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PHOTOOXIDATION OF D-FRUCTOSE WITH IRON(III) CHLORIDE UNDER AEROBIC CONDITION

Koji ARAKI,* Masato SAKUMA, and Shinsaku SHIRAISHI*
Institute of Industrial Science, The University of Tokyo
7-22-1 Roppongi, Minato-ku, Tokyo 106

D-Fructose is oxidatively degraded to D-erythrose with iron(III) chloride by photo-irradiation through Pyrex under aerobic as well as anaerobic condition. The reaction is suggested to proceed via formation of iron(III)-D-fructose complex and subsequent photo-redox process.

Carbohydrates and iron are widely distributed in nature. Complex formation of carbohydrates with iron and other metal ions has been studied because of their physiological and clinical importance,1) though little is known as to the photoreactivities of these complexes. Charley and his co-workers stated in their report that iron(III)-D-fructose complex does not undergo appreciable photooxidation under normal labolatory lighting.2) On the other hand, the photooxidation of organic substrates by aqueous iron(III) ion has long been studied,3) and alcohols are known to be oxidized to carbonyl compounds under anaerobic condition but not under aerobic one.4) In this letter, we wish to report that iron(III)-D-fructose system does undergo photo-redox reaction to give D-erythrose even under aerobic condition.

Upon addition of D-fructose (0.5 M5)) into a solution of iron(III) chrolide (0.25 M, pH 1.42), the pale yellow solution becomes reddish with a slight decrease in pH (1.38), indicating the formation of iron(III)-D-fructose complex. The difference spectrum before and after addition of D-fructose, which is considered to represent the absorption due to the complex,2) is shown in Fig. 1.

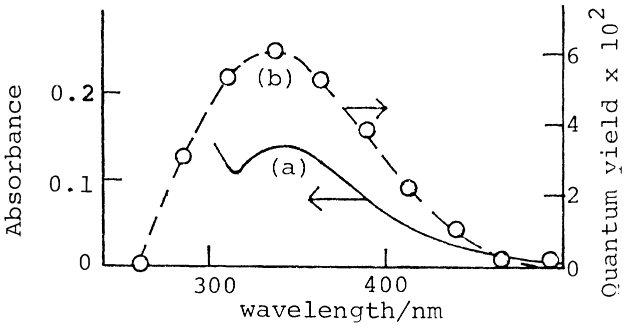

Fig. 1 The Difference Spectrum and Quantum Yields of $FeCl_3$ (2 mM)-D-Fructose (500 mM) Aqueous Solution (pH 1.38) under Aerobic Condition
(a) The difference spectrum before and after addition of D-fructose
(b) Quantum yields for reduction of Fe(III)

A solution (70 ml) containing D-fructose (0.5 M) and iron(III) chloride (0.25 M) was subjected to photo-irradiation at 20°C with a 100 W high-pressure mercury lamp through a Pyrex jacket under aerobic or anaerobic (degassed by three times of freeze-thaw cycles) condition. About 90% of initial iron(III) was reduced to iron(II) with considerable pH decrease after 2.5 h of the irradiation.6) Table 1 shows that 2 mol of iron(III) oxidizes 1 mol of D-fructose to form 2 mol of H^+ and iron(II). The reaction does not

Table 1. Changes in the Solution Composition after 2.5 h of Irradiation at 20°C

condition	D-fructose(M)$^{a)}$	$FeCl_3$(M)$^{a)}$	H^+(M)$^{a)}$	D-erythrose(M) (conversion mol%)$^{b)}$
aerobic	-0.112	-0.226	+0.222	+0.097 (87%)
anaerobic	-0.112	-0.224	+0.220	+0.092 (82%)

Initial concentration of D-fructose and $FeCl_3$ were 0.5 M and 0.25 M, respectively. a) See Ref. 6. b) Conversion based on the D-fructose oxidized. Determined by GLC.

proceed without irradiation or in the absence of any one of the substrates. The irradiated solution was deionized and condensed to give a colorless syrup (Yield 95-98 wt% to the initial D-fructose), and the syrup was analyzed by HPLC,$^{6)}$ TLC after pretreatment with 2,4-dinitrophenylhydrazine according to the methods of Honda et. al$^{7)}$ and Byrne$^{8)}$, and GLC for preacetylated sample with acetic anhydride-N-methylimidazole system according to the method of Wachowiak and Connors.$^{9)}$ These analyses confirmed that the main oxidation product was D-erythrose, the yield of which is more than 80 mol% of D-fructose oxidized. Glyoxal, glyceraldehyde, and formaldehyde were identified as minor products by TLC. It is interesting to note that the photooxidation of D-fructose with iron(III) ion took place similarly to the oxidation with lead tetraacetate, where a glycolic ester of D-erythrose has been reported to be formed via oxidative cleavage of the bond between C-2 and C-3.$^{10)}$

The results shown in Table 1 demonstrate that the photochemical oxidation of D-fructose with a concomitant reduction of iron(III) takes place even under aerobic condition, and only a little difference was observed between the reactions under aerobic and anaerobic conditions. Since the presence of air has little effect on the reaction, oxidation of D-fructose can best be explained by the initial formation of iron(III)-D-fructose complex and subsequent photo-redox process rather than by the free radical process resulting from the formation of hydroxyl radical from photo-excited iron(III) ion.$^{3)}$ This view is further supported by the result shown in Fig. 1(b), where quantum yields of the reduction of iron(III) at different wavelength are presented. Highest quantum yield was observed at 338 nm, indicating that a iron(III)-D-fructose complex is the photo-reactive species. More detailed studies as to the photochemical properties of metal-carbohydrate complexes are now under way.

References

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