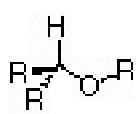
Guidelines for the Safe Handling of Peroxidizable Chemicals

A wide variety of organic compounds spontaneously form peroxides by a free radical reaction of the hydrocarbon with molecular oxygen. Under normal storage conditions, formed peroxides can accumulate in the chemical container and may explode when subjected to heat, friction or mechanical shock. Peroxides tend to explode violently and are capable of causing serious injury or death to researchers in the laboratory. For this reason, it is imperative that all researchers learn to recognize and safely handle peroxidizable compounds.

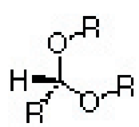
Recognition of Compounds Prone to Peroxide Formation

The first step in learning how to handle peroxidizable compounds safely is to learn how to recognize materials which are prone to hazardous peroxide formation. Although ethers are the most notorious peroxide formers, other peroxidizable organic materials include acetals, certain allylic alkenes (olefins), chloro- and fluoroalkenes, dienes, aldehydes, amides, lactams, ureas, some alkylarenes, ketones, vinyl monomers, and some alcohols. Figure 1 presents peroxidizable chemical structures in decreasing hazard.

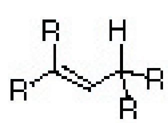
Figure 1: Structures of Peroxidizable Compounds



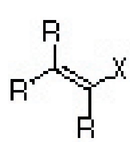
Ethers with alpha hydrogen atoms: e.g. isopropyl ether, ethyl ether, glyme



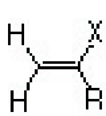
Acetals with alpha hydrogen atoms: e.g. acetal, benzylacetal



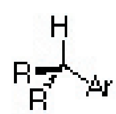
Olefins with allylic hydrogen atoms: e.g. butene, cyclohexene



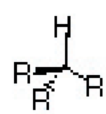
Chloroolefins and fluoroolefins: e.g. tetrafluoroethylene



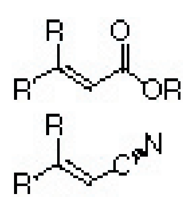
Vinyl halides, esters and ethers: e.g. vinylidene chloride, vinyl chloride, vinyl acetate



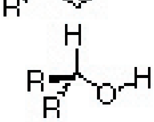
Alkylarenes that contain tertiary hydrogen atoms: e.g. isopropyl benzene



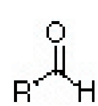
Alkanes and cycloalkanes that contain tertiary hydrogen atoms: e.g. ethylcyclohexane



Acrylates, methacrylates and acrylonitrile: e.g. methyl methacrylate

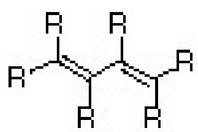


Secondary alcohols: e.g. sec-butyl alcohol

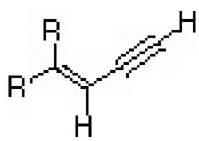


Aldehydes: e.g. benzaldehyde

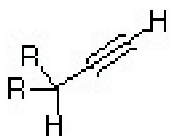
Figure 1 Continued



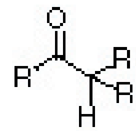
Dienes: e.g. butadiene, chloroprene



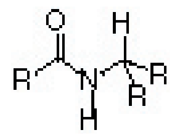
Vinylacetylenes with alpha hydrogen atoms: e.g. diacetylene, vinyl acetylene



Alkylacetylenes with alpha hydrogens: e.g. 3-methyl-1-butyne



Ketones with alpha hydrogen atoms: e.g. diisopropyl ketone, methyl ethyl ketone (MEK)



Ureas, amides, lactams with a hydrogen atom on the carbon attached to the nitrogen: e.g. N-ethylacetamide

Classes of Peroxide Formers

Different peroxidizable compounds tend to form dangerous levels of peroxides at different rates and under different conditions. For some materials, the concentration of peroxide reaches dangerous, shock sensitive levels without concentration. Other compounds do not usually accumulate potentially explosive concentrations of peroxides unless the volatile organic material is reduced in volume--i.e. through incidental evaporation or through distillation.

