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Preparation of OC¹⁴S, O¹⁸CS, OCS³³, and CH₃Cl³⁶*

By G. M. MATLACK, R. E. FERGUSON, J. F. HASKIN, AND G. GLOCKLER

In connection with a microwave absorption study of the nuclear spins of isotopes by Professor A. Roberts, formerly of the Physics Department of this University, we were asked to prepare samples of OC¹⁴S, O¹⁸CS, OCS³³, and of CH₃Cl³⁶, starting with small quantities of the materials containing the desired isotopes. We believe that the methods employed in the synthesis of these compounds may be of use to other investigators.

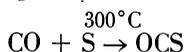
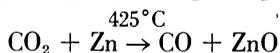
I. Preparations of Labelled OCS

The basic method chosen for the preparation of all of the OCS samples was that investigated by Lewis and Lacey¹ in which CO is heated with elemental sulfur; this reaction, on a large scale, is reported to give yields of 80% or better and it has the further advantage of being a "dry" method, suited to high vacuum operations.

A. Preparation of OC¹⁴S

In order that optimum intensity of the microwave absorption lines be achieved, it was essential that the synthesis be carried out with no dilution of the C¹⁴ with C¹², since the heavier isotope was available in concentrations of only 2-5% of total C at that time. As the conditions under which the absorption spectrum was examined required only about 3 x 10⁻⁸ mole of gas, we were also asked to scale down the synthesis so that no more than 1 milligram of starting material, BaCO₃ containing C¹⁴, would be used.

The preparation involved the following reactions:



All operations were carried out in a conventional chemical vacuum system. The BaCO₃ was placed in a 25 ml round-bottom flask and the flask was evacuated to 5 x 10⁻⁶ mm Hg or better. After isolation of the generating system from the pumps by a mercury cutoff, previously outgassed concentrated sulfuric acid was allowed to drip slowly into the BaCO₃. When the reaction had apparently ceased, the flask was heated gently with a smoky flame until it was hot to the touch. The CO₂ generated was condensed in a receiver cooled by

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¹G. N. Lewis and W. Lacey, J. Am. Chem. Soc., 37 1976 (1916).

liquid air; quantitative condensation was usually effected in 20 minutes as indicated by pressure-volume measurements. At this point any non-condensable material was pumped off.

The CO_2 was distilled from the receiver, now cooled with dry ice, into a small glass L-shaped reactor fitted with a break-seal containing zinc pellets in one leg and sulfur in the other, cooled by liquid air. Non-condensables were again pumped off and the reactor was sealed off from the vacuum line. The leg of the reactor containing the zinc was heated in a tube furnace at 425°C for 4 hours, then was removed and the leg containing the sulfur was inserted into the furnace and kept at 300°C for 24 hours. After the reactor had been resealed to the line, the condensable gases were frozen out with liquid air (about a half hour is required due to the presence of non-condensables from the out-gassing of the reactor tube walls), and the tube was opened with a magnetic hammer. Non-condensable gases were then pumped off and the condensable gases were distilled from the reactor, cooled by a dry ice bath, to receiver cooled by liquid air. 90% of the condensables containing OCS distilled over in 5 minutes.

In all, six runs were made in which the amount of BaCO_3 used was successively reduced. The purity of the OCS was estimated by the relative intensity of the S^{34} rotational line of the microwave spectra of the various samples. In runs made starting with 1 mg of BaCO_3 , the OCS was not as pure as that produced starting with 10 or 100 mg of BaCO_3 , the S^{34} line being just visible in the product from the small scale runs.

B. Preparation of OCS^{33}

In this synthesis we have limited the starting amount of sulfur to about 1 microgram. A typical run was as follows: The sulfur (enriched S from the Oak Ridge Laboratories) was dissolved in CH_2Cl_2 and the solution was pipetted into a 0.5 ml reactor made of glass tubing, one end of which was fitted with a breakoff seal. After the CH_2Cl_2 was evaporated with a water aspirator, the open end of the tube was sealed to the vacuum line and evacuated, the part of the tube containing the sulfur being cooled to reduce volatilization. The tube was filled with CO to about 500 mm Hg, sealed off from the line, and heated at 300°C for 24 hours. The breakoff seal end was then sealed to the vacuum line, the tube was cooled with liquid air, and the seal was broken with a magnetic hammer. Excess CO was pumped off and the OCS was distilled into a receiver cooled with liquid air.

