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Runaway Reaction Hazards in Processing Organic Nitro Compounds

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Abstract:
Pure organic nitro compounds, i.e., aromatic or aliphatic nitro compounds, decompose at high temperatures, exhibiting large decomposition exotherms. In most cases, the decomposition is violent or explosive. In practical process situations, nitro compounds are mixed with other chemicals or contaminated by impurities which lower their thermal stability. Contaminated nitro compounds or solutions of nitro compounds may decompose at much lower temperatures than the pure products. 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, and impurities may affect the organic nitro compounds' thermal stability and in which process situations this may be a hazard.

Introduction: Pure Organic Nitro Compounds

Pure organic nitro compounds, i.e., aromatic or aliphatic nitro compounds, decompose at high temperatures. Their decomposition is rapid and highly exothermic. Within a series of aromatic nitro compounds, 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 nitro compounds may have different causes: (1) an activation effect of the substituent on the nitro group through the aromatic ring; (2) the substituent's own thermal instability; (3) intramolecular redox reactions between the nitro group and the substituents as suggested by the thermal instability of 2-nitrobenzaldehyde; (4) intermolecular redox reactions or condensation reactions; (5) the instability of alkaline nitro compounds. Common examples of such instability are sodium or potassium nitrophenates exhibiting shock sensitivity and autocatalytic decomposition.

The thermal instability of 2-nitrobenzaldehyde is mentioned in the literature:[2,3] An incident occurred during the startup 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.[4]

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

(1) The decomposition occurs at high temperatures (250−350 °C), where chemical reactions are fast anyway.

(2) The heat of decomposition is very high (above 1050 $kJ \cdot kg^{-1}$). Consequently the thermal acceleration of the decomposition is large, due to a fast increase of the temperature under pseudoadiabatic conditions or in process situations.

(3) The decomposition activation energy is very high. Consequently the decomposition reaction, once initiated, becomes very fast even for a limited increase in temperature.

(4) The decomposition may exhibit a chemical acceleration phenomenon.

The decomposition reaction of nitro compounds 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 nitro compounds are known to exhibit an autocatalytic decomposition. For such compounds, the decomposition exhibits an isothermal induction period phenomenon at a temperature just below the decomposition onset temperature under temperature scan conditions.[5] This can be shown using a DTA apparatus.

In the case of organic nitro compounds, experimental proof of the decomposition autocatalytic behaviour is difficult to obtain due to the decomposition reactions high apparent activation energy.

The isothermal induction period may increase to 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, the test duration may be 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.

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(1) Grewer, Th. Int. Symp. Loss Prev. Saf. Promot. Process Ind. **1978**, No. 1, III-105−113.

(2) Incident during vacuum distillation of nitrobenzaldehyde. *IChemE Loss Prev. Bull.* **1989**, *87*, 27−29.

(3) Urben, P. G. *I.ChemE Loss Prev. Bull.* **1989**, *87*, 34.

(4) Grewer, Th. *Thermal Hazards of Chemical Reactions*; Industrial Safety Series, Vol. 4; Elsevier: Amsterdam, p 210.

(5) Gustin, J. L. Assessment of Runaway Reaction Hazards using the experimental methods of the Process Safety Laboratories. *International Symposium on Runaway Reactions and Pressure Relief Design, Boston, MA, Aug 2−4, 1995*; AIChE: New York, 1995; pp 150−185.

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A good example of the above-mentioned behaviour is the experimental investigation of a dinitrotoluene pipeline explosion by T. L. Bateman et al.[6]

Dinitrotoluene 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 and 230 °C in a closed vessel. The isothermal induction period for the production of decomposition gas was found to be 31 days at 150 °C. This induction period showed a 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 dinitrotoluene.

A list of organic nitro compounds exhibiting an autocatalytic decomposition phenomenon is given by Grewer.[7]

The thermal stability of “pure” organic nitro compounds 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 using 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 nitro compounds in DTA tests. Some laboratories use gold-plated cells to overcome this problem. However, gold may also present a wall effect with organic nitro compounds. The choice of the test cell wall material should be made to best represent the plant operating conditions.

