# Kinetic analysis of solids of the quasi-autocatalytic decomposition type: SADT determination of low-temperature polymorph of AIBN

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## ABSTRACT

Simulations of SADT values based on the heat balance of the system are presented for azobisisobutyronitrile (AIBN). These simulations used kinetic parameters obtained from heat flow calorimetry experiments performed at temperatures in the stability range of low-temperature (L-T) polymorph of AIBN. Thermal Activity Monitor (TAM) data were collected in the range of 55–70 °C. The simulated SADT value for L-T AIBN amounts to 46 °C. This is very similar to the computed results obtained in the BAM project (Malow et al., 2015; Roduit et al., 2015; Moukhina, 2015; Kossoy et al., 2015) for the high-temperature (H-T) form of AIBN which amounts to 47 °C and is also in full agreement with the large scale experimentally found SADT of AIBN (47 °C) (Malow et al., 2015). The prerequisites for collecting proper kinetic data for the quasi-AC type energetic materials in which the phase change phenomena (polymorphic transformation or melting) precedes the decomposition are discussed. The apparent paradox when the application of incorrect kinetics applied in narrow $\alpha$ or $T$ ranges may sometimes result in the correct predictions of such safety parameters, such as SADT, is also explained.

## 1. Introduction

The kinetic analysis of the reactions occurring in the solid state combined with the exact heat balance of the system is a very powerful tool for the prediction of the behavior of a material on a large scale, e.g. the results of the BAM Project [1–4] in which four laboratories successfully predicted the important safety parameter, Self Accelerating Decomposition Temperature (SADT) [5], of azobisisobutyronitrile (AIBN). During the calculation of safety parameters based on kinetic analysis, one has to take into account the correct temperature and reaction extent at which kinetic data are collected and calculated. If phenomena such as a polymorphic transformation and/or melting do not precede the decomposition, then the experimental window (the range of heating rates or temperatures) can be optimized relatively easily. However, in the case where the phase transitions occur very close to the beginning of the decomposition, the collection of the data required for the proper kinetic analysis may be very difficult. Such compounds belong, according to the widely used Kotoyori classification [6], to the solids of the quasi-autocatalytic decomposition type. It seems

obvious that the kinetics of the decomposition must be investigated for this phase which is stable at ambient temperatures during the long-term storage. These points are very well illustrated by the scenario observed during the determination of the SADT value of AIBN. This compound shows the polymorphic transformation (between 73–83 °C at the heating rate of 2 K min$^{-1}$), see Fig. 1, followed by melting (ca. 100 °C) which overlaps the beginning of the decomposition. The decomposition, after melting, obviously proceeds according to a different mechanism as in the solid phase; therefore, the kinetic parameters obtained for the reaction in the liquid phase are of little (if any) value for the prediction of the solid phase properties below 70 °C.

In the BAM project, the kinetic parameters of the AIBN decomposition were collected before melting in the range 80–90 °C and the simulated SADT values agreed well with those obtained experimentally. Three of the participants in that project proposed different kinetic approaches and models for the description of the decomposition course of H-T phase of AIBN. Despite these differences, they obtained very similar and fully acceptable agreement between simulated and experimental values of SADT.

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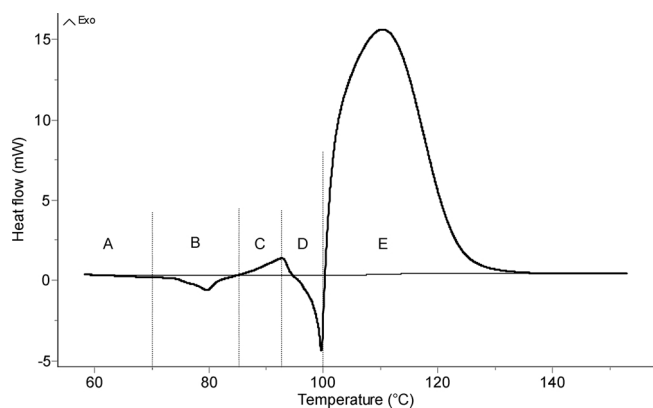
**Fig. 1.** Heat flow signal of AIBN recorded by DSC at a heating rate of $2 \, \text{K} \, \text{min}^{-1}$. The range between ambient and total decomposition temperature can be divided into 5 zones: A) range of existence of low temperature (L-T) polymorph of AIBN, B) the polymorphic transformation, C) decomposition of high temperature (H-T) phase of AIBN in solid state, D) melting of AIBN, and E) decomposition of AIBN in the liquid phase.

However, the careful consideration of the procedure applied in the BAM project may provoke critical comments as to whether the decomposition kinetics obtained after phase transformation i.e. for high-temperature (H-T) polymorph of AIBN is representative of the low-temperature (L-T) phase for which the SADT value was experimentally measured. During the ICTAC 2016 Conference in Orlando, Florida (USA) [7], some participants of the kinetic session expressed doubts as to whether such procedures as those applied in the BAM project are acceptable, and whether the kinetic data obtained for H-T polymorph can be used for the evaluation of SADT properties which are certainly linked to the properties of the L-T phase.