Using this procedure, 80% yields of OCS have been obtained from 2 micrograms of sulfur.

C. Synthesis of OCS with O¹⁸-enriched oxygen.

The enriched oxygen used in this preparation was supplied through the courtesy of Professor A.O.C. Nier of the University of Minnesota. The oxygen was said to contain about 50% of O¹⁸ and 1.5% of O¹⁷ together with a small amount of argon. The total pressure in the sample bulb was slightly less than 1 atmosphere.

Coarsely powdered charcoal was introduced into a vycor tube which was sealed to the stopcock of the oxygen container. The other end of the vycor tube was sealed to the vacuum line and the charcoal was evacuated with flaming with a large hot flame for one-half hour. The assembly was sealed off from the vacuum system and the oxygen was admitted to the tube containing the charcoal, which was in turn sealed off from the oxygen container. The vycor tube was heated to burn the carbon to CO₂, sealed to the vacuum line, cooled with liquid air, opened to the line through a break-seal, and the excess oxygen was pumped out. The CO₂ was reduced to CO which was heated with sulfur to produce OCS, as described above.

II. Preparation of CH₃Cl³⁶, starting with 0.5 N HCl³⁶ solution

This synthesis is described by the following series of reactions:

1. $\text{HCl}(\text{aq}) + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{HNO}_3$
2. $3\text{AgCl} + \text{Al} \rightarrow \text{AlCl}_3 + 3\text{Ag}$
3. $\text{CH}_3\text{OH} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{OH} \cdot \text{AlCl}_3$
4. $\text{CH}_3\text{OH} \cdot \text{AlCl}_3 \xrightarrow{140^\circ} \text{CH}_3\text{Cl} + \text{AlOCl} + \text{HCl}$

Reactions 3 and 4, investigated by Norris and Sturgis² were selected for the basic method and were adapted to the use of vacuum technique for this preparation.

The source of Cl³⁶ available was a 0.5 N solution of HCl, of concentration 0.0035 mc/ml in Cl³⁶, obtained from the Oak Ridge laboratories.

The chief problem was the preparation of AlCl₃ from the HCl solution; this was solved as follows:

0.2 ml of the HCl solution was pipetted into a sharply pointed, thin walled centrifuge tube of 1 ml capacity, and AgCl was precipitated by addition of 0.5 N AgNO₃ solution. After several washings the AgCl was packed into the bottom of the tube by centrifuging, and was dried in the tube at 70°C for 2 hours. The glass was

²J. F. Norris and B. M. Sturgis, *J. Am. Chem. Soc.*, 61, 1413 (1939).

cracked away from the pellet of AgCl ; the pellet was wrapped in pure Al foil and placed in a tube which was then sealed to the vacuum line. After evacuation the wrapped pellet was heated to induce reaction, which takes place very rapidly, covering the walls of the tube with a deposit of AlCl_3 . The AlCl_3 was caused to sublime to one spot in a small side neck of the tube.

Methyl alcohol was condensed upon the spot of AlCl_3 , air was admitted to the system, and the mixture was allowed to stand for 1 hour, after which the excess CH_3OH was pumped off, leaving a glassy deposit of the complex. The complex was decomposed by slow heating to 140°C and the resulting mixture of CH_3Cl and HCl was condensed in a trap cooled by liquid nitrogen. After several distillations from dry ice temperature to that of liquid nitrogen, the gases were stored in a glass break-seal sample bulb for later use. (The HCl can be removed, if desired, by distillation of the mixture over solid KOH).

The yield was 0.7 ml (S.C.) of condensable gas, the CH_3Cl content of which was estimated at 40% of the CH_3Cl - HCl mixture, by volume.

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