Reduction of Carbon Dioxide with Amalgams

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E. Drechsel[3] reported in 1868 that carbon dioxide reacted at the temperature of boiling mercury with sodium metal dispersed on sand, or with potassium amalgam at this temperature, to form a product which hydrolyzed in water forming oxalic acid. Numerous subsequent publications[4-7] have confirmed the formation of oxalic acid in comparable experiments utilizing various strongly electropositive metals or their amalgams. The other products which have been reported are carbon monoxide,[5,6] carbonate,[5-7] and an unidentified product which decolorized potassium permanganate solution upon warming.[5] Clusius and Mollet[8] treated carbon dioxide with cesium at room temperature and identified glycolic acid as the final hydrolysis product.

Earlier work by Hackspill *et al.*[9] had shown that carbon monoxide reacted with cesium to form cesium carbonyl which was hydrolyzed to glyoxal. Clusius and Mollet suggested in explanation of their own results that cesium and carbon dioxide formed cesium carbonyl plus cesium oxide, and that the carbonyl was hydrolyzed to glyoxal which then underwent a Cannizzaro reaction forming glycolic acid. The cesium–carbon dioxide reaction was further investigated[10] and it was shown that cesium formate was formed, which on heating liberated cesium and formed cesium oxalate which is hydrolyzed to oxalic acid.

Carbides and free carbon are among the products produced from carbon dioxide and sodium at elevated temperatures.[11]

It is evident that several mechanisms and products may be involved in the reduction of dry carbon dioxide by metal and amalgams. The formation of carbon-to-carbon bonds is unique since other reduction methods such as electrolysis, hydrogenation, complex metal hydrides, alkali metals in ammonia, or the reaction of wet carbon dioxide with metals or amalgams result almost exclusively in one-carbon products.[12,13] A preliminary investigation in this laboratory showed that the products obtained varied with reaction conditions and that products other than those previously reported in the literature could be produced. We have, therefore, re-examined the reaction utilizing modern analytical procedures.

Experimental

Reagents.—Reagent grade hydroxides or carbonates were used for the electrolytic preparation of amalgams of sodium, potassium, rubidium, cesium, lithium, calcium, strontium, and barium. Magnesium amalgam was prepared from reagent grade turnings. The mercury was purified by acid washing, distillation at reduced pressure, and air oxidation followed by filtration through a gold seal filter. Tank gases were checked for purity by mass spectrographic analyses: carbon dioxide—purity better than 99%, major impurity is air with smaller amounts of hydrogen and carbon monoxide. Carbon monoxide—98.4% carbon monoxide, 1.0% helium, and 0.6% carbon dioxide. Nitrogen—99.1% nitrogen, 0.2% oxygen, 0.1% argon, 0.6% hydrogen. Helium—no impurity other than a maximum of 0.2% air.

Amalgam Preparation.—Magnesium amalgam was prepared by mixing the metals in an inert atmosphere, since it cannot be prepared by the electrolysis of an aqueous solution at a mercury cathode. The other amalgams were prepared by the electrolysis of a concd. aqueous solution or suspension of the corresponding hydroxide or carbonate. The electrolytic apparatus used was the "Dyna-Cath" sold by the E. H. Sargent Co. Approximately 70–80 ml. of mercury was used as a cathode, the platinum ring assembly as an anode; 2 to 10 amperes of current was passed through the cell for 0.5 to 2 hr. The apparatus provides for cooling the electrolyte. When a proper amount of metal had been deposited in the mercury, the liquid amalgam was drained from the bottom of the electrolytic vessel through a pin hole filter into a storage bottle. An atmosphere of helium was maintained over all amalgams and a dry box filled with helium was used for transfers and other handling. Amalgam concentrations were measured by determining the loss in weight when washed with dilute acid; dilutions were made by the addition of mercury.

Reaction Procedure.—The reductions were run in a 500-ml. three-necked flask fitted with a mechanical stirrer. The amalgam was introduced from a burette into the evacuated flask and brought to temperature. Carbon dioxide was then admitted from a gas buret manually operated to maintain the pressure at approximately 1 atm. At the conclusion of the run a sample of residual gas was removed with a syringe, the system was flushed with helium, and the reaction mixture was hydrolyzed by introducing 20 ml. of 3 N sulfuric acid. The gas evolved on hydrolysis was measured and a sample taken with a syringe. The supernatant solution was adjusted to pH 10 with 3 N sodium hydroxide and removed for analysis.

During the reduction reaction the amalgam becomes pasty. When the active metal is nearly exhausted the amalgam ceases to wet the glass flask and separates into a black powder and liquid mercury. The hydrolysis of the black powder is rapid in the case of the alkali metals and much slower with the alkaline earths. There is frequently a small amount of black residue from the hydrolysis, equiva-

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[10] R. Setton, *Bull. Soc. Chim. France*, 1400 (**1958**); see also L. Hackspill and R. Setton, *Compt. Rend.*, **246**, 2430 (1958).

