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Autocatalytic decomposition reactions, hazards and detection

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Abstract

In the chemical industry, estimation methods based on dynamic Differential Scanning Calorimetry (DSC) measurements have been developed for a preliminary screening of the risk associated to a chemical operation. An important point for the assessment of thermal risk is the identification of autocatalytic reactions. These types of reactions require our special attention and should be clearly distinguished from *n*th order reactions. Until today, the most reliable tool for the identification of autocatalytic decompositions was an isothermal DSC measurement.

A new screening method based on dynamic DSC measurements for the identification of autocatalytic decompositions has been developed. The method consists of fitting a first order kinetic model to the measured heat release rate curve (from dynamic DSC measurement) and determining the apparent activation energy.

If the apparent activation energy is higher than 220 kJ/mol, the decomposition is autocatalytic.

By taking into account the cases with the border value of the apparent activation energy (180–220 kJ/mol), as well as the exception to this method, it should be possible to apply our new screening tool to about 80% of the cases.

Keywords: Autocatalysis; Decomposition; Thermal stability; DSC; Safety

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1. Introduction

An autocatalytic reaction is a chemical reaction where a product also acts as catalyst [1]. In such a reaction the observed rate of the reaction is often found to increase with conversion.

The term autocatalytic used in this paper may also refer to a molecular reaction mechanism; the exact mechanism is usually not known for decompositions, so the term autocatalytic stands here for the formal description of autocatalysis and is therefore not used in the molecular sense.

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The aim of this paper is not to study the mechanistic details of autocatalytic decompositions and their different types but rather to present a new screening tool to identify them on the basis of dynamic Differential Scanning Calorimetry (DSC) measurements, to save both time and money without loss of safety.

2. Hazards associated with autocatalytic decompositions

2.1. Behavior of autocatalytic decompositions compared to nth order reactions

Reactions often follow an *n*th order kinetic law. When performing a DSC-experiment at constant temperature, the heat release rate decreases uniformly with time. In the case of an autocatalytic decomposition, the behavior is quite different; an acceleration of the reaction with increasing conversion is observed (Fig. 1). The corresponding heat release rate passes through a maximum and then decreases again. Furthermore, the acceleration period is often preceded by an induction period where no thermal signal and therefore no noticeable thermal conversion can be observed.

If one considers the case of an adiabatic runaway these two reaction types will lead to totally different temperature versus time curves; with *n*th order reactions the temperature increase starts immediately after the cooling failure, while with autocatalytic reactions the temperature remains stable during the induction period and suddenly increases very sharply as shown in Fig. 2. This is due to the fact that an autocatalytic reaction initially shows no or only a small heat release. Thus the temperature increase is delayed and is only detected later after an induction period after which the reaction rate becomes sufficiently fast.

This has essential consequences for the design of emergency measures. A technical measure to prevent a runaway could be a temperature alarm. This works well with *n*th order

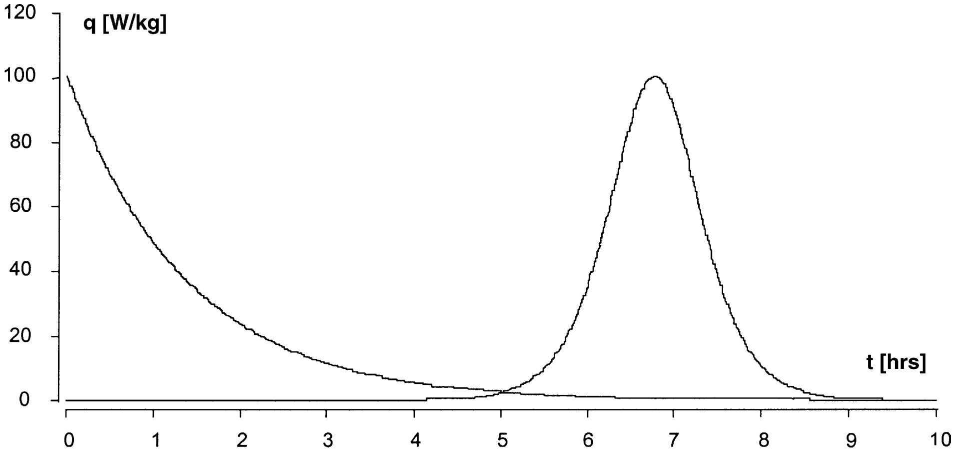

Fig. 1. Comparison of autocatalytic with *n*th order reactions during an isothermal DSC-experiment performed at 200 °C. Both reactions present a maximum heat release rate of 100 W/kg at 200 °C. The induction time of the autocatalytic reaction leads to a delay in the reaction course.

