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THE PRODUCTION OF SODIUM FORMATE-C^{14} BY THE LITHIUM BOROHYDRIDE PROCESS

J. G. Burr and H. E. Heller

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ABSTRACT

A method has been developed for the preparation of sodium formate-C^{14} by the reduction of carbon dioxide-C^{14} with an ethereal solution of lithium borohydride at $0^{o}C$. The method is equally applicable to low level synthesis using simple laboratory equipment and to high-level routine production.

By-products of the reaction are methanol (10-15%) and diborane. The mechanism of the reaction has as yet no simple interpretation.

Ethyl formate can be prepared in good yield from the sodium salt by the action of diethyl sulfate at $170^{o}C$.

A special apparatus has been built for routine production, which permits carefully controlled reaction conditions in an enclosed system. By this method 130 millicuries of high specific activity sodium formate has been prepared.

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THE PRODUCTION OF SODIUM FORMATE-C^{14} BY THE LITHIUM BOROHYDRIDE PROCESS

J. G. Burr and H. E. Heller

I. Introduction

A method has been devised for the preparation of sodium formate-C^{14} from carbon dioxide-C^{14} by reduction with lithium borohydride in ether solution. The method is important as a method of synthesis of formic acid-C^{14} since it does not require the use of elevated temperatures or pressures, or a prior conversion of carbon dioxide to carbon monoxide. The method is equally applicable to low-level synthesis using simple laboratory equipment (see Figure 1) and to high-level routine production for which a more elaborate apparatus has been designed (see Figure 2). By the use of the latter method, approximately 130 millicuries of high specific activity sodium formate has been produced.

II. Discussion of Results of Low-level and Non-radioactive Studies

A. Present Procedure

The procedure consists of sweeping carbon dioxide with dry nitrogen into a measured quantity of standardized ethereal lithium borohydride solution maintained at 0°C. Unreacted carbon dioxide (15-20%) is absorbed in two saturated barium hydroxide traps. At the completion of the run, the reaction product is hydrolyzed with dilute phosphoric acid, the aqueous formic acid is distilled under vacuum, and titrated with standard alkali.

Careful vacuum distillation of the aqueous formate solution to dryness removes neutral, volatile organic materials. The chemical yield may be based on the alkali titration value.

B. Effect of Variation in Reaction Conditions

The yield of formic acid is not increased by the use of excess carbon dioxide, and is considerably lowered with excess reducing agent. Elevation of the reaction temperature from 0°C. to 30°C. does not increase the yield but does reduce the carbon dioxide absorption. Below 0°C. the reaction velocity falls off rapidly.

Diethyl carbitol as solvent is found to increase the absorption of carbon dioxide but to lower the yield of formic acid. The reaction does not take place in tri-n-propyl amine.

C. By-products of the Reaction

Methanol-C^{14} to the extent of 13% was identified among the reaction products of tracer-scale preparations, but formaldehyde-C^{14} could not be detected. Although formaldehyde was detected during one non-radioactive run, to the extent of about 3%, this result could not be duplicated in other preparations.

During the reaction, part of the boron is converted to diborane, which appears in the barium hydroxide traps as boric acid. The remainder of the boron remains in the reaction flask as a precipitate of unknown composition. The exact distribution of the boron between the two flask does not appear to be reproducible.

D. Mechanism of the Reaction

The reduction of carbon dioxide to formate with the simultaneous production of diborane probably occurs by the process represented by equation (1).

$$(1) \quad LiBH_4 + CO_2 \longrightarrow LiOOCH + \tfrac{1}{2}B_2H_6$$

However, during the reaction, a precipitate forms which, when isolated in an inert atmosphere, was found to contain 0.78 moles of boron per mole of formate, and upon treatment with water to give off one mole of hydrogen per mole of formate. The anomolous composition of this precipitate and the variable ratio of diborane production to formate production make it evident that complex secondary processes must also take place.

