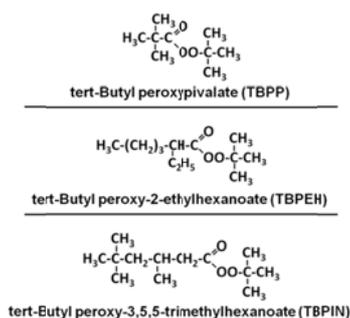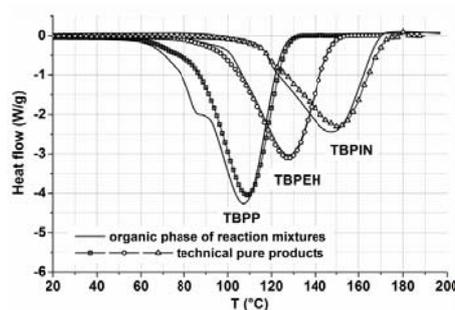

Figure 1: Examined Peroxyesters

Figure 2: Non-isothermal DSC measurements, heating rate 5 K/min

3.2 Measurements

Differential scanning calorimetry (DSC) was carried out with the DSC Pyris 1 by Perkin Elmer, a power compensated calorimeter. Calibration was done with Indium. As sample containers high pressure sealed crucibles made of stainless steel and gold coated venting discs were used. Nitrogen was applied as purge gas (20 mL/min). Sample mass varied between 3 mg and 7 mg. Figure 2 shows the normalised heat flows for the analysed peroxyesters.

To estimate the heat release criterion a Thermal activity monitoring device, TAM 227 by Thermometric (TAM family now belongs to TA Instruments) was used. The working principle is explained in Suurkuusk and Wadsö (1982). Calibration of instrument was done with a reference reaction according to Chen and Wadsö (1982). Signal noise was about 0.001 W/kg. The peroxyesters could not be measured in high concentrations due to possible overrun of measuring range of the calorimeter and possible harm to the calorimeter by high gas release. The peroxyesters were diluted with Isododecane, which was also used as thermal stable reference. Mass concentration of the diluted peroxyesters varied in the range from 2.5 w/w to almost 50 w/w depending on specific peroxyester and temperature (40 °C to 80 °C). Temperatures below 40 °C could not be measured because of lack of stable temperature conditions. Total sample mass was 2 g.

The normalised heat flow curves of the organic phase of TBPIN reaction mixture are exemplary shown in Figure 3. Normalisation of heat flow was done according to the mass of peroxyester. All other examined peroxyesters showed similar progression of the heat flow curves. The course of the heat flow indicates an nth order reaction mechanism.
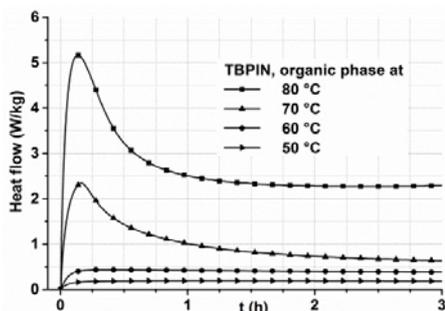

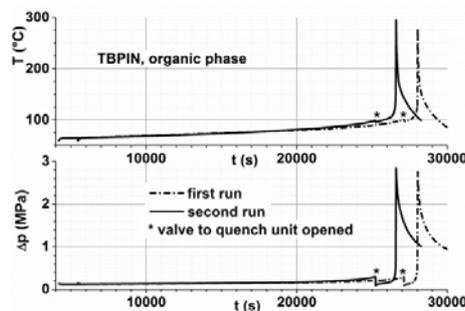Figure 3: Isothermal TAM measurements of TBPIN, organic phase of reaction product

Figure 4: Adiabatic measurements of TBPIN, organic phase of reaction product

Adiabatic measurement was done with PhiTec II apparatus by HEL Limited. This apparatus was designed primarily for vent-sizing purposes (Singh, 1993). Due to lack of cooling to subambient temperatures and a reasonable induction period only the peroxyester with the highest $T_{Onset\ DSC}$ could be measured. That was the organic phase of TBPIN reaction mixture. A quench unit (HEL, 2007) was installed because destruction of the containers during the decomposition of the high concentrated TBPIN could not be excluded. Figure 4 shows the temperature and pressure course for the two runs. The opening of the quench valve at 0.3 MPa is to be seen in Figure 4 at the point marked with an asterisk (*). After closing the quench valve temperature and pressure rose again. The total induction time of runaway was taken up to the opening of the quench valve for further evaluation according to Eq(1). That is incorrect but in a conservative sense. Induction time was corrected by the Phi factor, which was 1.17 for the experimental setup.

4. Results and discussion

4.1 Estimation of T_{Onset} (DSC)

Estimated $T_{Onset\ DSC}$ are listed together with the heat of decomposition (ΔH_d) of the peroxyesters in Table 1. Looking at these characteristic values no important differences between the organic phase (o. ph.) of reaction product and the corresponding technical pure (t. p.) grade product were observed.

Table 1: T_{Onset} values and decomposition energy estimated by DSC

	TBPP		TBPEH		TBPIN	
	o. ph.	t. p.	o. ph.	t. p.	o. ph.	t. p.
T_{Onset} (°C)	45	45	67	69	84	86
ΔH_d (J/g)	-1,430	-1,380	-1,120	-1,150	-1,060	-1,100

4.2 Estimation of $TMR_{ad}24$ (DSC and adiabatic calorimetry)

$TMR_{ad}24$ was estimated once with DSC measurements for the three peroxyesters and once with adiabatic calorimetry only for TBPIN as explained.

