



Kinetic Evaluations for the Transportation of Dangerous Chemical Compounds

Marco Dellavedova*, Christian Pasturenzi, Lucia Gigante, Angelo Lunghi

Innovhub-SSI, Divisione Stazione Sperimentale per i Combustibili, viale A. De Gasperi, 3 - 20097 San Donato Milanese (MI), Italy.
dellavedova@ssc.it

Current legislation about goods carriage (ADR - Agreement Concerning the International Carriage of Dangerous Goods by Road) sets the determination of several parameters related to the conditions of the used containers. Several of these parameters are required for the substance classification and the definition of the precautions to be adopted during transportation. One of the main potential hazards during freight is related to the thermal decomposition of the substance.

Testing for the identification of decomposition in the carriage conditions can be time consuming and expensive, therefore different solutions have been attempted to simulate thermal behaviour of chemical compounds during transportation.

This work focuses on the analysis of such methods and, in particular, on the model free methods for the determination of the decomposition kinetic of the studied compounds. This model is able to fit the kinetic behaviour of complex decomposition mechanisms more than others. The kinetic developed can be subsequently used to develop predictive models for the evaluation of transportation parameters, as for example the Self Accelerating Decomposition Temperature – SADT, but also to track the product quality during time aging.

Input data for this analysis are Differential Scanning Calorimetric (DSC) tests. They are safe, quick and cheap and can give important information about thermal behaviour of the studied substances.

The model free methodology and the SADT determination has been performed for the decomposition of two different organic peroxides and a solid compound.

1. Introduction

The chemical industry often requires the use of very reactive compounds as well as toxic and flammable substances.

The thermal decomposition of a substance stored in a container is a process that can be considered adiabatic; the heat generation can bring to an exponential increase of temperature, often with release of flammable vapours and toxic products; also explosions can occur. Therefore knowledge of the thermal stability and kinetics of decomposition of these substances is very important in order to define safe conditions of storage and transport.

The ADR (UN, 2011) regulates the transport of dangerous goods by road. Manual of Tests and Criteria by the United Nations (UN, 2003) separates reactive substances in nine categories.

In this work attention will be focused on self-reactive substances (class 4.1) and organic peroxides (class 5.2). A very important parameter to define the carriage conditions of these classes is the SADT: this parameter defines whether a temperature control is necessary during the transport. SADT is the

lowest temperature at which a self-heating of 6 °C or more within 7 days may occur for a certain substance in the commercial packaging used during carriage.

It is important to remind that SADT is not a chemical-physical parameter, but it derives from a combination of factors: room temperature, kinetics of decomposition, size of the container and heat transfer properties both of the substance and the container (UN, 2003).

The Manual of Tests and Criteria reports the four official tests for the determination of SADT (Table 1). SADT has to be measured for each commercial container used in transport. Official tests are very time consuming and, because of the big amount of sample, potentially dangerous. For these reasons new methods for the SADT calculation were developed; they are based on calorimetric techniques such as DSC and Accelerating Rate Calorimeter (ARC) (Fisher and Goetz, 1991; ASTM Standard E698, 2011). Another approach, called isoconversional method, well described by Roduit et al. (2008), finds interesting applications especially for decomposition reactions. Unlike traditional methods, that provide a single pair of Arrhenius parameters, the isoconversional method gives a trend of the activation energy and pre-exponential factor as function of the reaction progress. Following this approach only using a series of non-isothermal measurements, carried out at different heating rates, can bring to the necessary amount of information required for the identification of the studied process, as clearly described by Brown (2005).

In literature there are three options of the isoconversional method, as described by Budrugaec (2002): the Friedman method (Friedman, 1964), that is based on the differential evaluation of reaction progress as a function of time pre-exponential factor and decomposition activation energy, all dependent by the reaction progress itself; the Ozawa-Flynn-Wall method (Ozawa, 1965; Flynn and Wall, 1966) and the Vyazovkin method (Vyazovkin, 1997) that are based on the integration over small ranges of the reaction progress. It can be demonstrated that the use of isoconversional integral methods for too large ranges of the reaction progress can yield systematic errors. Using infinitesimal ranges of reaction progress such errors can be avoided but the isoconversional integral methods turns into the differential methods proposed by Friedman.

