LABORATORY HEALTH & SAFETY

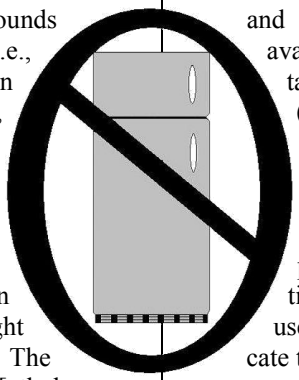
The care and feeding of organic peroxides

Here are some tips to avoid the old bump and grind game

Everyone who takes organic chemistry learns about the hazards of peroxide formation-sensitivityto light and air and the possibility of explosion in certain types of organic compounds. The best known is diethyl ether, probably because of its ubiquity, but peroxide formation is not restricted to ethers.

What's likely to form peroxides?

Some of the more common classes of chemicals that form peroxides are aldehydes; alkenes that contain the allylic structure; compounds with benzylic hydrogen atoms (i.e., hydrogen atoms attached to carbon directly to an aromatic ring); ethers, especially cyclic ethers and those with primary and secondary alcohol groups; and vinyl and vinylidene compounds.



Compounds prone to ready formation of peroxides after exposure to light and air are particularly troublesome. The most common include cellosolves [ethylene glycol mono- (and di-) methyl (or ethyl) ether];cyclohexene; cyclooctene; decalin (decahydronaphthalene) and tetralin (tetrahydronaphthalene); dibutyl, diethyl, and diisopropyl ether; p-dioxane; and tetrahydrofuran.

Managing use of these compounds

Some obvious administrative procedures should be followed: Know the hazards specific to the chemical; order only what is needed in small individual containers; read the MSDS; date the containers to indicate when they were received, when they were opened, and when they must be discarded; use an inventory system and label properly; use correct personal protective equipment; routinely test for peroxides; anticipate the unexpected (an accident) and know exactly what to do; and dispose of excess and waste properly.

A common misconception is that diethyl ether should be stored in a refrigerator. This is not a good practice because the flash point of diethyl ether is -45°C (-49°F). Problems arise when leaks occur or vapors build up from opened containers in closed spaces that are not explosion proof or when ignition sources are nearby.

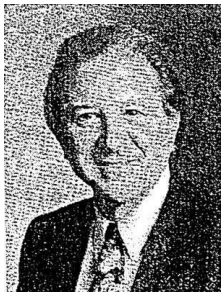
Usually the most important question to answer is how long these compounds should be stored. Peroxides can form within a few days after a container is opened; the time frame depends the specific compound, the conditions of storage and use, and whether stabilizers are present. To be safe, I dispose of such a compound if I haven't used the open container in two weeks and don't plan to do so in the immediate future.

Several tests can be used to detect peroxides, and dipstick-type kits are commercially available. Commonly, a solution of potassium iodide in glacial acetic acid (0.1 g/mL) is used; it turns brownish-yellow if peroxides are present. Water - moistened potassium iodide/starch paper turns violet when exposed to water soluble ethers if peroxides are present. For polymeric peroxides, titanium sulfate in 50% sulfuric acid is used; it turns yellow or orange to indicate their presence.

If peroxides are found, it's best to check with your chemical hygiene officer or safety office before proceeding. Procedures for peroxide removal are available (e.g., the National Safety Council's Data Sheet 655), but you will still have a waste disposal problem because the alumina used to absorb the material will be contaminated with peroxide and, consequently, flammable.

To recap

- Use minimum quantities of potential peroxide-forming compounds.
- Clean up spills immediately. Many peroxide formers are flammable, and if the material is volatile, peroxides may concentrate and increase the risk.
- Peroxides are usually shock and heat sensitive. This tendency can be reduced by dilution. Use wooden or ceramic spatulas rather than metal ones. Frozen peroxides become more sensitive, so avoid storage below the freezing point. It is also wise to avoid friction and grinding (i.e., don't use ground-glass stoppers and glass screw-cap containers).
- Anticipate, recognize, evaluate, and control. There is no substitute for knowledge! •



Doug Walters *is head of laboratory health and safety for the National Toxicology Program at the National Institute of Environmental Health Sciences.*