## THE REDUCTION OF CARBON DIOXIDE TO FORMALDEHYDE. 687

## LXIV.—The Reduction of Carbon Dioxide to Formaldehyde in Aqueous Solution.

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THE reduction of carbon dioxide in aqueous solution has always formed an attractive subject for investigation, not only from a purely chemical standpoint, but also from its important bearing on the problem of assimilation in plants. Interest in this question has recently received a fresh stimulus owing to the extremely suggestive summary

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of the subject which was given in the President's address at the last annual meeting of the Society. The practical demonstration of this reduction, by purely chemical methods, has been the object of a very large number of interesting researches, and, since the time when Baeyer first suggested his well-known hypothesis of carbon dioxide assimilation, one of the principal aims of these investigations has been the recognition of formaldehyde as a reduction product. If one excepts the somewhat inconclusive and yet unconfirmed experiment of Bach, in which palladium-hydrogen was employed as the reducer, to which attention will presently be drawn, it would appear that in no single case has formaldehyde been detected. This statement refers, of course, to the reduction in aqueous solution ; that formaldehyde can indirectly result as a reduction product of gaseous carbon dioxide in presence of moisture, under the influence of the silent discharge, appears to have been established by Löb (Zeitsch. Elektrochem., 1905, 11, 745, and 1906, 12, 282).

Maly, in 1865 (Annalen, 135, 119), acted on a concentrated solution of ammonium carbonate with dilute (liquid) sodium amalgam and showed that after acidification and distillation of the product a notable quantity of formic acid was obtained in the distillate.

Lieben (Monatsch., 1895, 16, 211, and 1897, 18, 582) extended this observation and made an exhaustive investigation of the reduction of carbonates, or carbon dioxide in presence of various metallic salts, by different metals. He found that when a slow stream of carbon dioxide was passed for some weeks through water to which, from time to time, small quantities of sodium amalgam were added, considerable quantities of formate could be obtained, and similar results were given by amalgams of barium or potassium. Aluminium amalgam alone did not reduce a solution of carbon dioxide, but in presence of sodium sulphate, sodium phosphate, or some other salts, good yields of formate resulted. When magnesium or platinised magnesium were used, alone or in presence of salts, under conditions which in the case of the other metals were found to be most favourable, the results were entirely negative, or at most traces only of formate In his second paper, the author draws particular were obtained. attention to this peculiarity of magnesium, and ascribes the results to the difference in the amount of energy set free in the liberation of hydrogen by the metals. Ballo (Ber., 1884, 17, 6) also prepared formates by reduction of bicarbonates with sodium or potassium, but with platinised magnesium only negative results were obtained.

The reduction of carbon dioxide in aqueous solution by the electrolytic method was first effected by Royer (*Compt. rend.*, 1870, 70, 731), the solution being subjected to what the author termed the

"intra-pilaire" current in a Grove or Bunsen cell. In this case again formic acid was the only product of reduction.

Coehn and Jahn (Ber., 1904, 37, 2836) made an extended study of the electrolytic reduction, and investigated the behaviour of different salts and the influence due to the nature of the cathode metal. The best results were obtained when a cold saturated solution of potassium sulphate was electrolysed, using an amalgamated zinc cathode, and a continuous current of carbon dioxide was conducted through the In this way the alkali formed at the cathode was at once solution. converted into bicarbonate. In order to examine the nature of the reduction product the anodic and cathodic solutions, which during electrolysis were separated by a porous cell, were mixed together and the acidity of the mixture determined after removal of the carbon dioxide in a current of air. An aliquot part of the solution was also titrated with permanganate, and the results, calculated as formic acid, usually agreed with the values calculated from the acidity. But in some experiments the oxidation values were higher than the acidity values, a circumstance which appeared to indicate a reduction product other than formic acid. No formaldehyde, however, could be detected.

Reduction was not obtained when normal carbonates were similarly electrolysed, and carbon dioxide, in presence of strong acids, also gave negative results, although an aqueous solution of carbon dioxide alone gave rise to formic acid, as in Royer's experiment. The authors therefore concluded that neither the  $CO_3$  ion nor the non-dissociated carbonic acid is reducible, and that formic acid results from the reduction of the  $HCO_3$  ion.

Ehrenfeld, however (*Ber.*, 1905, 38, 4138), shows that formate is also produced by the electrolytic reduction of a strongly ammoniacal solution of ammonium carbonate and considers that in this case the ion  $\mathrm{NH}_4\mathrm{CO}_3$  is reduced.

In all the above-named investigations the authors come to the conclusion that formic acid is the sole product of the reduction of carbon dioxide; in no case could formaldehyde be discovered.