Table I provides a list of the most common peroxidizable compounds found in many chemistry laboratories. The Table is divided into 4 parts, corresponding to different classifications of peroxidizable compounds which have unique safe handling requirements. Researchers should be familiar with safe handling procedures for the various compounds they are working with.

Table 1--Classes of Peroxidizable Chemicals

List A--Chemicals that form explosive levels of peroxides without concentration

Butadiene
Chloroprene
Divinylacetylene
Isopropyl ether
Tetrafluoroethylene
Vinylidene Chloride

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List B--Chemicals that form explosive levels of peroxides on concentration

Acetal	Diacetylene	3-Methyl-1-butanol	Tetrahydrofuran
Acetaldehyde	Dicyclopentadiene	Methylcyclopentane	Tetrahydronaphthalene
Benzyl alcohol	Diethyl ether	Methyl isobutyl ketone	Vinyl ethers
2-Butanol	Diglyme	4-Methyl-2-pentanol	Other secondary alcohols
Cumene	Dioxanes	2-Pentanol	
Cyclohexanol	Glyme	4-Penten-1-ol	
2-Cyclohexen-1-ol	4-Hepitanol	1-Phenylethanol	
Cyclohexene	2-Hexanol	2-Phenylethanol	
Decahydronaphthalene	Methylacetylene	2-Propanol	

List C--Chemicals that may autopolymerize as a result of peroxide accumulation

Acrylic acid	Vinyl acetate
Acrylonitrile	Vinylacetylene
Butadiene	Vinyl chloride
Chloroprene	Vinylpyridine
Chlorotrifluoroethylene	Vinyladiene chloride
Methyl methacrylate	
Styrene	
Tetrafluoroethylene	

List D--Chemicals that may form peroxides but cannot be clearly placed in Lists A-C

Acrolein	tert-Butyl methyl ether	Di(1-propynl) ether	n-Methylphenetole
Allyl ether	n-Butyl phenyl ether	Di(2-propynl) ether	2-Methyltetrahydrofuran
Allyl ethyl ether	n-Butyl vinyl ether	Di-n-propoxymethane	3-Methoxy-1-butyl acetate
Allyl phenyl ether	Chloroacetaldehyde diethylacetal	1,2-Epoxy-3-isopropoxypropane	2-Methoxyethanol
p-(n-Amyloxy)benzoyl chloride	2-Chlorobutadiene	1,2-Epoxy-3-phenoxypropane	3-Methoxyethyl acetate
n-Amyl ether	1-(2-Chloroethoxy)-2-phenoxyethane	p-Ethoxyacetophenone	2-Methoxyethyl vinyl ether
Benzyl n-butyl ether	Chloroethylene	1-(2-Ethoxyethoxy)ethyl acetate	Methoxy-1,3,5,7-cyclooctatetraene
Benzyl ether	Chloromethyl methyl ether	2-Ethoxyethyl acetate	b-Methoxypropionitrile
Benzyl ethyl ether	b-Chlorophenetole	(2-Ethoxyethyl)-a-benzoyl benzoate	m-Nitrophenetole
Benzyl methyl ether	o-Chorophenetole	1-Ethoxynaphthalene	1-Octene
Benzyl-1-napthyl ether	p-Chlorophenetole	o,p-Ethoxyphenyl isocyanate	Oxybis(2-ethyl acetate)
1,2-Bis(2-chloroethoxyl)ethane	Cyclooctene	1-Ethoxy-2-propyne	Oxybis(2-ethyl benzoate)
Bis(2-ethoxyethyl)ether	Cyclopropyl methyl ether	3-Ethoxypropionitrile	b,b-Oxydipropionitrile
Bis(2-(methoxyethoxy)ethyl) ether	Diallyl ether	2-Ethylacrylaldehyde oxime	1-Pentene
Bis(2-chloroethyl) ether	p-Di-n-butoxybenzene	2-Ethylbutanol	Phenoxyacetyl chloride
Bis(2-ethoxyethyl) adipate	1,2-Dibenzyloxyethane	Ethyl-b-ethoxypropionate	a-Phenoxypropionyl chloride
Bis(2-methoxyethyl) carbonate	p-Dibenzyloxybenzene	2-Ethylhexanal	Phenyl-o-propyl ether
Bis(2-methoxyethyl) ether	1,2-Dichloroethyl ethyl ether	Ethyl vinyl ether	p-Phenylphenetone
Bis(2-methoxyethyl) phthalate	2,4-Dichlorophenetole	Furan	n-Propyl ether
Bis(2-methoxymethyl) adipate	Diethoxymethane	2,5-Hexadiyn-1-ol	n-Propyl isopropyl ether

