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## Note

### The chromatographic preparation of high-purity solutions of tetrasulfur dinitride

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The study of the chemistry of tetrasulfur dinitride,  $S_4N_2$ , has been severely hindered by the difficulties associated with obtaining pure  $S_4N_2$ . Known reactions deal mainly with hydrolysis or oxidation of contained sulfur<sup>1-4</sup>.

The red compound, which melts at 23° (ref. 2), decomposes quite readily to sulfur and nitrogen in the solid state at 0° (ref. 5). However,  $S_4N_2$  is more stable when kept as a solution in organic solvents<sup>5</sup>. This is further evidenced by the fact that the correct molecular formula was not determined until 1951 by Meuwsen<sup>3</sup> although the compound was probably first prepared in 1850<sup>6</sup>.

Recent work by Nelson and Heal<sup>7</sup>, as well as work in this laboratory<sup>8</sup>, has shown that the compound is probably cyclic with the nitrogens in the one and three positions.

Presently, two methods are commonly employed for the synthesis of  $S_4N_2$ . The first method is a three-step synthesis involving the use of the salt  $Hg_5(NS)_8$  (refs. 3 and 9) while the second entails the heating of tetrasulfur tetranitride,  $S_4N_4$ , and sulfur in  $CS_2$  in an autoclave<sup>10</sup>. Both methods yield a complex mixture of products but are capable of producing pure  $S_4N_2$  (ref. 7).

Since we desired to study the reactions of  $S_4N_2$  with a large number of compounds it was desirable to develop a synthetic method that would lead to pure solutions of  $S_4N_2$  in a relatively efficient and easy manner.

We achieved this goal by utilizing a less common method of  $S_4N_2$  synthesis, that of refluxing tetrasulfur tetranitride and sulfur in toluene<sup>3</sup> with a subsequent use of column chromatography. Analysis of the solution was carried out by spectrophotometry and chemical analysis.

## EXPERIMENTAL

Tetrasulfur tetranitride was prepared according to Jolly<sup>11</sup>. However, for further purification the  $S_4N_4$  was washed twice with  $CS_2$  (ref. 12), instead of recrystallization from benzene, taking advantage of differences in solubility of  $S_4N_4$  and  $S_8$  in  $CS_2$ .

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(ref. 13). The purity was determined by infrared (IR) spectroscopy<sup>1</sup> and melting point (182°, with explosion). The sulfur used showed no absorbance in the 400–4000  $\text{cm}^{-1}$  region of the IR spectrum and was used without further purification.

The solvents toluene, carbon tetrachloride, and hexanes (ACS reagent chemical) were of reagent grade. They were further purified by refluxing over phosphorus pentoxide for 18 h and then distilled from calcium sulfate.

The silica gel powder, 60–200 mesh (J. T. Baker, Phillipsburgh, N.J., U.S.A.), used for columns was heated at 200° for 18 h prior to use<sup>14</sup>.

Thin-layer plates were prepared from a slurry of 70 g silica gel GF-254 (Anspec, Ann Arbor, Mich., U.S.A.) and 200 ml chloroform. The plates were heated at 110° for 12 h prior to use.

Absorbances in the ultraviolet–visible range were read on a Beckman DB spectrophotometer.

The IR spectrum of the hexanes solution of  $\text{S}_4\text{N}_2$  was observed in the potassium bromide region on a Perkin-Elmer Grating 457 spectrophotometer.

The  $\text{S}_4\text{N}_2$  was synthesized as follows. Tetrasulfur tetranitride (2 g) and sulfur (4 g) were refluxed in 40 ml toluene. The refluxing was stopped after 18–22 h and the reaction mixture was allowed to cool to room temperature. The toluene was removed by a stream of dry nitrogen gas. The  $\text{S}_4\text{N}_2$  was then dissolved in 5 ml of carbon tetrachloride and 5 ml of hexanes. The solution was then filtered through a sintered glass funnel and passed over a 0.37-m column (I.D. 2.5 cm) packed with 50 g silica gel powder in hexanes. The hexanes flow-rate was 5 ml/min.

Molecular sulfur was found to elute from the column approx. 8–10 cm ahead of the  $\text{S}_4\text{N}_2$  band. However, a trace amount of sulfur was still leaving the column when the  $\text{S}_4\text{N}_2$  began to elute. Therefore, the first 60 ml of the  $\text{S}_4\text{N}_2$  fractions were discarded. The remaining  $\text{S}_4\text{N}_2$  fractions were collected and found to be free of all contaminants as evidenced by thin-layer chromatography (TLC).

