Experimental study of thermal hazards during the hydrogenation of aromatic nitro compounds

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Catalytic hydrogenations of aromatic nitro compounds are known to be potentially hazardous reactions. Their safety depends both on the properties of compounds and on the operating conditions. The focus of this paper is on thermal hazards. Firstly, the thermal stability of the reaction mixtures determines the temperature range in which the reaction can be run safely. Secondly, accumulation of hydroxylamine is a potential hazard as it can lead to undesired side-reactions, which are highly exothermic and, in contrast to the hydrogenation, cannot be controlled by the hydrogen supply. Using a reaction calorimeter, the thermal data of the reactions, i.e. overall heat and heat flow during the reaction, can be measured. Conclusions on the accumulation of intermediates in the reaction mixture can also be drawn from these data. Finally, the thermal behaviour of the reactor in the case of a cooling failure can be predicted with a high accuracy.

(Keywords: aromatic nitro compounds; hydrogenation; thermal hazards)

Risk analysis of catalytic hydrogenations

The fine chemicals industry deals with a great number of very different processes. The risk management related to these necessitates a systematic risk analysis. The system used in our company consists of three steps:

1. systematic search for deviations, involving compilation of basic data and definition of safe conditions
2. evaluation of hazards, involving assessment of identified risks
3. definition of measures, involving assessment of the remaining risks

For chemical reactions the basic data must include the thermo-kinetic data of the reactive system.

The catalytic hydrogenation of aromatic nitro compounds is a well-defined class of reactions with a high hazard potential. In the fine chemicals industry a large amount of different aromatic nitro compounds are reduced to amines. Thus it is useful to apply a systematic approach of risk analysis for this reaction as a class. The purpose of this paper is to present a set of dedicated experiments which allow a fast and systematic assessment of the thermal hazards of this class of reactions.

Hazards in catalytic hydrogenations

The hazards of catalytic hydrogenations of aromatic nitro compounds can be enumerated according to the different compounds involved.

Hazards related to hydrogen

The very low density and viscosity of hydrogen in combination with high pressure makes it difficult to rule out leaks. These properties mean that the flow rate in case of a leak is 4 times higher than with air in similar conditions. Moreover hydrogen/air mixtures are explosive at a large range of concentrations (4–75% vol) and have a very low ignition energy (0.02 mJ). Thus ignition is very probable. Detonation is possible at a large range of concentrations (18–59% vol).

Hazards related to the catalyst

Hydrogenation catalysts like Ruppe or Raney nickel and platinum or palladium on carbon catalysts are pyrophoric when in contact with air.

Hazards related to the solvent

Often hydrogenations are run in organic solvents. The alcohols are the most frequently used solvents in catalytic reductions of aromatic nitro compounds. Since the reaction temperature is often above the boiling point, in case of a leak a flammable vapour cloud will emanate and most likely be ignited.

Hazards due to the high decomposition energy of aromatic nitro compounds

Aromatic nitro compounds are well known to have a high energy of decomposition (about 2000 kJ/mol). The decomposition reaction has a high activation energy and often follows a self-accelerating mechanism.
which causes the triggered decomposition of the pure compound to run very vigorously. Moreover it has been observed that the thermal stability of aromatic nitro compounds decreases in the presence of catalysts. Crystallized aromatic nitro compounds are often sensitive to shock.

Hazards due to the hydrogenation reaction
The reduction of nitro-aromatics is a very exothermic reaction (560 kJ/mol) in itself. In the case of loss of control of the reaction, decomposition of the aromatic nitro compound could easily be triggered. On the other hand, hydrogenation can be controlled by the stirring activity and by limiting the molar fraction of hydrogen present in the reactor.

Hazards related to unstable intermediates
The hydrogenation of aromatic nitro compounds involves a rather complex mechanism. Intermediate products such as N-phenyl-hydroxylamine can accumulate and lead to uncontrollable side-reactions.

The last three categories of hazards are directly related to thermal phenomena. This work focuses on these hazards only.