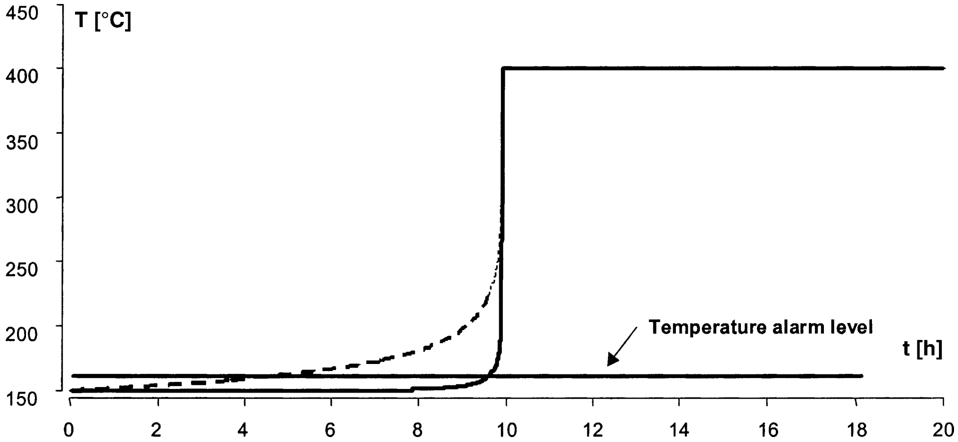

Fig. 2. Comparison of an autocatalytic (solid line) and an *n*th order reaction (dashed line) under adiabatic conditions starting from 150 °C. If an alarm level is set at 160 °C, the *n*th order reaction will reach the alarm level after 4 h and 15 min whereas the autocatalytic reaction reaches this level only after 9 h and 35 min.

reactions. Autocatalytic reactions however are not only accelerated by temperature but also by conversion. This can lead to a very sharp temperature increase. In the case shown in Fig. 2, a temperature alarm is not effective because there is no time left to take measures [2].

Therefore it is very important to know if a decomposition reaction is of autocatalytic nature or not, i.e. the safety measures must be adapted to this type of reaction.

2.2. *Catalysis of the reaction and influence of impurities*

Autocatalytic reactions are by definition catalyzed by their reaction products. These can be very stable and can often survive at room temperature or even at higher temperatures. Fresh material can therefore be contaminated when mixed with material that underwent thermal stress. This was the case when a distillation was performed at 200 °C batchwise, and in such a way that the residue originating from the previous batch was not removed. The isothermal DSC measurement of the initial mixture showed that it decomposed autocatalytically (Fig. 3). The same reactor was then used for the second distillation and again the residue was kept in the reactor. When the distillation was launched for a third run, an uncontrolled temperature increase was observed.

This can be explained on the basis of the isothermal DSC measurements of the reaction mixture before and after the first distillation (Figs. 3 and 4) and at the end of the second distillation (Fig. 5). A continuous decrease of the isothermal induction time (time between the beginning of the measurement and the maximum heat release rate) was observed between these different stages. At the end of the second distillation, the decomposition reaction started immediately at the distillation temperature (200 °C). The shift of the isothermal induction time was due to the fact that the autocatalyst was produced during the first and second run. At the beginning of the third run, the concentration of the formed autocatalyst

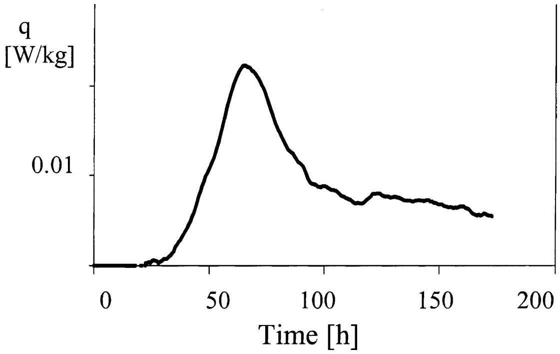

Fig. 3. Isothermal DSC measurement from starting material.