Thermal Stability of Organic Nitro Compounds in the Presence of Other Chemicals

In Nitration Processes. Organic nitro compounds are obtained in nitration processes where nitric acid is reacted with organic reactants in semibatch 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 into the reaction mixture as controlling reactant. The reaction mixture consists of two liquid phases: an acid phase and an organic phase.

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, and it has some catalytic effect.

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, help the separation of the acid and organic phases after the reaction, lower the organic nitro compounds solubility in the acid phase, and help to recover the desired product. Typical nitration solvents are 1,2-dichloroethane, dichloromethane, acetic acid, benzene, and toluene.

The acid phase contains sulfuric acid, excess nitric acid if any, and the soluble concentration of organic reactants and products in the acid phase.

The organic phase contains the organic nitro compounds, the solvent if any, and the soluble concentration of nitric acid and sulfuric acid in the organic phase.

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

The onset temperature of the decomposition exotherm of nitration products in spent 70% sulfuric acid, measured using DTA under 5 °C/min temperature scan conditions, is of the order of 200 °C in the absence of excess nitric acid. Decomposition gases are produced at a much lower temperature.

The final reaction mixture in concentrated nitric acid or in the presence of excess nitric acid would decompose at a much lower temperature, depending on possible subsequent nitration of the desired nitro compounds.

The presence of an organic solvent and concentrated nitric acid in the nitration reaction mixture allows possible secondary redox reactions between the solvent and nitric acid.

Mixtures of concentrated nitric acid and organic solvents used in nitration processes or organic nitro derivatives may present a detonation hazard in the condensed phase. This was shown by Kurbangalina,[8] Dubar and Calzia,[9] Vidal.[10] See also Gustin[11] and Grewer.[12]

The hazardous process deviations in nitration processes are (1) the loss of reactor cooling capacity causing the reaction mixture temperature rise, possible formation of unstable polynitro derivatives, reaction of the accumulated quantity of nitric acid, if any, and possible nitration reaction mixture decomposition; (2) the loss of agitation causing reactant accumulation, i.e., unreacted nitric acid (in most cases, the organic reactant and unreacted nitric acid are in two separate liquid phases; to restart agitation under such conditions is a critical operation); the loss of agitation causes also a loss of the reactor cooling capacity; (3) excess nitric acid or mixed acid due to wrong reactant feed rates, causing possible polynitro derivative formation and unreacted nitric acid accumulation in the reaction mixture (high concentrations of nitric acid in spent sulfuric acid may be obtained; this may be a hazard if spent acid is recycled in the nitration process); (4) too high a rate of nitric or mixed acid feed with respect to the reactor cooling capacity; (5) back-flow of organic phase in the nitric or mixed acid feed pipe; (6) nitration reaction occurring outside the reactor, in pipes or process vents; (7) back-flow of acid phase in the organic reactant feed pipe; (8) organic phase or acid phase enclosed

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(6) Bateman, T. L.; Small, F. H.; Snyder, G. E. Dinitrotoluene Pipeline Explosion. *AIChE CEP Loss Prev.* **1974**, *8*, 117−122.

(7) See ref 4.

(8) Kurbangalina, R. K. The detonating power of liquid explosive mixtures based on nitric acid. *Zh. Prikl. Khim.* **1959**, *32*, 1467−1470.

(9) Dubar, J.; Calzia, J. Propriétés explosives des mélanges d’acide nitrique, anhydride acetique et eau (Explosive properties of mixtures of nitric acid, acetic anhydride and water). *C. R. Seances Acad. Sci.* **1968**, *266*, pp 1114−1116.

(10) Vidal, P. Contribution à l’étude des conditions d’extinction de la détonation dans les mélanges liquides à base d’acide nitrique (Study of detonation quenching in liquid mixtures containing nitric acid). Thesis dissertation, Université de Poitiers, France, ENSMA, April 25, 1990.

(11) Gustin, J. L.; Vidal, P. Runaway reaction and detonation hazard in the manufacture of adipic acid. *Thermochim. Acta* **1993**, *225*, 223−238.