Bis(2-n-butoxyethyl) phthalate	2,2-Diethoxypropane	4,5-Hexadien-2-yn-1-ol	Sodium 8-11-14-eicosatetraenoate
Bis(2-phenoxyethyl) ether	Diethyl ethoxymethylenemalonate	n-Hexyl ether	Sodium ethoxyacetylide
Bis(4-chlorobutyl) ether	Diethyl fumarate	o.p-Iodophenetole	Tetrahydropyran
Bis(chloromethyl) ether	Diethyl acetal	Isoamyl benzyl ether	Triethylene glycol diacetate
2-Bromomethyl ethyl ether	Diethylketene	Isoamyl ether	Triethylene glycol dipropionate
beta-Bromophenetole	m,o,p-Diethoxybenzene	Isobutyl vinyl ether	1,3,3-Trimethoxypropene
o-Bromophenetole	1,2-Diethoxyethane	Isophorone	1,1,2,3-Tetrachloro-1,3-butadiene
p-Bromophenetole	Dimethoxymethane	b-Isopropoxypropionitrile	4-Vinyl cyclohexene
3-Bromopropyl phenyl ether	1,1-Dimethoxyethane	Isopropyl-2,4,5-trichlorophenoxy acetate	Vinylene carbonate
1,3-Butadiyne	Dimethylketene	Limonene	Vinylidene chloride
Buten-3-yne	3,3-Dimethoxypropene	1,5-p-Methadiene	
tert-Butyl ethyl ether	2,4-Dinitrophenetole	Methyl-p-(n-amyloxy)benzoate	
	1,3-Dioxepane	4-Methyl-2-pentanone	

Chemicals on list A in Table 1 may form explosive levels of peroxides without concentration by evaporation or distillation. These materials are particularly dangerous because they can be hazardous even if never opened. List B materials typically accumulate hazardous levels of peroxides only when evaporated, distilled or otherwise treated to concentrate the peroxides (e.g. deactivation or removal of peroxide inhibitors). Therefore, they have the potential of becoming far more hazardous after they are opened. List C chemicals have been associated with hazardous polymerization reactions that are initiated by peroxides which have accumulated in solution. These materials are typically stored with polymerization inhibitors to prevent these dangerous reactions. List D represents other peroxidizable chemicals which can not be placed into the other categories but nevertheless require handling with precautions.

Minimizing the hazards of peroxidizable compounds

Researchers who handle peroxidizable compounds must learn to handle these materials safely. Safe handling practices and procedures involves making effective purchasing decisions, implementing a storage control program, periodic testing for peroxides and proper disposal of hazardous containers. These elements are described below and are also presented in summary format in Table 2.

Purchasing

Ideally, purchases of peroxidizable chemicals should be restricted to ensure that these chemicals are used up completely before they can become peroxidized. This requires careful experiment planning on behalf of researchers. Researchers should purchase no more material than is needed to complete an experiment within the chemical's safe shelf life.

Storage and Shelf Life

Peroxides tend to form in materials as a function of age. Therefore, it is imperative that researchers are keenly aware of the age of their peroxidizable chemicals. Researchers must date each container of peroxidizable chemical upon arrival in the laboratory. Containers must be dated again when opened for the first time. Additional dates of testing should be added in certain cases (see below). Special labels as depicted in Figure 2 make dating of the containers convenient. These labels are available free of charge from CCHASP.

