# PEROXIDES

# AND

# PEROXIDE FORMING

# COMPOUNDS

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materials.  Readily oxidizable organic compounds such as alcohols, ketones, aldehydes, ketones, ethers, and dialkyl sulfoxides can react violently with concentrated perchloric acid. (25).  Digestion of organic material in boiling perchloric acid must be conducted is a chemical fume hood that is specifically designed for that purpose.  Perchloric acid fume hoods include a special wash-down feature to prevent buildup of explosive metallic peroxides.

Perchloric acid solutions are not combustible.  However, anhydrous perchloric acid is unstable and is subject to explosive decomposition at ordinary temperatures or in contact with many organic substances. The maximum concentration of perchloric acid commercially available is an aqueous solution of 70% $HClO_4$.  Cold 70% perchloric acid a strong acid but is not a strong oxidizing agent. The oxidizing power of perchloric acid increases with temperature and hot, concentrated solutions can be very dangerous. Perchloric acid solutions exceeding 70% may result from evaporation (e.g., spill or heated digestion procedure).
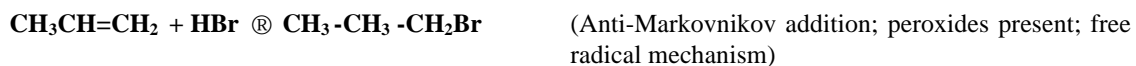
Furr included a review of the properties, hazards and use of perchlorates, including perchloric acid in the 4th edition of the CRC Handbook of Laboratory Safety (25).  He stated that "The most detailed available account of the chemistry of perchloric acid and a reference highly recommended to everyone who will be working with

content and oxygen balance increase (3).  Peroxide sensitivity may also be related to its heat of decomposition, activation energy and reaction kinetics. Some peroxides that are usually regarded as being relatively innocuous may become highly hazardous under certain conditions. Combination of hydrogen peroxide (>30%) and many organic compounds are potentially detonable (21). The potential energy of organic peroxides is low compared with that of conventional explosives, but high enough to be very hazardous. Hence, safety in dealing with organic peroxides depends on knowledgeable handling and storage.

Although physical properties may differ, the reactivity and toxicity of other percarboxylic acids are similar but less than those of peracetic acid. As a rule, longer-chain peroxycarboxylic acids are not shock sensitive, but may detonate when heated.  Peroxyformic and peroxyacetic acids are particularly explosive when relatively pure (21). Violent exothermic reactions may result when peracids contact ethers, metal chloride solutions, olefins, and some alcohols and ketones.  The reaction of these substances, as well as carboxylic anhydrides, with peracids can produce shock-sensitive peroxide derivatives.  "Run-away" peroxide decomposition may result from contact between peracids and some metal ions (e.g., iron, copper, cobalt, chromium, and manganese) (13).

Peracetic acid is probably the most toxic (chronic and acute) of the percarboxylic acids. The acute toxicity of peracetic acid is relatively low [oral $LD_{50}$ (rat) 1540 mg/kg; dermal $LD_{50}$ (rabbit) 1410 mg/kg].  It is highly irritating to skin, eyes and mucous membranes and may be weak carcinogen in mice. There is no such evidence to suggest carcinogenic, reproductive or developmental toxicity in humans. Other peracids (e.g., perbenzoic acid and m-chloroperbenzoic acid) are less toxic, less volatile and less hazardous to handle than peracetic acid (13).  Although the toxicity and irritation hazards of the organic peroxides are moderate, it is prudent to minimize exposure to peroxides and associated materials, including vapors and aerosols. Aliphatic peroxyacids have a sharp, unpleasant

as the peroxide radical abstracts a hydrogen atom from R-H (15). The catalytic potential of organic peroxides and the free radicals they generate, can change the course of a planned reaction, for example (11, 27):

$$CH_3CH=CH_2 + HBr \circledR CH_3\text{-}CHBr\text{-}CH_3$$        (Markovnikov addition; peroxides not present)

$$CH_3CH=CH_2 + HBr \circledR CH_3\text{-}CH_3\text{-}CH_2Br$$        (Anti-Markovnikov addition; peroxides present; free radical mechanism)

   The reversal of the orientation of the addition reaction is known as the "peroxide effect." The premise of free-radical mechanism is supported by the fact that very low levels of peroxide can alter the orientation of the reaction, and conversely, very small amounts of peroxide-inhibitor can prevent it (24). Thus, reagent purity can be extremely important for avoiding undesired results.

