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Student-Designed Experiment: Preparation and Mass Spectrum of Cyclohexasulfur

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Abstract: The teaching laboratory is an ideal environment for fostering active learning; yet, it is often criticized for being too "cookbook." In introductory courses, the high student population often dictates that many students perform the same experiment simultaneously. By working in discussion groups, with individual bench work, we are able to turn this communal effort into a strength. This article describes the revision of a recipe-style experiment into a student-designed procedure.

There are many reasons why a practical component is included in a chemistry course. One of our primary goals is to teach students how to perform experiments by design and by technique. It is unlikely that they will be required to perform exactly the same process later in life, but the method and approach to solving the problem presented should ideally be applicable to many situations. To this end, we have considered alternative ways of presenting traditional material. This paper [1] describes the synthesis of S_6 in two formats. Both, in our opinion, have value in their respective courses, and we wish to demonstrate to fellow chemical educators that, in some cases, the effectiveness of a teaching experiment can be influenced by the presentation more than by the choice of the specific chemical reaction.

The chemistry of this experiment has been known for about a century. Cyclo-S_6, sometimes known as Engel's sulfur, can be prepared by the acidification of an aqueous solution of sodium thiosulfate at low temperature [2]. The following sequence of reactions takes place.

$$HS_2O_3^- + S_2O_3^{2-} \xrightarrow{k_1} HS_3O_3^- + SO_3^{2-}$$

$$HS_3O_3^- + S_2O_3^{2-} \xrightarrow{k_2} HS_4O_3^- + SO_3^{2-}$$

$$HS_{n+1}O_3^- + S_2O_3^{2-} \xrightarrow{k_n} HS_{n+2}O_3^- + SO_3^{2-}$$

$$HS_{n+1}O_3^- \xrightarrow{k_r} + S_n + HSO_3^-$$

Ring closure to give cyclo-S_6 will occur if $k_r > k_n$, but above 10 °C, the formation of cyclo-S_8 and polycatenasulfur is highly favoured. The S_6 molecule has been shown crystallographically to be a puckered ring with the chair conformation [3].

The traditional procedure (see Supporting Material I) used in a senior class has a recipe-style synthesis followed by having the student record the mass spectrum [4] of the prepared compound at a low ionizing potential and compare the results with those found from a sample of cyclo-S_8. The purity of the S_6 sample, as determined by the mass spectroscopic analysis, is one of the criteria used for the evaluation of the student's performance.

In a second year course, the emphasis is placed on the procedure rather than the product (see Supporting Material II). The out-of-laboratory work to be done by each student is to plan the procedure. The following italicized information is given to the student. For the first 45 minutes of the class, students work in groups with the instructor to consolidate their procedural plan. The comments following the italicized information are the thoughts that we wish to inspire, sometimes needing provocative questioning by the instructor.

The acidification of aqueous sodium thiosulfate will generate the desired product, S_6, as described by the following equations.

$$H^+ + S_2O_3^{2-} \rightarrow HS_2O_3^-$$

$$HS_2O_3^- + S_2O_3^{2-} \rightarrow HS_3O_3^- + SO_3^{2-}$$

or, in general, this reaction can be continued as

$$HS_nO_3^- + S_2O_3^{2-} \rightarrow HS_{n+1}O_3^- + SO_3^{2-}$$

the final reaction has occurred when

$$HS_{n+1}O_3^- \rightarrow S_n + HSO_3^-$$

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Generate the net equation for the overall reaction. The net equation is:

$$H^+ + 6S_2O_3^{2-} \rightarrow S_6 + HSO_3^- + 5\,SO_3^{2-}$$

Breaking this down into steps gives:

