

## Chemicals That Form Peroxides: Handling and Storage

Peroxy compounds are examples of chemicals which present special problems in the laboratory because they can be violently reactive or explosive. Their handling deserves careful attention.

### Inorganic Peroxides

Inorganic peroxy compounds are generally stable as such, but in contact with organic compounds may generate organic peroxides and hydroperoxides. Their contact with any combustible material may lead to a fire or explosion. They must be stored, handled and used with much caution. Peroxides of alkali metals are not sensitive to shock, but are decomposed slowly by moisture and violently by bulk water. The most common inorganic peroxy compounds are sodium peroxide, hydrogen peroxide, sodium perborate, and sodium persulfate. The high weight alkali metals readily form superoxides, and ozonides such as  $KO_3$  are known.

Any of these peroxy compounds can pose a threat of fire or explosion when contacted by oxidizable materials. They can react violently with water and many other substances. Small spills can be treated cautiously with water and sodium bisulfite solution; larger ones should be taken up with inert solids such as vermiculite, sand or salt and treated with bisulfite in a safe area. Any person burned by these chemicals should be washed gently but thoroughly and given competent medical attention.

### Organic Peroxides and Hydroperoxides

Organic peroxy compounds fall largely into four classes: dialkyl or diarylalkyl peroxides, peracids, diacyl peroxides, and alkyl or arylalkyl hydroperoxides. All are unstable to some degree and generally are not offered in high purity for their hazards increase with concentration. The hazard decreases with increasing molecular weight because of the dilution effect. Those of lower molecular weight can deflagrate or detonate. Some of the most common ones are tert-butyl peroxide, tert-butyl hydroperoxide, peracetic acid, benzoyl peroxide and iso-propylbenzene (cumene) hydroperoxide.

Because peroxy compounds are unstable and decompose continuously, bulk quantities may generate enough heat to autoaccelerate up to ignition or explosion. They are sensitive to heat, friction, impact and light as well as to strong oxidizing and reducing agents. All organic peroxides are quite flammable and fires involving bulk quantities should be approached with extreme caution. Because they can generate free radicals with catalytic power, their presence as a contaminant in a reaction mixture can change the course of a planned reaction.

Organic peroxy compounds are generally more stable when water is present. For example, benzoyl peroxide is a solid (m.p. 104-106 dec.) which can ignite or explode from heat, impact or friction, and which must be kept moist in storage. The unscrewing of a lid covered with the dry chemical can set off the entire lot. No more than a short term supply should be kept on hand and the container must be checked at regular intervals. If in doubt, it is best to call an expert on disposal of dangerous chemicals.

### Peroxide Formers and Their Storage and Handling

Peroxide formers react with oxygen even at low concentrations and ordinary temperatures to form peroxy compounds which are usually hydroperoxides. In addition to any other hazards that they have, they pose a "peroxide threat"

especially if the oxygenated product crystallizes out or becomes concentrated by evaporation or distillation of the unoxidized part. Peroxide crystals may even form at the threads of a sealing plug or cap.

There are four main groups of compounds known to be peroxide precursors:

- ! Ethers with primary and/or secondary alkyl groups, including open chain and cyclic ethers, acetals and ketals
  - ! Hydrocarbons with allylic, benzylic or propargylic hydrogens
  - ! Conjugated dienes, enynes and diynes
  - ! Saturated hydrocarbons with exposed tertiary hydrogens
- Some specific and typical examples are diethyl ether, di-isopropyl ether, tetrahydrofuran (THF), p-dioxane, cyclohexane, isopropylbenzene (cumene), tetrahydronaphthalene (tetralin), divinylacetylene, decahydronaphthalene and 2,5-dimethylhexane.

Peroxidation is generally a problem of the liquid state. Solid peroxide formers present little problem except when finely divided, for the reaction, if any, will occur only at the surface. Peroxidation seems to be no problem within gases and vapors. For liquids, the peroxidation typically occurs when containers are not fully sealed and blanketed with inert gas. Breathing then occurs with changes in temperature and barometric pressure and oxygen gets into the containers. Peroxide buildup is usually slow because the exchange of atmosphere containing only twenty percent oxygen is usually slow.

