

**308.** *The Conversion of Carbon Dioxide into Acetylene on the Scale of 2—20 Micromoles.*

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A method is described for the conversion of carbon dioxide into acetylene in quantities of 50—500  $\mu$ l. at N.T.P. (2—20 micromoles) with yields generally upwards of 90%. The method is suitable for use with  $^{14}\text{CO}_2$  of high isotopic concentration.

THE synthesis of biologically important compounds labelled with  $^{14}\text{C}$  presents difficulties in technique, partly because the starting substance is carbon dioxide, and partly because it may be necessary to carry out synthesis on the very small scale of millimoles or less, if products of high specific radioactivity are to be obtained from the small quantities of labelled carbon dioxide available.

One compound important as an intermediate in several syntheses is acetylene. Cramer and Kistiakowski (*J. Biol. Chem.*, 1941, **137**, 549) and Vennesland *et al.* (*ibid.*, 1942, **142**, 371) developed methods for converting carbon dioxide labelled with  $^{14}\text{CO}_2$  into acetylene on the scale of 1—2½ millimoles with yields of about 50—70%. If  $^{14}\text{C}$  is to be used in place of  $^{13}\text{C}$ ,

these methods would entail the disadvantage of handling dry  $\text{Ba}^{14}\text{CO}_3$  and the loss of  $^{14}\text{C}$  occasioned by the moderate yield would be serious.

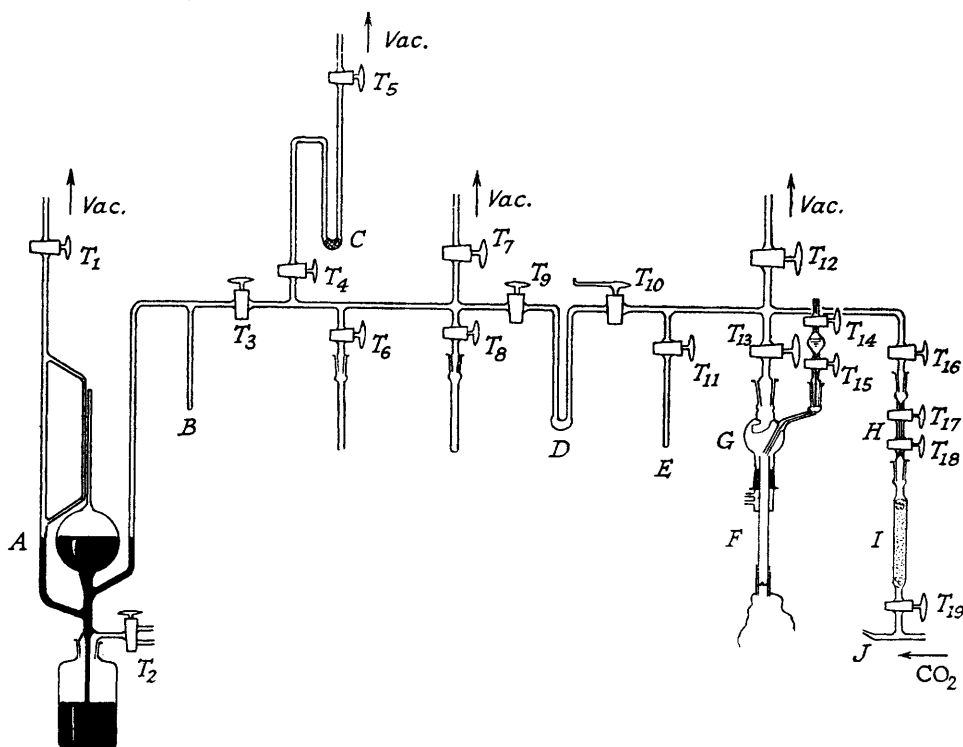
As it is hoped to carry out syntheses in which acetylene is an intermediate, a method has been developed for the conversion of carbon dioxide into acetylene in yields usually of more than 90%, working with quantities of carbon dioxide of 50 to 500  $\mu\text{l}$ . at N.T.P., this being of the order of the volume occupied by a millicurie of isotopically pure  $^{14}\text{CO}_2$ .

It is well known that when calcium is heated suddenly in an atmosphere of carbon dioxide some calcium carbide is formed, and even on a very small scale Chackett (unpublished work) obtained qualitative evidence of the presence of calcium carbide in the residue from a Soddy-type calcium furnace after this had been used to clean up hydrocarbons from inert-gas specimens. In the present experiments, barium heated in a stainless-steel vacuum furnace was found to absorb carbon dioxide to give barium carbide. The contents of the furnace after cooling were dissolved in water, and the acetylene from the barium carbide was separated from the resulting gas mixture.

#### EXPERIMENTAL.

The high-vacuum apparatus used is illustrated (not to scale) in Fig. 1. The tube *I* was filled with a sample of carbon dioxide from the vaporising solid, the gas sample being dried in *I* with magnesium

FIG. 1.

