Method for Preparation of Small Amounts of P4.

The following is a description of a technique I have used to prepare small amounts (< .5g at a time) of white (yellow) phosphorus from sodium hexametaphosphate (calgon). The chemistry for reduction of calgon using aluminum and silica was published by Franck more than a century ago and first mentioned near the beginning of this thread by Polverone 6 years ago.

$$6NaPO3 + 10Al + 3Si02 = 3Na2Si03 + 5Al203 + 3P2$$

The reaction, properly implemented, is self -sustaining and initiates at temperatures which can be obtained with a lab (Meker) burner and conducted in a test tube (18mmX150mm, pyrex), which can be re-used.

The reaction has the advantage of no hydrogen, hence no phosphine. Although the above stoichiometry calls for reactants in the ratio 3.4:1.5:1.0, by conducting several variations, I've achieved the best results by increasing the Al portion from 1.5 to 1.75. I've used several aluminum powders, including 20 micron spherical (Alfa) but the best results are with pyrotechnic (dark) Al. I have also tried Zn and Mg as reductants but was unable to initiate the reaction at relatively low temperature using Zn, and Mg was (as expected) explosive.

The silica used was in the form of silica flour- not as fine as fumed silica, but adequate.

The reactants are dried prior to mixing by careful heating. The Al and SiO3, already finely divided, are added to the NaPO3 and everything in 'whizzed' in a coffee grinder for a couple of minutes.

Exactly 3 grams of the mix are placed in the bottom of the test tube and a 2 inch (50mm) wide strip of paper towel is wrapped around the test tube at the neck. This is soaked in H20, which in the air current of the fume hood cools this portion of the tube.

For this experiment CO2 is used to provide a protective atmosphere. A 3-hole stopper is fitted with two glass tubes and a thermocouple probe. CO2 is fed to the test tube prior to heating and the gas from the test tube is exhausted through another tube immersed in 50ml of H2O within a 100ml grad cylinder to capture any P which may escape the tube.

Heating is begun (slowly) with the Meker (fed by propane) to compensate for the probe thermal inertia, and the temperature is monitored for signs of reaction. The bubbling in the cylinder increases audibly as the reaction begins. The reaction takes 3-4 seconds during which a dull red light is emitted. The temperature meter indicates reaction onset at about 500C with a peak temperature of ~ 700C being reached. With larger charges the test tube may be melted or cracked.

Following the reaction, the burner is kept at the bottom of the test tube for several seconds to drive any residual free P out of the ash (Na2Si03 + Al203) toward the cooler neck portion of the tube for condensing. The burner flame is slowly moved forward toward the neck driving the free P with it. After all visible P is at the cooler neck, heating is stopped and the tube is allowed to cool. Excellent separation is achieved which makes harvesting the P relatively simple. The tt is disassembled under water and the P scraped from the inside of the tube using a stainless steel spatula. If all white P is desired, the resulting mix of red and yellow P is added to another tube and sublimed to all white P (using the same configuration tt and cooling scheme).

Results: From 3 g of the above mentioned mix, .5 g of P4 is available. The resultant P4 (after re-subliming) weighed .25g or just 50% of theory. The residual ash weighed 2.64 g indicating that no more than .36g of P was released. These numbers are typical in my experience for small batch processing using this technique. Some P is undoubtedly lost due to small scale processing and, presumably, some is not released due to inefficiencies in reacting powdered solids intimately. Also, some may be lost in side reactions.

Fig. !: Ready to begin. Blue silicon rubber hose feeds CO2 in, yellow latex connects exhaust to tube immersed in 100ml cylinder. Thermocouple probe seen at far right.

