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Information on Pyrophoric Materials

Background

Pyrophoric materials have the potential to spontaneously ignite upon exposure to the oxygen in air, and in many cases are also water reactive. Exposure to air or moisture can cause them to generate heat and/or fire, as well as flammable and/or corrosive byproducts, by violent decompositions. Pyrophoric materials can take the form of solids, liquids, or gasses. In a chemistry research setting, they are often used in a flammable solvent solution, increasing the fire risk.

Examples of pyrophoric materials include, but are not limited to:

- Organolithium reagents (e.g., alkyl and aryl lithiums, lithium acetylide, lithium amide)
- Organohalogen or Grignard reagents (e.g., RMgX, where R=alkyl and X=halogen)
- Alkyl metal bases (e.g., butyllithiums, trimethylaluminum, triethylboron)
- Metal hydrides (e.g., sodium hydride, germane, lithium aluminum hydride)
- Finely divided metals (e.g., Raney nickel, aluminum powder, zinc dust)
- Used hydrogenation catalysts (e.g., palladium on carbon)
- Metal carbonyls (e.g., nickel carbonyl, iron pentacarbonyl)
- Organozincs (e.g., diethylzinc)
- Aluminum alkyls (e.g., trimethylaluminum)
- Silicon halides (e.g., dichloromethylsilane)
- Red and white phosphorus

The organolithium reagent *tert*-butyllithium (*t*-BuLi) is often the greatest cause for concern due to its extreme reactivity. In December 2008, a laboratory incident involving the use of *t*-BuLi resulted in severe burns and the subsequent death of a young researcher at UCLA. This chemical is highly hazardous and requires special training to handle properly; it is designated as a Restricted Chemical in the SU Chemical Hygiene Plan (Section 5.1), which requires PI approval prior to use. Section 5.2 of the Chemical Hygiene Plan lists methods for granting prior approval. For further information on the UCLA incident, visit this page.

What are the hazards?

Before beginning work, researchers must familiarize themselves with the specific hazards and toxicity of compounds**.** Performing a Risk Assessment is one way of completing this process. General information about risk assessments, with a link to a template, and training can be found on the Stanford EH&S website. A Standard Operating Procedure (SOP) is another method to complete a risk assessment.

General hazards for pyrophoric materials may include:

- Ignition on contact with air and/or water, potentially causing fires or explosions.
- Some are toxic and may come dissolved or immersed in a flammable solvent.
- Other common hazards include corrosivity, toxicity, teratogenicity, peroxide formation, or damage to the liver, kidneys, and central nervous system.

Specific hazard information may be found using manufacturer labels and safety data sheets (SDS) and/or from the following sources:

- Bretherick's Guide to Reactive Chemical Hazards
- e-EROS (Encyclopedia of Reagents for Organic Synthesis)
- Sittig's Handbook of Bretherick's handbook of reactive chemical hazards in SearchWorks catalogToxic and Hazardous Chemicals and Carcinogens
- Wiley Guide to Chemical Incompatibilities
- NIOSH Pocket Guide
- The Synthetic Organic Chemist's Companion
- Handbook of Synthetic Organic Chemistry
- CAMEO Chemicals
- Stanford Chemical Safety Database
- xSearch (Stanford Library custom chemical safety search engine)

How do I store this?

The storage of unused reagents is a key aspect of working safely with pyrophoric materials. Researchers may utilize the Stanford Compatible Storage Group Chemical Classification System to determine chemical compatibilities (pyrophoric materials are Storage Group B). To find the appropriate storage group for a given chemical, check your lab's online chemical inventory or search using Stanford's Chemical Safety Database.

- Store as directed by the manufacturer.
- Keep pyrophoric chemicals segregated from flammable/combustible materials or other incompatible chemicals.
- Avoid storage areas near to heat/flames, oxidizers, and water sources.
- Minimize quantities of pyrophoric material stored in the laboratory.
- Date all containers upon receipt and periodically check the condition of the container and material.
- Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name and hazard warning.
- Store pyrophoric materials in a secondary container of sufficient size, with only compatible materials in the secondary.