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[12] J. Hollander and L. Spialter, *J. Chem. Educ.*, **35**, 446 (1958).

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lent to considerably less than 1% of the total carbon involved in the reaction. Alkaline hydrolysis is much slower and generally less complete.

Analytical Procedures.—An exploratory examination, using the silica gel column procedure of Bulen, Varner, and Burrell,[14] showed that the hydrolysates consisted of mixtures of carboxylic acids. The analytical procedure adopted was gas chromatography of the ethyl esters. Dry samples were prepared from the basic reduction product solution by freeze drying which left the product in the form of a powder. The dried alkaline sample was extracted with ether in a miniature column. The sample was moistened with 30% sulfuric acid and 25 ml. of dry ether was added to elute the organic acids from the column. The ether solution was then evaporated in a stream of nitrogen to a final volume of about 0.4 ml. in a 6.5-ml. serum tube. The serum tube was closed with a rubber serum cap and a Drierite-filled vent tube was attached to a syringe needle through the cap.

Some preliminary trials were made on the preparation and esterification reactions of diazomethane, -ethane, -propane, -butane, and -pentane. Diazoethane gave the best over-all results. This material was prepared by the method of McKay[15] from *N*-ethyl-*N*-nitroso-*N'*-nitroguanidine and potassium hydroxide in 2-(ethoxyethoxy)ethanol. A suspension of 2 g. of ethylnitrosonitroguanidine in carbitol was added slowly to alkaline carbitol and the product diazoethane was distilled into a serum tube containing the sample. The sample was cooled to about −70° in a Dry Ice–acetone bath during the ethylation. The conclusion of the reaction was determined by the accumulation of yellow color due to excess diazoethane. The ether solution of esters was warmed to 0° and within 30 min. injected into the gas chromatograph system.

A Podbielniak chromatograph (4975-3V) was modified so that the detector (Gow-Mac No. 9285) was maintained at 158° separately from the column compartment. Helium carrier gas flow was adjusted to 75 ml. per minute using a soap film meter. In general, two 40-μl. samples were used, one with a 20% Octoil S on C-22 firebrick column, 12-ft. long programmed from 30° to 70°, and the other with a 25% silicone rubber on "Washed Chromosorb" column, 6 ft. long, programmed from 30° to 158°. The silicone rubber packing used was supplied by F and M Scientific Corp., New Castle, Del. 2,2,4-Trimethylpentane was used as an internal standard. Peak areas were measured by planimeter and were related to volume of component by individual calibration curves. All data were converted to m*M* carbon dioxide equivalents for comparison. The peaks were identified by infrared analysis and confirmed by co-chromatography with knowns.

The following compounds are adequately resolved by each of these columns:

Octoil-S, 30° to 70°	Silicone Rubber, 30° to 158°
1. Diethyl ether	1. Diethyl ether
2. Ethyl formate	2. Ethyl acetate
3. Acetone	3. 2,2,4-Trimethylpentane
4. Ethanol	4. Ethyl glycolate
5. Ethyl acetate	5. Ethyl ethoxyacetate
6. 2,2,4-Trimethylpentane	6. Ethyl oxalate
	7. Ethyl malonate
	8. Ethyl tartronate
	9. Ethyl ethoxymalonate

Results and Discussion

Amalgams adjusted to 0.2 *M* concentration were used to reduce carbon dioxide by three procedures: (1) carbon dioxide was admitted at 25° until an excess was present; (2) carbon dioxide was admitted at 25° until roughly half the active metal in the amalgam was consumed; and, (3) carbon dioxide was admitted at 180° until an excess was present. Table I shows the yields, rounded to 1%, calculated on the amount of carbon dioxide consumed.

The principal products can be accounted for by the following reactions, written for M as a monovalent metal:

$$CO_2 + 2M \longrightarrow \underline{MCOOM} \quad (1)$$

$$MCOOM \longrightarrow \underline{CO} + M_2O \quad (2)$$

$$MCOOM + CO_2 \longrightarrow \underline{MOCOCOOM} \quad (3)$$

$$MOCOCOOM + 2M \longrightarrow MOCOCM(OM)_2 \quad (4)$$

$$MOCOCM(OM)_2 + CO_2 \longrightarrow MOCOC(OM)_2COOM \quad (5)$$

$$MOCOC(OM)_2COOM \longrightarrow MOCOCOCOOM + M_2O \quad (6)$$

$$MOCOCOCOOM + 2M \longrightarrow \underline{MOCOCMOMCOOM} \quad (7)$$

$$M_2O + CO_2 \longrightarrow \underline{M_2CO_3} \quad (8)$$

$$(COOH)_2 + M + HA \longrightarrow \underline{CH_2OH{\cdot}COOH} + MA \quad (9)$$

$$MOCOCOOM + 2Mg \longrightarrow \underline{MgO + MOCMgCOOM} \quad (10)$$

In this tabulation those intermediates which are observed products, or hydrolyze to observed products, are underlined.

