

# Prediction of the self-accelerating decomposition temperature (SADT) for liquid organic peroxides from differential scanning calorimetry (DSC) measurements

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## Abstract

We present a prediction (estimation, calculation, screening) method for the estimation of the self-accelerating decomposition temperature (SADT) for liquid organic peroxides from differential scanning calorimetry (DSC) measurements based on the concepts of thermal explosion theory originally introduced by Semenov which are adopted to our problem assuming  $n$ th-order reaction kinetics. For the peroxides under investigation, we demonstrate good agreement with the experimental SADT. This method can be used as a quick and easy applicable method for the estimation of the critical temperatures.

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## 1. Introduction

The UN has published recommendations concerning the safe transport of dangerous goods in order to avoid incidents [1]. Specific testing schemes are described there, in order to achieve the identification and classification of dangerous goods of different classes and divisions. One group, Division 5.2, deals with organic peroxides (OPs). One important safety parameter of OPs is the self-accelerating decomposition temperature (SADT). The SADT is defined as the lowest temperature at which self-accelerating decomposition may occur with a substance in the packaging as used in transport. The SADT is a measure of the combined effect of the ambient temperature, the decomposition kinetics, the package size and the heat transfer properties of the substance and its packaging [2]. The UN manual [2] recommends several testing methods for the determination of the SADT. The heat accumulation storage test (HAST, UN H.4), which is also called the BAM-

Dewar-Test, is one of them. Briefly explained, a 500 cm<sup>3</sup> dewar is filled with 400 cm<sup>3</sup> of the OP to be tested. The dewar is closed with an appropriate closure system and heated to the desired storage temperature in a suitable test chamber. The temperature of the substance as well as the test chamber temperature is measured. If, within 7 days from the start of the storage time (the time at which the sample temperature reaches a temperature of 2 K below the test chamber temperature), a temperature increase of at least 6 K is measured, the SADT for that substance is reached. The pivotal point is that the heat loss of the dewar should be representative of the packaging filled with the substance. The SADTs listed in Table 1 were determined using the 500 ml dewar with heat loss characteristics between 11 and 13 h if filled with 400 ml of water.

Despite the fact that the recommended test procedures can be hazardous to the environment, e.g. due to the relative large sample mass and the possibility of a violent reaction, they are also time consuming and therefore alternatives have been sought since that time.

The most commonly used apparatus for SADT screening are the accelerating rate calorimeter (ARC) [3] alone or in

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Table 1

Investigated liquid OPs with literature values for the activation energy  $E$ , experimental onset temperatures  $T_{DSC}$ , literature values for the SADT, the SADT values as determined in our laboratory and the calculated  $T_{HAST}$

Peroxide	Abbreviation	$E$ (kJ/mol)	$T_{DSC}$ (°C) for a deflection limit of 5/10 mW/g	$T_{HAST}$ calculated (°C) for a deflection limit of 5/10 mW/g	SADT (BAM value) (°C)	SADT (literature) (°C)
<i>tert</i> -Amylperoxy-pivalate, t.p. <sup>c</sup>	TAPPI	127.76 <sup>a</sup>	44/47	20/22	20	25 <sup>a,d</sup>
<i>tert</i> -Amylperoxy-2-ethylhexanoate, t.p.	TAPEH	132.11 <sup>a</sup>	61/64	35/38	35	35 <sup>a</sup>
<i>tert</i> -Butylperoxy-2-ethylhexanoate, t.p.	TBPEH	124.90 <sup>a</sup> , 120.8 <sup>b</sup>	61/64	34/37	35	35 <sup>a</sup> , 29 <sup>b</sup>
<i>tert</i> -Butylperoxybenzoate, t.p.	TBPB	144.36 <sup>a</sup> , 145.6 <sup>b</sup>	91/95	63/68	65	60 <sup>a</sup> , 53 <sup>b</sup>
1,1-Di( <i>tert</i> -butylperoxy)3,3,5-trimethylcyclohexane	TMCH	127.52 <sup>a</sup>	84/87	55/57	65	60 <sup>a</sup>
1,1-Di( <i>tert</i> -butylperoxy)cyclohexane	DTBPCH	142.40 <sup>a</sup>	93/96	65/67	70	70 <sup>a,e</sup>
2,5-Dimethyl-2,5-di( <i>tert</i> -butylperoxy)-hexane	DHBP	155.49 <sup>a</sup>	104/109	76/81	85	80 <sup>a,f</sup>
Di- <i>tert</i> -butylperoxide, t.p.	DTBP	153.46 <sup>a</sup>	106/109	77/80	85	80 <sup>a</sup>

<sup>a</sup> Akzo Nobel [15].

