

Control of Potentially Explosive Chemicals in Laboratories

Many relatively common chemicals can become explosive when stored improperly or for excessive periods of time. This note contains background information on potentially *explosive and shock-sensitive chemicals*.

Peroxides and Peroxidizable chemicals

Peroxy compounds contain the characteristic peroxide oxygen-oxygen bond. They present special problems in the laboratory because they can be violently reactive or explosive. Their handling requires careful attention.

Inorganic Peroxides

They are generally stable but in contact with organic compounds they may generate organic peroxides and hydroperoxides. Their contact with any combustible materials may lead to fire or explosion. They must be stored, handled, and used with 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 peroxides are sodium peroxide, hydrogen peroxide, sodium perborate, and sodium persulfate. The higher atomic weight alkali metals readily form superoxides or ozonides. Sodium amide and many organometallic compounds can also autoxidize and form hazardous peroxides. These peroxy compounds can pose a threat of fire or explosion when contacted by oxidizable materials. Small spills can be treated cautiously with water and sodium bisulfite solution but larger ones should be taken up with inert solids such as vermiculite, sand, or salt and treated with bisulfite in a safe area.

Organic Peroxides

Organic peroxides are among the most hazardous chemicals handled in the chemical laboratory. The primary types of organic peroxides are hydroperoxides (R-O-O-H) and dialkyl peroxides (R-O-O-R'), where R and R' are alkyl groups. Organic peroxides are generally low-power explosives that are sensitive to shock, sparks, shaking, friction, heat or light. They are far more shock-sensitive than most primary explosives such as TNT. Organic peroxides fall largely into four classes: dialkyl or diarylalkyl peroxides, peracids, diacyl peroxides and alkyl or arylalkyl hydroperoxides. Those of low molecular weight can deflagrate or detonate. Examples of the most common ones are: *tert*-butyl peroxide, *tert*-butyl hydroperoxide, peracetic acid, benzoyl peroxide, and isopropylbenzene (cumene) hydroperoxide.

Peroxy compounds are unstable and decompose continuously and bulk quantities may generate enough heat to autoaccelerate up to ignition or explosion. Because they can generate free radicals with catalytic power their presence as 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 which is a solid at room temperature, can ignite or explode from heat, impact or friction must be kept moist on storage. The unscrewing of a lid covered with the dry chemical can set off the entire lot.

Peroxidizable Chemicals

A wide variety of organic chemicals react with molecular oxygen by a free radical reaction even at low concentrations and ordinary temperatures in a process of autoxidation to form peroxy compounds that are usually hydroperoxides and/or peroxides. Autoxidation of organic chemicals (solvents and other liquids, most frequently) proceeds by a free radical chain mechanism. For a chemical R-H, the chain may be initiated by ultraviolet light, by the presence of a radical source, and by the peroxide itself. Oxygen adds to the R radical, producing the peroxy radical R-O-O. The chain is propagated when the peroxy radical abstracts a hydrogen atom from R-H. The reaction can be initiated by light or by a contaminant. In addition to any other hazards they may have, these chemicals 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 form even on the threads of a sealing plug or cap. Ethers are the most notorious peroxide formers. However, not all chemicals which fall into these categories have been shown to form potentially dangerous peroxides. MSDS or other chemical literature for hazard potential of individual chemicals should be consulted.

Peroxidation is generally a problem of the liquid state. Solid peroxide formers present little problem except when finely divided because the reaction, if any occurs only at the surface. Peroxidation does not seem to be a problem in gases or vapours. For liquids, peroxidation usually occurs when containers are not fully sealed and blanketed with inert gas. In some cases, *stabilizers or inhibitors*, which are free radical scavengers that terminate the chain reaction, are added to the liquid to extend its storage lifetime. Examples of common inhibitors are: hydroquinone, 2,6-di-*tert*-butyl-*p*-methylphenol (butylated hydroxy toluene, BHT), diphenylamine which are added to the chemical in trace quantities. Iron will inhibit the formation of peroxides in diethyl ether, which is one reason that this chemical is usually sold in steel containers. However, iron or other metals will not inhibit peroxidation in isopropyl ether and are not known to be effective in other chemicals. Actually, iron may catalyze peroxidation in some chemicals. One should, however, be cautious that despite the use of inhibitors, peroxide explosions have occurred. Inhibitors are depleted as peroxides are formed and degraded. Eventually with the total depletion of inhibitors, the peroxide-forming chemical will act as an uninhibited chemical. This may result in rapid accumulation of peroxides in a chemical that has been stable for a long time. Table 3 lists common types of organic chemicals that autoxidize to peroxide and Table 4 provides information about shelf life for groups of peroxidizable chemicals. Table 5 is a fairly comprehensive list of peroxidizable organic laboratory chemicals.

