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DIFFERENTIAL SCANNING CALORIMETRIC STUDIES OF THE REACTION BETWEEN LIGNOCELLULOSIC MATERIALS AND HYDROGEN PEROXIDE USING MODEL COMPOUNDS

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ABSTRACT

Reaction of hydrogen peroxide with twenty lignocellulosic polymers and model compounds was studied by differential scanning calorimetry at 6722 kPa (975 psi) in nitrogen and oxygen atmospheres. Two exotherms were identified. Exotherm A peaked between 109 and 186°C in N_2 and O_2 with the heat of reaction ΔH_a ranging from 738 to 2638 cal g^{-1}. Exotherm B peaked between 180 and 254°C in either atmosphere with $\Delta H_b = 109–346$ cal g^{-1} in N_2 and with $\Delta H_b = 1356–4325$ cal g^{-1} in O_2. With one exception, exotherm B appeared in N_2 only in the case of the materials which possessed acetal or hemiacetal linkages. It was concluded that exotherm A resulted from decomposition of H_2O_2 under formation of O_2 and oxidation of organic compounds, while exotherm B resulted from oxidation of hydroxyl groups by O_2. A mechanism was proposed for the formation of O_2, which involved hydrolysis of acetal or hemiacetal linkages to aldehydes or ketones, formation of α-hydroxyperoxides by addition of H_2O_2, oxidation of α-hydroxyperoxides by hydroxyl radicals, decomposition of the resulting free radicals under formation of superoxyl radicals and oxidation of superoxyl radicals either by hydrogen peroxide or by hydroxyl radicals to oxygen.

INTRODUCTION

Our previous differential scanning calorimetric (DSC) studies of the reaction of hydrogen peroxide with lignocellulosic materials, in the absence of an added catalyst, resulted in identification of two exotherms designated as A and B [1–6]. Exotherm A appeared at temperatures between 140 and 198°C for cellulose, lignin, arabinoxylan or wood. The position of this exotherm and the corresponding heat of reaction changed only moderately with the change of atmosphere from nitrogen to oxygen. It was assumed that exotherm A resulted from decomposition of hydrogen peroxide to form, ultimately, oxygen and water, and/or from oxidation of organic substrates by hydrogen peroxide or its reactive decomposition products. The second exotherm B appeared between 200 and 255°C. It was absent for lignin run in a nitrogen atmosphere, but was present for all carbohydrates run in nitrogen or oxygen and also for lignin run in oxygen. While the position of this exotherm changed only moderately with the change in atmosphere, the

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heats of reaction increased drastically in oxygen. It was assumed that exotherm B arises from the reaction of oxygen with organic substrates, with the oxygen provided either by the atmosphere or generated by the decomposition of hydrogen peroxide. It was also apparent that decomposition of hydrogen peroxide under formation of oxygen required the presence of organics with certain structural features, as no oxygen was apparently produced with lignin, but only with carbohydrates.

This report deals with the determination of the structural features of lignocellulosics required for the production of oxygen in the exotherm A reaction as well as for the reaction of oxygen in the exotherm B reaction, using 14 mono- and oligomeric carbohydrates and their derivatives, microcrystalline cellulose, Kraft pulp, lignin, arabinoxylan, galactoglucomannan and wood powder.

EXPERIMENTAL

Mono- and oligosaccharides and their derivatives used as model compounds were of reagent grade, purchased from various commercial sources and were used without further treatment. Pinitol was isolated from *P. lambertiana* Douglas heartwood, and purified by crystallization to m.p. 182–184°C [7]. Microcrystalline cellulose was Sigmacell type 38 purchased from Sigma Chemical Co. Lignin was obtained from the brown cubical root of *Libocedrus decurrens* Torr., as previously described [3,8]. Arabinoxylan, galactoglucomannan and Kraft pulp were donated by M.M. Merriman of this laboratory and were prepared from wood of *Abies concolor* (Gord. and Glend.) Lindl. Wood powder was obtained by grinding wood of the same species to 60–80 mesh size and exhaustively extracting with ethanol and hot water.

