

UNITED STATES PATENT OFFICE

1,937,273

PROCESS FOR THE ELECTROLYTIC
OXIDATION OF ALDOSESEdward Leslie Helwig, Bristol Township, Bucks
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pany, a corporation of DelawareNo Drawing. Application February 8, 1930
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The oxidation of aldoses to the corresponding monocarboxylic acids has been successfully accomplished by the action of hypobromite or hypoiodite. Various attempts have been made to substitute hypochlorite for the more expensive hypobromite or hypoiodite but so far they have been unsuccessful due to the fact that the sugars are oxidized too far so that the desired products are contaminated with degradation products and unoxidized sugar, which impurities render the purification of the monocarboxylic acids very difficult.

Later it was found that the oxidation could be successfully carried on with hypochlorite provided some bromide was present in the reaction mixture (Journal of the Society of Chemical Industry, 41, pages 28—29, 1922).

In November, 1927, and February, 1929, U. S. Patents #1,648,368 and #1,703,755 were granted to Arthur Stoll and Walter Kussmaul, covering the oxidation of aldoses with hypochlorite in alkaline solution in the presence of iodides or bromides.

All the above methods have yielded the desired product mixed with a considerable quantity of alkali or alkaline earth salts from which it must be separated by crystallization. Furthermore, it is quite difficult to recover the bromide or iodide which was used in the reaction as it is mixed with a much larger quantity of chloride.

The new method which I herein describe has overcome these shortcomings and yields a very pure product even on the first crystallization.

The aldose is dissolved in water to which is added about one-tenth the equivalent amount of soluble bromide or iodide and a suspension of the calculated amount of calcium hydroxide, magnesium hydroxide or other base, the salt of which is desired. The mixture is then electrolyzed, using insoluble anodes. A number of the common metals, for instance copper, lead, iron or nickel, will serve as cathodes. No diaphragm is required. Sufficient agitation of the electrolyte is necessary to keep some of the base in suspension. When the theoretical amount of current has passed through the cell, the electrolysis is stopped, the solution is filtered, concentrated if necessary, and allowed to crystallize. The salt of the monocarboxylic acid so obtained is only contaminated with a trace of bromide or iodide from which it can easily be freed by one recrystallization. The mother liquors can be used to make up another batch of electrolyte by the addition of more aldose and base. Very little halogen is lost so it is only necessary to re-

place the little which is mechanically removed from the system. After a number of passages through the cell, the mother liquors finally become too foul, due to accumulation of degradation products, and it is then necessary to recover the halogen and begin over again. The recovery, however, is rendered much easier since the bromine or iodine is not associated with a lot of chlorine.

The amount of halogen required in the electrolyte depends on the current density employed. If an anode current density of 25 amperes per square foot is employed, the solution should preferably be about one-tenth molar with respect to iodine or bromine. At lower current densities, a smaller concentration of halogen will suffice, while at higher current densities a larger amount is necessary. The halogens might also be added in the form of their oxygen salts, which would soon be reduced to bromides or iodides.

The following examples serve to illustrate the nature of my invention but it is not limited to these special cases:

Example 1.—40 parts of glucose, 4 parts of potassium iodide, 9 parts of calcium hydroxide are mixed in 200 parts of water. This electrolyte is placed in a copper cup, which serves as a cathode, and a rotating graphite anode is placed in the center of the cup. The temperature is maintained at 10 to 15° C. and the solution is electrolyzed with an anode current density of 25 amperes per square foot. When the theoretical amount of current has passed through the cell, the electrolysis is stopped, solution filtered, evaporated, and allowed to crystallize. The product, calcium gluconate, crystallizes out after several hours and can be removed by filtration and purified by recrystallization.

Example 2.—An electrolyte is made up of 80 parts glucose, 5 parts calcium bromide, 18 parts calcium hydroxide, 200 parts of water; which is cooled to 15° C. while being circulated by means of a centrifugal pump and is electrolyzed between stationary copper cathodes and graphite anodes. A current density of 30 to 35 amperes per square foot is maintained until three-quarters of the theoretical current has passed through the cell, then it is tapered off gradually until a current density of 5 amperes per square foot is reached at the end of the electrolysis. After the theoretical current input, the electrolyte is removed from the cell, allowed to crystallize, filtered, and the filtrate and washings returned to the cell with the addition of 80 parts more or of glucose and 18 parts of calcium hy-

dioxide. The electrolysis is repeated and another crop of calcium gluconate crystals obtained.

Example 3.—40 parts glucose, 4 parts sodium iodide, 11 parts sodium carbonate are dissolved in 100 parts of water. This electrolyte is placed in a copper cup, which serves as a cathode, and a rotating graphite anode placed in the center. The temperature is maintained at 10° C. and the solution electrolyzed with an anode current density of 25 amperes per square foot. When the theoretical amount of current has passed through the cell, the electrolysis is stopped and the sodium gluconate precipitated out of solution by the addition of 4 parts of alcohol.

Example 4.—50 parts of lactose, 4 parts calcium bromide, 5.2 parts calcium hydroxide are dissolved in 200 parts of water. The mixture is electrolyzed between a stationary lead cathode and a rotating carbon anode at 20° C., current density 20 amperes per square foot. When the theoretical amount of current has passed through the cell, the electrolysis is stopped, solution filtered, and the calcium lactobionate is precipitated with 4 volumes of alcohol.

Example 5.—40 parts galactose, 4 parts of potassium iodide, 9 parts of calcium hydroxide are dissolved in 200 parts of water. This electrolyte is placed in a copper cup, which serves as a cathode, and a rotating graphite anode is placed in the center of the cup. The temperature is maintained at 10 to 15° C. and the solution is electrolyzed with an anode current density of 25 amperes per square foot. When the theoretical amount of current has passed through the cell, the electrolysis is stopped, solution filtered, evaporated, and allowed to crystallize. The product, calcium galactonate, crystallizes out after several hours and can be removed by filtration and purified by recrystallization.

What I claim is:

1. A process for the oxidation of aldoses to the corresponding monocarboxylic acids whereby the aldose is electrolyzed in alkaline solution with an insoluble anode in the presence of a salt containing a halogen of higher atomic weight than chlorine. 80
2. A process for the oxidation of glucose to gluconic acid whereby the glucose is electrolyzed in alkaline solution with an insoluble anode in the presence of a salt containing a halogen of higher atomic weight than chlorine. 85
3. A process for the oxidation of aldoses to the corresponding monocarboxylic acids in which the aldose is electrolyzed in the presence of a basic substance capable of neutralizing the monocarboxylic acid as it is formed and in the presence of a salt containing a halogen of higher atomic weight than chlorine. 90
4. The process of oxidizing an aldose sugar which comprises passing an electrical current through a solution containing an aldose sugar, a bromide and a base. 95
5. The process of oxidizing an aldose sugar which comprises passing an electrical current through a solution containing glucose, a bromide and a base. 100
6. The process of oxidizing lactose which comprises passing an electrical current through a solution containing lactose, a halogen of higher atomic weight than chlorine, and a base. 105
7. The process of oxidizing galactose which comprises passing an electrical current through a solution containing galactose, a halogen of higher atomic weight than chlorine, and a base. 110

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