   The hazards and consequences of fires and explosions during the laboratory synthesis and use of organic peroxides in the laboratory are widely recognized. There is no way to assure, with any degree of certainty that accidental explosions will not occur when working with such dangerous materials. Spontaneous or induced decomposition may culminate in a variety of ways, ranging from moderate gassing to spontaneous ignition or
 88mposition may culmin(3, 23 rea0.84    TD /F -0.0236  Tw ( ) Tj -160.2 -11.73.92D 0.0286  Tc -0.036  T3.584Tj -206Aur

fume hood.  All sources of accidental ignition must be excluded from areas where peroxides are used.

sensitive than the original solution. For example at $0^o$ C, crystals of acetyl peroxide (extremely impact-sensitive) can precipitate from a 25% solution in dimethyl phthalate.  Users of new or incompletely studied peroxy compounds (especially liquids and solutions) should be alert to the possibility of enhanced hazards on cooling. The appearance of a new phase is a very strong indicator of increased impact sensitivity (23).

   The consequences of storage at elevated temperature are highly scale-dependent. Container size is the primary determinant of the rate of decomposition without self-acceleration. Unless the self-decomposition rate is known to be low, experimental peroxide compositions should be handled and stored in small vessels (23). The self-accelerating decomposition test (SADT) is designed to deal with the scale-dependence phenomenon (17). The SADT (also called the "Temperature of No Return" or "Ignition Temperature") is the temperature at which a heat-sensitive compound can auto-ignite with rapid and violent decomposition. The SADT is used internationally to

diglyme).

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Autoxidation of isopropyl ether forms a variety of higher M.W. peroxides, including cyclic peroxides of acetone, which may be particularly explosive (3, 7).

The degree of peroxide accumulation is determined by the equilibrium established between peroxide formation and degradation, further reaction, and concentration of the peroxide. The equilibrium varies with compound and conditions (1). The structure-induced stability of the peroxide products varies greatly.  For example, α-phenylpropionyl peroxide is so unstable that it cannot be isolated under ambient conditions, whereas t-butyl hydroperoxide is stable for weeks when stored at ambient temperature and in the dark (4).

# USE AND STORAGE OF PEROXIDE-FORMING COMPOUNDS

The opportunistic peroxidation of susceptible solvents or solutions is a function of atmospheric oxygen, light and storage time. Ultraviolet light, including sunlight, promotes both autoxidation and depletion of the inhibitor. But the reaction cannot proceed in the absence of oxygen or oxidizers. The rate of peroxidation increases significantly when stored under conditions that do not exclude oxygen and actinic radiation (6). Since autoxidation is structure dependent, shelf life (before significant peroxidation occurs) and resulting products vary widely between compounds and storage conditions.

Laboratory chemicals known to form peroxides have been categorized into three groups based on their susceptibility to peroxide formation (Table 1).  (NOTE: Certain monomers included in Table 1 are not generally available in laboratory quantities).  The recommended maximum shelf life for each group is conditioned on the premise that the compounds are stored in opaque containers under an inert (oxygen-free) atmosphere, and are based upon time after opening the container. Susceptible solvents are normally supplied with an antioxidant or free-radical scavenger. These additives can slow, but not prevent peroxidation (19). Therefore, it is critical to include procedures to guard against unanticipated results.

The chemicals in Group A can form explosive peroxide levels even in an unopened container, and some will separate from solution. Isopropyl ether is particularly dangerous: the presence of two tertiary carbon atoms makes it readily peroxidizable to a hydroperoxide. The hydroperoxide then polymerizes to form a product that readily precipitates from the ether solution as an explosive crystalline solid (9, 13).