For DSC, the materials were vacuum-dried and mixed with 50% wt. of H_2O_2 in 8 : 1 compound-to-H_2O_2 ratio. The analyses were run in hermetically sealed plain aluminum pans with a pin-hole in the lids at 6722 kPa N_2 or O_2 pressure and 20°C min^{-1} heating rate. The analytical and calculation details were described in previous publications [1–6]. Due to the heterogeneous nature of the reactions, commonly involving three phases, the accuracy of the results was less than generally attained in DSC: this was particularly true for the figures for the heats of reaction in the case of exotherm B.

RESULTS

The values for the heats of reaction for exotherms A and B (ΔH_a and ΔH_b) and the temperatures of the corresponding peak maxima (T_a and T_b) are presented in Table 1.

In a nitrogen atmosphere, exotherm A was present for all materials studied and peaked between 109 and 186°C with the heats of reaction ranging from 738 to 2638 cal g^{-1}. Microcrystalline cellulose exhibited exotherm A at a particularly high temperature of $T_a = 186°C$, while Kraft pulp and hemicelluloses gave exotherms in the range $T_a = 140–148°C$. The heat of reaction was also somewhat lower for microcrystalline cellulose. This is probably due to the reduced accessibility to H_2O_2 of microcrystalline cellulose versus hemicelluloses and Kraft pulp, all of which are either amorphous or include appreciable portions of amorphous material, and thus less resistant to penetration. Furthermore, the T_a of the compounds with one hemiacetal linkage per carbohydrate repeat unit (H/M) was lower (109–136°C) than the T_a of the compounds with H/M less than one (131–186°C): this was most likely due to the generally higher susceptibility to hydrolysis of hemiacetalic compared to acetalic linkages.

In a nitrogen atmosphere, all materials containing hemiacetal and/or acetal linkages produced exotherm B, while all compounds which contained neither hemiacetal nor acetal linkages produced no exotherm B, with the exception of D-sorbitol: even in the case of D-sorbitol, however, the produced exotherm B was small with $\Delta H_b = 109$ cal g^{-1} only. Exotherm B generally peaked in the range $T_b = 197–254°C$, with the exception of D-α-methylglucoside, which peaked at 274°C. The heats of reaction for exotherm B (if present) were appreciably smaller than those of exotherm A and ranged between 109 and 346 cal g^{-1}.

In an oxygen atmosphere, the peak temperatures and the heats of reaction of exotherm A ($T_a = 133–185°C$ and $\Delta H_a = 805–2018$ cal g^{-1}) and the peak temperatures of exotherm B ($T_b = 180–253°C$) were only marginally different from the ones obtained in N_2. The heats of reaction of exotherm B increased, however, many times and appeared with all materials tested ($\Delta H_b = 1356–4325$ cal g^{-1}), including those not exhibiting exotherm B in N_2 (Table 2 and Fig. 1).

In our previous publications, we assigned exotherm B to the oxidation of organic materials, either by the introduced O_2, or by O_2 produced in the exotherm A reaction between H_2O_2 and the organic materials. This assignment was based essentially on the practically identical positions of exotherm B in N_2 and O_2, and on the drastic increase in the heat of reaction in O_2 [4]. To further strengthen this assignment, β-D-glucose was run in N_2 at 6722 kPa in a sealed pan with a pin-hole on top: immediately after exotherm A, at about 175°C, the pressure was released and the temperature was allowed to rise to 500°C at atmospheric pressure (101 kPa). No exotherm B could be detected in this case. This result was interpreted by the escape of O_2 formed during the exotherm A reaction through the pin-hole during the pressure release.

