

Kinetic parameter estimation for decomposition of organic peroxides by means of DSC measurements

I. Ben Talouba, L. Balland, N. Mouhab*, 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 stability of organic peroxides (cumene hydroperoxide 80 wt% and dicumyl peroxide) was studied by means of calorimetric measurement (DSC, TA Q1000) in an isotherm mode and a dynamic mode. Analysis of power profiles released in the isothermal mode was combined with the analysis of the decomposed compounds by a gas chromatograph/mass spectrometer (GC/MS) to determine the reaction mechanisms corresponding to each of the two reactions. In this work, a methodology for estimating kinetic parameters was based on the comparison of the power profile (dynamic mode) given by the model to that obtained experimentally by changing the parameters values. Parameter estimation is achieved using the mixed estimation method where a genetic algorithm is combined with a locally convergent method.

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1. Introduction

One of the aims of the fine organic chemistry is to produce at the best cost, with safety conditions more and more regulated. Indeed, among the main causes of the chemical process accidents, the thermal runaway of the reactional masses is one of most current (250 accidents occurred from 1976 to 1999) (Giovannini and Gaston, 2000). In this field, governmental institutions for industrial safety impose on the chemical industries to give proof of more and more complete knowledge of the physico-chemical phenomena associated with chemical process, as well as a description of the important parameters for safety (IPS) before the implementation of the process on an industrial scale. The knowledge of chemical and/or physical kinetic parameters, as well as associated energies, is necessary for the prediction of the reactive medium behavior as well for normal and degraded modes of operation. These parameters are generally unavailable in the literature and not easily calculable using models, from where need for an experimental determination.

Among the products which have a potential hazard, organic peroxides were checked off. These latter are widely used in the plastic and rubber industries because they are a source of free radicals which initiate a number of polymerization reactions (Luo et al., 2001). The organic peroxides are renowned by their

thermal instability and their explosive character. These decomposition reactions have the characteristic to be very exothermic and their activation energy being also very high, their kinetics is very sensitive to the temperature: not detectable at ambient temperature, their rate can quickly become important as soon as the temperature rises. Most often, the decomposition reaction can be initiated by many factors such as heat, mechanical shock, friction or impurities, especially in the presence of certain catalysts and promoters (acid, heavy metals,...) (Hou, Shu, & Duh, 2001; Uchida, Wakakura, Miyake, & Ogawa, 2008). This one can take place during storage, transport or industrial transformation (Yeh, Shu, & Duh, 2003). The instability origin of these peroxides lies on the specificity oxygen–oxygen linkage, which is known for its weak energy (80–200 kJ mol⁻¹).

Thus, the follow-up of such reactions seems to be practically impossible in calorimetric reactors because of the energy released during their implementation, and due to the risk of violent pressure rise. The follow-up of the heat balance can then be done in micro-calorimeters, according to several technologies: differential scanning calorimeter (DSC), thermo-gravimetric analysis (TGA), accelerating rate calorimeter (ARC) (Grewer, 1994).

In this work, the thermal decomposition of cumene hydroperoxide 80 wt% (CHP) with cumene solvent 20 wt% and of dicumyl peroxide (DCPO) was chosen. The thermal decomposition was carried out under dynamic and isothermal conditions. DSC technique was used for thermal analysis to obtain thermal kinetics data. The target of this research is to estimate the chemical kinetic

* Corresponding author. Tel.: +33 235522993.

E-mail address: nordine.mouhab@univ-rouen.fr (N. Mouhab).

parameters (rate constant k and activation energy). These parameters have a physical–chemical signification and help to calculate adiabatic time-to-maximum rate (TMR_{ad}) and adiabatic temperature rise (ΔT_{ad}) evaluated from ΔH (heat of decomposition) (Stoessel, 1993).

Using both the analysis of the decomposition reaction products given by a gas chromatograph coupled with the mass spectrometer (GC/MS) and the analysis of power profiles released in the isothermal mode, a reaction mechanism was proposed to the corresponding peroxides. The methodology for estimating kinetic parameters for both thermal decomposition reactions was reached by comparison of power profile given by the model to that obtained experimentally in dynamic mode. Parameters estimation was achieved using a mixed estimation method where a genetic algorithm is combined with a locally convergent method.

2. Experimental study

2.1. Calorimetric measurement

A calorimetric study both in isothermal and dynamic modes was performed by means of a microcalorimeter (DSC, TA Q1000) with purge using extra pure nitrogen (50 L min^{-1}). DSC detects the temperature change between the sample and reference for determining the heat flow, according to time and temperature. The type of crucibles used for the measurement is the gold-plated high pressure crucibles (M20 crucible 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 reactional mixtures. The sample mass of organic peroxides used in this work varies between 5 and 7 mg.

In isothermal mode, the thermal power profiles released by the decomposition of CHP 80 wt% and DCPO are represented in Figs. 1 and 2. The temperature is set at 129.6°C for CHP decomposition and at 149.5°C for DCPO decomposition.

