Guidelines for Handling Pyrophoric Materials

Introduction

Pyrophoric and water reactive materials can ignite spontaneously on contact with air, moisture in the air, oxygen, or water. Failure to follow proper safety procedures can result in fire or explosion, leading to serious injuries, death or significant damage to facilities. OSHA and US DOT respectively, defines pyrophoric as a chemical that will ignite spontaneously in air at a temperature of 130 ºF (54.4 ºC) or below. A material that is a liquid or solid, even in small quantities and without an external ignition source, can ignite within 5 minutes after contact with air.

This document describes how to properly handle, dispose, and respond to emergencies when working with pyrophoric materials.

NOTE: Handling of pyrophoric materials is high risk and must always be performed with appropriate engineering controls by at least two trained individuals.

Organolithium Compounds

Organolithium compounds fall into four board categories: alkyllithiums (exemplified by n-butyllithium), aryllithiums (such as phenyllithium), lithium amides (for example lithium diisopropylamide and lithium hexamethyldisilazide) and lithium alkoxides (such as lithium t-butoxide). They are all highly corrosive, flammable, and pyrophoric. Their inherent corrosive nature can result in severe chemical and thermal burns upon exposure if not handled properly. Furthermore the reagents are themselves flammable, and are typically supplied in organic solvents which intensify the flammability.

When planning to use alkyl lithium there are a number of factors that should be taken into consideration. For example, alkyl lithium having the same concentration pyrophoric effect would increase in order of n-butyllithium<sec-butyllithium<t-butyllithium. Note that as the concentration of alkyl lithium increases in formulation so does the pyrophoricity. Other factors that should be taken into consideration are the lower the flash point of the solvent the greater the pyrophoricity, as well as higher relative humidity and higher ambient temperature will also result in greater pyrophoricity.
Other examples of forms of pyrophoric/water reactive chemicals include:

- **Metal carbonyls**: Lithium carbonyl, nickel tetracarbonyl
- **Group I (Alkali) metals**: Lithium, potassium, sodium, sodium-potassium alloy (NaK), rubidium, cesium, francium
- **Metal powders (finely divided)**: Cobalt, iron, zinc, zirconium
- **Metal hydrides**: Sodium hydride, lithium aluminum hydride
- **Nonmetal hydrides**: Diethylarsine, diethylphosphine
- **Non-metal alkyls**: \( R_3B, R_3P, R_3As \); tetramethyl silane, tributyl phosphate
- **White and red phosphorus**

**Alternative Organolithium Reagents**

Although pyrophoric chemicals such as organolithium have proven to be important in the formulation of a variety of important precursors for different applications; there are several other innovative organolithium compounds that are safer to handle and have similar reactivity to the traditional reagents.

These alternatives should be considered in the synthetic process:

- 33 wt. % \( n \)-hexyllithium in hexanes, which has similar reactivity to the equivalent concentration of \( n \)-butyllithium in typical applications.
- Solutions of lithium diisopropylamide have been shown to be non-pyrophoric.
- \( t \)-butyl lithium in heptane, although still pyrophoric it is much safer to handle than the traditional pentane formulation because heptane has a much higher flash point (Fp = -1°C) than pentane (Fp = -49 °C).

**Controlling the Hazards**

Since these reagents are known to ignite on contact with air and/or water, they must be handled under an inert atmosphere and in a way that rigorously excludes air/moisture. Furthermore, some of these reagents are toxic and many come dissolved or immersed in a flammable solvent. Other common hazards include corrosivity, teratogenicity, water reactivity, peroxide formation, and can cause damage to the liver, kidneys, and central nervous system.

Therefore, prior to using/handling any pyrophoric chemical all workers should be trained on the hazards and specific chemical handling procedures:

