[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

The Reduction of Carbon Dioxide to Formic Acid[1]

BY JOHN G. BURR, JR., WELDON G. BROWN AND HOWARD E. HELLER

Carbon dioxide has been reduced to formate in yields of 69–88% by the action of lithium borohydride in ether solution. The yield of formate has averaged 73% of the carbon dioxide absorbed by the hydride solution; and the absorption of carbon dioxide has averaged 81% of the carbon dioxide charged. The method is superior to other methods for the preparation of isotopic sodium formate[2] in that it does not require the use of elevated temperatures, or pressures, and can be carried out in very simple equipment.

Methanol-C^{14} to the extent of about 13% was identified among the reaction products of the tracer runs, but formaldehyde could not be detected. Elevation of the reaction temperature from 0 to 30° did not increase the yield, but reduced the absorption of carbon dioxide. At −80° the reaction did not take place. Diethyl carbitol as solvent increased the absorption of carbon dioxide but lowered the yield of formic acid. The reaction did not take place in tripropylamine solution.

During the present reaction, a variable amount of boron was converted to diborane which appeared in the barium hydroxide traps as borate. At the same time, a solid precipitated in the reaction vessel. When this precipitate was isolated in inert atmosphere, it was found to contain 0.73 mole of boron per mole of formate and to evolve hydrogen when moistened.

The methanol formed was not produced by the action of lithium borohydride upon formate, since lithium formate was not reduced by lithium borohydride, alone or in the presence of methanol.

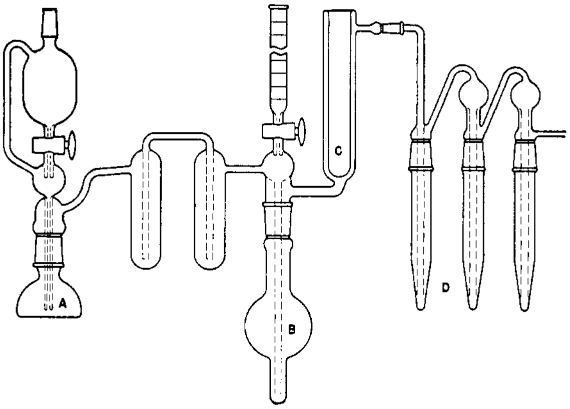

Fig. 1.—Sodium formate apparatus—low level

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

$$LiBH_4 + CO_2 \longrightarrow LiOOCH + {}^1/_2B_2H_6 \quad (1)$$

The production of methanol probably occurs through the competitive process represented by equation (2).

$$3LiBH_4 + 4CO_2 \longrightarrow LiB(OCH_3)_4 + 2LiBO_2 \quad (2)$$

This is analogous to the reduction of carbon dioxide to methanol by lithium aluminum hydride.[3] However, the ratio of diborane to formate was variable, and the solid formed in this reaction contained not only formate but also boron compounds and active hydrogen. Thus, it is evident that complex secondary processes must take place.

During exploratory and tracer runs, a simple apparatus shown in Fig. 1 proved quite adequate. However, to avoid open air transfers, the apparatus shown in Fig. 2 was used for the high-level production of sodium formate solution. In this apparatus, a total of 129 millicuries of aqueous sodium formate was produced in a series of five runs, with an over-all radiochemical yield of 75%.

Experimental

Lithium borohydride[4] was dissolved in ethyl ether. The solution was decanted from the considerable solid residue, and stored in a closed system. It was assayed by evaporating a sample under water-pump vacuum at 100°, and measuring the evolved hydrogen from dilute acid hydrolysis of the residue.

Sodium Formate-C^{14}.—In a typical run, carbon dioxide obtained from perchloric acid acidification of 1.974 g. (10 mmoles) of barium carbonate (containing 51 microcuries of activity,[5] and placed in vessel A, Fig. 1) was dried by passage through a trap at −80° and a second trap filled with Drierite, then swept by nitrogen during one and one-half hours into 27 ml. of 0.37 *M* lithium borohydride–ether solution (10 mmoles) maintained at 0°, and contained in vessel B, Fig. 1. Passage of the exit gases through saturated aqueous barium hydroxide (see vessels D, Fig. 1) led to the recovery of 0.2154 g. (1.09 mmoles) of isotopic barium carbonate containing 5.5 microcuries of activity. During the reaction volatilized ether was returned to the solution by a cold finger filled with Dry Ice (see C, Fig. 1). A heavy powdery precipitate formed in the reaction solution. The reaction solution was hydrolyzed with 6 ml. of water, and the ether was then removed in a strong stream of nitrogen. This ether contained 2–3% of the total radioactivity.

