reproduced by $n = 3$ and $c = 100$ applied in equation (B).[3] Areas so computed differ but little from those found by equation (2).

The occurrence of S-shaped isotherms (ethylene on porous glass and on III) would seem to imply adsorbed gas in a different state, possibly one corresponding to the solid rather than the liquid. The nature of an adsorbent might well influence the structure of an adsorbed film near the melting point of the vapor being adsorbed. These adsorbents appear to have the finest pores of any of the adsorbents, 50–60 Å. in diameter for porous glass and about 107 Å. for sulfuric acid anodic film.

Use of a larger value of P_0 extends the range of the BET equation for these two adsorbents but like the results of Anderson[19] the start of the linear region is displaced to higher pressures. In contrast to the case with the other isotherms, beyond the higher pressure limit of the linear range, points fall below the extrapolated straight line.

Surface Areas of the Adsorbents.—The large relative surface of the anodized aluminum agrees with the hypothesis of porous structure which has been recently supported by electron microscopic examination.[20] From the relative surface, 652, of V, the quantity of nitrogen required to fill the pores, 2.38×10^{-3} mole, and the thickness of the anodic film, 0.00125 cm., and assuming liquid packing, the average pore diameter is 107 Å. and the number of pores per sq. cm., 1.55×10^{11}. This agrees well with electron microscopic results.

The relative surface is roughly proportional to time of anodization. This also accords with a porous structure. For equal thicknesses the coatings formed in sulfuric acid have about three times the area of those formed in chromic acid. "Sealing" an anodic film forms boehmite, α-$Al_2O_3 \cdot H_2O$,[5] the growth of the crystals of which has been believed to seal the pores. Our surface area measurements support this view.

Anodic coating is amorphous to X-rays. That by chromic acid is substantially pure alumina[21] while that formed in sulfuric acid contains a little water[5,21] plus 13% sulfate.[21] Surfaces of the aluminum foil undoubtedly are covered by a layer of oxide a few molecules deep. The only surely crystalline surface studied in this investigation was the boehmite one.

Summary

The adsorption of ethylene at −183° has been applied to the determination of surface areas on aluminum foil subjected to various etching and anodic treatments.

The results accord with the hypothesis of porous structure of anodic coatings.

Two kinds of isotherms have been found, S-shaped ones and ones whose linear portions continue to the experimental saturation pressure. It is surmised that the nature of the adsorbent surface may influence the type of adsorption which occurs at temperatures for which the stable condensed phase is the solid.

(20a) Fischer and Kurz, *Korrosion u. Metallschutz*, **18**, 42 (1942). Upon electrolytically polished 99.99% aluminum anodized in 28% sulfuric acid at 12 volts, the average pore diameter is 150 Å., the average number per sq. cm., 0.8×10^{11}.

(20b) Edwards and Keller, *Trans. Am. Inst. Mining Met. Engrs., Inst. Metals Div.*, Tech. Pub. No. 1710 (1944). Upon 99.75% aluminum anodized in 7.5% sulfuric acid at 7.5 volts, the average pore number per sq. cm. is reported as 2.7×10^{11}, the average diameter appears to be slightly greater than 100 Å. The pore diameter in chromic acid anodic film is about 160 Å. but this is for anodization at but 5 volts in 1% solution.

[21] Pullen, *Metal Ind.* (*London*), **54**, 327 (1939).

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[CONTRIBUTION FROM THE RADIATION LABORATORY AND CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA]

Synthesis of Carbon Radioactive Methyl Iodide and Methanol from Carbon Dioxide[1]

BY B. M. TOLBERT

Carbon radioactive methyl iodide and methanol are of considerable importance in the synthetic chemistry of radioactive compounds for the introduction of labeled carbon. In this paper, a small scale (25 millimoles) and high yield (81–86% based on $C^{14}O_2$ taken) synthesis of these two compounds from carbon dioxide is presented.