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How can I work safely?

As part of the scientific process, researchers and PIs must continually consider how to minimize or eliminate exposure to workplace hazards. The most widely accepted system for controlling exposure to hazards is the Hierarchy of Controls from the National Institute for Occupational Safety and Health (NIOSH). In this system, researchers consider different methods to manage/reduce exposure, in order of effectiveness.

(1) Elimination: Remove the pyrophoric reagent from the process. This is the most effective risk reduction method and requires creativity.

- Develop alternative synthetic routes in which pyrophoric or highly reactive compounds are not required to accomplish your procedure successfully.
- Consider changing your target end product if other products may be equally effective for the application and do not require the use of pyrophoric reagents.

(2) Substitution: Use a less hazardous reagent.

- Resources such as March's advanced organic chemistry can be used to explore alternate reagents.
- For example, the following trends apply to estimate the pyrophoricity of metal alkyls.

Change in Property	Effect on Pyrophoricity
Metal Content ↑	Pyrophoricity ↑
Oxygen content ↑	Pyrophoricity ↓
Solvent vapor pressure ↑ (or boiling point ↓)	Pyrophoricity ↑
Temperature ↑	Pyrophoricity ↑

- Use less electronegative (higher atomic number) halogen components in organohalogen reagents (e.g., Grignard reagents) to reduce bond polarity, which also reduces reactivity and hazard.
    - Reactivity: C-F > C-Cl > C-Br >> C-I.
- Use organolithium reagents with less bulky alkyl groups to reduce reactivity.
    - *n*-butyllithium is significantly more stable, less reactive, and therefore less hazardous, than *tert*-butyllithium, although they are both pyrophoric.
    - Reactivity: *n*-BuLi < *sec*-BuLi < *t*-BuLi. This relationship holds for all organometal compounds.
    - Similarly, *n*-hexyllithium should be considered an alternative to *n*-butyllithium due to its lower tendency to ignite when compared to *n*-butyllithym.

(3) Engineering controls: Isolate people from the hazard.

- Perform work in a glove box or glove bag under inert atmosphere (e.g., nitrogen, argon) to reduce exposure to oxygen and/or water.
- Work in a fume hood, over a spill tray, using the appropriate sash height and working distance. For more information on proper fume hood use, please see the Laboratory Ventilation Management Program, Section 9.1.1.
- Use techniques that prevent the material from contacting air, such as vacuum manifold techniques (i.e., Schlenk technique) if working in a fume hood.
- Store pyrophoric gases in ventilated toxic gas cabinets.
- Utilize blast shields if there is a potential explosion hazard (these may be borrowed from the Stanford EH&S Safety Store).

(4) Administrative controls: Use safe work practices.

- Require proper training and practice before handling pyrophoric materials.
    - Never leave potentially hazardous experiments unattended; if this is unavoidable, post signage identifying the contents, hazards, and your contact information.
    - Do not work alone while handling pyrophoric materials, use an in-person buddy who is knowledgeable of the hazards and able to appropriately respond to an emergency.
    - Basic training requirements are the same as those identified in Section 10 of the Stanford University Chemical Hygiene Plan.
    - Specific training requirements include:
        - Fire Extinguisher Use in Labs (EHS-3700)
        - Laboratory-specific training, such as review of SDS for chemicals involved in process/experiment and review of the standard operating procedure (SOP)
        - PI Approval of each new user
        - Training can be documented on a PI-approved SOP
- Develop material- and lab-specific safe operating procedures (SOPs). Example considerations are listed below.
    - For reference, see Stanford's General Use SOP for Highly Reactive/Unstable Materials.
        - EH&S also provides a specific *tert*-butyllithium SOP template. While the techniques in this template are only *necessary* for *tert*-butyllithium, they are good practices for working with any pyrophoric material.
    - Use and purchase materials in the smallest quantities necessary and design experiments on the smallest scale or lowest concentration possible. The PI should set quantity limits for pyrophorics in their labs.
    - Larger volumes of pyrophoric liquids (> 20 mL) should be transferred by cannula directly into the reaction flask or a calibrated addition funnel.