Table 2 lists the safe shelf life of the different classes of peroxidizable compounds. Suggested time limits are given for retention or testing of these compounds. However, it must be noted that these shelf life durations are minimum criteria; many other references recommend more frequent testing for peroxides.

Peroxide forming chemicals should be stored in their original manufacturers container whenever possible. This is very important in the case of diethyl ether because the iron in the steel containers that this material is shipped in acts as a peroxide inhibitor. In general, peroxidizable chemicals should be stored in sealed, air-impermeable containers and should be kept away from light (light can initiate peroxide formation). Dark amber glass with a tight fitting cap is appropriate

Table 2--Safe storage period for peroxidizable chemicals

Peroxidizable Chemical Classification	Dispose or Test After...[1]
•Unopened chemicals from the manufacturer	18 months
•Opened containers	
List A, Table 1 materials	3 months
List B, Table 1 materials	12 months
List D, Table 1 materials	12 months
Uninhibited List C, Table 1 materials	24 hours
Inhibited List C, Table 1 materials	12 months[2]

Figure 2--Label for peroxide forming chemicals

> **Warning: May Form Explosive Peroxides**
>
> Store in tightly closed original container. Avoid exposure to light, air and heat. If crystals, discoloration or layering is visible, do not move or open and contact CCHASP immediately. Check for peroxides before distilling or concentrating.
>
> **This Chemical has a limited shelf life!**
>
> Date Received_______ Date Opened________
>
> Test or dispose ______ months after receipt or _____ months after opening.
> Do not use chemical if >100 PPM peroxides are detected
>
> Test date_______ Peroxides______PPM
> Test date_______ Peroxides______PPM

Testing for Peroxides

There is a great deal of uncertainty regarding the concentration at which peroxides pose a hazard to researchers. Various sources suggest that the minimum hazardous concentration of peroxides in organic solution is in the range 0.005 - 1.0% (50-10000 PPM). In most safety literature, a conservative concentration of 100 PPM peroxides is used as a control point.

By the end of the expiration date (as indicated in Table 2) for a particular peroxide forming chemical, the person using the chemical should either dispose of it or test it for peroxide content. Any container found to have a peroxide concentration greater than or equal to 100 PPM should be disposed of (call CCHASP for assistance). Materials which are older than the suggested shelf life but have been tested and have no detectable peroxides or peroxide concentrations less than 100 PPM may be retained but should be tested at frequent intervals. All chemicals which are to be distilled must be tested prior to distillation regardless of age. **Important note: Researchers should never test containers of unknown age or origin. Older containers are far more likely to have concentrated peroxides or peroxide crystallization in the cap threads and therefore can present a serious hazard when opened for testing. Please read section below on managing older containers.**

There are several methods that are commonly used to detect for peroxides in the laboratory. Perhaps the most convenient method is the use of peroxide test strips which are manufactured by Aldrich and several other suppliers. These strips are simple to use and can be obtained from CCHASP. For volatile organic chemicals, the test strip is immersed in the chemical for 1 second; then the tester breathes slowly on the strip for 15-30 seconds or until the color stabilizes. The color is then compared with a colormetric scale provided on the bottle. Strips that offer a 1-100 PPM peroxide range are useful for determining if the material is below the control point of 100 PPM. Other testing methods are available. Contact CCHASP for more information.

Management and disposal of old containers

Older containers of peroxidizable chemicals, or containers of unknown age or history, must be handled very carefully and should never be opened by researchers. Any peroxidizable chemical with visible discoloration, crystallization or liquid stratification should be treated as potentially explosive. Older steel containers that have visible rust may also be extremely dangerous. If any of these conditions are observed on a peroxidizable chemical or if the origin and age of the container are unknown, do not attempt to move or open the container. Please call CCHASP for assistance. We will arrange to have the container(s) inspected and if necessary will arrange for disposal.

(Footnotes)

[1] Never open or test containers of unknown origin or age or that have visible evidence of perioxides!

[2] Do not store under inert atmosphere