The production of methanol probably occurs through the competitive process represented by equation (2). It is not formed by the further action

$$(2) \quad 3LiBH_4 + CO_2 \longrightarrow LiB(OCH_3)_4 + 2LiBO_2$$

of lithium borohydride upon formate, since a suspension of lithium formate was not reduced by lithium borohydride, alone or in the presence of methanol. Although sodium trimethoxyborohydride will reduce carbon dioxide to formic acid in 60% yield[1], the corresponding lithium compound cannot be the

(1) Irving Sheft, M. S. Dissertation, the University of Chicago, March, 1944

intermediate here, since a solution of lithium borohydride containing two moles of methanol per mole of borohydride absorbed carbon dioxide very poorly and converted it to formate in very poor yield. However, a similar solution containing one mole of methanol per mole of borohydride reduced carbon dioxide to formate as efficiently as a solution containing no methanol. Table 1 shows the results of these experiments.

Table 1

Conditions	mmoles CO_2 charged	mmoles CO_2 reacted	mmoles $LiBH_4$	mmoles HCOOH (% yield)	mmoles B as B_2H_6	HCOOH in Rx ppt.	mmoles B in Rx ppt.	mmoles H_2 from Rx. ppt.
Preparative	5	2.94	4.50	2.19 (75%)	1.62	----	----	-
5 mmoles CH_3OH added to $LiBH_4$ solution	5	4.03	4.50	2.85 (71%)	2.24	----	----	-
10 mmoles CH_3OH added to $LiBH_4$ solution	5	2.20	4.50	0.91 (41%)	3.46	----	----	-
Rx ppt. filtered off	5	3.84	4.50	----	1.59	3.04 (79%)	2.24	3

III. Experimental

A. Tracer Experiments

1. Standardized $LiBH_4$ Solution. -- After dissolving lithium borohydride[2] in ethyl ether, the solution was decanted from the considerable

(2) Lithium borohydride must be handled in a dry box, preferably in an inert atmosphere, as some samples of the solid are spontaneously inflammable in moist air.

solid residue, and stored in a closed system. It was assayed by evaporating a sample to dryness under 15 mm. pressure at 100°C., and measuring the evolved hydrogen from dilute acid decomposition of the residue.

2. Sodium Formate-C^{14}. -- In a typical run, carbon dioxide obtained from 10 m. moles of barium carbonate (containing 51 microcuries of activity)[3]

(3) Radioactivities were determined by ion current measurements of CO_2 or volatile organic vapors using a dynamic condenser electrometer.

was dried by passage through a trap at -80°C. and a second trap filled with Drierite, then swept by nitrogen into 27 ml. of 0.37 M lithium borohydride-ether solution (10 m. moles) maintained at 0°C. Passage of the exit gases through saturated barium hydroxide led to the recovery of 0.2154 g. (1.09 m. moles) of isotopic barium carbonate containing 5.6 microcuries of activity. During the reaction, volatilized ether was returned to the solution by a cold finger filled with dry ice (see Figure 1). A heavy powdery precipitate formed in the reaction solution. The reaction mixture was hydrolyzed with 6 ml. of water, and the ether was removed by a stream of nitrogen. The collected ether contained 2-3% of the initial radioactivity. The aqueous