Since only the compounds possessing hemiacetalic or acetalic bonds generally gave exotherm B we hypothesized that the production of O_2 during the exotherm A reaction must be somehow connected with the hydrolysis of

TABLE 1

DSC characteristics of hydrogen peroxide treated carbohydrates and related compounds

No.	H/M [a]	HA/M [a]	Name of compound [b]	Thermal characteristics			
				Peak A		Peak B	
				T_a (°C)	ΔH_a (cal g^{-1})	T_b (°C)	ΔH_b (cal g^{-1})
(A) Nitrogen atmosphere							
1	1	1	β-D-glucopyranose (1)	135	1837	244	299
2	1	1	β-D-xylopyranose (1)	117	1397	218	346
3	1	1	α-L-fucopyranose (1)	136	1475	235	124
4	1	1	β-D-fructopyranose (1)	130	1239	220	330
5	0	1	Sucrose (2)	149	1042	230	250
6	0	1	Raffinose (3)	144	1657	218	258
7	1/2	1	Cellobiose (2)	154	1596	254	140
8	1	1	α-D-galacturonic acid (1)	109	1821	197	167
9	1	1	α-D-glucuronolactone (1)	134	1566	245	265
10	0	1	D-α-methylglucoside (1)	145	738	274 [c]	170 [c]
11	0	0	Pinitol (1)	152	1667	–	–
12	0	0	D-sorbitol (1)	152	2156	248	109
13	0	0	γ-D-ribonolactone (1)	151	1798	–	–
14	0	0	γ-D-galactonolactone (1)	131	1082	–	–
15	$\approx 1 \times 10^{-4}$	1	α-cellulose, microcrystalline (≈10.000)	186	1837	250	128
16	$\approx 1 \times 10^{-3}$	1	α-cellulose, Kraft pulp (≈1.000)	146	2638	215	(Shoulder)
17	$\approx 5 \times 10^{-3}$	1	Arabinoxylan (≈ 200)	140	1928	203	417
18	$\approx 1 \times 10^{-2}$	1	Galactoglucomannan (≈100)	148	1958	220	110
19	0	0	Lignin	154	2497	–	–
20	–	–	Wood powder	172	1937	257	127
(B) Oxygen atmosphere							
1	1	1	β-D-glucopyranose (1)	140	1513	238	1642
2	1	1	β-D-xylopyranose (1)	135	1364	190	4325
5	0	1	Sucrose (2)	142	805	205	3042
7	1/2	1	Cellobiose (2)	161	1206	212	3030
8	1	1	α-D-galacturonic acid (1)	133	1263	180	3842

10	0	1	D-α-methylglucoside (1)	164	1226	211 [d]	2728
11	0	0	Pinitol (1)	152	1628	234	2921
12	0	0	D-sorbitol (1)	155	1679	222	1356
13	0	0	γ-D-ribonolactone (1)	156	1636	217	2102
14	0	0	γ-D-galactonolactone (1)	168	1507	205	2620
15	$\approx 1\times10^{-4}$	1	α-cellulose, microcrystalline (≈ 10 000)	185	1446	235	2826
17	$\approx 5\times10^{-3}$	1	Arabinoxylan (≈ 200)	146	1302	210	3891
19	0	0	Lignin	153	2018	220	1863
20	–	–	Wood powder	182	1486	253	2028

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[a] H/M, number of hemiacetal linkages per monosaccharide unit; HA/M, number of hemiacetal and acetal linkages per monosaccharide unit.

[b] In parentheses is given the number of monosaccharide units in the molecule: for polymeric compounds such numbers are only approximations.

[c] Peak corresponds mainly to non-oxidative decomposition as discussed in text.

[d] Followed by a third exotherm at 335 °C, $\Delta H = 2845$ cal g^{-1}.

TABLE 2

Statistical evaluation of the influence of atmosphere on the thermal characteristics of the reaction mixtures [a]

Atmosphere	Thermal characteristic	Mean	Standard deviation	Difference in means	t-statistic	Number of values used	Significance of the difference in means
Nitrogen	Peak A, T_a	144.25	17.09	10.89	1.91	20	0.05
Oxygen	Peak A, T_a	155.14	15.90			14	
Nitrogen	Peak B, T_b	230.27	18.91	13.70	1.93	15	0.05
Oxygen	Peak B, T_b	216.57	19.37			14	
Nitrogen	Peak A, ΔH_a	1693.3	463.71	258.90	2.02	20	0.05
Oxygen	Peak A, ΔH_a	1434.2	282.35			14	
Nitrogen	Peak B, ΔH_b	219.29	102.79	2510.42	10.59	14	0.0005
Oxygen	Peak B, ΔH_b	2729.71	880.74			14	

[a] With exotherm B (nitrogen) the data for T_b of compounds 10, 11, 13, 14 and 19 were excluded as exotherm B was absent: the data for ΔH_b of compounds 10, 11, 13, 14, 16 and 19 were excluded for the same reason.