Control Measures

1. Purchase of peroxidizable chemicals should be restricted to ensure that the chemical is used completely before it can become peroxidized. Purchase ethers in the smallest practicable size (in no case larger than 1L) not in what seems to be the most economical size. Limit the stock of any such chemicals to *three months supply or less*, and dispose the remaining stock through the Environmental Health and Safety Office (EHSO) before the expiry date unless found to be essentially peroxide free. The storage limit for unopened containers is 12 months and 3-6 months for opened ones.
2. Containers of peroxidizable chemicals must be dated when received and again when opened. A University of Manitoba Hazardous Waste label should be used for this purpose (see the Hazardous Waste Disposal and Forms link listed in the right column of this web page). Many commercially purchased ethers have expiration dates printed on the containers beyond which they must not be used.
3. All peroxidizable chemicals should be stored in sealed, air impermeable containers. Dark amber glass container with a tight-fitting cap (but no screw-cap) should be appropriate. Containers with loose fitting lids and ground glass stoppers on glass bottles should not be used for storage. The chemicals should be stored in a tightly closed, properly labeled container inside a flammable storage safety cabinets or explosion proof refrigerator away from heat, flames, sources of ignition, light, oxidizers and oxidizing acids.
4. Promote routine testing for peroxides before distilling ethers. Distillation is notable for a number of accidents involving peroxidizable chemicals it has caused. A peroxidizable chemical should not be distilled if it contains more than 100 ppm of peroxide. Any distillation involving peroxidizable chemical should leave at least 20% bottoms. Peroxide may form from freshly distilled and unstabilized ethers in less than 2 weeks. There are reports that indicate the formation of peroxide in tetrahydrofuran after 3 days and in ethyl ether after 8 days. Very dry absolute ether undergoes oxidation much more readily.
5. A responsible user should annotate the general chemical inventory to indicate which chemicals are subject to peroxidation. Before the expiration date, the responsible user should either dispose of the chemical through the EHSO or test it for peroxide content. Any chemical with peroxide concentration greater than 100 ppm should be disposed of or decontaminated. (For chemicals containing less than 80 ppm peroxides, a "dash" of peroxide inhibitor, BHT should be added to the container to inhibit further peroxidation, unless it is determined that the inhibitor will adversely affect the experimental work.)

6. Old containers of peroxidizable chemicals or containers of unknown age and history must be handled with great caution. Any peroxidizable chemicals with visible discoloration, crystal formation or layering should be treated as potentially explosive. If the container shows no outward sign of deterioration, it may be possible to test the chemical by taking extra precautions against agitation and providing extra protection to the tester. Typically, an unopened container should be taken to a nearby fume hood by a person wearing chemical safety goggles, a face shield, heavy gloves, ear muffs and a heavy rubber apron. In the fume hood, with a protective blast shield and secondary containment, the person should test the chemical with the least possible amount of disturbance, by using a colorimetric peroxide strip. If high concentration of peroxide are detected, the container should be treated as a potential bomb. Contact EHSO immediately.

TABLE 3: Types of Compounds Known to Autooxidize to Form Peroxides

- Aldehydes
- Ethers, especially cyclic ethers and those containing primary and secondary alkyl groups (Never distill an ether before it has been shown to be free of peroxide)
- Compounds containing benzylic hydrogens
- Compounds containing allylic hydrogens (C=C-CH), including most alkenes: vinyl and vinylidene compounds
- Compounds containing a tertiary C-H group (e.g. decalin and 2,5- dimethylhexane)

TABLE 4: Peroxidizable Compounds – *classes of compounds that can form Peroxide upon aging*

Class I: Unsaturated Chemicals, especially those of low molecular weight, may polymerize violently and hazardously due to peroxide initiation – ***discard after 1 year.***