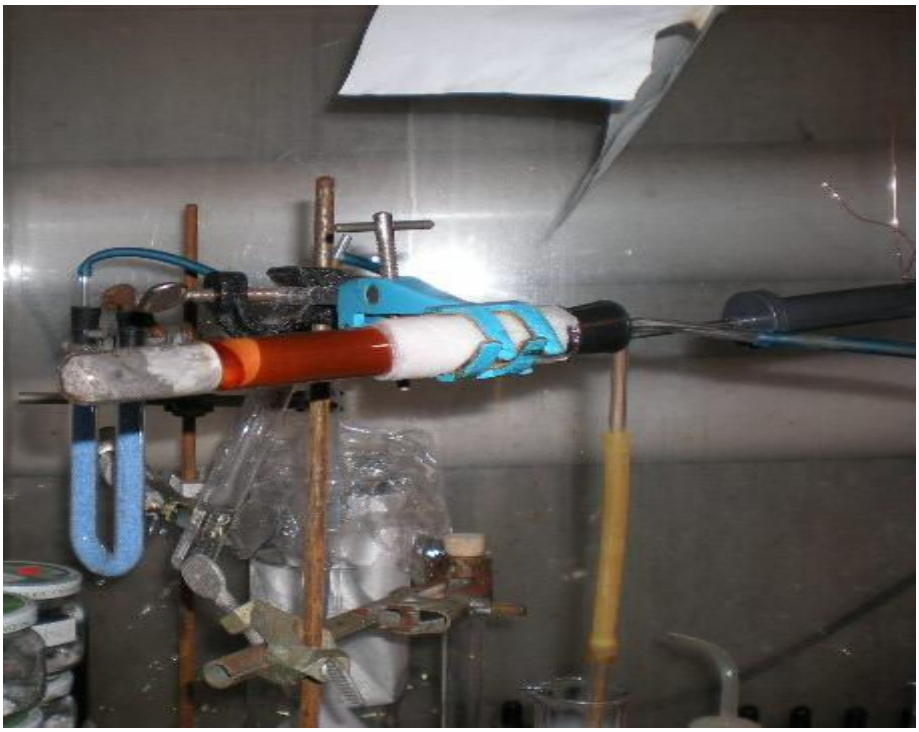

Fig. 2: Reaction complete. Interface between residual ash on left and red P on right seen.

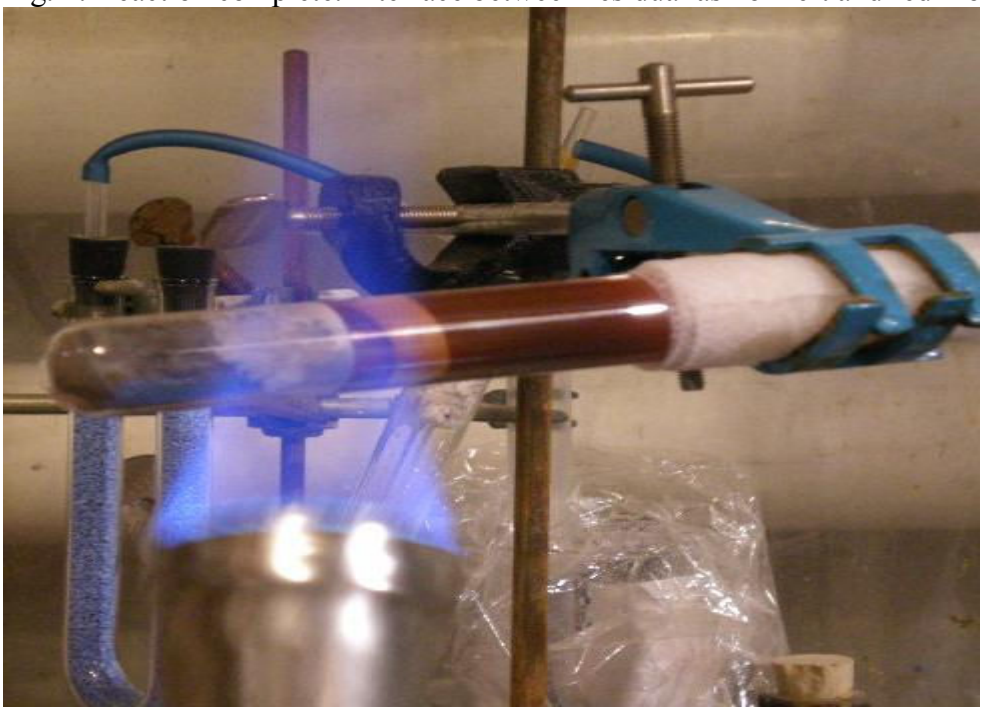

Fig. 3: Moving heat from left to right to drive P to cooler neck of tube.

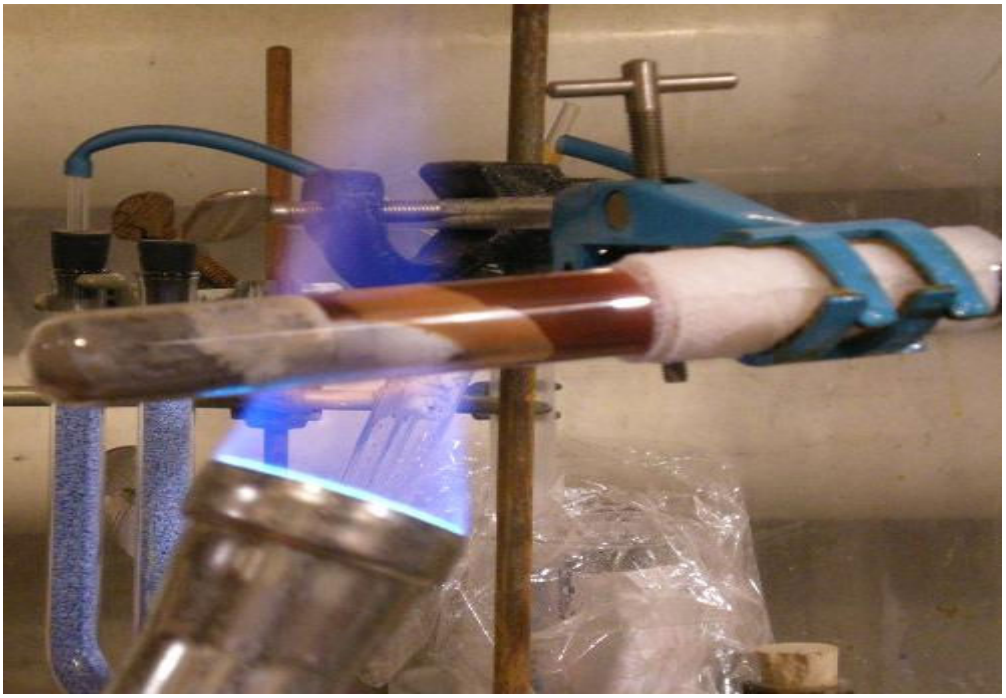

Fig. 4: some progress seen.

