

UNITED STATES PATENT OFFICE

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PROCESS OF OXIDIZING ALDOSE SUGARS
AND PRODUCTS RESULTING THERE-
FROM

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sented by the Secretary of Commerce

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amended April 30, 1928; 370 O. G. 757)

The invention described herein may be manu-
factured and used by or for the Government for
governmental purposes without the payment to
me of any royalty thereon.

5 The present invention relates to a process of
preparing monocarboxylic acids and their salts.

It is an object of the present invention to pro-
vide an improved process for the oxidation of
aldose sugars to their acids and salts. Other
10 objects of the invention will appear more fully
from the following specification.

Heretofore, various methods have been used
for the oxidation of aldose sugars, but these have
not been wholly satisfactory. For example, if
oxidation is effected by bromine or chlorine a
15 large quantity is necessary, and two molecules
of hydrogen bromide or hydrogen chloride are
formed for each molecule of sugar which is con-
verted to acid. This large amount of hydrogen
bromide or hydrogen chloride seriously interferes
20 with the separation of the desired product. Or,
if electrolytic oxidation is resorted to, a smooth
oxidation to the corresponding monocarboxylic
acid is not obtained, many degradation products
being produced which are difficult to separate and
25 which have little or no practical value.

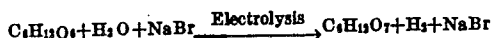
In accordance with the present invention, these
undesirable results are overcome by a process
wherein oxidation is effected electrolytically in
the presence of a catalyst. As a result, a nearly
30 quantitative oxidation of the sugar into its mono-
carboxylic acid is obtained, without objectionable
by-products. The catalyst, in addition to ex-
pediting the desired reaction, causes an increase
in the conductivity of the solution, thus reducing
35 its resistance and hence the amount of energy
required to effect the desired oxidation.

At the same time, the invention contemplates,
among other things, the use of a base or buffer in
the process, in the event that a salt of the sugar
40 acid is desired. The buffer has the additional
advantage that a nearly neutral solution may be
used in the process; and the current efficiency
(that is, actual oxidation divided by theoretical
oxidation) is remarkably increased.

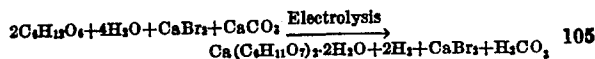
45 In the practice of the invention, satisfactory
results have been obtained with such catalysts
as bromine, hydrogen bromide, or halogen salts
of higher atomic weight than chlorine, such as
sodium bromide, calcium bromide, and iodides in
50 slightly alkaline solution. As a buffer or base,
satisfactory results have been obtained with lime,
calcium carbonate, barium carbonate and mag-
nesium oxide.

If the process of the present invention is used
55 in connection with such aldose sugars as glucose,

then the several steps are conveniently as fol-
lows: approximately 45 grams of glucose, 10
grams of a catalyst, say, sodium bromide, and
one liter of water are placed in an electrolytic
cell which may take the form of a container pro-
vided with a platinum cathode and a graphite
60 anode. It is noted that these proportions may
be varied within wide limits without departing
from the spirit and scope of the invention. About
14 ampere-hours of electricity are now passed
65 through the solution and, at the same time, the
solution is preferably agitated by means of a
conventional mechanical stirrer. When the
sugar determinations, by some such method as
iodine titration, show that the oxidation of the
70 aldose sugar to gluconic acid is substantially com-
plete, electrolytic action is terminated. Thus,
the sugar has been nearly quantitatively con-
verted into gluconic acid. The reaction is rep-
resented by the following equation:



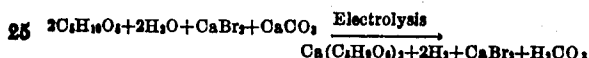
This gluconic acid may be used as such or it
may be separated as calcium gluconate in the
usual manner. Should it be desirable to form
80 the calcium gluconate direct, then the following
process may be used, it being noted that the pro-
portions are approximate only and given by way
of illustration: approximately 90 grams of glu-
cose, 10 grams of calcium bromide, 25 grams of a
85 buffer, such as calcium carbonate, and one liter of
water, are placed in an electrolytic cell provided,
say, with graphite electrodes and the conven-
tional mechanical stirrer. A direct current of
about 0.5 amperes is now passed through the so-
90 lution and the progress of the reaction followed
by sugar determinations. After 27 ampere-
hours of current has been used, the reaction is
practically complete, only a small amount of un-
converted sugar remaining in the solution. Upon
95 cooling the solution and nucleation, a good yield
of crystalline calcium gluconate is obtained which
is separated in the usual manner. The mother
liquors, which contain the catalyst, may be used
for a second oxidation by merely adding addition-
100 al glucose and calcium carbonate and repeating
the process. The foregoing reaction is repre-
sented by the following equation:



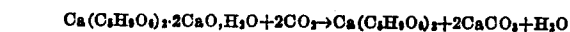
In thus forming the calcium gluconate direct,
in accordance with the formula and process just
described, the electrolyte contains a bromide com-
110 pound in the proportion of less than one equiva-

lent of the aldose originally present; and the reaction occurs on the acid side of neutrality, the latter being represented by pH 7. If it is desired to form the calcium gluconate, with the reaction on the alkaline side of neutrality, then a base such as lime and a catalyst such as an iodide may be used.