Determination of thermal data
First, we will consider the thermal stability of aromatic nitro compounds. The high energy of decomposition and the violence of the runaway necessitates the definition of conditions which rule out the occurrence of these reactions. We will then investigate the design of hydrogenation reactions and the choice of reaction parameters which provide a good control of its course. Finally, we will focus on the dynamic aspects of the hydrogenation of aromatic nitro compounds, particularly on the detection of accumulation of unstable intermediates during the reaction.

Thermal stability of nitro-aromatics
Requirement for data
The decomposition of pure aromatic nitro compounds is active only at elevated temperatures. However in solution, with the presence of catalyst and especially if the hydrogenation is run in the presence of alkaline, it may occur at quite low temperatures.

In the speciality and fine chemicals industry hydrogenations of aromatic nitro compounds are often run as batch reactions: the aromatic nitro compound is loaded at the start of the process of the reaction. Thus decomposition can be considered a parallel reaction which competes with hydrogenation. In practice the decomposition reaction becomes dominant only under heat accumulation conditions, which occur in the case of a cooling failure in a stirred autoclave or when the circulation pump fails in loop reactors. This kind of failure is a deviation from desired conditions which has to be accounted for in the risk analysis. Thus, the study of the decomposition will allow fixing of an upper temperature limit for the reaction mass containing the aromatic nitro compound. In terms of risk analysis we define safe conditions.

It is worth knowing the kinetics of the decomposition at the process temperature to predict the runaway time which in turn is needed to define preventive or corrective measures. The course of the decomposition can be well characterized by its heat effects, making calorimetric methods very effective for this purpose.

Experimental methods. Running a DSC (differential scanning calorimetry) experiment in a temperature scanned mode allows determination of the energy of decomposition and gives a rough indication of the temperature range at which this reaction is active (Figure 1). At process temperatures the decomposition is typically too slow to allow a direct measurement of its thermal effects by DSC. Therefore a series of isothermal DSC experiments are run at temperatures at which the reaction is fast enough to yield a measurable heat power (Figure 2). These results must be transformed in such a way that they can be used to predict the behaviour of the reaction mass in case of cooling failure.

Interpretation of the results. Adiabatic conditions are assumed to represent the worst case of cooling failure. In order to predict the behaviour of the aromatic nitro compound under adiabatic conditions, the results obtained by isothermal experiments are transformed to simulate adiabatic conditions. Since the heat power is a simple function of temperature (Arrhenius' law)
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and a more complex function of conversion, these two types of variable must be taken into account. The temperature dependence is obtained using an Arrhenius diagram which allows extrapolation to lower temperatures (Figure 3). The conversion dependence can be determined by three different methods.

The first method ignores the conversion term and therefore holds primarily for highly energetic decompositions. For these reactions zero order kinetics are a good approximation, i.e. heat release rates are assumed to be independent of conversion. In this case the induction time of the thermal explosion or time to maximum rate under adiabatic conditions (TMRad) can be estimated by the formula published by Townsend and Tou4:

\[ T_{\text{MRad}} = \frac{C_p \times R \times T_0}{q_0 \times E_a} \]

where \( R = \) universal gas constant = 8.31431 J/mol/K; \( T_0 = \) temperature (K); \( q_0 = \) heat power of the reaction at \( T_0 \) (W/kg); \( E_a = \) activation energy (J/mol); \( C_p = \) specific heat of the reaction mixture (J/kg/K).

For the nitro decomposition, which often has an autocatalytic character, the zero order assumption is a conservative approximation when using the highest heat evolution rates, \( q_0 \), observed in the isothermal experiments, i.e. the times calculated by this method are shorter than they would be if the reaction depletion and/or the delayed occurrence of the maximal heat evolution as a function of conversion were considered. The estimate is on the safe side.

The second method developed by Gygax5 uses the geometric similarity of the thermograms recorded at different temperatures (Figure 2). A number of representative points on one curve are interpolated using cubic splines. The temperature dependence of the isothermal curve is described by a single parameter. By changing the set temperature, the curve is stretched in time and compressed in height an equal amount to derive the isothermal curve of a lower temperature. In this way the isothermal heat flow curves can be predicted for any temperature. The adiabatic behaviour of the sample is simulated from this model by a numerical method. The temperature is considered constant for a small increment of conversion and the heat release, based on the polynomial description, is calculated for this increment. Then the temperature increase by the adiabatic temperature rise corresponding to the conversion of the first step is accounted for. This calculation is repeated for the new temperature and so on. This allows a numerical simulation of the adiabatic behaviour.

