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Note

Oxidation of carbohydrates by alkaline hydrogen peroxide in the presence and in the absence of ferrous ion

Horace S. Isbell and Paweł Czubarow
Department of Chemistry, The American University, Washington, DC 20016 (U.S.A.)

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It has been reported that degradation of carbohydrates by alkaline hydrogen peroxide can take place by the Fenton reaction[1–3], the Bayer–Villiger reaction[4], the alpha hydroxy hydroperoxide (αHHP) cleavage-reaction[5–7], the ester reaction[8], the dihydroxy–epoxide reaction[1,9], and the peroxy–radical reaction[10–12]. In addition, mechanisms for the degradation of carbohydrates by hydrogen peroxide in the presence and in the absence of ferrous ion have been described[1,13].

Originally, Fenton's reagent was used under acidic or neutral conditions. Isbell and co-workers[1] found that hydrogen peroxide and hydroperoxide anion, in both the presence and absence of ferrous ion, oxidatively degrade alditols, aldoses, and aldonic acids nearly completely to formic acid and water. Both systems involve the formation of hydroxyl radical, and reaction of this with the carbohydrate substrate. The similarity of the two systems was noted. With Fenton's reagent, hydroxyl radical, hydroxyl ion, and ferric ion are produced from hydrogen peroxide and ferrous ion (Eq. *1*). In the absence of ferrous ion, hydroxyl radical, hydroxyl ion, and hydroperoxide radical are formed from hydrogen peroxide and hydroperoxide anion (Eq. *2*). It was of interest to compare the effectiveness of the two systems.

Oxidation of an alditol to an aldose proceeds according to Eq. *3* and *4*. Addition of hydrogen peroxide to the resulting carbonyl form of the aldose produces an adduct (Eq. *5*) capable of decomposing by several mechanisms[13]. Important among these is the αHHP cleavage reaction. This may take place either heterolytically (Eq. *6*) or homolytically (Eq. *7*). Heterolytic cleavage is slow because the O–O bond is stable to hydrolysis. Homolytic cleavage is catayzed by hydroxyl radical, which abstracts the hydrogen of the 2-hydroxyl group, releasing an electron for homolytic cleavage of the C-2–C-1 bond. This produces the next lower aldose, formic acid, and water. Repetition of the process leads to complete conversion of the aldose into formic acid and water. The reaction is rapid, because it includes both the addition and elimination of the high-energy constituent, hydroxyl radical.

The experimental work described here shows that the oxidative reaction is significantly more rapid in the presence of a catalytic amount of ferrous ion than in its absence. The difference may be ascribed to the regeneration of ferrous ion from ferric

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TABLE I

Effect of ferrous ion on oxidation of D-glucitol at 4°

Time (h)	*Formic acid produced (mmol)*	
	Fe^{2+} present	*Fe^{2+} absent*
2.5	0.89	0.36
7.0	1.33	0.66
11.0	1.73	0.82
24.0	5.11	1.18

ion, and its subsequent reaction by Eq. *1* to yield more hydroxyl radicals. On the other hand, the hydroxyl radical produced during the reaction of hydroperoxide anion with hydrogen peroxide (Eq. *2*) is partially consumed by reaction with the accompanying hydroperoxide radical (Eq. *8*). Thus D-glucitol is converted into formic acid more rapidly in the presence of a catalytic amount of ferrous ion than in its absence (see Table I).

It was of interest to determine the effect of relatively large amounts of ferric salt on the oxidation reaction. The results showed that, in the absence of ferric ion, one mmol of D-glucitol was converted into 1.2 mmol of formic acid within 24 h. However, in the presence of one mmol of $FeNH_4(SO_4)_2 \cdot 12H_2O$, only 0.65 mmol of formic acid was formed. Presumably, retardation in the production of formic acid is caused by reaction of ferric ion with hydroperoxide radical, producing oxygen and ferrous ion (Eq. *9*). Reaction of the excess of ferrous ion with hydroxyl radical again produces ferric ion, and decomposes the hydroxyl radical (Eq. *10*), thus retarding the degradation of carbohydrates to formic acid. Retardation in the production of formic acid from degradation of D-glucitol in the presence of ferric ion may also be explained with the fact[14] that the reaction of Eq. *9* is energetically more favorable than the reaction of Eq. *11*.