(12) Grewer, Th. *Thermal Hazards of Chemical Reactions*; Industrial Safety Series, Vol. 4; Elsevier: Amsterdam, 1994; pp 173−175.

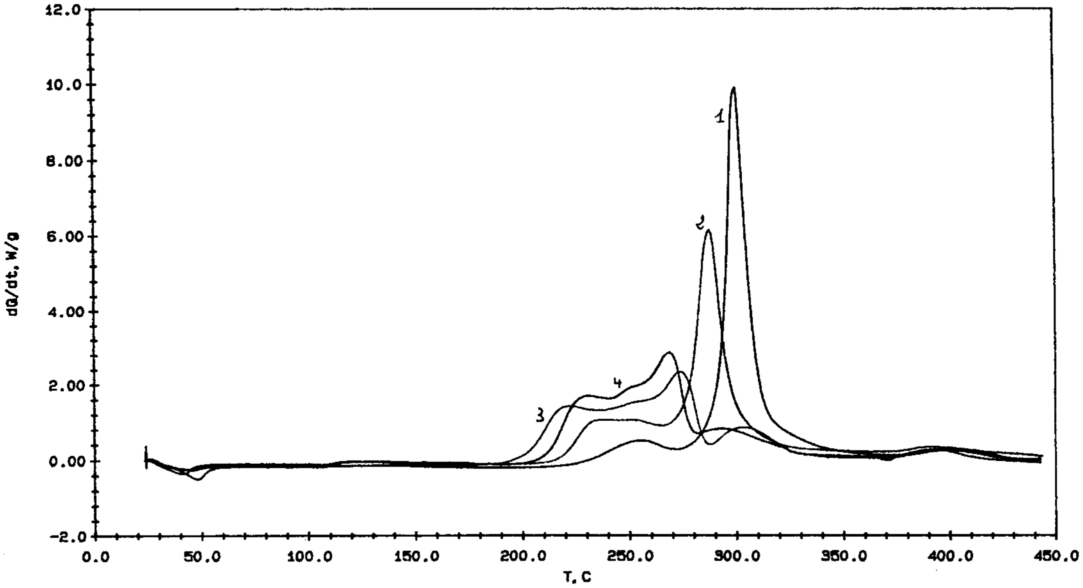

Figure 1. **DTA thermograms, under 5 °C/min temperature scan conditions, of a nitro chloro methyl ester aromatic derivative with different proportions of 95% sulfuric acid: 1 = 4.6 wt %; 2 = 10 wt %; 3 = 20 wt %; 4 = 27 wt %. Obtained in Setaram DSC 111, stainless steel closed cell. Heat flux refers to unit sample mass.**

in traced pipes; (9) excess residence time of the reaction mixture in the reactor when the process is stopped, allowing self-heating of the reaction mixture or possible autocatalytic decomposition.

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

An example of the influence of sulfuric acid and nitric acid on the thermal stability of nitro compounds 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 3.5 h, although pure dinitrotoluene is stable until 250 °C. The nitric acid concentration and the presence of free sulfuric acid were sufficient to depress the thermal stability of dinitrotoluene, leading to an explosion.[13]

Washing of Nitration Products. After the nitration step, organic nitro compounds 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 nitro compounds. The washing and decantation process should include the following steps: (1) separation of the acid phase from the organic phase; (2) washing of the organic phase with water to remove the acids as much as possible and lower the residual concentration in sulfuric and nitric ions; (3) washing of the organic phase with diluted caustic soda to neutralize mineral acidity and allow the salification of oxidation products such as nitrophenols or organic nitro acids whose sodium salts are soluble in water; (4) washing of the organic phase with water to remove the sodium salts formed and excess caustic soda; (5) acidification, in some instances, with clean acid to remove residual sodium salts which would be detrimental to thermal stability.

If the organic phase is processed in further operations such as drying by water evaporation, solvent removal by evaporation, purification or isomeric distillation, or separation of heavies or detarring, the washing and decantation process becomes critical due to the possible decomposition of contaminated nitro compounds under high-temperature conditions.

