

RUNAWAY REACTION HAZARDS IN PROCESSING ORGANIC NITROCOMPOUNDS

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Pure organic nitrocompounds i.e. aromatic or aliphatic nitrocompounds decompose at high temperature exhibiting a large decomposition exotherm. In most cases, the decomposition is violent or explosive. In practical process situations nitrocompounds are mixed with other chemicals or contaminated by impurities which lower their thermal stability. Contaminated nitrocompounds or solutions of nitrocompounds may decompose at much lower temperature than the pure product. Their decomposition is less rapid but remains highly exothermic.

Therefore for practical reasons, the most relevant information in the field of Process Safety is to describe how reactants, solvents, impurities may affect the organic nitrocompounds' thermal stability and in which process situation this may be a hazard.

Keywords : Nitrocompounds, Thermal stability, Runaway reactions.

INTRODUCTION-PURE ORGANIC NITROCOMPOUNDS

Pure organic nitrocompounds, aromatic or aliphatic nitrocompounds, decompose at high temperature. Their decomposition is rapid and highly exothermic. Within a series of aromatic nitrocompounds, the thermal stability and decomposition exotherm are influenced by the type, position and number of substituents (1).

The influence of substituents on the thermal stability of aromatic nitrocompounds may be due to their activation effect on the nitro group through the aromatic ring, or to the substituent's own thermal instability.

The thermal stability of aromatic nitrocompounds may also be reduced by red-ox reactions between the nitro group and the substituents, as suggested by the following example :

An incident occurred during the start up of a batch distillation of 2 nitrobenzaldehyde from a mixture of mononitrobenzaldehyde isomers. The initial temperature of the product mixture was as low as 132°C when the decomposition exotherm was observed. This is close to the decomposition onset temperature of pure 2 nitrobenzaldehyde which is known to exhibit an autocatalytic decomposition phenomenon (2) (3).

The decomposition of pure nitrocompounds is rapid or explosive. This is due to the following factors :

- The decomposition occurs at high temperature (250°C - 350°C) where chemical reactions are fast anyway.
- The heat of decomposition is very high (above 1050 kJ.kg⁻¹). Consequently the thermal acceleration of the decomposition is large, due to a fast increase of the temperature under pseudo adiabatic conditions or in process situations.
- The decomposition activation energy is very high. Consequently the decomposition reaction, once initiated, becomes very fast even for a limited increase in temperature.

The decomposition reaction of nitrocompounds may be autocatalytic i.e. exhibit a chemical acceleration under constant temperature conditions or follow an Arrhenius n-Order rate equation.

Some authors consider that with such a high decomposition activation energy, the decomposition must be autocatalytic. However this is not a good criterion. Some nitrocompounds are known to exhibit an autocatalytic decomposition. Their decomposition exhibits an isothermal induction period phenomenon at temperature just below the decomposition onset temperature under temperature scan conditions (4). This can be shown using a DTA machine.

In the case of organic nitrocompounds, the experimental proof of the decomposition autocatalytic behaviour is difficult to obtain due to the decomposition reaction high apparent activation energy. The isothermal induction period may increase by a large extent for a small decrease in the test isothermal temperature. For practical short duration calorimetric tests, not exceeding a few hours, the temperature range where a chemical acceleration phenomenon can be observed may not exceed 10°C and may remain undetected.

When Process Safety is considered, the isothermal exposure test temperature and duration must be representative of the process conditions. Therefore, test duration may be of several weeks. Monitoring of pressure or gas generation in the test vessel is recommended because the detection of gas generation is more sensitive than the detection of heat production by the sample.

A good example of the above-mentioned behaviour is the experimental investigation of a DNT pipeline explosion by T.L. Bateman *et al* (5).