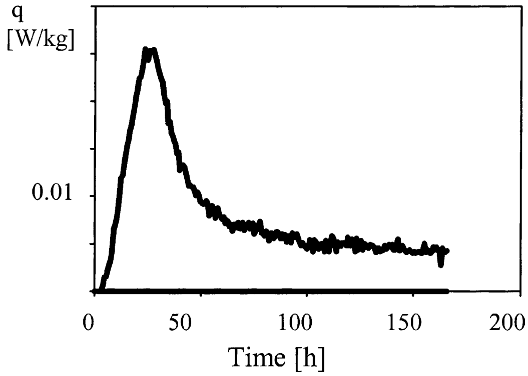

Fig. 4. Isothermal DSC measurement at the end of the first distillation.

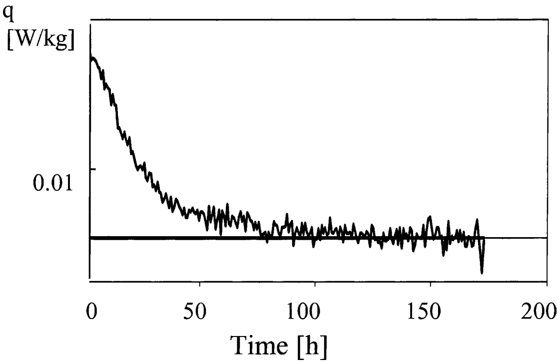

Fig. 5. Isothermal DSC measurement after the second distillation.

was so high that the decomposition reaction already started at the distillation temperature. This explained the unusual temperature increase observed.

In addition, autocatalytic reactions are also catalyzed by impurities such as heavy metals or acid. A well-known example is dimethylsulfoxide, which is known to decompose autocatalytically. Quite a few accidents that actually happened during its distillation are described in literature [3]. The decomposition characteristics and especially the isothermal induction time vary with the type and amount of impurities and these are not an intrinsic property of the substance itself, but rather vary from one supplier to another and depend therefore on the quality of the product and sometimes even on the batch.

3. Classical detection methods of autocatalytic decompositions

3.1. Compounds known to decompose autocatalytically

Autocatalytic decompositions occur with many sorts of substances, organic as well as inorganic ones. Certain classes of compounds as, for example aromatic nitro compounds, chlorinated aromatic amines or cyanuric chloride are known to decompose by an autocatalytic mechanism. A list of compounds decomposing autocatalytically can be found in the literature [4].

3.2. Chemical detection

An autocatalytic decomposition can be followed by isothermal aging and periodic sampling and subsequent chemical analysis of the reaction mass. The reactant concentration first remains constant and decreases after an induction period (Fig. 6). This is characteristic for self accelerating or autocatalytic behavior.

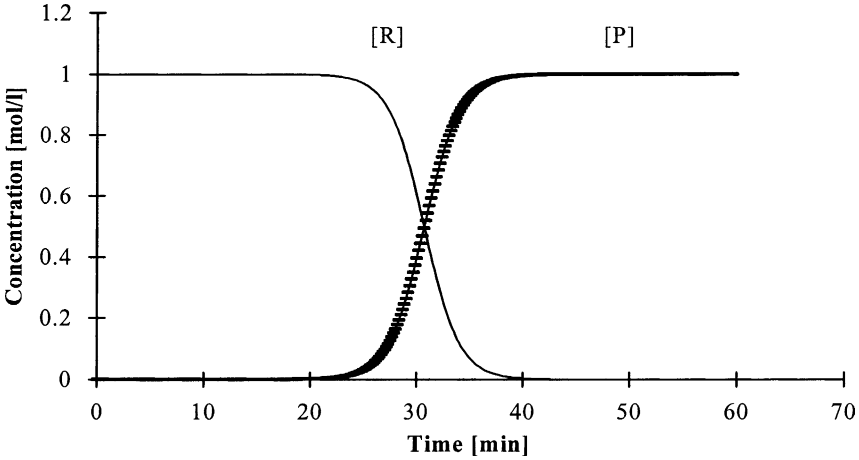

Fig. 6. Variation of concentration as a function of time: R is reactant and P is product.