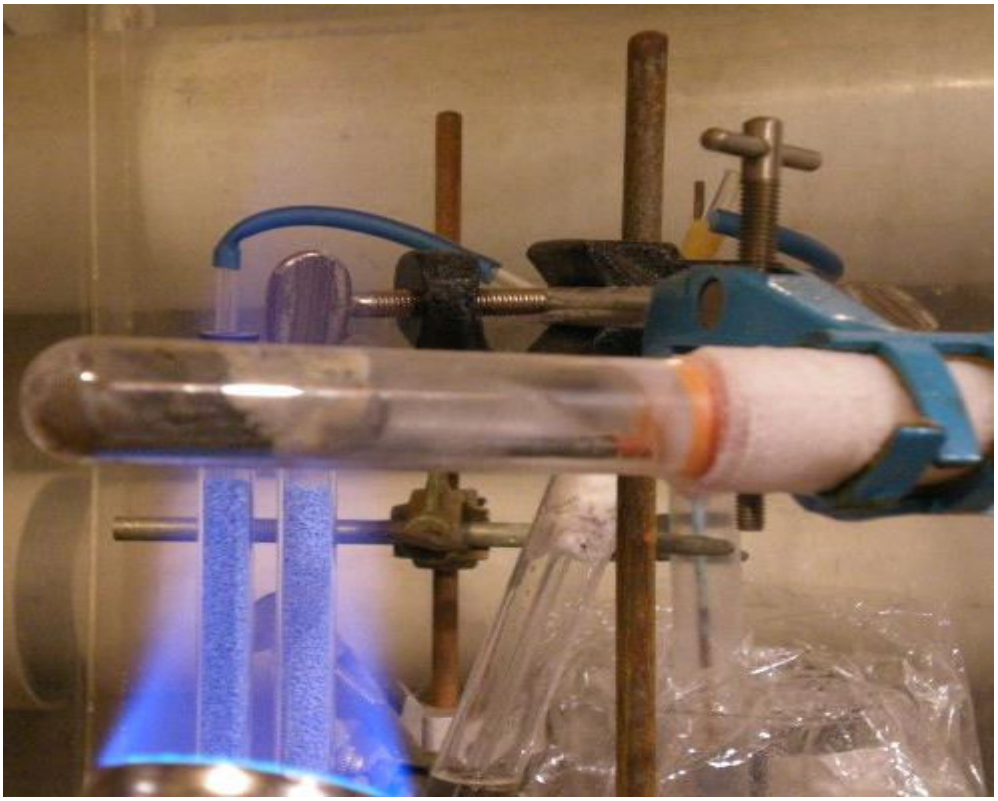

Fig. 5: Separation essentially complete.

Fig. 6: Ash on left, then clear tube and red/yellow/white P on right.

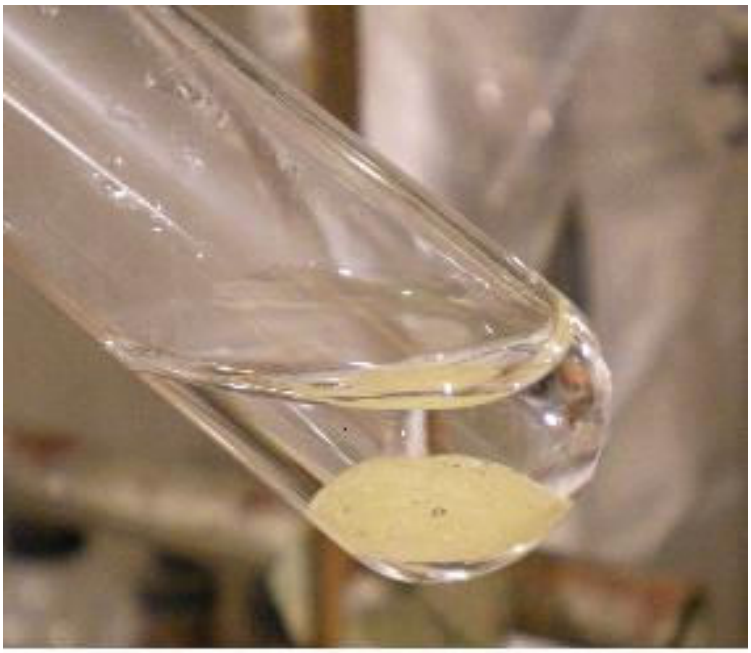

Fig 7: Final product after subliming P harvested from 6 above and re-melting under water.