

# SYNTHESIS OF A SOLID ACID, 12-Tungstosilicic acid, $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 7\text{H}_2\text{O}$

## REFERENCES:

- E. North, *Inorg. Syntheses*, **1**, 129 (1939).
- N. N. Greenwood and A. Earnshaw, "Chemistry of the Elements" Pergamon Press, 1984, pp 1171-1186.
- F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th Edition, pp 811-818.
- D. M. Adams and J. B. Raynor, *Advanced Practical Inorganic Chemistry*.

## 1. INTRODUCTION

The condensation of oxometalate anions in acidic solutions is a commonly encountered reaction in inorganic chemistry. For example, the following equilibria between molybdenum species are highly dependent on pH:



These ions are only two of the many complex species which occur in solution, and hydration, protonation and further condensation or hydrolysis reactions can increase the diversity of these systems. The basic building block of these isopolyanions is the  $\text{MoO}_6$  octahedron, and these units can be connected by sharing corners, edges, but not faces. In some structures  $\text{MoO}_4$  tetrahedra can also be found. Tungsten exhibits very similar chemistry in this regard.

There has been renewed interest in these types of compounds, largely as a result of their potential and actual, use as catalysts. They have found use in selective oxidation and acid catalyzed reactions.

In this laboratory exercise you will prepare a heteropolymetalate species which is a solid acid. The object of the experiment is to:

- a) Prepare the compound 12-tungstosilicic acid using a solvent extraction method.
- b) Quantitatively determine the available protons in this material.
- C) To test the material as a solid acid catalyst.

## 2. PROCEDURE

*This entire procedure should be carried out in the fumehood. Ensure that there is no naked flame in the hood or close to you.*

Dissolve 15 g of sodium tungstate dihydrate,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , in 30 ml of water and add 1.16 g of sodium silicate solution (density  $1.38 \text{ g/cm}^3$ ). Stir the solution vigorously at just below the boiling point, and add concentrated hydrochloric acid (10 mL) dropwise over a period of about 30 minutes, using a dropping funnel. Cool the solution to room temperature, then filter it, add a further 5 mL of concentrated hydrochloric acid slowly, and transfer it into a separatory funnel. Shake the solution with diethyl ether (12 mL); at this point you should observe three layers in the funnel. If not, add a little more ether, shake and again allow to separate. Withdraw the bottom, oily ether layer and save it in a beaker. Repeat the extraction process several times, until the yellow product in the middle layer has been completely removed. Discard the liquid left in the funnel (put it in the residues bottle), rinse out the funnel, and return the ether extracts to the funnel, together with a solution of 4 mL of concentrated hydrochloric acid in 12 mL of water, and an additional 4 mL of ether. After shaking, run off the lower (ether) layer into an evaporating dish and allow the solvent to evaporate. Dry the white crystalline product at  $70^\circ \text{C}$  for about two hours, then put it into a tared sample vial, reweigh the vial and record your yield.

**DO NOT USE A METAL SPATULA TO HANDLE YOUR PRODUCT, OR IT WILL TURN BLUE!**

### 3. Determination of the acidity of the product

Weigh out about four grams of the product and dissolve it in deionized water, and dilute to 100 mL in a volumetric flask. Titrate 40 mL aliquots of the solution with the 0.1 M NaOH solution provided, using an appropriate indicator (e.g. methyl orange or chlorophenol red). Assuming the formula given in the title, calculate the moles of titratable protons per mole of compound.

### 4. Test of $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot \text{XH}_2\text{O}$ as a Solid Acid

Add 6 drops of cyclohexanol to 3 mL of cyclohexane. Shake to dissolve. Add ca. 0.2 g of  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  and shake for a few minutes. Filter to remove the solid acid from the solution A. Prepare a second solution B of 6 drops of cyclohexanol in 3 mL of cyclohexane. Add ca. 10 drops of dilute bromine water (pale brown color) - 20 drops of saturated  $\text{Br}_2$  water in 20 mL of distilled water - to each of the cyclohexane solutions and shake. Solution A should decolor, and a white precipitate of  $\text{C}_6\text{H}_{10}\text{Br}_2$  may appear in the organic layer.

Solution B will extract the brown  $\text{Br}_2$  out of the  $\text{Br}_2$  water into the organic layer, but the organic layer will not decolor.



**NB:** It is important to filter out the solid acid after reaction with cyclohexanol since it appears to react with bromine water by itself.

## Post-lab questions

1. What is a Keggin unit? Without giving a complex diagram briefly describe what is meant by this term.
2. Give two examples, other than that made in this experiment, of compounds which are "solid acids" and which can be used as acid catalysts.
3. What other atoms can occupy the tetrahedral position in the center of the  $M_{12}$  polyanion in which the Si is found in  $H_4SiW_{12}O_{40} \cdot 7H_2O$  ?