Section 5.28 Title: Generating and Quenching Reactive Gases

Revision Date: 11/01/19

Prepared By: Daniel SantaLucia and Michael Roy **P.I.:** Prof. John F. Berry

Prior Approval: This procedure **IS** considered hazardous enough that prior approval is needed from the Principal Investigator.

Involves Use of Particularly Hazardous Substance (PHS)? Yes

___ Carcinogen ___ Reproductive Toxin _X_ High Acute Toxicity

Does this procedure require medical surveillance? No

Does this require use of a fit-tested respirator? No

Brief Description of Procedure:

Generation of reactive gases (CO, H_2S, and Cl_2) used in the Berry lab with general apparatus. Quenching of gases included within apparatus.

Location: *List the locations (buildings/rooms) where this procedure may be performed. For use of a PHS indicate a more precise location within the room, if appropriate, as a designated area.*

Daniels Chemistry - All Berry group labs

Chemicals Involved:

Chemical	Physical or Health Hazard (e.g. carcinogen, corrosive)
Methanesulfonyl chloride	Toxic, corrosive, lachrymator
Formic acid	Corrosive
Triethylamine	Irritant, corrosive
Copper (II) oxide	
Carbon monoxide	Toxic
Iron (II) sulfide	
Hydrochloric acid	Corrosive
Copper (II) sulfate pentahydrate	
Hydrogen sulfide	Toxic, flammable
Bleach (NaOCl)	Oxidizer
Sodium hydroxide	corrosive
Chlorine gas	Toxic, irritant, strong oxidizer
Organic solvents	Flammable, carcinogenic (some)

Other Hazards: *Include hazards, other than chemical, that may be present during operation of the procedure.*

Flammable solvents; needles; potential for pressure buildup.

Exposure Controls: *(Check all that apply)*

PPE: _X_ Safety Glasses ___ Face Shield ___Chemical Splash Goggles

___Chemical Apron _X_ Gloves (Nitrile) _X_ Lab Coat

___Respirator (type) ___Other:

Engineering Controls:

_X_ Fume Hood ___Biosafety Cabinet _X_ Glove box
___ Vented gas cabinet ___Other:

Administrative Controls: *List any specific work practices needed to perform this procedure (e.g., cannot be performed alone, must notify other staff members before beginning, etc.).*

Notify other lab members when generating reactive gases. Receive training from JFB before generating reactive gases. Never generate reactive gases alone.

Task Hazard Control Table: *For procedures involving numerous steps, it may be convenient to indicate specific requirements for individual tasks in the table below:*

N/A

Waste Disposal: *Describe any chemical waste generated and the disposal method used.*

Dispose of organic solvents in the appropriate carboy. Aqueous solutions can be neutralized and disposed of down the drain. Excess solids can be disposed of in the trash.

Accidental Spills: *Describe the procedure for handling small chemical spills that may occur during this procedure. Note that for large spills it may be appropriate to call 911.*

Small spills may be cleaned with an absorbing material. The material should be placed in a fume hood to dry after the spill has been cleaned.

Decontamination Procedures (required for PHS use): *Describe the procedure for decontamination of personnel and equipment.*

N/A

Training: *Describe any training needed prior to performing this procedure. Include training performed in-lab and any required demonstrations of competency.*

Formal training and documentation is required. Training is done on an individual basis by Prof. Berry.

Principle Investigator Approval: I have reviewed this procedure and approved it for use. Note: Modifications to the procedure may require update to this form.

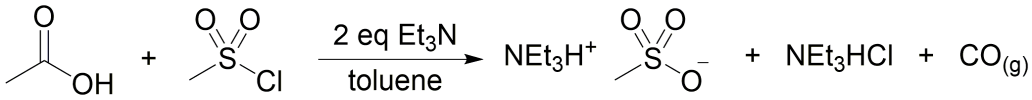
Name: John F. Berry Signature: _____ Date: _____

Generating and Quenching Reactive Gases

General Notes

- First/most important question: is there a better way to do your chemistry that *doesn't* involve generating these gases?
- Ensure that Tygon tubing is used (be careful if using wet Cl_2 to wash tubes out after use, as this tubing will not hold up as well under prolonged exposure according to: https://www.usplastic.com/catalog/files/charts/Tygon%20CC.pdf. The Tygon is chemically resistant to dry Cl_2 and the other gases in this SOP).

CO:



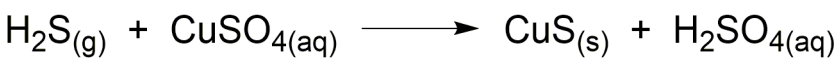
Source: *React. Chem. Eng.* **2016**, *1*, 142 – 146.

