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Interaction of Iron(III) Chloride with D-Fructose in an Acidic Solution

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Synopsis. Complex formation between Fe(III) and D-fructose in an acidic solution was studied by electronic and CD spectroscopy, and the role of the complex in the photochemically-induced oxidation of D-fructose by Fe(III) was discussed.

An Fe(III)-monosaccharide complex was suggested to play an essential role in the photochemically-induced oxidation of monosaccharides by $FeCl_3$.[1-3] The reaction was assumed to proceed via an Fe(III)-D-fructose complex, and irradiation of near-UV light caused oxidative cleavages of C-C bonds of monosaccharides with high specificity.[1] Though interactions between monosaccharides and a variety of metal ions have been the subject of intense studies,[4-6] only a little has been known as to the interaction of Fe(III) with monosaccharides in solutions.[6,7] Because of the physiological importance of the Fe(III)-monosaccharide systems,[3,8] we report here the interaction of Fe(III) with D-fructose in an acidic solution and clarify further the role of the Fe(III)-D-fructose complex in the photooxidation of D-fructose.

Experimental

Photoirradiation was carried out according to the method described previously.[1,3] Electronic and CD spectra (path length 10 mm) were recorded with JASCO UVIDEC-505 and J-20 spectrophotometers, respectively.

Results and Discussion

An aqua complex of Fe(III) shows a strong ligand-to-metal charge-transfer (LMCT) band in near-UV region.[9] Upon addition of D-fructose to an acidic $FeCl_3$ solution, the initial brown solution becomes reddish with concomitant decrease in pH. Difference spectra of the $FeCl_3$ solutions before and after addition of D-fructose showed appearance of the absorption band at 300—350 nm along with the band at 280 nm due to an acyclic form of D-fructose (Fig. 1).[10] The absorption at 300—350 nm in the difference spectra increased as the D-fructose concentration increased, though D-fructose alone had no absorption in this range. Therefore, this absorption band is ascribed to the Fe(III)-D-fructose complex. CD spectra of an $FeCl_3$-D-fructose solution further supported this assignment (Fig. 2). In addition to a strong positive absorption at 280 nm presumably due to the acyclic form of D-fructose, the CD spectra showed a weak negative absorption at 320 nm. The presence of the CD absorption at 320 nm indicated the contirbution of D-fructose to this absorption band, confirming the formation of the Fe(III)-D-fructose complex. Thus, the band observed at 300—350 nm in the difference spectra is ascribed to the LMCT band of the Fe(III)-D-fructose complex. Upon photoirradiation, the CD absorption at 320 nm disappeared (Fig. 2b). As the highest quantum yield for the photooxidation of D-fructose was observed at around 330 nm,[1] the result presented here confirmed that the reaction proceeded by the excitation of the LMCT band of the Fe(III)-D-fructose complex.

Apparent stability constants (K_{app}) of the Fe(III)-D-fructose complex in aqueous acidic solutions (pH 1—3) at 20 °C were determined from the electronic (380 nm) and CD (337 nm) spectra by the Benesi-Hildebrand and Rose-Drago methods.[11,12] The plots obtained by assuming a formation of the 1:1 complexes (Eq. 1) in the presence of a large excess amount of D-fructose gave satisfactory results. Typical Benesi-Hildebrand plots are shown in Fig. 3, and

$$\mathrm{Fe(III)} + \text{D-fructose} \overset{K_{app}}{\rightleftharpoons} \text{complex};$$
$$K_{app} = \frac{[\text{complex}]}{[\mathrm{Fe(III)}][\text{D-fructose}]} \qquad (1)$$

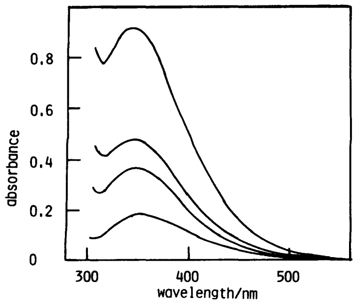

Fig. 1. Difference spectra of of $FeCl_3$(1×10^{-3} mol dm^{-3} solutions before and after addition of D-fructose; D-fructose concentrations are 0.4, 0.8, 1, and 2 mol dm^{-3}, respectively.