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

Other impurities such as metal chlorides (NaCl, $CaCl_2$) may be introduced by brine intrusion if brine is used as a cooling fluid.

Drying may concentrate inorganic impurities in the organic phase and lower its thermal stability.

Dehydrochlorination of chloro nitro compounds at medium or high temperature may contribute to metal chloride contamination of the organic phase.

The formation of heavies, polynitro derivatives, nitro polymers, and oxidation products, which are not removed by the washing and decantation process, may also lower organic nitro compounds thermal stability.

Simplifications in the organic phase washing/decantation process may lead to good results but with a lower reliability for contaminant removal. For example, if the first washing of the organic phase with water is omitted, concentrated caustic soda must be used for the neutralization of inorganic acidity. This makes the elimination of excess caustic soda

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(13) Explosion in a dinitrotoluene pipeline. *IChemE Loss Prev. Bull.* **1989**, *88*, 13−16.

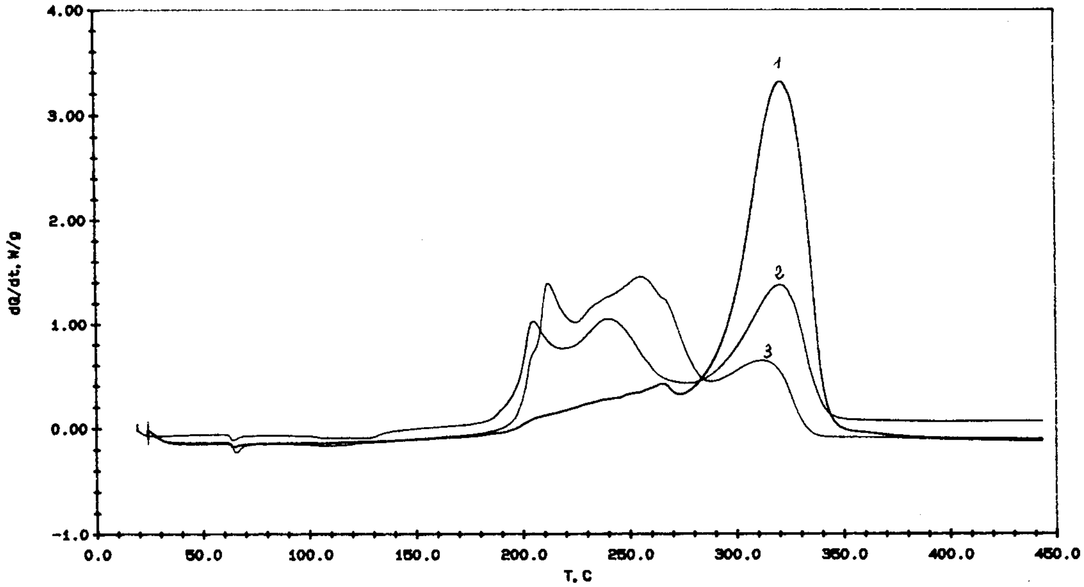

Figure 2. **DTA thermograms, under 5 °C/min temperature scan conditions, of a nitrocumene isomer mixture with different proportions of pure caustic soda: 1 = 5 wt %; 2 = 10 wt %; 3 = 15 wt %. Obtained in Setaram DSC 111, stainless steel closed cell. Heat flux refers to unit sample mass.**

and other salts more difficult by subsequent washing with water.

This simplified washing process is more expensive and less reliable than the recommended process.

The most dangerous simplification of the washing process is to omit alkaline washing, which would not allow proper elimination of salts and oxidation products from the organic phase.

The influence of possible contaminants on the organic nitro compounds' thermal stability is as follows.

Caustic Soda. Contamination of nitro compounds with caustic soda reduces their thermal stability. As an example, Figure 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. In these DTA thermograms, obtained under 5 °C/min temperature scan conditions, the decomposition exotherm of the nitrocumene isomer mixture is shifted toward lower temperature with increased caustic soda concentration in the sample.

Sodium Sulfate. Sodium sulfate has a limited influence on the thermal stability of organic nitro compounds.

