Laboratory Safety Bulletin

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Location: Essex Hall / B-37 • Hours: 8:30 am to 4:30 pm (M-F)

Peroxides in the Laboratory

Peroxide-forming chemicals can react with oxygen, even at low concentrations, to form peroxy compounds (O-O). Substances that are susceptible to peroxide formation are ones that typically react with air, moisture or impurities over a period of time and produce a change in their chemical composition in normal storage even if the containers have not been opened.

Organic Peroxides

Organic peroxides are a special class of compounds with unusual stability problems. They are low-power explosives and are among the most hazardous substances encountered in the chemical laboratory.

They are hazardous because they are sensitive to shock, sparks, heat, friction and other accidental ignition. They are far more sensitive to shock than primary explosives (TNT)

Chemical families of organic peroxides formers:

- Ethers and ethers derived from alcohols.
- Aldehydes
- Ketones, especially cyclic ketones
- Vinyl and vinylidene compounds
- Compounds containing benzylic hydrogen atoms.
- Compounds containing the allylic (CH2=CHCH2-) structure, including most alkenes.

Inorganic Peroxides

Inorganic peroxides are generally more stable; however, in contact with organic compounds they may generate organic peroxides.

As well, their contact with any combustible materials may lead to fire or explosion. They must be stored, handled and used with caution.

Chemical families of inorganic peroxides formers:

- Alkali metals: potassium, rubidium, cesium
- Alkali metal alkoxides and amides
- Organometallics with a metal bonded to carbon.

Examples of chemicals that can form potentially hazardous concentrations of peroxides when exposed to air:

- Cyclohexene
- Cyclooctene
- Decahydronaphthalene (Decalin)
- p-Dioxane
- Ethyl ether
- Isopropyl ether
- Tetrahydronaphthalene (Tetralin)
- Tetrahydrofuran (THF)

Recommended work practices:

- Label the containers of peroxide-forming chemicals with the date the chemical was received and opened.
- Test all ethers and other peroxide-forming compounds for peroxide concentration at regular intervals and preferably before each use. Testing can be done with a commercial test strip. If peroxide concentrations are acceptable, re-date the container. If peroxide concentrations are greater than 100 ppm the chemical should be disposed of as hazardous waste (contact Chemical Control Centre) for instructions on disposal procedures.

- Familiarize yourself with the storage limits of peroxide formers used in your laboratory[1] *For example: Unopened containers of ethers should be discarded after one year, unless inhibitors have been added. However, once these bottles have been opened, they should only be kept for 6 months.*

- Store in air-tight, amber glass bottles, in a dark location and under inert atmosphere if possible.

- If the peroxide-forming chemical is flammable and requires refrigeration, then use an explosion-proof refrigerator.

- Never distill, evaporate or concentrate a peroxide-forming chemical until you have first tested it for the presence of peroxides and even then do not distill to dryness. Always leave a minimum of 20% bottoms. (Peroxides are usually less volatile than their parent material and will tend to concentrate in the hot distillation pot).

- Never touch or attempt to open a container of a peroxide-forming liquid if there are whitish crystals around the cap and/or in the bottle. The friction of screwing the cap may detonate the bottle. If you encounter such a bottle, contact the CCC immediately for removal. DO NOT TOUCH OR MOVE THE SUSPECTED BOTTLE YOURSELF FOR ANY REASON

- Never scrape or scrub glassware or containers that have been used with peroxide-forming compounds if you see an oily or crusty residue.

- Follow individual chemical's MSDS for the recommendations of the appropriate PPE. Usually standard PPE should be worn (safety glasses with side shields, laboratory coats and closed toed shoes). Additional PPE such as face shields, chemical aprons, disposable coveralls, chemically resistant gloves and respiratory protection shall be worn as appropriate.

- Use a fume hood or other appropriate exhaust ventilation when handling peroxide forming chemicals in a manner that may produce an airborne hazard. This includes procedures such as transferring, preparation of mixtures, blending, sonification, spraying, heating, evaporation and distilling. Place safety shields in front of reaction vessels, distillation columns and other apparatuses when fire, explosion or detonation may occur.

The list is not exhaustive and you should always check the MSDS of your chemical or other chemical literature before use to determine if it forms peroxide and ensure the proper work practice. MSDS are available online at www.uwindsor.ca/msds

For more information on Peroxides, please visit the Chemical Control Centre's Laboratory Safety, Assurance, and Compliance website at www.uwindsor.ca/ccc or by phone (ext. 3523)

References:

1. http://www.lbl.gov/ehs/chsp/html/reactives.shtml#Peroxide
2. *Prudent Practices in the Laboratory: Handling and Disposal of Chemicals*, 1995 National Research Council, National Academy Press, Washington, D.C.
3. Kelly, R.J. "Review of Safety Guidelines for Peroxidizable Organic Chemicals" Chemical Health and Safety, Sep. /Oct. 1996, pp28-38.
4. Academic Chemistry Laboratories: Accident Prevention for College and University Students, 2003 American Chemical Society, Washington, D.C.
5. *Safety in Academic Chemistry Laboratories: Accident Prevention for College and University Students*, American Chemical Society, pp 24-25.