The aim of this study is to test the robustness of the isoconversional method in order to obtain the kinetic behaviour of a substance or a mixture. This kinetic will be consequently used to develop predictive models of the studied chemicals during storage conditions in order to determine the SADT of the studied packaging. Input data for this analysis are DSC tests data entered in the Friedman method.

Table 1: Official tests for the determination of SADT.

The United States SADT test (US SADT test) H1
Adiabatic storage test (AST) H2
Isothermal storage test (IST) H3
Heat accumulation storage test (HAST) H4

2. Experimental

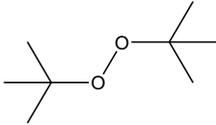
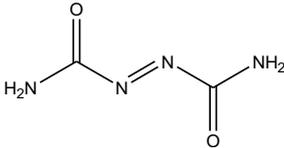
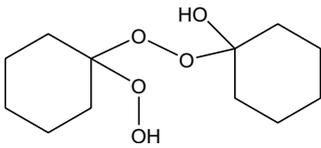
The used methodology, for the determination of SADT, is based on four simple steps listed in Table 2.

Table 2: Steps for the determination of SADT.

1	Four DSC tests at different scanning rates were run, using a DSC823 Mettler-Toledo, from 20 °C to 280 °C (this temperature was chosen because all the detected thermal effects happen at a lower temperature). Sealed crucibles and inert atmosphere were used. Sample amount was about 3-5 mg.
2	Calculation of the kinetic of the decomposition reaction. The software <i>AKTS Thermokinetics</i> (extension of Friedman isoconversional method) was used.
3	Validation of the kinetic data through an adiabatic ARC test (ARC2000 Columbia Instruments). Sample amount was about 2-3 g.
4	SADT evaluation using the simulation commercial software <i>AKTS thermal safety</i> .

Three samples were analyzed: di-tert-butylperoxide (DTBP), azodicarbonamide (ADCA) and a commercial mixture of cyclohexanone peroxide (CHP) (Table 3).

Table 3: Analyzed samples.

DTBP	ADCA	CHP
		
Cas n° 110-05-4	Cas n° 123-77-3	Cas n° 12262-58-7

SADT was calculated in a 25 L HDPE container for the two organic peroxides and in a 30 L HDPE container for ADCA.

The four steps for the calculation of SADT are shown for di-tert-butylperoxide (DTBP).

2.1 Step 1: DSC tests

The very first step of the experimentation consists in running four DSC tests at different scanning rates: 1 °C/min, 2 °C/min, 4 °C/min and 8 °C/min (Figure 1).

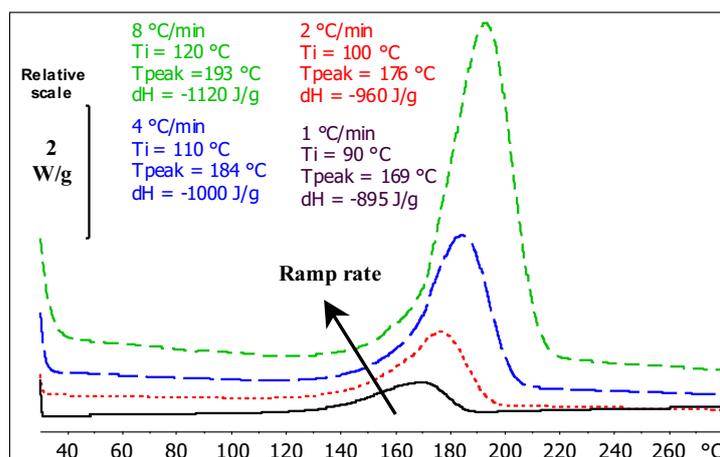


Figure 1: DSC tests at different scanning rates (DTBP). T_i is the detected onset temperature of the decomposition reaction, T_{peak} is the temperature corresponding to the maximum heat rate, dH is the decomposition enthalpy normalized to the sample mass

2.2 Step 2: Calculation of the kinetic data

Using the Friedman's isoconversional method it is possible to determine both the activation energy and pre-exponential factor as a function of the reaction progress (Figure 2).