<sup>b</sup> Hordjik and De Groot [10].

<sup>c</sup> Technical pure (t.p.) means the concentration of the peroxide is  $\geq 95\%$ .

<sup>d</sup> For a formulation containing 75% of the peroxide.

<sup>e</sup> For a formulation containing 50% of the peroxide.

<sup>f</sup> For a formulation containing 92% of the peroxide.

combination with the thermal activity monitor (TAM) [4], the heat flux calorimeter (C80D) [5,6] and the DTA [7,8] or DSC [9], respectively.

Hordjik and De Groot [10] investigated the decomposition kinetics of different peroxides in detail using different experimental methods. They calculated the SADT from the kinetic parameters and found good agreement to experimental values.

Very recently, Yang et al. [11] presented the prediction of the SADT of organic peroxides based on the non-isothermal decomposition behaviour utilising a new approach for the description of the decomposition kinetics. Opposed to the well-established Arrhenius-like behaviour, they introduced the reaction temperature range parameter in combination with the end temperature of the decomposition process to describe the fractional conversion of the apparent elementary reaction. The predicted SADT values agreed well with the literature values.

In this paper, we utilise the derivation for the prediction of the SADT first given by Klais and Steinbach [7] and extended by Antelmann in her thesis [8]. They used a DTA as the small-scale screening device. On the basis of the standard theory of explosion of Semonov, a simple transfer equation for the calculation of SADT data from DTA onsets and vice versa was derived. In this paper, we present some first results for the determination of the SADT from experiments using a DSC as the small-scale device. The differences and similarities compared to the DTA as the small-scale device are pointed out.

## 2. The transfer equation

The detailed derivation of the transfer equation can be found in [8]. The basis of this derivation is the well-known Semonov Model of explosion where the competing effects

of the heat generation of the system on the one hand and the heat transfer to the environment on the other hand, are considered. The critical temperature for a given geometry is reached if the heat production rate equals the heat loss of the system. Quantifying the responsible effects for the dewar and the DTA cell, it is shown [8] that

$$\frac{r_0(T_{DTA})m_{DTA}U_{HAST}A_{HAST}(T_{HAST} - T_K)}{r_0(T_{HAST})m_{HAST}U_{DTA}A_{DTA}(T_{DTA} - T_K)} = 1 \quad (1)$$

where  $r_0(T_i)$  are the temperature dependant initial reaction rates,  $m_i$  the sample masses,  $U_i$  the heat transfer coefficients,  $A_i$  the heat exchange areas and  $T_i$  the sample temperature and  $T_K$  is the ambient temperature. The index  $i$  specifies HAST or DTA, respectively.

To derive the final transfer equation some important assumptions are to be made, one of those affects the relationship between the heat exchange areas  $A_{HAST}/A_{DTA}$ . The ratio of the heat exchange areas can be calculated if some simple geometric parameters are known. For a standard 500 ml dewar vessel and for a standard DTA cell, a height:diameter ( $h:d$ ) of 2 is appropriate [8]. Assuming cylinder geometry for both vessels the ratio of the heat exchange areas can be calculated according to Eq. (2)

$$\frac{A_{DTA}}{A_{HAST}} = f \frac{m_{DTA}}{m_{HAST}} \sqrt[3]{\frac{m_{HAST}}{m_{DTA}}} \quad (2)$$

where  $A_i$  are the heat exchange areas,  $f=1$  and  $m_i$  are the masses, respectively.

The geometry of our DSC crucibles, which are more pan like, implies that a  $h:d$  of 2 is not adequate anymore and has to be changed to 1/2. This obviously leads to a new relationship for the heat exchange areas that means the factor  $f$  in Eq. (2) has to be changed to  $f=1.0079$ .

