

INTERACTION OF SULFUR DIOXIDE AND NITRIC OXIDE WITH PHOTOIRRADIATED WOOD SURFACES

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ABSTRACT

Photoinduced free radicals on a southern pine surface were examined by electron spin resonance (ESR) spectroscopy. Phenoxy and carbon radicals were generated in cellulose, hemicelluloses, and lignin. While most of the phenoxy radicals were stable at 25 C, carbon and alkoxy radicals were unstable at that temperature. Nitric oxide readily reacted with carbon and alkoxy radicals to produce nonradical nitroso and nitrite products, respectively. However, only a portion of carbon radicals reacted with sulfur dioxide to produce sulfonyl radicals. Alkoxy radicals were reactive with sulfur dioxide to produce sulfite radicals. Sulfonyl and sulfite radicals were unstable at 25 C and terminated rapidly to form sulfinic acid and sulfonate ester, respectively. Phenoxy radicals were inert toward sulfur dioxide and nitric oxide. Reaction mechanisms among photoinduced free radicals, sulfur dioxide, and nitric oxide are discussed.

Keywords: ESR, electron spin resonance, cellulose, hemicelluloses, lignin, sulfonyl radical, sulfite radical, nitroso, nitrite, sulfinic acid, sulfonate ester.

INTRODUCTION

Photodegradation of wood surfaces has been known to occur via numerous free radical chain reactions. Several types of free radicals with different reactivity generated in cellulose, hemicelluloses, and lignin that are distributed on the photoirradiated wood surfaces have been recognized (Hon 1991). Some of these free radicals are active toward oxygen to produce hydroperoxide (Hon 1985; Hon and Feist 1992). The chemistry and kinetics of hydroperoxidation in the wood surface have been reported recently, and the formation of hydroperoxyl radicals and hydroperoxide end products have been confirmed (Hon 1985; Hon and Feist 1992).

In addition to oxygen, sulfur dioxide (SO₂) and nitric oxide (NO) are important gases in air pollution. Because of their high reactivity, these gases are likely to have ill-effects on the surface quality of wood when it is exposed to them. We have reported earlier that acid rain, which is developed due to the reaction among water, sulfur dioxide, and nitric oxide, has significant detrimental effects on chemical composition of exposed wood surfaces as well as their mechanical properties (Hon 1985, 1992). Although the consequence and the mechanisms of interaction between active gases and synthetic polymers have been known (Jellinek and Flajsman 1969a, b; Jellinek 1970), the mechanisms of the reaction between wood sur-

faces and gases have not been established. In this study, we investigated the interaction of sulfur dioxide and nitric oxide with wood surfaces that had been activated by ultraviolet light. The rate of interaction of photoinduced wood free radicals with sulfur dioxide and nitric oxide was monitored by an electron spin resonance (ESR) spectrometer. The formation of sulfonyl and sulfite radicals and nonradical products of nitrite and nitroso is discussed.

MATERIALS AND METHODS

Southern yellow pine (*Pinus* spp.) was used as the wood material. High purity sulfur dioxide and nitric oxide obtained from Union Carbide were used for this study. The surface of a radial section of the wood was microtomed and cut into a strip with a dimension of 30 mm \times 2 mm \times 100 μ m. The sample was inserted into a clear fused-quartz Surprasil tube and sealed in vacuum (10^{-6} mm Hg). It was then irradiated with a high-pressure quartz xenon-pact mercury lamp with a shortest wavelength of 223 nm at liquid nitrogen temperature, i.e., -196°C or 77 K. The reaction of sulfur dioxide and nitric oxide with a photoirradiated wood surface was performed by introducing each gas into the sample tube at a specific temperature, after breaking the seal at -196°C . Sulfur dioxide and nitric oxide were condensed rapidly into liquid at that temperature. After the photoirradiated wood contacted the liquid sulfur dioxide or nitric oxide for 5 min, the liquids were pumped off from the sample tube. The ESR studies were then performed. It is noteworthy that if the liquid sulfur dioxide and nitric oxide were left in the sample tubes, they would interfere with the ESR signals of wood specimens because of their paramagnetic characteristics.

A Varian E-12 ESR spectrometer with a 100-kHz magnetic field modulation, and equipped with a variable-temperature accessory, was used. The free radicals were monitored at 9,400 Mc/sec and 3,300 gauss. The g value was measured by comparison with Mn^{2+} in ZnS.

RESULTS AND DISCUSSION

Free radical characteristics of wood, sulfur dioxide, and nitric oxide

Wood does not contain any intrinsic free radicals (Hon et al. 1980). However, stable free radicals are frequently found on the wood surfaces, which can be easily detected by ESR spectroscopy. These stable free radicals are believed to be the phenoxy radicals generated in lignin during wood preparation, by oxidation, or by ultraviolet light irradiation (Hon 1987; Simkovic 1986).

