

solution was added to make the solution alkaline; it was then acidified with 10 per cent acetic acid. Mucic and oxalic acids in mixture were determined by the author's method,¹⁰ oxalic acid when alone by the usual volumetric method. Galactose, mucic acid, and oxalic acid were the substances chosen for oxidation.

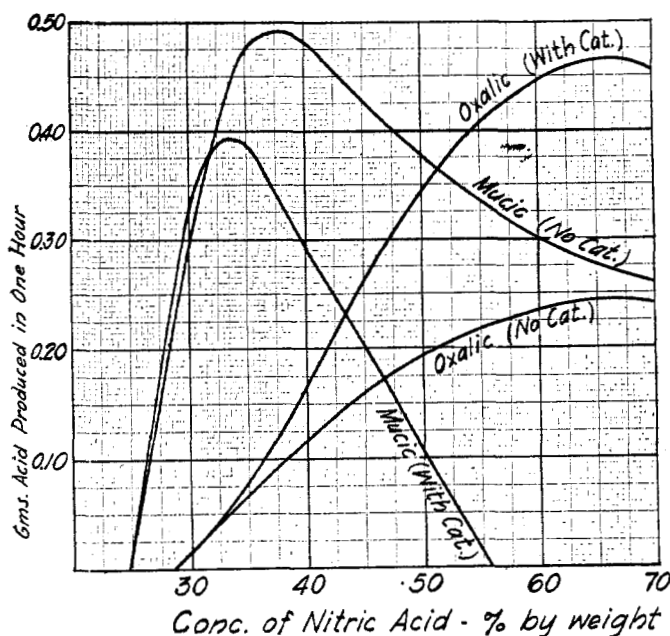


FIG. 1

Vanadium pentoxide was the only substance that showed any effect on the oxidation of galactose by nitric acid. Its most pronounced effects were in the higher nitric acid concentrations, where it caused the amount of mucic acid formed to be greatly reduced and the amounts of oxalic and carbonic acids to be increased.

Nitric acid does not attack mucic acid perceptibly under the conditions of these experiments, except when vanadium is present. In the presence of vanadium, 70 per cent nitric acid oxidized approximately 30 per cent of the mucic acid present, 60 per cent nitric acid oxidized approximately 22 per cent, 50 per cent nitric acid approximately 12 per cent, and 40 per cent nitric acid only a trace. Oxalic and carbonic acids were produced in approximately equal quantities. The oxidation of oxalic acid was catalyzed by vanadium pentoxide, cerium nitrate, and manganese nitrate. The relative activity of the catalysts, and the influence of concentration of oxidizing agent and of catalyst are shown in Table I. This table is also of interest in connection with the yields of oxalic acid from the oxidation of galactose, as shown in Table II.

TABLE I—INFLUENCE OF CATALYSTS, CONCENTRATION OF CATALYST, AND CONCENTRATION OF OXIDIZING AGENT ON NITRIC ACID OXIDATION OF OXALIC ACID

Catalyst Gram Atoms	Concentration of HNO ₃				
	70%	60%	50%	40%	30%
None	7.7	5.5	0.0	0.0	0.0
0.0001 cerium	18.0	9.8	7.7	6.4	2.1
0.0001 manganese	30.7	21.3	14.7	11.3	7.4
0.0001 vanadium	90.6	52.7	36.0	12.7	9.5
0.0002 vanadium	95.6	72.0	54.3	28.0	18.3
0.0004 vanadium	99.9	93.7	69.1	37.8	23.0

An extended series of oxidations of galactose was then carried out according to the procedure previously described. The concentrations of nitric acid ranged from 25 per cent by weight to 70 per cent by weight. The catalyst used was 0.0091 gram vanadium pentoxide—e. g., 0.0001 gram atom vanadium. This set of conditions was selected because over

nearly the whole range of acid concentrations the reactions were proceeding in a practically identical manner throughout the time of reaction and were incomplete at the end of the reaction period. Consequently, none of the values given approach the yields of mucic acid obtainable when the reaction is allowed to continue for a longer time. The results are recorded in Table II and plotted in Fig. 1. Each value given is the average of several oxidations.

TABLE II—OXIDATION OF GALACTOSE BY NITRIC ACID
Temperature, 85° C. Time, 1 hour 1 gram galactose
17.5 grams actual HNO₃ Catalyst, 0.0091 gram V₂O₅

HNO ₃ Concn. Per cent by Weight	OXALIC ACID		MUCIC ACID	
	Not Catalyzed Grams	Catalyzed Grams	Not Catalyzed Grams	Catalyzed Grams
25	0.0000	0.0000	0.0000	0.0000
30	0.0103	0.0190	0.2985	0.3274
35	0.0525	0.0817	0.4765	0.3873
40	0.1166	0.1550	0.4812	0.2840
45	0.1896	0.2596	0.3792	0.1996
50	0.1696	0.3067	0.3843	0.0290
55	0.2197	0.4236	0.3582	0.0180
60	0.2510	0.4256	0.3176	0.0000
65	0.2151	0.4693	0.2728	0.0000
70	0.2391	0.4542	0.2591	0.0000

DISCUSSION

The changes in curvature of the plotted values at 60 per cent nitric acid concentration are due partially to the slowing down before the end of the hour of the reactions at these high concentrations, and partially—in the case of the oxalic acid curves—to oxidation of oxalic acid. The principal reactions taking place at low nitric acid concentrations are the oxidation of galactose to mucic acid and oxidation of galactose to oxalic acid. At higher concentrations of the acid, galactose is evidently oxidized directly to carbon dioxide and water, even in the absence of vanadium. The optimum concentration of nitric acid for maximum mucic acid production at 85° C. is in the vicinity of 35 per cent. At this concentration oxalic acid is formed, but in comparatively small amounts. At lower concentrations the rate of production of both acids falls off rapidly. At higher concentrations the amount of mucic acid formed in a given time is less, and the amount of oxalic acid is greater, than at 35 per cent. Vanadium apparently catalyzes positively, but to a slight degree, the oxidation of galactose to mucic acid by 30 per cent nitric acid. It appears to have the opposite effect at higher concentrations but this apparent effect is probably due to the preponderance of the reactions producing oxalic and carbonic acids, which are both accelerated by vanadium. The catalytic effect of vanadium on the oxidation of galactose to oxalic acid is clearly evident, even at the higher nitric acid concentrations where the oxidation of the oxalic acid itself is being catalyzed.

The large number of factors involved in these reactions makes a discussion from the standpoint of the law of mass action impracticable.

Industrial Standards in Advertising Matter

As a definition of policy concerning the use of references in advertising matter to standards approved by the American Engineering Standards Committee, the following resolution has been adopted:

Resolved, that in the opinion of the American Engineering Standards Committee the use, in the advertising of products which comply with specifications and other standards approved by the Committee, of proper references to such standards, is advantageous and makes for industrial economy; accordingly, the Committee desires to encourage the use of such references in trade catalogs and other advertising media, but the Committee will in no case pass upon the merit of products, or upon their compliance with specifications or other standards, which questions it will leave to the commercial and legal agencies equipped for such work.

Such references are frequently made by foreign manufacturers in advertising products made in accordance with the standards of their national standardizing bodies, particularly in Great Britain and Germany. Both the British and Canadian associations have adopted official trade marks for use on goods manufactured in accordance with their specifications.

¹⁰ Whittier, *J. Am. Chem. Soc.*, **45**, 1391 (1923).