The photo-reduction of carbon dioxide in presence of uranyl acetate was said by Bach (*Compt. rend.*, 1893, 116, 1145) to give rise to formaldehyde, and Usher and Priestley (*Proc. Roy. Soc.*, 1906, 77, 370) state that they have confirmed this result. The method of proof, however, is not given. Moreover, the last named authors have since shown (*loc. cit.*, 78, 322) that no formaldehyde can be detected if uranyl sulphate is substituted for the acetate, and, as regards the precipitation of uranium hydroxides, Euler has shown that a similar result is obtained when nitrogen is substituted for the carbon dioxide

(Ber., 1904, 37, 3415). The supposed formation of formaldehyde when dimethylaniline was used as catalyser, in place of the uranyl salt, has also been disproved by Euler (loc. cit., 3416); compare also Pilhashy (J. Amer. Chem. Soc., 1900, 22, 132). Bach has also stated (Compt. rend., 1898, 126, 479) that formaldehyde is produced when a solution of carbon dioxide is reduced by hydrogen-palladium; the nature of his experiment and the method of proof will be gathered from the following statement. Ten grams of spongy palladium and 2.85 grams of palladium foil were charged with hydrogen and introduced into water which had been boiled and cooled in a stream of carbon dioxide. Carbon dioxide was passed into the mixture for three days and the solution was filtered after thirty days. The addition of aqueous aniline gave "un faible dépôt blanc," which, from its appearance when crystallised and its melting point, was considered to be methylene-The melting point of the product is not stated. aniline. Another portion of the liquid when evaporated to dryness with excess of ammonia left a residue which, when dissolved in a little water, gave a yellow precipitate with bromine water.

## EXPERIMENTAL.

Since it has been established by the various authors referred to in the foregoing summary that carbon dioxide is readily reduced, in various ways, to formic acid, it appeared interesting to attempt the further reduction of formic acid to formaldehyde. If this attempt were successful the practical demonstration of the reduction of carbon dioxide to formaldehyde would be complete. The systematic and direct reduction of acids to corresponding aldehydes has hitherto succeeded only in the case of hydroxy-acids which can yield lactones, the lactone, in fact, being the product which undergoes reduction (Fischer, *Ber.*, 1889, 22, 2204, and 1890, 23, 930). It was altogether improbable therefore that the desired object, in the present case, would be attained by the use of sodium. But, in the course of a series of experiments with other reducing agents, it was found that metallic magnesium readily reduces formic acid to formaldehyde.

When a rod of magnesium was introduced into a solution of pure formic acid (about 10 per cent.) a vigorous reaction ensued and the solution, after some minutes, showed strongly-marked reactions of formaldehyde with the colour tests mentioned below. After the action had proceeded for about half an hour the solution, when neutralised with sodium carbonate and boiled, gave off a strong odour of the aldehyde. In order to complete the identification of the product, a few drops of phenylhydrazine acetate were added, and the resulting nearly white precipitate was washed with water, a little alcohol, and ether, and was then recrystallised from a mixture of absolute alcohol and toluene. The product so obtained crystallised in lustrous, white plates which melted at 184—185° (compare Wallace Walker, Trans., 1896, **69**, 1278). With hydrogen sulphide the solution gave, on standing, a bulky, white, crystalline precipitate; aqueous aniline gave a white precipitate, and ammoniacal silver nitrate was reduced in the cold.

The yield of formaldehyde, estimated by Romijn's iodine method, amounted to about 1 to 2 per cent. of the formic acid used; the greater part of the acid is of course rendered inert, as regards reduction, by conversion into magnesium formate. By suitable treatment with acids and regulation of the temperature and concentration, it would doubtless be possible to obtain very much larger yields. Ammonium formate, in solution, reacts violently with metallic magnesium; a large quantity of ammonia is evolved, and the solution after a few minutes gives, strongly, the reactions of formaldehyde. If the resulting solution is evaporated to dryness on a water-bath and the residue extracted with chloroform, notable quantities of hexamethylenetetramine are obtained and can be identified in the manner indicated below.

The results obtained, therefore, show that carbon dioxide can be reduced to formaldehyde with formic acid as the intermediate stage. But it still remained a matter of interest to ascertain whether the complete reduction could be demonstrated in one operation. This again is found to be possible with the aid of metallic magnesium, if certain conditions are employed. In this case there is no evidence that the formic acid stage is passed through, and, judging from the results of Lieben and of Ballo, the occurrence of this stage would appear to be improbable.