The following reactions were used for the several steps

$$\underset{0.025\text{ mole}}{BaC^*O_3} \xrightarrow{H_2SO_4} C^*O_2 \qquad 100\% \quad (1)$$

$$C^*O_2 + 3H_2 \xrightarrow[\text{KCuAl}_2\text{O}_3\text{ catalyst}]{\text{460 atm. pressure}} C^*H_3OH + H_2O \qquad 80\text{–}90\% \quad (2)$$

$$C^*H_3OH \xrightarrow[H_2O]{I_2 + \text{Red } P_4} C^*H_3I \qquad 95\text{–}100\% \quad (3)$$

Special techniques are necessary for the handling of small amounts of volatile organic compounds. Thus all reactions, washings and transfers were done in a closed system that had been evacuated to 10 microns or less pressure. Purification methods were chosen that could be adapted to vacuum line work. Liquid nitrogen was used to freeze contents of reaction vessels and traps during evacuation. Quantitative transfers were effected by distilling compounds from one vessel to another using liquid nitrogen. The vacuum line used for this work (see Fig. 1) was developed for general organic synthesis. Reaction tubes and vessels may be closed off, removed from the line, and as

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(1) This paper is based on work performed under Contract #W-7405-Eng-48 with the Manhattan Project in connection with the Radiation Laboratory, University of California.

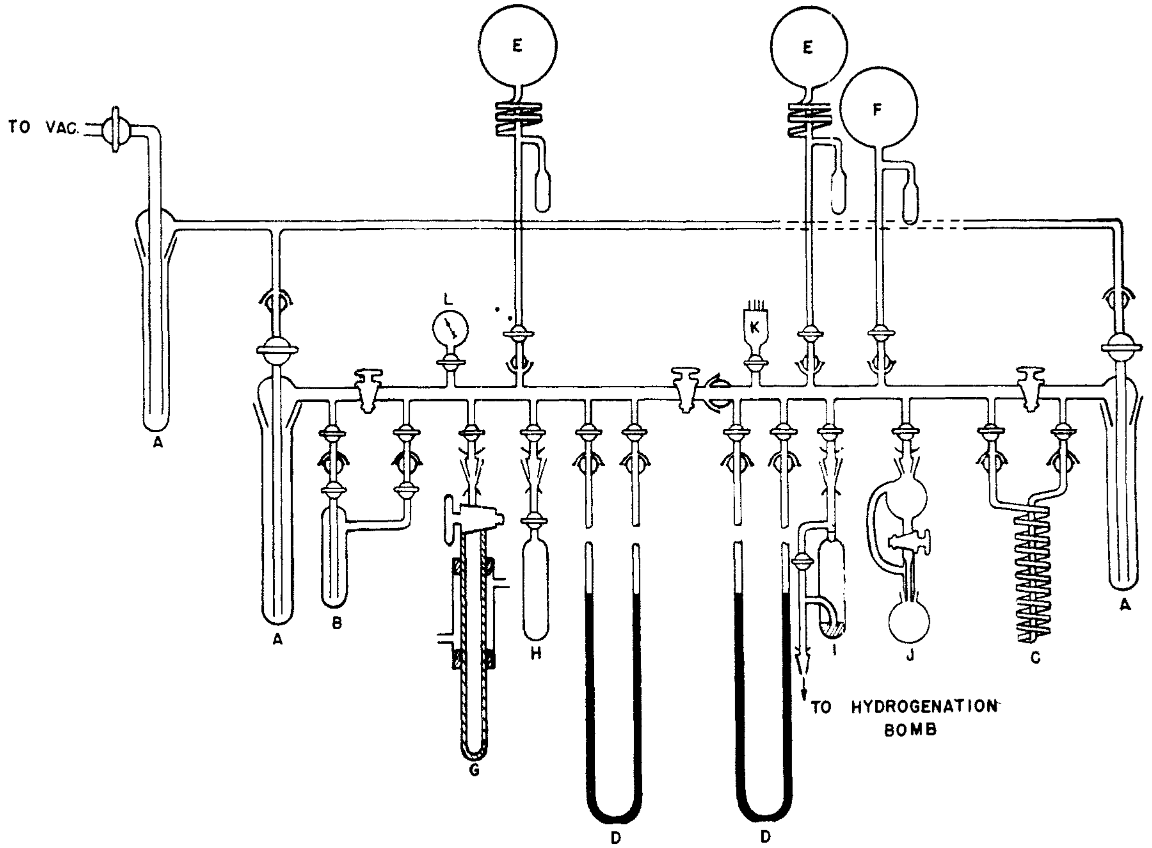

Fig. 1.—High vacuum line for organic synthesis: A, large liquid nitrogen traps; B and C, removable traps; D, mercury manometers; E and F, gas storage and aliquoting bulbs with leg to permit freezing of condensable vapors from the line into the storage bulb; G, iodination glass bomb; H, reaction or storage vessel; I, mercury bubbler with bypass, used to observe rate of hydrogen removal from high pressure bomb; J, pressure equalizing dropping funnel for carbon dioxide generation; K, thermocouple vacuum gage[2]; L, brass vacuum gage.