3.3. Detection by isothermal DSC

Until today, isothermal (calorimetry at constant temperature) DSC measurements have been the only reliable way to detect and characterize an autocatalytic decomposition. As mentioned before, the heat release rate curve of an autocatalytic decomposition under isothermal conditions has a characteristical shape. The corresponding heat release rate passes through a maximum and then decreases again. In addition to that, the acceleration period is often preceded by an induction period where no thermal signal and therefore no noticeable thermal conversion can be observed (so called strong autocatalysis).

To detect an autocatalytic decomposition reliably by isothermal DSC measurements certain precautions have to be taken. For those measurements, the choice of the experiment temperature is crucial [5]. At too low a temperature, the induction time may be longer than the experiment time, suggesting that there is no decomposition at all. This false interpretation can be avoided by comparison with the dynamic DSC-experiment; the measured energy must be the same in both experiments. At too high temperature, the induction time may be so short that only the decreasing part of the signal is detected, suggesting a non-autocatalytic decomposition. At a correct temperature level, the typical form of the signal as shown in Fig. 1 can be identified; the reaction rate first increases passes through a maximum and decreases again.

4. Detection of autocatalytic decomposition by the new method based on dynamic DSC

4.1. Background of the new method

Whereas isothermal DSC measurements are not common and can be very time consuming, dynamic, i.e. temperature programmed DSC measurements are widely used as a screening tool in industry [6]. Temperature programmed DSC measurements with autocatalytic reactions have a characteristic shape. They show narrow signals with a high heat release rate maximum. It was also found that an experienced person could identify such decompositions based on the characteristic shape of their signal. Therefore, it seemed possible to develop a reliable autocatalytic screening tool to detect autocatalytic decompositions.

The fact that the peak appears sharp and narrow with a high maximum heat release rate may be expressed in a quantitative way. The first idea is to measure the peak height and width and to use their ratio, in order to determine if the reaction is autocatalytic or not. Even if this method looks very simple, its drawback is that only a few points are used to describe the peak. The statistic significance of such an evaluation is very poor by nature.

Therefore a more efficient and reliable method, which has higher statistic significance, was developed.

In fact the beginning of the reaction (or of the peak) determines the behavior of the reaction mass under adiabatic conditions. It can be shown that at small conversion any reaction kinetics can (at least formally) be described by a first order reaction. Therefore a simple first order model is fitted to the beginning of the peak by adjusting three parameters of the model: the decomposition energy, the activation energy and a heat production rate at a certain temperature. The latter can be extracted from the DSC-signal, if the baseline is known. The resulting activation energy from the fit is an *apparent* activation energy and characterizes the steepness of the peak, i.e. the higher is its value the greater is the probability that the reaction is autocatalytic. It is important to notice that the apparent activation energy has absolutely no physical significance. It is just used as a criterion to distinguish between autocatalytic and non-autocatalytic decompositions.

4.2. Experimental part

For the general applicability of the method, the following approach was chosen. The kinetic model was written as spreadsheet (MS-Excel®). The mathematical background of the model is given in Appendix A. The dynamic DSC measurements were not required to exist as ASCII-files, but they usually existed as graphs (from, e.g. a scanner) and were imported in bitmap form where they formed a background picture to the Excel graphics showing the simulated curve. By varying the parameters of the simulation the simulated and the measured curves could be superposed. Sloping baselines could also be corrected.

During the study, it became clear that the border value of the apparent activation energy distinguishing between autocatalytic and non-autocatalytic reactions was around 200 kJ/mol. Accordingly the examples were chosen to narrow this limit.

4.3. Results

The proposed method was tested with 100 samples. For every one of these a temperature programmed as well as a isothermal DSC curve was available.

