The fact that some other experimental results at fairly low concentrations have led to smaller values of the numerical coefficient than those given by these equations can be attributed to variations of the dielectric constant only if it be assumed that the solutions investigated were still too concentrated to make the limiting law strictly applicable.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO]

NITROGEN TETRASULFIDE AND NITROGEN TETRASELENIDE[1]

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Nitrogen Tetrasulfide

Preparation.—Various investigators have stated that sulfur monochloride is inferior to sulfur dichloride for the preparation of nitrogen tetrasulfide, but we found that the monochloride serves very well. Ruff and Geisel[2] were able to obtain only 57% of the calculated yield from sulfur dichloride and ammonia, while the monochloride gives a yield of about 65%. We used the following method in the preparation: 5 cc. of sulfur monochloride was diluted to about 150 cc. with ether and a stream of dry ammonia was passed through. The reaction is $16\ NH_3 + 6\ S_2Cl_2 = 12\ NH_4Cl + N_4S_4 + 8\ S$. The yield is greatest when the gas is passed through at the rate of 900–1000 cc. per minute. The mixture turns brown at first, but after about half an hour becomes orange. On standing, an orange precipitate separates out, leaving a bright red solution. The precipitate is extracted with ether and the solution is allowed to evaporate in the air, leaving orange-yellow crystals having a very strong, characteristic odor. When the solution is evaporated by heating, most of the crystals decompose into sulfur, nitrogen and perhaps some other sulfide of nitrogen. In order to avoid the loss of ether while the reaction between the sulfur monochloride and ammonia is taking place, the flask should be immersed in an ice-bath and fitted with a reflux condenser. Even with these precautions, a large part of the ether is lost and the supply may have to be replenished before the completion of the experiment. It is interesting to note that, while the solution formed in this manner is bright red, we did not find it possible to prepare a red solution by dissolving crystals of nitrogen tetrasulfide in ether.

We tried benzene and carbon disulfide as solvents in place of ether, but the yield was not nearly so good in either case as when ether was used. Benzene, however, gave better results than carbon disulfide.

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[1] Adapted from a thesis submitted by John C. Bailar, Jr., in partial fulfilment of the requirements for the degree of Master of Arts in Chemistry at the University of Colorado.

[2] Ruff and Geisel, *Ber.*, **38**, 2659 (1905).

We attempted to prepare nitrogen tetrasulfide from sulfur monochloride and liquid ammonia, also. When the two liquids were mixed, a black solid formed. As this warmed to room temperature it became orange, but only a few crystals of nitrogen tetrasulfide could be seen in the mixture. The remainder was sulfur.

Molecular Weight.—As an aid to the identification of our compound, we determined its molecular weight cryoscopically, using benzene as the solvent, and checked the most recent determination.[3] The data are as follows.

Mol. wt. Subs., 0.052: 46.84 g. of solvent; Δt (lowering), 0.030°; cryoscopic constant for benzene, 51.2. Calcd. for N_4S_4: mol. wt., 184. Found: 189.

Hydrolysis Products.—Fordos and Gelis[4] state that nitrogen tetrasulfide decomposes in water, giving ammonium thiosulfate, ammonium trithionate and free ammonia. Ruff and Geisel[5] state that the solution contains ammonia and sulfuric, sulfurous, thiosulfuric and pentathionic acids. The ammonia, according to them, is in excess. We carried out the hydrolysis in the following manner: 0.2 g. of the material was shaken with 400 cc. of freshly-boiled, distilled water at room temperature for 24 hours. Only a little less than 0.1 g. dissolved, indicating that the saturated solution was less than 0.0013 *M*. The solution contained pentathionic acid, sulfurous acid, free sulfur and ammonia. It was neutral to both methyl red and methyl orange. Negative tests for sulfides were obtained with silver nitrate, lead nitrate and copper sulfate. The test for thiosulfate was as follows: 1 cc. of the solution was mixed with 1 cc. of a 10% solution of ammonium molybdate and 5 cc. of concd. sulfuric acid was poured down the side of the tube, so that it formed a layer on the bottom. We could obtain no coloration in the zone of contact, although a known thiosulfate solution gave a blue color. The tests for the thionic acids showed that only pentathionic acid was present, but it is known that all of the polythionic acids hydrolyze to form pentathionic acid. To determine the amount of this acid present, we used a method worked out by Riesenfeld and Feld.[6] According to them, pentathionic acid is converted quantitatively into thiosulfuric acid by boiling with potassium hydroxide. The thiosulfuric acid formed is then titrated with standard iodine solution. We found that 50 cc. of our solution, boiled with potassium hydroxide, required 1.3 cc. of 0.02 *N* iodine solution. This means that 21.3% of the sulfur in the nitrogen tetrasulfide was converted into pentathionic acid.

Barium chloride gave a slight opalescence with the acidified solution; this test for sulfates was doubtless due to the sulfites which were present

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[3] Andreocci, *Z. anorg. Chem.*, **14**, 246 (1897).

[4] Fordos and Gelis, *Compt. rend.*, **31**, 702 (1850).

