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Methods for the Safe Storage, Handling, and Disposal of Pyrophoric Liquids and Solids in the Laboratory

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Introduction

Pyrophoric reagents represent an important class of reactants because they can participate in many different types of reactions. They are very useful in organic synthesis and in industrial applications[1-6]. The Occupational Safety and Health Administration (OSHA)[7] and the National Fire Protection Association (NFPA)[8,9] define Pyrophorics as substances that will self-ignite in air at temperatures of 130°F (54.4°C) or less. However, the U.S. Department of Transportation (DOT) uses criteria different from the auto-ignition temperature criterion. The DOT defines[10] a pyrophoric material as a liquid or solid that, even in small quantities and without an external ignition source, can ignite within five minutes after coming in contact with air when tested according to the United Nations Manual of Tests and Criteria[11]. The Environmental Protection Agency has adopted the DOT definition. Regardless of which definition is used, oxidation of the pyrophoric reagents by oxygen or exothermic reactions with moisture in the air (resulting in the generation of a flammable gas such as hydrogen) is so rapid that ignition occurs spontaneously.

Due to the inherent nature of pyrophoric substances to ignite spontaneously upon exposure to air, special precautions must be taken to ensure their safe handling and use. Pyrophoric gases (such as diborane, dichloroborane, phosphine, etc.) are typically the easiest class of pyrophoric substances to handle since the gas can be plumbed directly to the application and used remotely. Pyrophoric solids and liquids, however, require the user to physically manipulate them when transferring them from one container to another. Failure to follow proper safety precautions could result in serious injury or unintended consequences to laboratory personnel.[12] Because of this danger, pyrophorics should be handled only by experienced personnel. Users with limited experience must be trained on how to handle pyrophoric reagents and consult with a knowledgeable staff member prior to performing the experimental task. The purpose of this article is three fold: 1) to provide guidelines and general safety precautions to avoid accidents, 2) describe proper techniques on how to successfully handle, store, and dispose of pyrophoric liquids and solids, and 3) illustrate best practices for working with this class of reactants in a laboratory environment.

Pyrophoric Storage

Storage of pyrophoric reagents should be minimized. They should be purchased just-in-time in the quantity required for the application and any excess disposed of immediately after use. Pyrophoric liquids should not be stored for extended periods because the integrity of the reagent may be compromised. Concentrations of solutions of pyrophoric materials may be different from what is given on the label, higher due to solvent evaporation or lower from decomposition due to

air/water (moisture) infiltration. Air intrusion through an old, used septum may also have a more serious consequence (e.g., fire) than altering product quality. Lastly, storage of pyrophoric liquids for extended periods only increases the risk of an accident through routine handling of reagent bottles, especially if made of glass.

The storage of pyrophoric solids should be minimized even when the solids are stored under a protective material such as mineral oil or in an inert atmosphere like nitrogen. Some metals, such as sodium or potassium, will form superoxides on their surface even when stored under kerosene or oil[13]. These superoxides are very unstable and dangerous. Only the amount of material required should be procured and then the excess disposed of after use.

Pyrophoric materials in storage should be kept away from sources of heat and ignition, flammable and combustible materials, oxidizers, and other incompatible substances (such as air and water in the case of water-reactive pyrophorics).

Use of Pyrophoric Liquids

Pyrophoric liquids are present in two forms – pure liquids and solutions. Examples of pure liquids include diethylzinc, trimethylaluminum, triethylborane, and tributylphosphine. Mixtures typically contain metal alkyl substances such as methyllithium, n-butyllithium, sec-butyllithium, and t-butyllithium dissolved in a solvent such as hexane, pentane, diethyl ether or tetrahydrofuran. Pyrophoric liquids are typically packaged in glass bottles under an inert atmosphere, such as dry nitrogen or argon, and sealed with a septum to prevent air intrusion.

