



Reactive chemical hazards of diazonium salts



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ABSTRACT

Many diazonium salts are thermally unstable and sensitive to friction and shock. Most diazonium salts are known for their violent decomposition hazard in the solid state. There are many industrial and laboratory incidents caused by this group of chemicals. For safety purposes, the hazards related to the preparation and the handling of diazonium salts are discussed. Twelve cardinal rules are provided:

1. Use only a stoichiometric amount of sodium nitrite when generating diazonium salts, avoiding excess sodium nitrite.
2. Check for the excess of nitrous acid by starch–potassium iodide papers and neutralize it.
3. Minimize the presence of nitrous acid by combining amine and acid first, then subsequently adding the sodium nitrite.
4. Keep the temperature below 5 °C.
5. Always vent the gases generated.
6. Determine the thermal stability of diazonium compounds in your system.
7. Understand the explosive properties of diazonium salts. If unknown, always assume they are explosive.
8. Never allow the undesired precipitation of diazonium salts out of solution.
9. Analyze the residual diazo compounds in the final product, especially for new process conditions.
10. Quench the remaining diazonium salts before any further treatments.
11. Isolate no more than 0.75 mmol of explosive diazonium salts at one time; also consider the addition of an inert material to stabilize the diazonium salts.
12. Use a plastic spatula when handling the solid. The dried powder should not be “scratched” with a metal spatula or ground finely.

An example of a testing strategy and data interpretation is provided for a process which has multiple steps and two diazonium compounds. Differential Scanning Calorimetry (DSC) and Heat of Mixing calorimetry (HOM) successfully serve as efficient tests to screen thermal stability and gas generation, identifying the candidates for advanced tests.

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1. Introduction

Diazonium salts ($R-N^+ \equiv N \cdot X^-$) are important intermediates for the preparation of halides and azo compounds. They are commonly used in the Sandmeyer and Sandmeyer-like reactions by reacting with other pseudohalide-type electrophiles (Fig. 1). However, diazonium salts are known for violent decomposition hazards at temperatures slightly higher than ambient, so they normally are made in situ and used immediately in further reactions (Fierz, 1952). Some diazonium salts are so unstable, even at ambient

conditions, that they are only metastable and are able to explode unpredictably or spontaneously with shock, impact, friction, heat, vibration, or static discharge. There have been multiple historical incidents reported which are related to diazonium salts (Urban, 1999). Ullrich (Ullrich, 1993) mentioned an explosion triggered by mechanically cleaning a valve with unexpected precipitated and dried diazonium salts. A major accident report system (MARS) incident (UKCRHF) described an explosion of about 2 kg of “diazonium solid particulate” upon falling to the ground during inspection of a clarification press, which caused one fatality, six injuries and \$3 million in damages. The UK Chemical Reaction Hazards Forum (UKCRHF) recorded a decomposition explosion of wetted 2,4,6-tribromophenyl diazonium bromide salt triggered by friction or impact. Another fatal accident caused by the detonation

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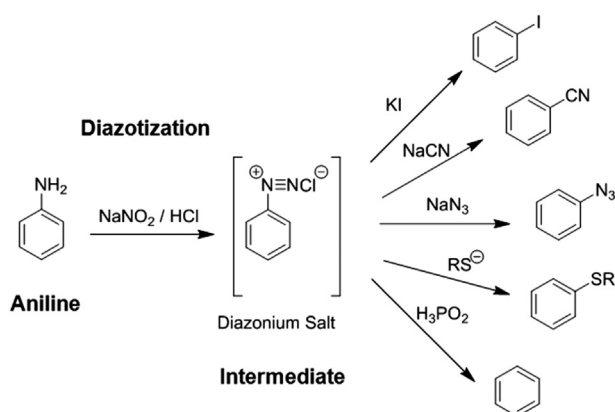


Fig. 1. Sandmeyer and Sandmeyer-like reaction examples.

of supersaturated diazonium chloride salt was reported by UKCRHF as well. There was a reported detonation of benzenediazonium-2-carboxylate hydrochloride when the student touched the material with a metal spatula (Kittsley, 1971). Recently, one of Dow's R&D labs experienced an explosion due to 8 g of a dry product made from a diazonium chloride intermediate (Dow, 2014).

To reduce the occurrence of such incidents, a good awareness of the hazards associated with diazonium salts is necessary and appropriate safety rules should be followed.

