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Safe use of Hydrogen Peroxide in the Organic Lab
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Leading references
The monograph, *Applications of Hydrogen Peroxide and Derivatives* offers a very useful introduction to preparation, properties, use as an oxidant in the presence of catalysts, synthetic application, and environmental applications.¹ The web sites of several suppliers and a paper industry trade group offer information on: physical properties, safety, guidelines for handling/storage/usage, and regulatory requirements.² Information on aq. H₂O₂ solutions is available in the American Chemical Society *Reagent Chemicals* series.³ Safety data sheets for commercially available solutions are available from all major vendors; a link to a safety portal from a major trade group is provided.⁴ A review describing industrial synthesis of H₂O₂ is available.⁵

Toxicity
Exposure to odorless (no odor threshold is known) hydrogen peroxide vapors has resulted in injuries to several dozen employee.⁶ H₂O₂ (vapor, mist, or aerosol) is considered to hold immediate danger to life and health; the IDLH level is 75 ppm;⁷ the threshold limit value (TLV) for time-weighted exposure is 1.0 ppm.⁸ Dermal exposure to 30% H₂O₂ can produce skin
damage in a few minutes and serious eye damage in only a few seconds.\textsuperscript{9,10} Although relatively modest acute toxicities (LD50) are reported for oral and dermal exposure in rodent models (2-4 g/kg and > 10 g/kg, respectively),\textsuperscript{1} accidental human ingestion of one pint of 30\% aq. H\textsubscript{2}O\textsubscript{2} resulted in a near fatality.\textsuperscript{11}

**Physical properties**

Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}, [7722-84-1], is an odorless and colorless molecule with a boiling point of approximately 150 °C.\textsuperscript{1,2} Gaseous mixtures rich in H\textsubscript{2}O\textsubscript{2} can explode violently and without warning; under no conditions should ambient pressure distillation be attempted. The melting point of highly concentrated H\textsubscript{2}O\textsubscript{2} is just below 0 °C but the freezing point of aqueous solutions is typically much lower.\textsuperscript{1} Cooling of dilute aqueous solutions typically results in separation of water ice (and some concentration of the hydrogen peroxide) while cooling of concentrated solutions can result in supercooling.\textsuperscript{12} A useful summary of physical properties of H\textsubscript{2}O\textsubscript{2} solutions, including molarity/density/composition, is available online.\textsuperscript{2a}

**Chemical properties**

**Acidity:** The pKa of H\textsubscript{2}O\textsubscript{2} is ~ 12. Concentrated solutions can have pH values as low as 4.3,\textsuperscript{1} and reaction of 30\% H\textsubscript{2}O\textsubscript{2} with carbonyls to form 1,1-dihydroperoxides has been reported to occur in ethereal solvents in the absence of added acid.\textsuperscript{13}

**As oxidant:** H\textsubscript{2}O\textsubscript{2} is a powerful oxidant; the E\textsubscript{0} of 1.8 V places it between KMnO\textsubscript{4} and O\textsubscript{3} in oxidizing strength.\textsuperscript{1,2} Although catalysts are often required to achieve high rates of oxidation, exposure of concentrated H\textsubscript{2}O\textsubscript{2} solutions to flammable or combustible materials (including wood palettes, paper), can result in fires.\textsuperscript{2,11}

**Stability and incompatibilities**
Incompatibilities: Concentrated solutions of H₂O₂ can be highly reactive towards organics and combustible materials and can decompose with considerable force;¹,²,¹⁴ mixtures of hydrogen peroxide and organics may explode upon heating even in the absence of metals.¹⁵ Hydrogen peroxide should never be used in ketone solvents or stored in the presence of aliphatic ketones or almost any aldehydes. In the presence of even moderate amounts of strong acids, such mixtures can be converted to highly explosive 1,2,4,5-tetraoxanes (ketone peroxide dimers), or 1,2,4,5,7,8-hexaoxanones (trimers), or polymeric peroxides.¹⁶ The curious stabilization of H₂O₂ solutions by small amounts of aryl alkyl ketones is discussed below.

Stabilization of aqueous solutions:

Highly pure aqueous solutions may lose only a few percent of activity each year.² However, in the words of Shanley and Greenspan "Hydrogen peroxide is remarkable for the number and variety of decomposition catalysts and for the minute quantities required to give large effect."¹⁴ These and other authors note a remarkable acceleration in the rate of decomposition under basic conditions. Commercially marketed aqueous solutions of hydrogen peroxide typically contain one or more inorganic or organic stabilizers. A recent report describing aryl alkyl ketone stabilizers provides an entry to this discussion.¹⁷

Solutions of H₂O₂ in organic solvents: Hydrogen peroxide has good solubility in many organic solvents and experimenters unable to access the highly concentrated (e.g., 90%, > 30 M)² solutions described in many older synthetic procedures¹⁴ have sometimes turned to organic solutions prepared via extraction of 30 or 50% aqueous solutions with ether or dichloromethane.¹⁸,¹⁹,²⁰ These "anhydrous" solutions, which can be up to 3M in peroxide, should be considered inherently unstable; our group, for example, limits preparation to a maximum of 10 mL. Ethereal solutions of H₂O₂ should never be concentrated or stored, but immediately consumed or quenched. A recent article describes safety issues related to generation and ignition of O₂ head gas within organic solutions of H₂O₂.²¹ Attempts to further concentrate ethereal solutions of H₂O₂ through evaporation or distillation are ineffective and represent needless hazard.²² A recently described alternative involves dissolution of amino acid
perhydrates into organic solvents.\textsuperscript{23} The urea•H\textsubscript{2}O\textsubscript{2} complex, as well as salts of perborates and percarbonates, are sometimes applied as substitutes for H\textsubscript{2}O\textsubscript{2},\textsuperscript{24,25} however, these have limited solubility in aprotic solvents.\textsuperscript{26}

\textbf{Confinement/pressure:}

H\textsubscript{2}O\textsubscript{2} readily decomposes to liberate O\textsubscript{2} and the resulting enrichment of oxygen in the headspace of containers and reactors can dramatically increase fire hazards.\textsuperscript{1} Over the range of 20-100 °C, the rate of decomposition increases approximately 2.2 fold for each rise of 10 °C and confined reactions should be avoided unless adequate precautions have been taken to avoid unintentional over pressurization.\textsuperscript{2} Solutions of hydrogen peroxide are best stored with venting caps. Guidelines for safe storage and handling are available.\textsuperscript{2}

\textbf{Literature on accidents}

The following references discuss accidents related to hydrogen peroxide.\textsuperscript{6,9,11,15}

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\textsuperscript{3} "Hydrogen Peroxide Solutions" ACS Reagent Chemicals (updated January 1, 2017); DOI:10.1021/acsreagents.4167.


18 Extraction into ether has been long known. See, for example: *J. Chem. Soc. Industry*, **1900**, *19*, 777.

19 In our experience, extraction of 1-2 mL of 30% aq. H$_2$O$_2$ with 10 mL of diethyl ether furnishes a 1-2 M ethereal solution.


