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THE RELATIVE BEHAVIOR OF BENZYLIC ALCOHOLS AND MERCAPTANS TOWARD
OXIDATION BY SODIUM ANTHRAQUINONE-1-MONOSULFONATE (AMS)

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ABSTRACT

The reactions of 1-phenylethanol and 1-phenylethanethiol, either alone or together, with AMS in alkaline 50% aqueous dioxane at 88° have been studied. The mercaptan is oxidized several hundred times faster than the alcohol. The results imply that benzyl mercaptans, such as those produced during the kraft pulping of wood, could serve as reaction partners in the reduction of anthraquinone to anthrahydroquinone during kraft/anthraquinone pulping.

INTRODUCTION

A simple redox cycle (Figure 1) involving anthraquinone (AQ), anthrahydroquinone (AHQ), carbohydrates, and lignin has been proposed to account for the increased yields and fast delignification rates observed during the pulping of wood with catalytic amounts of AQ.¹⁻³ Although substantial evidence exists for the reactions proposed in Figure 1, the likelihood that they occur simultaneously is low because of the timing of the steps. In general, the principal yield-reducing carbohydrate degradation reactions occur in the early stages of pulping, and the lignin reactions dominate the later stages.⁴

Viscosity-reducing chain cleavage reactions of carbohydrates occur late in pulping; however, a rough calculation indicates that the number of carbohydrate reducing end groups liberated in this

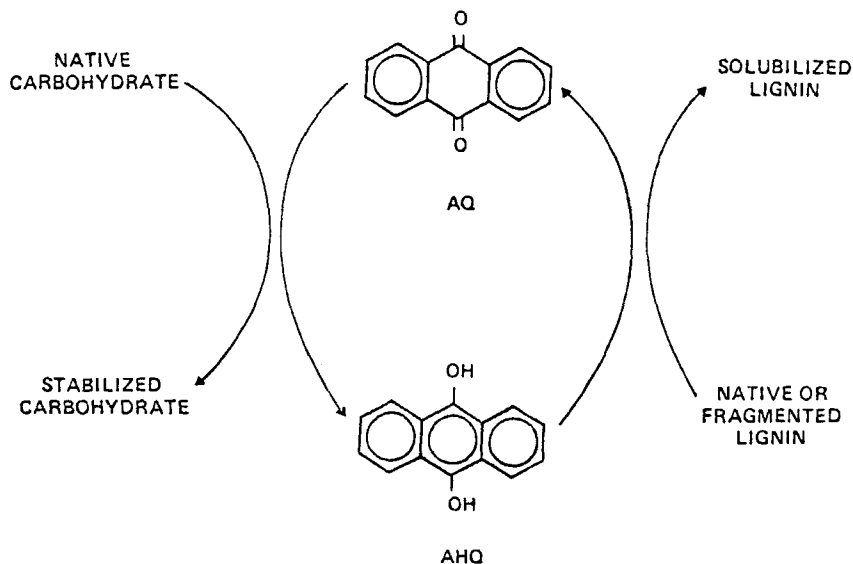
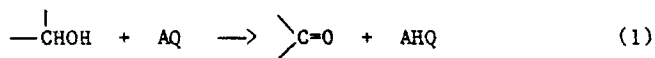


Figure 1. A redox cycle proposal to explain the action of anthraquinone during pulping.

way is only about 1/100 of the number of lignin units that could potentially be cleaved by AHQ. Possibly, short-lived carbohydrate by-products from "peeling," after chain cleavage, could reduce some AQ to AHQ. The oxidation of alcohol groups of lignin or carbohydrates by AQ may provide another source of AHQ at 170° (equation 1). Reactions of this type may be responsible for carbohydrate chain cleavage reactions, as has been observed with amylose.⁵



Gratzl and co-workers^{6,7} have studied the reactions of AQ with lignin model fragments and have proposed the following relative ease of oxidation of functional groups: carbohydrate reducing end groups > coniferyl alcohol >> phenolic benzyl alcohols > nonphenolic benzyl alcohols. Also, the α -carbonyl group content of lignin precipitated from soda/AQ and kraft/AQ black liquors is significantly higher than comparable control runs.⁹ These findings suggest that there probably are a collection of "internal" redox

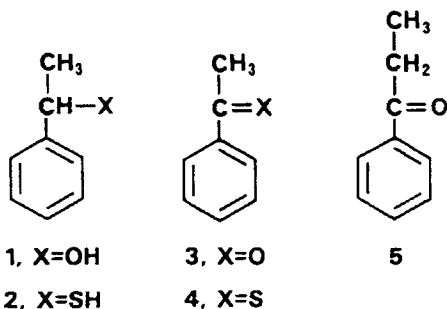
cycles in which both carbohydrates and lignin are being oxidized and reduced. Redox cycles involving the extractive components of wood do not appear to be significant.⁸

Benzyl mercaptans are believed to be produced during kraft pulping.⁹ Mercaptan-AQ redox couples might rapidly regenerate AHQ, a potent delignification promoter, and thereby facilitate pulping rates and improve viscosities.¹⁰⁻¹⁴ How rapidly would benzyl mercaptans be oxidized by AQ?

