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Organic Peroxides: Safety Issues

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Safe use of Hydrogen Peroxide in the Organic Lab

Patrick Dussault
University of Nebraska-Lincoln, pdussault1@unl.edu

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Pat Dussault
Department of Chemistry, University of Nebraska-Lincoln
e-mail: pdussault1@unl.edu phone: 402-472-6951

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Leading references

Applications of Hydrogen Peroxide and Derivatives offers a very useful introduction, including discussions of: methods for 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. H_2O_2 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;[2] a link to a safety data sheet portal is provided.[4] A review describing industrial synthesis of H_2O_2 is available.[5]

Toxicity

Exposure to odorless (no odor threshold is known) hydrogen peroxide vapors has resulted in injuries to several dozen employee.[6] H_2O_2 (vapor, mist , or aerosol) is considered to hold immediate danger to life and health (IDLH) at 75 ppm; [7] the threshold limit value (TLV) for time-weighted exposure is 1.0 ppm.[8] Dermal exposure to 30% H_2O_2 can produce skin damage in a few minutes and serious eye damage in only a few seconds. [9,10] Although relatively modest acute toxicities (LD50) are reported for oral and dermal exposure in rodent models (2-4 g/kg and

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> 10 g/kg, respectively),[1] accidental human ingestion of one pint of 30% aq. H_2O_2 resulted in a near fatality.[11]

Physical properties

Hydrogen peroxide (H_2O_2, [7722-84-1], is an odorless and colorless molecule with a boiling point of approximately 150 °C.[1,2] Gaseous mixtures rich in H_2O_2 can explode violently and without warning; under no conditions should ambient pressure distillation be attempted. The melting point of highly concentrated H_2O_2 is just below 0 °C but the freezing point of aqueous solutions is typically much lower.[1] Cooling of dilute aqueous solutions typically results in separation of water ice (and some concentration of the hydrogen peroxide) while concentrated solutions can undergo supercooling.[12] A useful summary of physical properties of H_2O_2 solutions is available.[2a]

Chemical properties

Acidity*:* The pK_a of H_2O_2 is ~ 12 and concentrated aqueous solutions can have pH values as low as 4.3.[1] As a result, self-catalyzed reactions of 30% H_2O_2 with carbonyls to form 1,1-dihydroperoxides can occur.[13]

As oxidant: H_2O_2 is a powerful oxidant, with an E_0 (1.8 V) falling between $KMnO_4$ and O_3.[1,2] Although catalysts are often required to achieve high rates of oxidation, exposure of concentrated H_2O_2 solutions to flammable or combustible materials (including wood palettes, paper) can result in fires and must be avoided.[2,11]

Stability and incompatibilities

Safe Handling and Storage: Many of the hazards, warnings, and mitigation principles described in the following section are nicely laid out in technical bulletins, many of which are maintained on vendor web sites.[2a-d, 14] The short version: handling, storage, and/or transport of hydrogen peroxide must take into account decomposition (and attendant generation of oxygen) but also the high reactivity towards many organic materials, (including simple combustibles such as paper and wood), many inorganics, (particularly reducing agents), many metals (why container choice can be important), and many redox-active metal ions.

Incompatibilities: Concentrated solutions of H_2O_2 can be highly reactive towards organics and combustible materials and can decompose with considerable force;[1,2, 15] mixtures of hydrogen peroxide and organics may explode upon heating even in the absence of metals. [16] 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-hexaoxanonanes (trimers), or polymeric peroxides,[17] and formation of these and other ketone/ H_2O_2 adducts has been observed even in the absence of acid. [13,18] The curious stabilization of H_2O_2 solutions by small amounts of aryl alkyl ketones is discussed below.

Reactions of hydrogen peroxide, including disproportionation, are often catalyzed by redox-active transition metals ($Fe^{+2/+3}$ and $Cu^{+/+2}$ are two of the best known systems) and exposure of concentrated solutions to metal ions or precursors of metal ions should be avoided at all costs. Thus, transfer of aq. H_2O_2 should employ Teflon needles; if it is absolutely necessary to use a metal needle for extremely small volumes, then approximate amount of H_2O_2should be transferred first to a small vial and any leftover reagent discarded into running water.

Cleaning solutions based upon mixtures of H_2O_2 and strong acids. for example, sulfuric ("Piranha" solution) or nitric) are remarkably corrosive, and call for great care in terms of procedure, personal protective equipment, <u>and choice of vessel/container</u> (the solutions are very destructive of many plastics). [19] Under strongly acidic conditions, H_2O_2 can undergo relatively rapid decomposition with liberation of oxygen;[20] bottles must be vented to avoid over pressurization. Acetone and any other low-molecular weight carbonyl compound <u>must not be introduced</u> into acidic solutions of peroxides: see: http://cenblog.org/the-safety-zone/2015/01/piranha-solution-explosions/

<u>Stabilization of aqueous solutions:</u>

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.[21]

<u>Solutions of H_2O_2 in organic solvents:</u> 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 procedures[14] have sometimes turned to organic solutions prepared via extraction of 30 or 50% aqueous solutions with ether or dichloromethane.[22,23,24] These "anhydrous" solutions, which are typically 1-2 M in H_2O_2, should be considered inherently unstable;[2d] our group, for example, limits preparation to a maximum of 10 mL. A recent article describes safety issues related to generation and ignition of O_2 head gas within organic solutions of H_2O_2.[25] Attempts to further concentrate ethereal solutions of H_2O_2 through evaporation or distillation are ineffective and represent needless hazard.[26] Similarly, ethereal solutions of H_2O_2 should never be stored, but immediately consumed or quenched. The urea•H_2O_2 complex, as well as salts of perborates and percarbonates, are sometimes applied as substitutes for H_2O_2;[27,28] however, these have limited solubility in aprotic solvents.[29] A recently described alternative approach for generation of dry H_2O_2 involves dissolution of amino acid perhydrates into organic solvents.[30] Note that several recent publications describe the incompatibility of even dilute solutions of H_2O_2 with acetone and other ketones or aldehydes.[14] A statement from Solvay's guide on handling and storage is useful to remember: "Investigation of new applications involving hydrogen peroxide and other chemicals should be carried out on a small scale, with adequate precautions taken for dealing with uncontrolled and potentially explosive reactions.[2d]

Confinement/pressure/temperature.

H_2O_2 readily decomposes to liberate O_2 and the resulting enrichment of oxygen in the headspace of containers and reactors can dramatically increase fire hazards.[1] Over the range of 20-100 °C, the rate of decomposition increases more than two-fold for each rise of 10 °C and confined reactions should be avoided unless adequate precautions have been taken to avoid unintentional over pressurization.[2] Solutions of hydrogen peroxide are best stored with venting caps. Guidelines for safe storage and handling are available.[2a-d.]

Literature on accidents. The listed references discuss accidents related to hydrogen peroxide.[6,9,11,15]

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c. http://www.peroxychem.com/chemistries/hydrogen-peroxide (accessed August 2018); d.

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[20] In a solution of 4M nitric acid at elevated temperatures, the half-live for hydrogen peroxide can be less than two hours: "Rate of Hydrogen Peroxide Decomposition in Nitric Acid Solutions" Miner, F. J.; Hagan, R. G. *Ind. Eng. Chem. Proc. Des. Dev.* **1972** *11*, 547-549; DOI: 10.1021/i260044a017

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