Experiment A
Synthesis and Characterization of Potassium Nitrosodisulfonate, $K_4[ON(SO_3)_2]_2$, Fremy's Salt

Introduction. The nitrosodisulfonate ion, $ON(SO_3)_2^{2-}$ is an example of a relatively rare type of molecule, the free radical or odd-electron molecule. Most such molecules are difficult to prepare because they have a strong tendency to dimerize and thus permit the pairing of the odd electrons.

The nitrosodisulfonate ion is also unusual because it is a paramagnetic ion that contains no metallic element. We shall make use of such properties as the magnetic susceptibility, electronic absorption spectrum (color), and electron spin resonance to study some forms of Fremy's salt and related compounds.

Procedure. The reactions employed in this synthesis are represented by the following (unbalanced) equations:

$$HNO_2 + HSO_3^- \rightarrow HON(SO_3)_2^{2-} + H_2O \qquad \text{(I)}$$

$$HON(SO_3)_2^{2-} + MnO_4^- \rightarrow ON(SO_3)_2^{2-} + MnO_2(s) \qquad \text{(II)}$$

$$ON(SO_3)_2^{2-} + K^+ \rightarrow K_4[ON(SO_3)_2]_2(s) \qquad \text{(III)}$$

Before starting the synthesis, prepare your filtration equipment so that it will be ready for immediate use. For a Buchner funnel of 75 mm diameter you will need 15 g. of Filter-aid (diatomaceous earth). Prepare a slurry of the Filter-aid in 75 ml of 6 M NH_3. Pour the slurry into the Buchner funnel, until a layer of the Filter-aid about 5 - 8 mm thick covers the paper. Remove the dilute ammonia solution by suction and discard.

Carry out the synthesis in a 600-ml beaker immersed in an ice bath. It is essential that this reaction be carried out at a low temperature (5 ˚C or lower) and with continuous stirring with a mechanical stirrer to obtain a good yield.

Place a freshly prepared solution of 14 g of $NaNO_2$ in 40 ml of water in the 600-ml beaker. After stirring for at least 3 minutes, add 80 g of crushed ice. Add a freshly prepared solution of 21 g of $NaHSO_3$ in 40 ml of water over a period of 1 minute. Then add 8 ml of glacial acetic acid, and after 3 minutes, add 15 ml of concentrated aqueous NH_3. Next (using your separatory funnel) add, over a span of 5 minutes, a solution of 5 g of $KMnO_4$ in 160 ml of water. A dark brown color will develop. Stir for 2 minutes, and filter with suction into a 500-ml or 1-liter flask containing 100 ml of a saturated solution of KCl (saturated at 0˚ C). Immerse the flask in an ice bath during the filtration. A layer of very finely-divided MnO_2 will form on the surface of the Filter-aid. If the rate of filtration diminishes drastically, the MnO_2 layer can be partially removed by scraping gently with a spatula. If any decomposition occurs in the unfiltered reaction mixture during the course of the filtration, as indicated by effervescence or bleaching of the purple supernatant liquid, the filtration should be stopped immediately. Usually it is possible to filter at least 200 ml of liquid before decomposition is evident. A precipitate of beautiful orange-yellow crystals will form in the filter flask. Collect the precipitate by suction filtration. Quickly transfer the filtrate back to the 600-ml beaker immersed in the ice bath. Transfer the precipitate to a 250-ml beaker and add a cold (<5˚) wash mixture of 5 ml of concentrated NH_3 and 75 ml of methanol. Stir to wash the precipitate and refilter on a clean filter paper. Repeat this washing and filtering procedure to insure complete removal of $KMnO_4$. After the washing, additional saturated KCl solution may be added to the original filtrate in the beaker to precipitate more Fremy's salt. Dry your sample in a vacuum dessicator over $CaSO_4$ ("Drierite") at 0.1 torr for several hours. Seal your product in a screw cap bottle, store in the refrigerator. Do not seal your sample until it has been pumped dry or an explosion may occur.

Characterization. Potassium nitrosodisulfonate is a bright yellow solid, but its aqueous solutions are bright violet. The solid is diamagnetic, whereas the solution is paramagnetic. In acidic solutions nitrosodisulfonate decomposes very quickly.

$$4ON(SO_3)_2^{2-} + 3H_2O \rightarrow 2HON(SO_3)^{2-} + 4HSO_4^- + N_2O$$

The decomposition in basic solution is much slower, to yield a complex product containing NO_2^- ion and hydroxylamine trisulfonate among the products. If the nitrosodisulfonate ion is crystallized with large anions, such as Cs^+, or $(CH_3)_4N^+$, a purple paramagnetic solid is formed

Analysis. Potassium nitrosodisulfonate may be analyzed iodimetrically.

$$2ON(SO_3)_2^{2-} + 3I^- + 2H^+ \rightarrow 2HON(SO_3)_2^{2-} + I_3^-$$

Measure 25 ml of 0.1 M KI solution into each of three iodine determination flasks. Acidify each sample with 3 M H_2SO_4 just before use. Accurately weigh three samples of Fremy's salt (ca. 0.2 g per sample), immediately adding each sample to one of the KI solutions. Without delay, titrate each solution with standardized $Na_2S_2O_3$, using a starch indicator. Keep each iodine flask stoppered until ready to titrate. The first titration should be carried out relatively slowly in the presence of the starch indicator because the end-point is unknown, but in the later titrations add the thiosulfate solution rapidly until the end-point is near. At this point add a few drops of the starch indicator and proceed to the end-point. If no permanent end-point is found, it indicates that your sample is contaminated with nitrite ion.