RESULTS

A study was undertaken to compare the relative ease of oxidation of 1-phenylethanol (1) and 1-phenylethanethiol (2) by sodium anthraquinone-1-monosulfonate (AMS) in 50% aqueous dioxane containing sodium hydroxide. Anthraquinone was initially examined as a reactant. However, the reactions were slow due to poor solubilities, and AMS was then selected. The choice of substrates and conditions was dictated by our desire to study homogeneous reactions and by the ease of preparation and analysis of the products. The mercaptan 2 was prepared from 1 by treating with thiourea and then with sodium hydroxide. Both 1 and 2, upon oxidation, should yield the same product, acetophenone (3); the production of the latter from 2 would involve the expected rapid hydrolysis of thioacetophenone (4) by base.

The oxidations were done under a nitrogen atmosphere at 87.8°C (solvent reflux) with equimolar amounts of AMS and substrate and 4 equivalents of NaOH. Aliquots of the reaction mixture were



removed at regular intervals, quenched, and analyzed by gas chromatography (GC) for acetophenone and/or starting material content relative to propiophenone (5) as an internal standard.

A steady, but slow, production of acetophenone was observed during the oxidation of 1-phenylethanol (Figure 2). Only about 13% oxidation had occurred in 20.8 hours. A pseudo first-order rate of $6.64 \times 10^{-3} \text{ hour}^{-1}$ was observed, and a half-life of 104 hours was calculated. A red color developed during the reaction; this was taken as qualitative evidence for the production of sodium anthrahydroquinonel-monosulfonate (AHMS). No other products were observed.

The treatment of 1-phenylethanesithiol (2) with AMS resulted in a rapid consumption of mercaptan and production of a red color. The disappearance of mercaptan did not follow first-order kinetics throughout the course of the run, probably because the concentra-

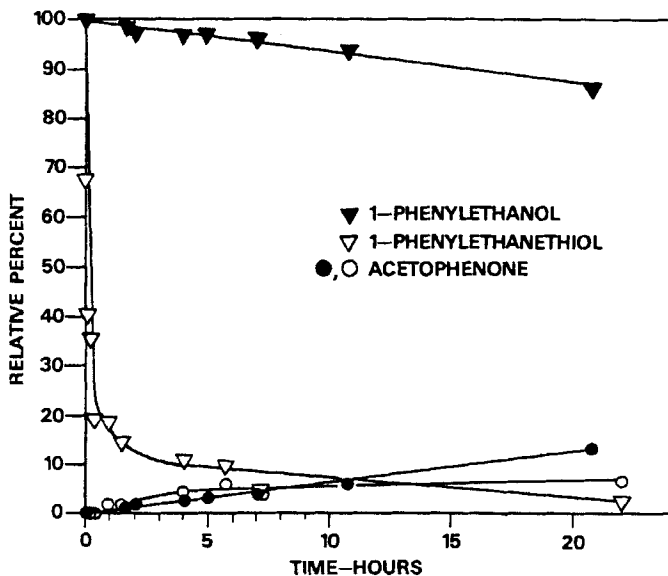
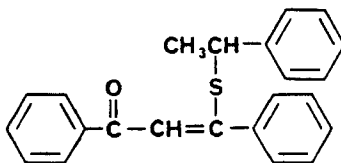


Figure 2. The product compositions for the AMS oxidations of 1-phenylethanol (∇ , \circ) and 1-phenylethanesithiol (∇ , \circ), each done separately.



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tion of AMS changed significantly with time (Figure 2). The initial pseudo first-order rate constant for the disappearance of mercaptan was 5.2 hour^{-1} , and the half-life was 7 minutes. The rate of acetophenone production was much less than mercaptan disappearance, suggesting that thioacetophenone (4) hydrolysis was relatively slow or that acetophenone was being consumed in side reactions. Thioacetophenone was not observed by GC-mass spectroscopy (MS).

A gold-colored precipitate was isolated from the 1-phenylethanthiol oxidation product mixture. The spectral evidence (^1H and ^{13}C -NMR, IR and GC-MS) for the gold precipitate suggested structure 6 (see Experimental Section). Attempts to confirm the structure 6 by synthesis were repressed by the strongly offensive odors of the compounds involved. There is no straight forward mechanism which could account for a structure such as 6 being produced from oxidation of 2.

