[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA]

The Action of Barium Hydroxide on Certain of the Monobasic Sugar Acids

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Introduction

This paper presents the results of a quantitative study of the decomposition products resulting from the action of barium hydroxide on four sugar acids at a temperature of 140° for twenty-four hours. The compounds studied were *d*-gluconic, *l*-arabonic, *dl*-glyceric and *dl*-lactic acids.

While numerous studies of the action of alkalies on the sugars have been made, there is little work available on the action of alkalies on the sugar acids. It usually has been assumed that acids formed in the degradation of sugars with alkalies are relatively stable under the conditions employed. The experiments recorded in this paper indicate that this assumption is not always justified, particularly when higher concentrations of alkali and temperatures above 100° are employed.

Experimental

Materials.—Barium *d*-gluconate was prepared from commercial calcium *d*-gluconate. Barium *l*-arabonate was prepared from calcium *l*-arabonate made from *l*-arabinose by oxidation with bromine in the presence of calcium carbonate. Barium *dl*-glycerate was prepared from calcium *dl*-glycerate made from glycerol according to the method of Debus.[1] The purity of the salts was established by means of barium determinations. The *dl*-lactic acid was prepared from pure zinc lactate by precipitation of the zinc ion as the sulfide and extraction of the lactic acid from the filtrate with ether. The concentration of the aqueous solution was determined by titrating weighed portions with standard sodium hydroxide solution.

Procedure.—One-half equivalent of the barium salt was placed in a 500-ml. round-bottomed flask with one and one-half equivalents of barium hydroxide which had been dissolved in hot water and filtered. The solution in the flask was made up to 500 ml., the solution boiled and a rubber stopper wired in place. The stoppered flask was partially immersed in water in a cast iron bomb which was heated in an oil-bath by an electric hot-plate. The temperature within, which was indicated by the reading of a pressure gage on the bomb, was held at 140° for twenty-four hours. After this heating period the reaction mixture was treated as outlined below.

A solid residue consisting of barium carbonate and barium oxalate was filtered out of the slightly colored solution. Some additional barium oxalate usually precipitated when the solution was diluted to 1500 ml. and heated. The solids were dissolved in hydrochloric acid. Calcium oxalate was precipitated and reprecipitated from solution in the usual manner, and dried in air to constant weight.

After the solid residue had been taken out, the barium ion was removed from the filtrate with sulfuric acid until only a trace of barium remained. The free organic acids were then separated into a volatile and a non-volatile fraction by distillation *in vacuo* from a water-bath at 60°. Two 50-ml. portions of water were added, each of which was distilled to dryness.

The total acidity and the acidity due to formic acid were determined by the method of Evans and Hass[2] on aliquot portions.

The remaining part of the volatile acids was neutralized with sodium hydroxide and evaporated to dryness. Upon distillation with sulfuric acid the dry sodium salts from gluconic, arabonic and glyceric acids each yielded acetic acid, as determined by the Duclaux constants and the derivative formed with *p*-toluidine. Acetic acid was not found among the decomposition products of lactic acid.

The non-volatile acids were dissolved in water and separated into two portions by extraction with ether for forty-eight hours.[3] The extract was converted to the zinc salts and the zinc lactate removed as completely as possible. Its purity was determined frequently by igniting samples well dried in air and weighing the zinc oxide. The gummy residue remaining after the removal of zinc lactate was converted into brucine salts which were recrystallized until substances having constant melting points were obtained. An unidentified salt which darkened at 192° before melting at 197–199° was obtained from arabonic acid. From gluconic acid small amounts of salts melting at 186–188° and 221° were obtained. The former may be the brucine salt of 1,3-dihydroxybutyric acid, and the latter that of *dl*-glyceric acid. The amounts were too small for certain identification.

From the portion of non-volatile acids not soluble in ether a small amount of a very insoluble calcium salt was obtained which has been identified as calcium meso-α,α'-dihydroxyadipate.

Anal. Calcd. for $CaC_6H_8O_6$: Ca, 18.54. Found: Ca, 18.39.

The free acid obtained from the calcium salt melted at 172° (corr.) after being recrystallized once from ethyl acetate and twice from glacial acetic acid. The acid was found to be optically inactive.

Anal. Calcd. for $C_6H_{10}O_6$: C, 40.43; H, 5.66. Found: C, 40.77; H, 5.89.

A sample of pure phenylhydrazide prepared from the acid melted at 215° (corr.). This is a new compound.

Anal. Calcd. for $C_{18}H_{22}N_4O_4$: C, 60.30; H, 6.19. Found: C, 60.32, 60.34; H, 6.69, 6.73.

For the purpose of identification some meso-α,α'-dihy-

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[1] Debus *Ann.*, **106**, 79 (1858).

[2] Evans and Hass, THIS JOURNAL, **48**, 2703 (1926).

[3] Evans, Edgar and Hoff, *ibid.*, **48**, 2665 (1926).

droxyadipic acid was prepared according to the method of Le Sueur.[4] It melted at 172° (corr.) and melting points of mixtures were unchanged. Some of this acid was converted into the phenylhydrazide which melted at 215.5° (corr.). Melting points of several mixtures of this phenylhydrazide with that obtained above were also 215°. The acid was thus identified as meso-α,α'-dihydroxyadipic acid.