needed, heated, refluxed or shaken. The connecting lines are re-evacuated when the vessels are returned to the system.

Ipatieff and Monroe[3] report high yield synthesis of methanol from carbon dioxide and hydrogen over copper–alumina catalyst using a flow type apparatus. Starting with their data, a small scale batchwise reduction was developed. The yield of methanol, as such, was never determined, although its boiling point and index of refraction were checked in a separate experiment. The identity of the methyl iodide was similarly checked and its yield was used as a criterion of the completeness of the reduction of the carbon dioxide to methanol.

The completeness of the reduction of carbon dioxide to methanol was found to be very dependent on pressure. After six hours of heating at 285° at a hydrogen pressure of 410 atm., 86% of the carbon dioxide had reacted, but the yield of methyl iodide on the basis of carbon dioxide used up was only 60%. With a hydrogen pressure of 450 atm. 95–97% of the carbon dioxide reacted and of this amount 83–90% was converted to methyl iodide (see Table I).

TABLE I

REDUCTION OF C^*O_2 AT 285° AND 450 ATM. HYDROGEN PRESSURE

Reaction time, hours	2	4	5	6	6	6
% C^*O_2 reacted	59	80.9	92.7	97.2	95.1	97.0
% yield C^*H_3I	31	52	68	85	86	81
% yield C^*H_3I on basis of CO_2 reacted	53	64	72	87	90	83

The catalyst used for these experiments was suggested and supplied by the Shell Development Company[4] and contained 10% cupric oxide and 2% potassium hydroxide on 8–12 mesh alumina. It is not known whether the potassium in this catalyst is necessary. Several reductions of carbon dioxide were tried using catalysts containing 10–20% copper on powdered gamma active alumina. These reductions gave methanol in yields of about 50% of those obtained with the coarser catalyst containing the potassium.

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(2) Thermocouple gage, Type E, National Research Corporation, Boston, Mass.

(3) V. N. Ipatieff and G. S. Monroe, THIS JOURNAL, **67**, 2168 (1945).

(4) Shell Development Co., Emeryville, California.

The specific activity [1.53 × 10^3 counts/min./mg. barium carbonate[5]] of the carbon in the carbon dioxide and in the methyl iodide checked within counting errors (±3%). To obtain a material balance of the radioactive carbon, the residues from the several steps of a synthesis (last reduction, Table I) and material from the traps of the vacuum line were collected together and an attempt made to oxidize out the residual carbon. Large quantities of chlorine and iodine obtained on acid oxidation of these residues hindered this operation so very little of this material was recovered. The following radio material balance was obtained: counts in initial $C^{14}O_2$, 7.5 × 10^6; amount of $C^{14}O_2$ recovered, 2.2 × 10^5 counts; activity recovered from the residues, 4.5 × 10^3 counts; counts in the methyl iodide, 6.05 × 10^6. Thus 83.4% of the radioactive carbon was readily recovered or accounted for. Part of the activity may have been lost as methane and carbon monoxide with the hydrogen from the reduction bomb.

Although the experiments were done on a 25 millimole scale, this could have been reduced considerably without serious loss of yield. Some preliminary reductions of 15 millimoles of carbon dioxide gave yields of methyl iodide of comparable percentage to the larger scale runs.

The author wishes to thank Professor Melvin Calvin for his encouragement and advice in these experiments.

Experimental

The carbon dioxide was generated in the evacuated system from barium carbonate by the action of concentrated sulfuric acid using a pressure equalizing dropping funnel. The liberated carbon dioxide was condensed in a liquid nitrogen trap and entrapped air released from the crystals of barium carbonate pumped off. The amount of carbon dioxide used in a run was determined by measuring the pressure in a system of known volume; this value checked the weight of barium carbonate taken.