General Precautions

Pyrophoric liquids should generally be handled inside of inert gloveboxes. When this is not possible, pyrophoric liquids can be transferred by either a syringe or double-tipped needle (cannula) outside the glovebox **only** if the transfer takes place under an inert atmosphere using proper handling techniques. No matter what transfer method is used, the following safety measures must be observed:

- Do not work alone when handling pyrophoric liquids. A colleague needs to be present (i.e., the Buddy System) while working with these materials. If you become unable to respond to a situation due to an injury, the colleague can provide immediate assistance.
- At a minimum, safety glasses must be worn at all times when working with pyrophoric reagents. Fire-retardant laboratory coats and fire-retardant gloves should be mandatory. Fire-retardant gloves can also absorb hazardous liquids and consideration should be given to using the gloves in conjunction with appropriate chemically-resistant gloves.
- Extreme caution must be exercised to mitigate skin exposure or spillage when handling pyrophoric reagents. Avoid wearing synthetic clothing while working with pyrophoric reagents as they do not provide the required protection. Natural fiber clothing tends to char instead of melting when exposed to flames or high temperatures and is preferable to synthetic fibers. (Figure 1)

Figure 1. Transfer Assembly in Fume Hood with Researcher in Proper PPE (Chemically resistant gloves topped with fire resistant pilot glove, fire resistant lab coat, and safety glasses with side shield) Note how the sash has been lowered to reduce potential splash hazards.

- Any spill of a pyrophoric liquid onto a person should be considered an emergency in the extreme. Flooding quantities of water from a safety shower for at least 15-20 minutes until all the chemicals have been washed away is the preferred method of dealing with this type of spill. Other fire extinguishing methods such as the use of fire extinguishers, fire blankets, or stop, drop, and roll, may be attempted, but, given the nature of pyrophoric liquids, they may not be effective.
- Practice your experimental technique with non-hazardous materials to refine your technique and identify points that require heightened care.
- Read the manufacturer's MSDSs, and understand the technical information associated with handling the materials. If uncertain of how to handle pyrophoric reagents, users must also consult a knowledgeable staff member prior to performing the experimental task,
- Work should be performed inside a fume hood with the sash down as far as possible for protection against chemical splashes and unexpected ignition events. (Figure 1)
- All nonessential flammable/combustible materials should be removed from the hood to reduce the hazard in case of a fire.
- Pyrophoric reagent bottles should be secured to a stand with a clamp before use to prevent them from tipping over. Controlling the bottle with one hand while handling the syringe with the other hand is strongly discouraged.
- Use a long needle to reach the solvent level. Do not invert the bottle as such action dislodges sediments that may clog the needle.

- Use a wide bore needle of 18-gauge or larger. The use of a smaller bore needle can slow down the transfer process and cause the needle to clog.
- Use a Luer-lock syringe with long needle when possible and be sure that the assembly does not leak. Make sure that the needle is secured in the Luer-lock and does not separate from the barrel during the transfer.
- Disposable plastic syringes should only be used within the confinement of a glovebox. Used syringes must be rinsed with a non-reacting solvent and neutralized as appropriate prior to their removal from the glovebox for disposal.
- All equipment, such as syringes and glassware, should be free of moisture and purged with an inert gas prior to use.
- Pyrophoric reagent should be slowly added to the reaction vessel in a cooling bath to control reaction rate and heat dissipation.
- A container with residual pyrophoric reagents must never be opened. Such (nearly empty) containers must be rinsed with an inert solvent and neutralized, with adequate cooling, prior to disposal. (see Neutralization and Disposal of Pyrophoric Liquids and Solids below)
- Products from pyrophoric reagents should be handled as potentially highly-reactive materials.

Using a Syringe to Transfer Pyrophoric Liquids

When a syringe is used, extreme caution must be exercised to prevent the plunger from separating from the syringe. Luer-lock airtight syringes (18 gauge or larger) should be used for the transfer and should have a minimum volume of twice that being transferred. Transfers of a large volume (> 10 mL) from the pyrophoric reagent bottle should be avoided when using syringes. Double-tipped needle methods (described below) should be used when large volumes are to be transferred. At the conclusion of the transfer, the syringe needs to be cleaned to minimize the chance of the plunger from sticking/freezing in the barrel.