- Conduct a risk assessment before starting experiment; if possible use safer chemical alternatives.
- Remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric or water reactive chemicals will be used. This will minimize the risk if a fire should occur.
- Keep combustible materials, including paper towels and Kimwipes, away from reactive reagents.
- Keep the amount of pyrophoric or water reactive material present in the lab to the smallest practical amount.
- Use and handle the smallest quantity possible. It is better to do multiple transfers of small volumes than attempt to handle larger quantities at once.
• A “dry-run” of the experiment should be performed using low-hazard materials, such as water or solvent, as appropriate.
• Use the “buddy system”. Do not work alone with pyrophorics.
• Conduct the procedure only after a supervisor has observed you performing the proper technique unassisted.
• All glassware used for pyrophorics should be oven-dried and free of moisture.
• Keep an appropriate fire extinguisher or extinguishing material close at hand.
• Remove all other flammable material from the hood, as well as any clutter.
• Secure the pyrophoric reagent bottle to a stand.
• Pyrophoric liquid transfer:
  o Sigma-Aldrich recommends the use of a long needle, 1-2 foot, and a syringe that is twice the volume of liquid to be transferred.
  o The syringe needs to be secured so if the plunger blows out of the body it, and the contents will not splash anyone.
  o Use a syringe to transfer small volumes (< 20 mL). The cannula technique is recommended for larger volumes.

Personal Protective Equipment

ALWAYS wear proper PPE at all times when handling pyrophoric materials.

Eye Protection:

• Chemical splash goggles, or safety glasses, must be worn whenever handling pyrophoric chemicals.
• A face shield is required any time there is a risk of explosion, large splash hazard or a highly exothermic reaction.

Skin Protection:

• Gloves must be worn when handling pyrophoric chemicals. See the Hand Protection for Pyrophorics chemical safety update for the appropriate glove choice. Please also refer to the Hand Protection for Handling Liquid Pyrophorics Frequently Asked Questions.
• A buttoned appropriately fitted fire resistant Nomex lab coat must always be worn. Never wear synthetic clothing.
• No open toe shoes are allowed.
Engineering Controls

Ensure that all use and handling of pyrophoric material is performed in an appropriate glove box or in a chemical fume hood using techniques to ensure isolation from air/moisture (see Aldrich technical bulletins 134 and 164).

Glove (dry) box:

A Glove box is an excellent control device when inert or dry atmospheres are required. Pyrophoric solids must be handled in an appropriate glove box and it is strongly recommended for liquids and gases, particularly transfers.

Fume Hood:

If an inert atmosphere glove box is not available and a pyrophoric reagent such as t-butyllithium solution needs to be used, the solution can be safely transferred in a fume hood using either a syringe or double-tipped needle (cannula). This must take place under an inert atmosphere using proper handing techniques (see Aldrich technical bulletins 134 and 164).

Some pyrophoric materials are stored under kerosene (or other flammable solvent); the use of a fume hood is required to prevent the release of flammable vapors into the laboratory. Many pyrophoric chemicals release noxious or flammable gases and should be handled with the fume hood sash down at the lowest feasible position.

Storage

Avoid areas with heat/flames, oxidizers, and water sources. Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name and hazard warning. Pyrophoric chemicals should be stored under an atmosphere of inert gas or under kerosene, oil, or within a solvent as appropriate [the material must be preserved during storage and while dispensing]. Do NOT allow pyrophoric chemicals stored in solvent to dry out. Check periodically to ensure there is a visible amount of solvent in the bottle.

Disposal

- Prior to disposal of small residue of pyrophoric materials it should be quenched by hydrolysis and/or neutralization with adequate cooling using an inert solvent such as heptane.
- All materials that contain or are contaminated with pyrophoric chemicals should be disposed of as hazardous waste.
- A container with residual material must NEVER be opened to the atmosphere.
- If the pyrophoric chemical was originally stored in solvent and is dried, hydrate the chemical with an appropriate solvent before pick-up; use the same solvent used for the original reagent.
Emergency Procedures

- Pyrophoric specific spill adsorbents such as: dry sand, powdered soda ash (sodium carbonate), calcium oxide (lime) or clay-based kitty litter should be kept at arm’s length. Copious amounts of these materials should be used to completely cover/smother any spill that occurs.
- If a person is exposed, or on fire, use the stop, drop, and roll method. A safety shower, a fire blanket, or fire extinguishers are the most effective means of controlling clothing on fire.
- The recommended fire extinguisher is a standard dry powder (ABC) type. Class D extinguishers are recommended for combustible solid metal fires (such as sodium).
- Call 9+911 from a campus phone or 476-6911 from a cell phone for emergency assistance.

References

6. A fatal 2009 laboratory incident at UCLA involved an accident with t-butyllithium. A detailed account of the accident is available courtesy of the American Chemical Society.
7. "Safe handling of organolithium compounds in the laboratory" Schwindeman, J.A.; Woltermann, C.J.; Letchford, R.J.; *Chemical Health & Safety*, May/June 2002, 6-11
8. Working with Pyrophorics Safety Video