

CATALYSIS OF HYDROGEN PEROXIDE OXIDATION OF CARBOHYDRATES BY IRON AND COPPER SALTS¹CLIFFORD F. GASTINEAU, FAY SHEPPARD, and MARK R. EVERETT
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As part of a systematic investigation of salt catalysis in carbohydrate oxidation (Crews *et al* 1940; Everett and Sheppard 1940; Sheppard *et al* 1938, 1940; Sheppard and Everett 1939), we are reporting the results of quantitative studies of the oxidation of 1 per cent solutions of carbohydrate derivatives by hydrogen peroxide at 25° C, in the presence of iron salts, copper salts, potassium bicarbonate or potassium tungstate. These were found by Everett and Sheppard (1940) to be the most effective of an extensive series of salts in catalysis of oxidation by hydrogen peroxide.

After decomposition of excess hydrogen peroxide by agitation with manganese dioxide, the iron cations were removed by cupferron, and the excess of the latter by means of copper sulfate and hydrogen sulfide. Copper cations were removed by hydrogen sulfide alone. The optical rotations of the resultant solutions were determined. After neutralization with potassium hydroxide, the quantitative reducing values were determined by the Sumner and Folin-Wu methods. Qualitative color tests were also performed.

The ferric compounds employed as catalysts included the carbonate, chloride, hydroxide and sulfate; the ferrous salts, the acetate, carbonate and sulfate; the cupric salts, the acetate, carbonate and sulfate; and also cuprous carbonate. The sulfates of iron and copper exhibited maximal effectiveness, and their use facilitated the analytical technique. Freshly precipitated ferric carbonate was less effective; this salt remained practically undissolved except in the presence of carbohydrate derivatives having a *trans* pyranoid structure (Everett and Sheppard 1938). When soluble salts of iron and copper were employed, the yields of reducing material were not related to the *cis-trans* structure of the carbohydrates in the manner previously reported for bromine oxidation (Everett and Sheppard 1936). Maximal yields resulted with 0.1 molar equivalent (with respect to the carbohydrates) of ferrous sulfate and 2 molar equivalents of hydrogen peroxide, or with 2 molar equivalents of cupric sulfate and 1 molar equivalent of hydrogen peroxide. Using ferrous sulfate under these conditions, the approximate reducing values (in terms of equivalent glucose by Sumner's method) were: hexitols, 56 per cent (chiefly aldoses); glycerol, 28 per cent; hexonic lactones, 33 to 46 per cent (aldopentoses and keturonic acids); pentonic lactones, 22 to 38 per cent (aldotetroses and keturonic acids); and *D*-saccharic acid, 33 per cent. The presence of sufficient bromide, phosphate, methanol or ethanol inhibited the iron-catalyzed oxidation. Cupric sulfate catalysis has not been studied so extensively. The reducing values at present available are: hexitols, 11 to 18 per cent; and *D*-gluconolactone, 34 ± 6 per cent.

In the presence of 4 molar equivalents of potassium bicarbonate, 2 molar equivalents of hydrogen peroxide produced 20 to 39 per cent of reducing material from hexonic lactones, and 16 to 29 per cent from pentonic lactones. This salt was less effective with sugar alcohols as substrates (2 to 8 per cent yields of reducing material). Potassium tungstate (2 molar equivalents) was an effective catalyst in the oxidation of hexitols and *D*-gluconolactone. The values for reducing material are not reported because of possible analytical inaccuracies.

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The oxidation products produced by hydrogen peroxide from any given carbohydrate, or derivative, appear to differ characteristically for the several catalysts mentioned. Experiments are in progress to elucidate the nature of the products and the mechanism of salt catalysis.

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