Should the invention be used in connection with such aldose sugars as xylose for the preparation of calcium xylonate, the procedure may be conveniently as follows, the proportions given being approximate only: ten grams of calcium bromide, 40 grams of xylose, 15 grams of a buffer, such as calcium carbonate, and one liter of water are placed in an electrolytic cell of the usual type and a current of about 0.3 amperes passed through the solution. After 15 ampere-hours of current, a Fehling's test for sugar is negative, indicating that substantially all the xylose had been converted into xylonic acid, which in turn has reacted with the calcium carbonate to give calcium xylonate. The action may be represented by the following equation:



In accordance with the present invention, the calcium xylonate may be separated from the solution in the following manner: the solution preferably is concentrated to a convenient volume, say, 200 ml., and an excess of lime, say 25 grams, is added. After standing a short time, an insoluble basic salt precipitates which may be separated in the usual manner. This salt is a new substance which affords a convenient method for the separation of calcium xylonate. The normal calcium xylonate may be obtained from this new basic salt by removing the lime with carbon dioxide, the reaction being represented by the following equation:



Should the free acid be desired, it may be formed in accordance with the present invention by removing the calcium with an acid, say, sulphuric or oxalic acid, in the usual manner. Or, the free acid may be obtained directly from xylose by electrolytic oxidation in the presence of a catalyst such as bromine or a bromide.

As a further illustration of the invention, the application of the process to the aldose sugar galactose is as follows, the proportions being approximate only and given by way of illustration: about 50 grams of galactose are dissolved in one liter of water containing seven grams of hydrogen bromide. The solution is conveniently placed in the anode compartment of a diaphragm type of cell containing a mechanical stirrer. A direct current of about 0.4 amperes is then passed between the electrodes. After about 15 ampere-hours of current has been used, the reaction is practically complete. The hydrogen bromide preferably is removed at the end of the reaction by continuing the electrolysis which converts the hydrogen bromide into free bromine and hydrogen. Removal of the bromine is expedited by blowing a stream of air through the solution, the resulting bromine vapors being conveniently recovered by absorption in an alkali. A nearly pure solution of galactonic acid is obtained by this means from which crystalline galactonic lactone may be obtained by evaporation to a thick syrup.

While the invention has been discussed in detail in connection with certain aldose sugars, it is also applicable to other sugars of this group

such as lactose, mannose, and arabinose. It is also noted that the foregoing proportions are susceptible of change within relatively wide limits and are set forth by way of illustration only. The invention may be further modified and embodied within the scope of the subjoined claims.

I claim:

1. The process which comprises the electrolytic oxidation of an aldose sugar in the presence of a halogen salt of higher atomic weight than chlorine.

2. The process which comprises the electrolytic oxidation of an aldose sugar in the presence of bromine.

3. The process of oxidizing an aldose sugar which comprises passing an electrical current through a solution containing an aldose sugar, a bromide and a calcium compound adapted to combine with an organic acid to form a salt.

4. The process which comprises the electrolytic oxidation of xylose in the presence of a bromide and a calcium compound adapted to combine with xylonic acid to form calcium xylonate.

5. As a new product, a basic calcium xylonate having the formula $\text{Ca}(\text{C}_5\text{H}_9\text{O}_6)_2 \cdot 2\text{CaO} \cdot \text{H}_2\text{O}$.

6. The process which comprises the electrolytic oxidation of xylose in the presence of a bromide and a calcium compound adapted to combine with xylonic acid to form calcium xylonate, and then adding at least two molecular equivalents of lime for each equivalent of calcium xylonate so as to cause the separation of a basic calcium xylonate.

7. The process of forming xylonic acid which comprises removing the calcium from



H_2O by means of an acid which forms a difficultly soluble calcium salt.

8. The process of forming xylonic acid which comprises the electrolytic oxidation of xylose in the presence of a bromide.

9. The process which comprises the electrolytic oxidation of an aldose sugar in the presence of a bromide, and then reclaiming bromine from the bromide by further electrolysis.

10. Process for converting an aldose into the corresponding aldonic acid, comprising electrolyzing an aqueous solution of the aldose in the presence of a bromide.

11. Process for converting an aldose into the corresponding aldonic acid, comprising electrolyzing an aqueous solution of the aldose on a carbon anode in the presence of a halogen salt of higher atomic weight than chlorine.

12. An electrolyte for the electrolytic conversion of an aldose into the corresponding aldonic acid, comprising an aqueous solution of the aldose containing a bromide compound in the proportion of less than 1 equivalent of the aldose present.

13. A process for converting an aldose into the corresponding aldonic acid, comprising electrolyzing through a diaphragm an aqueous solution of the aldose in the presence of a bromide.

14. A process for converting an aldose into the corresponding aldonic acid, comprising electrolyzing an aqueous solution of the aldose in the presence of a bromide, the reaction of the solution being on the acid side of neutrality.

15. The process of oxidizing an aldose sugar which comprises passing an electrical current through a solution containing an aldose sugar, a bromide and calcium carbonate.

16. The process which comprises the electro-

lytic oxidation of glucose in the presence of a bromide and a calcium compound capable of combining with gluconic acid to form calcium gluconate, the reaction occurring on the acid side of neutrality.	5	tion of less than 1 equivalent of the aldose pres- ent.	
17. The process which comprises the electro- lytic oxidation of glucose in the presence of a bromide and calcium carbonate.	10	19. The process which comprises the electro- lytic oxidation of xylose in the presence of a hal- ogen salt of higher atomic weight than chlorine, while maintaining the reaction nearly neutral.	80
18. An electrolyte for the electrolytic oxidation of an aldose, comprising a solution of the aldose containing a bromide compound in the propor-		20. The process which comprises the electro- lytic oxidation of an aldose sugar in the presence of a halogen salt of higher atomic weight than chlorine, while maintaining the reaction nearly neutral.	85
		HORACE S. ISBELL.	
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