The third method is more work intensive. A kinetic law is fitted to the thermograms allowing an analytical or a numerical integration of the differential equations by classical methods. The identification of a kinetic law is only possible in rare cases and may also require analytical data.

Any of the three methods delivers TMR as a function of temperature (Table 1).

Use of TMRad in risk analysis. In the case of a cooling breakdown in hydrogenation reactors, the batch is submitted to heat accumulation conditions meaning that even a slow reaction can eventually lead to a thermal runaway. Thus, measures have to be taken which bring the situation under control. Typical measures are emergency cooling, slow pressure release with condensation of the solvent (cooling by evaporation), transfer of the batch to a cooled tank etc. These interventions need a certain time depending on the nature of the measure and the organization of the plant.

It must be ensured that the TMRad is considerably longer than the time needed for the intervention after the cooling breakdown. Thus the maximum temperature allowed for the reaction mass is determined. Usually a temperature leading to a TMRad in 10 to 24 h will be accepted.

Mastering the heat of reaction
The catalytic reduction of aromatic nitro compounds is a very exothermic reaction, but in most cases easy to control. In fact, this multiphase reaction is affected by mass transfer. Hence the reaction speed can be controlled by the amount of catalyst, the hydrogen pressure and the mixing intensity. Changing the stirrer speed or the flow rate in the loop provides easy means to slow down the reaction and thus to reduce or stop the heat flow. In terms of risk analysis the knowledge of the influence of these parameters on the heat release of the reaction will allow definition of safe

Figure 2 Isothermal DSC thermograms at different temperatures

Figure 3 Arrhenius diagram
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Table 1 Example of thermal adiabatic TMR estimations from isothermal DSC experiments

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>195</th>
<th>205</th>
<th>220</th>
<th>230</th>
<th>240</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Calculated</td>
<td>Calculated</td>
<td>Measured</td>
<td>Measured</td>
<td>Measured</td>
<td>Measured</td>
</tr>
<tr>
<td>Heat power (W/kg)</td>
<td>4</td>
<td>8</td>
<td>28</td>
<td>50</td>
<td>115</td>
<td>200</td>
</tr>
<tr>
<td>Isothermal time to maximum rate (h)</td>
<td>50</td>
<td>17</td>
<td>6.5</td>
<td>2.3</td>
<td>1.6</td>
<td>0.3</td>
</tr>
<tr>
<td>TMR\textsubscript{cal} (h) (spline polynomials)</td>
<td>7</td>
<td>3.0</td>
<td>1.2</td>
<td>0.6</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>TMR\textsubscript{cal} (h) (Townsend formula)</td>
<td>1.2</td>
<td>0.6</td>
<td>0.2</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

conditions for the reaction and also investigation of the thermal effects of possible deviations from safe conditions.

Reactions calorimetry provides a means of investigation of reactions under conditions very similar to plant operation\textsuperscript{6,7}. We use a special version of the Mettler reaction calorimeter RC1 with a 1 litre autoclave designed for pressures up to 150 bar and temperatures up to 300°C. This calorimeter is equipped with a high speed turbine agitator and baffles to ensure a good gas dispersion. The hydrogen uptake is monitored via pressure drop in a calibrated reservoir and by flow measurement. The thermal effects of the reaction and its hydrogen uptake are recorded simultaneously. Sample curves are provided in Figures 4 and 5.

These data can be directly used for the design of the plant reactor. The effect of reaction parameters such as concentration of nitro-aromatic, pressure and flow rate of hydrogen, turbulence in the reactor and concentration of catalyst on the kinetics of the reaction and therefore on the heat flow can easily be studied. This technique provides a good way for optimization of the mentioned reaction parameters with respect to the technical possibilities of a given plant reactor or vice versa, and allows the design of a reactor for pre-defined reaction parameters.

For the design of a safe hydrogenation it is also important to know the course of the heat output of the hydrogenation: whether the heat flow is constant (Figure 4) or if it varies with time as in Figure 5. These data are particularly useful in predicting the behaviour of the reactor by loss of cooling even after shutting off the hydrogen supply. The knowledge of the temperature which can be reached after such an event is important for the definition of preventive or corrective measures.

