Reaction of Disulphur Monoxide with Silicon Tetrafluoride

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Disulphur monoxide (S₂O) reacts with silicon tetrafluoride at low temperatures to form an adduct SiF₄·SO. This gaseous adduct is found to be stable at room temperature in the absence of moisture. The infrared spectrum is suggestive of silicon-sulphur bonding in the adduct.

Silicon tetrafluoride forms a variety of adducts with amines¹⁻⁴, thiazoles⁵ and dimethyl sulphoxide⁶. In all these adducts the bonding to silicon occurs through nitrogen or oxygen of the ligand. The adducts having silicon-sulphur bond do not appear to have been reported in literature. Therefore, it was of interest to investigate whether a lower oxide of sulphur would promote bonding. Preliminary experiments indicated such a reaction with disulphur monoxide (S₂O). The gaseous adduct formed was stable at room temperature for several days in the absence of moisture. Details of its preparation and identification are given below.

Disulphur monoxide (S₂O) was prepared⁷ by heating copper oxide (2 g) and elemental sulphur (10 g) at 300-400°C for 1 hr in vacuo. The evolved S₂O gas was trapped in a vessel cooled under liquid nitrogen. To this orange red condensate of S₂O in the trap at liquid nitrogen temperature was condensed a known weight of silicon tetrafluoride (100-200 mg). The reactant gases were then slowly thawed to room temperature during 1 hr.

The IR spectrum of the gaseous product, recorded in a 10 cm gas cell fitted with KBr windows on a Perkin-Elmer model 599 spectrophotometer, displayed a shift in the vSi–F at 1031 cm⁻¹ to the region 900-1000 cm⁻¹ indicating that the reaction between S₂O and SiF₄ had occurred. The intensity of this band at 900-1000 cm⁻¹ did not increase with time suggesting the completion of the reaction before the attainment of room temperature.

In a separate experiment the disulphur monoxide was thawed to room temperature and then treated with known weight of silicon tetrafluoride. The two gases were then cooled under liquid nitrogen and then thawed up to room temperature. The IR spectrum of the combined reactant gases did not display any shift in vSi–F. This indicated that no reaction occurred under the above conditions.

It is well known⁹ that disulphur monoxide decomposes at room temperature to sulphur and sulphur dioxide via sulphur monoxide in accordance with Eq. (1). In order to eliminate the possibility (SₙO)ₙ→ₙSO+(m−1)nS; 3SO→S₂O+SO₂;

\[ 2S₂O \rightarrow 3S + SO₂ \]  

of the reaction between sulphur dioxide and SiF₄, known amounts of SO₂ (bottled) were treated with aliquots of silicon tetrafluoride at different temperatures (25°C, -40°C, -80°C, -196°C) for different time intervals (1-16 hr) and then thawed to room temperature. Here again, the IR spectrum of the reactant gases did not indicate any compound formation.

Disulphur monoxide is a bent triatomic molecule with two stretching modes¹⁵ (vSO at 1165 and vSS at 679 cm⁻¹) and one bending mode (388 cm⁻¹). In the IR spectrum of the product gas (Table I), the vSS is absent, indicating that S₂O is not a coordinating species. If SO is the coordinating species, then the coordination can occur through sulphur or oxygen of sulphur monoxide. In a wide variety of dimethyl sulphoxide¹⁶ complexes it has been shown that if vSO occurs at lower frequencies than that of the free ligand, then the ligand is bonded through the oxygen of the SO bond. However, if the ligands are bound through the sulphur atom, the vSO occurs at lower frequencies.

<table>
<thead>
<tr>
<th>Compd</th>
<th>Geometry</th>
<th>Spectral frequencies cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO·SiF₄</td>
<td>Trigonal bipyramidal</td>
<td>Experimental: 1270, 950, 910, 820, 500, 360</td>
</tr>
<tr>
<td>NH₃·SiF₄</td>
<td>-do-</td>
<td>Reported⁶: 1253, 952, 854, 706, 456, 409</td>
</tr>
<tr>
<td>SF₄</td>
<td>-do-</td>
<td>Reported¹²: 1744, 1281, 889, 867, 728, 557, 532</td>
</tr>
<tr>
<td>SiF₄</td>
<td>Tetrahedral</td>
<td>Reported¹²: 1294(w), 1191(m), 1161(w), 1065(w), 1031(s), 780(w), 389(s)</td>
</tr>
<tr>
<td>S₂O</td>
<td>Bent</td>
<td>Reported¹³: 1165(doublet), 679 (triplet), 388</td>
</tr>
<tr>
<td>SO₂</td>
<td>Bent</td>
<td>Reported¹⁴: 1361, 1151, 517</td>
</tr>
</tbody>
</table>

Table I—Infrared Spectral Data of a Few Silicon and Sulphur Compounds
higher frequency as compared to that in the free ligand. In the present case, shift of $v_{SO}$ from 1165 cm$^{-1}$ to 1270 cm$^{-1}$ suggests bonding of silicon through sulphur. The band at 500 cm$^{-1}$ could be assigned to $v_{Si-S}$ or $v_{Si-S-Si}$ by comparing with some reported values. The product gas could, therefore, be SiF$_4$.SO or (SiF$_4$)$_2$SO. The infrared bands have fine contour indicating a lighter molecule, and it could thus be SiF$_4$.SO that is formed. The number of exhibited vibrations (Table 1) indicate that the molecule could be trigonal bipyramidal in structure due to pentacoordination of silicon.

The product gas on hydrolysis with alkali (2N), indicated the formation of sulphite and fluorosilicate of sodium. This suggested that the oxidation state of sulphur in the compound was four, indicating preferred formation of (SiF$_4$)$_2$SO. Since, the yield was of the order of 10% and also it was found difficult to separate the product gas from sulphur dioxide by fractional distillation it was rather difficult to ascertain the number of SiF$_4$ molecules associated with SO.

References
7. Satyanarayana S R & Murthy A R V. *Z anorg allg chem.* 330 (1964) 245.