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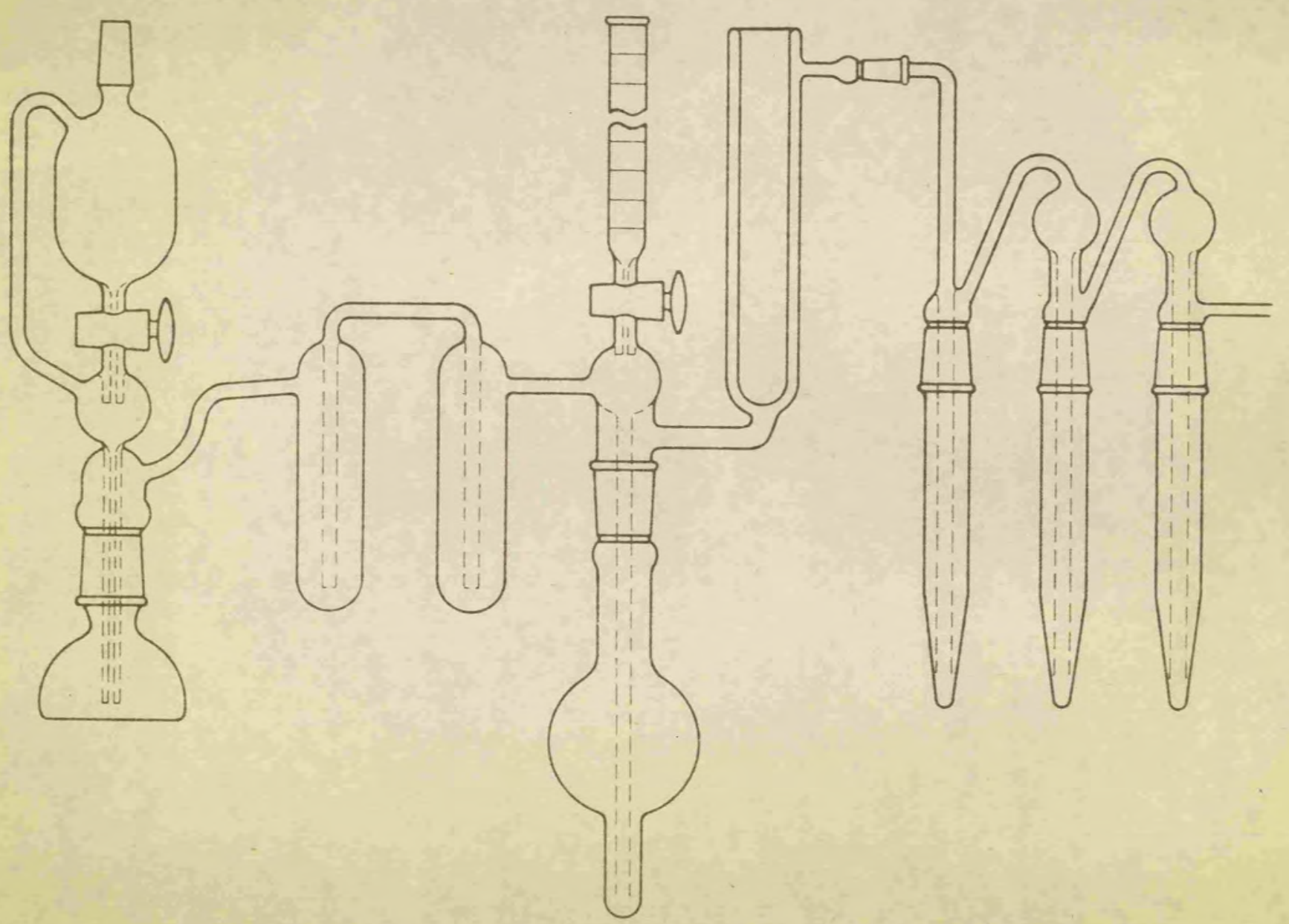

FIG. 1
SODIUM FORMATE APPARATUS-LOW LEVEL

solution was acidified with 1.5 ml. of 85% phosphoric acid. High vacuum distillation gave a product containing, by titration with standard NaOH, 6.3 m. moles (71%) of formic acid; the phosphomolybdate test revealed the presence of a trace of phosphate, and turmeric proved the absence of borate. The radiochemical yield was determined by adding 0.50 g. of inactive sodium formate to an aliquot of the neutralized distillate, and preparing the S-benzylthiuronium salt. Assay of this derivative indicated a radiochemical yield for sodium formate-C^{14} of 6.1 m. moles, (69% of CO_2 reacted). The remaining formate solution was distilled to dryness under high vacuum at room temperature.

During exploratory non-radioactive experiments, the aqueous solution obtained after hydrolysis with water was subjected to qualitative tests: Formic acid was identified as the S-benzylthiuronium salt, and by the mercuric chloride reaction; methanol was detected by the Eegrine test[4]; formalde-

(4) E. Eegrine, Microchem. Acta. 2, 329 (1937).

hyde was shown absent, except in one case, by the Eegrine test and by the dimedon test. The formate content was also determined by boiling the aqueous solution to remove volatile organic substances, and oxidizing with alkaline permanganate[5].

(5) Newer Methods of Volumetric Analysis, 2nd Edit., W. Bottger, Editor, Van Nostrand Co., New York (1938), p. 58..

3. Ethyl Formate-C^{14}. -- A 4.7 m. mole portion of the dry sodium formate-C^{14} containing 24 microcuries of carbon-14 was mixed with 20 m. moles of inactive sodium formate, and refluxed for 10 minutes at 170° with 10 ml.

of vacuum-distilled diethyl sulfate. The ethyl formate was distilled under high vacuum, and after redistillation at 10 mm. pressure weighed 1.253 g. (69% yield) had a vapor pressure of $0^{o}C$. of 79 mm. and had a specific activity of 0.98 microcuries per mole. Exploratory runs carried out upon this reaction gave yields of 96-98% of ethyl formate with a similar vapor pressure, and a refractive index at 25° of 1.3562. It was found that if the reaction temperature was allowed to rise above 185°, the product was heavily contaminated with a more volatile impurity.