Figures 2 and 3 show the complete assembly of reagent transfer using an airtight glass syringe and a bubbler, for pressure release, under an inert atmosphere. The volume of reagent to be transferred is not to exceed 10 mL. Special instructions/precautions when using this method are:

- Ensure that the glassware being used is dry, and the assembly is purged and maintained under an inert atmosphere prior to reagent transfer.
- Ensure that a needle is attached to the inert gas line, equipped with a bubbler and a shut-off valve, and purged prior to reagent transfer.
- Insert the inert gas supply needle through the septum into the headspace above the reagent to maintain a slight positive pressure inside the pyrophoric reagent bottle.
- Insert the long needle of a Luer-lock, airtight, dry syringe through the septum into the reagent.

- Pull the plunger back slowly to fill the syringe with the required volume of reagent. Always keep the plunger in your grasp and avoid pulling back the plunger quickly as this action causes leaks and creates gas bubbles.
- Once the required volume is attained, slowly pull up the syringe needle from the pyrophoric reagent to the overhead space above the liquid.
- Pull the plunger up slowly and allow the inert gas to push the reagent trapped in the needle into the syringe.
- Shut the inert gas line off and slowly pull the needle out from the assembly to complete the transfer.
- At the conclusion of the transfer, the syringe and needle need to be rinsed with a non-reacting solvent and the residue quenched, as appropriate, under an inert atmosphere (see Neutralization and Disposal of Pyrophoric Liquids and Solids below).

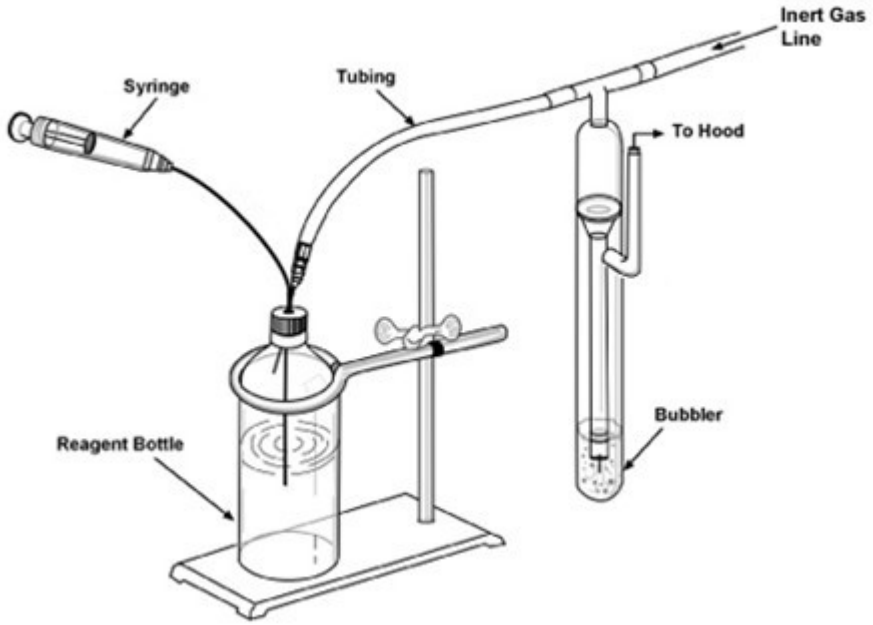

Figure 2. Syringe Transfer Assembly Equipped with an Inert Gas Line and a Bubbler during Reagent Transfer

Figure 3. Syringe Transfer Assembly with Inert Gas Line (1), Bubbler (2), Secure Reagent Bottle (3), and Fire Resistant Gloves

Using a Double-Tipped to Transfer Pyrophoric Liquids

There are two similar methods that can be used for transferring pyrophoric liquids using a double-tipped needle. The first is shown in Figure 4. It shows the complete assembly for reagent transfer using a double-tipped needle under low pressure (< 1 psig) from an inert gas line. Note that a bubbler is connected to the reaction vessel to avoid pressure build up in the assembly. Special instructions/precautions when using this method are:

