Office of Research Safety
Laboratory Safety Manual
807 Peroxidizable Materials

1. What are organic peroxides?

2. Organic peroxides are a class of compounds that have unusual stability problems that make them among the most hazardous substances found in the laboratory. The lack of stability is due to the presence of an oxidation and reduction center within the same molecule.

R-O-O-R

R = organic side chains

O-O = Peroxo bridge

As a class, organic peroxides are considered to be powerful explosives and are sensitive to heat, friction, impact, light, as well as to strong oxidizing and reducing agents. Peroxide formers react with oxygen even at low concentrations to form peroxy compounds. Autoxidation of organic material proceeds by a free-radical chain mechanism and commonly affects organic solvents.

R-H ▶ R- ▶ R-O-O ▶ R-O-O-R (In the presence of oxygen)

The instability of the molecule (R-O-O-R) can cause auto-decomposition simply by bumping or jarring the container, addition of heat, light, or opening the cap. The risk associated with the peroxide increases if the peroxide crystallizes or becomes concentrated by evaporation or distillation. Peroxide crystals may form on the container plug or the threads of the cap and detonate as a result of twisting the lid.

3. Classes of Peroxide Formers

- Aldehydes
- Ethers - especially cyclic ethers and those containing primary and secondary alcohol groups
- Compounds containing benzylic hydrogen atoms (particularly if the hydrogens are on tertiary carbon atoms)
- Compounds containing the allylic structure, including most alkenes.
- Vinyl and vinylidene compounds.

4. Preventing Formation of Organic Peroxides

No single method of inhibition of peroxide formation is suitable for all peroxide formers. Use of different inhibitors is discussed in the literature (0.001 to 0.01% hydroquinone, 4-tert-butylcatechol (TBC) or 2,6-di-tert-butyl-p-methylphenol (BHT)); however, limiting size of container and regular testing (every 3 months) and disposal is probably more effective (and certainly easier) for managing peroxide formation.

Ethers and other organic peroxide formers should be stored in cans, amber bottles, or other opaque containers, and ideally under a blanket of inert gas, such as nitrogen. It is preferable to use small containers that can be completely emptied rather than take small amounts from a large container over time. Containers of ether and other peroxide-forming chemicals should be marked with the date they are opened, and marked with the date of required disposal.

5. Common laboratory chemicals that form peroxides during storage include:

Acetal	Diisopropyl ether	Sodium amide

Butadiene	Dioxane	Styrene
Cumene	Dimethyl ether	Tetrahydrofuran
Cyclohexene	Divinyl acetylene	Tetrahydronaphthalene
Cyclooctene	Ethyl ether	Tetralin
Decahydronaphthalene	Ethylene glycol dimethyl ether (glyme)	Vinyl acetate
Decalin	Isopropyl ether	Vinyl actylene
Diacetylene	Methyl acetylene	Vinyl choride
Dicyclopentadiene	Methylcyclopentane	Vinyl ethers
Diethylene glycol	Potassium metal	Vinylidene chloride

6. Peroxide Detection Tests

From *Prudent Practices in the Laboratory: Handling and Disposal of Chemicals*, 1995

The following tests will detect most (but not all) peroxy compounds and all hyperperoxides. NOTE: These tests should not be used for testing materials potentially contaminated with inorganic peroxides (i.e., potassium).

Option 1. Add 1-3 ml of the liquid to be tested to an equal volume of acetic acid, add a few drops of 5% potassium iodide (KI) solution and shake. The appearance of a yellow to brown color indicates the presence of peroxides.

Option 2. Addition of 1 ml of a freshly prepared 10% KI and 10 ml of an organic solution in a 25 ml glass cylinder should produce a yellow color if peroxides are present.

Option 3. Add 0.5 ml of the liquid to be tested to a mixture of 1 ml of 10% KI solution and 0.5 ml of dilute hydrochloric acid to which a few drops of starch solution have been added just before the test. The presence of a blue-black color within a minute indicates the presence of peroxides.

Option 4. Peroxide test strips that turn an indicative color in the presence of peroxides. Care must be taken to follow manufacturer instructions for effective detection. In general, the strips must be air dried until the solvent evaporates and then exposed to moisture for proper operation.

Results of peroxide detection tests must be indicated on the container with test date, test results/method, and initials of the authorized person conducting the test.

7. Peroxidizable Materials Handling

Peroxidizable materials should be purchased in amounts that are expected to be used within six months to one year. This practice will help ensure that others are used up before the manufacturer's expiration date.

Peroxidizable materials, either opened or unopened, should be disposed of or tested for peroxides upon reaching the manufacturer's expiration date, or upon one year after receipt. If positive for peroxides, the peroxides may be removed or the materials may be disposed of by submitting a "Request for Chemical Pick-up" to Chemical Hygiene Officer. Please be sure to label the date that the test for peroxides was performed and the date peroxides removed (if applicable). The new expiration date will be three months after the date tested for materials in List A, and one year after the date tested for materials in List B.

Containers should be marked with the date opened and, in the absence of a manufacturer's expiration date, with the date received. Containers should also be marked with the date that the last test for peroxides was done.

Ethers should be disposed of without opening if there are visible crystals around the cap, or if the container is in a grossly corroded condition. Crystals visible in the container should be brought to the attention of the instructor, principal investigator or staff research assistant.

Leave at least 10 percent bottoms when distilling peroxidizable materials. The flask can be rinsed with equal amounts of a solvent such as ethanol and considered as waste.

Test for peroxides before distilling (even previously unopened ethers) and upon three months after opening List A and after one year of opening List B materials:

List A Peroxide hazard on storage

Test or dispose in 3 months

Isopropyl ether; Divinyl acetylene; Vinylidene chloride; Potassium metal;Sodium amide

List B Peroxide hazard on concentration

Test or dispose in 12 months

Isopropyl ether; Diethyl ether; Divinyl acetylene; Tetrahydrofuran; Vinylidene chloride
Diacetylene; Potassium metal; Methyl acetylene; Sodium amide; Dioxane; Acetal
Decahydronaphthalene (Decalin); Tetrahydronaphthalene (Tetralin)
Ethylene glycol dimethyl ether; Cyclohexene; Vinyl ethers
Diethylene glycol dimethyl ether; Dicyclopentadiene