For apparent activation energies between 50 and 180 kJ/mol, the decomposition was found to be non-autocatalytic. For apparent activation energies between 220 and 1000 kJ/mol, the decompositions were of autocatalytic nature. Thus a general rule can be deduced: if the apparent activation energy is higher than 220 kJ/mol, the decomposition is very likely to be autocatalytic. An error margin of 10% is taken into consideration for the determination of the apparent activation energy. The error margin was determined on basis of experiments

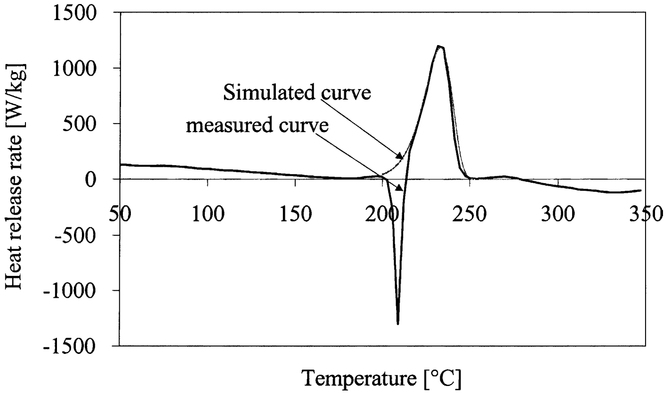

Fig. 7. Fit procedure in case when the exothermicity is preceded by an endothermic effect.

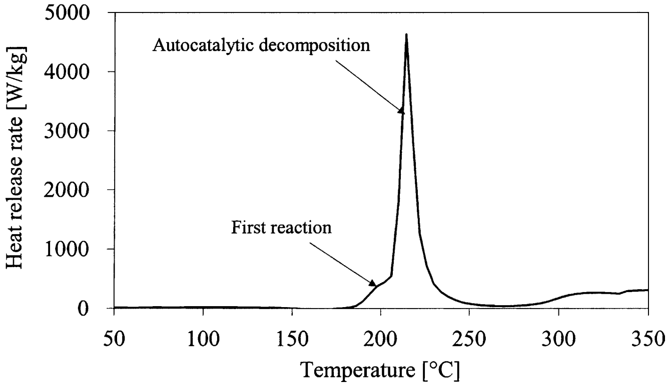

Fig. 8. DSC measurement with more than one exothermal peak.

where several persons had to fit the same curve. For apparent activation energies lying between 180 and 220 kJ/mol, we recommend to perform isothermal DSC measurements.

We also found that for some cases fitting is not possible or leads to erroneous results. Nevertheless, we were able to identify the cases where the described method cannot be applied.

When an endothermic process precedes the exothermic decomposition, no fitting is possible (Fig. 7), since the real onset of the exothermic reaction necessary to perform the fit cannot be determined. Therefore the method cannot be applied in those cases. However, it is known that decompositions from the melt have a formally autocatalytic decomposition mechanism. Problems may also occur with consecutive reactions, where the autocatalytic reaction is preceded by an *n*th order reaction. By fitting the curve, the calculated apparent activation energy will reflect the first reaction which is *n*th order and not the autocatalytic one (Fig. 8).

It is important to notice that in these cases the dynamic DSC measurement clearly shows the presence of several reactions causing different well distinguishable peaks.

5. Statistical study and practical consequences while handling autocatalytically decomposing substances

A study involving 100 fine chemicals commonly used in the fine chemical industry has shown that 20% of the analyzed substances had apparent activation energies between 180 and 220 kJ/mol, and 60% of the decompositions had activation energies higher than 220 kJ/mol and were thus based on the described method considered to be autocatalytic. A similar observation was made by Grewer and Klais [7].

Unfortunately there is no general rule to deal with autocatalytic decompositions; however these guidelines have proved to be useful whenever autocatalytic decomposition reactions are to be expected at handling temperatures:

- Try to characterize and specify the relevant impurities, and to determine whether they catalyze the decomposition reaction. This can be made on the basis of a dynamic DSC measurement, where a peak shift is observed in case a catalysis occurs. The knowledge of the thermal history of the compound in those cases could be very helpful.

- Be aware that autocatalytic decompositions can be catalyzed by impurities such as acids, rust, heavy metals. After storage of the product, carry out a thermal analysis before running a reaction.
- Reduce transfer operations: every transfer operation can lead to contamination of the product. Use one-way drums or use recycle drums or containers only after thorough cleaning.
- In case of distillation avoid the accumulation of residues. Also if you have compounds containing stabilizer, do not forget that you will remove it by distillation.
- Perform a dynamic DSC measurement before submitting the product to any thermal stress.

