

SYNTHESIS OF ^{14}C AND ^{35}S LABELLED CARBONYL SULFIDE

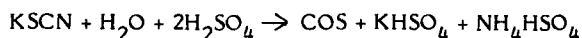
SUMMARY

Carbonyl sulfide (COS) was prepared by a replacement reaction from potassium thiocyanate (KSCN) in 50% sulfuric acid. ^{14}C -COS or ^{35}S -COS can be prepared by the same method, depending on the position of the label in the starting KSCN. The yield of the final product is in excess of 60%, and radiochemical purity was 99.5%.

Key Words: carbonyl sulfide, carbon-14 and sulfur-35

INTRODUCTION

The recent note by Kerr and Ott (1) on the synthesis of ^{13}C -carbonyl sulfide (COS: Carbon oxysulfide) has prompted us to report on our laboratory scale synthesis of radiolabelled COS. This method uses the reaction of sulfuric acid and potassium thiocyanate, as reported by Mellor (2).



The predominant contaminant, CO_2 is removed by passing the product gas through 33% potassium hydroxide (KOH). The product may be selectively labelled by using either ^{35}S or ^{14}C -thiocyanate as the starting material, with the resulting COS having the same specific activity as the starting thiocyanate.

MATERIALS AND METHODS

^{35}S -potassium thiocyanate (specific activity 19 $\mu\text{Ci}/\mu\text{mole}$) was obtained from New England Nuclear (Boston, Mass.), while ^{14}C -potassium thiocyanate (specific activity 59 $\mu\text{Ci}/\mu\text{mole}$) was purchased from Amersham Searle (Arlington Heights, Ill.). Unlabelled COS was obtained from Matheson (Marrow, Georgia).

Gas chromatography was performed with a Varian Model 3700 aerograph, while the infrared spectrum was obtained using a Perkin Elmer model 337 I-R spectrophotometer specially equipped with a 10 cm gas cell.

EXPERIMENTAL

A 25 mL Erlenmeyer flask was sealed with a rubber sleeved serum stopper, evacuated by water aspiration through a hypodermic needle, and placed in an ice bath. Next, 9.5 mL ice cold 50% sulfuric acid was injected into the vial, followed by 0.5 mL 5.0 M ice cold KSCN (in H₂O) carrying the desired label. The reaction flask was then refrigerated at 4° for 24 hours (the reaction is exothermic). The evolved COS escapes into the evacuated head space of the reaction flask.

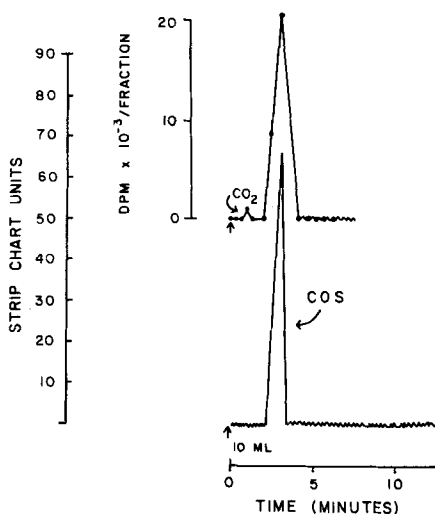


Fig. 1: The identity of the synthesized radiolabelled carbonyl sulfide (COS) was determined by gas chromatography using a flame (sulfur sensitive) photometric detector. Separation was affected using a 100 cm x 4 mm aluminum column packed with deactigel (3). The column temperature was programmed as follows: initial, 122° C for 2 min., then increased at 80° C/min to a final temperature of 242° C, which was continued for one min. Inlet pressure was 18 psig. The retention times were 1.5 min for CO₂, 2.4 min. for COS, and 4.5 min for CS₂.

Radioactivity was determined by collecting the gas chromatographic column eluent in ethanolamine at thirty second intervals. Trapped radioactivity was determined by liquid scintillation counting.

The labelled COS in the head space of the reaction vessel was removed with a 50 mL syringe and passed through a small gas washing flask containing 33% KOH to remove contaminating CO_2 . A dilute (0.05 M) hydrochloric acid solution, connected to the reaction vessel by way of a siphon, was used to correct for the volume and pressure change in the reaction flask. The COS was immediately injected into an evacuated sealed 25 mL Erlenmeyer flask; the yield was determined by gas chromatography (Fig. 1). When stored at -60°C , the gas was stable for at least a month.

Gas-radiochromatography revealed that with either ^{14}C - or ^{35}S -KSCN as starting material (see Figure 1), the major radiolabelled peak obtained corresponded to COS. No CS_2 , and little ($> 1\%$) CO_2 was detected in the final product. The identity of the product as COS was also confirmed by its infrared spectrum, which was identical with that of commercially available COS (I). The normal yield was between 50 and 60%. The method described provides a simple, relatively inexpensive synthesis of radiolabelled carbonyl sulfide for laboratory scale projects.

ACKNOWLEDGEMENT

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