



Thermal decomposition kinetic of 1,1-di(tert-butylperoxy)cyclohexane in organic solvents



I. Ben Talouba*, N. Bensahlam, H. Medjkoune, N. Mouhab, L. Balland, M.A. Abdelghani-Idrissi

Université de Rouen/INSA-Rouen, Laboratoire de Sécurité des Procédés Chimiques (LSPC), Avenue de l'Université, BP 8, F-76801 Saint-Étienne-du-Rouvray Cedex, France

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ABSTRACT

The thermal decomposition reaction of 1,1-di(tert-butylperoxy)cyclohexane (BPCH) was studied in pure solvents (anisole, xylene and ethylbenzene) and alone. The kinetics of each system was explored by means of microcalorimetric measurements (DSC) in isothermal and non-isothermal conditions. Analysis of heat flow profiles released in the isothermal mode combined with the analysis of the decomposed compounds by a gas chromatograph/mass spectrometer allowed to propose a chemical decomposition model. An empirical n th order rate equation was used to describe the decomposition of BPCH alone. In pure solvent, the mechanism was modeled by two parallel reactions. The first one followed an empirical n th order rate equation. The second one was modeled by a transfer reaction of the radical to the solvent. The kinetic parameters estimation was achieved using a mixed estimation method where a genetic algorithm is combined with a locally convergent method.

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1. Introduction

For chemical industry processes, reducing the risk of accidents at source still requires investigation and research efforts. The thermal runaway of the reaction mass is the most prominent cause of these accidents. Tools and methodologies for prediction and characterization are still subject of research. The consequences of such accidents are often important insofar as unwanted or uncontrolled chemical reactions are likely to give both explosion and release of toxic or flammable substances in environment.

Among the products which have a potential hazard, organic peroxides were checked off. They are widely used in the plastic and rubber industries because they are a source of free radicals which initiate numerous polymerization reactions [1]. The unstable origin of these peroxides lies on the specificity oxygen–oxygen linkage, which is known for its weak energy ($80\text{--}200\text{ kJ mol}^{-1}$) [2].

Most often, the decomposition reaction of these compounds can be initiated by many factors such as heat, mechanical shock, friction or impurities, especially in presence of certain catalysts and promoters (acid, heavy metals, . . .) [3–7]. This one can take place during production, but also during storage, transport or industrial transformation [8]. Adiabatic temperature rise (ΔT_{ad}) is

evaluated from enthalpy of decomposition (ΔH). The knowledge of kinetics data (activation energy, frequency factor and reaction order) is necessary to calculate adiabatic time-to-maximum rate (TMR_{ad}). These criterions help to carry out hazard assessments to design more effective control systems to prevent runaway during preparation, processing, storage and shipping.

Most studies of peroxide decomposition reaction were carried out mainly on pure compounds. However, these products exist rarely pure. They are generally diluted in a solvent or in presence of other substances. The latter may be reactive with the peroxide. Presence of solvent can drastically change mechanism and kinetics of the decomposition [9,10]. The change is linked to interactions between the peroxide and the solvent, according to Iglesias et al. [11]. This interaction may depend on the solvent polarity. It may even result in appearance of a radical transfer reaction between the peroxide and the solvent [12].

The purpose of this study is to evaluate the thermokinetic parameters of the decomposition reaction of 1,1-di(tert-butylperoxy)cyclohexane (BPCH) alone and mixed to an organic solvent (anisole, ethylbenzene and xylene). The BPCH is a bifunctional peroxide. An advantage of polyfunctional peroxides is due to the nature of their thermal decomposition which can affect the polymerization kinetics and increase or maintain the molecular weight of formed polymers [13,14].

A differential scanning calorimeter (DSC) was used for thermal analysis to obtain thermokinetics data. A gas chromatograph

* Corresponding author. Tel.: +33 235522996.

E-mail address: imed.bentalouba@univ-rouen.fr (I. B. Talouba).

Nomenclature

C (mol m^{-3})	concentration
E_a (J mol^{-1})	activation energy
ΔH (J mol^{-1})	molar enthalpy
k (variable)	kinetic constant
k_∞ (variable)	pre-exponential factor
NR (–)	number of reactions
dQ/dt (W)	heat flow
r ($\text{mol s}^{-1} \text{m}^{-3}$)	reaction rate
R ($\text{J mol}^{-1} \text{K}^{-1}$)	general gas constant
T (K)	temperature
V (m^{-3})	volume

Superscripts

cal	calculated
exp	experimental

Subscripts

i	reaction number
max	maximum
n	order of reaction
S	solvent

coupled with mass spectrometer (GC/MS) has allowed to identify the compounds of the decomposition reaction. This information coupled with the heat flow profiles were used to propose a thermal decomposition model including the effect of organic solvents. To avoid the trap of local minima, a mixed method based on a global optimization method (genetic algorithm) combined to a local convergent method (Rosenbrock's method) was selected to estimate the kinetic parameters.