Separate portions of the barium salts one twenty-fifth as large as those used above, were heated in 25 × 100 mm. stoppered Pyrex test-tubes for the carbon dioxide determinations. An apparatus described by Clowes and Coleman[5] was modified slightly for the determinations.

Discussion of Results

With very few exceptions the figures presented below are averages of three to six or more determinations.

TABLE I

CARBON RETURNED IN PERCENTAGE OF TOTAL CARBON

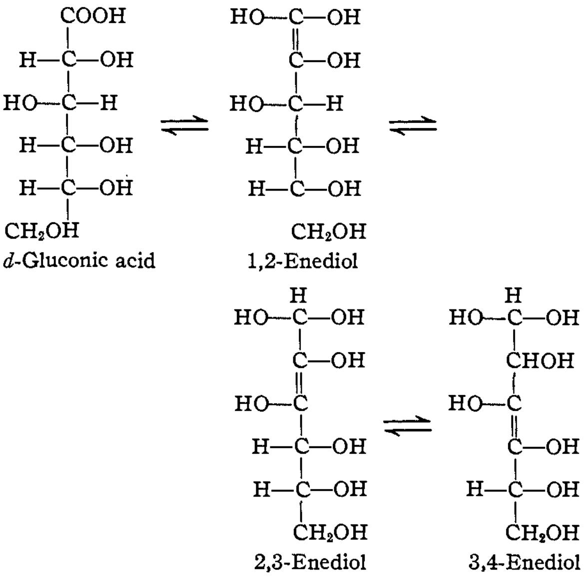
Acid	Formic	Other volatile	Oxalic	Lactic	Carbonic	Total
Gluconic	3.28	1.97	1.49	65.2	1.92	73.9
Arabonic	1.92	6.36	5.7	59.9	2.58	76.5
Glyceric	8.93	3.20	4.0	65.2	5.09	86.4
Lactic	0.17	0.53	..	98.2	..	98.9

The main constituent of the "other volatile acids" is acetic acid from all starting substances except lactic acid. Traces of lactic acid were present in every distillate since it is somewhat volatile. Traces of unchanged gluconic and arabonic acids were isolated as the phenylhydrazides from the original reaction mixture.

Since barium hydroxide is not an oxidizing or a reducing agent, some product must be oxidation products if others are reduction products of the sugar acid molecule. It is evident from the empirical formulas that lactic and acetic acids are reduction products while formic, oxalic and carbonic acids are oxidation products of glyceric, arabonic and gluconic acids.

When the theory of enediol formation[6] as developed from studies of the action of alkalies on the sugars, is applied to the sugar acids, the following possibilities may be presented.

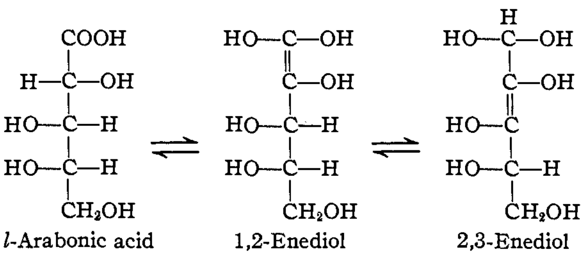
Evans and Conaway[7] state that it is generally accepted that pyruvic aldehyde formation is the forerunner of lactic acid in the alkaline decomposition of sugars.


d-Gluconic acid

1,2-Enediol

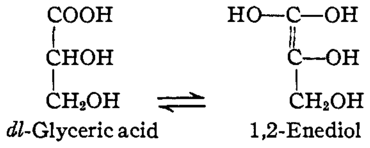
2,3-Enediol

3,4-Enediol


l-Arabonic acid

1,2-Enediol

2,3-Enediol


dl-Glyceric acid

1,2-Enediol

The formation of lactic acid from the active form of glyceric aldehyde resulting from the action of alkali on gluconic and arabonic acids may be explained by a mechanism presented by Evans and Hass.[2] Its formation from glyceric acid may be explained if we suppose that glyceric acid is reduced first to glyceric aldehyde. Such a reduction is entirely possible since combustible gases which contain hydrogen as one constituent were formed in small amounts in all experiments of this type. The second C_3 fission product of gluconic acid resulting from the breaking of the 3,4-enediol must also be capable of yielding lactic acid since approximately 65% of the carbon of this acid is returned as lactic acid. This breaking product is tartronic aldehyde, which may be converted to glyceric aldehyde upon reduction.

Since nearly 60% of the carbon of arabonic acid is returned as lactic acid and since no acetic acid is obtained from lactic acid, acetic acid must come from C_2 residues and not from the oxidation of pyruvic aldehyde, pyruvic acid or lactic acid. Its formation from the C_2 fission product of gly-

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[4] Le Sueur, *J. Chem. Soc.*, **93**, 716 (1908).

[5] Clowes and Coleman, "Quantitative Chemical Analysis," P. P. Blakiston's Son and Co., Philadelphia, 1914, p. 103.