DNT was contained in a transfer line for 10 days and was probably exposed to temperatures of about 210°C. The transfer line finally exploded in several places. Isothermal exposure tests were performed at temperatures between 150°C and 230°C in a closed vessel. The isothermal induction period for the decomposition gas production was found to be of 31 days at 150°C. This induction period showed linear variation in log scale, as a function of the temperature in reciprocal scale, thus proving the autocatalytic nature of the phenomenon. Traces of Na_2CO_3 are shown to lower the thermal stability of DNT.

A list of organic nitrocompounds exhibiting an autocatalytic decomposition phenomenon is given by Grever (6).

The thermal stability of "pure" organic nitrocompounds may be reduced by traces of impurities from the process and, in DTA tests, by the test cell wall material. For example the kinetics of decomposition of a mixture of nitrocumene isomers measured in DTA under temperature scan conditions, depend on the test cell material : stainless steel, Hastelloy C, titanium, glass. Graphite test cells are known to lower the thermal stability of organic nitrocompounds in DTA tests. Some laboratories use gold plated cells to overcome this problem.

THERMAL STABILITY OF ORGANIC NITROCOMPOUNDS IN THE PRESENCE OF OTHER CHEMICALS

In nitration process

Organic nitrocompounds are obtained in nitration processes where nitric acid is reacted with organic reactants in semi-batch or continuous operations. Some nitrations are made in concentrated nitric acid. However, in most industrial processes, the organic reactant is dispersed in sulfuric acid and nitric acid or mixed acid is injected slowly in the reaction mixture as controlling reactant.

Sulfuric acid is used to provide some dilution of the reactants and products, control the reaction mixture temperature, remove the water produced by the reaction and provide some solubility of the reactants necessary for the reaction to take place.

In some cases, solvents are added to the reaction mixture, to allow the organic reactants and products to remain in the liquid phase at the low process temperature. Typical nitration solvents are 1,2 Dichloroethane, dichloromethane, acetic acid, benzene, toluene, etc...

The thermal stability of the final reaction mixture is lower than that of the pure nitrocompounds.

The onset temperature of the decomposition exotherm of nitration products in spent 70 % sulfuric acid is of the order of 200°C. Decomposition gases are produced at a much lower temperature.

The final reaction mixture in concentrated nitric acid would decompose at much lower temperature, depending on possible subsequent nitration of the wanted nitrocompounds.

The contamination of nitrocompounds with concentrated sulfuric acid lowers their decomposition onset temperature by a large extent, depending on the ratio of sulfuric acid to nitrocompound. An example of this effect is shown for a nitrochloro methyl ester aromatic derivative using DTA tests under temperature scan conditions on fig.1.

An example of the influence of sulfuric acid and nitric acid on nitrocompounds thermal stability is the following.

A 4,5 m length of 38 mm nominal bore stainless steel pipe was completely destroyed by the thermal explosion of crude dinitrotoluene. During nitration, dinitrotoluene extracts nitric acid. Some crude dinitrotoluene was enclosed in a pipe, at a temperature of about 130°C. The explosion occurred after three and a half hours, although pure dinitrotoluene is stable until 250°C. The nitric acid concentration and the presence of free sulphuric acid were sufficient to depress the stability of dinitrotoluene, leading to an explosion (7).

