Cost-Effective Teacher

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Harold H. Harris
University of Missouri–St. Louis
St. Louis, MO 63121

A System for Cooling Inside a Glove Box

Martial Sanz
Departamento de Química Inorgánica, Universidad de Alcalá, Edificio de Farmacia, Campus Universitario, 28871 Alcalá de Henares, Spain
marcial.sanz@uah.es

Reacting air- and moisture-sensitive compounds in a dry, inert atmosphere has always been a priority for chemists. Three methods are currently available for producing these reactions in a relatively safe, efficient air- and moisture-free manner: (a) the inert atmosphere balloon technique *(1)*; (b) the dual-manifold *(2)* vacuum inert atmosphere technique, used in conjunction with glass Schlenk tubes *(2)*; and (c) the dry, inert atmosphere glove box technique including the temporary dry, inert atmosphere polyethylene glove bag technique *(2)*, used in conjunction with glass Schlenk tubes or glass vials.

Organometallic chemists often must carry out reactions at controlled, low temperatures. In the dual-manifold vacuum technique, the Schlenk tube where the reaction takes place is placed in a low- and controlled-temperature bath. However, the use of the dry, inert atmosphere glove box presents various technical challenges. The introduction of a volatile heat-transfer medium is not practical because of the danger of contaminating the glove-box purification system. Most commercial glove boxes can be equipped with an internal cooler or freezer, specifically designed for storing such products at low temperatures. However, such equipment is expensive and may represent an excessive demand on many chemists' research budgets. Although several articles have been published in this *Journal* and elsewhere describing how to build a glove box *(3, 4)* or make related modifications *(5)* or improvements *(6, 7)*, I have not found a description that includes the construction of a cooler system inside the glove box to achieve air- and moisture-sensitive reactions at controlled, low temperatures.

We have successfully designed a simple, effective, low-cost, flexible, reliable system whose key component is a simple circulating pump for controlling the below-ambient temperature of reactions inside of a glove box.

Chemicals and Equipment

Methylcyclohexane (99% purity) was purchased from Aldrich and used as received. Finely divided sea sand was purchased from SDS. A dry, inert atmosphere glove box, a well-ventilated fume hood, and a simple recirculating pump are needed.

Hazards

Although the vapor pressure of methylcyclohexane remains low at low temperatures and there is no reference to this chemical as a carcinogen, the use of methylcyclohexane nevertheless represents a minor fire and health hazard.

Design Using a Glove Box

Before building an external cooler connected to the glove box, three parameters must be considered: (i) choice of an inert, nonvolatile heat-transfer medium placed inside the glove box to avoid contamination of the glove-box purification system; (ii) choice of a reliable, efficient cooling system attached to glove-box connections; and (iii) choice of the low-temperature range.

Heat-transfer media are extensively used for heat transfer in research. Although dried, finely divided alumina or silica can be used for this purpose, dried, finely divided sea sand is preferred due to its low cost.

The cooling system must be based on materials that are inexpensive and accessible in a laboratory. The system described here is composed of (a) a reservoir to contain the cooling fluid, comprising a Dewar flask or more simply, a cylindrical metal container externally insulated with polystyrene with a volume of at least 10 times the inner volume of the flexible tubing; (b) insulating materials; (c) two, 1 m lengths and one, 2 m length of flexible tubing with inside and outside diameters of 16 mm and 20 mm, respectively;[1] (d) one 1 L glass beaker; (e) various hose connector clamps or other material to ensure a tight fit; (f) two low-temperature thermometers; and (g) recirculating pump. Generally, commercial or self-built glove boxes have at least two stainless steel tubing connections with internal and external manual valves that can be used for the cooling circulation.

To construct the cooling system, the 1 L glass beaker, dry sea sand, 2 m length of flexible tubing, thermometer, insulating material, and various hose connector clamps are placed inside the glove box. One end of the 2 m length of tubing is tightly attached to one of the internal manual connection valves in the glove box (Figure 1). Starting at about 50 cm along the tubing, a coil is formed in the beaker in such a way that the flexible tubing principally occupies the bottom and sides of the beaker. The other end of the flexible tubing is secured tightly to another internal manual valve. To ensure immobility of the flexible tubing in the beaker, the sea sand is uniformly added and carefully packed down. The Schlenk tube or vial in which the reaction is performed is then gently pushed down through the sea sand toward the bottom of the beaker. The thermometer is placed in the sea sand near to the Schlenk tube or vial to obtain reliable temperature readings. The visible part of the 2 m length of flexible tubing is covered with insulating material to avoid heat transfer. Outside of the glove box, the two ends of both 1 m lengths of flexible, tubing are secured tightly to the external manual valves (Figure 1) and the other ends are connected tightly to the recirculating pump above the reservoir. The pump and reservoir must be placed inside a fume hood. The cooler system with a simple recirculating pump coupled to the inert atmosphere glove box is thus constructed as shown in Figure 1.