The basic reactions are metalation of the carbonyl bond (reactions 1, 4, 7) and addition of carbon dioxide to the resulting metal alkyl intermediate (reactions 3, 5). Both reaction types are familiar.[16] Direct decomposition of the first intermediate could result in carbon monoxide formation (reaction 2). Comparing the distribution of products from sodium and potassium amalgams, it appears that reaction 3 proceeds less readily with potassium, which would explain the formation of carbon monoxide and especially the formation of formic acid when the concentration of potassium in the amalgam is high. A further series of metalations, carboxylations, and reductions (reactions 4–7) forms the precursor of tartronic acid. Carbonate formation from metal oxide (reaction 8) should and does accompany the formation of carbon monoxide or tartronic acid.

The formation of glycolic acid by reaction 9 is a secondary reduction of oxalate or its precursor, which occurs when there is excess sodium left in the amalgam at hydrolysis.

The alkaline earth metals, especially magnesium, give a greater range of products including acetate (reaction 10) and acetylene and other hydrocarbons indicating the formation of carbides. In Table I, there are cases where not all the carbon dioxide has been accounted for. Either the identification of product material has not been made, or the analysis for the amount present is not complete.

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TABLE I

YIELDS BASED ON CO_2 CONSUMED

	CO_2 Excess, 25°									Metal Excess, 25°									CO_2 Excess, 180°								
	Na	K	Li	Mg	Ca	Rb	Cs	Sr	Ba	Na	K	Li	Mg	Ca	Rb	Cs	Sr	Ba	Na	K	Li	Mg	Ca	Rb	Cs	Sr	B
Carbon monoxide	0	27	0	7	3	29	30	3	2	0	20	0	10	2	29	30	1	1	0	4	0	25	7	20	34	4	4
Carbonate	5	38	28	24	27	63	66	30	26	1	20	20	27	26	35	37	32	19	8	6	20	20	29	24	35	31	32
Formate	1	2	1	2	1	1	1	0	0	3	49	6	2	3	25	32	2	0	2	2	1	1	1	0	0	0	0
Acetate	0	1	0	10	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	2	0	17	2	0	0	0	0
Glycolate	6	0	0	2	4	0	0	0	0	68	1	3	4	6	3	0	4	0	0	0	4	0	5	0	0	0	0
Oxalate	83	20	19	27	16	3	0	46	63	7	4	1	6	12	2	0	2	33	87	84	18	4	31	55	30	32	45
Malonate	0	3	2	6	3	0	0	2	1	0	2	6	4	7	0	0	8	0	1	1	1	3	4	0	0	3	2
Tartronic	2	8	43	7	40	3	1	19	8	1	3	59	23	5	5	1	39	22	2	1	50	10	19	1	1	30	17
Total CO_2	97	99	93	85	94	99	100	100	100	80	99	95	76	61	99	100	88	75	100	100	94	80	98	100	100	100	100

In other experiments it has been found that carbon monoxide does not react under the conditions used to obtain the data of Table I; hence, carbon monoxide is not an intermediate step in the formation of other products. The reduction of carbon dioxide occurred only in the presence of an alkali or alkaline earth metal, no reduction was obtained with amalgams of manganese, zinc, cadmium, gallium, or with mercury alone.

Certain other reducing systems were investigated in cursory fashion. A 50:50 solution of sodium in mercury has formic acid as the chief product at 100°; at 280° the products were formate (10%), malonate (25%), oxalate (45%), and tartronate (20%). A 50:50 mixture of sodium and potassium at 80° gave oxalate and glycolate. A mixture of sodium in Woods metal at 170° produced formate.

Labeling Fatty Acids by Exposure to Tritium Gas. III. Methyl Stearolate and Methyl Linolenate

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Saturated fatty acid methyl esters, to C_{18} as previously shown,[1] are labeled in high specific activity by the Wilzbach method[2] of exposure to tritium gas; tritium substitutes for hydrogen in the aliphatic chain as was predicted.[2] It was discovered, however, that on exposure of methyl oleate, tritium exclusively added to the double bond, yielding radioactive methyl stearate.[3] Further, the 12,13- and the 9,10-double bonds of methyl linoleate were shown to add tritium in a ratio of 1.4 to 1, respectively.

The acetylenic fatty acid ester—methyl stearolate—on exposure to tritium and on subsequent analysis is shown herein to yield *cis*- and *trans*-9,10-tritioöctadecenoate as the major radiochemical product and to give minor amounts of radioactive methyl stearate (saturation) and stearolate (substitution) as shown in Table I. Radioactivity observed in the C_9 dibasic and C_9 monobasic acids results from substitution by tritium for the carbon-bonded hydrogen at carbon atoms other than numbers 9 and 10. Radioactivity in the C_9 mono- and dibasic acids corresponds to the 3–4% tritiated methyl stearolate isolated by liquid-liquid chromatograph and gas-liquid chromatography be-

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