Using the obtained kinetic data, it is possible to simulate the reaction rate and the reaction progress for the decomposition reaction.

A comparison between experimental reaction rate and the simulated one is reported in Figure 3. It is possible to note a good agreement between simulated and experimental data.

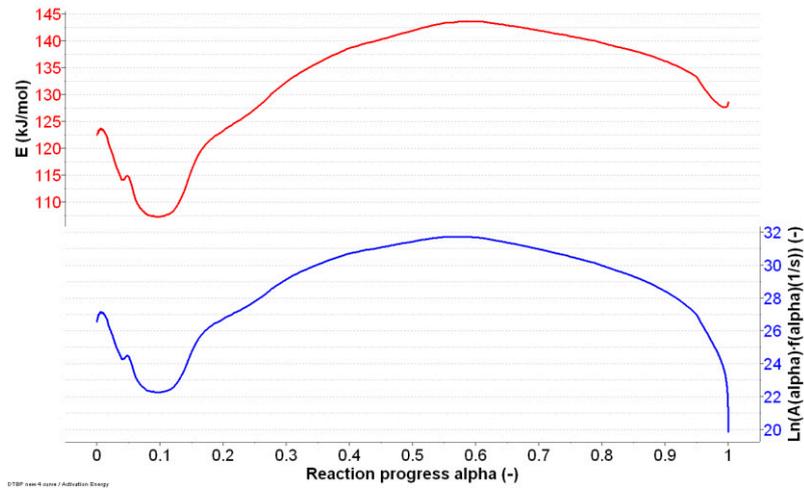


Figure 2: Activation energy and pre-exponential factor vs. reaction progress (DTBP)

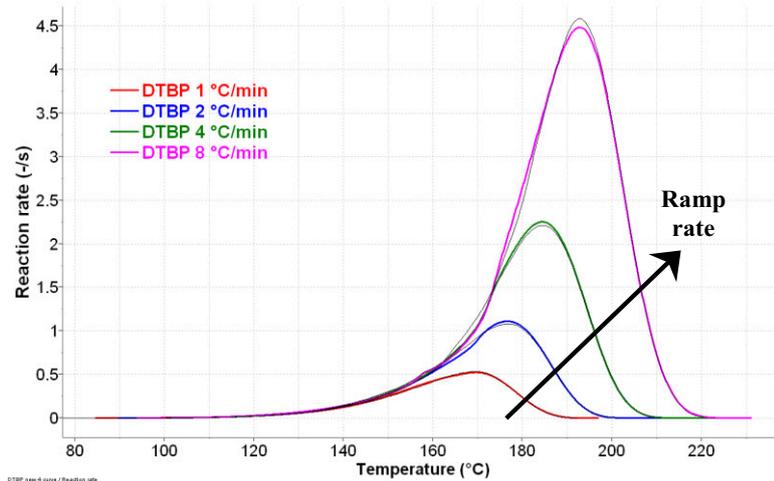


Figure 3: Comparison between the experimental reaction rates (dashed line) and the simulated ones (solid lines)

2.3 Step 3: Validation of kinetic data

Before using the kinetic data to calculate the SADT, a validation test of the obtained parameters in different conditions than dynamic heating with DSC needs to be run: in this case an isoaging ARC test at 80 °C. Figure 4 shows the comparison between the experimental adiabatic ARC test (solid line) and the simulated one (circles).

The simulated data have been obtained evaluating the reaction progress at each temperature using the model free equation of Friedman. In this method it is not used a fixed kinetic law but the kinetic parameters change step by step with the progression of the reaction. The heat balance equation is also used for the simulation of adiabatic condition during the test once that the sample has reached 80 °C after the first heat. During the simulation the reaction rate, at each temperature, generates an amount of heat depending by the time at which that temperature is maintained. The generated heat increases the sample temperature and modifies the reaction rate, calculated through the new set of kinetic parameters, at the reached reaction progress.

There is a good correlation between the experimental temperature profile and the simulated one.