A solvent that has a melting point lower than the reaction temperature must be chosen, so that its viscosity at low temperature under atmospheric pressure will not impede ease of circulation throughout the length of the flexible tubing. Because temperatures near the dry ice sublimation temperature of −78 °C are often used for low-temperature reactions, methylcyclohexane is an appropriate choice for the heat-transfer liquid. It has a melting point of

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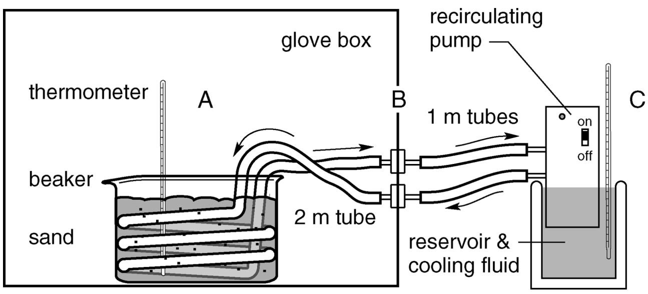

Figure 1. Schematic representation of the cooler system coupled to the inert-atmosphere glove box: (A) 1 L glass beaker, thermometer, 2 m length of flexible tubing; (B) glove-box wall with internal and external manual valves equipped with stainless steel connection tubing; and (C) solid walled Dewar, a recirculating pump, two 1 m lengths of flexible tubing, and thermometer. Insulating materials, hose connector clamps, the glove box's internal and external manual valves, and the fume hood for the methylcyclohexane reservoir are omitted for clarity.

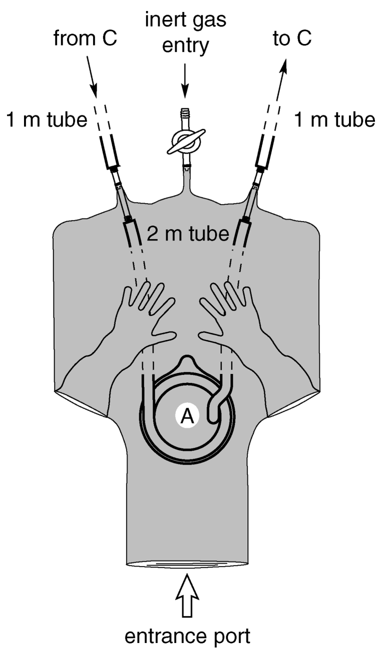

Figure 2. Schematic representation of the modification of the inert-atmosphere polyethylene glovebag. The letters refer to Figure 1.

−126 °C and acceptably low viscosity at −78 °C. Consequently, the temperature range using methylcyclohexane can be from room temperature to −78 °C.

The reservoir is loaded with methylcyclohexane, which is then cooled gradually to the desired temperature by carefully adding small portions of solid CO_2 or liquid nitrogen to reach and maintain a relatively stable temperature. When thermometer readings of the reservoir show that the desired temperature has been obtained and is stable, the recirculating pump is switched on and the decrease of the temperature of the sea sand bath is monitored until the desired temperature is reached.

Design Using a Glove Bag

If an inert-atmosphere polyethylene glove bag is used, the construction is as follows. Two holes, approximately 20 cm apart, are made in the polyethylene glove bag (Figure 2). The hole diameter should be slightly smaller than the external diameter of the glass or metal connector. Gently force the connector through the hole and seal the polyethylene glove bag and connector with glue or tape to ensure a tight fit. Introduce the cooler system described in the previous section (part A of Figure 1) into the glove bag and tightly connect the flexible tubes of the cooler system to the internal glove-bag connectors. Tightly connect the corresponding tubes of the recirculating pump (part C of Figure 1) to the external glove-bag connectors. Connect the inert gas entry and introduce all materials necessary to achieve an air- and moisture-sensitive synthesis. Set a positive pressure of inert gas[2] to flush both air and humidity inside the glove bag for roughly 2 h.[3] The entrance port of the glove bag should be folded several times in such a manner that there is a small leak of gas while the chamber remains inflated. After 2 h, the folded entrance port is tightly secured for the preparation of air- and moisture-sensitive compounds.

Conclusion

The construction of a cooler system using a simple recirculating pump represents a reliable and successful method to prepare air- and moisture-sensitive substances inside a dry, inert atmosphere glove box as well as a dry, inert atmosphere glove bag. This method has been used during postgraduate studies to routinely achieve the low-temperature preparation of some basic air- and moisture-sensitive organometallic compounds such as transmetalation of vinyl bromide derivatives with *tert*-butyllithium or preparation of tetrabenzyl and tetrakis(dimethylamido) group 4 complexes.

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Notes

1. The tubing must be suitable for use at low temperatures, where the chosen liquid would circulate easily when cooled under controlled temperature.
2. A heavy, inert gas such as argon is recommended.
3. To rapidly eliminate humidity, introduce a glass beaker containing freshly divided P_4O_{10}.

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