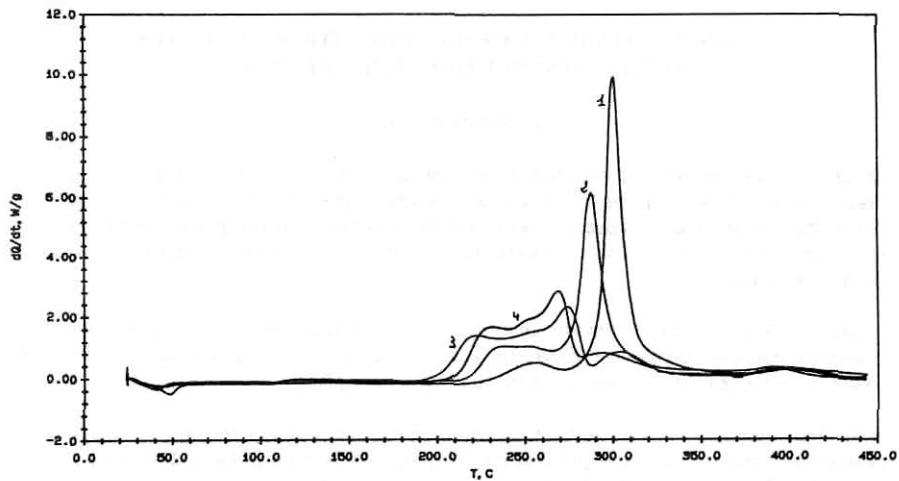


Fig. 1: DTA thermograms under 5°C/min temperature scan conditions of a nitrochloro methylester aromatic derivative with different proportions of 95 % sulfuric acid : 1 = 4,6 % wt - 2 = 10 % wt - 3 = 20 % wt - 4 = 27 % wt. Obtained in Setaram DSC 111 - Stainless steel closed cell. Heat-flux refers to unit sample mass.

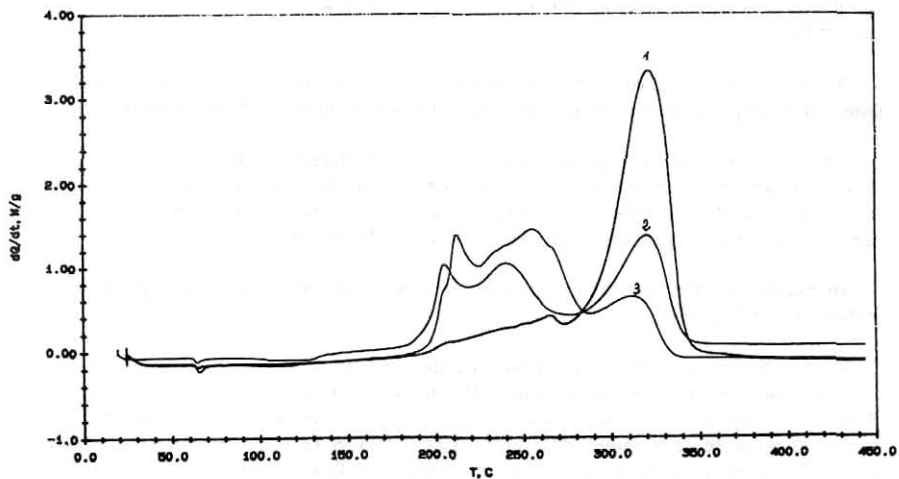


Fig. 2: DTA thermograms under 5°C/min temperature scan conditions of a nitrocumene isomer mixture with different proportions of pure caustic soda : 1 = 5 % wt - 2 = 10 % wt - 3 = 15 % wt. Obtained in Setaram DSC 111 - Stainless steel closed cell. Heat-flux refers to unit sample mass.

Washing of nitration products

After the nitration step, organic nitrocompounds are separated from the acid phase and washed to remove the acids and water soluble impurities. This operation must be performed carefully to obtain uncontaminated stable nitrocompounds. The washing and decantation process should include the following steps :

- Separation of the acid phase from the organic phase.
- Washing of the organic phase with water to remove as well as possible the acids and lower the residual concentration in sulfuric and nitric ions.
- Washing of the organic phase with diluted caustic soda to neutralise mineral acidity and allow the salification of oxidation products such as nitrophenols or organic nitro acids which sodium salts are soluble in water.
- Washing of the organic phase with water to remove the sodium salts formed and excess caustic soda.
- Acidification, in some instances, with clean acid to remove residual sodium salts which would be detrimental to thermal stability.

Maloperation in the washing/decantation steps may cause contamination of the nitrocompounds with caustic soda and salts such as sodium sulfate, sodium nitrate, other metal salts, nitrophenols, nitrophenates, which may decrease the wanted nitrocompounds thermal stability.