$$H^+ + S_2O_3^{2-} \rightarrow HS_2O_3^-$$

$$HS_2O_3^- + S_2O_3^{2-} \rightarrow HS_3O_3^- + SO_3^{2-}$$

$$HS_3O_3^- + S_2O_3^{2-} \rightarrow HS_4O_3^- + SO_3^{2-}$$

$$HS_4O_3^- + S_2O_3^{2-} \rightarrow HS_5O_3^- + SO_3^{2-}$$

$$HS_5O_3^- + S_2O_3^{2-} \rightarrow HS_6O_3^- + SO_3^{2-}$$

$$HS_6O_3^- + S_2O_3^{2-} \rightarrow HS_7O_3^- + SO_3^{2-}$$

$$HS_7O_3^- \rightarrow S_6 + HSO_3^-$$

If the temperature is not kept low enough, the break-up of the $HS_nO_3^-$ *ion will occur at different values of n, generating a mixture of sulfur species. Thus, the reaction must be carried out at –10 °C, which is low enough to prevent other forms of* S_n *from forming, but high enough to allow the reaction to take place.* At this stage, one might ask what sort of container will be used for the reaction. How will the temperature be kept low enough?

Ice mixed with a little methanol will create a bath cold enough to cool a flask to –15°. Surprisingly little methanol is needed to get low temperatures with ice; 50 mL will suffice for a full pan of ice. Where should the thermometer be placed, in the ice or the liquid below? The addition of rock salt can also help to maintain the low temperature. Shaved ice may not work as well as ice chunks.

The reaction is best carried out with a minimum of water present (25 mL). This information, combined with knowledge of the solubility of sodium thiosulfate, will tell the students how much solid to weigh out. About 12.5 g of the anhydrous salt should give a saturated solution. It does not matter if they use an excess, except that it has to be filtered off and is wasted. Using a saturated solution ensures that the minimum of water is employed.

The sodium thiosulfate must be in solution. The scale of the reaction should be the largest possible. This means that the sodium sulfate solution should be saturated. At this point, it is wise to confirm that everyone has checked the Material Safety Data Sheets (MSDS). Sodium thiosulfate is hygroscopic and an irritant.

The solubility of anhydrous sodium thiosulfate is 500 g L^{-1}. $Na_2S_2O_3{\bullet}5H_2O$, MW = 248.18 g mol^{-1} [CAS registry #10102-17-7]; anhydrous $Na_2S_2O_3$, MW 158.11 g mol^{-1} [CAS registry #7772-98-7]. The solubility of the pentahydrate is 79.4 g in 100 mL at 0 °C and 291.1 g in 100 mL at 45 °C. The solubility of the anhydrous salt is reported to be about 50 g in 100 mL at room temperature.

The acid should be concentrated and used in excess; 100 mL will be sufficient. The choice of acid should be discussed. Obviously, it will center on the common acids: nitric, sulfuric, and hydrochloric. Nitric is a common oxidizing acid and may well change the chemistry of the reaction. Thiosulfate has sulfur in the +6 and –2 oxidation states. The redox reaction for the net equation can be viewed as the oxidation of terminal S^{2-} to S^0 in S_6 and the reduction of the central S^{6+} atom to S^{+4} in the sulfite, or hydrogen sulfite. It is probably not a good idea to introduce more sulfate, so HCl [CAS registry #7647-01-0] is the safe choice. Remind the students of its corrosive properties.

The reaction is exothermic and spontaneous. So, a hot plate will not be necessary, but a stirrer is a good idea. Because low temperature is desired, it is beneficial to add one reagent slowly to the other. Cooling the largest volume at first makes sense; thus, have acid in the flask. Normally, one adds acid to water, but in this case, with a slow addition and controlled temperature, that rule can be bent. This needs to be discussed thoroughly with the students, **particularly the slow addition of the water solution to the acid.**

A precipitate (not the product) will form, which must be removed from the solution before the extraction of the product can be attempted. This will require that a vacuum filtration be done such that the solutions are still kept cool, even after filtering. This requires some prior planning to have the appropriate flasks chilled. The precipitate forms immediately on addition of thiosulfate solution, no matter how fast the addition.