Group B compounds can form explosive levels of peroxides, but usually become hazardous only if the peroxides are concentrated by evaporation, distillation, etc. The common laboratory solvents (e.g., diethyl ether, THF, cyclohexene, the glycol ethers, and isopropanol) become increas0Rnly hazardous when evaporatiol

impurities in higher boiling point chemicals (e.g. long-chain alkyl ethers and the glycol ethers) usually undergo thermal decomposition at distillation temperatures. However, this may not be true in reduced-pressure procedures and dangerous peroxide levels may develop (6).

Peroxides are less volatile than the parent compound, therefore become concentrated upon evaporation of the parent solvent.  It is prudent to test potential peroxide-formers immediately prior to distillation or evaporation. It can be extremely dangerous to distill or significantly concentrate any uninhibited solvent in Groups A or B unless known to be fre

non-hazardous light source (e.g. a flashlight).    The light source should provide back light or side light the bottle to avoid distortion. Visible indicators of peroxide presence include:

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Larger quantities of organic peroxide may require special handling.  Handling, storage and disposal requirements are

(< 1 gm).  Review of the properties of analogous materials can provide valuable guidance in determining risk. Hazard always increases (pattern not necessarily predictable) with increased active-oxygen content. Virtually all organic peroxides become less prone to violent reaction if diluted (23).  A large excess of aqueous sodium hydroxide can be used to hydrolyze and deactivate a reaction mixture (23).

Organic peroxide compositions should be treated with extreme caution until the hazard is determined. Laboratory-scale tests for mechanical and heat sensitivity of organic peroxides have been developed (23). The synthesis of organic peroxides frequently starts from hydrogen peroxide. Mixtures of concentrated hydrogen peroxide and organic substances are powerful and sensitive explosives within certain concentration ranges. This is extremely important in organic syntheses involving hydrogen peroxide (23).

# REFERENCES

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3.  Bretherick, L., in *Improving Safety in the Chemical Laboratory: A Practical Guide*, J..A. Young, Editor, John Wiley & Sons, New York, 1987.
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5.  Hall, Stephen, K., *Chemical Safety in the Laboratory*, Lewis Publishers, Ann Aubor, 1994.
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# TABLE 1.                                    Peroxide-Forming Chemicals (9, 13, 15, 16, 19)

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|---|---|
| A. | Chemicals that form explosive levels of peroxides without concentration.  Severe peroxide hazard after prolonged storage, especially after exposure to air.  All have been responsible for fatalities. *Test for peroxide formation before using or discard after 3 months.* |

| | | |
|---|---|---|
| Butadiene[a] | Isopropyl ether | Sodium amide |
| Chloroprene[a] | Potassium amide | Tetrafluoroethylene[a] Divinyl acetylene |
| Potassium metal | | Vinylidene chloride |

| | |
|---|---|
| B. | Peroxide hazards on concentration. *Test for peroxide formation before distillation or evaporation. Test for peroxide formation or discard after 1 year.* |

| | | |
|---|---|---|
| Acetal | Dicyclopentadiene | 2-Pentanol |
| Acetaldehyde | Diethylene glycol dimethyl ether (diglyme) | 4-Penten-1-ol |
| Benzyl alcohol | Diethyl ether | 1-Phenylethanol |
| 2-Butanol Dioxanes | Ethylene glycol ether acetates (cellosolves) | 2-Phenylethanol |
| Chlorofluoroethylene | Furan | Tetrahydrofuran |
| Cumene (isopropylbenzene) | 4-Heptanol | Tetrahydronaphthalene |
| Cyclohexene | 2-Hexanol | Vinyl ethers |
| 2-Cyclohexen-1-ol | Methyl acetylene | Other    secondary    alcohols |
| Cyclopentene | 3-Methyl-1-butanol | |
| Decahydronaphthalene (decalin) | Methyl-isobutyl ketone | |
| Diacetylene (butadiyne) | 4-Methyl-2-pentanol | |

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|---|---|
| C. | Chemicals, which are hazardous due to, peroxide initiation of autopolymerization. The peroxide-forming potential increases for liquids of this group, especially for butadiene, chloroprene and tetrafluoroethylene, such that these materials should be considered as a peroxide hazard. *Test for peroxide formation or discard liquids after 6 months; discard gases after 1 year.* |

| | | |
|---|---|---|
| Butadiene[b] | Chlorotrifluoroethylene | Vinyl acetylene |
| Chlorobutadiene | Styrene | Vinyl chloride |
| Chloroprene[b] | Tetrafluoroethylene[b] | Vinyl pyridine |
| | Vinyl acetate | Vinyldiene chloride |

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[a]When stored as a liquid monomer.    [b]Can form explosive levels of peroxides when stored as liquid.  When stored as gas, peroxide accumulation may cause autopolymerization.