The analysis of these power profiles and consequently the decomposition rate shows that the reaction mechanisms of these organic peroxides are different. It is concluded that the CHP decomposition is autocatalytic (Gold, Loening, & Sehmi, 1987; Hou et al., 2001) because the rate of the reaction is found to increase with conversion. The maximum exothermic peak appeared after the induction time (Fig. 1). However, the DCPO decomposition is n th order because the maximum rate of heat release occurs at 0% conversion reaction (appearance of the maximum exothermic peak as soon as the isotherm begins, Fig. 2).

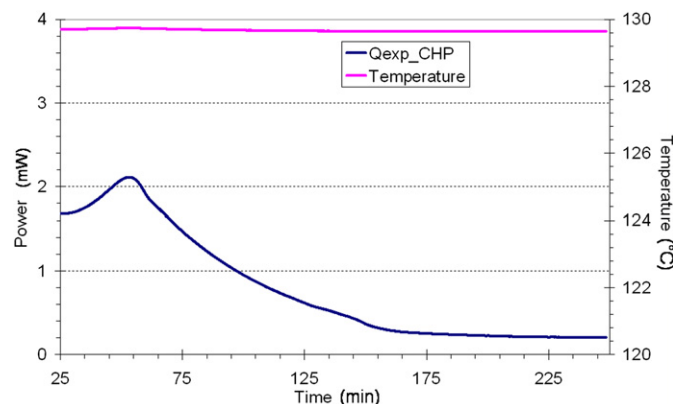


Fig. 1. CHP decomposition in the isotherm condition.

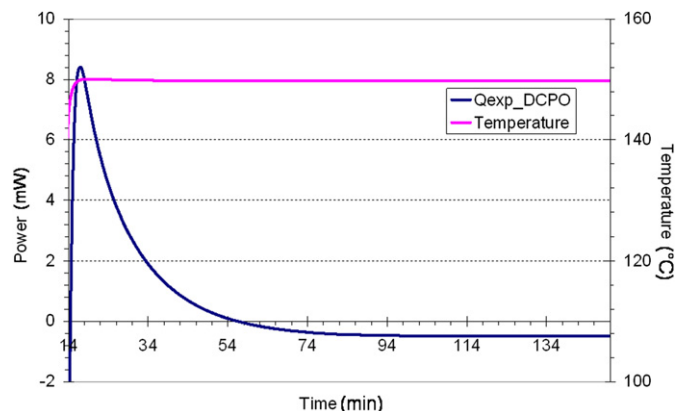


Fig. 2. DCPO decomposition in the isotherm condition.

To estimate the chemical kinetic parameters for these two reactions, measurement of the thermal power profiles in a dynamic mode is necessary. Figs. 3 and 4 illustrate respectively the heat flow versus temperature of CHP decomposition and of DCPO decomposition at various heating rate ($5, 7.5$ and $10^\circ\text{C min}^{-1}$) at the range of 50 – 350°C . The start-temperature is chosen to avoid the endothermic peak: a sharp endothermic peak appears at 41°C due to fusion of DCPO. The effects of the heating rate on the heat of decomposition (ΔH), exothermic onset temperature (T_0) and the temperature maximum (T_{max}) of both peroxides can be obtained directly by DSC dynamic scanning tests. From Figs. 3 and 4, it is evident that the decomposition enthalpies measured for the same solution are very close.

The average heat released is respectively equal to 1538 J g^{-1} for the CHP decomposition and 861.5 J g^{-1} for the DCPO decomposition.

2.2. Chemical analysis and reaction mechanism

In order to shed some light on the mechanism of the thermal decomposition process of the organic peroxides studied in this work, the chemical analyses of products resulting from the decomposition reaction of CHP and DCPO, in dynamic mode were used. A gas chromatograph coupled with the mass spectrometer (GCMS-QP2010, Shimadzu Corp., Japan) was used. Figs. 5 and 6 illustrate the chromatograms. After identification by mass spectrometry, the main identified products are respectively cumene already present in the starting product; acetophenone (Fig. 7-3) and α -methylstyrene (Fig. 7-5) during the CHP decomposition (the

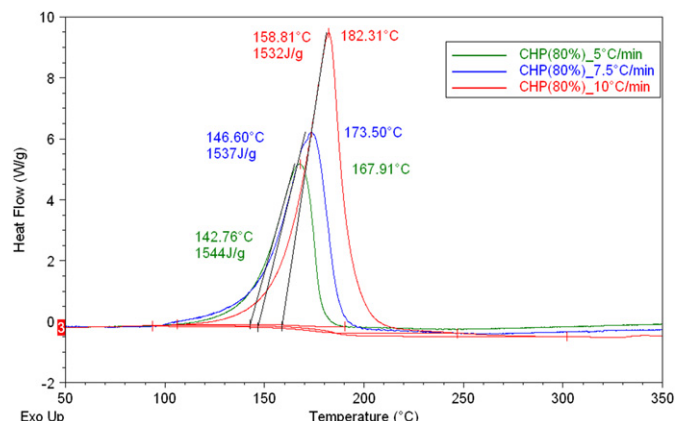


Fig. 3. Heat flow during DSC experiments on CHP at various heating rates.

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