    - If using a syringe, purchase a Luer lock with a long reusable needle and hard plastic or glass plunger, and only fill the syringe to half of its working volume to avoid accidental exposure.
        - Never reuse a syringe for more than one transfer, as this can lead to clogging of the barrel
        - Do not transfer more than 20 mL of pyrophoric liquids by syringe.
    - If the original manufacturer's container that has an air-sensitive seal or cap, use a non-coring needle no larger than 16-gauge and create a new puncture hole each time, which avoids enlarging existing holes.
        - Note: Sigma-Aldrich warns that the SureSeal cap (and similar caps from other suppliers) may lose integrity over multiple uses. If the bottle will be used multiple times and stored, they recommend transferring the contents to Schlenkware or using an Oxford Valve Cap or similar covering the SureSeal. See AL-134 and AL-195.
    - Dry all glassware, syringes, needles, atmosphere, solvents, and other reagents when working with water-reactive compounds.
        - Glassware and metal syringes can be dried by flaming under vacuum or in an oven overnight. Allow the flask to cool in a dry atmosphere, such as a Schlenk line or in a desiccator.
        - Compatible plastic syringes can be dried by storing in a desiccator with the plunger removed.
        - Solvents can be dried using a solvent system or by adding dried molecular sieves to a fresh bottle. Please note that solvent stills are discouraged due to excessive quantities of flammable solvents, water reactive drying agents (e.g., sodium metal) in combination with heat and a nearby water-cooled condenser.
- Maintain good housekeeping practices.
    - Remove clutter from your work area.
    - Keep all combustible and flammable materials away from pyrophoric materials.
    - Follow manufacturer's recommendations for use and storage.
    - Dispose of old bottles with excessive precipitates or unreliable concentrations.

(5) PPE: Protect the worker with personal protective equipment as a last line of defense.

- Always wear a fire resistant (FR) lab coat with tight cuffs.
- Wear protective eyewear, such as fully enclosed safety goggles or face shield with safety glasses or goggles.
- Wear appropriate gloves, such as flame-resistant Nomex gloves under nitrile gloves.
- Tie back hair to avoid catching it on fire, exposing it to chemicals, or having it interfere with your vision.
- Wear long pants (or equivalent) and closed-toe shoes that cover the whole foot.
- Avoid loose sleeves that may get caught or knock something over.
- Wear natural fabrics like cotton; avoid synthetic fibers, which can melt when ignited.

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How do I respond to emergencies?

As part of the scientific process, researchers and PIs must carefully review all aspects of an experiment to anticipate incidents that might occur, and to be ready to respond quickly to emergencies. There is always the potential for unwanted events to happen, even when hazards are recognized, assessed, and minimized. Preparing for emergencies is critical for mitigating the effects of any exposure or damage that might occur.

Prepare

- Familiarize yourself with the location of the eyewash and safety shower.
- Locate your laboratory first aid and spill kits.
- Locate an appropriate fire extinguisher.
    - Many pyrophoric chemicals, like metal hydrides, require the use of a Class D fire extinguisher, check your chemical supplier's SDS for more information.
    - If your fire extinguisher needs to be repaired, replaced, or you need a new one installed, submit a Stanford SUFMO Work Request.

Exposure

- If a hazardous material has come into contact with your body, remove contaminated clothing and use either the eyewash or safety shower for 15 minutes before seeking further medical attention.
    - Call for help if needed.
    - If only one eye is affected, be careful not to flush contaminated water into the other eye by keeping the affected eye lower.
    - **Use the eyewash or safety shower even if materials are water reactive**, as the high flow rate will deprive the fire of oxygen and rapidly cool flammable materials.
- If an incident occurs, bring along a copy of the SDS(s) when seeking medical attention.
- For all serious injuries that require medical attention, call 911 or go to the Stanford Hospital Emergency Department (1199 Welch Road, Palo Alto).
    - After the injured person and the scene is secure, report the serious injury to EH&S by calling 650-725-9999 (answered 24 hours a day, 7 days a week).
- For non-emergency injuries and illnesses, go to the Stanford Occupational Health Center (484 Oak Road, Stanford). Contact 650-725-5308 for consultation (open Monday through Friday, 8 am - 4 pm).
    - After hours, the Stanford Hospital Emergency Department is available for prompt medical attention.
- After any incident (spills, near-miss, fire, or injury), complete the Incident Report (SU-17) form.

