

Columbia University Environmental Health and Safety

The Safe Use of Pyrophoric Reagents

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EXECUTIVE SUMMARY

November, 2009—Due to a recent incident involving the use of dry powder *sodium hydride*, EH&S has made some additions to this document to place greater emphasis on the use of solid pyrophorics. A brief section has been added before the techniques outlining the manipulation of liquid reagents to address issues concerning the use of metallic hydrides. All other material erstwhile contained herein is still held to be valid.

INTRODUCTION

In light of the recent fatal accident at UCLA, Columbia University EH&S has developed the following bulletin to serve as a guide for those who currently, or might in the future, use pyrophoric reagents. This guide is NOT to serve as a replacement for formal training in lab techniques or lab safety. Only qualified and experienced laboratory workers should ever attempt to manipulate these materials, and only after they have extensively researched and consulted knowledgeable peers with regard to the correct techniques for doing so. Failure to follow proper handling precautions can result in the exposure of these materials to the atmosphere, with consequences including serious injury or death.

Pyrophoric compounds are widely used in labs at Columbia. Here are some examples of the more common reagents:

- Organolithiums, such as t-Butyllithium
- Organozincs, such as diethylzinc
- Organomagnesiums (Grignard reagents)
- Aluminum alkyls, such as trimethyl aluminum
- Metallic hydrides, such as sodium hydride, potassium hydride, lithium aluminum hydride and some boranes.
- Finely divided metals, such as: aluminum, lithium, magnesium, titanium, zinc, zirconium, sodium, and potassium.

HAZARD INFORMATION

Pyrophoric reagents are extremely reactive to oxygen and moisture, and precautions must always be taken to prevent their exposure to air, which usually leads to spontaneous ignition. The danger of this reactivity is often exacerbated by the fact that these reagents are sold in solvents that are extremely flammable, such as ethyl ether, tetrahydrofuran (THF), or pentanes. When possible, compounds stored in pentanes or hexanes should be avoided, as storage in heptanes is *slightly* less hazardous.

The hazards from using these chemicals stem from fires that could result from the chemicals themselves and the solvents containing them, as well as any secondary fires that may spread to nearby flammable or combustible materials. Segregating combustible materials from storage as well as work areas is the best way to prevent dangerous secondary fires that could cause serious property damage and personal injury.

CONTROL MEASURES

Engineering Controls

- Solid pyrophorics must only be handled in an inert atmosphere glove box. Less expensive inert atmosphere glove bags are also available (<http://www.sigmaaldrich.com/labware/products/aldrich-atmosbag.html>).
- Pyrophoric liquids, or compounds dissolved in a liquid, should be stored in sealed containers with PTFE-lined septa to prevent air exposure.
- Handling of liquid pyrophorics must be conducted via cannula or syringe transfer to prevent exposure to air if not manipulated within an inert atmosphere (see below for more details).
- Manipulation of these reagents via syringe or cannula should always be conducted in a certified chemical fume hood, over a spill tray if possible, with the sash at the lowest practicable working height.
- Needles should be equipped with locking mechanisms to prevent accidental disconnection and release of reagents.
- Mineral oil bubblers must be employed at all times to release excess pressure from reagent or reaction vessels that can contribute to accidents. Balloons used for air-sensitive reagents are not suitable with pyrophorics.
- A blast shield is excellent, if available.

Administrative Controls/Safe Work Practices

- All users of pyrophoric reagents must first go through EH&S Lab Safety and Fire Safety training before working in a lab (<http://www.ehs.columbia.edu/Training.html>).
- Users must be trained thoroughly by a qualified and experienced supervisor on techniques for handling pyrophorics, and must be directly supervised when first starting with these techniques. It is best to try a few “dry runs” with the techniques using something less hazardous prior to using an actual pyrophoric material. Supervisors must also understand the hazards associated with these materials along with emergency response procedures, and relay this information to new users.

THE SAFE USE OF PYROPHORIC REAGENTS

Pyrophoric materials must only be used while other knowledgeable and experienced lab workers are present and aware of the procedure.

Pyrophoric materials must be used and stored away from all other flammable and combustible materials such as paper, bench liners, and solvents. Even open containers of water should be kept away due to the potential for a violent reaction.