The product is isolated by extracting the acidic solution with toluene (30 mL). One extraction is sufficient, but stir well (best to keep it in the flask at this stage). The separatory/dropping funnel used for the slow addition can be re-used for the separation. Toluene [CAS registry #108-88-3] is a toxic, flammable liquid.

The temperature may be allowed to warm slowly (no heating) to room conditions during the extraction phase. Warming at this stage does not seem to affect the product significantly and allows the toluene to dissolve the product, which it does not do at low temperature. The solution starts to turn yellow once the solvent mixture warms to room temperature.

The toluene extract can be dried with anhydrous magnesium sulfate. It will take about 15 minutes to take up the residual moisture. Add about a scoop of anhydrous magnesium sulfate [CAS registry #7487-88-9] and watch. If it clumps, then add more. Once the solvent is dry, the remaining powder will be obvious. Gravity filter to separate.

Crystals of product can be obtained by leaving the toluene solution at –15 °C for ~1 h.. Stopper the flask. It may have to be periodically shaken or scratched. Thorough cooling is necessary. Cover with foil. If all else fails, immerse in a dry ice/acetone bath instead. This tends to crash out the powder rather than form crystals. S_6 is very orange in color and S_8 (the obvious contaminant) is lemon yellow.

The yield of S_6 *is typically less than 5% of the theoretical value. What would the theoretical yield be? What is 5% of this value?* Assuming all 12.5 g of anhydrous $Na_2S_2O_3$ was used, 2.53 g would be the theoretical yield and 5% or this value is 0.127 g.

What options do you have for isolating this amount of material? Vacuum filtering seems to be the favorite answer, but there is a good chance that all the product will be lost by using vacuum filtration on such a small quantity. Gravity filtering might be better, but if the crystals have grown slowly, then they will likely stick to the glassware. In this case the solvent can be decanted from the product.

This experiment is offered as the last experiment in a ten-week course. The student groups have been the same for the duration of the course, so a working familiarity has been established. As you can imagine, most groups generate a procedure that is similar for every member, but not every group has the same approach. For instance, some choose to use a dropping funnel for the slow-addition step; others use a disposable pipette to deliver small aliquots of reagent. We encourage instructors to encourage any nonhazardous method as viable, although inefficient or bad practices will generate some discussion at the end. The report is written up in class, which is atypical for the course, but appropriate for the last week. Emphasis is placed on the detail of the procedure, which is not usual for a laboratory report of a traditional-style experiment.

The laboratory skills of a student at the second-year level are lower than those of a fourth-year student. In many cases, we suspect that S_8, rather than S_6, is produced because the temperature has been allowed to rise. Nevertheless, the advantages of encouraging independent thought in a student at this level outweighs the goal of producing the target product! The analysis done by these students is by mass spectroscopy, but because of the number of students, previously recorded spectra for S_6 and S_8 are issued. If the equipment is available, it is highly desirable for students to obtain the mass spectrum in order to evaluate the purity of their product.

Conclusion

Students at the second-year level have responded favorably to a final experiment in which they are encouraged to develop a procedure. At this stage in their learning of laboratory skills, it is not convincing that all experiments in the course should be converted to this format. We are, at present, rewriting another traditional experiment, the synthesis of tin(IV) iodide, in a similar style. Information about this experiment, as well as any current revisions of the sulfur experiment, are available by email request (from DB).

As a final note, this experiment is best first performed by the instructor before the class. The experience significantly adds to the effectiveness of the instruction.

Supporting Materials. Supporting Materials I is the traditional-style experimental procedure as given to the senior-level students. Supporting Materials II is the information given to the students in the second-year course, together with the teaching notes given to the laboratory instructors. Both are available as Adobe PDF files in a single compressed WinZip file (http://dx.doi.org/10.1007/s00897000458b).

Notes and References

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