The Thermal Risk of Autocatalytic Decompositions: A Kinetic Study

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Abstract. A method is presented for the estimation of the ‘time to maximum rate under adiabatic conditions’ of autocatalytic decompositions and for their safety assessment. This method is based on the kinetics: a first-order reaction in competition with a Proudt-Tompkins step was chosen. Isothermal or temperature-programmed Differential Scanning Calorimeter curves were used to obtain the kinetic parameters. The method requires the heat release rates at the start of the reaction and at its maximum. It is in agreement with previously published ones, but is more easy to apply and allows, therefore, to perform a quick assessment of the safety of a process. Results found for the adiabatic case were confirmed by Accelerating Rate Calorimeter experiments.

1. Introduction

Traditionally, risk is defined as the product of the severity of a potential incident by its probability of occurrence. Considering chemical decompositions, their reaction energy can be taken as a measure of the severity whereas their probability is linked to the time to Explosion.

Very often an originally desired reaction is the cause of an incident. A desired reaction can constitute a thermal risk, if its control is lost and a runaway reaction is, therefore, triggered. Hence, it is necessary to understand how a reaction can change from its normal course to a runaway reaction, and then to plan countermeasures. This can best be done within the frame of a risk analysis which is based on a systematic approach, such as a defined runaway scenario [1]. Since in a large reactor (>1 m³) without an efficient and active cooling system, heat dissipation is negligible compared to the heat-release rate of the reaction going on in the batch, the situation can be considered adiabatic.

Such a scenario will, therefore, describe the temperature time behavior in the adiabatic case. The resulting temperature increase is proportional to the severity of the potential incident: the higher the temperature and the pressure, the more heavy are the consequences. The kinetics of the reaction, on the other hand, determines the runaway time: countermeasures cannot be taken and the risk, therefore, not be controlled, if the reaction is too fast or the time to explosion too short. An estimate of this time can be obtained by using the concept of the Time to Maximum Rate under adiabatic conditions ($T_{MR}$).

$$T_{MR} = \frac{c_p R T_0 E_q}{(q_0 E_p)}$$

This approximation [2] is valid for reactions of zero order. The error is low for other reaction orders, if the reaction in question is very exothermic. In this case, the temperature increase is high even at low conversion, and the reaction rate is almost independent of the conversion.

A decomposition reaction has, however, often an autocatalytic mechanism. Such a reaction can be formally represented by a mechanism involving two parallel steps: the first one is a first-order reaction, whereas the second one is of a second order, Proudt-Tompkins, reaction type:

$$A \xrightarrow{k_1} B$$

$$A + B \xrightarrow{k_2} 2B$$

Sometimes the reaction seems to be preceded by an induction time during which no exothermic reaction can be observed. In this case, one could calculate the activation energy and the $T_{MR}$ using the maximum rate of heat release and neglecting the induction time. This leads to induction times which are too short and therefore, to enormous safety margins in time. The apparent risk could eventually prevent an interesting process from being commercially exploited.

The aim of this paper is to develop an estimation method for the time to explo-
sion under adiabatic conditions in the case of autocatalytic decomposition reactions.

The method should be reliable and easy to use. It should require only instruments commonly used in thermal safety laboratories like Differential Scanning Calorimeters (DSC) and possibly an Accelerating Rate Calorimeters (ARC). The method is demonstrated using 2,4-dinitrophenol (2,4-DNP) as a test substance.

2. Definition of an Autocatalytic Reaction and of the Macro-Kinetic Model

Reactions often follow an nth order kinetic law. Under isothermal conditions, i.e., conditions, where the temperature remains constant, the heat release rate decreases uniformly in time. In the case of an autocatalytic decomposition, the behaviour is quite different (Fig. 1).

An acceleration of the reaction rate with time is observed. The corresponding heat-release rate passes through a maximum and then decreases again. Hence, an isothermal DSC experiment will immediately show to which type a reaction belongs. In the case of an adiabatic runaway, these two types of reaction will lead to totally different temperature vs. time curves: with nth order reactions, the temperature increase starts immediately after the cooling failure, while with autocatalytic reactions the temperature remains stable during the induction period and then suddenly increases very sharply (Fig. 2).