6. Conclusion

The new screening method for the identification of autocatalytic decomposition can be used as a tool to detect autocatalytic decomposition. For apparent activation energies (obtained by fitting a first order kinetic model on the measured heat release rate of a dynamic DSC) higher than 220 kJ/mol the decomposition was shown to be autocatalytic. The method is not applicable in cases where the exothermic signal is directly preceded by an endothermal signal. The method has to be used with care when serial reactions occur (several peaks can be distinguished in the thermogram). By taking into account the cases with the border value of the apparent activation energy (180–220 kJ/mol), as well as the cases where fitting is not possible, the new screening could be applied to about 80% of the cases. This allows reducing the number of isothermal experiments required.

Acknowledgements

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Appendix A. Mathematical background of the new screening tool

The mathematical background of our new method is simple. A simulated DSC curve based on first order kinetics is fitted to the measured heat release rate curve from a dynamic DSC. The signal-baseline must either be known or be based on a reasonable assumption. The heat release rate $\dot{q}(T)$ (W/kg) for a first order mechanism assuming an Arrhenius model is given by Eq. (A.1):

$$\dot{q}(T) = \dot{q}_0 \exp\left(\frac{-E_\mathrm{a}}{RT}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right)\left(1 - \frac{\Delta H(t)}{\Delta H_\mathrm{R}}\right) \tag{A.1}$$

where T_0 (K) is the onset temperature and is defined as the temperature at which the heat rate signal can first be differentiated from the baseline temperature reading, $\dot{q}_0$ (W kg^{-1})

the heat release rate at the onset temperature, E_a (kJ mol^{-1} K^{-1}) the activation energy, R the ideal gas constant (kJ mol^{-1} K^{-1}), T (K) the temperature, $\Delta H(t)$ the partial reaction enthalpy at a given time t (s), ΔH_R the global reaction enthalpy and the ratio $\Delta H(t)/\Delta H_R$ (–) the conversion.

For a temperature-programmed measurement, the temperature is defined by the following equation:

$$T(t) = T_{\text{start}} + \alpha t \tag{A.2}$$

where T_{start} is the start temperature of the measurement and α a constant heating rate in (K/s).

Eq. (A.1) using the temperature function Eq. (A.2) can only be integrated numerically.

For the numerical simulation of the DSC curve the value of the partial reaction enthalpy at a time $t + \Delta t$ is needed and can be given by

$$\dot{q}(t+\Delta t) = \dot{q}_0 \exp\left(\frac{-E_a}{R}\left(\frac{1}{T(t+\Delta t)} - \frac{1}{T_0}\right)\right)\left(1 - \frac{\Delta H(t+\Delta t)}{\Delta H_R}\right) \tag{A.3}$$

However the value of the partial reaction enthalpy at $t+\Delta t$ is unknown. A first approximation (Euler) is used to evaluate this value. The approximated value is given by $\Delta H^*(t+\Delta t)$ and can be expressed by

$$\Delta H^*(t+\Delta t) = \Delta H(t) + \dot{q}(t)\Delta t \tag{A.4}$$

By replacing $\Delta H^*(t+\Delta t)$ by its approximation we get

$$\dot{q}(t+\Delta t) = \dot{q}_0 \exp\left(\frac{-E_a}{R}\left(\frac{1}{T(t+\Delta t)} - \frac{1}{T_0}\right)\right)\left(1 - \frac{\Delta H^*(t+\Delta t)}{\Delta H_R}\right) \tag{A.5}$$

Knowing the value of the heat release rate at $t + \Delta t$ a better approximation of the specific heat of the reaction at $t + \Delta t$ can be calculated (trapezoid integration):

$$\Delta H(t+\Delta t) = (\dot{q}(t) + \dot{q}(t+\Delta t))\tfrac{1}{2}\Delta t \tag{A.6}$$

Eq. (A.6) of the heat of reaction at $t + \Delta t$ is then introduced into Eq. (A.3) describing the heat release rate at $t + \Delta t$ and the simulated curve is then calculated.

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