- Ensure that the glassware being used is dry, and the assembly is purged and maintained under an inert atmosphere prior to reagent transfer.
- Insert one end of the double-tipped needle through the septum into the reaction vessel or addition funnel in order to flush the needle.
- Insert the other end of the double-tipped needle through the septum of the reagent bottle into the headspace above the liquid.
- A needle attached to a very low pressure inert gas line (< 1 psig) is inserted through the septum into the headspace and kept above the solution of the pyrophoric reagent bottle.
- The liquid is transferred from the reagent bottle into the reaction vessel or the addition funnel by pushing the end of the double-tipped needle in the reagent bottle down into the liquid.
- At all times during the transfer, the reaction vessel must be vented through a mineral oil bubbler and kept under a positive pressure of an inert atmosphere to prevent air from entering the system.

- Once the required volume is transferred, the end of the double-tipped needle in the pyrophoric reagent should be slowly pulled up so that it is no longer in the liquid, but still through the septum and in the headspace above the liquid. This allows the inert gas to flow through the needle to push the trapped reagent in the needle to the reaction vessel or the addition funnel.
- At the conclusion of the transfer, the double-tipped needle needs to be rinsed with a non-reacting solvent and the residue quenched, as appropriate, under an inert atmosphere (see Neutralization and Disposal of Pyrophoric Liquids and Solids below).

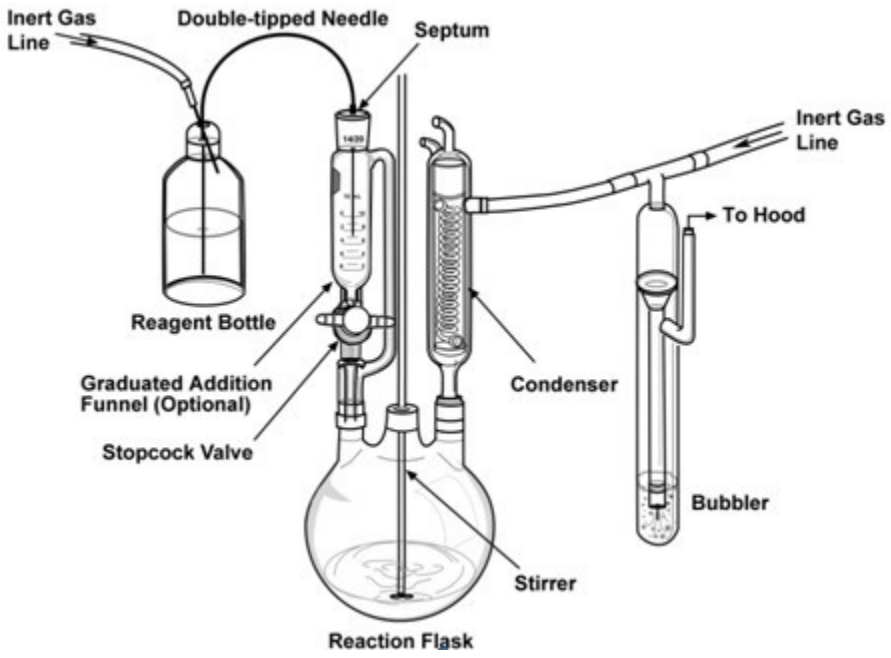

Figure 4. Double-Tipped Needle Assembly Equipped with a Bubbler and Kept Under an Inert Atmosphere during Reagent Transfer

The second method that can be used for transferring pyrophoric liquids using a double-tipped needle is shown in Figure 5. This shows the complete assembly for reagent transfer using the double-tipped needle under slight vacuum and connected to an inert gas line through a bubbler. Special instructions/precautions when using this method are:

- Make sure that the reaction vessel being used is dry and that the assembly is purged and maintained under an inert atmosphere prior to reagent transfer.
- Insert the double-tipped needle through the septum into the reaction vessel or addition funnel to purge the needle with inert gas.
- Insert the other end of the double-tipped needle into the head space above the liquid of the pyrophoric reagent bottle.
- Connect a vacuum line (vacuum pump or house line) with a **shutoff** valve to the reaction vessel (Figure 5).