For the design of emergency measures, it is very important to know to which of the two types a decomposition reaction belongs. For example, temperature alarms will only be useful with decomposition reactions following an nth order kinetic law, as only in these cases the warning time will be sufficiently long.

Several existing models describe the autocatalytic behavior of a reaction. The best known and the oldest one (1945) is the Prout-Tompkins model [3-8]:

\[ A + B \xrightarrow{k} 2B \]

This model was developed to describe the thermal decomposition of permanganates. The reaction rate \( r = k[A][B] \) shows a quadratic dependence.

A corresponding cubic dependence [9-11] can be described by:

\[ A + 2B \xrightarrow{k} 3B \]

and the reaction rate becomes \( r = k[A][B]^2 \).

To describe the decomposition of many apparently pure products, these models are not suitable as the impurity, i.e., the catalyst, must be already present. Therefore, an initiation reaction which produces the catalyst is postulated, resulting in the following model [12]:

\[ v_1 A \xrightarrow{k_1} v_1 B \]

\[ v_2 A + v_3 B \xrightarrow{k_2} (v_3 + 1)B \]

where

\[ r = k_1 [A]^a - k_2 [A]^b[B]^c \]

As simplification we set \( v_1 = v_2 = v_3 = 1 \) and \( a = b = c = 1 \):

\[ A \xrightarrow{k_1} B \]

\[ A + B \xrightarrow{k_2} 2B \]

\[ r = k_1 [A] - k_2 [A][B] \]

This simplification will in general underestimate the adiabatic runaway time of reactions of higher orders. This error is on the safe side and can be tolerated.

This model has already been discussed by Schmid and Sapunov [13], Boldyrev [14], Chen and Reagan [15], Benito-Perez et al. [16,17], Ordax and Arriazabalaga [18], Greucer and Klais [19] gave special attention to the thermal process safety.

It should be noted that there is a difference between self-accelerating and autocatalytic reactions. Self-accelerating reactions are not always autocatalytic. The rate of autocatalytic reactions increases with the concentration of a catalyst [B] formed by the reaction itself.

A delay in product formation or heat release rate and, therefore, a self acceleration of the reaction can, however, be produced by another than an autocatalytic mechanism. Let us consider a system with two consecutive reactions

\[ C \xrightarrow{k_1} D \xrightarrow{k_2} E \]

The rate of reaction \( \frac{d[D]}{dt} \) will reach a maximum when

\[ \frac{d[D]}{dt} = k_1[C] - k_2[D] = 0 \]

at the time \( [20-22] t_{max} = \frac{k_1 \ln [k_1/k_2]}{1-(k_2/k_1)} \)

if, moreover, only the second step is exothermic or very fast, a delay in the heat release rate will be observed (Fig. 3).

3. Experiments

2,4-Dinitrophenol (2,4-DNP, Fluka 424160) was used without further purification and its initial concentration in all experiments is \([A]_0 = 5.43 \text{ mol} \cdot \text{kg}^{-1}\). DSC curves were obtained using sealed stainless crucibles purchased from Mettler-Toledo. The study was carried out under different atmospheres: Ar-\(\text{N}_2-\text{O}_2\)-ambient air and compressed air. No reproducible results were obtained in ambient air under isothermal conditions. The induction time of the decomposition obviously depends on the moisture content of the air (Fig. 4). Therefore, all DSC and ARC experiments with this substance were carried out under an Ar atmosphere.
4. Thermal History of Samples

Fig. 6 shows the overall induction time, under isothermal conditions, for samples with different temperature-time treatment. The sample is kept for a certain time at 240°C (first heating period), cooled down and heated again to 240°C (second heating period). An acceleration of the decomposition is observed, compared to the freshly prepared sample (first experiment). However, the induction time (sum of the first and the second one) is nearly the same regardless of the thermal treatment.