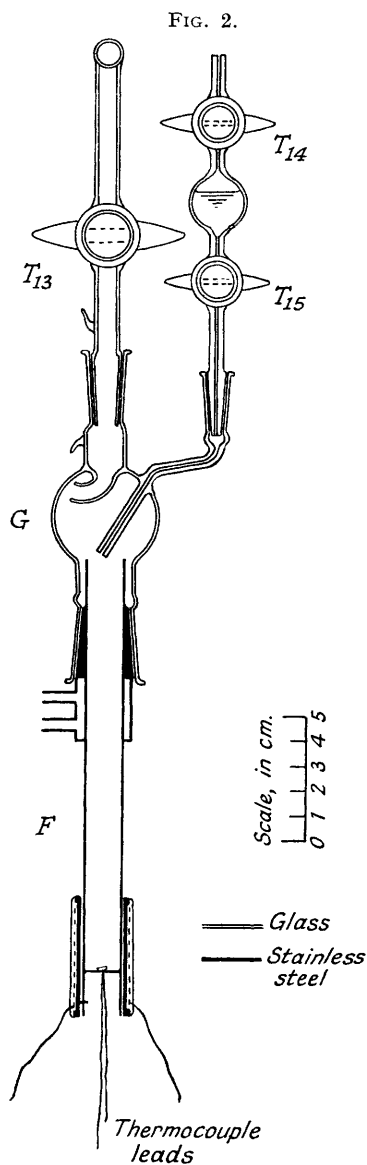


perchlorate. With all stopcocks to vacuum closed, carbon dioxide was admitted to the apparatus in doses through the dosing tube *H*, condensed into the McLeod gauge trap *B*, and, with stopcock  $T_3$  closed, evaporated and its pressure measured so that the volume of carbon dioxide taken could be corrected to N.T.P. In fact, the volume measured was corrected to normal pressure and laboratory temperature since at this stage only relative measurements of gases were required.

A very pure specimen of barium was scraped as clean as possible. About 40 mg. were cut off, weighed, and placed in a stainless-steel vacuum furnace *F* fitted with a splash-head *G*, the whole being evacuated through  $T_{13}$  and  $T_{12}$  (Fig. 2). With all stopcocks to vacuum closed, the measured specimen of carbon dioxide was condensed into a reservoir *E*, and  $T_{10}$  was closed; *E* was warmed to room temperature, and with  $T_{11}$  and  $T_{13}$  open, the furnace was heated with a bayonet fitting heater wound on a stainless-steel former, the temperature being measured from outside with a platinum-platinum-rhodium thermocouple. It may be seen from Fig. 2 that the design of *F* is such that both the barium and the thermojunction are about at the centre of the heating element. The gas began to disappear at a temperature of about  $480^\circ$ , and in about 5 minutes, by which time the furnace had reached a temperature of  $600^\circ$ , all the gas

except for perhaps 1% or less had disappeared. With the heating element removed, the furnace temperature fell rapidly to room temperature.

The next stage of the process was the decomposition of the contents of the furnace with water. Preliminary analytical experiments on the composition of the mixed gases obtained showed the mixture to consist of a large excess of hydrogen and water vapour together with acetylene, ammonia from the



barium nitride on the surface of the barium, and a very small amount of a gas which had physical properties consistent with its being ethylene, although the amount obtained never exceeded 2% of the total  $C_2$  hydrocarbons and was too small for chemical identification. With  $T_{15}$  closed, distilled water was introduced into a dosing bulb through  $T_{14}$  by means of a narrow metal tube which was then used to pass hydrogen through the water for a few minutes to remove dissolved gases. On withdrawing the tube and closing  $T_{14}$ , hydrogen was left above the water surface at 1 atm. pressure. With  $T_{13}$  closed,  $T_{15}$  was opened cautiously, water passed into  $F$ , and the contents of  $F$  rapidly dissolved.

In preparation for the removal of acetylene from the gas mixture, the charcoal trap  $C$  and the rough drying trap  $D$  were cooled to  $-78^\circ$ ;  $T_4$ ,  $T_5$ ,  $T_3$ , and  $T_{13}$  were opened while  $T_2$ ,  $T_{10}$ , and all other stopcocks were closed.  $T_{10}$  was a control stopcock, having a long handle on the plug and shallow file cuts on opposite sides of the plug leading into the bore so that it could be opened very gradually.

Tap  $T_{10}$  was opened cautiously, and the gas mixture from  $F$  passed at low pressure through  $D$ , where most of the water vapour was frozen out without carrying down any acetylene with it. The mixture, consisting now of hydrogen, water vapour, acetylene, ammonia, and the trace of ethylene, passed into  $C$ , where the last four gases were stripped completely from the hydrogen which was pumped away. By this time the solution in  $F$  had boiled and become very cold;  $T_{10}$  was therefore closed, and  $F$  heated gently with the heating element. The boiling-off process and gas transfer were repeated twice.

