

NOTES

PREPARATION OF CARBON-¹³C DISULFIDE AND CARBON-¹³C OXSULFIDE

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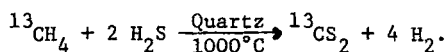
SUMMARY

Carbon-¹³C disulfide was synthesized from methane-¹³C with hydrogen sulfide in a heated quartz chamber. Carbon-¹³C oxysulfide was made from carbon-¹³C monoxide with elemental sulfur heated in the presence of sodium methylate.

Key Words: Carbon-¹³C disulfide, Carbon-¹³C oxysulfide, Methane-¹³C, Carbon-¹³C monoxide

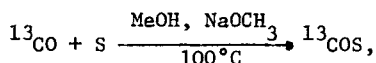
INTRODUCTION

A carbon-¹³C disulfide synthesis has been developed by modification of the process of Waterman and Vlodrop (1) in accordance with the following scheme:



The reaction tube, with successive preparations, developed a stable carbon mirror along its heated length; however, no apparent change in yield was seen with repetition of several preparations while using the same tube. The flow rate was chosen in preliminary experiments with the aid of infrared spectra of the emergent gas stream by decreasing the rate until methane was absent while maintaining an excess of 30-40% of hydrogen sulfide. Residence time of the gases in the tube was about 40 seconds, and a contact time-surface area relationship can be calculated as 1.5×10^{-8} mol of methane per second per square centimeter of quartz surface. The effect of very slow flow rates was not determined.

Carbon oxysulfide was prepared by a method modeled on the work of Swakon and Field (2). The reaction scheme, as follows,



gave yields between 70 and 75%. Extending the time for the reaction did not produce any significant change. There is apparently an equilibrium established under the conditions used which is limiting.

MATERIALS AND METHODS

Carbon- ^{13}C monoxide (ca. 93 mol % ^{13}C) was produced by the Los Alamos Scientific Laboratory Stable Isotopes Separation Facility (3). Methane- ^{13}C was prepared from carbon- ^{13}C monoxide or dioxide by catalytic hydrogenation (4). Infrared spectra were taken with a Perkin-Elmer Model 710 spectrophotometer using 10-cm gas cells; absorption bands for material with natural abundance carbon are shown in parentheses for comparison.

EXPERIMENTAL

Carbon- ^{13}C Disulfide--A quartz combustion tube (24 mm i.d. x 90 cm) was packed along 70 cm of its length with quartz tubing (5 mm o.d., 3 mm i.d., x 25 mm) (17 pieces in cross section) which afforded ca. 3500 cm² of quartz surface area and ca. 250 cm³ free volume. The tube was heated in an electric furnace at 975-1000°C, and a mixture of methane- ^{13}C and excess hydrogen sulfide was passed over the glowing quartz at flow rates of approximately 275 ml/min for the hydrogen sulfide and 100 ml/min for the methane. The exit reaction gas was led through an air-cooled condenser, then a Dry Ice-cooled condenser into a flask cooled to -20°C with alcohol and ice. A second Dry Ice condenser was placed on the outflow from the flask, and this was connected to a cold trap immersed in a Dry Ice bath to assure collection of all product. Over 99% of the product was collected in the first flask.

Reaction runs using 1.5-2.0 mol of methane were completed in 9 hr, giving crude yields of 76-80%. Redistillation of the product (bp 39.5°C, 590 torr) was accomplished with 92% recovery. A small amount of residual, elemental sulfur remained in the distillation flask. Ir (gas): s 1480, 1490 (s 1530, 1540); w 2130, 2140 (w 2180, 2195) cm⁻¹.

Carbon- ^{13}C Oxydisulfide--Into a 1-liter stainless steel pressure vessel equipped with a thermometer, pressure gauge, and heating jacket were placed 32 g (1 mol) of elemental sulfur, 2 g of sodium methoxide, and 50 ml of anhydrous methanol. The vessel was partially evacuated to remove air, and carbon- ^{13}C monoxide was added to 200 psi (0.45 mol, 12.9 g). The vessel was heated to 100-105°C, and

the contents were agitated by shaking. As heat was applied, the pressure in the flask increased initially to 250-260 psi, then fell and leveled off at near 200 psi. After a reaction time of 18-20 hr, purification of the product was performed by slowly venting the reaction vessel through a train which consisted of two traps held at -40°C to trap methanol, then a tube containing Lithasorb to remove by-product carbon dioxide, and then three traps in series cooled to -70°C with Dry Ice (almost all of the product was retained in the first trap). When the reaction vessel was exhausted, the train was clamped off so as to isolate the product traps, and these were connected to a 300-ml stainless steel pressure vessel which had been evacuated and chilled with liquid nitrogen. The traps were allowed to warm to room temperature with transfer of product to the pressure vessel. Found 19.6 g (71%); ir (gas): w 840, 860 (w 840, 860); w 1000, 1025 (w 1040, 1055); w 1690, 1710 (w 1700, 1720); w 1850, 1870 (w 1885, 1905); s 2010, 2040 (s 2065, 2085); w 2945, 2955 (w 2945, 2955); w 3025, 3050 (w 3110, 3140) cm^{-1} .

ACKNOWLEDGMENT

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