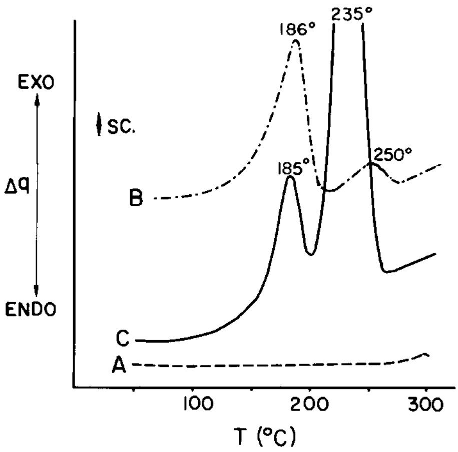


Fig. 1. DSC of microcrystalline cellulose: (A) in N_2, 2.1 mg, no H_2O_2; (B) in N_2, 1.4 mg, with H_2O_2; (C) in O_2, 1.4 mg, with H_2O_2. Runs made at 6722 kPa, 20°C min^{-1}. Ordinate scale: SC = 2 mcal s^{-1}.

hemiacetalic and acetalic bonds to corresponding aldehyde and ketone groups which reacted with H_2O_2 under production of O_2. In order to verify this hypothesis, *n*-tetradecyl aldehyde was reacted in N_2 with H_2O_2, both in the absence and presence of pinitol (5-*O*-methyl-D-inositol), as polyhydroxy compound (weight ratios: 4:1 and 4:1:4, respectively). The results are given in Fig. 2. In the absence of pinitol, *n*-tetradecyl aldehyde exhibited a melting endotherm at about 80°C and an exotherm at about 140°C corresponding to exotherm A: no exotherm B was observed. In the presence of pinitol, however, which, per se, does not produce exotherm B with H_2O_2 in N_2 (Table 1), a well defined additional exotherm in the temperature range 175–235°C was produced (exotherm B). These experiments demonstrate a definite link between the reaction of H_2O_2 with an aldehyde group and the production of O_2 giving exotherm B in N_2. The experiments also demonstrate that the exotherm B reaction with O_2 requires the presence of hydroxyl groups.

On the basis of all our experiments and the literature data [9–13] the following mechanism for the reaction of lignocellulosic materials with H_2O_2 can be proposed. In the absence of organic materials, H_2O_2 decomposes catalytically with formation of H_2O and O_2, and, specifically in our case, the surface of the aluminum pans could serve as a catalyst:

$$3H_2O_2 + Al \rightarrow Al^{3+} + 3OH^- + 3HO \tag{1}$$

$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \tag{2}$$

$$HO_2^{\cdot} + HO^{\cdot} \rightarrow H_2O + O_2 \tag{3}$$

$$HO_2^{\cdot} + H_2O_2 \rightarrow HO^{\cdot} + H_2O + O_2 \tag{4}$$

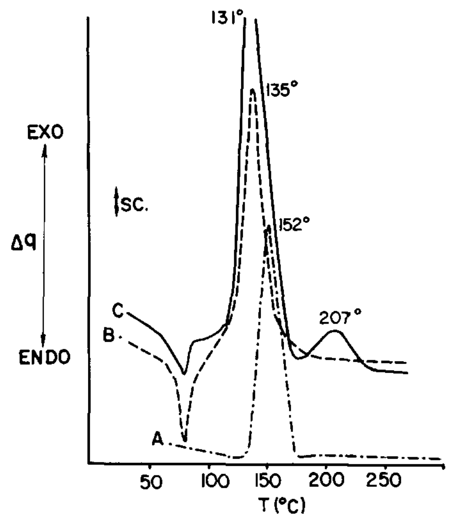


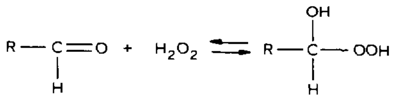
Fig. 2. DSC of tetradecylaldehyde: (A) pinitol, 3.6 mg, with H_2O_2; (B) tetradecylaldehyde, 3.6 mg, with H_2O_2; (C) tetradecylaldehyde, 3.6 mg, and pinitol, 6.0 mg, with H_2O_2. Runs made in N_2, at 6722 kPa, 20°C min^{-1}. Ordinate scale: SC = 2 mcal s^{-1}.

In the presence of organic materials, hydroxyl radicals can react with these materials forming organic radicals:

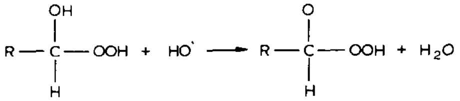
$$HO + R\text{-}CH_2OH \rightarrow R\text{-}\dot{C}HOH + H_2O \qquad (5)$$

Our experiments with various polyols lacking a ketone or aldehyde group indicated that no oxygen was formed during oxidation with H_2O_2, as detectable by exotherm B: this suggests that reaction (5) under our conditions is much faster than reaction (2). Similar relationships have been previously demonstrated by other investigators [9–13]. The formation of oxygen for compounds including aldehyde, ketone, hemiacetal or acetal linkages must then take place other than by routes (2–4).

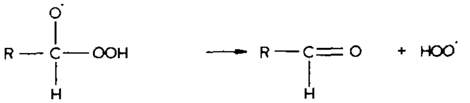
The well-known reversible formation of α-hydroxyperoxides by reaction of carbonyl compounds (either free or formed by hemiacetal or acetal hydrolysis) with H_2O_2 most probably represents the first step [14]. A number of routes leading from α-hydroxyperoxides to O_2 can be formulated [14], but the experiments do not allow us to definitely decide between them. The simplest two explanations would involve oxidation of the α-hydroxyl group, or of the peroxyl group to radicals which would decompose under formation of the original carbonyl compounds and a superoxyl radical (routes 7–8 or 9–10) with the latter producing O_2 via routes (3) and (4). Carbonyl compounds would thus act as true catalysts for decomposition of H_2O_2 to H_2O and O_2:



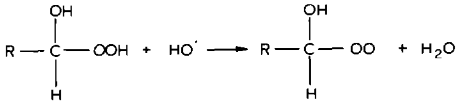
$$\underset{\displaystyle H}{\underset{|}{R-C}}=O + H_2O_2 \rightleftharpoons R-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-OOH \qquad (6)$$



$$R-\underset{H}{\overset{OH}{C}}-OOH + HO^{\cdot} \longrightarrow R-\underset{H}{\overset{O}{C}}-OOH + H_2O \tag{7}$$



$$R-\underset{H}{\overset{O^{\cdot}}{C}}-OOH \longrightarrow R-\underset{H}{C}=O + HOO^{\cdot} \tag{8}$$



$$R-\underset{H}{\overset{OH}{C}}-OOH + HO^{\cdot} \longrightarrow R-\underset{H}{\overset{OH}{C}}-OO + H_2O \tag{9}$$

(10)

As mentioned previously, D-sorbitol and methyl-α-D-glucoside behaved abnormally: the first compound, possessing no hemiacetalic or acetalic linkages, produced a weak exotherm B while the second compound, possessing an acetalic linkage produced exotherm B at an abnormally high temperature (Table 1). The experiments of Fenton and Jackson [15] indicate, however, that D-sorbitol is particularly readily and quantitatively oxidized to glucose and mannose by the H_2O_2/Fe^{2+} reagent. The O_2 produced in this case must thus arise from the interaction of H_2O_2 with these sugars, after they are formed by oxidation of D-sorbitol.