Accumulation of intermediates

Chemical aspects. The catalytic reduction of nitro-aromatic compounds is not, however, a one step reaction. It is well known\textsuperscript{8-10} that this reaction involves a series of different intermediates, among them N-phenylhydroxylamine. This compound disproportionate exothermically\textsuperscript{11,12} and may lead to other side-reactions such as the formation of azo- and azoxybenzene. These reactions are not controlled by the hydrogen mass transfer and therefore cannot be stopped by reducing the turbulence.

An incident due to the accumulation of N-phenylhydroxylamine followed by exothermal disproportionation has been reported\textsuperscript{13}. Therefore, for a complete risk assessment of catalytic reductions of aromatic nitro compounds it is necessary to know if accumulation of intermediates occurs and what the consequences are for the thermal safety of the process. The instability of the intermediates makes the detection of accumulation and the recognition of conditions favourable to accumulation a difficult problem. Therefore we require a method which allows the detection of accumulation of instable intermediates while the hydrogenation is running.

Experimental methods. Different methods all based on calorimetry can be used for this purpose:

* sampling and DSC analysis
* conversion curves from reaction calorimetry
* simulation of cooling failure at intermediate process times

The first method consists of taking samples from an autoclave while the hydrogenation is running. In
the samples, ongoing reactions are instantaneously quenched by cooling and storing under argon before they are analysed by DSC. This method allows a direct measurement of the energy potential of the samples. It enables us to predict runaway courses of the reaction described in the previous section. A set of such thermograms is shown in Figure 6.

The inconvenience of the method is related to the sampling itself. Industrial reduction processes are often run at high concentrations and the aromatic nitro compound is not necessarily dissolved. Thus it is difficult to draw representative samples. The information delivered by the sampling method must be expected to be qualitative only.

The second method is based on the comparison of the chemical and thermal conversion curves. The reduction is performed under the conditions corresponding to plant conditions. The heat flow and the hydrogen uptake are recorded simultaneously. The principle of the method can be explained by looking more closely at the different steps involved in the reduction of aromatic nitro compounds.

The reduction mechanism can be written as follows:

\[ R-\text{NO}_2 + \text{H}_2 \rightarrow R-\text{NO} + \text{H}_2\text{O} \quad (R = \text{Phenyl}) \]

\[ R-\text{NO} + \text{H}_2 \rightarrow R-\text{NHOH} \]

\[ R-\text{NHOH} + \text{H}_2 \rightarrow R-\text{NH}_2 + \text{H}_2\text{O} \]

Considering only the two steps leading to the N-phenylhydroxylamine and assuming that the heat of reaction is mainly due to the heat of formation of water, then it becomes obvious that the hydrogen uptake will be 2/3 of the total, while the heat produced will be roughly half of the total up to the hydroxylamine stage. Thus accumulation of phenylhydroxylamine can be obtained by monitoring the difference between the chemical conversion measured as hydrogen uptake and the thermal conversion measured in the calorimeter.

This observation can be exploited to detect the accumulation at the hydroxylamine step. Sample conversion curves are provided in Figure 7.

The validity of the method has been established experimentally. Nitrobenzene was hydrogenated in the presence of dimethyl-sulfoxide (DMSO) and ammonia in tetrahydrofurane with a 5% Pt/C catalyst. The DMSO is also reduced during the hydrogenation and the sulphur compound obtained poisons the catalyst. Thus the speed of the reduction is affected. In this way, a selective hydrogenation leading to the N-phenylhydroxylamine is obtained. Under these conditions the hydrogenation course shows an interesting thermal behaviour. Two steps of the hydrogenation are distinctly visible in the thermogram obtained by reaction calorimetry (Figure 8). The first step corresponds to the reduction of nitrobenzene to phenylhydroxylamine and runs with a quasi constant heat flow corresponding to overall zero order kinetics. The heat of reaction is 320 kJ/mol nitrobenzene and the hydrogen uptake is 2 mol/mol nitrobenzene. The second step is slower and runs with an exponentially decreasing heat flow corresponding approximately to first order kinetics. The heat of reaction is 225 kJ/mol and the hydrogen uptake is 1 mol/mol nitrobenzene.