Spills

- Exert extreme caution due to potential spontaneous combustion and potential ignition of flammable solvents or other materials in the area.
- Only clean up a spill of a pyrophoric material if it is not on fire, smoking, or otherwise showing signs of instability.
- If a spill is on fire, smoking, or otherwise showing signs of instability, pull the fire alarm and call 911.
- To report a hazardous material spill or any other incidents which may affect health, safety, or the environment, call 650-725-9999 (answered 24 hours a day, 7 days a week), even if you have also called 911.
- After any incident (spills, near-miss, fire, or injury), complete the Incident Report (SU-17) form.

Fires

- If the fire is small (less than knee height) and has not spread from the point of origin, you may use the appropriate fire extinguisher, if you have been trained and are comfortable doing so.
    - Pull the fire alarm and call 911 for any fire that is larger than knee height or has spread.
    - NEVER use more than one fire extinguisher. If it's not out after one, you cannot fight it.
- Pyrophoric chemicals typically require a Class D fire extinguisher.
    - Check the SDS of your specific material to verify the correct fire extinguisher.
    - For example, *tert*-butyllithium and other pyrophoric solutions require ABC fire extinguishers.
- To report the incident, call 650-725-9999 (answered 24 hours a day, 7 days a week), even if you have also called 911.
- After any incident (spills, near-miss, fire, or injury), complete the Incident Report (SU-17) form.

How do I dispose of this?

Disposal is often the final step in ensuring that a researcher and EH&S Environmental Protection staff safely handle pyrophoric materials. Improper disposal can lead to fires or other mishaps, injuries, or lasting effects on the environment. General guidelines are listed below. However, please reach out to the Stanford Environmental Protection team for any questions about waste disposal.

- Handling and disposal should be done in accordance with the lab protocol approved by the Principal Investigator (PI).
- Reactions should be quenched before disposal. Ensure proper training before quenching procedures are attempted.

- Bulk materials, like excess reagent in the original manufacturer's container, should not be quenched prior to disposal, they can be tagged with a waste tag at wastetag.stanford.edu.
- Ensure proper containment before removal of a potentially pyrophoric material from a glove box or other inert atmosphere (e.g., original manufacturer's container or properly sealed vessel).
- Information about waste disposal procedures can be found on the Stanford EH&S website here.

Additional Related Resources

- Aldrich Technical Bulletin AL-164
- e-Eros Encyclopedia of Reagents for Organic Synthesis: *t*-Butyllithium
- PNNL Technical Report on Handling Pyrophoric Reagents
- LBL Chemical Hygiene and Safety Plan
- Lessons learned
  - *C&EN* Lessons Of The Tragedy At UCLA
  - Stanford *n*-Butyllithium Lessons Learned
  - UC Davis Pyrophoric Metal Fire Lessons Learned
  - UCI Pyrophoric Materials Cause Chemical Fume Hood Fire Lessons Learned
  - BNL Silane Safety/Lessons Learned and Accident Prevention
  - Safety Partners Titanium: Beautiful but Dangerous Incidents, Accidents, and Near Misses
- Resources from other universities
  - Princeton Pyrophoric Materials
  - UIUC Handling Pyrophoric and other Air/Water Reactive Materials
  - UMN Pyrophoric Chemicals Guide
  - UCSB Safe Use of Pyrophoric/ Water Reactive Reagents Fact Sheet
  - CMich Pyrophoric & Water-Reactive Chemicals Appendix
  - CMU Pyrophoric Handling Procedure