Acyclic Acid	Chlorotrifluoroethylene	Tetrafluoroethylene	Vinyl chloride
Butadiene	Methyl methacrylate	Vinyl acetate	Vinyl pyridine
Chlorobutadiene	Styrene	Vinyl acetylene	Vinylidene chloride

Class II: The following chemicals are a peroxide hazard upon concentration (distillation/evaporation). A test for peroxide should be performed if concentration is intended or suspected - ***discard after 1 year.***

Acetal	Dicyclopentadiene	Methyl acetylene
Cumene	Diethylene glycol dimethyl ether (diglyme)	Methyl cyclopentane
Cyclohexene	Diethyl ether	Methyl isobutyl ketone
Cyclooctene	Dioxane (ρ -dioxane)	Tetrahydrofuran (THF)
Cyclopentene	Ethylene glycol dimethyl ether (glyme)	Tetrahydronaphthalene
Diacetylene	Furan	Vinyl ethers

Class III: Peroxides derived from the following compounds may explode without concentration – ***discard after 3 months.***

Organic	Inorganic
Divinyl ether	Potassium metal
Divinyl acetylene	Potassium amide
Isopropyl ether	Sodium amide (sodamide)
Vinylidene chloride	

Detection of Peroxides

1. **Iodide Tests.** The presence of most (but not all) peroxy compounds, including hydroperoxides, can be detected by this method: Add 1 mL of the liquid to be tested to an equal volume of glacial acetic acid in a test tube, add a few drops of freshly prepared 5% aqueous potassium iodide solution and shake. A yellow colour indicates a low concentration of peroxide (40-100 ppm as hydrogen peroxide). A brown colour indicates higher concentration of peroxide. Run a blank to make sure the test is really positive. (The test solution has a very short shelf life and will give high blank values if stored for any length of time). Alternatively, addition of 1 mL of a freshly prepared 10% aqueous solution of potassium iodide to 10 mL of an organic liquid in a 25 mL glass cylinder should produce a yellow colour if peroxides are present.
2. Add 0.5 mL of the liquid to be tested to a mixture of 1 mL of 10% aqueous potassium iodide solution and 0.5 mL of dilute hydrochloric acid to which has been added a few drops of starch solution just prior to the test. The appearance of a blue or blue-black colour within a minute indicates the presence of peroxides.

Caution: Alkali metals and their amides may form peroxides on their surfaces. Do not apply standard peroxide tests to such materials because they are both water and oxygen reactive.

3. **Dip strips:** Peroxide test strips, which turn to an indicative colour in the presence of peroxides, are available commercially. E. Merck and Aldrich Chemical Co. make dip strips for semiquantitative detection of peroxides in inorganic and organic solutions. The strip incorporates the enzyme peroxidase, which transfers oxygen from peroxide to an incorporated organic redox indicator. The indicator turns blue in the presence of peroxides. Comparison colour scales are provided for organic and aqueous tests. The strips have limited shelf life.

For volatile organic chemicals, immerse the test strip in the chemical for 1 sec; move the strip slightly to and fro for 3-30 sec until the solvent evaporates. Then breathe slowly on the test strip for 15-30 sec or until the colour stabilizes. The appearance of any blue colour within 3 minutes indicates the presence of peroxide. The colour is then compared with the scale provided on the bottle. If a deep dark blue to brown colour or a green to brown colour is produced, the peroxide concentration is too high for the colour scale.

Modifications of this procedure are required to test non-volatile organic compounds.

For water-miscible compounds, add 3 drops of water to 1 drop of the chemical to be tested. Wet the dip strip in the mixture, wait 2-3 min or until the colour stabilizes, compare with the colour scale provided and multiply the result by 4. For water-immiscible compounds, mix 3 drops of petroleum ether (boiling range 40-60 C) with 1 drop of the low volatility compound to be tested. Wet the dip strip in the mixture and breathe on the reaction zone of the dip strip for 30-60 sec or until the colour stabilizes, and multiply the measured value by 4.

Dip strips provide the highest sensitivity and most accurate quantitation of peroxide concentration for routine testing. They are easier, faster, and safer to use than other methods and they detect a wider range of peroxides.

Other Shock Sensitive Chemicals

Other shock sensitive chemicals include acetylides, azides, nitrogen triiodides, organic nitrates, nitrocompounds, perchlorate salts (especially those of heavy metals such as ruthenium and osmium) and compounds containing diazo, halamine, nitroso and ozonide functional groups. Table 1 lists a number of functional groups in explosive compounds. Some are set off by friction such as the action of a metal spatula on the solid; some are so sensitive that they are set off by the action of their own crystal formation. For example, diazomethane and organic azides may explode when exposed to a ground glass joint.

