

Saccharic Acid Preparation by the Nitric Acid Oxidation of Glucose*

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Saccharic acid has long been known as a product of the oxidation of glucose, but its preparation has never become industrially important. At present it is priced far too high. It is believed that it could be manufactured and sold in competition with tartaric acid. Derivatives of these two acids have common properties. Tartaric acid is manufactured almost solely from wine lees (1), but because of recent shortages, interest has been aroused in its synthesis from other sources (2). Several patents exist for its direct manufacture by the nitric acid oxidation of starch, or indirectly from 5-ketogluconic acid (6).

In a search for other derivatives that could be prepared by the oxidation of glucose, interest centered on saccharic acid. It is commonly prepared by the method of Fischer as modified by Kiliani (3), but the method has been insufficiently studied for application to large scale production. In this work a study was made of the methods of improving the yields and simplifying the procedure.

One of the best known of the nitric acid oxidations of carbohydrates is that of galactosides to yield mucic acid. A study has been reported also of the oxidation of xylose (5), as a possible outlet for the utilization of waste pentosans. The most extensive study of the oxidation of glucose has been that of Kiliani (4).

Although the methods used in the preparation of saccharic acid are much the same as those used for the manufacture of mucic acid, they are complicated by the fact that the former is soluble in the oxidation mixture. As a result of extensive studies, Kiliani was able to obtain only a 25% yield (3). By the simple procedure described in this report it has been possible to obtain greater than 30% yields, and in some cases as high as 50%.

Proposed Procedure

The proposed method is the result of an extensive study of the conditions necessary for obtaining good yields of saccharic acid from the nitric acid oxidation of glucose.

Glucose, or starch, is dissolved in 20-50% nitric acid. If nitric acid of density 1.15 (about 25%) is used, this solution should be prepared in the ratio of 1 g. of glucose to 3.5 ml. of nitric acid. For the laboratory

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preparation of saccharic acid these concentrations of reagents have been found best, but certain adjustments would have to be made for larger scale production. A catalyst has not been found that will significantly increase the yield. If the above ratio of reagents is used, the solution should be heated until it has evaporated to $\frac{1}{2}$ of the weight of the ingredients. The method used for the heating has not been found to be very important, but a slight advantage is found if the solutions are rapidly heated at first, and then allowed to continue to completion at 70-80°. The oxidation starts when the temperature reaches 75°, and then rapidly rises due to an exothermic reaction, until the temperature reaches 95°. At the onset of the oxidation NO_2 fumes are very strong and continue to be vigorously evolved for several minutes after the temperature reaches 95°. The vigorous oxidation then suddenly ceases and the temperature begins to drop, if the solution is not heated excessively. At this point practically no oxidation product can be isolated in the regular manner, but with continued heating at about 75°, the amount of recoverable saccharic acid goes through a maximum. This maximum is attained when the weight has been reduced to about $\frac{1}{3}$ that of the original ingredients. If the oxidation mixture is cooled to 0° at the termination of the oxidation, about $\frac{1}{2}$ of the oxalic acid will crystalize out, which will decrease the amount that will have to be removed by extraction.

The oxidation mixture is then extracted with ether until the extraction residue is almost devoid of nitric acid. At this point the oxalic acid will also be removed. The oxalic acid can be recovered from the ether extract by any convenient means, but care must be exerted to see that the extract is not evaporated to the point at which the oxalic acid will be vigorously oxidized. Solvents other than ether might be advantageously used, and in a large scale production the extraction could be carried out by pumping the solvent through the solutions to be extracted. This extraction must be carried out not far above room temperature, because of the dangers involved in vigorous oxidations at elevated temperatures.

The extraction residue is then made alkaline with potassium hydroxide, and sufficient time is allowed to saponify the lactone completely. This solution is then half acidified with a second batch of the extraction residue, and the potassium bisaccharate filtered off after it is completely precipitated. This filtrate is then made alkaline and the process repeated. Acetic acid can be used for the half acidification of the alkaline solution if sufficient is added to bring the pH to about 3.5. The potassium bisaccharate does not precipitate completely. It is only about 1.1% soluble in water, but is apparently more soluble in the presence of impurities. Additional product can be recovered from the potassium bisaccharate filtrate by the addition of calcium chloride. In many cases the salt has a CaO equivalent corresponding to that of calcium saccharate, and it is possible to convert a large portion of it to potassium bisaccharate. It is likely that if various fractions could be worked, products other than oxalic and saccharic acids could be recovered, but this has not been found feasible in small scale preparations.

Some results are recorded in Tables 1, 2, and 3 and presented graphically in Figures I, II, and III.

TABLE 1. Acid Catalysts with Nitric Acid

	Cat.	Ratio	Oxalic		KH-salts		N. E.
1.	H ₂ SO ₄	1/3	1.40	2.9	10.65	33.0	256.0
2.	H ₃ PO ₄	1/1	2.55	5.3	10.30	32.8	256.8
3.	HClO ₄	1/20	0.55	1.2	12.20	38.8	253.7
4.	H ₃ BO ₃	1/35	1.20	2.5	10.30	32.9	249.1

Column 2 is molar ratio of catalyst to glucose, 3 is g. of oxalic acid, 4 is % C returned as oxalic acid, 5 is g. of K bisaccharate, 6 is % C returned as K bisaccharate, and 7 is the neutral equivalent.