**FIGURE 1. Peroxidizable Organic Moieties: Ordered From Most to Least Likely to From Dangerous Peroxides (3, 13, 15)**
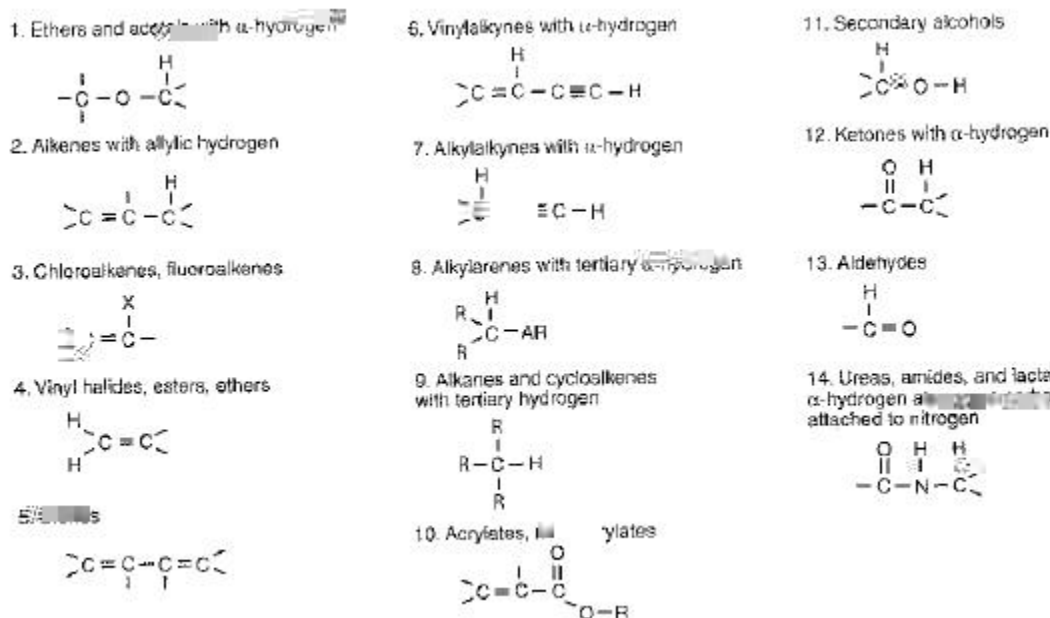


**FIGURE 2. Oxidative Conversion of Isopropyl Ether to the Corresponding Hydroperoxide**
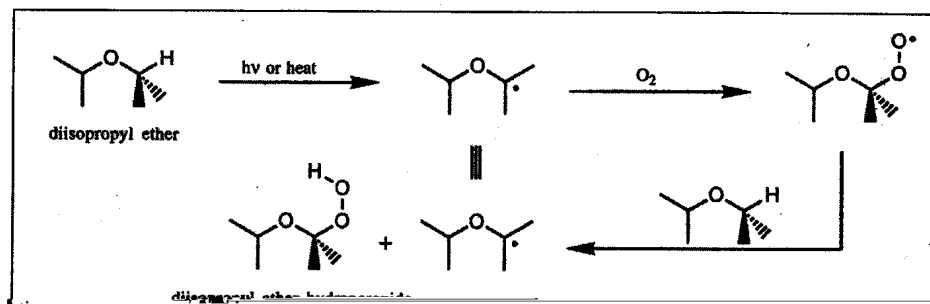


Heat or light generally initiates the free-radical process. The pathway to the hydroperoxide involves subsequent reaction of the ether radical with molecular oxygen to form the peroxy radical, which abstracts hydrogen from another ether molecule to form the hydroperoxide and consequently propagate the chain reaction (8, 15).