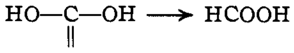
[6] Fischer, *Ber.*, **28**, 1145 (1895); Wohl and Neuberg, *ibid.*, **33**, 3095 (1900); Nef, *Ann.*, **403**, 205 (1914); Glattfeld, *Am. Chem. J.*, **50**, 137 (1913).

[7] Evans and Conaway, THIS JOURNAL, **52**, 3680 (1930).

ceric acid may be explained by a mechanism recently advanced by Evans and Hockett.[8] The C_2 fission product from gluconic and arabonic acids, unlike that from glyceric acid, would rearrange to form glyoxal. As is well known, alkalies convert glyoxal into glycolic acid even at 20°. The formation of acetic acid from glycolic acid may be explained by the method of Evans and Hockett if we suppose that the glycolic acid is first reduced to glycolic aldehyde.

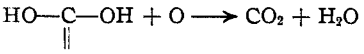
Oxalic acid may arise from the oxidation of any C_2 fission product.

Formic acid must arise directly from the rearrangement of dihydroxymethylene, a fission product of 1,2 enediols.



$$\underset{\Vert}{\mathrm{HO—C—OH}} \longrightarrow \mathrm{HCOOH}$$

The oxidation of dihydroxymethylene will account for carbon dioxide.



$$\underset{\Vert}{\mathrm{HO—C—OH}} + \mathrm{O} \longrightarrow \mathrm{CO_2} + \mathrm{H_2O}$$

The formation of meso-α,α'-dihydroxyadipic acid from gluconic acid may be explained by means of a double mechanism of the type leading to the formation of metasaccharinic acids. The mechanism presented by Evans, Edgar and Hoff[3] will apply readily to the transformation if one assumes that an aldehyde group is first formed at each end of the molecule by the reduction of the carboxyl group and the oxidation of the primary alcohol group.

$$\mathrm{OH{-}{-}C—CHOH—CHOH—CHOH—CHOH—CHO} \longrightarrow$$
$$\mathrm{HOOC—CHOH—CH_2—CH_2—CHOH—COOH}$$

The action of barium hydroxide on the sugar acids is somewhat related to the work of Evans and his students on the action of potassium hydroxide on *d*-glucose,[3] *l*-arabinose[7] and *dl*-glyceric aldehyde[2,9] the corresponding sugars. The part of the work of Evans which deals with the treatment of the three sugars with 3 *N* potassium hydroxide at 50° is summarized in the following table for the purpose of comparing his results with those of the present work.

The proportion of carbon accounted for as formic, acetic and lactic acids is much less in every case in the experiments with the hexoses, than with the corresponding acids. While a total of 13.2–37.5% of the carbon is accounted for by Evans and his students, 73.7–86.4% is accounted for in the present work.

TABLE II

PERCENTAGE OF CARBON RETURNED IN TERMS OF TOTAL CARBON FROM SUGAR AND SUGAR ACIDS

Acid......	Formic	Acetic	Oxalic	Lactic	Carbonic	Total
d-Glucose	0.29	0.68	..	24.5	..	25.5
d-Gluconic acid	3.28	1.97	1.49	65.2	1.92	73.9
l-Arabinose	1.63	0.80	..	10.8	..	13.2
l-Arabonic acid	1.92	6.36	5.7	59.5	2.58	76.5
dl-Glyceric ald.	1.1	1.4	..	35.0	..	37.5
dl-Glyceric acid	8.93	3.20	4.0	65.2	5.09	86.4

Since Evans used lower temperatures, it seemed of interest to find the effect of 3 *N* barium hydroxide on glucose at 140°. Accordingly, one experiment was carried out with this end in view.

One-half mole of anhydrous *d*-glucose was treated in exactly the same manner as the barium salt of the acid had been treated. No oxalic acid was found and no determination of carbon dioxide was made. The amounts of the carbon accounted for as formic, acetic and lactic acids were 8.8, 5.0 and 29.8%, respectively. These values are considerably higher than those obtained by Evans at 50° and values for formic and acetic acids are also higher than those obtained with gluconic acid. This indicates that the higher temperature favors the formation of the volatile acids in the action of alkalies on the hexoses. The significant difference between the sugars and the sugar acids is the relatively much higher percentage of lactic acid obtained from the latter.

Summary

1. Barium salts of *d*-gluconic, *l*-arabonic, *dl*-glyceric and *dl*-lactic acids have been treated with three normal barium hydroxide for twenty-four hours at 140° and the decomposition products have been determined quantitatively.

2. Gluconic, arabonic and glyceric acids are practically completely decomposed into simpler substances while lactic acid is almost unaffected by the treatment.

3. The amounts of the carbon recovered as lactic acid are three-fifths of the total carbon of arabonic acid, almost two-thirds of that of gluconic and glyceric acids, and 98% of that of lactic acid. The proportion of oxalic and acetic acids is greater by far from arabonic acid than from the others.

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[8] Evans and Hockett, THIS JOURNAL, **52**, 4065 (1930).

[9] Evans and Cornthwaite, *ibid.*, **50**, 486 (1928).