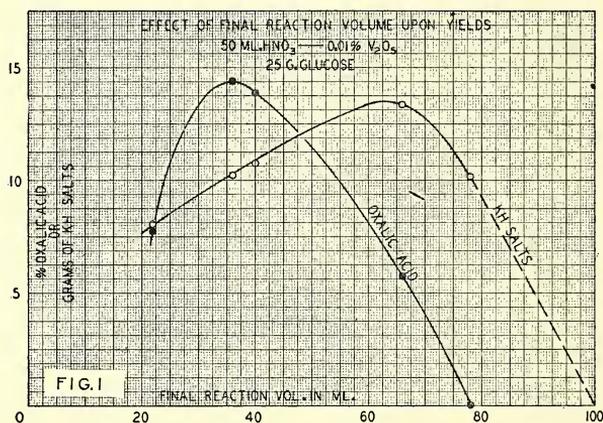


TABLE 2. Salt Catalyst with Nitric Acid

	Cat.	%	Oxalic		KH-salts		N. E.
1.	AlCl ₃	1.0	0.20	0.4	11.85	37.0	246.9
		10.0	0.20	0.4	10.80	34.5	248.7
2.	SnCl ₂	0.5	10.65	34.0	249.3
		10.0	3.15	10.2	250.4
3.	NH ₄ Cl	1.0	1.00	2.1	10.15	32.3	250.6
		10.0	0.55	1.2	9.15	29.2	251.3
4.	ZnCl ₂	0.5	1.10	2.3	10.75	34.3	245.5
		10.0	12.30	37.7	257.7

Legend: See Table 1. Column 2 is % conc. of catalyst.

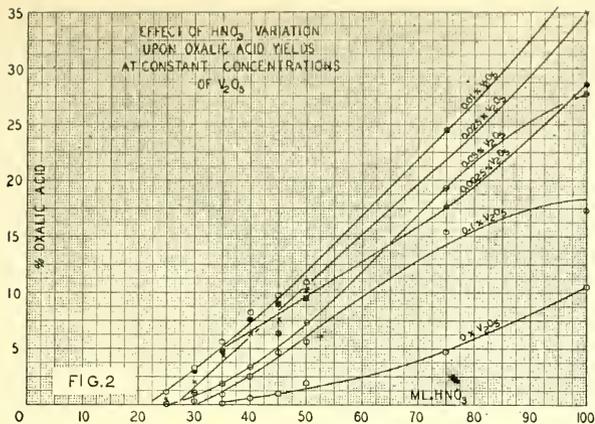
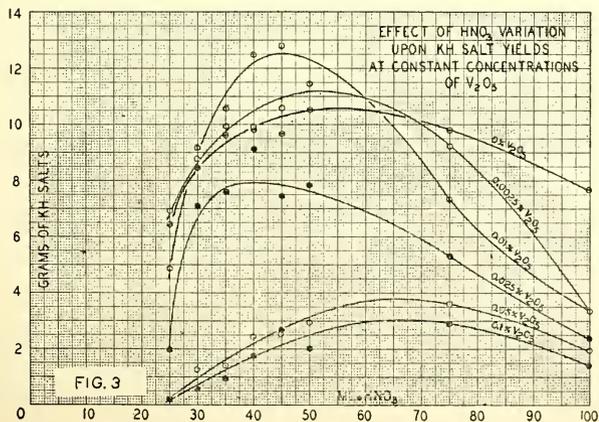


TABLE 3. Oxide Catalysts with Nitric Acid

Cat.	1%	Oxalic	KH-salts		N.E.		
1.	SiO ₂	1.0	11.00	35.0	248.8
2.	CoO	0.6	3.30	7.4	10.60	33.8	323.0
3.	CuO	0.6	3.90	8.2	8.45	29.7	273.7
4.	Cr ₂ O ₃	0.6	4.15	8.7	8.90	28.4	248.6
5.	Fe ₂ O ₃	0.1	5.25	11.0	8.00	25.5	251.7
6.	NiO	0.2	4.30	9.0	9.25	29.4	298.2
7.	WO ₃	0.2	4.70	9.8	7.50	24.0	261.8
8.	MoO ₃	.05	6.95	14.0	9.75	31.0	276.8
9.	MnO ₂	0.2	4.50	9.4	9.20	29.3	253.6
10.	V ₂ O ₅	.05	13.9	29.0	1.95	5.5	187.7

Legend: See Table I. Column 2 is % conc. of catalyst.



Summary

Oxalic and nitric acids can be extracted from the oxidation mixture with ether, and the extraction residue can then be worked for potassium bisaccharate. The oxalic acid can be recovered.

Best yields of potassium bisaccharate are obtained if it is precipitated by half acidification of dipotassium saccharate. After the addition of acid, sufficient time must be allowed for the lactone to saponify.

It is believed that by the methods described in this portion of the thesis, saccharic acid derivatives can be manufactured in competition with corresponding derivatives of tartaric acid.

Bibliography

1. Black, J. W., *Ind. Chemist*, **14**:443-4, 483, 521-4. (1938); **15**:100-1. (1939).
2. Coghill, R. D., *Abstr. St. Louis Meeting*, Amer. Chem. Soc., Section K, 2 (April, 1941).
3. Kiliani, H., *Ber.* 58B, 2344-62. (1925).
4. Kiliani, H., *J. Chem. Education*, **8**:1908-14. (1932).
5. Kline, G. M., and Acree, S. F., *Ind. Eng. Chem.*, **22**:975-80. (1930).
6. Pasternack, R., and Brown, E. V., (to Charles Pfizer and Co.), U. S. Patent 2,197,021 (April 16, 1940).