During exploratory runs, the aqueous solution obtained at this point was subjected to qualitative tests: Formic

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[1] This document is based upon work performed under Contract Number W-7405, eng. 26 for the Atomic Energy Project at the Oak Ridge National Laboratory. It was presented in part at the spring meeting of the American Chemical Society in San Francisco, California, March 28, 1949.

[2] Calvin, Heidelberger, Reid, Tolbert and Yankwich, "Isotopic Carbon," John Wiley and Sons, New York N. Y., 1949, p. 64.

[3] Nystrom, Yanko and Brown, THIS JOURNAL, **70**, 441 (1948).

[4] Lithium borohydride must be handled in a dry box, preferably in an inert atmosphere, as some samples of the solid are spontaneously flammable in moist air.

[5] Radioactivities were determined by ion current measurements of carbon dioxide using a dynamic condenser electrometer.

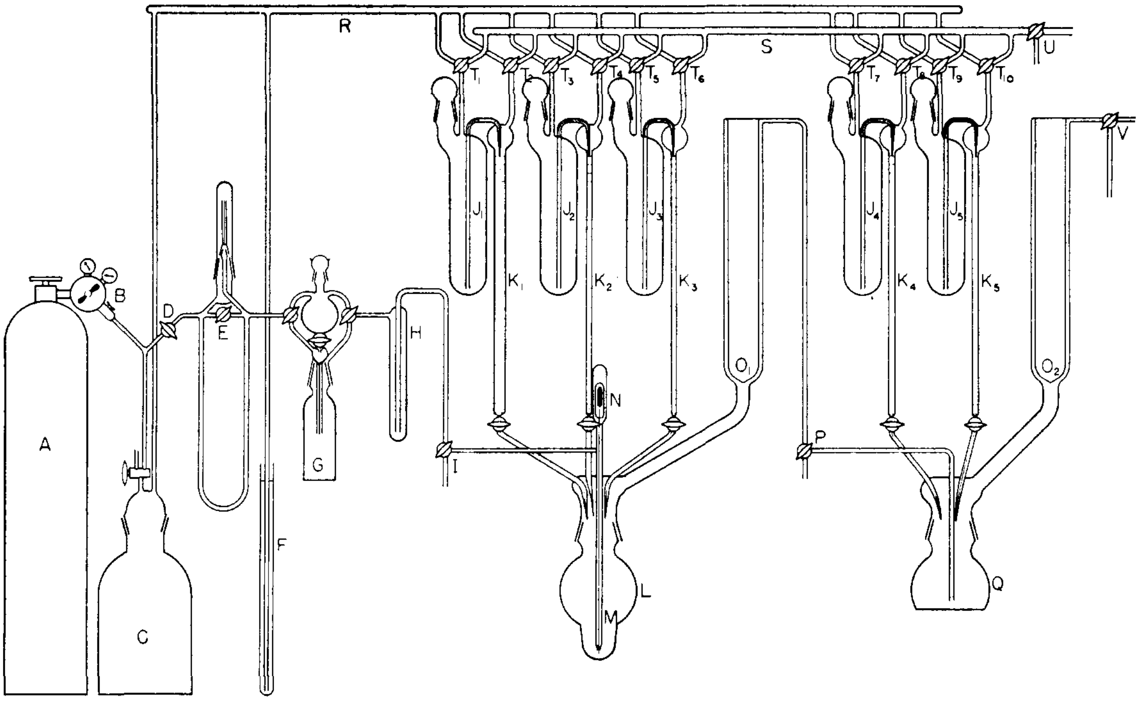

Fig. 2.—A, Nitrogen tank; B, pressure-reducing valve; C, pressure reservoir for actuating burets; D, stopcock with notches filed in the core for fine adjustment of gas flow through the system; E, flowmeter; F, mercury-filled pressure release for buret system; G, carbon dioxide generator; H, trap for water vapor; I, three-way stopcock; J, K. . . J_1K_1 pressure-actuated burets for adding reagents to reaction system without exposing the mixtures to the air; L, reaction vessel holding ethereal lithium borohydride solution; 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, vessel for titration of formic acid and for reaction of sodium formate with diethyl sulfate; R, pressure manifold for burets; S, outlet manifold for burets; T_1. . . . . T_{10}, stopcocks for controlling filling and emptying of the burets; 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.

acid was identified as the S-benzylthiuronium salt, and by the mercuric chloride reaction. The formate content was also determined by boiling the aqueous solution to remove volatile organic substances, and oxidizing the residual material with alkaline permanganate.[6] Methanol was detected by the Eegrine test.[7] Formaldehyde was shown absent by the Eegrine test and by the dimedon test.

In the experiments with isotopic carbon dioxide, the aqueous solution obtained was acidified with 1.5 ml. of 85% phosphoric acid. High vacuum distillation gave a product containing, by titration with NaOH, 6.4 mmoles (71%) of formic acid; the phosphomolybdate test revealed the presence of a trace of phosphate, and turmeric indicated the absence of borate. The radiochemical yield was determined by mixing 0.50 g. of inactive sodium formate with one-tenth of the neutralized distillate, and preparing the S-benzylthiuronium salt. Combustion of this derivative and ion chamber assay of the carbon dioxide produced gave a radiochemical yield for sodium formate-C^{14} of 6.1 mmoles (69% of carbon dioxide reacted). The remaining formate solution was distilled to dryness in high vacuum at room temperature.