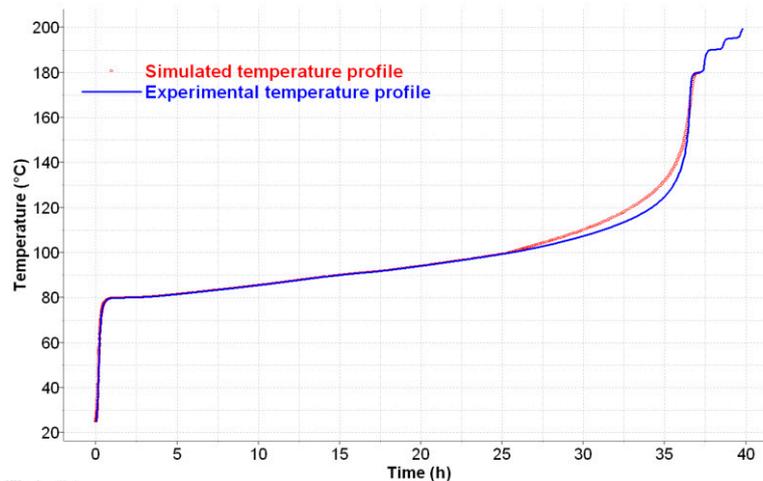


Figure 4: ARC test - isoageing at 80 °C (DTBP)

2.4 Step 4: SADT calculation

The last step is the SADT calculation using the validated kinetic data. Figure 5 shows the SADT calculation. SADT, calculated for the system DTBP in a 25 L HDPE container, is 92 °C. This value is in good agreement with literature (Fisher and Goetz, 1991).

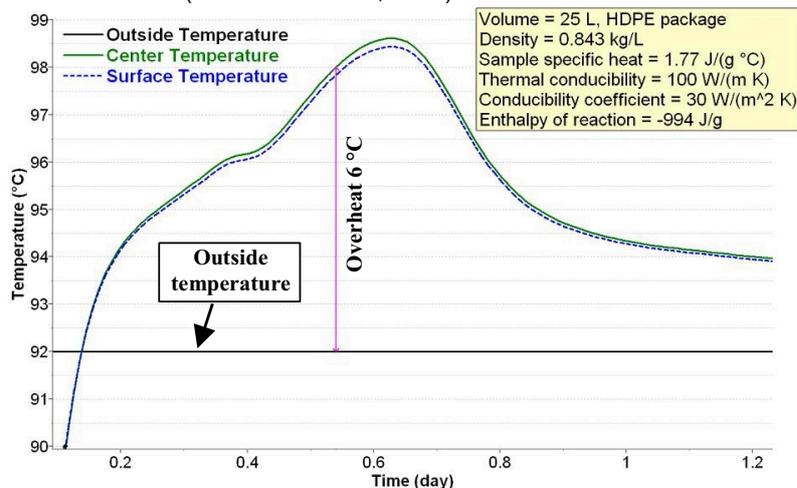


Figure 5: SADT calculation (DTBP)

3. Results and discussion

The use of Friedman's isoconversional method provides the results shown in Table 4. SADT was calculated for the three compounds: DTBP, ADCA and a commercial mixture of CHP. For the two organic peroxides a 25 L HDPE container has been considered while a 30 L HDPE container has been considered for ADCA.

As shown in Table 4, the obtained results are in good agreement with public data. There is a small overestimation, of few degrees, in all the cases using the simulation compare with the published data. In spite of that, the possibility to avoid an expensive and time consuming testing methodology make the small differences not relevant for the determination of the transportation characteristics of a compound.

Moreover, the differences could be reduced knowing the exact characteristics of the test apparatus used for the SADT experimental determination in terms of thermal exchanged parameters.

Table 4: SADT results.

Sample	SADT (isoconversional method)	SADT (public data)
DTBP	92 °C	90 °C (Fisher and Goetz, 1991)
CHP mixture	62 °C	> 60 °C (CHP-Hardener, 2010)
ADCA	116 °C	115 °C (Whitmore and Wilberforce, 1993)

4. Conclusions

The SADT calculation used in this work is based on the collection of experimental data (DSC dynamic tests), the usage of isoconversional method for the kinetic parameters determination and validation. These methods are a real alternative to the official ones: the obtained results are in good agreement with public data; they are less time consuming and cheaper. Moreover the sample amount in calorimetric tests is very small, so the risk, connected with experimentation, is lower.

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