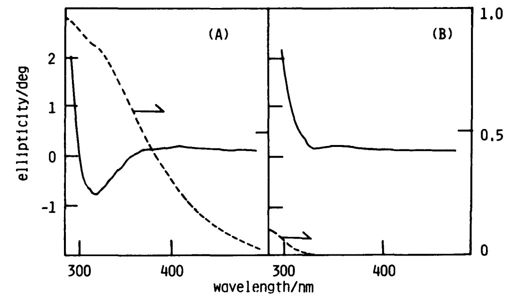

Fig. 2. CD(——) and electronic (----) sectra of $FeCl_3$ (1×10^{-3} mol dm^{-3})-D-fructose(0.4 mol dm^{-3}) solution (A) before and (B) after irradiation of Pyrex-filtered light at 20 °C.

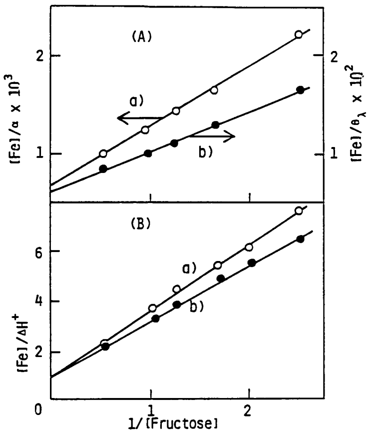

Fig. 3. Benesi–Hildebrand plots ([Fe]/absorbance vs. 1/[Fructose], where [Fructose]$\gg$[Fe]) for the complex formation between Fe(III) and D-fructose at 20 °C. (A) Applied for the (○) electronic (380 nm) and (●) CD (337 nm) spectra of the $FeCl_3$(5×10^{-4} mol dm^{-3})–D-fructose solutions at pH 2.82; (B) Applied for the amounts of H^+ liberated upon addition of D-fructose to (○) $FeCl_3$ and (●)$Fe(NO_3)_3$ solutions (4×10^{-3} mol dm^{-3}) at pH 2.50.

the results are summarized in Table 1. When pH of a solution was below 2, the absorption bands due to the complex was too small to determine the K_{app} values, and a rough estimation was made only from the electronic spectra. The stability constants could also be estimated from the amounts of H^+ liberated ($\Delta[H^+]$) on addition of D-fructose to FeCl3 solutions. The $\Delta[H^+]$ values were estimated from pH decreases of freshly-prepared FeCl3 solutions on addition of a large excess amount of D-fructose. If we assume that n H^+ are liberated upon formation of the 1:1 complex, the concentration of the complex is expressed as $\Delta[H^+]/n$ and the Benesi–Hildebrand plot can be applied by replacing absorbance and molar extinction coefficient with $\Delta[H^+]$ and n, respectively.[11] The plot gave a linear line yielding $1/(n\ K_{app})$ as a slope and $1/n$ as an intercept (Fig. 3), and the K_{app} values obtained here were in good agreement with those obtained from the electronic and CD spectra (Table 1). Therefore, formation of the complex can be written as follows (Eq. 2), and $\log K_s$ is estimated to be −2.8.

$$\text{Fe(III)} + \text{D-fructose} \overset{K_s}{\rightleftharpoons} \text{complex} + \text{H}^+ \qquad (2)$$

$$K_s = \frac{[\text{complex}][\text{H}^+]}{[\text{Fe(III)}][\text{D-fructose}]}$$

Table 1. Apparent Stability Constants (K_{app}) at 20 °C.

pH	Fe(III) salt	K_{app}
2.82	$FeCl_3$	1.03(UV); 1.04(CD)
2.50	$FeCl_3$	0.4(UV); 0.4(CD); 0.40(pH)
	$Fe(NO_3)_3$	0.37(pH)
1.20	$Fe(NO_3)_3$	0.03(UV)

K_{app} values were estimated from (UV): the electronic spectra (380 nm), (CD): the CD spectra (337 nm), and (pH): the amounts of H^+ liberated.

We previously reported that the quantum yield of the reduction of Fe(III) in the photochemically-induced oxidation of D-fructose (0.5 mol dm^{-3}) by Fe(III) (2×10^{-3} mol dm^{-3}) was 0.061 at 338 nm.[1] Since the action spectrum of the reaction coincided well with the absorption spectrum of the complex,[1] the reaction was assumed only to proceed by the light absorption of the complex but not by that of free Fe(III). Proportion of the light absorbed by the complex was determined from the electronic and difference spectra, and concentration of the complex was estimated from the K_s value obtained here. Thus, the quantum yield for the photoreactivity of the complex was estimated to be 0.3, showing that the excitation of the LMCT band of the complex efficiently induced reduction of Fe(III) with concomitant oxidation of D-fructose.

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