Reagent bottles typically come in secondary containment within metal cans. If it is resealable, keep the manufacturer's can for storage of your reagents when not in use, and for disposal of the bottle after completion of the experiment involving the material. Otherwise, store in a clean, dry desiccator.

Highly flammable synthetic clothing is to be avoided, as well as loose clothing. Always wear long pants and closed-toe shoes in the lab. Tie back all loose hair to prevent ignition in the event of a flash fire.

Purchase only the smallest amounts necessary for your work, and discard old materials promptly. Reagents should be viewed with skepticism if older than six months, or if the septa have been pierced more than six times.

Personal Protective Equipment (PPE)

At a minimum, gloves, safety glasses, and a protective lab coat must be worn.

A lab coat made of fire resistant material, such as Nomex, is preferred to polyester or cotton.

It is recommended that you wear leather or Kevlar gloves beneath nitrile gloves for fire protection purposes.

Fully enclosed safety goggles or a face shield are preferred, if available, as they offer greater facial protection than safety glasses.

Emergency Preparedness and Response

Always know the exact location of your eyewash and shower and how to use all emergency equipment. Test your eyewash regularly. Keep the area around them clear from obstruction at all times.

It is best to choose the chemical fume hood closest to the safety shower to perform this work.

Users may encounter small fires at the tips of needles – know to expect this, and do not panic. A beaker of sand is useful for extinguishing this “pilot light”.

For skin exposures, if there are no severe burns, rinse with water for 15 minutes and seek first aid.

Keep a container of soda ash or sand within arm's reach in case a small fire occurs, as this can be safely used to smother the flames.

Class ABC dry chemical extinguishers can be safely used for most organometallic reagents that are dissolved in organic solvents, such as T-Butyllithium in heptanes.

For aluminum alkyl fires involving neat reagents, use MET-L-KYL® extinguishing powder, made by Ansul, Inc.

If you have access to Class D fire extinguishing material, know where it is and how to use it. Typically, Class D extinguishing material is used for large quantities of fires involving combustible metals. Contact EH&S at (212) 854-8749 (Morningside) or (212) 305-6780 (CUMC) to determine what type of extinguishing material is needed.

DO NOT use a CO₂ extinguisher to attempt to quench a fire with pyrophoric reagents – this can greatly exacerbate the problem.

Sodium Hydride (and other metallic hydrides)—Special Considerations

Sodium hydride is extremely reactive toward water, to the point that it will spontaneously react with moisture in air and ignite. As such, it should be treated with extreme caution as a solid pyrophoric material. It is strongly recommended that you substitute a mineral oil dispersion of sodium hydride for the “dry powder” form whenever possible. If this substitution cannot be made, “dry powder” sodium hydride, or any other metallic hydride such as lithium aluminum hydride or potassium hydride, must only be manipulated in an inert atmosphere, and must never be exposed to air. If a fire ever results during the use of a metallic hydride, use copious amounts of sand to smother the flames and the reagent. Never use an ABC fire extinguisher in an effort to put out a fire involving sodium hydride, as the force from the extinguisher can rapidly disperse fine powders.

TECHNIQUES FOR REAGENT TRANSFER

Equipment Preparation

Locate a needle of appropriate length and gauge. A sixteen-gauge needle is recommended if you plan to draw from the reagent container several times, as anything larger than this will leave a hole too large for the Teflon septum on the reagent bottle to reseal. A long needle is best if using a syringe. A long double-tipped flexible needle can be used for cannula transfer. Luer lock needles, or needles otherwise equipped with a locking mechanism, are highly recommended as a guard against the needles becoming detached.



Fig. 1 Drawing reagent into syringe from reagent container, with inert gas line inserted

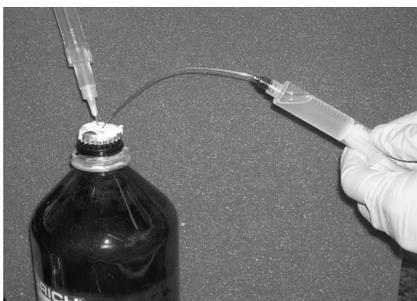


Fig. 2 Syringe is flipped needle-up after drawing liquid to allow inert gas bubbles to rise to needle



