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SEPARATION OF \( S_8 \), \( S_7NH \), AND \( S_4N_4 \) BY
ADSORPTION CHROMATOGRAPHY

M. Villena-Blanco and W. L. Jolly

August 1964
Separation of $S_8$, $S_7\text{NH}$, and $S_4\text{N}_4$ by Adsorption Chromatography

Sir: Sulfur, heptasulfur imide and tetrasulfur tetranitride are products of the reaction of ammonia with $S_2\text{Cl}_2$ and are formed in various reactions involving sulfur-nitrogen compounds (2). 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 (1, 3-5) have mentioned the use of adsorption chromatography in the separation of $S_8$ from $S_7\text{NH}$ and related materials, but no details have been given. We describe here a method involving elution with benzene from alumina for the separation of $S_4\text{N}_4$ from $S_7\text{NH}$ and $S_8$, and a method involving elution with carbon tetrachloride from silica gel for the separation of $S_7\text{NH}$ 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 hours at 150°C and 200°C, respectively. The solvents were dried over $\text{P}_2\text{O}_5$ 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.

Table I. Chromatographic Separation of Known Mixtures of $S_8$, $S_{7NH}$ and $S_4N_4$.

<table>
<thead>
<tr>
<th></th>
<th>$S_8$, g.</th>
<th>$S_{7NH}$, g.</th>
<th>$S_4N_4$, g.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Non-dried Alumina</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taken</td>
<td>0.2352</td>
<td>0.0105</td>
<td>0.1242</td>
</tr>
<tr>
<td>Recovered</td>
<td>0.2345</td>
<td>0.0092</td>
<td>0.0882</td>
</tr>
<tr>
<td><strong>Dried Alumina</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taken</td>
<td>0.1765</td>
<td>0.0227</td>
<td>0.3311</td>
</tr>
<tr>
<td>Recovered</td>
<td>0.1952</td>
<td></td>
<td>0.3106</td>
</tr>
<tr>
<td><strong>Non-dried Silica Gel</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taken</td>
<td>0.1906</td>
<td>0.2015</td>
<td>0.1283</td>
</tr>
<tr>
<td>Recovered</td>
<td>0.1900</td>
<td>0.2051</td>
<td>0.0394</td>
</tr>
<tr>
<td><strong>Dried Silica Gel</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taken</td>
<td>0.1770</td>
<td>0.1900</td>
<td>0.2002</td>
</tr>
<tr>
<td>Recovered</td>
<td>0.3652</td>
<td>0.1621</td>
<td></td>
</tr>
</tbody>
</table>
The melting points of \( \text{S}_4\text{N}_4 \) and \( \text{S}_7\text{NH} \) (187-187.5\(^\circ\) and 113.5\(^\circ\), resp.) are good criteria of purity; the purity of \( \text{S}_8 \) may be ascertained from its infrared spectrum, which should show no bands in the NaCl region. Eluate containing \( \text{S}_4\text{N}_4 \) is readily recognized by its orange color. Eluate containing \( \text{S}_7\text{NH} \) 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 \( \text{S}_8 \) gives no color, but, as is also the case with \( \text{S}_7\text{NH} \), 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 \( \text{S}_4\text{N}_4 \)) was used for its elution. When columns of either undried alumina or undried silica gel were used, very poor recoveries of \( \text{S}_4\text{N}_4 \) were achieved (see Table I), and non-elutable sulfur compounds were retained in the columns. We believe that \( \text{S}_4\text{N}_4 \) undergoes hydrolysis on the undried adsorbents to form various sulfur oxyacids which are insoluble in benzene. About 90\% recovery of \( \text{S}_4\text{N}_4 \) was 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 \( \text{S}_4\text{N}_4 \) from \( \text{S}_7\text{NH} \) and \( \text{S}_8 \).

Both \( \text{S}_7\text{NH} \) and \( \text{S}_8 \) 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 \( \text{S}_7\text{NH} \) and \( \text{S}_8 \) came out together with the solvent front. When undried adsorbents were used, the \( \text{S}_7\text{NH} \) was eluted in a
well-separated band ($R_f = 0.15$) after the $S_8$. We believe the $S_\gamma$NH is held by hydrogen bonding to the water of hydration of the undried adsorbent. Both $S_\gamma$NH 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.

LITERATURE CITED


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