To the distillate, 3.00 ml. (74.2 mmoles) of inactive methanol was added, and the solution was very slowly distilled through a Widmer column (an exploratory dead run under identical conditions gave methanol with a refractive index at 28° of 1.3247, lit.[8] at 25° is 1.3276). Two small samples of methanol were withdrawn from the column. Radiochemical assay[9] of these samples proved the presence of 1.1 mmoles of methanol-C^{14} in the distillate (13% of carbon dioxide reacted).

Ethyl Formate-C^{14}.—A 4.7-mmole portion of the dry sodium formate-C^{14} containing 24 microcuries of carbon-14 was mixed with 20 mmoles of inactive sodium formate, and heated for ten minutes at 170° with 10 ml. of vacuum-distilled ethyl sulfate. The ethyl formate was distilled under high vacuum, and after redistillation at 10 mm. pressure weighed 1.253 g. (69% based on sodium formate), had a vapor-pressure at 0° of 79 mm. and had a specific activity[9] of 0.98 microcuries per mmole. Exploratory runs carried out with inactive material gave yields of 96–98% of ethyl formate with a similar vapor pressure, and a refractive index at 25° of 1.3562 (lit.[10] 1.3575). It was found that if the reaction temperature was allowed to rise above 185°, the product was heavily contaminated with a more volatile impurity.

Formation of Diborane.—The alkaline hydrolysis solution from the reaction of 5.0 mmoles of inactive carbon dioxide with 4.9 mmoles 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

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[6] "Newer Methods of Volumetric Analysis," 2nd edit., W. Bottger, Editor, Van Nostrand Co., New York, N. Y., 1938, p. 58.

[7] E. Eegrine, *Microchem. Acta*, **2**, 329 (1937).

[8] Walden, *Z. physik. Chem.*, **59**, 935 (1906).

[9] These compounds were vaporized into the ion chamber and assayed directly.

[10] Munch, THIS JOURNAL, **48**, 997 (1926).

acid, boiled, and then titrated in the presence of glycerol for boric acid. A total of 3.3 mmoles of boric acid was found. The formate produced in this reaction was 2.2 mmoles as determined by permanganate titration. The solution in the carbon dioxide absorption traps at the end of the reaction train (see Fig. 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 gave a white crystalline sublimate melting at 92–95° (lit.[11] for trimethylamine borine, 94–95°).

