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# Preparation of Tetrasulphur Tetranitride from Sulphur Monobromide

D. K. PADMA, V. SUBRAHMANYA BHAT and
A. R. VANSUDEVA MURTHY

*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India*

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The standard method for the preparation of tetrasulphur tetranitride is based on the reaction between sulphur chloride ($S_2Cl_2$) saturated with chlorine and ammonia in carbon tetrachloride medium [1, 2]. While exploring the possibilities of finding an alternative method, it has been found in the present investigation that the reaction between sulphur monobromide ($S_2Br_2$) and ammonia could be conveniently employed with advantage. The details of the procedure are given below.

## Experimental

Sulphur monobromide could be prepared easily by reacting the elements in stoichiometric proportions in a closed vessel at 50 °C on a water bath for 24 hours [3, 4]. In a typical case 25g of resublimed sulphur and 63g (21 ml) of bromine will give 88g (34 ml) of sulphur monobromide.

25 ml(65g) of sulphur monobromide is dissolved in 400 ml of dry carbon tetrachloride and taken to a three necked flask (IL) fitted with an inlet, outlet and a mechanical stirrer. The contents are cooled to 10 °C to control the exothermic reaction between ammonia and sulphur bromide by dipping into cooled water. A fast stream of ammonia (25 litres per hour for the first one hour and 36 litres per hour for the next two hours) from the cylinder is bubbled through the solution. A series of colour changes are observed (brown, grey–green, dark brown–yellow, salmon red) during this interval. When the entire mixture has turned salmon red, the ammonia gas flow is stopped and the stirring is continued for another ten minutes. The reaction mixture is then filtered on a large sintered glass or Buchner funnel. The solid damp material is vigorously stirred with a litre of water for 10 minutes to dissolve out ammonium bromide. The remaining yellow solid is filtered and dried in a desiccator over calcium chloride. The dry yellow solid residue is shaken with ether to remove any $S_7NH$ that might be formed. It is of interest to point out that the ether layer contained only small amount (less than 100 mg) of $S_7NH$. The undissolved yellow residue is transferred on to a thimble of a Soxhlet and extracted with pure and dry dioxane (250 ml). Alternatively the yellow residue is shaken with 25 ml portions of warm dioxan (50 °C) till the elute is only weakly coloured orange–yellow. When the eluate is cooled to room temperature some tetrasulphur tetranitride crystallizes out. This material is filtered and dried. The filtrate is evaporated to dryness at a temperature below 50 °C. The yield of the two crops of tetrasulphur tetranitride is found to be 8.5g. These crystals are dissolved in carbon tetrachloride or dioxane. This solution is shaken with a pellet of mercury to remove any free sulphur that is associated with the crystals of tetrasulphur tetranitride. The sulphur is converted to mercuric sulphide. The yellow solution is filtered and the filtrate evaporated as above. The residue is dissolved in hot benzene and on cooling bright orange–yellow needles of tetrasulphur tetranitride separate out. The crystals had a melting point of 187 °C. The reported value in literature for the melting point of tetrasulphur tetranitride ranges from 187–189 °C. This is observed to depend on the purity of the crystals. Presence of traces of sulphur could account for the variation in the melting point. In the present case elemental sulphur has been removed by shaking with mercury. It is reported that repeated crystallizations from benzene or by purification on an alumina chromatographic column [5] or by vacuum sublimation [6] has yielded purer crystals with higher melting point (189 °C).

The purity of the sample prepared above has been found to be over 99.6%. This is based on chemical analysis (calculated, S, 69.6, N, 30.4%; found, S, 69.3, N, 30.2%). The purity of the sample was confirmed by recording the i.r. spectra of the solid on a UR-10 (Carl Zeiss). Reported 519.3, 529.7, 553.2, 701, 726, 760, 766, 925 $cm^{-1}$. Found 520, 530, 552, 702, 728, 764, 768, 928 $cm^{-1}$.

The percentage yield varied from 25–30%, based on the amount of sulphur taken. Theoretically a yield of 33% is expected from the equation:

$$6S_2Br_2 + 16\ NH_3 \rightarrow S_4N_4 + 8S + 12\ NH_4Br$$

It is interesting to point out that a few milligrams (0.24) of tetrasulphur tetranitride could readily be prepared from 1 ml of sulphur bromide dissolved in 25 ml of carbon tetrachloride and ammonia. The salmon red colour appears in about 15 minutes. The residue is filtered, washed with water, shaken with ether and extracted with dioxane (50 °C). The yellow residue obtained when dioxane is evaporated is recrystallized from benzene. M.pt.179 °C. This small scale preparation requires less than 2 hours.

*CAUTION: Sulphur nitride should be handled with care. It explodes when heated above 100 °C or when struck. Even the small amount of material contained in a melting point capillary can explode violently.*

## References

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