In order to clarify these logical questions which are very general and have to be considered during the kinetic analyses of all compounds in which phase changes are observed very close to the beginning of the decomposition, a study was performed to evaluate the kinetics of AIBN decomposition from data obtained below the phase transformation of (i.e. at temperatures lower than 70 °C). However, with a maximal sample mass of ca. 14–15 mg loaded in 50μl high pressure sealed crucibles [8], the sensitivity of a conventional DSC apparatus is not suitable to provide quantitatively usable signals in this temperature range. The traces of AIBN recorded by DSC under isothermal conditions at temperatures of 78–80 °C have the maximal values of the heat flow in the range of ca. 1 mW [9]. To quantify such weak signals in the present study, more sensitive, although very time and effort consuming experiments were done by means of a Thermal Activity Monitor (TAM) heat flow calorimeter.

The studies of the decomposition of AIBN clearly illustrate the difficulties of the experimental collection of the data best suited for further kinetic analysis. Moreover, the kinetics of the decomposition of solids is often evaluated using simplified kinetic assumptions depicted by the common expression "let us assume that the reaction is first-order" (e.g. the majority of kinetic evaluations of the data obtained by an Accelerating Rate Calorimetry (ARC) technique). It surprisingly often happens that this procedure, leading to a totally incorrect kinetic description of the process, has a minor influence on the correctness of the prediction of some safety parameters. It may happen that the data collected in these narrow temperature and/or reaction extent windows and elaborated with simplified kinetic assumptions result in the improper determination of the kinetics of the decomposition, yet surprisingly, may allow for acceptable simulations of some safety parameters such as the SADT. Such a scenario is particularly possible when the kinetic analysis used for the prediction of certain properties is evaluated from the data collected in the very narrow range of the decomposition ($\alpha$ between 0 and 0.05).

Because incorrect kinetic analysis sometimes results in an acceptable prediction of the SADT value, this scenario has to be undoubtedly clarified. In this study, an explanation of this apparent paradox is given. It will also be shown why even a correct determination of SADT value of AIBN using a first order kinetic model approach, being very often applied using data collected by ARC, is not convincing proof that the first order kinetic model is the correct kinetic description of the decomposition of AIBN. The conclusions illustrated by the evaluation of the decomposition kinetics of the L-T polymorph of AIBN are general and applicable for all types of materials.

## 2. Experimental

An investigation was done for the kinetics of the decomposition of the azobisisobutyronitrile (AIBN), CAS Number 78-67-1, purum, $\geq 98.0\%$ (GC) supplied by Sigma-Aldrich. A TAM III multi-channel heat flow calorimeter (TA Instruments) was used for the ultra-sensitive heat flow measurements. With average temperature fluctuation in the range of $\pm 10 \, \mu\text{K}$ between 15 and 150 °C and drift over 24 h within $\pm 100 \, \mu\text{K}$, this instrument achieves a sensitivity about 1000 times better than in DSC. In order to combine high sensitivity and operational safety, hermetically sealed high pressure DSC crucibles with internal volumes of 50 μl provided by TÜV SÜD [8] were placed inside of the glass ampoule of the microcalorimeter [10]. Sample masses of AIBN between 14 and 15 mg were used. The TAM heat flow traces recorded at 55, 60, 65, and 70 °C are shown in Fig. 2. The values of the heat of AIBN decomposition at 55, 60, 65, and 70 °C are presented in Table 1.

Due to the very high sensitivity of the heat flow calorimeter, it was possible to record even such small heat flows as those observed at 55 °C (duration of the experiment ca. 40–50 days, maximal heat flow amounted to ca. 35 μW). The measurements at 60, 65, and 70 °C (Fig. 2) were:

- repeated with new samples to check the reproducibility of the heat flow traces,
- verified by experiments with another AIBN batch and using another TAM III-device, and
- performed with two crucibles in the same glass ampoule of the TAM-microcalorimeter to obtain doubled heat flow intensities.

All traces reported in Fig. 2 show an acceleration period followed by one of deceleration, which is characteristic of autocatalytic behavior. Similar behavior of the AIBN decomposition below phase transformation was reported by Li et al. [11]. Results presented here as well as results from Li et al. clearly indicate that the proper description of L-T heat flow traces of AIBN with a *1st- order* kinetic model is incorrect. With this reaction model, the maximal rate of the reaction under isothermal conditions occurs at the beginning of the reaction which is certainly not the case for the aforementioned results.

## 3. Determination of the kinetic parameters and the predictions of the reaction course

In order to use the heat flow signals collected by heat flow calorimetry in the kinetic analysis, it is necessary to convert them into the reaction rate, $d\alpha/dt$, and the reaction progress, $\alpha$. As the baseline is horizontal and well defined, the integration of heat flow signal is precise.

There exist two main approaches used for the evaluation of the kinetic parameters in the solid state kinetic analysis, particularly the activation energy $E$ and the pre-exponential factor $A$: (i) so-called model fitting and (ii) isoconversional approaches. In this study, because the decomposition mechanism of AIBN is not fully known, the kinetic analysis is based on the isoconversional method, used also in previous studies on AIBN [2,9]. Based on the Arrhenius equation, the logarithm of the conversion rate, $d\alpha/dt$, as a function of the reciprocal