High Level Preparation of Aqueous Sodium Formate.—In the apparatus shown in Fig. 2, a total of 11.896 g. of isotopic barium carbonate, containing an estimated[12] 203 millicuries of C^{14}, was processed as above, in five runs. From these runs, the recovered barium carbonate weighed 1.947 g. (9.84 mmoles, 16.3%), and contained an estimated 32 millicuries of C^{14}. By titration, the total amount of formic acid produced was 33.35 mmoles (66% based on the absorbed 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 mmoles) 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 salt showed an average specific activity of 0.0206 microcuries per mg. This corresponds to a total yield of 129 ± 2 millicuries of sodium formate. 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 derivative led to the same result, within experimental error, as assay of 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 assays, however, gave the same value within experimental error.

Summary

Carbon dioxide has been reduced to formic acid in 69–88% yield by passage of the gas into an ether solution of lithium borohydride at 0°. Carbon-14 dioxide yields formic acid-C^{14} on similar treatment. By the use of this method, 129 millicuries of formic acid-C^{14} as aqueous sodium formate-C^{14} has been prepared.

Ethyl formate-C^{14} has been prepared at the microcurie level by the reaction of sodium formate-C^{14} with diethyl sulfate at 170°.

During the reduction diborane is liberated, and a small amount of methanol-C^{14} is produced. No formaldehyde was detected as a product of the reaction.

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[11] Burg and Schlesinger, THIS JOURNAL, **59**, 780 (1937).

[12] The barium carbonate was obtained from the Operations Division of the Oak Ridge National Laboratory, and was assayed by an indirect solid counting method developed and used by that group.

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Application of Polarization Theory to Sorption of Water Vapor by High Polymers[2,3]

BY SAM R. HOOVER AND EDWARD F. MELLON

Introduction

In our studies of water absorption by proteins we found that the sorption of water at high relative humidity depends on the prior sorption on active sorptive groups such as the free amino and peptide groups.[4,5]

This dependence was not only qualitatively true; attempts to fit the data to various possible equations showed that many of our data can be described by the simple relationship $\log a = kp/p_0 + b$ when a = amount absorbed, p/p_0 = relative vapor pressure, and k and b are empirical constants.[5] This equation fitted the data from 30 to 90% relative humidity. Expressed in words, it says that the amount absorbed in this region as the relative humidity increases is proportional to the amount already adsorbed. Moreover, the slope constant k was the same for three proteins and two synthetic polyglycines. As stated previously,[5] "This fact indicates that all the water absorbed in this humidity region is held by hydrogen bonds of about the same strength." These results seemed to be best interpreted as sorption of water in water, and further analysis was made in an attempt to put this idea on a more quantitative basis.

Current treatments of sorption phenomena have been based primarily on the Brunauer–Emmett–Teller (BET) extension of the Langmuir isotherm to multimolecular adsorption,[6,7,8,9] and the Flory–Huggins solution theory.[10,11] The BET theory was developed originally to describe the adsorption at low temperature and pressure of gases on surfaces with succeeding layers held by van der Waals forces. The original two-constant equation for an unlimited number of layers and the modified three-constant equation, wherein n, the number of layers, is introduced, give valuable information in the lower portion of

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] Paper V in the series "Water Absorption of Proteins."

[3] Presented at the American Chemical Society meeting in Atlantic City, N. J., September, 1949.

[4] Mellon, Korn and Hoover, THIS JOURNAL, **69**, 827 (1947).

[5] Mellon, Korn and Hoover, *ibid.*, **70**, 3040 (1948).

[6] Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938).

[7] Bull, *ibid.*, **66**, 1499 (1944).

[8] Dole and McLaren, *ibid.*, **69**, 651 (1947).

[9] Dole, *J. Chem. Phys.*, **16**, 25 (1948).

[10] Simha and Rowen, THIS JOURNAL, **70**, 1663 (1948); Rowen and Simha, *J. Phys. Colloid Chem.*, **53**, 921 (1949).

[11] Cutler and McLaren, *J. Polymer Sci.*, **3**, 792 (1948).