Caustic soda

Contamination of nitrocompounds with caustic soda reduces their thermal stability. As an example, fig.2 shows the influence of various amounts of caustic soda on the thermal stability of a nitrocumene isomer mixture, measured in DTA under temperature scan conditions.

Sodium sulfate

Sodium sulfate has limited influence on the thermal stability of organic nitrocompounds.

Metallic nitrates

Sodium nitrate and nitrates of other metal impurities may reduce thermal stability by initiating nitric oxidation of organics above 140°C.

Purification of organic nitrocompounds

The manufacture of nitrocompounds may require purification steps i.e. drying, separation of lights and heavies, isomeric distillation and crystallization.

Elimination of water by evaporation may concentrate the water soluble impurities in the organic phase.

Distillation steps requiring high temperature make the whole process critical due to possible contamination.

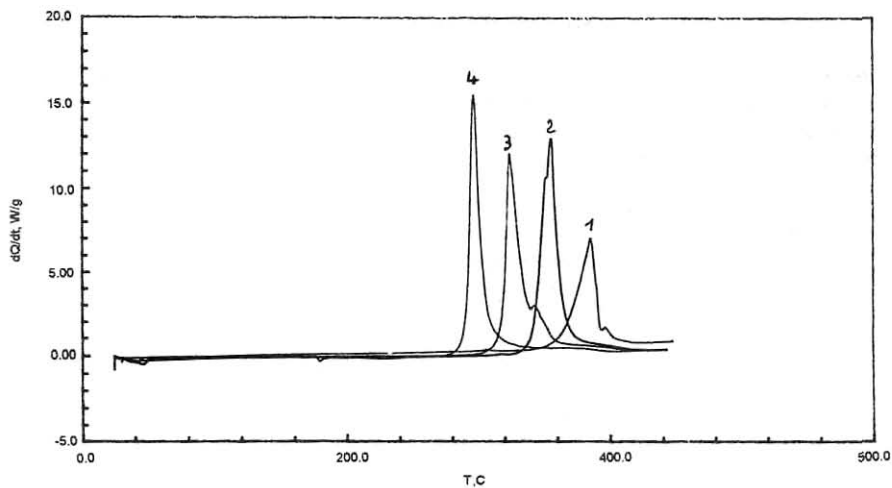


Fig. 3 : DTA thermograms under 5°C/min. temperature scan conditions of nitrochloromethylester aromatic derivative with different proportions of Ca Cl₂ : 1 = pure - 2 = 1,49 % wt - 3 = 4,84 % wt - 4 = 13 % wt. Obtained in Setaram DSC 111 - Stainless steel closed cell. Heat-flux refers to unit sample mass.

The influence of metal ions on nitrocompounds thermal stability is often investigated using metal chlorides (8) (9) for practical reasons. Metal chlorides are water soluble and are easily dispersed in organic liquids.

In true process situations chlorides may contaminate the product due to brine ingress (NaCl, CaCl₂). Corrosion may provide the other metal chlorides. Dehydrochlorination of aromatic chloronitrocompounds under moderate or high temperature may also cause metal chloride contamination. As shown in ref. (8) (9), metal chlorides influence to a large extent the organic nitrocompounds thermal stability. As an example, fig.3 shows the influence of calcium chloride on the thermal stability of a nitro chloro methyl ester aromatic derivative, studied in DTA under temperature scan conditions.

The screening of thermal stability of contaminated organic nitrocompounds using DTA in temperature scan mode, does not imply that the thermal decomposition obtained follows Arrhenius n-order kinetics. In some instances, the decomposition may be autocatalytic and could be initiated at lower temperature after an isothermal induction period.

Formation and separation of heavies

In refining steps, the formation and separation of heavies of nitro organic compounds may be a hazard. Unless the heavies are well identified products and remain liquid, in most instances the heavies are contaminated nitrated tars and solids because the process is not clean.