The appearance of exotherm B in the case of methyl-α-D-glucoside at a particularly high temperature (274°C) in N_2 raises the question as to

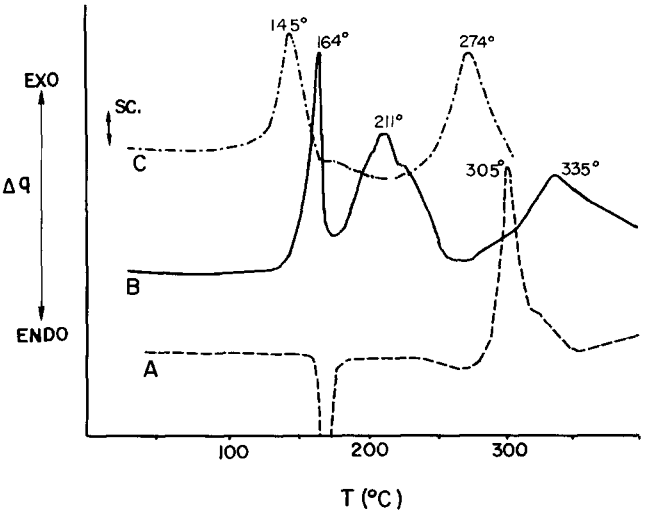


Fig. 3. DSC of methyl-α-D-glucoside: (A) in N_2, 2.8 mg, no H_2O_2; (B) in O_2, 2.0 mg, with H_2O_2; (C) in N_2, 3.6 mg, with H_2O_2. Runs made at 6722 kPa, 20°C min^{-1}. Ordinate scale: SC = 2 mcal s^{-1}.

whether we are dealing with the oxidation of hydroxyls by O_2 in this case. This suspicion is strengthened by the appearance of the exotherm B at the normal position (211°C) in O_2 (Fig. 3). In N_2, in the absence of H_2O_2, methyl-α-D-glucoside gave a sharp melting endotherm at 168°C and a strong exotherm at 305°C, preceeded by a weak endotherm starting at 250°C (Fig. 3). Shafizadeh et al. [16,17] studied by DTA the pyrolysis of phenyl-β-D-glucopyranoside and phenyl-α-D-glucopyranoside in N_2 at ambient pressure and reported, in addition to the endotherms arising from the loss of water of crystallization and melting, a broad endotherm at 305° with a shoulder at 330°C, arising from pyrolytic reactions. The absence of exotherms is probably due to the concurrent endothermic evaporation of the products of decomposition: this evaporation should have been suppressed by the 6722 kPa pressure used in our experiments. Hendrix et al. [18] also observed an endotherm between 270 and 310°C followed by an exotherm at 310°C in DTA of methyl-α-D-glucoside run in air at ambient pressure: they explained the two processes by the decomposition of the compound followed by the condensation reactions of the products of decomposition, respectively. In our experiments, the addition of H_2O_2 lowered the above endotherm and exotherm to 220 and 274°C, respectively (Fig. 2): this lowering could be due to differences in pressure, as well as from an increased acidity resulting from oxidation of the substrate by H_2O_2, catalyzing both the decomposition and condensation reactions.

While it appears that the methyl-α-D-glucoside exotherm at 274°C results from the condensation reactions, rather than from O_2 oxidation, it cannot be excluded that the peak includes a weak oxidation exotherm B, which is not registered due to its merger with the strong condensation reaction exotherm. The absence of a strong exotherm B for methyl-α-D-glucoside is in sharp contrast with much stronger exotherm B produced by the equally fully acetalic sucrose and raffinose. Most probably, the difference relates to the higher hydrolytic susceptibility of the furanosidic linkages in the two oligosaccharides compared to the pyranosidic linkage in methyl-α-D-glucoside. Thus Haworth reported $K = 25 \times 10^{-5}$ min^{-1} for the rate constant of the methyl-α-D-glucoside hydrolysis in 0.01 N HCl at 95–100°C, compared to 5000×10^{-5} min^{-1} for sucrose hydrolysis under the same conditions [19]. Other authors reported similar results for these and other sugars [20,21]. The ease of hydrolysis of the furanosidic linkage is most likely also responsible for the stronger exotherm B in partly furanosidic arabinogalactan compared to pyranosidic galactoglucomannan and cellulose.

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