The carbon dioxide was reduced in a micro hydrogenation bomb[6] with a free volume of 300 cc. The catalyst, 10% cupric oxide and 2% potassium hydroxide on alumina was prepared by impregnation of 8 to 12 mesh alumina[7] with the copper nitrate, drying at 130°, absorbing a potassium hydroxide solution, redrying, igniting at 500° for four hours and finally reducing at 285° and 330 atm. hydrogen pressure for three hours. After introduction of five grams of this catalyst the bomb was evacuated on the high vacuum line to a pressure of 10 microns. The bomb was then half immersed in liquid nitrogen and the $C^{14}O_2$ frozen into it. After introduction of an initial pressure of 3500 p.s.i. hydrogen at room temperature, the bomb was heated for six hours at 285°.

The products of the reduction and the unreacted carbon dioxide were condensed in a series of three liquid nitrogen traps. The hydrogen, at a pressure of about 1 cm. mercury, was passed through the traps at a slow rate (0.3 mole per hour) to insure complete condensation. The remaining products were vacuum distilled from the warmed bomb into the traps. The carbon dioxide that had not been reduced was then separated from the water–methanol mixture by distillation through a Dry Ice-trap. The residual pressure of carbon dioxide in the original measuring system gave the necessary data to determine the per cent. of carbon dioxide that reacted.

The methanol was converted to methyl iodide in a heavy-walled glass bomb tube closed with an eight-mm. stopcock held in by a simple clamp. The upper half of the tube was jacketed to permit the reaction mixture to be refluxed. Ten grams of iodine was introduced through a long stemmed funnel. The tube was chilled in liquid nitrogen and 2 g. of red phosphorus and 3 ml. of water were added. The tube was evacuated and the methanol-water mixture distilled into it. The reaction mixture was refluxed on the steam-bath for two hours in the closed and clamped tube. The exact pressure in this tube was not known but exceeded one atmosphere during refluxing. The water reduces the pressure considerably by dissolving the hydrogen iodide and did not interfere with the conversion of the methanol to methyl iodide. The reaction tube was warmed and evacuated until all the methyl iodide was caught in a liquid nitrogen trap.

This methyl iodide was purified by two methods. In the first the impure methyl iodide was distilled into a reaction vessel containing 10 ml. of water. This vessel was removed from the line, shaken and returned to the vacuum line. The methyl iodide was distilled through a 15-ml. calcium chloride tube into a storage vessel for weighing. The boiling point of the methyl iodide, $n^{21}D$ 1.525, was 42 to 43°. In the second procedure, the methyl iodide was distilled into a reaction tube containing 3 to 4 g. of phosphorus pentoxide. After shaking at room temperature for five minutes, the methyl iodide was distilled into a storage vessel for weighing; $n^{22}D$ of the methyl iodide, 1.5280. The methyl iodide made by either of these two purification methods has been found satisfactory for Grignard reactions.

The identity of the methanol was established by fractional distillation of 2 ml. of a water–methanol mixture from a reduction. About 0.75 ml. of methanol boiling over the range of 62 to 70°, $n^{22}D$ 1.3332, was recovered. Almost all the methanol distilled at 65°.

Summary

1. Carbon radioactive methyl iodide has been synthesized on a 25 millimole scale from $C^{14}O_2$ with yields of 81–86% by the high pressure catalytic reduction of carbon dioxide with hydrogen to methanol and the conversion of methanol to methyl iodide using phosphorus and iodine.

2. High vacuum technique was employed for manipulation of the small quantities of organic gases and liquids.

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(5) Measurements of radioactivity were made with a thin mica-window Geiger–Müller tube on a scale of 64 circuit with a geometry of 12.5 disintegrations per count. The activity was determined with thin uniform layers of barium carbonate according to the procedures of Dauben, Reid and Yankwich (paper in preparation) and Yankwich, Norris and Huston, *Anal. Chem.*, **16**, in press.

(6) Micro bomb, American Instrument Co., Silver Springs, Md.

(7) High surface alumina with approximately 100 sq. meters surface area per g. Aluminum Ore Co. of America, Pittsburgh, Pa.