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

Metallic Chlorides. The influence of metal ions on the thermal stability of nitro compounds is often investigated using metal chlorides[14,15] for practical reasons. Metal chlorides are water soluble and are easily dispersed in organic liquids.

As shown in refs 14 and 15, metal chlorides influence the thermal stability of organic nitro compounds to a large extent. As an example, Figure 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 nitro compounds using DTA in the temperature scan mode is used to compare the sample thermal stability on a standard basis.

This does not imply that the thermal decomposition obtained follows Arrhenius *n*-order kinetics. In some instances, the decomposition may be autocatalytic, i.e., may present a chemical acceleration phenomenon and could be initiated at a 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 they are contaminated nitrated tars and solids because the process is not clean.

The processing of these heavies at high temperatures 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 the production of heavies. Accidental decomposition of heavies is frequently reported.[16]

Further Processing of Nitro Compounds

The production of nitro compounds is often not the process final step. Organic nitro compounds are further processed in various operations such as (1) hydrogenation, (2) hydrolysis of chloro nitro compounds, (3) condensation reaction to produce diphenyl ethers, (4) substitution reaction under alkaline conditions, (5) pressure amination of chloro nitro compounds, (6) Friedel−Crafts reaction, and (7) recovery of nitro compounds from solutions by solvent evaporation.

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(14) Grewer, Th.; Klais, O. *Exotherme Zersetzung, Schriftenreihe "Humanisierung des Arbeitslebens" Band 84*; VDI-Verlag: Düsseldorf, 1988.

(15) Grewer, Th.; Rogers, R. L. Exothermic secondary reactions. *Thermochim. Acta,* **1993**, *225,* 289−301.

(16) The fire at Hickson and Welch Ltd, Sept 21, 1992, HSE books, 1994.

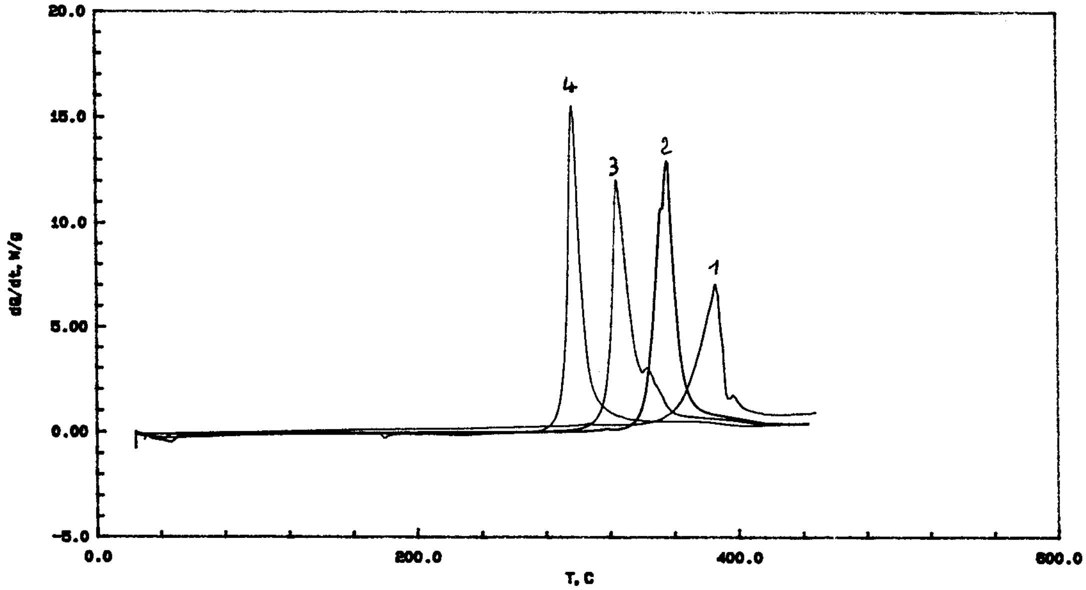

Figure 3. **DTA thermograms, under 5 °C/min temperature scan conditions, of a nitro chloro methyl ester aromatic derivative with different proportions of $CaCl_2$: 1 = pure; 2 = 1.49 wt %; 3 = 4.84 wt %; 4 = 13 wt %. Obtained in Setaram DSC 111, stainless steel closed cell. Heat flux refers to unit sample mass.**

Hydrogenation. Organic nitro compounds are hydrogenated to produce amines. In hydrogenation processes organic nitro compounds react with hydrogenation catalysts, carbon-supported precious metals or Raney nickel, under hydrogen pressure ranging from a few bars to a few hundred bars.