An oxidation of an equal molar mixture of 1 and 2 with two equivalents of AMS produced the data shown in Fig. 3. The results again confirmed the high reactivity of the benzyl mercaptan relative to the alcohol; however, the reactivity was only about 1/3 of that observed in the previous experiment. The reactivity of the benzyl alcohol was also quite different (initially 180 times faster) from that observed previously. After the initial rapid loss, the alcohol concentration leveled off to about 60% of its original value. The acetophenone concentration steadily increased but not enough to account for substrate losses.

The above behavior suggests that the mercaptan is rapidly oxidized to thioacetophenone and that the latter can incorporate

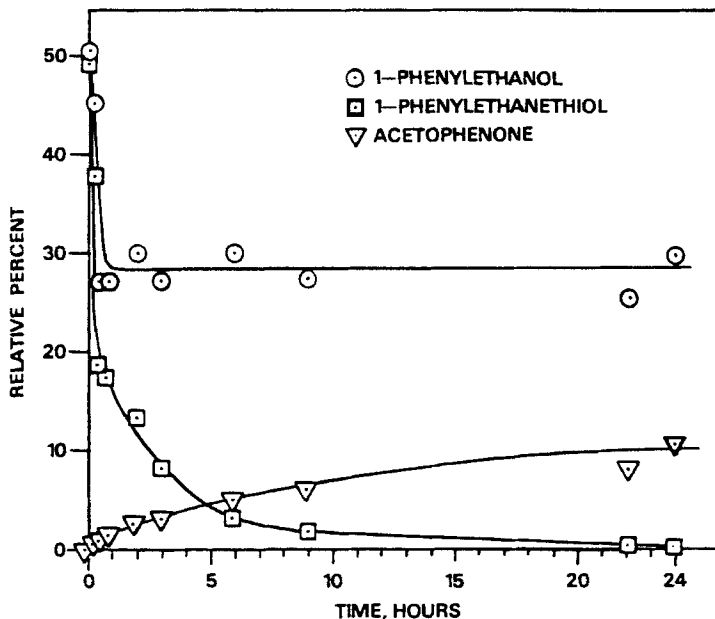


Figure 3. Product composition for the AMS oxidation of a 50/50 mixture of 1-phenylethanol and 1-phenylethanethiol.

molecules of either mercaptan or alcohol toward the production of secondary products. Alternatively, the mercaptan oxidation synergized the alcohol oxidation; this, however, should have given higher yields of acetophenone.

The competitive experiment also produced a precipitate. Analysis by GC-MS showed two principal components: the one (75% of the volatile products) was identical to the previously described material (mol.wt. 344), and the other (20% of the volatiles) had an apparent molecular weight of 274. One of the minor components had an apparent molecular weight of 240. The 274 and 240 molecular weights could result by combining 2 (mol.wt. 138) and 4 (mol.wt. 136), followed by loss of H_2S (mol.wt. 34), or 1 (mol.wt. 122) and 4, followed by loss of H_2O (mol.wt. 18).

DISCUSSION

Our results demonstrate that benzyl mercaptans oxidize much more rapidly than benzyl alcohols (half-lives of a few minutes vs.

about 100 hours) with AMS. The products of the mercaptan oxidation were acetophenone and an unknown (6). Since the principal product could not be thoroughly characterized, we are not certain as to what portion of the loss of the mercaptan was due to oxidation and what portion was due to secondary reactions with oxidized products. The mercaptan 2 was shown to be stable to the reaction conditions in the absence of AMS.

The reaction of a mixed system, benzyl mercaptan 2 and alcohol 1, with AMS produced some unusual data which suggest that benzyl alcohols can also be consumed by benzyl mercaptan oxidation products.

The redox potentials of the AQ/AHQ and derivative systems are low, in the range of 150-250 mV. Thus, any oxidative and reductive processes should be highly selective and limited to only certain components of wood. Assuming that the reactivities shown in this work for AMS and a model mercaptan can be projected to AQ and pulping, we believe that benzylic lignin mercaptans will participate in AQ/AHQ redox cycles. In the kraft/AQ pulping process, the oxidation of mercaptan components by AQ may provide unique, favorable alternatives for regenerating AHQ and, thus, influence the efficiency of delignification. A redox cycle involving mercaptans, rather than carbohydrate material, may serve to protect the carbohydrates from degrading oxidative reactions at 170°.

EXPERIMENTAL

A detailed description of the instrumentation used is given elsewhere.¹⁵ The GC analyses employed a column packed with 10% EGGS-XI on chromosorb P at 130°. Acetophenone, propiophenone, and 1-phenylethanol were purchased from Aldrich Chemical Company, Milwaukee, WI. Elemental analyses were done by MicroTech Laboratories, Skokie, IL.

