Solvent Pots

Na/Ph_2CO ketyl solvent pots are used for performing reactions with anhydrous solvents on the high vacuum line, for further drying of tough-to-dry solvents from the solvent columns (THF, Et_2O), and for drying small quantities of "valuable" solvents – deuterated NMR solvents, for example. Solvents are then "vacuum transferred" to destination/reaction vessels through vacuum distillation instead of thermal distillation. For related procedures, see the Vacuum Transfer SOP and the Freeze/Pump/Thaw Degas SOP.

Similar pots can be generated with CaH_2 or other drying agents. Refer to *Purification of Laboratory Chemicals* for ideal drying agent/solvent combinations.

Halogenated solvents and other easily reduced solvents (e.g. nitriles, DMF, acetone) react violently with sodium metal. DO NOT ATTEMPT TO MAKE A KETYL POT WITH THESE SOLVENTS!!

We do not run solvent stills in the lab. Ever. Only vacuum, NEVER heat, should be applied to a ketyl pot to distill the solvent.

We should not have more than 1 of each type of solvent pot in the group. Standing solvent (especially standing solvent over Na) is a fire hazard that needs to be minimized as much as possible.

A. General Safety Guidelines & PPE:

- Making and working with solvent pots involves the use of potentially pyrophoric material.

Full PPE (goggles or facemask, gloves, and labcoat) must be worn at all times, and manipulations should be carried out in a working fume hood. Be aware of the location and use of fire safety equipment in the lab prior to using a solvent pot. This is especially critical when quenching pyrophoric pots (Part D).

B. Solvent Pot Synthesis:

Materials:

1 cm^3 Na^0 per 500 mL solvent, cut into smaller chunks (approx.)
1 g of Ph_2CO per 500 mL solvent (approx.)
1 180° 24/40 Adapter
1 500 mL (or smaller) round bottom flask
1 stirbar

Preparing a ketyl pot with these amounts of Na and Ph_2CO should result in a roughly 0.01 M solution of ketyl radical, with Ph_2CO as the limiting reagent. A purple solution indicates a mixture of the radical anion (blue-green) and the radical dianion (deep red). When the pot is purple and the ketyl

radical mixture is present, it is indicative that the H_2O content is under 10 ppm. There should be excess sodium at the bottom of the pot.

The preferred way to make a ketyl pot is to mix the Na chunks and benzophenone in the round bottom flask in the glovebox. The flask can then be sealed with the 180° adapter, removed from the box and evacuated on the high vacuum line.

After evacuation, solvent can be collected into the pot *via* the solvent system, or benchtop solvent can be sucked into the flask by pouring solvent in to the top of the 180° adapter and slightly opening the stopcock. These two methods significantly minimize the amount of air and water that the solvent pot is exposed to, which will prolong its life.

After addition of solvent *via* whatever method is most appropriate, the solvent pot should be degassed, sealed under vacuum, and left to stir overnight. Overnight, the pot should turn from colorless to blue to purple, although the rates of ketyl radical formation vary as a function of solvent, Na chunk size, and amount of water in the starting solvent. ***If the pot is not purple, it is not < 10 ppm H_2O and should not be used***.

C. Common Issues:

- My solvent pot is blue (green)! Can I use it?

  Blue solvent indicates a significant amount of water (or O_2) is present preventing the formation of the radical dianion. This is probably not dry enough to use for most sensitive applications in our group.

- My solvent pot is yellow/orange, and stuff has precipitated out of it! What do I do?

  This is a result of reductive decomposition of benzophenone, or pinacol coupling of the radicals and commonly occurs in older pots or pots that have been frequently refilled. If there is still visible Na^0 in the flask, you can add more benzophenone to fix this problem. If there is not, it is probably not worth adding more; you should quench the remaining material and start over.

- My pot won't turn purple!!

  This could be due to a number of factors: the two most common are that your reaction vessel isn't properly degassed (see free/pump/thaw degassing SOP), or the ketyl isn't very soluble in your solvent (common for hydrocarbons like hexane). To improve solubility, you can add a small (< 1%) amount of a nonvolatile ethereal solvent such as tetraglyme. Be aware that glyme solvents are *notoriously* wet, so you may need to add more Na or Ph_2CO after adding.

- How do I add more Na or Ph_2CO?

  Put the pot under N_2, then quickly yet carefully remove the 180° adapter. Add in your additional reagent, then seal the adapter back in place. You will need to degas the pot afterward.

D. Quenching Solvent Pots:

It is often necessary to dry solvents using a sodium/benzophenone solvent pot in the lab. If done correctly, excess sodium will need to be disposed of after the solvent has been dried. To safely quench the sodium pots:

1. Always quench pots in a clean and empty hood, away from bottles of flammable solvents.

2. The pot should be completely dried of solvent. This can be done by vacuum transferring (see vacuum transfer SOP) the remaining solvent or just pumping down into a solvent trap.

3. Carefully open the pot to the air, and salvage any large pieces of Na that might remain for later use. If your pot was made correctly this will not be necessary, but let's face it—there are a lot of incorrectly-made pots in the world with way too much Na in them.

4. A N_2 stream should be flowing through the flask. If you have a single neck flask, then use a N_2 hose attached to house nitrogen to blow N_2 in and continue to flush through the remaining steps. If you have a two or three neck flask, blow N_2 in through one neck and leave one of the remaining necks open.

5. Add toluene to the pot and begin stirring. The stirring should be fast enough to get adequate mixing of the sodium chunks and the benzophenone.

6. Slowly add isopropanol. Make sure that the flask is still under N_2 flush. If the bubbling or reflux becomes too vigorous, stop adding isopropanol and wait for the bubbling to subside. It should take about 15 mL of isopropanol for every gram of sodium in the pot.

7. Once the pot stops bubbling after further isopropanol addition, allow the mixture to stir for at least one hour.

8. After stirring, slowly add methanol to the mixture. The amount of methanol added to the pot should match the amount of isopropanol added in step 5.

9. Stir the mixture overnight.

10. After stirring overnight, check for remaining sodium chunks in the pot. If sodium persists, repeat steps 5-7. If there is no visible sodium, add water dropwise to the pot. If there is no immediate reactivity, add 15 mL of water for every gram of sodium that was originally in the pot.

11. Dispose of waste into the appropriate waste containers.

By signing below, you indicate that you have read and understand the content of this document.

Name: _____ Date: _____