The results are summarized in Table 2.

As predicted, the heat of reduction of the nitro
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The calorimeter is heated up with a linear temperature programme while the thermal effects due to side-reaction of the accumulated intermediates are recorded.

The heat flow curve of such an experiment is shown in Figure 9. The advantage of this method is that the sampling problems are avoided and the measured thermal effects are quantitative. For the sake of safety in the laboratory, the method requires good supervision. In practice we use it only after the thermal behaviour of the reaction mass has been roughly explored by sampling and DSC analysis (first method). This allows the determination of an acceptable temperature range for this experiment.

Relevance for risk analysis. In practice we use these methods in combination with each other. The first method provides a qualitative answer to the question of whether accumulation of intermediates occurs or not. With the second method the process time of maximum accumulation can be determined. Then the thermal effects of accumulation at that instant are investigated by the third method.

Additionally, experiments are run under different operating conditions in the reaction calorimeter. The recorded conversion curves allow conclusions on the accumulation of intermediates to be drawn. Typically the effects of catalyst, of pressure, of hydrogen supply (flow limitation), of temperature etc., can be easily investigated.

These data are directly used to define safe operating conditions and to assess the risks related to deviation from safe conditions. Since the measurements of the thermal effects due to accumulation are quantitative it is possible to design tailored preventive measures for the case of cooling failure. The accumulation of

Figure 8 Hydrogenation of nitrobenzene with poisoned catalyst

Table 2 Hydrogenation of nitrobenzene with poisoned catalyst in a reaction calorimeter

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>Heat of reaction</th>
<th>Hydrogen uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>kJ/mol</td>
<td>mol/mol %</td>
</tr>
<tr>
<td>1+2</td>
<td>R-NO₂ → RNHOH</td>
<td>320</td>
<td>2 67</td>
</tr>
<tr>
<td>3</td>
<td>R-NHOH → R-NH₂</td>
<td>225</td>
<td>1 33</td>
</tr>
<tr>
<td>1+2+3</td>
<td>R-NO₂ → R-NH₂</td>
<td>545</td>
<td>3 100</td>
</tr>
</tbody>
</table>

group to the hydroxylamine corresponds to about half (56%) of the heat of reduction of the nitro group to the amine. The hydrogen uptake for the first two steps is, of course, 2/3 of the total.

These measurements confirm the assumptions made above and validate the method. The accumulation of intermediates is indicated by a discrepancy between the chemical and the thermal conversion curves.

This method is also well suited for screening purposes. In addition, important information concerning the heat of reaction and the dynamics of the reaction are delivered. Nevertheless, since the method delivers no information on the course of the runaway reaction, it must be complemented by a further type of experiment.

The effect of a cooling failure in the course of the process can be directly investigated in the reaction calorimeter by shutting off the hydrogen supply. After the hydrogen remaining in the autoclave has been consumed, the reaction stops. In the experiment, the moment of interruption can be chosen such that the reaction terminates at the point of maximum accumulation of unstable intermediates. Afterwards,
intermediates can be reduced or avoided in different ways. Among them are the progressive addition of the aromatic nitro compound, the choice of catalyst, the use of higher temperature, different solvents etc.

Conclusion

The calorimetric methods are powerful tools to investigate the thermal safety of the hydrogenation of nitro-aromatics. The methods presented are useful for the determination of safe conditions, the search for deviations, the assessment of risk and the design of preventive measures.

Different aspects of thermal safety can be investigated by calorimetric methods:

- the thermal stability of the reaction mixtures at the start, during the process and at the end of the desired reaction
- the heat flow of the reaction under different operating conditions
- the detection of accumulation of thermally unstable intermediates in the course of the reaction and its effect on the thermal behaviour of the reaction mass, information which is relevant in the case of a cooling failure.

Since risk analysis in the sense discussed in this paper relates to thermal and kinetic data, it is strongly linked to process design. This opens up the opportunity to integrate economy, quality and safety requirements rather than having these goals oppose each other in a sequential approach. The simultaneous variation of all degrees of freedom in the same optimization procedure always gives a greater chance of finding the optimum solution.

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