The collected  $\text{S}_4\text{N}_2$  was analyzed by observing the absorbance of the solutions at  $\lambda_{\text{max}}$  = 377 and 455  $\text{nm}^7$  as a function of concentration (Fig. 1), with  $\epsilon_{\text{max}}$ , (377) =

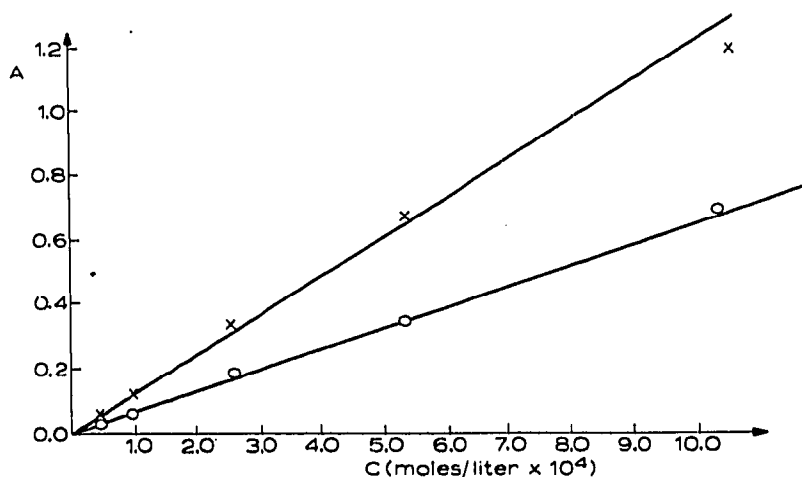


Fig. 1. Lambert-Beer law plot for  $\text{S}_4\text{N}_2$  in hexanes.  $\times$ — $\times$ , 377 nm;  $\circ$ — $\circ$ , 455 nm.

1296 and  $\epsilon_{\text{max.}}(455) = 670$ . Concentrations were determined by Kjeldahl analysis of the parent solution. This method produced 180–210 mg of  $\text{S}_4\text{N}_2$ .

## RESULTS

TLC of the reaction mixture revealed five products when exposed to iodine vapors (Table I).  $R_F$  values were determined for carbon tetrachloride, hexanes and toluene. From Table I one can see that hexanes will effectively separate any  $\text{S}_4\text{N}_2$  and sulfur from the other compounds.

TABLE I  
 $R_F$  VALUES OF  $\text{S}_4\text{N}_4$  AND  $\text{S}_8$  REACTION PRODUCTS

Compound	Solvent		
	Carbon tetrachloride	Hexanes	Toluene
$\text{S}_8$	0.78	0.73	0.65
$\text{S}_4\text{N}_2$	0.65	0.28	0.62
$\text{S}_4\text{N}_4$	0.23	0.09	0.48
Unknown 1	0.45	0.10	0.61
Unknown 2	0.01	0.0	0.10

The absence of sulfur in the collected  $\text{S}_4\text{N}_2$  was established by TLC. A TLC plate, developed in carbon tetrachloride, indicated the presence of no sulfur upon exposure to iodine vapors for 8 h. To determine the limit of detection of  $\text{S}_8$  by the iodine vapor technique a series of sulfur solutions of known concentrations were made. Each solution was analyzed as above. The results showed that the limit of detection for sulfur by this method is  $4 \times 10^{-3}$  g per 250 ml of solution.

The results of the Kjeldahl analysis were 41.3 mg  $\text{S}_4\text{N}_2$  for both 50-ml aliquots 1 and 2. It was assumed that two moles of  $\text{NH}_3$  are produced from one mole of  $\text{S}_4\text{N}_2$ .

## CONCLUSIONS

The present method produced  $\text{S}_4\text{N}_2$  in smaller yields than the two more common methods of synthesis<sup>3,10</sup>. However, no attempts were made to find the conditions which give the maximum yields such as time of refluxing and the weight ratio ( $\text{S}_4\text{N}_4$ )/( $\text{S}_8$ ).

The procedure obviates the need of autoclaves, sublimation or the synthesis of the salt  $\text{Hg}_5(\text{NS})_8$  and the compound  $\text{S}_4\text{N}_4\text{H}_4$ , and thus offers an attractive alternative to existing syntheses.

Quantitative analysis of  $\text{S}_4\text{N}_2$  is possible as hexanes solutions of this dinitride closely follow the Lambert-Beer law, at wavelengths of 377 and 455 nm. The results demonstrate that the produced  $\text{S}_4\text{N}_2$  is free of  $\text{S}_8$  or any other contaminant.

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