2. Hazards during the preparation of diazonium salts

The most common method to make diazonium salts is treatment of primary amines such as aniline with an aqueous solution of nitrous acid (HNO_2) prepared from sodium nitrite (NaNO_2) and a mineral acid (e.g. HCl , H_2SO_4). Normally, a considerably greater amount of mineral acid than the two equivalents necessary on the basis of the stoichiometry of diazotization should be used. This helps the formation of the nitrosating agent and then accelerates the formation of diazonium products. However, a stoichiometric amount of sodium nitrite often is used to prevent an excess of nitrous acid, which exerts a very unfavorable effect on the stability of diazonium salts and potentially interferes with further transformations. Due to the potential instability of diazonium salts, it is important to use the amount of nitrite required for the reaction as accurately as possible. Some researchers recommended testing for excess of nitrous acid by starch–potassium iodide papers and neutralizing it by adding urea, sulfamic acid, or hydrazine at the end of the diazotization reaction. Even in the process of making diazonium salts, the presence of nitrous acid should be minimized. A high concentration of nitrous acid is subject to a rapid decomposition releasing toxic gases of NO_x . Under certain conditions, this gas generation is much faster than that from the decomposition of diazonium salts, which results in a large venting of gas and low yield of the desired products. Therefore, combining the primary amine and mineral acid, and subsequently adding sodium nitrite, is more practical and widely used.

During the preparation of diazonium salts, the reaction temperature is a key safety parameter. In aqueous solutions, most diazonium salts are unstable at temperatures above 5°C , with the diazo functional group tending to be lost as nitrogen gas. To retain the diazo group for further steps, low temperatures need to be maintained as long as the diazonium salts are present in the system. On the other hand, the formation of the diazo group from a primary amine and nitrous acid is an exothermic reaction, with a

reaction enthalpy of between -65 kJ/mol and -150 kJ/mol , depending on the mineral acid used (Grewer, 1999). Meanwhile, most aqueous diazotization reactions are fast reactions at -10 to 5°C . For example, the reaction rates of the diazotization reaction in aqueous hydrochloric and hydrobromic acids are close to the rate of diffusion in the solution. In order to control the reaction temperature, either sufficient cooling capacity is required to quickly remove the heat of reaction, or the feed rate controlled to limit the heat generation rate. Direct pre-add of ice into the reactor is an effective heat removal method and widely used in the dye industry.

In semi-batch process mode utilizing simultaneous temperature and feed control, extra caution is needed. For example, Partington (Partington, 2002) investigated a 500-gallon reactor failure with a manual temperature control system. The vessel failure was caused by the reactant accumulation due to over cooling and fast heat release from those reactants during the following heating step, triggering the decomposition of the diazonium salt. Gas generation from decomposition of diazonium salt is another safety consideration in the preparation of diazonium salts, especially when high nitrous acid is present. A gas venting system is suggested to prevent the pressure buildup in the reactor, as well as safety relief devices to protect the equipment.

In addition, it was reported that several diazonium salts were produced by organic nitrites (typically pentyl nitrite) in organic solvents such as acetic acid, ethanol, or dioxane (Zollinger, 1996). The diazonium salts were either separated from the solution by vacuum distillation or precipitated by addition of a nonpolar solvent. Such an isolation operation is not recommended before understanding the stability of the diazonium salts. An example of a stability study is provided in a later section.

3. Violent decomposition of diazonium salts

Although in most cases, the diazonium salts are made in situ and immediately consumed in further treatment, the violent decomposition hazard and the potential explosive property of those materials brings a significant safety concern. Diazo compounds tend to decompose at low temperature compared to other high energy function groups. As Grewer (Grewer, 1999) reported, typical ADT_{24} (temperature at which the adiabatic induction period is 24 h) for the decomposition of diazonium salts was 80°C , while ADT_{24} for chemicals with nitro groups was between 190°C and 280°C (depending on the other substituents). They also gave a reaction enthalpy of -160 kJ/mol and -180 kJ/mol associated with the decomposition of the diazo functional group. Other researchers reported that bases, transition metal impurities (e.g. Cu , Sn), excess of nitrous acid and direct sunlight significantly accelerated the decomposition behavior and greatly lowered the detected onset temperature. For example, the detected onset temperature of benzenediazonium chloride in one reaction mixture was determined to be 35°C by DSC in our lab, which is significantly lower than the literature data, 80°C . The thermal stability characterization data from the literature may not necessarily apply across all experimental conditions. Therefore, thermal stability studies of diazonium compounds should be considered for each new process.

4. Explosion hazard of diazonium salts

Besides the violent decomposition hazard, many diazonium salts tend to be explosive in the solid state. Of those, chromates, nitrates, picrates, sulfides, triiodides, xanthates, and particularly perchlorates are highly explosive and sensitive to friction, shock, heat and radiation. Chloride and bromide salts also exhibit a highly explosive potential. Ullrich (Ullrich, 1993) gave a list of the selected explosive diazonium salts. From a safety standpoint, diazonium

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