[5] Ruff and Geisel, *Ber.*, **37**, 1573 (1904).

[6] Riesenfeld and Feld, *Z. anorg. Chem.*, **119**, 225 (1921).

in relatively large amount, for after oxidation with bromine water, barium chloride gave a much heavier precipitate than the pentathionic acid alone could give.

The residue from the hydrolysis solution was treated with ether which dissolved the undecomposed nitrogen tetrasulfide, leaving only free sulfur, since sulfur is but slightly soluble in ether. In one determination 0.0733 g. of nitrogen tetrasulfide (containing 0.0510 g. of sulfur) was decomposed, and 0.0192 g. of free sulfur was left, indicating that 37.6% of the sulfur had been liberated. In a second experiment, 0.0865 g. of nitrogen tetrasulfide (containing 0.0602 g. of sulfur) was decomposed, and 0.0232 g. of sulfur was left, indicating that 38.5% of the sulfur had been liberated. An average of these values gives 38.1%.

The rest of the sulfur must have been converted into sulfites. By difference, the percentage of sulfur in the form of sulfites must be 40.6.

By distilling the hydrolysis solution with sodium hydroxide, and catching the distillate in standard sulfuric acid, we found that all of the nitrogen present in the nitrogen tetrasulfide had been converted into ammonia.

These results show only the final products of the reaction, which are pentathionic acid, sulfurous acid, free sulfur and ammonia. It is quite clear that secondary reactions have taken place, since no simple equation can account for the conversion of nitrogen tetrasulfide into these products.

Action of Ammonia on Nitrogen Tetrasulfide.—Ruff and Geisel[5] state that at —40° liquid ammonia and nitrogen tetrasulfide form a compound, $N_4S_4.2NH_3$, which loses ammonia when heated.

We found that when a stream of ammonia gas is passed through an ether solution of sulfur monochloride for much longer than half an hour, or when a solution of nitrogen tetrasulfide in ether, in carbon disulfide, or in benzene is treated with dry ammonia at 20–25° the solution becomes dark red by transmitted light, but blue by reflected light. On spontaneous evaporation, this solution yields a very dark red, viscous liquid with the odor of rotten beef. This compound does not lose ammonia when heated. Two determinations of the molecular weight of this compound, by the cryoscopic method, using benzene as the solvent, gave 106.7 and 107.9. The nitrogen content was found by two analyses by the modified Kjeldahl method to be 12.56 and 12.74%, and the sulfur by the Carius method to be 13.73 and 15.01%. Other determinations gave results in this same neighborhood, also. No explanation is offered for these rather surprising results.

Michaelis[7] says that at 100° a solution of nitrogen tetrasulfide in ether, and ammonia, give a white compound that sublimes. We found that in the preparation of nitrogen tetrasulfide, although the ether was not at 100°, a white sublimate formed in the reflux condenser. This may be the compound that Michaelis noticed.

Nitrogen Tetraselenide

Preparation.—We prepared nitrogen tetraselenide in the same way that we prepared the tetrasulfide, except in two minor respects. First, we used carbon disulfide as the diluent instead of ether, since it gave a better yield,

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[7] Michaelis, *Jena. Z.*, **6**, 79 (1870); *Z. Chem.*, **6**, 460 (1870).

and second, we made the solution more dilute than in the case of the sulfur monochloride, for the same reason.

Molecular Weight.—Strecker and Claus[8] suppose that the actual formula of this compound is N_4Se_4, rather than NSe, but state that they could find no solvent suitable for making a molecular-weight determination. They mention having tried only diphenyl, naphthol and liquid sulfur dioxide. According to them, nitrogen selenide decomposes in, or unites with, many organic solvents.

We determined the molecular weight by the cryoscopic method, using glacial acetic acid as the solvent, and found the formula to correspond to N_4Se_4.

Mol. wt. Subs., 0.0468, 0.0140: 12.800, 12.002 g. of solvent; Δt (lowering), 0.040°, 0.014°; cryoscopic constant for glac. acetic acid, 39. Calcd. for N_4Se_4: mol. wt., 372.8. Found: 356.5, 341.2.

Compound with Ammonia.—When ammonia is passed through a solution of nitrogen tetraselenide in carbon disulfide for half an hour, a red solution is formed. On evaporation, this yields a dark red, heavy liquid, very similar to the compound formed by ammonia and nitrogen tetrasulfide in the same manner.

Summary

1. Methods of preparation giving satisfactory yields have been worked out for nitrogen tetrasulfide and nitrogen tetraselenide.
2. The molecular weight of nitrogen tetrasulfide has been redetermined, and has been found to agree with the value obtained by other investigators. The molecular weight of nitrogen tetraselenide has been found to correspond to the formula N_4Se_4.
3. The hydrolysis products of nitrogen tetrasulfide have been studied and have been found to be pentathionic acid, sulfurous acid, free sulfur and ammonia.
4. The compounds that ammonia forms with nitrogen tetrasulfide and nitrogen tetraselenide have been prepared and described.

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[8] Strecker and Claus, *Ber.*, **56**, 362 (1923).