4. Methanol-C^{14}. -- To the distillate from the neutral formate solution, 3.00 ml. (74.2 m. moles) of inactive methanol was added, and the solution was very slowly distilled through a Widmer column (an exploratory dead run under identical conditions gave pure methanol). Two small samples of methanol were withdrawn from the column. Radiochemical assay of these samples proved the presence of 1.1 m. moles of methanol-C^{14} in the distillate (12% of CO_2 reacted).

5. Diborane. -- The alkaline hydrolysis solution from the reaction of 5.0 m. moles of inactive carbon dioxide with 4.9 m. moles of lithium borohydride was evaporated carefully to dryness (overheating at this point caused extensive conversion to oxalate), and the residue was dissolved in water. The solution was made strongly acid, boiled, and then titrated in the presence of glycerine for boric acid. A total of 3.3 m. moles of boric acid was found. The formate produced in this reaction was 2.2 m. moles as determined by permanganate titration. The solution in the carbon dioxide absorption traps at the end of the reaction train (see Figure 1) was similarly found to contain 1.6 mmoles of boric acid. The amount of boric

acid in the bubblers was always less than the amount of formate produced in the reaction, but there was no simple relationship. From a Dry Ice-cooled trap containing anhydrous ethereal trimethylamine inserted in the system before the barium hydroxide bubblers, a solid compound could be recovered which yielded a white crystalline sublimate melting at 92-95°C. (Lit.[6] for trimethylamine borine: 94-95°).

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(6) Burg and Schlesinger, J. Am. Chem. Soc. 59, 780 (1937).

B. Apparatus and Procedure for High-level Production of Sodium Formate-C^{14}

The apparatus is shown in Figure 2 (not to scale).

A magnetic stirring-bar was placed in the lower vessel of G and the required amount of $BaCO_3$ was weighed in. The solid was covered with water, a drop of octyl alcohol was added to prevent foaming during the decomposition, and the vessel was placed in position on the generator. The upper vessel of G was filled with 30% HClO and capped. A Dry-Ice filled Dewar was placed around H, and two $Ba(OH)_2$ bubblers filled with 100 ml. of half-saturated $Ba(OH)_2$ each were connected in series to the external outlet of P. Reservoir G was filled with nitrogen from A to provide pressure to actuate the system of burettes J_1K_1 . . . .J_5K_5, the stopcocks on G were adjusted so that both chambers of G would be washed with gas, and the entire system from G through H, I, L, internal condenser O_1, P, and the $Ba(OH)_2$ bubblers was rinsed with nitrogen for thirty minutes.

The gas flow was reduced to about 10 cc./min., $LiBH_4$-ether reagent was added from burette J_1K_1, O_1 was filled with Dry Ice, and the stopcock at