The processing of these heavies at high temperature is a hazard. The heavies should not be allowed to accumulate and a process hazard review should be prompted on the nitration and washing steps to reduce or suppress heavies production. Accidental decomposition of heavies are frequently reported (10).

FURTHER PROCESSING OF NITROCOMPOUNDS

The production of nitro compounds is often not the process final step. Organic nitro compounds are further processed in various operations such as :

- hydrogenation
- amination under pressure of chloro nitrocompounds
- hydrolysis of chloro nitrocompounds
- substitution reaction in alkaline conditions.

Hydrogenation

Organic nitrocompounds are hydrogenated to produce amines. In hydrogenation processes organic nitrocompounds react with hydrogenation catalysts, precious metals or Raney nickel, under hydrogen pressure. The process temperature range, 80°C - 200°C, is the temperature at which the nitrocompounds react in the presence of the catalyst i.e. the thermal stability of the nitrocompound is reduced to the process temperature. Contamination of nitrocompounds with hydrogen containing catalyst may cause accidents because the heat of hydrogenation by the active catalyst is very large (11) (12) (13).

In addition, as hydrogenation proceeds in normal process conditions, unstable intermediates are formed and can accumulate, which are phenyl nitroso and phenyl hydroxylamine derivatives if precious metals catalyst is used, and azo derivatives if Raney Nickel is used (13).

Tong and al. (14) described an incident during the hydrogenation of 3,4 dichloronitrobenzene (3,4 DCNB) in an agitated autoclave. During this operation the unstable intermediate 3,4 dichlorophenylhydroxylamine (DCPHA) could accumulate due to the reactant contamination by impurities. The subsequent decomposition of the accumulated intermediate caused the reactor explosion. The intermediate DCPHA mentioned in (14) implies that the catalyst used was a precious metal which would be sensitive to reactant impurities. This accident was further discussed by Mac Nab (13), Stoessel (12) and Grewer (15).

Hydrolysis

The hydrolysis of nitro halo derivatives using sodium hydroxide, potassium hydroxide, or any alkaline reactant is subject to frequent accidents due to the instability of the nitro group under alkaline conditions. In alkaline conditions, unstable nitrophenols and nitrophenates are obtained which further decompose. The decomposition of nitrophenates exhibits autocatalytic behaviour. Explosion may occur when the reactor is cooled down, thus allowing nitrophenate to crystallize on the vessel wall.

This type of incident occurred in a process where parachloronitrobenzene is hydrolysed with 50 % caustic soda, in a batch operation, to produce paranitrophenol. As the conversion ratio of the wanted reaction was low, the operator thought that the correct amount of caustic soda had not been properly introduced and decided to introduce a second charge of caustic soda in the reaction vessel. After reaction completion, the reaction mixture was cooled down.

The reactor exploded during cooling. The cause of the explosion was the crystallisation of sodium paranitrophenate on the reactor wall. Solid sodium paranitrophenate exhibits an autocatalytic decomposition. The unstable aci form of paranitrophenate is red and can be easily recognized. The aci form of nitrophenates is also possible for the ortho derivative but not for the meta derivative which should be more stable.

The occurrence of a condensed phase explosion, during reactor cooling, when aromatic chloronitro derivatives and caustic soda or potassium hydroxide are present, should lead to consider nitrophenate formation.

The same circumstances are known in the manufacture of nitrodiphenylethers if an excess of caustic soda or potassium hydroxide is introduced.

The possible explosion initiation by the agitator impact on the solid deposit or by autocatalysis is controversial.

Hydrolysis may not be the intended reaction. Any reaction involving organic nitrocompounds and alkaline reactants such as NaOH, KOH, may lead to unstable final reaction mixture. Any process deviation may initiate the final reaction mixture decomposition.