Fig. 3 Inert gas bubbles and excess liquid are forced back into reagent bottle

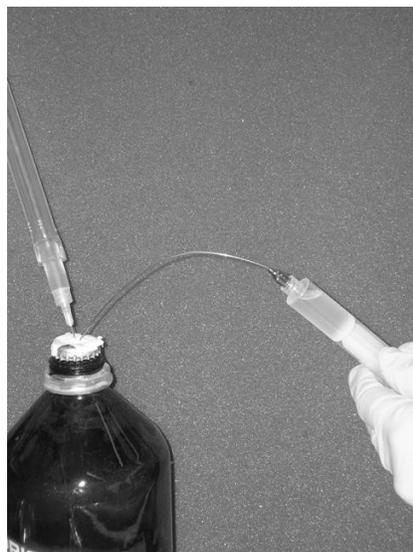


Fig. 4 Needle tip is brought into head-space of bottle, and an inert gas layer is drawn into syringe



Fig. 5 Needle is carefully withdrawn from reagent bottle. Syringe is kept needle-up to prevent spilling

Flush your syringe-needle assembly, if using one, with dry, high-quality inert gas such as nitrogen or argon before starting. Ensure that it is leak-free by inserting the needle into a rubber stopper. You should be able to compress the syringe to half its original volume without any leaks. The needle can be left in the rubber stopper when not in use to prevent the entry of air.

Ensure that all glassware and other equipment involved in the procedure are clean and dry. Glassware should be heated in an oven to remove moisture, and cooled in an inert atmosphere.

Prepare an inert gas line for supplying positive pressure to the reagent container. Use a dry, high quality inert gas cylinder with a pressure regulator set to the lowest pressure sufficient for your work (no more than 5 psi), attached to flexible plastic tubing. A mineral oil bubbler should be added to the line, typically off of a manifold, to release excess pressure. A hypodermic needle at the end of the tubing can be used to insert the line through the septum of the reagent container. This needle can be inserted into a rubber stopper when not in use to prevent the entry of air.

The reaction vessel will also need to be supplied with a small amount of positive pressure during the reaction to prevent any pressure reversals that could cause air to enter the vessel. An inert gas line equipped with a mineral oil bubbler to relieve excess pressure will be needed for this. Run the reaction in a Schlenk flask that is under positive pressure from the inert gas line, connected via the tubing adapter. If the reaction vessel has a septum inlet, a hypodermic needle attached to the gas line can be pushed through the rubber septum to the reaction vessel, though the Schlenk vessel is better suited for controlling the atmosphere.

Syringe Transfer

Transfer of pyrophoric reagents via syringe is convenient, but should not be used for 20 mL or more.

Clamp your reagent container firmly. You will need a small amount of positive pressure in the reagent container in order to draw the reagent

into a syringe. Insert an inert gas line with low positive pressure (1-2 psi). Ensure that excess pressure is released through the mineral oil bubbler that is attached to the gas line. Simply sticking a needle through the septum, or using a balloon to relieve pressure, is not safe for pyrophoric reagents.

Prior to starting the procedure, ensure that the reaction vessel you plan to deposit your reagent into has a mineral oil bubbler to relieve pressure (if a bubbler is not already on the gas line), and that it is thoroughly flushed with inert gas prior to use. Again, do not use a balloon, and do not simply stick a needle through the septum to relieve pressure.

Before beginning, set aside an Erlenmeyer flask with the same solvent in which your reagent is dissolved. If it is a neat reagent, use a solvent that is inert and unreactive towards that reagent. Aliquot slightly more than the volume you will be transferring with the syringe. This flask will need to be immediately available after the transfer for flushing out your syringe.

Draw slightly more than you need initially. Be careful to pull only very gently on the plunger as pulling too strongly can cause leaks and create air bubbles. Always keep a good grip on BOTH the needle and the plunger to ensure that neither comes off. If the plunger is ejected with its contents due to excess pressure, you will have a dangerous fire on your hands. (Fig. 1)

Flip the syringe needle-up, so that the inert gas bubbles rise to the top (a long needle is needed for this). It is best to avoid allowing the reagent in the bottle to come into contact with the septum to prevent degradation. Tap the syringe a couple of times and look to make sure all the air/gas has been collected at the tip. (Fig. 2)

Push the plunger down to eject the inert gas and excess reagent back into the reagent vessel, stopping once the volume you need for your experiment is reached. (Fig. 3)

Pull the needle into the headspace of the reagent bottle and draw a small amount of inert gas into the syringe. This prevents spilling, and very importantly protects the liquid from exposure to air during transfer. (Fig. 4)

The needle can now be removed from the bottle, keeping the inert gas layer at the syringe tip. If you see a small flame at the tip of the needle, do not panic. You can use a beaker of sand to extinguish this. (Fig. 5)

Insert the syringe into the septum of the reaction vessel, keeping the inert gas layer between the syringe and needle, if you have a long needle. Ensure that the vessel is equipped with an inert gas line to provide positive pressure, and a mineral oil bubbler to relieve excess pressure. Holding the plunger down, inject the inert gas cushion in your reaction first, and then inject your liquid into the flask.