2. Calorimetric study

2.1. Samples

The 1,1-di(tert-butylperoxy)cyclohexane (BPCH) used was purchased directly from Sigma–Aldrich and was stored in a refrigerator at 4 °C. It is a bifunctional peroxide (containing two oxygen–oxygen bonds in their structure) 75% w/w in white spirit. Organic solvents (anisole, xylene: isomer mixture and ethylbenzene) are high purity chemical reactants for laboratory analysis supplied by VWR.

2.2. Differential scanning calorimetry (DSC)

A calorimetric study both in isothermal and non-isothermal conditions was performed by means of a microcalorimeter DSC Q20 manufactured by TA Instruments with purge using extra pure nitrogen (50 mL min^{-1}). DSC Q20 measures temperature with an accuracy of $\pm 0.05 \text{ K}$ and the specific sensitivity is 1 mW kg^{-1} . DSC detects temperature change between the sample and the reference to determine heat flow, according to time and temperature. The type of crucibles used for measurement is the gold-plated high pressure crucibles (M20 crucibles from Swiss Institute for the Promotion of Safety and Security). This study allows to characterize the reactive medium during the initial phase of the thermal runaway and consequently to know the stability limit for pure compounds or reaction mixtures.

2.3. Thermal decomposition of BPCH alone

Two experiments under isothermal condition at 125 °C and 150 °C, and a set of three experiments under non-isothermal

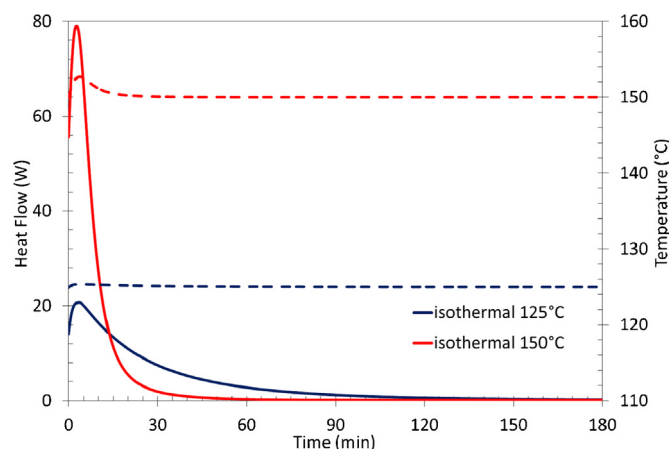


Fig. 1. BPCH decomposition in the isothermal condition.

conditions were carried out in M20 crucibles. In non-isothermal condition, a temperature ramp from 35 °C to 300 °C is imposed upon various heating rates (1, 5 and 10 °C min^{-1}). The sample masses in all experiments in this work are limited to $7.8 \pm 0.1 \text{ mg}$ and measured with precision 0.01 mg.

In isothermal mode, the heat flow profiles released by the decomposition of BPCH (solid line) are represented in Fig. 1 with temperature curve (dotted line).

The heat flow profiles on Fig. 1 reach their maximum when temperature approaches its setpoint. The maximum rate of heat release occurs at the beginning of the reaction. It indicates that the reaction mechanism follows a kinetic law of n th order [15].

Temperature control at the beginning of isothermal experiment is not enough efficient to measure temperature inside sample. To better estimate the chemical kinetic parameters, measurement of heat flow profiles in non-isothermal condition is chosen. These profiles are illustrated in Fig. 2 and they allowed to directly determine the maximum temperature (T_{max}) and the exothermic onset temperature (T_{onset}). This temperature is defined as the point of intersection of the tangent drawn at the point of greatest slope on the leading edge of the peak with the extrapolated baseline [16]. These last two parameters and the signal intensity of heat flow increase with the heating rate. The reaction enthalpy of decomposition (ΔH) was determined as:

$$\Delta H = \frac{\int_{t_{\text{begin}}}^{t_{\text{end}}} dQ_R^{\text{exp}}/dt \times dt}{m} \quad (1)$$

where dQ_R^{exp}/dt represents experimental heat flow and m represents the mass of BPCH.

2.4. Thermal decomposition of BPCH in solvent

To study the effect of solvent on the decomposition of BPCH, three organic solvents (anisole, xylene and ethylbenzene) were selected. These solvents are commonly used in free radical solution polymerization processes. For each solution of BPCH, two mass ratio (50% and 90% w/w) are used. Mass ratio is defined as mass of solvent over total mass (solvent + BPCH).

Choosing heating rate required to consider two constraints: on one hand, thermal inertia of crucibles (0.492 J K^{-1}) [17] can lead to temperature drift at high heating rate; on the other hand, the dilution of solution decreases the measured heat flow and avoid to use low heating rate. The heating rate was chosen at 5 °C min^{-1} . This rate is also recommended by the United Nations [16].

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