LABORATORY SAFETY FACT SHEET #17

Peroxides and Distillations

Extractions

Before pouring a liquid into a separatory funnel, make sure the stopcock is closed and has been lubricated. Use a stirring rod to direct the flow of the liquid being poured. Keep a beaker under the funnel in the event the stopcock comes open unexpectedly. Do not attempt to extract a solution until it is cooler than the boiling point of the extractant. When a volatile solvent is used, the unstoppered separatory funnel should first be swirled to allow some mixing. Shake with a swirl holding the stopper in place and immediately open the stopcock. Repeat until it is evident that there is no excessive pressure. Swirl again as the funnel is racked, immediately remove the stopper, and separate when appropriate.

Distillations

Ethers must never be distilled unless known to be free of peroxides. Most ethers, including cyclic ethers, form **dangerously explosive peroxides** on exposure to air and light.

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

where, R = organic side chains and 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. 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. 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	Decalin	Dimethyl ether	Methylcyclopentane	Tetralin
Butadiene	Diacetylene	Divinyl acetylene	Potassium metal	Vinyl acetate
Cumene	Dicyclopentadiene	Ethyl ether	Sodium amide	Vinyl actylene
Cyclohexene	Diethylene glycol	Ethylene glycol dimethyl ether	Styrene	Vinyl choride
Cyclooctene	Diisopropyl ether	Isopropyl ether	Tetrahydrofuran	Vinyl ethers
Decahydronaphthalene	Dioxane	Methyl acetylene	Tetrahydronaphthalene	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.

NOTE: If material is old (> 1 year past label expiration date) then minimize handling and DO NOT OPEN OR ATTEMPT TO TEST! Call EHS (x-3293) 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!

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. 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. 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. Take care 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.