The process temperature range, 80−200 °C, is the temperature at which the nitro compounds reacts in the presence of the catalyst, i.e., the thermal stability of the nitro compounds is reduced to the process temperature.

Contamination of nitro compounds with hydrogen containing catalyst may cause accidents because the heat of hydrogenation by the active catalyst, 525 kJ/mol, is very large.[17−19]

In addition, as hydrogenation proceeds under normal process conditions, unstable intermediates are formed and can accumulate, which are phenyl nitroso and phenyl hydroxylamine derivatives if precious metal catalysts are used, azo and azoxy derivatives if Raney nickel is used.[19]

Tong et al.[20] 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 reactant contamination by nitrate ion impurities. The subsequent decomposition of the accumulated intermediate caused the reactor explosion. The intermediate DCPHA mentioned in ref 20 implies that the catalyst used was a precious metal which would be sensitive to reactant impurities. This accident was further discussed by Macnab,[19] Stoessel,[18] and Grewer.[21]

The main causes of significant unstable intermediate accumulation in hydrogenation processes are (1) wrong choice of catalyst, (2) catalyst being killed by impurities (the most active impurities are (a) metal salts and metal nitrates, (b) sulfur-containing compounds, (c) the wrong lubrication oil, and (d) carbon monoxide in hydrogen), (3) too low a concentration of catalyst, (4) too low a hydrogen feed rate or hydrogen feed interruption, and (5) not enough agitation.

The formation of azo and azoxy derivatives may cause an increase of the reaction mixture viscosity, lowering the reactor cooling capacity.

When the hydrogenation reaction is fast, the probability of unstable intermediate accumulation is low.

If the hydrogenation reaction exhibits an unexpected slow rate, the unstable intermediate accumulation hazard is high and one should immediately investigate the causes of the abnormal situation.

Figure 4 shows the DTA thermogram of hydrogenation reaction mixtures of a nitrocumene isomer mixture. In this example, the small exotherm observed at low temperature, below 100 °C, shows that only limited unstable intermediate accumulation occurs, due to good hydrogenation conditions. The principal exotherm obtained at high temperature decreases with the hydrogenation conversion ratio, showing the absence of interaction between the amine and the nitro groups.

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. Under 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

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(17) David, D. J. *Anal. Chem.* **1965**, *37* (1), 82−85.

(18) Stoessel, F. 6th International Symposium Loss Prevention, Oslo, 1989; Paper 77.

(19) Macnab, J. I. *IChemE Symp. Ser.* **1981**, No. 68.

(20) Tong, W. R.; Seagrave, R. L.; Wiederhorn, R. *AIChE Loss Prev.* **1977**, *11*, 71−75.

(21) Grewer, Th. *Thermal hazards of chemical reactions*; Industrial Safety Series, Vol. 4; Elsevier: Amsterdam, 1994; pp 310−312.