An example of such a situation is the accident in Griesheim, 1993, in a semi-batch process to manufacture orthonitroanisole by reacting methanolic caustic soda on orthochloronitrobenzene, where caustic soda was the controlling reactant. Due to the absence of agitation, caustic soda could accumulate and further react when agitation was restarted, initiating the decomposition of the final reaction mixture (16). The same accident in the same process had already occurred in Japan in 1973 (17).

Amination

The pressure amination of 4 chloronitrobenzene is known to have experienced numerous explosions (18) (19). This can be related to the poor thermal stability of the final reaction mixture due to the excess of ammonia in the final reaction mixture.

In this process, 4 chloronitrobenzene is reacted with 28 % ammonia solution in a batch operation, to produce 4 nitroaniline (18). The heat of reaction of the wanted reaction is high enough to initiate the final reaction mixture decomposition. The wanted reaction exotherm onset temperature is approximately 160°C. However, the temperature versus time profile of the process is such that the conversion ratio is high enough, when the reaction is allowed to proceed in adiabatic mode, to prevent the wanted reaction final temperature to reach the final reaction mixture decomposition onset temperature. Many process deviations may cause problems.

G.C. Vincent (19) described an accidental explosion of such a batch which occurred at Sauget, Illinois, in 1969. In this accident, the operators decided to inject additional ammonia when the initial reaction mixture had reached 160°C, because the autoclave pressure was too low. Then the reaction mixture conversion ratio may have been low enough to allow the wanted reaction final temperature to initiate the final reaction mixture decomposition. There was possibly too high a charge of ammonia.

A double charge of 4 chloronitrobenzene is known to have caused incidents. This can be shown using a VSP experiment where the process conditions are reproduced with the process deviation considered. *Normal process conditions are "safe"*.

Another example of aromatic nitrocompound thermal instability in alkaline conditions is the following : the preparation of a potassium hydroxide solution in methanol, followed by the introduction of nitrobenzene in a 6000 litre reactor, led to an explosion (20).

A review on decomposition reactions involving organic nitrocompounds in alkaline conditions is given by D. Gickel (21).

Decomposition of nitrocompounds in the presence of metal halides

As discussed above, metal halides lower the thermal stability of aromatic nitrocompounds.

AlCl_3 is used in Friedel-Crafts reactions in conjunction with nitrobenzene as solvent. Nitrobenzene is also a good solvent to clean AlCl_3 deposits. Several accidents occurred due to the decomposition of AlCl_3 - nitrobenzene mixtures (18) (22).

Recovery of nitrocompounds from solutions

The batch concentration of nitrocompound + solvent solutions may be a critical operation, specially in second crop recovery. Several examples of explosive decomposition are known during concentration of impure nitrocompound solutions. Impurities may lower the solution thermal stability. A further unfavourable circumstance seems to be the decreasing level of the liquid solution in batch evaporation. Projection of solution on the vessel wall by the agitator may allow concentrated nitrocompounds to decompose on the hot unwetted reactor wall. The presence of active carbon used to decolourise impure product may also contribute to the decomposition initiation. As mentioned above, active carbon or graphite lowers the thermal stability of organic nitrocompounds. The concentration of impurities on active carbon may also contribute to this effect.

CONCLUSION

A good knowledge of the factors influencing organic nitrocompounds thermal stability is essential in preventing accidents. The identification of dangerous process situations based on general considerations of hazard factors such as those described in this paper helps to make the decision of making Process Hazard Reviews and investigating thermal stability and runaway reaction hazard on a detailed experimental basis.

A review of accidents described in the literature may help in understanding which type of process is dangerous, where high frequency of accidents is observed.

In the field of runaway reaction prevention and mitigation, the design of safe processes must be considered first.

It is often considered that the decomposition of nitrocompounds is so violent that protection by venting is not possible. This may not be true for contaminated nitrocompounds whose decomposition is less rapid.

Contaminated nitrocompound decompositions are often gassy reactions producing foaming viscous heavies which can possibly be vented. The problem is again to guess where decomposition will occur.

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