- Insert the needle connected to the inert gas line (bubbler) through the septum into the headspace of the reagent bottle to keep the space above the solution under a blanket of an inert gas.
- Ensure the assembly is in proper configuration and the inert gas is flowing through the bubbler.
- Push the end of the double-tipped needle in the reagent bottle down into the pyrophoric reagent.
- Apply a slight vacuum to the reaction vessel assembly by opening the vacuum valve slowly to transfer the desired volume from the reagent bottle to the reaction vessel through the double-tipped needle. Note the vacuum line will only need to be opened intermittently in order to transfer the pyrophoric reagent. High or continuous vacuum may allow air to enter the system through the bubbler.
- Once the required volume is transferred, pull up slowly on the end of the double-tipped needle in the pyrophoric reagent so that it is no longer in the liquid, but still through the septum and in the headspace above the liquid. Allow the inert gas to flow through the double-tipped needle to push the trapped reagent in the needle to the reaction vessel.
- Close the vacuum valve and connect the reaction flask to an inert gas line.
- At the conclusion of the transfer, the double-tipped needle needs to be rinsed with a non-reacting solvent and the residue quenched, as appropriate, under an inert atmosphere (see Neutralization and Disposal of Pyrophoric Liquids and Solids below).

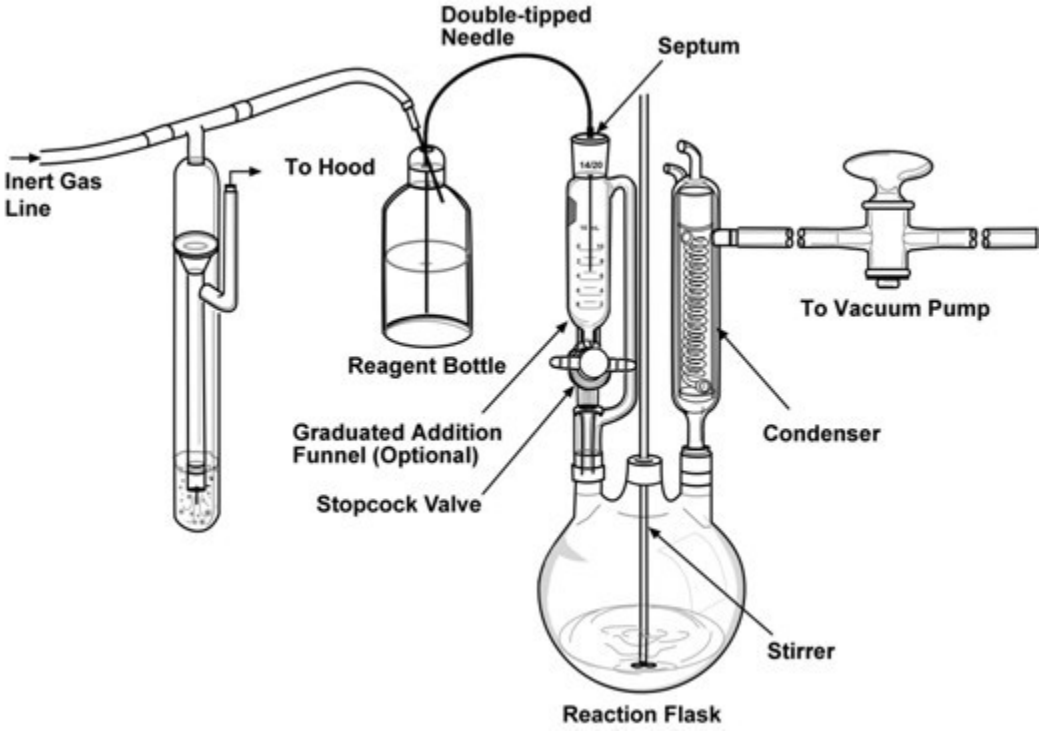

Figure 5. Double-Tipped Needle Assembly Equipped with a Vacuum Pump and Kept Under an Inert Atmosphere during Reagent Transfer