1. Set up a 3-neck round bottom flask with a stir bar and add appropriate amount of formic acid and methanesulfonyl chloride (mesyl chloride) to flask in a 1:1 molar ratio dissolved in dry degassed toluene (make sure concentration of each reagent is ~ 0.5 M); use an appropriate sized flask for this reaction: the solvent level should not be more than halfway up the flask.
2. Attach an N_2 inlet with valve to the 3-neck round bottom flask.
3. Attach a pressure-equalized addition funnel to the center neck of the flask; stopper off top.
4. Attach an outlet hose to the 3-neck flask; the outlet hose should be hooked up to a needle, which can be used to bubble CO through the desired solution in a separate flask. If the chemistry is water sensitive, it is advised to have a section of $CaSO_4$ desiccant in a drying tube between the generating flask and the needle to remove any H_2O vapor before the gas reaches the reaction.
5. To the addition funnel, add two equivalents of NEt_3, ensuring valve is closed. Make sure to stopper off the top. Make sure all ground-glass joints are greased and secured with keck clips or rubber bands.
6. The separate flask containing the reaction through which CO is being bubbled should have an outlet hose that allows excess CO to pass through a column containing powdered CuO. This will oxidize any excess CO to CO_2 and form Cu metal. Make sure to use at least two equivalents of CuO you need in case you make too much CO.

7. If doing air-sensitive chemistry, pre-flush system with N_2. When ready, begin stirring in the generating flask, close the N_2 inlet, and slowly open the addition funnel valve to allow for NEt_3 to drip at a slow rate (recommend rate: ~2 drops/second) into the stirring solution. Allow for all of the NEt_3 to drip into the stirring solution before moving on.
8. When the reaction is finished, open the N_2 valve on the inlet to flush the system with N_2 and remove any residual CO. When no more Cu metal forms in the quenching column, the apparatus is safe to disassemble.

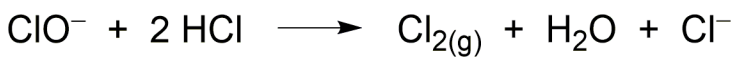
H_2S:

1. Set up a 3-neck round bottom flask with a stir bar and add the appropriate amount of solid FeS to the flask.
2. Attach an N_2 inlet with a valve to the 3-neck round bottom flask.
3. Attach a pressure-equalized addition funnel to the center neck of flask; stopper off the top.
4. Attach an outlet hose to the 3-neck flask; the outlet hose should be hooked up to a needle, which can be used to bubble H_2S through the desired solution in a separate flask. If the chemistry is water sensitive, it is advised to have a section of $CaSO_4$ desiccant in a drying tube between the generating flask and the needle to remove any H_2O vapor before the gas reaches the reaction.
5. To the addition funnel, add 15% HCl (4.94 M; 2 equivalents) ensuring the valve is closed. Make sure to stopper off the top. Make sure all ground-glass joints are greased and secured with keck clips or rubber bands.
6. A separate flask containing the reaction through which H_2S will be bubbled should have an outlet hose that allows excess H_2S to bubble into a beaker containing a saturated aqueous solution of $CuSO_4 \cdot 5\ H_2O$. This quenches any excess H_2S not used by reaction by forming solid CuS. Use *twice* the required amount of $CuSO_4 \cdot 5\ H_2O$ that you need (i.e. two equivalents) in case you make too much H_2S. Make sure the hose doesn't get blocked with solid CuS; jostle it occasionally to break up any chunks.



7. If doing air-sensitive chemistry, pre-flush system the with N_2. When ready, begin stirring in the FeS flask, close the N_2 inlet, and slowly open the addition funnel valve to allow for HCl solution to drip at a slow rate (recommended rate: ~2 drops/second) onto the FeS. Allow for all of the HCl solution to drip into the stirring FeS mixture before moving on.
8. When the reaction is finished, open the N_2 valve on the inlet to flush the system with N_2 and remove any residual H_2S. When no more CuS forms in the quenching beaker, the apparatus is safe to disassemble.

Cl_2:



1. Set up a 3-neck round bottom flask with a stir bar. Add the desired amount of concentrated 37% HCl (12.18 M). Use an appropriate sized flask for scale you're doing: the solvent level should not be more than half-way up the flask.
2. Attach an N_2 inlet with a valve to the 3-neck round bottom flask.
3. Attach a pressure-equalized addition funnel to the center neck of flask; stopper off the top.
4. Attach an outlet hose to the 3-neck flask; the outlet hose should be hooked up to a glass tube, NOT a needle (Cl_2 reacts with stainless steel), which can be used to bubble Cl_2 through the desired solution in a separate flask. If the chemistry is water sensitive, it is

advised to have a section of $CaSO_4$ desiccant in a drying tube between the generating flask and the glass tube to remove any H_2O vapor before the gas reaches the reaction.