Part II – Characterization of Fremy's Salt

Bis(benzyltriphenylphosphonium)nitrosodisulfonate

Dissolve 2.9 g of benzyltriphenylphosphonium chloride, $(C_6H_5CH_2)(C_6H_5)_3PCl$, in 20 ml of water. The mixture may be warmed to hasten the solution process, but cool it to between 25° and 30° before proceeding to the next step. Add 1.0 g of your Fremy's salt, and stir vigorously. A violet precipitate of $[(C_6H_5CH_2)(C_6H_5)_3P]_2ON(SO_3)_2$ will form immediately. Cool the mixture to below 5° in ice, and separate the precipitate by suction filtration. Wash the product with at least five 10-ml portions of ice-cold distilled water, followed by three 5-ml portions of anhydrous ether (Hood!). Allow the crystals to dry by drawing air through the precipitate on the filter for at least 5 minutes. Store the crystals in an open container inside a dessicator for at least 12 hours. The product is quite stable if protected from moist air. Calculate the per cent yield of this compound.

Magnetic Measurements

Measure the magnetic susceptibility by the Gouy method (see Appendix I).

(1) a sample of your Fremy's salt preparation

(2) a sample of your bis(benzyltriphenylphosphonium) salt

Report the magnetic moment of the nitrosodisulfonate ion and compare this with the value expected for one unpaired electron. You must make the correction for the inherent diamagnetism. This is important and a little tricky. It is best to use values for the atomic diamagnetic correctons which are close to the type of atom in your compound. The oxygen atoms are closest to those in SO_4^{2-} rather than O^{2-}. Why is this? Give some thought to this and use the corrections for atoms which are closest in charge to the ones in your compound.

Electron spin resonance (ESR)

Consult your teaching assistant concerning this measurement. Obtain the ESR spectrum (see Appendix II) of the nitrosodisulfonate ion from an approximately 1×10^{-4} M solution of the bis(benzyltriphenylphosphonium) salt in dichloromethane. This solution should be light violet in color and can be qualitatively made up. Use an NMR tube for this experiment.

Include in your write-up

1. Calculations of percent yield and total yield of $K_4[ON(SO_3)_2]_2$ and $[(C_6H_5CH_2)(C_6H_5)_3P]_2ON(SO_3)_2$
2. Calculations of percent purity via titration.
3. Have your sample checked and approved by a TA.

In your report summarize the following aspects of your ESR spectrum.

(1) The approximate magnetic field strength at which resonance occurs.
(2) The number and "splitting" of the lines in the spectrum.
(3) Identification of the interaction that is responsible for each line in the spectrum.

Report the values of the magnetic susceptibility and magnetic moment for the two compounds. Show all calculations. Report the yield of the compound.

Preliminary Questions for Experiment A

1. Write electron dot formulas for the molecules CN and NO. In what neutral structural forms do these exist at room temperature?
2. Draw the molecular orbital diagrams for the CN and NO molecules. (This is the energy level diagram, not the pictures of the MO's.)
3. Using either the electron dot formulae or the molecular orbital diagrams, explain why the behavior of CN differs so greatly from that of NO at room temperature. (Hint: Consider the number of bonds.)
4. Draw the electron dot formula for the nitrosodisulfonate ion, $ON(SO_3)_2^{2-}$.
5. Draw the electron dot formula for the dimer.
6. Balance equations I, II, and III.
7. How do the relative quantities of $NaNO_2$, $NaHSO_3$, and $KMnO_4$ called for in the preparations differ from those in equations I, II, and III? What is the limiting reagent for the overall reaction?
8. What would be a 100% yield of bis(benzyltriphenylphosphonium) nitrosodisulfonate (=bis(BTPP) nitrosodisulfonate)?
9. Using the table of diamagnetic corrections in Appendix I, estimate χ_M for BTPP chloride.
10. What do you expect the magnetic moment to be for your Fremy's salt, $K_4[ON(SO_3)_2]_2$ and for the bis(benzyltriphenylphosphonium) salt of $ON(SO_3)_2^{2-}$? Calculate the magnetic moments in Bohr magneton units.

References

1. D. J. Cram and R. A. Reeves, *J. Am. Chem. Soc.* **80**, 3094 (1958).
2. W. Moser and R. A. Howie, *J. Chem. Soc. (A)*, 3039, 3043 (1968).
3. B. J. Wilson and D. M. Ritter, *Inorg. Chem.* **2**, 974 (1963).
4. D. L. Fillmore and B. J. Wilson, *Inorg. Chem.* **7**, 1592 (1968).