The formed catalyst is stable even at low temperatures and accelerates the decomposition. This has important consequences for industrial processes with pronounced residence times, e.g. continuous rectification or batch distillations. It is indeed usual in production that the distillation residue is left in the kettle and mixed with the following batch. In such a case the decomposition will be accelerated.

5. Evaluation of DSC Measurements

The heat-release rate of a chemical reaction is a function of both temperature and conversion rate. The complete thermokinetic description of a decomposition reaction involves, therefore, the knowl-
5.1. The Isothermal Mode

The decrease of species A can be described by Bernoulli's differential equation:

$$\frac{d[A]}{dt} = k_1 [A] + k_2 [A] ([A]_0 - [A]) \quad (1)$$

The solution of Eqn. 1 is given by Benito-Perez [17]:

$$[A] = \frac{k_1 + k_2 [A]_0}{k_2 + \frac{1}{[A]_0} - \exp \left((k_1 + k_2 [A]_0) t \right)} \quad (2)$$

The instantaneous heat release rate, \(dq/dt\), as measured by DSC, is proportional to \(d[a]/dt\) where \(a\) is the conversion:

$$d[a]/dt = (-\Delta H_a) \frac{da}{dt} \quad (4)$$

Insertion of \([A]\) as defined by Eqn. 2 in Eqsns. 3 and 4 gives:

$$\frac{dq}{dt} = -\Delta H_a \frac{k_1 (k_1 + k_2 [A]_0)^2 \exp \left((k_1 + k_2 [A]_0) t \right)}{(k_2 [A]_0 + k_1 \exp \left((k_1 + k_2 [A]_0) t \right))^2} \quad (5)$$

Simplification: For the most common case where \(k_2 [A]_0 >> k_1\), Eqn. 5 becomes:

$$\frac{dq}{dt} = -\Delta H_a \frac{k_1 \exp \left(k_1 [A]_0 t \right)}{(k_2 [A]_0 + k_1 \exp \left(k_2 [A]_0 t \right))^2} \quad (6)$$

and the conversion:

$$a = \frac{k_1 \exp \left(k_1 [A]_0 t \right)}{k_2 [A]_0 + k_1 \exp \left(k_2 [A]_0 t \right)} \quad (7)$$

Conversion at the maximum heat release rate: It can be shown that the maximum \(a_{\text{max}}\) of \(a = f(t)\) is found for \(d^2[a]/dt^2 = 0\), which corresponds to the maximum heat release rate in Eqn. 5.

$$a_{\text{max}} = \frac{k_2 [A]_0}{2 k_2 [A]_0} \quad (8)$$

Using Eqn. 8 with \(k_2 [A]_0 >> k_1\), \(a_{\text{max}}\) is shown to be 0.5.

Therefore, the maximum heat-release rate is obtained when half of the reactant \([A]\) is used.

5.1.1. Determination of Kinetic Parameters: First Method

In isothermal mode, the kinetic parameters are both rate constants, \(k_1\) and \(k_2\), and the activation energies, \(E_a1\) and \(E_a2\).

The rate of increase of the product B is given by:

$$\frac{d[B]}{dt} = k_2 [A][B] + k_1 [A] \quad (10)$$

If \([B] = \alpha [A]_0\) then:

$$[A] = [A]_0 - \alpha [A]_0 \quad (11)$$

Using Eqn. 11, 10 becomes:

$$\frac{d[a]}{dt} = k_2 (1-\alpha) \frac{k_1}{k_2 [A]_0} \quad (12)$$

Eqn. 12 is similar to Grewer's expression [27] with \(\alpha = u, k_2 = k\) and \(\beta = \alpha/k_2 [A]_0\) as \(u, k\) and \(\beta\) being notations used by this author.

Application: \(\alpha\) is the conversion yield of the reaction referred to intermediate products, i.e., products directly responsible for the autocatalysis. \(\alpha\) is thus deduced from isothermal DSC measurements.

Thus, \(f(\alpha) = \ln [\alpha/(1-\alpha)]\) may be plotted as function of time. The slope of the straight line (Fig. 7) is then \(k_2 [A]_0\) furthermore, for \(\ln [\alpha/(1-\alpha)] = 0\), the following equation is obtained:

$$\ln \alpha = -k_2 \frac{[A]_0}{\alpha}$$

\(\alpha_0\) can be considered as the degree of autocatalysis of the reaction. A small value of \(\alpha_0\) corresponds to a high degree of autocatalysis.

