Lesson Learned - Peroxide Explosion Injures Campus Researcher

Hazardous peroxide contaminants formed in old solvent and exploded after concentration.

What happened?
An undergraduate student researcher was working at the laboratory bench when the apparatus she was using exploded, sending glass fragments into her face and upper torso. The researcher was using a rotary evaporator (rotovap) to remove organic solvents from an azobenzene precipitate. She adjusted the bottom flask which then exploded sending glass towards her face, hitting her safety goggles and forehead. Lab personnel helped her to the safety shower and called 911. She was taken by ambulance to the hospital where she received stitches above her eyes and other treatment for her injuries. She was released from the hospital the same day.

What was the cause of the explosion?
Most likely, the explosion was caused by peroxide contaminants in the solvents that had concentrated to the point of being unstable. Both tetrahydrofuran (THF) and diethyl ether were used in the reaction, and both of these solvents form peroxides over time. In this case, the THF used did not contain a stabilizer (such as BHT) to slow the rate of peroxide formation and the four-liter bottle was nearly empty. A sample from the THF bottle was later analyzed with a simple test and found to contain excessive peroxides (more than 100 mg/l). The evaporation in the rotovap concentrated the peroxides in the bottom of the glass reaction vessel and any movement of the vessel could cause the now dry and shock sensitive peroxides crystals to explode.

Below is a photo of what remained after the explosion. Note that the lower round-bottomed flask from the rotovap exploded inside the metal water bath.

What corrective action has been taken?
Since the accident, the laboratory members met to discuss the incident and take corrective action. All the lab users were asked to become familiar with peroxide forming chemicals by reading the Safe Operating Procedures for Peroxidizable Compounds: https://berkeley.app.box.com/v/ccehss-section7-insert17 and the College of Chemistry's Chemical Hygiene Plan: https://chemistry.berkeley.edu/ccehss/manual/section-5, which contains a list of common peroxide forming chemicals. Also, there was a sweep of the laboratory and ALL peroxide forming chemicals in the laboratory were removed and disposed of. Peroxide forming chemicals are considered to have a limited shelf life for safe use. When the safe period is exceeded, the chemical should be tested for peroxides or disposed of.

Now that the lab has been cleaned-out ALL new peroxide forming chemicals will be labeled with the date they are received and opened. Every two weeks there will be a safety inspection of all the lab space for a variety of items including verification that all chemical containers are labeled and properly stored.

One of the chemicals added in the reaction is referred to as Ethereal HCL, which is hydrochloric acid in ether. This material is >95% di-ethyl ether, which can form peroxides over time. Users of such materials in ether or THF should realize that peroxides could form.

Other changes are also being made because of this incident. EH&S and the College of Chemistry (CoC) Health and Safety Program are improving their guidance on safely working with peroxide forming chemicals. While primarily used in Chemistry, these materials are found in labs across campus. One change will be the addition of further training on peroxide formation to the laboratory safety training for new researchers. Also, EH&S plans to add peroxide formation information to the chemical inventory database, and it will identify HCl in ether as a potential peroxide former. Both CoC (for CoC researchers) and EH&S now offer the peroxide dip tip test strips for researchers to test for peroxides. Contact EH&S at 642-3073 or the College of Chemistry Health and Safety Program at 643-0648 for information on this service.

Lessons Learned

How can incidents like this be prevented?

1) Manage peroxide forming chemicals properly. If your research uses peroxide formers, it must be understood that explosive peroxides will form over time and need to be identified as materials containing peroxides. Researchers need to be trained on how to properly use these potentially hazardous materials safely. The safe procedures should be listed or described in the lab's Chemical Hygiene Plan.

1a) Limit purchases. Purchase small quantities and try to completely use materials so that remaining peroxide forming material is not left in the container. Larger containers may sit around longer increasing the chance of forming peroxides. Whenever possible, purchase material with **stabilizer added** so the rate of peroxide formation is decreased. If peroxidizable material does not have a stabilizer, it should be tested every time it is used. The lab that had the accident no longer buys most materials in four-liter bottles, choosing instead to purchase 500 ml containers.

1b) Store properly. Peroxide formers should be stored away from air and light. They should be stored in their original containers, usually dark colored bottles or metal cans, with a tight fitting cap. Some unstabilized peroxide formers are best stored under inert atmospheres. In this case, the laboratory was aware that peroxides could form in the unstabilized THF, but thought that the use of inert atmosphere in the bottle (as the manufacturer recommended) would be sufficient to prevent formation of peroxides. Apparently, the use of inert atmosphere was not enough.

1c) Always date containers of peroxide formers with the date received and the date opened. After a container is opened, it should be labeled with an expiration date. The campus EH&S office and web site have guidance on "potentially explosive chemicals", including information on expiration protocols and labeling. (See the links below.) EH&S also has labels available for marking such containers. Also, the manufacturer's label may include the manufacture date and recommendations for storage. **Do not use old containers of peroxide formers or containers undated without testing for peroxide contamination.**

1d) Dispose of old peroxide forming chemicals through the chemical waste program or contact EH&S. If you notice a viscous liquid or crystalline solids in the solvent, stop immediately and get assistance from EH&S. It is possible that old crystals may be shock, friction, or impact sensitive and could explode.

2) Wear proper personal protective equipment (PPE) in the lab. Fortunately, the researcher in this lab was wearing laboratory safety goggles, which protected her from the exploded glass fragments and chemicals. Wearing a lab coat would have better protected her personal clothing and minimized the need for decontamination in the safety shower before she was sent on to the hospital.

3) Work behind a safety sash, such as a fume hood sash when working with potentially explosive chemicals.

4) Know where the emergency eyewash and safety shower is so that decontamination is taken care of quickly.

5) Give safety training to everyone in the lab on the unique hazards of their work. Undergraduate researchers may need additional safety training and perhaps should not be asked to work on hazardous reactions alone. Since this accident, the laboratory now has a policy of direct supervision for undergraduates until they have worked in the lab for more than one semester.

Resources

Campus-EH&S Guidelines for Explosive and Potentially Explosive Chemical Safe Storage and Handling:
http://ehs.berkeley.edu/sites/default/files/lines-of-services/hazardous-materials/pecguidelines.pdf
Specific information about Peroxide forming chemicals can be found in Appendix II of the guideline.

The College of Chemistry Safety Manual, Guidelines for the Safe Handling of Peroxidizable Chemicals: https://berkeley.app.box.com/v/ccehss-section7-insert17