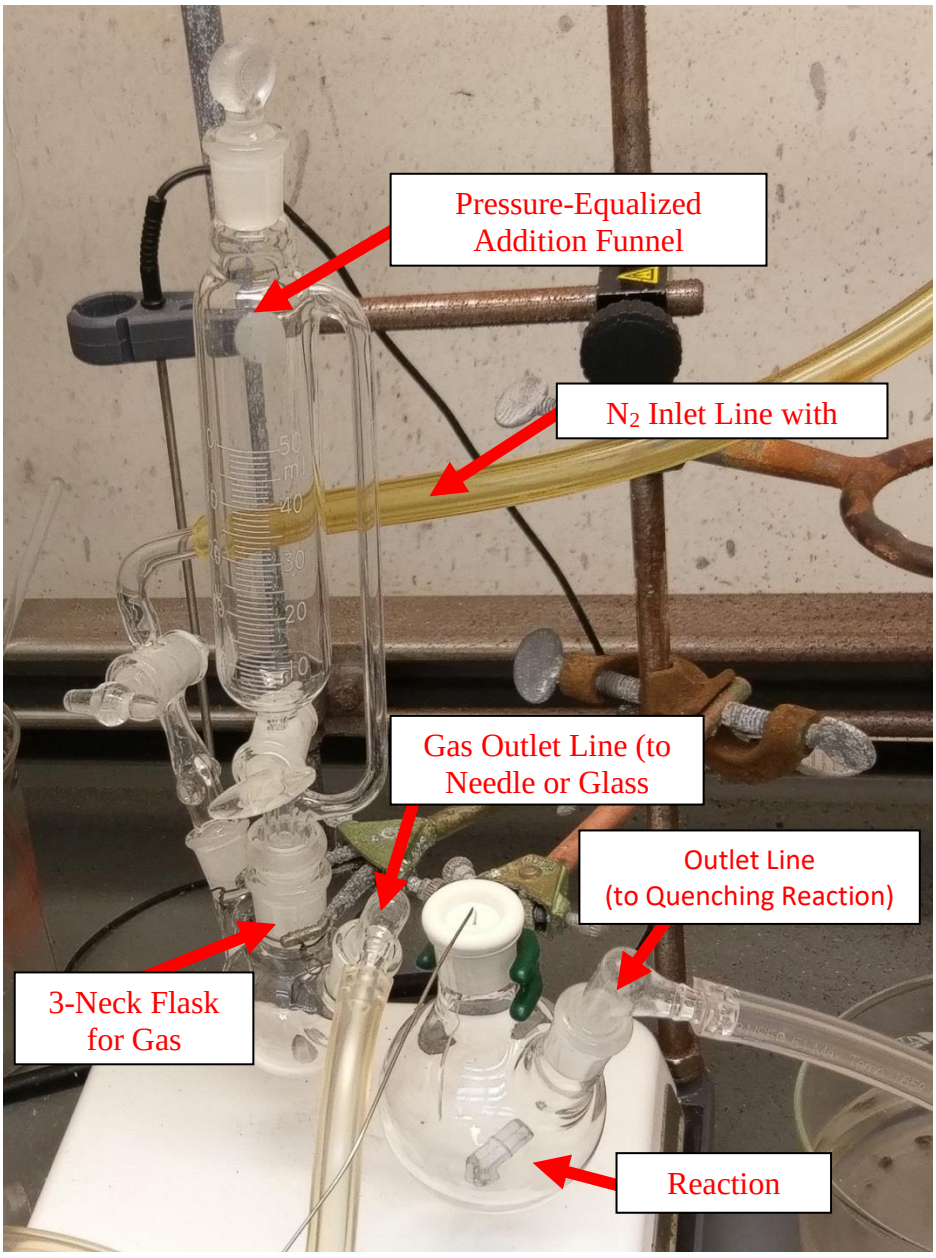
5. To the addition funnel, add the appropriate amount of aqueous bleach (NaOCl; Clorox brand bleach is sufficient unless you need to be more precise) ensuring the valve is closed. Make sure to stopper off the top. Make sure all ground-glass joints are greased and secured with keck clips or rubber bands.
6. A separate flask containing the reaction through which Cl_2 is being bubbled should have an outlet hose that allows excess Cl_2 to bubble into a beaker containing a 50% aqueous solution of NaOH (18.94 M); put the beaker in an ice bath to keep the quenching solution cold. This quenches any excess Cl_2 not used by the reaction by forming ClO^-, ClO_3^-, and Cl^- anions. Use *twice* the required amount (i.e. two equivalents) of NaOH that you need in case you make too much Cl_2.

$$Cl_{2(g)} + 2\ NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + NaClO_{(aq)} + H_2O$$

$$3\ NaClO_{(aq)} \longrightarrow 2\ NaCl_{(aq)} + NaClO_{3(aq)}$$

7. If doing air-sensitive chemistry, pre-flush the system with N_2. When ready, begin stirring in concentrated HCl flask, close the N_2 inlet, and slowly open the addition funnel valve to allow for the bleach solution to drip at a slow rate (recommended rate: ~2 drops/second) into the stirring HCl solution. Allow for all of the bleach solution to drip into the stirring HCl solution before moving on.
8. When the reaction is finished, open the N_2 valve on the inlet to flush the system with N_2 and remove any residual Cl_2. When no more green color is visible in the apparatus, blow N_2 through apparatus for another 20 minutes; the apparatus is then safe to disassemble.

Gas Generation Apparatus



*NOTE: All ground glass joints need to be secured with keck clips or rubber bands (not depicted in the diagram above).