The adiabatic measurement was evaluated according to Eq(1). The total induction time (t_{ind}) was 6.4 h for the first run and 6.0 h for the second run.

To calculate $TMR_{ad}24$ from DSC measurements Eq(2) and Eq(3), and additionally Eq(4) were used. $T_{Onset\ DSC}$ was taken as T_{ref}. For estimation of the experimental onset temperature ($T_{Onset\ DSC}$) a deflection from the baseline of the threefold value of signal noise, 9 mW/g, was used. This value was set as reference heat flow q_{ref} in Eq(3). Specific heat capacity c_p, was set to 2 kJ/kgK for all samples. The values for activation energy Ea were taken from TAM measurements (Table 3). Table 2 shows the results.

The calculated values of $TMR(T_0,i)$ are plotted in Figure 5 versus the inverse absolute temperature (1/T). $TMR_{ad}24$ was derived by extrapolation. It was calculated to be in the range between 43 °C and 45 °C.
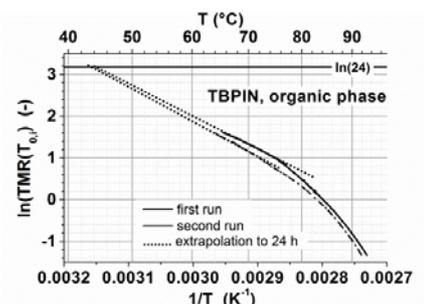
Figure 5: TMR$_{ad}$24 derived from adiabatic measurements of TBPIN, organic phase of reaction product

Table 2: TMR$_{ad}$24 values estimated by DSC and adiabatic calorimetry

	TBPP		TBPEH		TBPIN	
	o. ph.	t. p.	o. ph.	t. p.	o. ph.	t. p.
TMR$_{ad}$24 by DSC (Eq2+Eq3) (°C)	19	15	37	39	54	58
TMR$_{ad}$24 by DSC (Eq4) (°C)	-6	-6	8	7	20	18
TMR$_{ad}$24 by adiabatic cal. (°C)	-	-	-	-	43	-

4.3 Estimation of heat release criterion (0.1 W/kg)

The maximum heat flows (W/kg) of the individual peroxyesters, estimated with TAM, were plotted in dependency on the temperature in an Arrhenius diagram. The temperature, which corresponds to the heat flow of 0.1 W/kg, was derived from the plot. As mentioned above TAM measurements were used to determine Ea value of peroxyester decomposition primarily for the organic phase of reaction mixture, where no data exist in literature. Temperature values and activation energy are shown in table 3.

Table 3: Temperature, where heat flow is 0.1 W/kg (heat release criterion), and activation energy

	TBPP		TBPEH		TBPIN	
	o. ph.	t. p.	o. ph.	t. p.	o. ph.	t. p.
T (°C)	19	16	33	35	47	55
Ea (kJ/mol)	125	108	118	133	120	163

5. Conclusions

An overview of T$_{exo}$ values, estimated by the used approaches, gives table 4.

Table 4: T$_{exo}$ values in °C estimated by the different approaches

	TBPP		TBPEH		TBPIN	
	o. ph.	t. p.	o. ph.	t. p.	o. ph.	t. p.
100 K rule	-55	-55	-33	-31	-16	-14
Heat release criterion	9	6	23	25	37	45
TMR$_{ad}$24						
DSC (Eq2+Eq3)	9	5	27	29	44	48
DSC (Eq4)	-16	-16	-2	-3	10	8
adiabatic	-	-	-	-	33	-

Based on the used approaches to the estimation of T$_{exo}$ of the examined peroxyesters, the heat release criterion is in our opinion the method of choice. It has the benefit that low heat releases can be measured, which makes it possible to estimate the temperature at a heat flow which is as low as 0.1 W/kg. Error margins can be minimized.

Investigation falls somehow short, as far as adiabatic measurement for estimation of TMR$_{ad}$24 is concerned. For reasons already mentioned, only one substance was studied. The result for T$_{exo}$ is similar

to the one won from the heat release criterion, but not reliable enough to allow a general conclusion for the examined peroxyesters.

Instead of adiabatic measurements dynamic DSC runs were used to estimate $TMR_{ad}24$ values for all samples following the evaluation proposed by Keller et al. (1997) and by Pastré et al. (2000). Calculation of $TMR_{ad}24$ by Eq(2) and Eq(3) led to values for T_{exo}, which are similar to the ones estimated by the heat release criterion. This approach is only applicable when the activation energy is known for the reaction or decomposition, respectively. Otherwise an assumption for the Ea value, preferably a low one, has to be made.

In a second evaluation of DSC measurements $TMR_{ad}24$ values were estimated using the empiric established Eq(4). The resulting T_{exo} values are for our examples on the safe, conservative side. In all cases the limit temperature was lower than the one established by the heat release criterion.

The application of the 100 K rule for estimation of T_{exo} gave conservative results for the investigated samples. For all peroxyesters T_{exo} was found to be below 0°C. The application of T_{exo} value as synthesis temperature seems to be very safe, but accumulation will probably cause a problem, and crystallisation of water and produced potassium chloride too, which are both involved in the specific synthesis route.

As final result it can be concluded that for the investigated peroxyesters all three approaches led to T_{exo} values, which were on the safe side – taken the T_{exo} value estimated by the heat release criterion as reference. Evaluation of the decomposition was based on the assumption of a zero order reaction. That is a very conservative point of view which is justified due to the high hazard potential of the organic peroxides.

Acknowledgements

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