Use of Pyrophoric Solids

Examples of pyrophoric solids are alkali metals (such as potassium, sodium), finely divided metal powders (e.g., aluminum, cobalt, iron, magnesium, titanium, zirconium, zinc), metal hydrides (e.g., sodium hydride, lithium aluminum hydride), alloys of reactive metals (e.g., sodium-potassium alloy) and white phosphorus. Because some solid pyrophorics are more stable in air, manufacturers sell some formulations that do not require the use of an inert atmosphere until immediately before use. Reagents such as sodium hydride or lithium aluminum hydride are sold as powders mixed with mineral oil (dispersions). Metals such as potassium and sodium may be sold as large pieces submerged under mineral oil. To use these materials, one simply measures out the amount of material required, places the material under an inert atmosphere, and removes the mineral oil by repeated washings with a solvent such as hexane.

General precautions

Although pyrophoric solids are more stable in air than pyrophoric liquids, caution must be exercised during their handling.

- Wear personal protective equipment (PPE) and practice your experimental process with non-hazardous materials to refine your technique and identify points that require heightened care. Make sure to have suitable fire suppression materials (e.g., Class D dry powders, dry sand, dry sodium chloride, and dry soda ash are effective in fighting alkali metal fires) at hand and practice emergency response to the release and ignition of pyrophoric solids.
- Because many pyrophoric solids release flammable and harmful gases upon exposure air or moisture, these materials should only be handled in a fume hood or dry glovebox.
- Pyrophoric solids that are discolored or have any unusual appearance should never be used. These materials may be dangerously unstable. When these conditions are found, one should obtain immediate assistance and utilize proper disposal techniques.
- Store pyrophoric solids under an inert atmosphere and away from water, oxidizers, and sources of heat or ignition. To avoid uncontrollable ignition, do not leave containers with residues of pyrophoric materials open to the atmosphere.
- All containers must be labeled appropriately with the chemical name and hazard warning.
- Do not cut pieces of sodium metal or other pyrophoric metals on paper towels or other combustible materials and do not clean up residues from these procedure using paper towels, unless the reactive materials have positively been quenched. A common problem is subsequent ignition when these contaminated towels are disposed of in waste receptacles.
- A spill control plan should be developed and necessary spill control materials should be on hand prior to any work with pyrophoric solids.

Neutralization and Disposal of Pyrophoric Liquids and Solids

Neutralization of excess reagents and the cleaning of used glassware should be done carefully. When a syringe, a double-tipped needle (cannula), or spatula is used in handling pyrophoric reagents, the assembly should be rinsed with an inert solvent and the rinse transferred to a flask under an inert atmosphere for subsequent neutralization. Excess pyrophoric reagent should also be dissolved/dispersed in an inert solvent. Rinsates or solvents containing pyrophoric reagents should then be cooled in a cooling bath (dry ice/acetone) prior to the addition of isopropyl alcohol to initiate a quenching reaction. Isopropanol should continue to be added until no further heat is released. Methanol is then added followed by copious amounts of water (stronger neutralization agent) to complete the quenching. The resulting mixture should then be dispositioned using the organization's waste disposal processes.

Conclusion

Pyrophoric materials are an important reactant in the laboratory. Because of their inherently hazardous properties, caution must be exercised at all times when dealing with pyrophoric reagents. However, it is clear that more attention must be paid to the safe use of these materials. The U.S. Chemical Safety Board is beginning to undertake a closer examination of laboratories practices because of the injuries and deaths resulting from laboratory incidents involving pyrophoric and other hazardous materials[14]. While the U.S. Chemical Safety Board will provide insights into causal details, the ways to minimize or prevent injuries from handling pyrophoric reagents are known: through proper training, vigilance, complying with regulatory requirements, and following safe guidelines such as the ones in this article.

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