This method [28] was used by Loronova et al. [29], Boldyreva [14], and Sakurai et al. [30] in a different area of thermal analysis. Results of this method are summarized in Table 1. Values found using this method allow an estimate of activation energies and pre-exponential factors (Table 2) using a simple Arrhenius diagram.
5.1.2. Determination of Kinetic Parameters: Second Method

This simple method is applicable only for a low degree of autocatalysis, i.e., for cases with a measurable initial heat release rate.

Using Eqn. 5 we obtain \(k_1 (-\Delta H_r)\) for \(t = 0\), which corresponds to the initial heat release rate \(q_{ref1}\) as measured by DSC. Thus an estimate of \(k_1\) may be obtained:

\[
k_1 = q_{ref1}(-\Delta H_r).
\]

Using Eqn. 2 and its derivative with respect to time \(d[A]/dt\), it can be written:

\[
\frac{1}{[A]^2} \frac{d[A]}{dt} (-\Delta H_r) = \frac{-k_1}{[A]_0} (-\Delta H_r) \exp \left[ \left( k_1 + k_2 [A]_0 \right) t \right]
\]

Also using Eqn. 3, the left hand side of Eqn. 22 can be expressed as:

\[
\frac{1}{[A]^2} \frac{d[A]}{dt} (-\Delta H_r) = \frac{1}{[A]_0 (1-\alpha)^2} (-\Delta H_r) \frac{d\alpha}{dt}
\]

Using Eqns. 7 and 9, the time \(t_{max}\) at which the maximum heat release rate is observed, is given by:

\[
t_{max} = \frac{1}{(k_1 + k_2 [A]_0)} \ln k_2 [A]_0 / k_1
\]

Eqns. 22 and 23 can be set equal for \(t = t_{max}\) and \(\alpha = \alpha_{max} = 0.5\):

\[
4 (-\Delta H_r) \left( \frac{d\alpha}{dt} \right) t = t_{max} = -k_2 [A]_0 (-\Delta H_r)
\]

The maximum heat release rate \(q_{ref2}\) in the left hand side of Eqn. 25 can be expressed as:

\[
q_{ref2} = (-\Delta H_r) \left( \frac{d\alpha}{dt} \right) t = t_{max}
\]

The rate constant of the autocatalytic reaction may then be written using Eqns. 25 and 26:

\[
k_2 = \frac{4 q_{ref2}}{(-\Delta H_r) [A]_0}
\]

Comparison of both methods: The second method is compared to the first one in Table 1. Values of activation energies can be seen in Table 2.

Both methods give, within 1%, the same results. Small variations (\(-1\%\)) in activation energy values have no influence on the result of the simulation. Simulated curves can be superimposed. Using the above determined parameters and Eqn. 6, isothermal DSC curves can be numerically calculated (Fig. 8).

In general, the first method is always more precise, because all the points of the curves are used to estimate parameters. Only two points are used in the second one.

The second method is, therefore, more easy to apply, as only reference powers are required. This method may thus be used for a quick decision on the probability of occurrence. But it is unsuitable when there is no measurable initial heat release rate, that is to say, when \(q_{ref1}\) is lower than the detection limit of the DSC device i.e. for a high degree of autocatalysis.

5.2. The Temperature-Programmed Mode

This mode allows an estimate of the energy and of the temperature range within which the undesired reaction will occur.