Cannula/Double-Tipped Needle Transfer

Transfer of pyrophoric reagents via cannula is recommended for 20 mL or more.

Clamp your reagent container firmly. You will need to create a small amount of positive pressure in the reagent container in order to force the reagent through your double-tipped needle. Connect it to an inert gas line to provide low positive pressure (1-2 psi). Ensure that the line is equipped with a mineral oil bubbler to relieve excess pressure. Using a balloon or simply sticking a needle through the septum to relieve pressure is not safe for pyrophoric reagents.

Make sure, before starting, that the reaction vessel into which you plan to deposit your reagent has a pressure release mechanism such as a mineral oil bubbler on the inert gas line, and that it is thoroughly flushed with inert gas prior to use. Again, do not use a balloon or simply stick a needle through the septum to relieve pressure.

Insert one end of the double-tipped needle into the headspace of the reagent vessel and allow the positive pressure from your inert gas line to flush the needle free of air.

Insert the other end of the double-tipped needle through the septum of the reaction vessel. To allow for a measured transfer, you can use a sealed, measured funnel attached to the reaction flask, with the septum at the top of the funnel.

When ready to transfer, push the needle that is in the headspace of the reagent container down into the liquid. The pressure from the inert gas line will begin forcing the liquid through the double-tipped needle.

When the desired volume has been transferred, pull the end of the needle in the reagent container up into the inert gas headspace and allow it to be flushed with inert gas again. Remove the end of the needle from the reaction flask first, and then from the reagent container. If, upon removal, a flame is lit at either tip, extinguish it in a beaker of sand.

Equipment Cleanup

If you use a syringe transfer, the syringe will have a small amount of the reagent remaining. Fill an Erlenmeyer flask with a small amount of the same solvent in which the reagent was stored, using slightly more than the volume which the syringe was used to transfer. If the syringe was used for a neat reagent, use a solvent that is inert and unreactive toward the reagent. Ensure that any flame at the tip of the needle is extinguished first, and put the tip of the needle beneath the liquid in the flask, keeping it beneath the solvent. Carefully draw the solvent into the syringe and eject it to flush the syringe, and repeat for a total of three rinses. Afterwards, the syringe can be disposed of by putting it into a sharps container, if it is disposable. The solvent in the flask, with trace amounts of the pyrophoric compound, should be added to your solvent waste container. Be sure to list all of the components on the chemical/hazardous waste label.

For a cannula transfer, the double-tipped needle should have been purged with inert gas before you removed it. The needle can be placed in a sink in the absence of any solvents or other combustible materials. Flush the needle with water, collecting the effluent for disposal with your aqueous waste. Making sure that there is no longer any reactivity, use a wash bottle to flush the needle with acetone, collecting the effluent with your solvent waste.

DISPOSAL

For any significant amount of reagent remaining in the reagent bottle, first ensure that the bottle is purged with inert gas. Place a secondary container such as a sealable plastic bag, or the manufacturer's can in which the bottle was shipped, into an inert atmosphere and purge it with inert gas. Put the reagent bottle into this purged secondary container and seal, then complete a chemical/hazardous waste label and submit an online chemical waste pickup request at <http://vesta.cumc.columbia.edu/ehs/wastepickup/>.

If only trace amounts of the reagent remain, use the solvent in which the reagent was originally stored to triple rinse the bottle (under positive pressure from an inert gas line when purging), collecting the rinse in your solvent waste container. If the bottle contained a neat reagent, perform this procedure with a solvent that is inert and unreactive toward the reagent. When finished, purge the bottle once more with inert gas and seal inside a secondary container, such as the metal can that came with the reagent. Complete the chemical/hazardous waste label and submit an online pickup request.

Sources

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Photos courtesy of Dr. Uttam Tambar.