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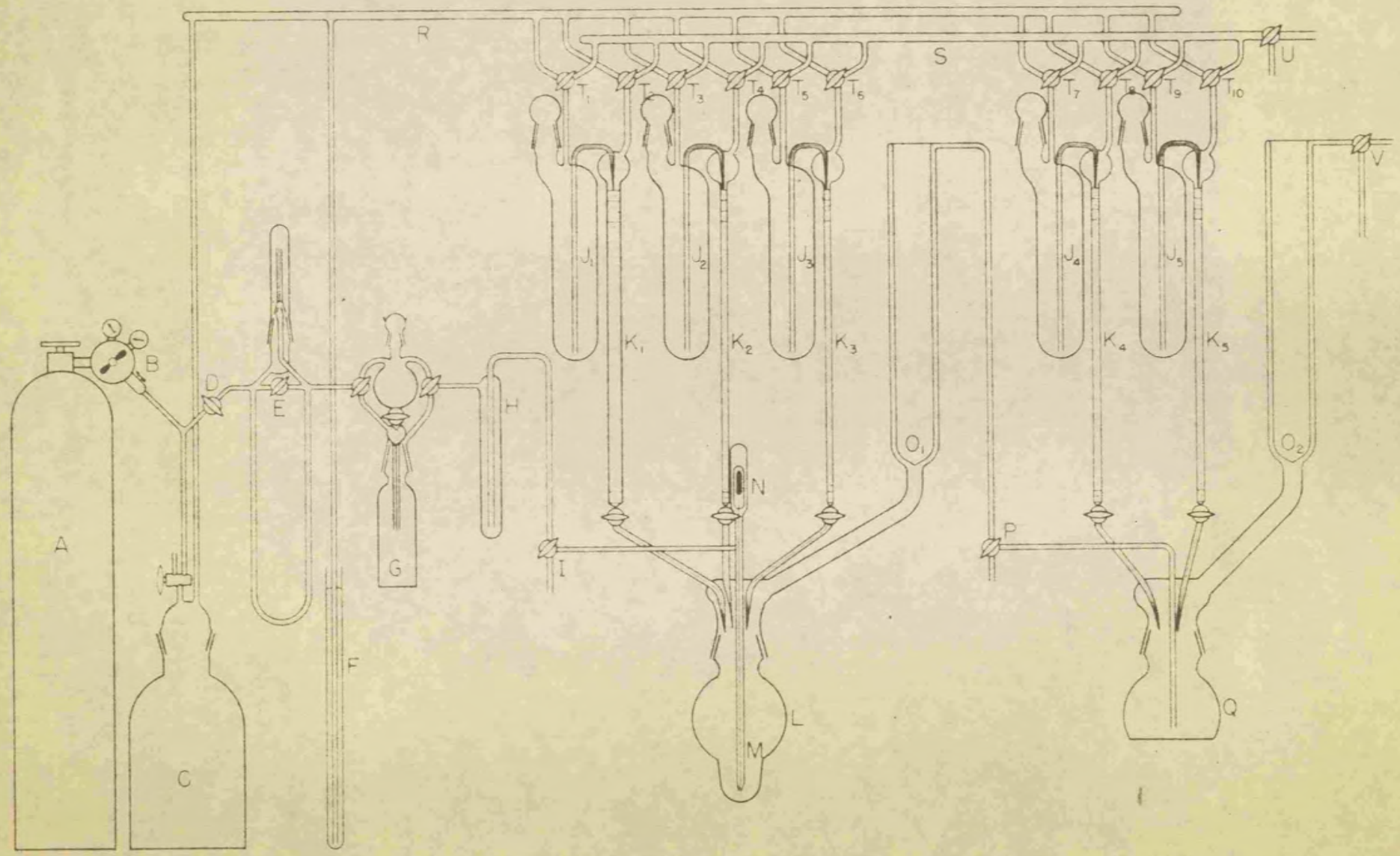

FIG. 2

Key to Figure 2

A. Nitrogen tank.

B. Pressure-reducing valve.

C. Pressure reservoir for actuating burettes.

D. Stopcock with notches filed in the core for fine adjustment of gas flow through the system.

E. Flowmeter.

F. Mercury-filled pressure release for burette system.

G. CO_2 generator.

H. Trap for water vapor.

I. Three-way stopcock.

J.K. . . . J_1K_1. Pressure-actuated burettes for adding reagents to the reaction system without exposing the mixtures to the air.

L. Reaction vessel.

M. Tip of gas-introduction line.

N. Magnetically operated tungsten wire plunger for clearing M of precipitated solids.

O_1, O_2. Internal condensers.

P. Three way stopcock.

Q. Reaction vessel.

R. Pressure manifold for burettes.

S. Outlet manifold for burettes.

T_1. . . . T_{10}. Stopcocks for controlling filling and emptying of the burettes.

U. Three way stopcock connecting outlet manifold to the air or to vacuum.

V. Three-way stopcock connecting the entire reaction system to the air or to high vacuum.

the bottom of the upper chamber of G was adjusted to give two drops of $HClO_4$ per minute to the lower chamber of G. The gas flow through G was adjusted to pass through the lower chamber only, and vessel L was immersed in an ice-water bath. The CO_2 generation and subsequent sweeping required about an hour and a half for a 10 m. mole run. After about the first half hour CO_2 began to show up in the first $Ba(OH)_2$ bubbler as precipitated $BaCO_3$, but none was found in the second bubbler until after the addition of a few ml. of water from burette J_2K_2 to decompose the reaction mixture in L. From time to time during the reduction and decomposition, it was necessary to clear tip M of precipitated material by agitating plunger N with a small magnet. When the violent reaction resulting from addition of water had subsided, the Dry-Ice remaining in O_1 was removed by a stream of air, the $Ba(OH)_2$ bubblers were disconnected from P and replaced by a hose leading to the main vent of the California hood in which the apparatus was built, and the ether was evaporated from the mixture by increasing the gas flow through the system to several hundred cc./min.