Picric acid and other polynitroaromatic compounds

Picric acid is commonly used in laboratories and is relatively safe in the form in which it is sold . It is generally sold with 10% water added to stabilize it. However, picric acid can become explosive when it is allowed to dry out or when it forms some metal salts. The following steps should be taken for safe storage and handling of picric acid:

1. Never allow picric acid to be stored in containers with metal caps or to come in contact with any metals.
2. Monitor the picric acid frequently to ensure that it remains damp. Add water if needed.
3. Never try to open a bottle of old or very dry picric acid. Contact EHSO if you find any old or dry picric acid.

Other nitro compounds to mention are: nitroglycerine, trinitrotoluene, nitrocellulose, ethyl nitrate, dinitrophenylhydrazine.

Sodium azide

Sodium azide, though inherently not unstable, may form highly explosive heavy metal azides if contaminated or used improperly. Improper disposal of sodium azide to the sewer may cause the formation of potentially explosive lead or copper azide in plumbing. Do not store sodium azide in container with metal components.

Table 5 is on next page.

TABLE 5 Classes of peroxidizable Compounds³

A. Chemicals that form explosive levels of peroxides without concentration

Butadiene ^a	Divinylacetylene	Tetrafluoroethylene ^a	Vinylidene chloride
Chloroprene ^a	Isopropyl ether		

B. Chemicals that form explosive levels of peroxides on concentration

Acetal	Diacetylene	2-Hexanol	2-Phenylethanol
Acetaldehyde	Dicyclopentadiene	Methylacetylene	2-Propanol
Benzyl alcohol	Diethyl ether	3-Methyl-1-butanol	Tetrahydrofuran
2-Butanol	Diethylene glycol dimethyl ether	Methylcyclopentane	Tetrahydronaphthalene
Cumene	(diglyme)	Methyl isobutyl ketone	Vinyl ethers
Cyclohexanol	Dioxanes	4-Methyl-2-pentanol	Other secondary alcohols
2-Cyclohexen-1-ol	Ethylene glycol dimethyl ether	2-Pentanol	
Cyclohexane	(glyme)	4-Penten-1-ol	
Decahydronaphthalene	4-Heptanol	1-Phenylethanol	

C. Chemicals that may autopolymerize as a result of peroxide accumulation

Acrylic acid ^b	Chlorotrifluoroethylene	Vinyl acetate	Vinylidene chloride
Acrylonitrile ^b	Methyl methacrylate ^b	Vinylacetylene	
Butadiene ^c	Styrene	Vinyl chloride	
Chloroprene ^c	Tetrafluoroethylene ^c	Vinylpyridine	

