

Rauchfuss Group Prep of $\text{Fe}_2\text{S}_2(\text{CO})_6$

Large Scale Synthesis of $\text{Fe}_2\text{S}_2(\text{CO})_6$.

A three neck, 5-liter round-bottomed flask was fitted with a good mechanical stirrer, a N_2 -inlet adapter, and an addition funnel with a septum connected to a bubbler. After being flushed with N_2 (strong flow) for 20 min, the flask was charged with 208 g (3.7 mol, 6.5 equiv, pellets) of KOH followed by 500 mL of degassed MeOH and 200 mL of degassed water. The solution was cooled to 0 °C with an ice bath before 75 mL (0.57 mol, 1 equiv) of $\text{Fe}(\text{CO})_5$ were added to the addition funnel and added dropwise to the reaction over the course of 30 min. The mixture was then stirred for an additional 30 min. To this mixture ($\text{HFe}(\text{CO})_4^-$) was added 182 g (5.7 mol, 10 equiv) of elemental sulfur, delivered in two portions over 10 min. *Caution: this step is extremely vigorous.* The black mixture was stirred for 30 min at 0 °C, then 500 mL of H_2O and 2000 mL of pentane were added to the reaction flask. Finally 1000 mL (10,26 mol, 18 equiv) of HCl (37%) were added dropwise over the course of 3 h. *Caution! evolution of H_2S .* The ice bath was then removed, and the reaction mixture was stirred at room temperature for 1 h.

The resulting reaction mixture consists of a dark red pentane layer a black precipitate suspended between the pentane layer and the clear aqueous phase. The pentane layer was cannulated into a beaker (do not cannulate out the black mud) and filtered through a pad of ca. 400 mL of Celite. The reaction mixture was extracted with pentane until the extracts were no longer red (4x extracts, 1.5 L), these pentane extracts were also passed through the Celite. Solvent was reduced under reduced pressure at a rotary evaporator to approximately 500 mL. This solution was washed with equal volume of water (three washes) then dried over MgSO_4 . Evaporation of the solution on a rotary evaporator gave several grams of deep red solid. This material is stored in a refrigerator in a sealed container and worked up as described below.

Chromatographic Work-Up

A 20-gram portion of the crude solid from the previous procedure was dissolved in 60 mL of pentanes. If any solid appears, do not try to dissolve it, and definitely do not put the solid on the column. It is elemental sulfur. This solution was chromatographed on an 8 x 25-cm silica column eluting with pentanes. The first red orange band was collected, and solvent was removed using a rotary evaporator. The solid was extracted into 30 mL of pentanes, and this extract was filtered through a small plug of Celite to remove elemental sulfur. Solvent was removed, and the solid was briefly dried on the vacuum line. Yield 17 g. *Note:* $\text{Fe}_2\text{S}_2(\text{CO})_6$

sublimes readily at room temperature and reduced pressure. We do not recommend sublimation as a method of purification.

IR (pentanes): 2084 (s), 2044 (m), 2008 (m), 1993 (s), 1967(vs), 1957 (vs) cm^{-1} .

The second chromatographic band ($\text{Fe}_3\text{S}_2(\text{CO})_9$) is darker red. IR (pentanes): 2063 (m), possibly 2044 (m), 2024 (m), 1984 (vs) cm^{-1} .

Note: if the column is not long enough, $\text{Fe}_2\text{S}_2(\text{CO})_6$ and $\text{Fe}_3\text{S}_2(\text{CO})_6$ will not separate.

Note: do not use any CH_2Cl_2 in the chromatography

Areas for further optimization

The following should be tested at a scale reduced from the above for ease of workup.

- 1- Use a different stirring apparatus to efficiently mix the two phases (water and pentane) and the solid that forms at the interphase. Also when you add acid, the acid lays on top of the solid and doesn't reach the water phase continuously but in big aliquots causing local increasing of temperature therefore pentane to boil and even the threat of explosions!
- 2- Use a different solvent (higher boiling point) to extract the formed $\text{Fe}_2\text{S}_2(\text{CO})_6$ like hexane or heptane. Possibly even DCM so that the aqueous phase is at the top. A major impurity using pentane is elemental sulfur, but DCM may extract way excessive amounts of impurities!
- 3- Temperature may play an important role. Examine increases in the temperature to 40-50 $^{\circ}\text{C}$ before adding the acid.
- 4- Vary the amount of acid and sulfur, which are used in large excess.
- 5- Conduct the reaction in the dark since $\text{Fe}_2\text{S}_2(\text{CO})_6$ decomposes with light.
- 6- Test if the formed $\text{Fe}_2\text{S}_2(\text{CO})_6$ decomposes over time with reaction conditions. For example stir a pentane solution of it with water and conc. HCl and monitor the IR spectrum.