

## Procedures for using peroxide (organic peracid; H<sub>2</sub>O<sub>2</sub>; etc.)

Peroxides and peracids are useful oxidants in synthesis. However, their reactions are often very exothermic and therefore can be dangerous. Furthermore, in pure form, they are explosive. Precautions need to be taken to handle these chemicals.

### Storage:

In separated areas reserved for oxidants, well-vented, and no organic compounds/solvents around. Store away from light and heat.

### Use:

1. Make sure peroxides and peracids remain in solution, not as pure solids. Use less concentrated ones: e.g., < 35% H<sub>2</sub>O<sub>2</sub>.
- 2. Never evaporate or distill a solution that contains peroxides.**
3. Carry out new reactions in small scale.
4. Always plan reactions.
- 5. Always add the peroxide to the organic materials (except with acid anhydride) to avoid explosion.**
- 6. Addition of peroxide solutions should be slow.**
7. Ensure the content of peroxide does not exceed 20% during reaction.
8. Provide efficient agitation.
9. Control temperature. Provide adequate cooling to the reaction.
10. Pre-set temperature. Do not increase temperature after addition if no reaction takes place.
- 11. Remove any residual/unreacted peroxides before distillation or evaporation. Perform peroxide test to make sure no peroxide left.**
- 12. Never use acetone or other lower aliphatic ketons as a solvent or co-solvent for extraction or cleaning. (Because explosive acetone peroxide may form!!)**
13. Use nitrogen to reduce the danger of flammable atmospheres (oxygen is produced sometime from reaction).

## Procedure for removal

### (1) Removing from organic reaction mixture for GC analysis

Washing with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution is the safest. Extraction with water might be sufficient for analysis. After analysis, it is better to remove the residual peroxide by extraction with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. The concentration of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> can be from 0.1 to 1 M. It is better to use fresh solutions.

### (2) Removing from aqueous solution before putting in aqueous waste container.

Remove residual peroxides using excess of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The reaction can be exothermic so drop-wise addition is recommended. Alternative, solid Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> can be used, but with ice-bath to control the temperature. **Don't rush!**

Do the math so you know the maximum amount of peroxide, and use excess Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

Use peroxide test to make sure peroxide is gone.

### **(3) Removing from organic reaction mixture for separation of products**

**Be cautions.** Washing with excess of aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution to remove residual peroxide. Do it slowly to make sure no over-heating of the system. Do the test to make sure no peroxide is left. When use rotar-vap, use shields if possible. Wear protection.

### **Reagents that can remove peroxide**

Soluble reductants such as  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_4$ ,  $\text{Na}_2\text{SO}_3$  have been used, while most organic chemists use  $\text{Na}_2\text{S}_3\text{O}_3$ .

Insoluble reductants such as  $\text{MnO}_2$  have also been used. They serve as catalysts to decompose peroxide. The reactions release gases and heat so care need to be applied.

1 M solution of  $\text{Na}_2\text{S}_3\text{O}_3$  is commonly used.

### **Test for complete removable of peroxides.**

(1). Some people used KI-starch test paper to test. In principle this is the most convenient test. The sensitivity is not clear.

(2) Manual KI-starch test. A 1M solution of  $\text{H}_2\text{SO}_4$  (20 mL) containing 1 mmol of potassium iodide and a small amount of starch was prepared. The solution to be tested is diluted. An aliquot of the solution to be tested is added to a portion (1 mL, e.g.) of the KI/starch solution (e.g., 1 mL). The mixture would turn purple if there is peroxide left.

(3) Iron sulfate test. Prepare an approximately 1% solution of ferrous ammonium sulfate. Transfer 5 mL to each of two test tubes and add 0.5 mL of 0.5 M sulfuric acid and 0.5 mL of 0.1 M potassium thiocyanate solution to each tube. Add 5 mL of the methylene chloride solution of the solution to be tested to one of the test tubes and shake well. The aqueous phase in the methylene chloride tube should not develop a brown-red color when examined parallel to the blank.

To be absolutely sure, a combination of (1) and (3), or (2) and (3) is needed. This is essential if you want to evaporate/distill the organic phase to have isolated yields.

**Determination of oxidation efficiency.**

Sometimes it is necessary to check how much oxidant is left after reaction. The following procedure can be applied.

After reaction, the mixture is diluted by methanol to 20 mL. The mole of remaining oxidant can be determined by iodometric titration. A portion (1.0 ml) of the diluted methanol solution was added to 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution (20 ml) containing 1mmol potassium iodide and a small amount of starch. The mixture turned purple due to generation of I<sub>2</sub>. Then, the mixture was titrated with 0.02 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution until the color disappeared.

Ref. First chapter, Application of hydrogen peroxide and derivatives, by C. W. Jones, RSC clean technology monograph, E-book available online for EPFL. Link:

<http://pubs.rsc.org/en/content/ebook/978-0-85404-536-5>.

Chem. Comm. 2006, 4016-4018. And its supporting info.