When a stream of carbon dioxide is passed to saturation for about eighteen to twenty-four hours through pure water in contact with several rods of amalgamated magnesium, the solution obtained gives slight but unmistakable indications of formaldehyde with the colour tests to be mentioned. It was afterwards found that if small quantities of ammonia, aniline, phenylhydrazine, or piperidine are first added to the water, the indications of formaldehyde are much more marked; aluminium hydroxide, ferric hydroxide, and calcium carbonate all show a similar influence, especially if the mixtures are warmed. Ammonia and phenylhydrazine appear to give the best results, and in presence of either of these reagents it is easy to demonstrate the production of formaldehyde even after a few minutes. An aqueous solution of phenylhydrazine, for example, when mixed with excess of magnesium powder and subjected to a rapid stream of carbon dioxide, allowing the temperature to rise to  $60-70^\circ$ , gives, after about ten minutes, an intense blue colour with test No. I (see p. 693). Aniline gives similar results; in this case and with phenylhydrazine the solutions begin to precipitate on standing for some time. The products, however, are very likely impure, since phenylhydrazine probably undergoes some reduction to aniline and ammonia, and methyleneaniline, as shown by Miller and Plöchl (*Ber.*, 1902, 25, 2020), is easily reducible to methylaniline.

When ammonia or ammonium carbonate is used in contact with amalgamated magnesium rods, or more rapidly with magnesium powder, the product gives, after acidification in the cold, only slight indications of formaldehyde, but if the mixture is heated to boiling after acidification, the reactions are strongly marked. The aldehvde is in fact "fixed," as fast as formed, as hexamethylenetetramine. If the ammoniacal solution is evaporated \* just to dryness, and the residue extracted with chloroform, a small quantity of crystalline residue is obtained, from the chloroform solution, which is easily recognised as hexamethylenetetramine by Legler's method (Ber., 1885, 18, 3350: compare also Horton, *ibid.*, 1888, 21, 1999). When exposed to the vapours of bromine it swells and turns dark brick-red; on exposure to air bromine is evolved, and a sulphur-yellow powder is left. These products are the tetra- and di-bromides respectively. The aqueous solution gives, with bromine water, a yellow precipitate. Silver nitrate gives a white precipitate which dissolves and is reduced to a mirror on heating, and iodine in aqueous-alcoholic solution gives a dark reddishbrown, crystalline precipitate.

It was noticed in some experiments that on heating the mixture obtained by the action of carbon dioxide on magnesium in presence of ammonium carbonate with caustic soda there appeared at some stage of the operation a distinct "fishy" odour of the methylamines. This result is to be expected since hexamethylenetetramine, as shown by Delépine (*Bull. Soc. Chim.*, 1895, [iii], 13, 135), can be reduced by zinc to trimethylamine. The formation of mono-, di-, and tri-methylamines from formaldehyde and ammonia, and from hexamethylenetetramine, has also been shown by other authors (compare Eschweiler, *Ber.*, 1905, 38, 880; Ischidzu and Inouye, *Jour. Pharm. Soc. Japan*, Jan. 1, 1906, &c.).

The latter observation appears to be of interest in connexion with the fact that trimethylamine is of frequent occurrence in certain plants and also as regards the close relationship of this substance to betaine.

The quantities of formaldehyde, or its derivatives, which are

\* Since a considerable loss of the product occurs when the solution is completely evaporated at 100°, it is best to finish the evaporation in a vacuum desiccator at the ordinary temperature.

obtained in the manner above indicated are of necessity only small. The actual mass of carbon dioxide available for reduction in solution is limited, of course, by the small solubility of the gas at the tempera-The best results are obtained when the gas is ture employed. "rushed" through the solution at a rapid rate, since, so far, no convenient apparatus has been available for working under increased Further, the magnesium rapidly loses its activity, probably pressure. owing to a superficial coating of basic carbonate, and attempts to remedy this by addition of mineral acids yield only negative results. When the magnesium is used in the form of powder it appears to be advantageous first to saturate the solution with magnesium bicarbonate; this moderates, to some extent, the over-rapid action of the metal and probably increases the potential concentration of the carbon dioxide (or HCO, ions) at the temperature employed (compare Rinne, Chem. Zeit., 1907, 31, 125).

In the course of the foregoing investigation a considerable number of the well-known tests for formaldehyde have been compared and studied. In the authors' opinion the following three are the most delicate and most satisfactory of the colour-reactions, and to these preference is given in the order named.

I. To the solution to be examined is added a few drops each of dilute solutions of phenylhydrazine hydrochloride, sodium nitroprusside, and caustic soda; the result is a bright but transient Prussian-blue colour (Rimini's test).

II. The solution is mixed with a few drops of an alcoholic solution of gallic acid, and the mixture is carefully poured on to pure concentrated sulphuric acid; a bright blue ring appears where the liquids meet.

III. An aqueous solution of resorcinol is substituted for the alcoholic gallic acid in II; the result is a red or reddish-violet ring (compare Mulliken, *Identification of Carbon Compounds*, p. 24).

The conditions of formation of formaldehyde from carbon dioxide and the behaviour of metallic magnesium towards other acids are being further studied. Acetic acid gives recognisable quantities of acetaldehyde when treated with magnesium, but negative results have so far been obtained with propionic and *n*-butyric acids.