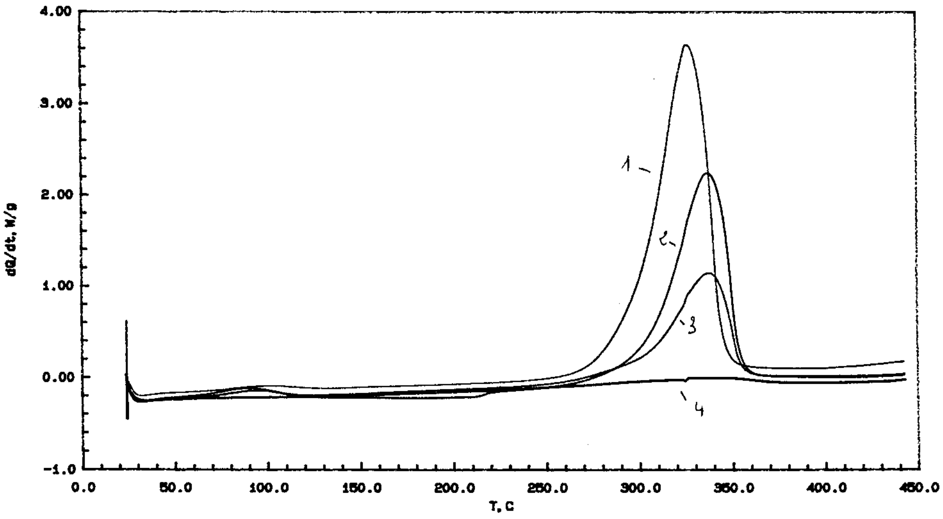
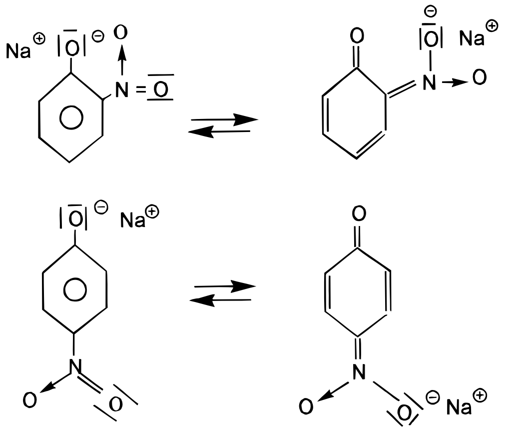


Figure 4. **DTA thermograms, under 5 °C/min temperature scan conditions, of hydrogenation reaction mixtures of a nitrocumene isomer mixture. Thermal stability as a function of residual nitro derivative concentration: 1 = 86.5 wt %; 2 = 56 wt %; 3 = 25.5 wt %; 4 = <100 ppm nitro compound. Note the low unstable intermediate accumulation. Stainless steel closed cell. Heat flux refers to unit sample mass.**

Scheme 1



down, thus allowing nitrophenate to crystallize on the vessel wall.

This type of incident occurred in a process where *p*-chloronitrobenzene was hydrolyzed with 50% caustic soda, in a batch operation, to produce *p*-nitrophenol. 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 into the reaction vessel. After reaction completion, the reaction mixture was cooled down. The reactor exploded during cooling.

The cause of the explosion was the crystallization of sodium *p*-nitrophenate on the reactor wall. Solid sodium *p*-nitrophenate 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. See Scheme 1.

The occurrence of a condensed-phase explosion, during reactor cooling, when aromatic chloro nitro derivatives and caustic soda or potassium hydroxide are present, strongly suggests nitrophenate formation.

The same circumstances are known in the manufacture of nitro diphenyl ethers 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.

Substitution Reaction under Alkaline Conditions. Hydrolysis may not be the intended reaction. Any reaction involving organic nitro compounds and alkaline reactants such as NaOH and KOH may lead to an unstable final reaction mixture. Any process deviation may initiate decomposition of the final reaction mixture.

An example of such a situation is the accident in Griesheim, 1993, in a semibatch process to manufacture *o*-nitroanisole by reacting methanolic caustic soda with *o*-chloronitrobenzene, where caustic soda was the controlling reactant. Due to the absence of agitation, unreacted caustic soda could accumulate in the reaction mixture where two separate liquid phases were present, one containing *o*-chloronitrobenzene, the other methanolic caustic soda. When agitation was restarted, the reactants present reacted at too high a temperature, initiating decomposition of the final reaction mixture.[22]

The same accident in the same process had already occurred in Japan in 1973.[23] In this accident, caustic soda was charged to the reactor, and *o*-chloronitrobenzene was the controlling reactant. The other circumstances are similar to those of the Griesheim 1993 accident.

Pressure Amination. The pressure amination of 4-chloronitrobenzene is known to have experienced numerous explosions.[24,25] 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.

