The Reactions of Alkaline Hydrogen Peroxide with Lignin Model Dimers.

Part 2. Guaiacylglycerol-β-Guaiacyl Ether *

S. Omori and C. W. Dence
Empire State Paper Research Institute, SUNY College of Environmental Science and Forestry, Syracuse, New York

Summary. Guaiacylglycerol-β-guaiacyl ether (I) was treated with alkaline hydrogen peroxide under simulated technical bleaching conditions in the presence and absence of a peroxide stabilization reagent, Na₅DTPA (sodium diethylenetriaminepentaacetate) and with molecular oxygen under similar conditions. The reaction products were characterized and their yields determined using a combination of gas chromatography and gas chromatography mass spectrometry.

In the reaction of I with peroxide, the principal reaction consisted of the displacement of the side chain (Dakin-like reaction) initiated by molecular oxygen and/or other peroxide decomposition products. The displaced side chain, α-0-(2-methoxyphenyl)glyceraldehyde, subsequently was dehydrated to α-guaiacoxycrolein which was oxidized by peroxide to guaiacol and glycolic acid. α-Guaiacoxycrolein also gave evidence of undergoing competing condensation reactions in the alkaline medium. The influence of Na₅DTPA in controlling peroxide decomposition was evident after comparing the yields and types of products formed when I was reacted with peroxide in the presence and absence of this stabilizer.

The findings are discussed in terms of their relationship to technical peroxide bleaching.

Introduction

In the previous paper in this series (Omori, Dence 1981), the behavior of three lignin model dimers of the phenacyl α-aryl ether type toward alkaline hydrogen peroxide under simulated technical bleaching conditions was examined. By conducting the reactions in the presence and absence of a peroxide stabilizer such as Na₅DTPA, the effect of peroxide decomposition into oxygen on the types and amounts of reaction products was assessed. Under the conditions imposed in these experiments, the dimers tested were found to be essentially unreactive toward oxygen. On the other hand, peroxide itself was found to have a pivotal role in such reactions as evidenced by the fact that the yields of certain products were enhanced by the addition of a peroxide stabilizer.

* Contribution No. 140 from the Empire State Paper Research Institute, State University of New York College of Environmental Science and Forestry, Syracuse, New York. The authors gratefully acknowledge financial support received from the Empire State Paper Research Associates, Inc.
In the work described below, guaiacylglycerol-β-guaiacyl ether, a dimer representing the most abundant structural element in lignin, was selected for a study paralleling the one cited above. Previous studies (Bailey, Dence 1969; Kempf, Dence 1975) involving the reaction of hydrogen peroxide with α-methylvanillyl and α-methylsyringyl alcohols confirmed the occurrence of a “Dakin like” reaction characterized previously by Kratzl et al. (1967). The latter authors portrayed the hydroperoxide radical as the active oxidant in the process:

More recently, Agnemo and Gellerstedt (1979) have reported that α-methylvanillyl alcohol, α-methylsyringyl alcohol, and creosol are completely stable in Na₅DTPA- or silicate stabilized peroxide solutions. These authors credited the reactions of compounds of this type to singlet oxygen formed by decomposition of unstabilized peroxide. With the foregoing in mind, the reactions of guaiacylglycerol-β-guaiacyl ether with alkaline hydrogen peroxide were examined, not only for the purpose of product characterization but also with a view to demonstrating the relationship between peroxide and its various decomposition products and the types and amounts of products generated in the reaction.

Results and Discussion

The compounds identified in the reaction of guaiacylglycerol-β-guaiacyl ether (I) with alkaline hydrogen peroxide and oxygen under various reaction conditions, together with their yields, are compiled in Table 1. The recovery of unreacted dimer is seen to be very nearly quantitative in the case where the peroxide was stabilized with Na₅DTPA, and in this respect the results duplicate the findings of Agnemo and Gellerstedt (1979). The relatively minor amounts of products which were detected in this particular instance may have resulted in part from a slight decomposition (estimated to be <2%) of the peroxide to oxygen even in the presence of the stabilizer. Hosoya et al. (1979) similarly have noted the unreactivity of I toward silicate-stabilized peroxide.

Sequences depicting the various reactions of guaiacylglycerol-β-guaiacyl ether with alkaline hydrogen peroxide are outlined in Fig. 1. Transformations yielding guaiacylglycerol (X), vanillin (XI), and vanillic acid (XII) account for only a very small fraction of the total amount of I consumed and will not be discussed further. The primary route accounting for the breakdown of the model dimer appears to consist of side chain displacement (Dakin-like reaction) and further modification of the two compounds formed thereby. These compounds, α-O-(2-methoxyphenyl)glyceraldehyde (II) and methoxy-p-benzoquinone (III), were not detected, however, as a consequence of their penchant for reacting further with alkali. The former compound was additionally oxidized to a very minor degree to α-O-(2-methoxyphenyl)glyceric acid (IX). The reactivity of II was established by heating an authentic sample in aqueous sodium hydroxide (pH 10.5) in the absence of peroxide but under conditions otherwise identical to those used in the presence of peroxide. As a result of this treatment, no