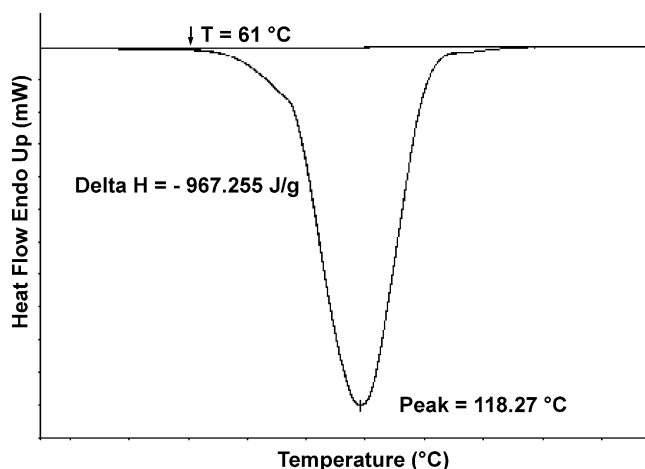


Fig. 1. DSC run for TAPEH. The arrow in the plot denotes the temperature of 61 °C at which the deflection of the signal from the baseline is 5 mW/g.

Following the other assumptions given in [8] we derive Eq. (3), the transfer equation applicable for  $n$ th-order reactions

$$\frac{1}{f} \left( \frac{T_{\text{HAST}}}{T_{\text{DSC}}} \right)^2 \sqrt[3]{\frac{m_{\text{DSC}}}{m_{\text{HAST}}}} \exp \left( \frac{E}{R} \left( \frac{1}{T_{\text{HAST}}} - \frac{1}{T_{\text{DSC}}} \right) \right) = 1 \quad (3)$$

where  $E$  is the activation energy and  $R$  is the gas constant.

If  $T_{\text{DSC}}$  is known, the  $T_{\text{HAST}}$  can be calculated from Eq. (3). This equation is solved using the Levenberg–Marquardt algorithm, which is available in the Mathcad software [12]. The differences in going from DTA to DSC can be accounted for by the factor  $f$  representing the different heat exchange areas in the DTA and DSC cells.

### 3. Experimental method

All experiments were carried out using a Perkin Elmer Pyris Diamond Differential Scanning Calorimeter. The calorimeter was calibrated with Indium at each heating rate for temperature and heat flow. High pressure stainless steel capsules were used for all experiments and a 20 ml/min  $\text{N}_2$  purge gas was applied. Heating rates of 3–5 K/min were used. Sample masses were about 4–5 mg. For each peroxide at least two runs at the same heating rate have been performed. A typical run for TAPEH at 5 K/min is shown in Fig. 1.

For all liquid OPs the HAST (UN test H.4) has been performed in our laboratory according to the UN recommendations.

### 4. Results and discussion

The investigated liquid OPs are summarised in Table 1. Some literature values for the activation energy of the de-

composition process as well as the SADT are also shown. The SADT as determined in our laboratory is also given in Table 1. The most commonly found SADTs for OPs (20–85 °C) are covered by this selection.

The agreement between the literature and the BAM SADT values is good. Nevertheless, it seems remarkable that our SADTs tend to be slightly higher than the literature values. Differences in the dewar heat losses may be responsible for some shift in the SADT. An example is the DTBPCH. We determined a value of 70 °C. At this storage temperature, the temperature increase was 6 K, which is exactly the SADT criterion according to the UN recommendations. For DHBP a similar behaviour was obtained. During storage at 80 °C the temperature increase was 5.5 K. Therefore, the SADT is 85 °C. These two examples represent borderline cases that mean that the actual SADT is strongly influenced by the actual heat loss of the dewar vessel.

As pointed out in Section 2 the  $T_{\text{HAST}}$  can be estimated with Eq. (3). The experimental onset temperature  $T_{\text{DSC}}$  is taken at the point where deflection from the baseline is observed, i.e. where the deflection from the baseline is 5 mW/g. The arrow indicates this temperature in Fig. 1. Additionally, we used a deflection limit of 10 mW/g. Besides the  $T_{\text{DSC}}$ , the mass scale factor  $m_{\text{DSC}}/m_{\text{HAST}}$  is known. In our calculations, we took an average value of  $m_{\text{HAST}} = 350$  g, but if the density of the liquid OP is known the exact mass for a volume of 400  $\text{cm}^3$  may be determined instead. For the calculation of the  $T_{\text{HAST}}$  according to Eq. (3), the only parameter remaining unknown is the activation energy. In principle, this value can be determined from DSC measurements as well [13,14]. For this work the values are taken from the info brochure published by Akzo Nobel [15]. The experimental  $T_{\text{DSC}}$  and the calculated  $T_{\text{HAST}}$  for both deflection limits are shown in Table 1. The SADT values determined in our laboratory are given in Table 1 additionally.