If abundant oxygen is supplied to a fast peroxide former, typically there is an induction period, then a relatively fast accumulation of hydroperoxide which tapers off at a maximum level, perhaps 5-15%. Then, the concentration will stabilize or even decrease because the hydroperoxide itself undergoes decomposition and forms byproducts such as alcohols and water which interfere with the free radical chain reaction or peroxidation. The byproduct content may continue to grow, but the peroxide content does not. CAUTION: This scenario does not apply when peroxides separate in solid form. Then the peroxy substance is undiluted by solvent or byproducts and is an immediate threat.

Peroxide formers cannot form peroxy compounds without exposure to oxygen or oxidizers. Therefore their containers should always be tightly sealed. Air should always be flushed out of the free space with an inert gas (usually nitrogen) before sealing. Plastic caps, stoppers and plugs should be used to reduce corrosion and friction.

Precautions for storing and handling peroxide formers are summarized here:

- (a) Label the chemicals as known peroxide formers or (in some cases) as possible peroxide formers.
- (b) Limit the stock of any item to three months supply or less, and discard remaining stock unless found to be essentially peroxide free.
- (c) Always maintain an inert atmosphere (nitrogen or argon) in the free space of each container. Either flush with a stream of the gas, or use pressure siphoning with the gas when withdrawals are made.
- (d) Unless it would compromise the material's usefulness, add an oxidation inhibitor to it. The recommended amount is from 0.001 to 0.01% of inhibitors such as hydroquinone, 4-tert-butylcatechol (TBC) or 2,6-di-tert-butyl-p-methylphenol (BHT).
- (e) Before distilling any known or suspected peroxide former, check it carefully for peroxide. If any is present, eliminate it by chemical treatment or percolation, or add an inert high boiling substance (such as mineral oil) to prevent the peroxide from concentrating to a dangerous level.

A variety of chemicals used as solvents or in synthesis, even alcohols, have been found to contain significant amounts of peroxides (as high as 0.1 percent). Such small amounts could arise from impurities which are peroxide formers. However, a severe laboratory explosion in the distillation of 2-propanol has been attributed

to peroxide content. Pending further investigation, prudence suggests that all oxidizable organic liquids should be checked for peroxides before distillation or use in reactions sensitive to peroxide catalysis.

### **Detection and Determination of Peroxides**

The presence of most peroxy compounds, including all hydroperoxides, can be detected by this test: Mix 1-3 mL of the liquid to be tested and an equal volume of acetic acid in a test tube, add a few drops of five percent potassium iodide solution, and shake. The appearance of a yellow-to-brown color indicates presence of a peroxide. If the color is faint, run a blank to make sure the test is really positive. A semi-quantitative testing kit using treated paper strips is available. Quantitative titration procedures are available.

### **Disposal of Peroxides**

CAUTION. Only a "bomb squad" should dispose of pure peroxides. Peroxides normally must be diluted before disposal.

Small quantities (25 g or less) of peroxides are generally disposed of by diluting with water to a concentration of 2% or less and then transferring them to a polyethylene disposal bottle containing an aqueous solution of a reducing agent such as ferrous sulfate or sodium bisulfite. The material is then handled like any other waste chemical, but it must not be mixed with other chemicals for disposal. Spilled peroxides should be absorbed on vermiculite as quickly as possible. The vermiculite-peroxide mixture may then be burned directly or may be stirred with a suitable solvent to form a slurry, which is then treated as above. CAUTION: Never flush organic peroxides down the drain.

Large quantities (more than 25 g) of peroxide require special handling. Each case should be considered separately and a handling, storage and disposal procedure, determined by the physical and chemical properties of the particular peroxide and prevailing regulations, established. In Preparing a disposal procedure, consult "Destroying Peroxides of Isopropyl Ether," by A. C. Hamstead, Ind. Eng. Chem., 1964, 56(6), 37.

Reprinted from "Safety in Academic Chemistry Laboratories." Published by The American Chemical Society.