D. Chemicals that may form peroxides but cannot clearly be placed in sections A-C

Acrolein	<i>tert</i> -Butyl methyl ether	Di(1-propynyl) ether ^d	4-Methyl-2-pentanone
Allyl ether ^d	<i>n</i> -Butyl phenyl ether	Di(2-propynyl) ether	<i>n</i> -Methylphenetole
Allyl ethyl ether	<i>n</i> -Butyl vinyl ether	Di- <i>n</i> -propoxymethane ^d	2-Methyltetrahydrofuran
Allyl phenyl ether	Chloroacetaldehyde diethylacetal ^d	1,2-Epoxy-3-isopropoxypropane ^d	3-Methoxy-1-butyl acetate
<i>p</i> -(<i>n</i> -Amyloxy)benzoyl chloride	2-Chlorobutadiene	1,2-Epoxy-3-phenoxypropane	2-Methoxyethanol
<i>n</i> -Amyl ether	1-(2-Chloroethoxy)-2-phen- oxyethane	<i>p</i> -Ethoxyacetophenone	3-Methoxyethyl acetate
Benzyl <i>n</i> -butyl ether ^d	Chloroethylene	1-(2-Ethoxyethoxy)ethyl acetate	2-Methoxyethyl vinyl ether
Benzyl ether ^d	Chloromethyl methyl ether ^d	2-Ethoxyethyl acetate	Methoxy-1,3,5,7-cycloocta- tetraene
Benzyl ethyl ether ^d	β -Chlorophenetole	(2-Ethoxyethyl)- <i>o</i> -benzoyl benzoate	β -Methoxypropionitrile
Benzyl methyl ether	<i>o</i> -Chlorophenetole	1-Ethoxynaphthalene	<i>m</i> -Nitrophenetole
Benzyl 1-naphthyl ether ^d	<i>p</i> -Chlorophenetole	<i>o,p</i> -Ethoxyphenyl isocyanate	1-Octene
1,2-Bis(2-chloroethoxy)ethane	Cyclooctene ^d	1-Ethoxy-2-propyne	Oxybis(2-ethyl acetate)
Bis(2-ethoxyethyl) ether	Cyclopropyl methyl ether	3-Ethoxypropionitrile	Oxybis(2-ethyl benzoate)
Bis(2-(methoxyethoxy)ethyl) ether	Diallyl ether ^d	2-Ethylacrylaldehyde oxime	β,β -Oxydipropionitrile
Bis(2-chloroethyl) ether	<i>p</i> -Di- <i>n</i> -butoxybenzene	2-Ethylbutanol	1-Pentene
Bis(2-ethoxyethyl) adipate	1,2-Dibenzoyloxyethane ^d	Ethyl β -ethoxypropionate	Phenoxyacetyl chloride
Bis(2-ethoxyethyl) phthalate	<i>p</i> -Dibenzoyloxybenzene ^d	2-Ethylhexanal	α -Phenoxypropionyl chloride
Bis(2-methoxyethyl) carbonate	1,2-Dichloroethyl ethyl ether	Ethyl vinyl ether	Phenyl <i>o</i> -propyl ether
Bis(2-methoxyethyl) ether	2,4-Dichlorophenetole	Furan	<i>p</i> -Phenylphenetone
Bis(2-methoxyethyl) phthalate	Diethoxymethane ^d	2,5-Hexadien-1-ol	<i>n</i> -Propyl ether
Bis(2-methoxyethyl) adipate	2,2-Diethoxypropane	4,5-Hexadien-2-yn-1-ol	<i>n</i> -Propyl isopropyl ether
Bis(2- <i>n</i> -butoxyethyl) phthalate	Diethyl ethoxymethylenemalonate	<i>n</i> -Hexyl ether	Sodium 8,11,14-eicosa- tetraenoate
Bis(2-phenoxyethyl) ether	Diethyl fumarate ^d	<i>o,p</i> -Iodophenetole	Sodium ethoxyacetylde ^d
Bis(4-chlorobutyl) ether	Diethyl acetal ^d	Isoamyl benzyl ether ^d	Tetrahydroxy: 7
Bis(chloromethyl) ether ^d	Diethylketene ^d	Isoamyl ether ^d	Triethylene glycol diacetate
2-Bromomethyl ethyl ether	<i>m,o,p</i> -Diethoxybenzene	Isobutyl vinyl ether	Triethylene glycol dipropionate
β -Bromophenetole	1,2-Diethoxyethane	Isophorone ^d	1,3,3-Trimethoxypropene ^d
<i>o</i> -Bromophenetole	Dimethoxymethane ^d	β -Isopropoxypropionitrile ^d	1,1,2,3-Tetrachloro-1,3-butadiene
<i>p</i> -Bromophenetole	1,1-Dimethoxyethane ^d	Isopropyl 2,4,5-trichlorophenoxy- acetalate	4-Vinyl cyclohexene
3-Bromopropyl phenyl ether	Dimethylketene ^d	Limonene	Vinylene carbonate
1,3-Butadiyne	3,3-Dimethoxypropene	1,5- <i>p</i> -Methadiene	Vinylidene chloride ^d
Buten-3-yne	2,4-Dinitrophenetole	Methyl <i>p</i> -(<i>n</i> -amyloxy)benzoate	
<i>tert</i> -Butyl ethyl ether	1,3-Dioxepane ^d		

Notes

^a When stored as a liquid monomer.

^b Although these chemicals form peroxides, no explosions involving these monomers have been reported.

^c When stored in liquid form, these chemicals form explosive levels of peroxides without concentration. They may also be stored as a gas in gas cylinders. When stored as a gas, these chemicals may autopolymerize as a result of peroxide accumulation.

^d These chemicals easily form peroxides and should probably be considered under Part B.

^e OSHA regulated carcinogen.