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Preliminary communication

Formation of organic peroxides from methyl β-D-glucopyranoside in alkaline hydrogen peroxide solutions

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During the course of investigations on the degradation of cellulose with peroxidic solutions, the reaction of alkaline hydrogen peroxide with methyl β-D-glucopyranoside was studied in a teflon-lined reactor with 1 25M NaOH, with and without mM $MgSO_4$, over a range of temperatures (60–90°), glucoside concentrations (0.01–0 03M), peroxide concentrations (0 1–0.4M), and various contents of transition-metal ions The trace quantity of magnesium ion was frequently added to ensure reproducible rates of degradation, and its catalytic behavior will be the subject of another communication.

Each reaction was analyzed as a function of time for methyl β-D-glucoside (by g.l.c.), methanol (by the method of Boos[1] employing chromotropic acid), hydrogen peroxide, organic peroxide, and evolved oxygen Because of the explosive nature of concentrated peroxides, the samples for g l c. analysis were reduced with sodium hydrogensulfite before trimethylsilylating the products. Sodium hydrogensulfite also buffers the alkaline solution to lower pH and reacts with any carbonyl groups present to form hydrogensulfite addition-compounds

The concentrations of H_2O_2 and organic peroxides were determined by a colorimetric, titanium sulfate method[2,3]. In this procedure, H_2O_2 forms a titanium complex immediately, and can thus be differentiated from organic peroxides [which undergo acid hydrolysis (pH 1–2) slowly to form H_2O_2] by measuring the increase in color (420 nm) intensity in the sample with time In the present study, the concentration of organic peroxides was determined from the difference between two large numbers However, in these experiments, the probability that the difference was significant was 99% The average concentrations of organic peroxide, and their 95% confidence limits, from three replicate reactions are shown in Fig 1

The reactions with glucoside were characterized by a rapid initial loss of glucoside followed by a slower, almost constant, rate of degradation (Fig. 1) During the rapid, initial phase of the reaction, the concentration of organic peroxides reached a maximum The correlation apparent in Fig 1 between the maximum concentration of organic peroxide and a high rate of reaction of methyl β-D-glucopyranoside suggests that an organic peroxide is acting as a reactive intermediate in these reactions Similar reaction-patterns at this stage were exhibited under all conditions studied, regardless of the presence or absence of magnesium, cobalt, or chromium ions

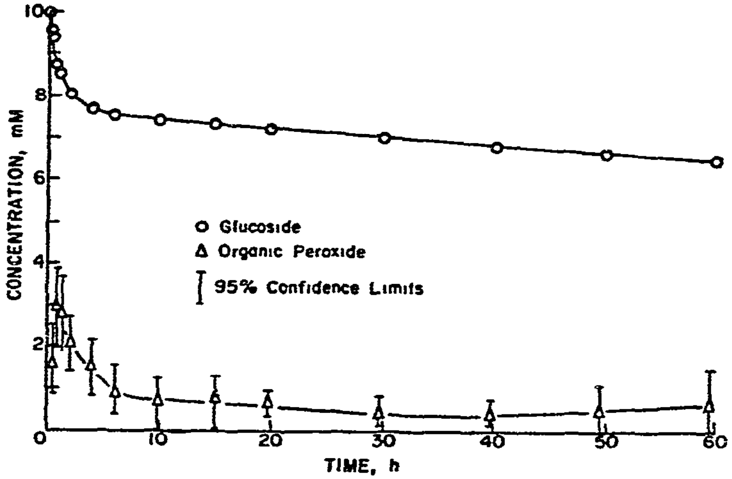

Fig.1. Degradation of methyl β-D-glucopyranoside and resultant formation of organic peroxide in 200 mM H_2O_2 and 1.25M NaOH with mM $MgSO_4$ stabilizer at 60°

As the organic peroxide was only moderately stable, it could not be separated from hydrogen peroxide for more than a few minutes, and it was converted into degradation products and hydrogen peroxide when attempts were made to isolate it.

Gas-chromatographic analysis of the products as a function of time for the reaction at 60° gave a concentration–time profile for one product that was similar to that for the organic peroxide, as detected by colorimetric analysis (see Table I). Analysis of the per-*O*-trimethylsilyl derivative of this product by g.l.c.–mass spectrometry was consistent with its being a methyl hexopyranosidulose. Peaks at *m/e* 408 (M), 393 (M–15), and 377 ($M-CH_3O$) established the molecular weight and glycosidic character of the product, and well-characterized fragments at *m/e* 204, 133, 129, and 103 indicated that the carbonyl group is probably[4] at C-2. The known lability of aldopyranosiduloses in alkali[5] makes it unlikely that the identified product existed to any significant extent as such in

TABLE I

RELATIVE CONCENTRATIONS OF ORGANIC PEROXIDE AND HEXOPYRANOSIDULOSE AS A FUNCTION OF TIME[a]

Time, h	*Organic peroxide* [b]	*Hexopyranosidulose* [c]
1.0	0.30	0.35
9.0	0.08	0.06
20.0	0.07	0.05
44.0	0.04	0.03

[a] Methyl β-D-glucoside, 10 mM; H_2O_2, 200 mM; NaOH, 1.25 M, $MgSO_4$, mM; 60°. [b] Ratio of organic peroxide concentration to concentration of unreacted glucoside. [c] Ratio of hexopyranosidulose to unreacted glucoside, g.l.c. peak areas.

$$HO{-}\overset{|}{\underset{|}{C}}{-}OOH + HSO_3^- \longrightarrow \overset{|}{\underset{|}{C}}{=}O + H_2O + HSO_4^- \quad (1)$$

$$HO{-}\overset{|}{\underset{|}{C}}{-}OOH \rightleftharpoons \overset{|}{\underset{|}{C}}{=}O + H_2O_2 \quad (2)$$

the alkaline peroxide solution, although it may have been stabilized as a magnesium complex[6] Instead, it is considered that the aldopyranosidulose is derived chiefly from the corresponding α-hydroxyhydroperoxide during sodium hydrogensulfite treatment and neutralization of the samples in the gas-chromatographic analysis procedure. The aldopyranosidulose could result either from reduction of the α-hydroxyhydroperoxide [Eq (*1*)] or from the α-hydroxyhydroperoxide as the H_2O_2 is decomposed [Eq. (*2*)][7,8]. α-Hydroxyhydroperoxides have often been proposed as intermediates in similar oxidation systems[9]. The subsequent degradation of these peroxides is profoundly influenced by magnesium ions and transition-metal ions, and this aspect will be the subject of other communications

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