The reactions previously described are accompanied by formation of peroxy radical by oxidation of the anion of the adduct of Eq. *5* (Eq. *12*). The peroxy radical also decomposes, with formation of the next lower aldose, formic acid, and hydroxyl radical. This is an important reaction for degradation of aldoses by alkaline hydrogen peroxide. Formation and cleavage of peroxy radicals constitutes an interesting chapter in carbohydrate chemistry which will be considered in future papers.

Equations:

$$H_2O_2 + Fe^{2+} \rightarrow \cdot OH + OH^- + Fe^{3+} \quad (1)$$
$$H_2O_2 + OOH^- \rightarrow \cdot OH + OH^- + \cdot OOH \quad (2)$$
$$RCH_2OH + \cdot OH \rightarrow \cdot CH(OH){-}R + H_2O \quad (3)$$
$$\cdot CH(OH){-}R + Fe^{3+} + OH^- \rightarrow RHC{=}O + Fe^{2+} + H_2O \quad (4)$$
$$\cdot RHC(OH){-}HC{=}O + H_2O_2 \rightarrow \cdot RHC(OH){-}HC(OH){-}OOH \quad (5)$$

$$\cdot RHC(OH)-HC(OH)-OOH \xrightarrow{\pm\ ^{-}OH} \cdot RHC{=}O + HCO_2H + H_2O \tag{6}$$

$$\cdot RHC(OH)-HC(OH)-OOH \xrightarrow{\pm\ ^{-}OH} \cdot RHC{=}O + HCO_2H + H_2O \tag{7}$$

$$\cdot OH + \cdot OOH \rightarrow H_2O + O_2 \tag{8}$$

$$Fe^{3+} + \cdot OOH + OH^- \rightarrow O_2 + Fe^{2+} + H_2O \tag{9}$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \tag{10}$$

$$Fe^{3+} + H_2O_2 \rightarrow \text{no reaction} \tag{11}$$

$$RHC(OH)-HC(OH)-O-O\cdot \rightarrow RHC{=}O + H_2C{=}O + \cdot OOH \tag{12}$$

EXPERIMENTAL

Oxidation in the presence of ferrous ion. — A solution of 4 mmol of D-glucitol in 10 mL of water, 10 mL of 30% H_2O_2, and 1 mL of milimolar $FeSO_4$ was stirred at 4°C, and treated with 24 mL of 2M KOH added dropwise during the course of 30 min. The solution was kept at 4°, and aliquots were taken after 2.5, 7, 11, and 24 h and analyzed for HCO_2H by the $HgCl_2$ method[9].

Oxidation in the presence of hydroperoxy anion. — A solution of 4 mmol of D-glucitol in 10 mL of water was stirred with 10 mL of 30% H_2O_2 at 4°C, and treated with 24 mL of 2M KOH added dropwise during 30 min. The solution was kept at 4°, aliquots were taken after 2.5, 7, 11, and 24 h and analyzed for HCO_2H by the $HgCl_2$ method[9].

Oxidation in the presence of a ferric salt. — A solution of 1 mmol of D-glucitol in 10 mL of water was stirred with 10 mL of 30% H_2O_2, and 1 mmol of $FeNH_4(SO_4)_2 \cdot 12H_2O$ was added at 4°. After 24 h an aliquot was taken and analyzed for HCO_2H by the $HgCl_2$ method[9]. The results showed that only 0.65 mmol of HCO_2H was formed, whereas in the absence of the ferric salt, 1.2 mmol was produced.

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