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**Table 1. Reference Powers (each value is the mean of 6 experimental values) and Estimating of Rate Constant, Based on Method 1 and 2**

| Temp. [°C] | \(q_{ref1}\) [W/kg] | \(q_{ref2}\) [W/kg] | \(k_1\) \cdot 1000 [s\(^{-1}\)] | \(k_2\) \cdot 1000 [kg \cdot mol\(^{-1}\) \cdot s\(^{-1}\)] |
|-----------|----------------|----------------|-----------------|------------------|
| 230       | 8              | 169            | 0.0025          | 0.0026           |
| 240       | 10             | 371            | 0.0032          | 0.0031           |
| 250       | 13             | 814            | 0.0042          | 0.0042           |
| 260       | 36             | 987            | 0.0110          | 0.0115           |
| 270       | 76             | 1894           | 0.0236          | 0.0233           |

**Fig. 7. Illustration of the first method: Eqn. 19 as a function of the time for different isothermal temperatures**
All optimizations and simulations were made with the Netzsch program. Fig. 9 shows the comparison between experimental and simulated curves. The so obtained kinetic parameters are listed in Table 3.

Analogy between autocatalysis and first-order reaction: The temperature-programmed mode is the most commonly used method in thermoanalysis, but such DSC curves are difficult to simulate compared to the isothermal ones, because the reactant concentration and the rate constants are both a function of time and of temperature. The dependence of the rate constants on the temperature is given by the Arrhenius equation:

$$k(T) = a \exp \left( \frac{-E_A}{RT} \right)$$  (28)

To estimate the reactant concentration, the integrated form of Eqn. 28 is needed:

$$I(T) = a \int \exp \left( \frac{-E_A}{RT} \right) dT$$  (29)

However no algebraic solution of Eqn. 29 can be found without simplifications [31]. If $E_A/RT \gg 1$, a semi-convergent series can be used to simplify this integral:

$$I(T) = -aT \exp \left( \frac{-E_A}{RT} \right) \sum_{n=1}^{\infty} \left( -1 \right)^n \frac{RT}{E_A} \right)$$  (30)

Using the following substitution of variables:

$$\frac{d[A]}{dt} = \beta \frac{d[A]}{dT} = \beta \frac{d[A]}{dT}$$  (31)

Fig. 8. Experimental and simulated curves of an isothermal measurement of 2,4-DNP; $T_{iso} = 270^\circ$C

Table 2. Estimates of Activation Energies and of Pre-exponential Using Methods 1 and 2

| Reaction Type       | First method | Second method |
|---------------------|--------------|---------------|
| initiation reaction | 129.3        | 128.6         |
| $\log_{10} (a_1)$  | 8.8          | 8.6           |
| autocatalytic reaction | 132.2        | 133.6         |
| $\log_{10} (a_2)$  | 9.4          | 9.4           |

Fig. 9. Experimental (points) and simulated (lines) DSC curves: temperature-programmed mode

Using the following substitution of variables:
We assume the reactant concentration to be:

\[ [A] = x(T) \exp \left( -\frac{1}{\beta} (I_1(T) + I_2(T)) \right) \]  

where \( x(T) \) is an unknown function of the temperature. \( I_1(T) \) and \( I_2(T) \) correspond to the initiation and the catalysis reaction, respectively. \( x(T) \) can be found by introducing Eqn. 33 in Eqn. 32. The solution of this differential equation is as follows:

\[ [A] = \frac{\exp \left( -\frac{1}{\beta} (I_1(T) + I_2(T)) \right)}{1/[A]_0 - \frac{k_2}{\beta} \int_{T_0}^{T} \exp \left( -\frac{1}{\beta} (I_1(T) + I_2(T)) \right) dT} \]  

If \( T \to T_0 \), then \([A] \to [A]_{T \to T_0} \) \(([A]_{T_0} = [A]_0)\)

thus Eqn. 34 becomes:

\[ [A]_{T \to T_0} = [A]_0 \exp \left( -\frac{1}{\beta} (I_1(T) + I_2(T)) \right) \]  

This expression (Eqn. 35) can be compared with the expression found for a first-order reaction under the temperature-programmed mode:

\[ [A] = [A]_0 \exp \left( -\frac{1}{\beta} H \right) \]  

Adiabatic conditions are realized when no heat exchange between the reaction mixture and the surroundings takes place. When a cooling failure occurs, the effectiveness of the cooling system is suddenly reduced to very low values. Hence, adiabaticity is a good approximation for the heat balance after a cooling failure has occurred.

