

SYNTHESIS OF DIMETHYL- ^{35}S SULPHIDE

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SUMMARY

The synthesis of dimethyl- ^{35}S sulphide in high yield from the contact of hydrogen- ^{35}S sulphide and methanol over a $\gamma\text{Al}_2\text{O}_3 \cdot 1\% \text{SiO}_2$ catalyst is described. The procedure produces high yields of dimethyl- ^{35}S sulphide of low specific activity compared to that of the hydrogen- ^{35}S sulphide starting material.

Key Words: Dimethyl- ^{35}S sulphide, hydrogen- ^{35}S sulphide,
methanol, alumina catalyst.

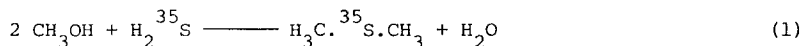
INTRODUCTION

Dimethyl sulphide (DMS) has been detected in wines(1), beers(2), foods(3), plants(4), algae(5), soils(6), and many other sections of the environment(7). The availability of dimethyl- ^{35}S sulphide would enable radiochemical techniques to be employed to study its behaviour in these systems.

On the industrial scale, DMS, together with methanethiol, is produced by contacting hydrogen sulphide, carbon disulphide (or carbonyl sulphide) with methanol (or dimethyl ether) over a heated catalyst (8, 9, 10, 11). The ratio of products obtained is determined by the composition, temperature and pretreatment of the catalyst, by the mole ratio of the reactants, and by the contact time (12, 13). The choice of catalyst composition is however fundamental in determining the nature of the product, be it thiol or sulphide, while operating conditions, although important, play a secondary role. Studies carried

out by Folkins and Miller(12) showed that acidic catalysts such as activated alumina impregnated with about 2% silica gave the best results for DMS synthesis from hydrogen sulphide and methanol.

The title process used hydrogen-³⁵S]sulphide and methanol as reactants together with a γ Al₂O₃.1% SiO₂ catalyst. The reaction was as in equation (1):



Side reactions producing methane-³⁵S]thiol, dimethyl ether and, to a lesser extent, carbon dioxide, carbon monoxide, hydrogen, and methane may also occur. Reaction (1) indicates that the hydrogen-³⁵S]sulphide:methanol ratio must be at least 1:2 for high DM³⁵S yield.

EXPERIMENTAL

Catalyst

Reagent grade aluminium sulphate (50.00g) was dissolved in distilled water (1000 ml) and 10 drops of concentrated sulphuric acid were added. A solution of sodium disilicate (0.14g, Na₂Si₂O₅.2.5 H₂O) in 20 ml of distilled water, to which 10 drops of concentrated sulphuric acid were added, was prepared. The two cooled solutions were mixed well and ammonium hydroxide was slowly added until no further precipitation occurred. The precipitate was washed with distilled water until the washings were free of sulphate ions. It was dried overnight at 110°C and ground to a small particle size. Activation was carried out at 1100°C for 3 hours. Analysis showed the catalyst to be γ Al₂O₃.1.11% SiO₂.

Synthesis of dimethyl-³⁵S]sulphide

Analytical reagent grade methanol was vapourised in a closed

container on a water bath. The vapour was swept by a 20ml min^{-1} flow of oxygen-free nitrogen to a pyrex U-tube (arm length 26cm, internal diameter 8mm) containing 26ml of catalyst. The mass flow rate of methanol through the U-tube was about $500\ \mu\text{mol min}^{-1}$. The U-tube was mounted in an oven held at $360 \pm 5^\circ\text{C}$. A dilute mixture of hydrogen sulphide (purity 99.5%) in oxygen-free nitrogen at a pressure of 2MPa was used to supply hydrogen sulphide to the methanol/nitrogen gas stream immediately prior to the U-tube at a mass flow rate of $6\ \mu\text{mol min}^{-1}$.

Hydrogen- ^{35}S sulphide (supplied by Amersham International plc, Amersham, England) was transferred on a vacuum line to a U-tube where it was held as a solid at liquid nitrogen temperature. This U-tube was attached to the DMS synthesis apparatus so that the hydrogen- ^{32}S sulphide/nitrogen gas stream could be diverted through it. The hydrogen- ^{35}S sulphide was thus carried to the methanol vapour flow and subsequently to the catalyst bed. The transfer of hydrogen- ^{35}S sulphide to the catalyst took 2 minutes after commencing the hydrogen- ^{32}S sulphide flow through the apparatus.

The products of the reaction were collected in a cryogenic trap held at liquid nitrogen temperature. The trap was constructed of pyrex glass (15cm length, 4cm diameter) and was filled with pyrex glass beads of diameter 5mm. Both the trap and the beads were precoated with a 1% (w/w) solution of benzyltriphenyl phosphonium chloride in methylene chloride in order to prevent surface sorption problems with the products (14).

The cryogenic trap was cooled immediately prior to the addition of hydrogen- ^{35}S sulphide to the catalyst. The reaction was allowed to continue for a further 10 minutes and then oxygen-free nitrogen was passed through the column for 5 minutes to remove all products.

Purification of dimethyl- ^{35}S sulphide in the cryogenic trap was by

vapour transfer under vacuum. The trap was attached to a vacuum system and the temperature raised to -100°C by application of a dry ice-diethyl ether slush bath. The major side product of the reaction, dimethyl ether, was removed in this way.

In a typical preparation, 0.8mCi of hydrogen-³⁵S]sulphide of specific activity 1.0mCi mmol^{-1} produced dimethyl-³⁵S]sulphide of specific activity $2 \mu\text{Ci mmol}^{-1}$. Higher product specific activity is possible by increasing the specific activity of hydrogen-³⁵S]sulphide which is available up to 200mCi mmol^{-1} , or by varying the proportion of hydrogen-³²S]sulphide carrier. Conversion of total ³⁵S-activity to product is in excess of 99%.

Analysis of Dimethyl sulphide

The product gases were analysed using a "Tracor" model 270HA sulphur gas analyser modified to separate the sulphur gases on a Porapak QS column as described by de Souza et al. (15). The detector in this gas analyser is a flame photometric system filtered for specificity for sulphur. The same column was used for separation and detection of dimethyl ether however, in this case, a flame ionisation detector was used.

Storage of dimethyl-³⁵S]sulphide

Purified dimethyl-³⁵S]sulphide was stored in a permeation tube constructed of stainless steel, and fitted with a PTFE plug (15). Transfer to the permeation tube from the cryogenic trap was by vapour transfer on a vacuum line. The permeation tube enabled storage and use of the product gas which permeated from the tube through the plug at a constant rate at a given temperature. Arrangements were made to seal the space about the plug when the tube was not in use.

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