Short Communication

Separation of S_8, S_7NH, and S_4N_4 by adsorption chromatography

Sulfur, heptasulfur imide and tetrasulfur tetranitride are products of the reaction of ammonia with S_2Cl_2 and are formed in various reactions involving sulfur–nitrogen compounds[1]. Characterization of these reactions has been delayed because of the difficulty of quantitatively analyzing the product mixtures. As might be expected from the fact that the three substances have similar molecular structures (puckered eight-membered rings), they have similar solubilities in organic solvents and are difficult to separate from one another. Various investigators[2–5] have mentioned the use of adsorption chromatography in the separation of S_8 from S_7NH and related materials, but no details have been given. We describe here a method involving elution with benzene from alumina for the separation of S_4N_4 from S_7NH and S_8, and a method involving elution with carbon tetrachloride from silica gel for the separation of S_7NH from S_8.

Experimental

Commercial alumina (M. Woelm-Eschwege, acid, activity grade 1) and silica gel (J. T. Baker Chemical Co., "suitable for chromatographic use") were used. When required, "dried" alumina and silica gel were prepared by heating for 12 h at 150° and 200°, respectively. The solvents were dried over P_2O_5 and distilled. The column beds were 18 cm long and 2.54 cm in diameter; a flowrate of 1 ml/min was used. Known mixtures of S_8, S_7NH and S_4N_4 were prepared by weighing out the pure materials; the chromatographic fractions were evaporated to dryness and weighed. Data are presented in Table I.

The melting points of S_4N_4 and S_7NH (187–187.5° and 113.5°, respectively) are good criteria of purity; the purity of S_8 may be ascertained from its infrared spectrum, which should show no bands in the NaCl region. Eluate containing S_4N_4 is readily recognized by its orange color. Eluate containing S_7NH is colorless, but may be identified by the purple-violet color which forms on treating a small portion with an equal volume of a 10 % solution of KOH in anhydrous methanol. Similar treatment of eluate containing only S_8 gives no color, but, as is also the case with S_7NH, a yellow color forms on heating the mixture.

Discussion

Tetrasulfur tetranitride is held very tenaciously by alumina and silica gel; benzene (a good solvent for S_4N_4) was used for its elution. When columns of either undried alumina or undried silica gel were used, very poor recoveries of S_4N_4 were achieved (see Table I), and non-elutable sulfur compounds were retained in the columns. We believe that S_4N_4 undergoes hydrolysis on the undried adsorbents to form various sulfur oxyacids which are insoluble in benzene. About 90 % recovery of S_4N_4 was

TABLE I

CHROMATOGRAPHIC SEPARATION OF KNOWN MIXTURES OF S_8, S_7NH AND S_4N_4

	S_8 (g)	S_7NH (g)	S_4N_4 (g)
Non-dried alumina			
Taken	0.2352	0.0105	0.1242
Recovered	0.2345	0.0092	0.0882
Dried alumina			
Taken	0.1765	0.0227	0.3311
Recovered	0.1952		0.3106
Non-dried silica gel			
Taken	0.1906	0.2015	0.1283
Recovered	0.1900	0.2051	0.0394
Dried silica gel			
Taken	0.1770	0.1900	0.2002
Recovered	0.3652		0.1821

achieved using dried silica gel, and about 95 % recovery was achieved using dried alumina (R_F 0.15); we recommend use of the latter adsorbent for the separation of S_4N_4 from S_7NH and S_8.

Both S_7NH and S_8 are weakly held by alumina and silica gel; the relatively poor solvent carbon tetrachloride was used for the elution of these compounds. When columns of either dried alumina or dried silica gel were used, both S_7NH and S_8 came out together with the solvent front. When undried adsorbents were used, the S_7NH was eluted in a well-separated band (R_F 0.15) after the S_8. We believe the S_7NH is held by hydrogen bonding to the water of hydration of the undried adsorbent. Both S_7NH and S_8 were consistently recovered in 98–102 % yield with undried silica gel columns, and we recommend use of the latter adsorbent for the separation of these compounds.

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