The increase in temperature can be written as:

\[ \Delta T_{ad} = T_f - T_i = \frac{-\Delta H_i}{c_p} \]  

and the conversion becomes:

\[ \alpha = \frac{(T - T_i)}{\Delta T_{ad}} \]  

The single variable is the temperature which is a function of time. According to Eqns. 1, 3, 37, and 38:

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**Table 3. Estimates of Activation Energies and Pre-exponential Factors Using the Temperature Programmed Mode**

| Activation energy | Initiation reaction | Autocatalytic reaction | First-order reaction |
|-------------------|---------------------|------------------------|---------------------|
| 128.8 kJ/mol      | 132.6 kJ/mol        | 346.2 kJ/mol           |
| Pre-exponential factor \( \log_{10}(a_i) \) | 8.8 | 9.4 | 12.3 |

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**Fig. 10.** Experimental (points) and simulated (line) DSC curves using a model of first order with the temperature-programmed mode.
with \( k_1(T) = a_1 \exp \left( - \frac{E_{a1}}{RT} \right) \) and \( k_2(T) = a_2 \exp \left( - \frac{E_{a2}}{RT} \right) \).

No analytical solution of this equation was found. Eqn. 39 was solved numerically.

The simulation parameters were chosen in such a way that always slightly shorter times than in reality were obtained (Figs. 11 and 12).

The corresponding results are shown in Table 4.

Thus, the adiabatic case can be well modelled using isothermal measurements, as can be seen from a comparison of Tables 2 and 4. Simulations with errors of \( \pm 1\% \) in \( E_{a1} \) and \( E_{a2} \) give a scatter of values for the TMRad in a range of 15\% around the true value.

### 7. Conclusion

It has been shown that the adiabatic behavior of autocatalytic decompositions can be described using kinetic parameters deduced from isothermal DSC curves. The second method presented is easy to apply, reliable, and takes very little time. Experience within our company shows that de-

### Table 4. Estimates of Activation Energies from ARC-experiments

| Reaction Type                        | Heat-wait-search mode | "Isothermal age" mode |
|--------------------------------------|-----------------------|-----------------------|
| Initiation reaction \( E_{a1} \) [kJ/mol] | 128.9                 | 129.2                 |
| Autocatalytic reaction \( E_{a2} \) [kJ/mol] | 129.6                 | 132.2                 |
composition reactions of many nitro compounds can be treated in the same way. Compared to a simplified zero-order approximation the time to explosion is increased by a factor of 10 depending on the nature of the substance, i.e., on the kinetic parameters. This allows to work at higher temperatures without increasing the risk of a runaway. This result can be achieved due to a more comprehensive knowledge of the decomposition kinetics.

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List of symbols

- $T_{\text{max}}$: time to maximum rate under adiabatic conditions
- $[A]$: concentration of reactant A
- $[A]_0$: initial concentration of reactant A
- $[B]$: concentration of catalyst B
- $[B]_0$: initial concentration of catalyst B
- $a_1$: pre-exponential factor for the initiation reaction
- $a_2$: pre-exponential factor for the autocatalytic reaction
- $k_1$: rate constant of the initiation reaction
- $k_2$: rate constant of the autocatalytic reaction
- $E_{a1}$: activation energy of the initial reaction
- $E_{a2}$: activation energy of the autocatalytic reaction
- $-\Delta H_f$: partial reaction enthalpy until the time $t$
- $\Delta H_f$: total reaction enthalpy until the time $t$
- $r$: time
- $T$: temperature
- $T_{\text{ad}}$: temperature increase under adiabatic conditions
- $T_i$: initial temperature
- $T_f$: final temperature
- $c_p$: specific heat capacity at constant pressure
- $R$: ideal gas constant
- $q$: heat release rate
- $q_j$: heat release rate at the beginning
- $q_{\text{max}}$: heat release rate at the maximum
- $\alpha$: conversion
- $\phi$: degree of autocatalysis
- $i$: stoichiometric coefficient of substance $i$
- $a, b, c$: reaction orders
- $\lambda(T)$: Arrhenius integral

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