With  $T_6$ ,  $T_7$ , and  $T_9$  closed and  $T_3$  and  $T_4$  open, the temperature of  $C$  was raised to  $0^\circ$ , and  $B$  cooled with liquid nitrogen. At  $0^\circ$ , appreciable proportions of acetylene and ethylene were found to be desorbed from charcoal while all the water vapour and ammonia were still adsorbed. The hydrocarbons therefore were condensed into  $B$ , the transfer rate falling off not quite exponentially. In about 10 minutes most of the acetylene had been recovered together with the trace of ethylene, and with  $T_3$  closed the gases could be evaporated into the McLeod gauge at room temperature and measured.

The McLeod gauge used had a bulb of 250-ml. capacity and a closed capillary 20 cm. long by 3 mm. internal diameter. An accuracy of about  $\pm 1$ –2% was obtainable with amounts of gas varying from 2 to 500  $\mu$ l. at N.T.P.

Methods of identification and analysis of the gases involved in this work included measurement of vapour pressures at very low temperatures and chemical absorption in standard reagents in the reaction vessels below  $T_6$  and  $T_8$ . Carbon dioxide was absorbed in a wet pellet of potassium or sodium hydroxide, ammonia in viscid metaphosphoric acid, and acetylene in a paste of cuprous chloride and potassium hydroxide solution. With all but very small amounts of acetylene, absorption in this reagent gave a red precipitate of copper acetylide.

*Results.*—Some typical results are given below. Volumes of gases quoted are at N.P. and laboratory temperature ignoring dead space of the McLeod gauge. The volume measurements are relatively accurate and, because the dead space correction and temperature correction are in opposite senses, very nearly at N.T.P.

$CO_2$ taken, $\mu$ l.	$C_2H_2(+C_2H_4)$ found, $\mu$ l.	$C_2H_2$ in blank.	Yield, %.	$CO_2$ taken, $\mu$ l.	$C_2H_2(+C_2H_4)$ found, $\mu$ l.	$C_2H_2$ in blank.	Yield, %.
335	178	14	98	62	25.5	1.1	79
273	133	12	89	558	265	3	94
300	140	3	91	566	260	2	91
305	140	3	90	50	21.5	1.8	79

*Discussion.*—The process described above is a standard procedure which was found to be satisfactory. In earlier work, however, considerable difficulties were encountered. For example, it was found to be important to use stainless-steel as a furnace material. From mild steel, relatively large amounts of acetylene were produced in blank experiments; and a fused

silica envelope fitted with a nickel thimble was found, after it had been used with calcium and barium, to absorb carbon dioxide when hot even though no calcium or barium was present.

The condensation at low temperature of a mixture of acetylene, water vapour, and ammonia all together with mercury (as opposed to adsorption on charcoal) is to be avoided, since acetylene disappears when the trap is warmed, presumably because of the formation of mercury acetylide.

In carrying out the absorption of carbon dioxide in hot barium in the stainless-steel furnace, it was found that when the pressure at which the gas was admitted was less than  $10^{-1}$  mm. of Hg, the yield of acetylene was variable and only about 45%. A similar tendency to low yield (79%) is seen in two experiments where the maximum pressure which could be exerted in our apparatus was lower than usual.

The formation of barium carbide is certainly the result not of a single reaction but probably of several which result partly in the formation of elementary carbon and of barium carbonate from barium oxide and carbon dioxide. Barium carbonate is known to react with hot barium to form carbide and oxide, while elementary carbon intimately mixed with barium might be expected to react appreciably even at  $600^{\circ}$  by analogy with the direct combination of carbon and calcium investigated by Botolfsen (*Ann. Chim.*, 1922, 18, 5). If carbon dioxide is admitted to a barium furnace at  $600^{\circ}$ , at which temperature the barium is distilling quite freely, it will react with the metal vapour, and any elementary carbon or carbonate formed will condense with excess of barium on a cold part of the furnace and will not be reheated with the barium. If, however, the carbon dioxide is present in contact with the barium while this is being heated, vaporisation of the metal will be inhibited and reaction will take place on the surface, the reaction products being further heated in contact with metallic barium. Better yields of carbide would be expected in the second case than in the first.

The scale on which this conversion to acetylene has been carried out is about two orders of magnitude less than has been employed in most syntheses involving  $^{14}\text{CO}_2$ . The scale could fairly easily be increased with probably almost quantitative yields, but could not be decreased very far without the difficulties being encountered of low yield and inconvenience in manipulation and measurement.

We wish to thank Professor W. H. Linnell for his interest and support, many others for helpful conversations, the Research Laboratories of the General Electric Co. Ltd. for a specimen of very pure barium metal, and also to acknowledge generous grants from the Therapeutic Research Corporation, the Royal Society, the Medical Research Council, and the Central Research Fund of the University of London. One of us (R. G.) is a Keddey Fletcher-Warr Student of London University.

COLLEGE OF THE PHARMACEUTICAL SOCIETY,  
UNIVERSITY OF LONDON.

[Received, September 5th, 1947.]

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