Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary Information – Important Safety Considerations

Synthesis and utilisation of disulfur dinitride, S_2N_2, should not be attempted without thorough understanding of the practical procedure as outlined in our prior work,[1, 2] and careful appreciation of the points noted below. Though these cover many of the pertinent issues, continued care and attention is imperative when working with these materials as it is impossible to list all potentially dangerous scenarios.

Purified S_4N_4 (the process in question requires the use of high purity, and thus more sensitive, material) is a potentially pernicious friction sensitive explosive and **amounts as small as 50 mg (or less in some circumstances) have the potential to inflict serious injury, particularly if glassware breaks in the process.** When used with due care and attention these risks can, however, be significantly reduced - as attested to by the fact that during the course of our work we have run the S_2N_2 generation process in excess of 100 times with no problems. S_4N_4 can be safely stored (as noted below) and we know of no reports of spontaneous problems at ambient temperature and in the absence of friction. **However**, the following scenarios **must** be avoided

- **Use of metal spatulas.** When weighing out the material, Teflon coated or plastic spatulas should be used. Care should be taken to avoid excessive pressure on samples – given that the crystallised material is quite free flowing there should be no need to "dig" into samples. As noted below it is sensible to store the bulk material in separate vials of ca 1g, and take samples for accurate weighing from these.
- **Trapping of even small crystalline samples within ground glass joints.** Even in the presence of vacuum grease this is potentially hazardous as even a very minor initiation can have an amplified effect on the stressed glass.
- **Overheating of solid material.** It is crucial that the temperature of any heating unit set up to start the volatalization process is carefully controlled and regulated – see the experimental in reference 1.

As the S_2N_2 generated is used *in situ* it follows that its friction sensitivity is less of an issue; however the following important points should be noted:

- If a run is interrupted (e.g. by loss of vacuum) and thus residual S_2N_2 remains to be dealt with, the apparatus should be left open to air at ambient temperature at least overnight, thereby ensuring polymerisation/hydrolysis of the material.
- All residues from runs (i.e. the bulk polymer which coats the apparatus or residues from the above scenario) should be assumed to potentially contain small amounts of S_4N_4 or S_2N_2. Thus cleaning (see below) must not involve scraping of solids from the side of the reaction vessel.

S_4N_4 preparation

Tetrasulfur tetranitride, S_4N_4, may be prepared in crude form following synthetic routes outlined by Villena-Blanco and Jolly.[3] As SCl_2 is less commercially available now, S_2Cl_2 can be employed with chlorination prior to reaction with ammonia. In such cases **it is**

important to purge the reaction vessel thoroughly with nitrogen gas prior to ammonia introduction in order to avoid accidental synthesis of NCl_3. **In contrast to some literature sources we would strongly recommend that purification of the crude material *via* Soxhlet extraction with 1,4-dioxane is NOT performed** as this leads to the risk of hot-spot formation and serious detonation. Instead, recrystallization from toluene can be performed, though in this case it is important that:

- The toluene solutions are not overheated. Thus if performed in a conical flask care must be taken to make sure evaporation of the toluene from the meniscus does not leave overly heated solid S_4N_4.
- The mixtures should be efficiently stirred to make sure solid samples at the bottom of the flask do not overheat.
- Decanting of the hot solutions from impurity residues, followed by slow cooling, generates high quality crystals of S_4N_4; cooling should not be all the way to ambient (and certainly not to ice) temperature in order to avoid sulfur crystallisation.
- Filtration of the final material should be onto paper **NOT** sintered glass.

Storage of the recrystallised product should be in well protected, screw-top plastic sample vials with no more than *ca.* 1 g of product per vial.

$(SN)_x$

Once exposed to S_2N_2, all fingerprints are developed in the form of polythiazyl, $(SN)_x$. Under usual handling conditions, this material poses no inherent safety risk, although some decomposition to S_4N_4 is inevitable with time. $(SN)_x$ can be stored under nitrogen or sealed under vacuum for indefinite lengths of time and trace S_4N_4 contamination can be removed by washing samples in CH_2Cl_2 until the filtrate runs clear.

Cleaning Regime

Thin film coatings of $(SN)_x$ on the inside of the apparatus may be removed by first washing with CH_2Cl_2 and acetone before soaking in a KOH/IMS bath for 10-30 mins.

Residues containing S_4N_4 (e.g.the washings above) can be accumulated in a dedicated vessel, allowed to evaporate to dryness then slurried with water for *ca.* 24 h. Addition of sodium hypochlorite solution may then be safely facilitated and the resulting sulfur residues should be disposed of as per usual laboratory practice.

References

1 R. S. P. King, P. F. Kelly, S. E. Dann, R. J. Mortimer, *Chem. Commun.*, 2007, 4812-4814.
2 R. S. P. King, P. F. Kelly, R. J. Mortimer, *Chem. Commun.*, 2008, 6111-6113.
3 M. Villena-Blanco, W. L. Jolly, *Inorg. Synth.*, 1967, **9**, 98-102.