1-Phenylethanethiol (2). - To a mixture of 38.1 g (0.50 moles) of thiourea in 50 mL of water at room temperature was added, 40 mL of concentrated hydrochloric acid followed by 60.3 mL (0.50 moles) of 1-phenylethanol. After refluxing for 28 hours, the mixture was

made basic by the dropwise addition of 22 g of sodium hydroxide in 30 mL of water and refluxed an additional 14 hours. Two phases resulted. The orange organic phase was separated and washed with a saturated salt solution and then pure water. The material, which possessed an extremely unpleasant odor, was vacuum distilled using an alkaline KMnO_4 trap to prevent the odor from escaping to afford 1-phenylethanethiol (51% yield): bp 76–79°/ 10–11 mm (lit.¹⁶ 83°/10 mm); IR (neat) 700, 762, 1450, and 1490 cm^{-1} and a marked absence of C–O–H signals; NMR (CDCl_3) δ 1.60 (d, 3, CH_3), 1.97 (d, 1, SH), 4.21 (q of d, 1, CH) and 7.31 (m, 5, aryl).

Oxidation of 1-phenylethanol (1). – A mixture of 2.66 g (4 equivalents) of NaOH and 5.16 g (1 equivalent) of AMS in 300 mL of 50/50 water/p-dioxane was refluxed under nitrogen for 90 minutes to dissolve the AMS. To the hot solution was added, 2.0 mL (1 equivalent) of 1-phenylethanol and the heating and stirring were continued. The color of the reaction mixture changed from light amber to a light cloudy red with the addition of 1-phenylethanol and after 20 minutes was deep red. At various times ranging from minutes to 25 hours, 10-mL aliquots of the reaction mixture were removed, quenched with 10 mL of 0.2N H_2SO_4 , and extracted with 10 mL of chloroform containing an internal standard (1.0 mL of propiophenone in 250 mL of CHCl_3). The chloroform extracts were collected, dried (Na_2SO_4), and analyzed by GC for the relative amounts of components compared with the propiophenone standard. The results were then compared with previously determined GC response factors for known mixtures. Figure 2 shows the data for acetophenone production from 1-phenylethanol. A plot of the natural logarithm of the ratio of the moles of 1 to the moles of 5 vs. time results in a straight line whose slope is $6.64 \times 10^{-3} \text{ hour}^{-1}$ (correlation coefficient of 0.99).

Oxidation of 1-phenylethanethiol (2). – The procedure was completely analogous to the 1-phenylethanol oxidation. Upon introduction of the mercaptan to the refluxing mixture, a very deep red color appeared instantaneously. The GC analysis produced the data shown in Fig. 2. A plot of the $\ln [2]/[5]$ vs. time gave

a line whose slope is 5.2 hour^{-1} (correlation coefficient of 0.99) for the first three data points (0-10 minutes).

Upon quenching the aliquots and the final reaction mixture with acid, we observed a gold-colored precipitate. Attempts to recrystallize the precipitate were not successful. It reprecipitated from ethanol-water as a granular material. In a blank reaction without AMS, no gold precipitate was produced; only 1-phenylethanethiol was recovered. A GC-MS analysis (OV-17 packing) of the precipitate showed one major volatile component (ca. 95%) and several minor components. The mass spectra consist of: m/e (%) electron impact 344 (10, M), 240 (37, M-PhCH=CH₂), 239 (89, M-PhCHCH₃), 139(10), 105 (100, PhCHCH₃ and/or PhCO), 79(11) and 77(12), chemical ionization (CH₄) 373 (8, M + C₂H₅), 345 (53, M + H), 241 (14, M + H - styrene) and 105 (100).

The ¹H-NMR (CDCl₃) showed δ 1.75 (d, 3, CH₃), 4.60 (q, 1, CH), 7.2-8.4 (M, 15, =CH and aryl) and minor signals at 1.6, 2.6, and 4.65. The ¹³C-NMR (CDCl₃) spectrum of the gold precipitate showed nine major signals in the aryl, vinyl region (123-134 ppm), a methyl signal at 23.4 (q), and a methine signal at 45.1 ppm (d). The NMR data clearly show only two aliphatic carbons, those of CH₃CH₂^X_{Ph}; by comparison, the methine signal when X = OH was at 4.8 and when X=SH was at 4.2 δ . The observed intermediate value of 4.6 and the abundance of aryl signals suggested structure 6.

Anal. calc. for C₂₃H₂₀OS (6): C, 80.23; H, 5.81; O, 4.65; S, 9.30. Found for the unpurified gold precipitate: C, 71.01; H, 4.23; O, 9.92; S, 11.17.

Competitive Oxidation of 1-phenylethanol and 1-phenylethanethiol. - The procedure was identical to the individual oxidations described above, except 2 equivalents of AMS were used for 1 equivalent each of 1 and 2, and less internal standard was employed. The results are given in Fig. 3. Quenching the reaction mixture with acid again gave a gold-colored precipitate, the analysis of which is described in the Results Section.

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