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(22) Klais, O. Seminar on Safety of Runaway Reactions, Frankfurt, Nov 7−8, 1994.

(23) Sumitomo Chemical Co Ltd. Accident case history of reactive chemicals in Japan between 1971 and 1981.

(24) Grewer, Th. *Thermal Hazards of Chemical Reactions*; Industrial Safety Series, Vol. 4; Elsevier: Amsterdam, 1994; pp 308−310.

(25) Vincent, G. C. Loss Prevention. *Chem. Eng. Prog.* **1971**, *5*, 46−52.

In this process, 4-chloronitrobenzene is reacted with 28% ammonia solution in a batch operation to produce 4-nitroaniline.[24] The autoclave is heated to 175 °C in 3 h and then allowed to self-heat to 189 °C in approximately 1 h and then to about 196 °C for 5 h. The final pressure is 42 bars absolute.

The heat of reaction of the desired reaction is high enough to initiate decomposition of the final reaction mixture above 200 °C. The desired reaction exotherm onset temperature measured in DTA tests is 160 °C.

The temperature versus time profile of the process is such that the conversion ratio of the desired reaction is high enough, when the reaction mixture is allowed to self-heat in an adiabatic mode, to prevent the autoclave final temperature from reaching 200 °C. Many process deviations may cause problems.

Too fast a reactor heating rate results in a lower reactant conversion ratio when the reaction is allowed to proceed in an adiabatic mode, without application of cooling. Under such conditions, a higher final temperature of the desired reaction is obtained, which may allow the initiation of decomposition of the final reaction mixture.

G. C. Vincent[25] described an accidental explosion of such a batch which occurred at Sauget, IL, 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 final temperature of the desired reaction to initiate decomposition of the final reaction mixture. 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 (vent sizing package) experiment where the process conditions are reproduced with the process deviation considered. Grewer[24] mentioned eight explosions concerning this process, but the process deviations involved in most accidents are not known. Normal process conditions are “safe”.

Miscellaneous Accidents under Alkaline Conditions. Another example of aromatic nitro compounds thermal instability under alkaline conditions is the following: the preparation of a potassium hydroxide solution in methanol, followed by the introduction of nitrobenzene in a 6000 L reactor, led to an explosion.[26]

A review on decomposition reactions involving organic nitro compounds under alkaline conditions is given by D. Gickel.[27]

Decomposition of Nitro Compounds in the Presence of Metal Halides. As discussed above, metal halides lower the thermal stability of aromatic nitro compounds. $AlCl_3$ 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.[27,28]

Recovery of Nitro Compounds from Solutions. The batch concentration of nitro compounds−solvent solutions may be a critical operation, especially in second-crop recovery. Several examples are known of explosive decomposition during the concentration of impure nitro compounds 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 nitro compounds to decompose on the hot unwetted reactor wall. The presence of active carbon used to decolourise impure product may also contribute to the initiation of decomposition. As mentioned above, active carbon or graphite lowers the thermal stability of organic nitro compounds. The concentration of impurities on active carbon may also contribute to this effect.

Conclusion

A good knowledge of the factors influencing the thermal stability of organic nitro compounds 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 performing process hazard reviews and investigating thermal stability and runaway reaction hazards on a detailed experimental basis.

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

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 nitro compounds is so violent that protection by venting is not possible. This may not be true for contaminated nitro compounds whose decomposition is less rapid.

Contaminated nitro compounds decompositions are often gassy reactions producing foaming viscous heavies which can possibly be vented. The problem is again to determine in which part of the plant the decomposition will occur.

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(26) Bretherick, L. *Chem. Ind.* **1975**, 1060.

(27) Gickel, D. La réaction dangereuse de décomposition des dérivés nitrés en présence de bases (The dangerous reaction of nitro derivative decomposition in alkaline conditions). CNAM Thesis, Centre du Haut Rhin, Université de Mulhouse, France, 1983.

(28) Riethmann, J.; et al. *Chem.-Ing.-Tech.* **1976**, *48*, 729.

⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1997.