When the ether had evaporated, concentrated H_3PO_4 was added from burette J_3K_3 causing a further violent evolution of gas. When this had subsided, stopcock I was closed to vessel L, L and Q were connected through P, L was frozen down in liquid nitrogen, and stopcock V was opened to the high vacuum system, Q was immersed in liquid nitrogen, and when a good vacuum was obtained, L was allowed to warm so that distillation of the mixture of water, methanol, and formic acid to Q occurred. In the final stages of the distillation, L was warmed very strongly with a smoky flame to drive over the last traces of acid.

When the distillation was complete, Q was allowed to warm and the system was opened to the air. Q was momentarily removed and a drop of phenolphthalein indicator was added. The formic acid was then titrated with 5 N NaOH from burette J_4K_4. The slightly basic titration mixture was set aside for combination with the products from other runs.

The results obtained with this apparatus are summarized in Table II. A total of 11.8962 g. of isotopic barium carbonate, containing an estimated 203 millicuries of C^{14}, was processed as above in five runs. From these runs, the recovered barium carbonate weighed 1.9469 g. (9.84 m. moles, 16.3%), and contained an estimated 32 millicuries of C^{14}. By titration, the total amount of formic acid produced was 33.4 m. moles (67% based on the reacted carbon dioxide). The neutralized formate solutions (containing a slight excess of alkali) were combined and vacuum distilled almost to dryness. The residue was taken up in distilled water, centrifuged, and made up to 100.0 ml. From this solution, two 100 λ samples were taken, and each pipetted into a solution of 2.000 g. (29.4 m. moles) of sodium formate in 10 ml. of water. The S-benzylthiuronium salts were then prepared and recrystallized from ethanol. Duplicate assay of each sample of the salts showed an average specific activity of 0.0206 microcuries per mg. This corresponds to a total yield of 129 $\pm$ 2 millicuries of sodium formate (75% based on reacted carbon dioxide activity). Crystallization of the derivatives was so carried out as to produce a considerable fractionation should more than one acidic species be present; however, assay of the crude derivatives led to the same result, within experimental error, as assay of

Table II

Run	$BaCO_3$ Decomposed (mmoles)	CO_2 Reduced to Acid[a] mmoles	per cent	CO_2 Recovered[b] mmoles	per cent	CO_2 Remainder[f] mmoles	per cent
1	9.42[c,d]	----	----	----	----	----	----
2	9.51[d]	4.34	45.7	3.79	39.9	1.36	14.4
3	10.00[d]	5.47	54.7	3.64	36.4	0.89	8.9
4	" [d]	5.94	59.4	3.06	30.6	1.00	10.0
5	" [d]	5.72	57.2	1.79	17.9	2.49	24.9
6	10.87	4.18	38.4	1.51	13.9	5.18	52.3[e]
7	10.00	5.84	58.4	2.87	28.7	1.29	12.9
8	12.81	7.96	62.2	1.33	10.4	3.52	27.4
9	15.82	9.55	60.3	2.36	14.9	3.91	24.8
10	10.00	5.72	57.2	1.77	17.7	2.51	25.1

[a]Determined by titration with standard NaOH solution.

[b]Determined by weighing the $BaCO_3$ precipitated in the after bubblers.

[c]Bubble tip M (Figure 1) plugged during this run. As a result of this, the plunger N was added to the apparatus to allow clearing of the plugged tip without opening the apparatus.

[d]These runs were testing experiments for the apparatus, and were carried out with inactive $BaCO_3$.

[e]The $BaCO_3$ used in this run foamed badly on contact with the $HClO_4$, and much CO_2 was lost when the apparatus was dismantled for cleaning.

[f]These figures include the carbon dioxide lost by accident, as well as that converted to recoverable by-products, e.g. methanol.

the recrystallized salt. If radioactive species other than formate were present in the solution, direct assay of the solution should give a higher value than assay through a formate derivative; both types of assay, however, gave the same value within experimental error.