What are organic peroxides?

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.

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.

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.

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

Storing Peroxide Formers

Mark on containers of time-sensitive materials both the date of receipt and the date the container is first opened. Time-sensitive materials should be marked with a tag to make them easily identified. No materials should be used or tested after the manufacturers' expiration date unless evidence of current stability has been obtained via direct testing *prior* to the expiration date. Refillable dispensing containers holding peroxide formers must be dated with the fill date.

NOTE: If material is old (> 1 year past label expiration date) then minimize handling and DO NOT OPEN OR ATTEMPT TO TEST! Call (330-672-1977), or email lwilso51@kent.edu to request special disposal for this item. Isolate the container from possible inadvertent use until picked up. If the material is very old or shows evidence of conversion to a hazardous status (i.e., crystalline materials in/under cap of ethers), do not move the container! Call the Laboratory Safety Manager at 2-1977 for assistance.

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/tag with test date, test results/method, and initials of the authorized person conducting the test.