Even though only  $n$ th-order decomposition kinetics is assumed in the derivation of the transfer equation – a possible contribution of autocatalysis is neglected – the results show very nice agreement with the experimental SADT. The  $T_{\text{HAST}}$  values calculated for a deflection limit of 5 and 10 mW/g are quite similar and the majority of the calculated temperatures lie within the typical experimental increment of 5 K. Especially for low SADTs we find excellent agreement. Particularly with regard to temperature control these temperatures are exceptionally significant. The larger deviations, e.g. for TMCH are on the safe side.

The calculation of the SADT of liquid OPs using this procedure seems to produce reliable values nevertheless, using this procedure, as a full alternative to the H.4 test needs some more verification. This is not only because reliable reaction kinetics are needed. A more versatile tool should of course incorporate more complex kinetic models, e.g. autocatalysis.

Obviously, the presented method works very well as a screening device to narrow down the temperatures to be tested in a large-scale test.

## 5. Conclusion

A procedure for the estimation of the SADT for liquid OPs based on DSC measurements is presented. An existing transfer equation for DTA cells is extended to the application of DSC measurements. Important parameters in this derivation are the heat exchange areas of the large- and the small-scale testing device. These areas are changing, going from DTA to DSC cells. By incorporating these differences it turned out that the factor in the transfer equation has to be changed from 1 to 1.0079 when going from DTA to DSC cells. In practice this hardly affects the results. Nevertheless, the determination of this factor is of great importance for the transferability of the equation to our cell geometry. The results for some liquid OPs confirm that this method may be used as a quick and easy applicable screening procedure for an estimation of SADT values. To our opinion this method may be seen as an additional tool for the estimation of critical temperatures and is capable in saving precious time. Nevertheless, the determination of the SADT value should still be performed according to the UN recommendations.

## References

- [1] UN Recommendations on the Transport of Dangerous Goods, Model Regulations, 13th revised ed., United Nations, New York and Geneva, 2003.
- [2] UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Section 28, fourth revised ed., United Nations, New York and Geneva, 2003.
- [3] H.G. Fisher, D.D. Goetz, Determination of self-accelerating decomposition temperatures for self-reactive substances, *J. Loss Prev. Process Ind.* 6 (3) (1993) 183–194.
- [4] M.W. Whitmore, J.K. Wilberforce, Use of the accelerating rate calorimeter and the thermal activity monitor to estimate stability temperatures, *J. Loss Prev. Process Ind.* 6 (2) (1993) 95–101.
- [5] Y.H. Yu, K. Hasegawa, Derivation of the self-accelerating decomposition temperature for self-reactive substances using isothermal calorimetry, *J. Hazard. Mater.* 45 (2–3) (1996) 193–205.
- [6] J.H. Sun, Y.F. Li, K. Hasegawa, A study of self-accelerating decomposition temperature (SADT) using reaction calorimetry, *J. Loss Prev. Process Ind.* 14 (5) (2001) 331–336.
- [7] O. Klais, J. Steinbach, Prediction of self-reactive properties from DTA-measurements, in: *HAZARD XIII Symposium, Process Safety—The Future*, Manchester, 1997.
- [8] O. Antelmann, Erkennung und Charakterisierung gefährlicher selbstzersetzlicher Substanzen, in: *Fakultät III Prozesswissenschaften, Thesis, Technische Universität, Berlin, 2001*, [http://edocs.tu-berlin.de/diss/2001/antelmann\\_olivia.htm](http://edocs.tu-berlin.de/diss/2001/antelmann_olivia.htm).
- [9] E. Gimzewski, G. Audley, Thermal hazards: calculating adiabatic behaviour from differential scanning calorimetry (DSC) data, *Thermochim. Acta* 214 (1) (1993) 129–140.
- [10] A.C. Hordijk, J.J. De Groot, Experimental data on the thermal kinetics of organic peroxides, *Thermochim. Acta* 101 (1986) 45–63.
- [11] D. Yang, H. Koseki, K. Hasegawa, Predicting the self-accelerating decomposition temperature (SADT) of organic peroxides based on non-isothermal decomposition behavior, *J. Loss Prev. Process Ind.* 16 (5) (2003) 411–416.
- [12] Mathcad, Mathsoft Engineering & Education, Inc., 2001.
- [13] H.E. Kissinger, Reaction kinetics in differential thermal analysis, *Anal. Chem.* 29 (11) (1957) 1702–1706.
- [14] T. Ozawa, Estimation of activation energy by isoconversion methods, *Thermochim. Acta* 203 (1992) 159–165.
- [15] Akzo Nobel, Organic Peroxide Initiators, Product Brochure, 2001.