Sulfur dioxide and nitric oxide accommodate unpaired electrons; hence they possess a paramagnetic property that can be detected by ESR. Since these gases are free radicals in nature, there is a high possibility that they will react with photoinduced free radicals in wood, which have been shown to be quite active toward oxygen, to create new free radicals (Hon 1985; Hon and Feist 1992). These free radicals could undergo secondary reactions that influence surface properties of wood.

Formation of free radicals in wood by ultraviolet light

Wood contains small amounts of stable free radicals. Much higher amounts of free radicals are generated on the wood surface when it is exposed to ultraviolet light. However, these photoinduced free radicals are very active, decaying rapidly at ambient temperature, and are capable of reacting with oxygen molecules to produce peroxy radicals. The decay, or secondary free radical reaction, of wood radicals usually leads to discoloration and loss of reflectance of the wood surface (Hon 1991). In order to trap these unstable free radicals, photoirradiation was conducted at -196°C (i.e., 77 K) to immobilize the labile free radical. Such trapped radicals exhibited a multiplet ESR signal as shown in Fig. 1. A strong singlet signal located at the center of the spectrum with one weaker signal at the low magnetic field and two weaker signals at the high magnetic field were observed. When the irradiated specimen was warmed from -196°C to -155°C for 60 sec

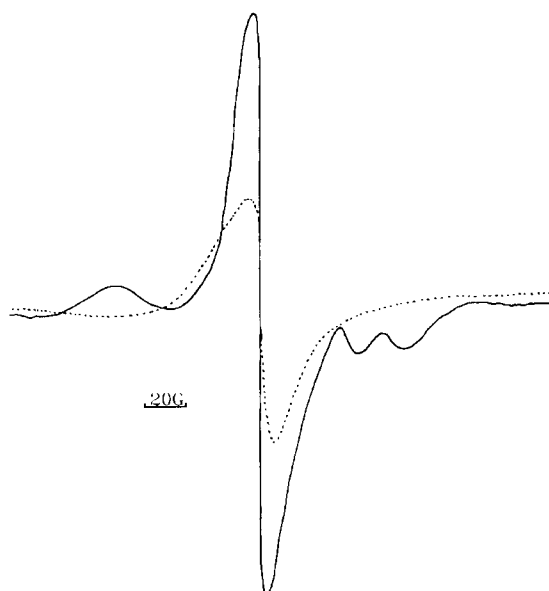


FIG. 1. A typical ESR spectrum of wood irradiated with ultraviolet light at -196°C . The dotted line signal was recorded at -196°C after the specimen was warmed to 25°C for 60 sec, and recorded at -196°C .

and the ESR recorded again at -196°C , no change of ESR signal intensity was observed. Likewise, no change was noticed for a specimen warmed to -50°C for 5 min. These warm-up experiments demonstrated that photoinduced free radicals were stable between -196°C and -50°C . However, when the specimen was warmed to 25°C for 60 sec and recorded again at -196°C , only a singlet signal with reduced intensity was registered. This implied that certain free radicals having short lives were decayed at 25°C . On the basis of our previous studies (Hon 1983, 1991), it is known that certain phenoxy radicals from lignin and alkoxy radicals from cellulose, which make up the major portion of the centered singlet signal, as well as carbon radicals generated from both cellulose and lignin, which make up the side-peak signals, decayed rapidly. These unstable free radicals served as the reaction sites to trigger additional free radical chain reactions. It should be noted that some of the phenoxy radicals located in the rigid structure, such as in a biphenyl structure, were stable even at 25°C .

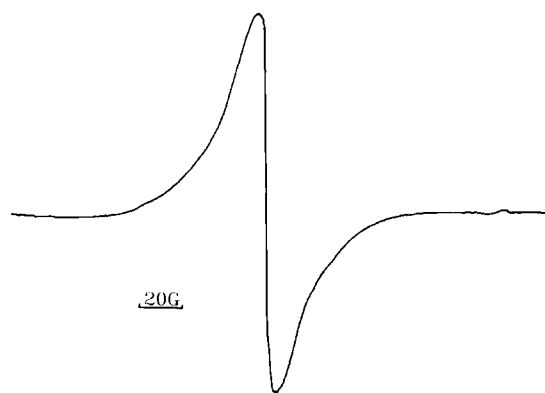


FIG. 2. A typical ESR signal of stable free radicals in wood. This signal was not influenced by the presence of NO and SO_2 .

Reaction of phenoxy radicals with active gases

When an unirradiated specimen was placed into an ESR sample tube and inserted into the ESR cavity at -196°C , a singlet signal with a line width of 15 gauss and a g value of 2.003 was detected due to the stable phenoxy radicals (Fig. 2). Sulfur dioxide and nitric oxide were introduced separately into the sample tubes at -50°C and -155°C , respectively. They were condensed inside the test tubes and allowed to contact the phenoxy radicals for 5 min. Sulfur dioxide and nitric oxide were then pumped out from the sample tubes, and ESR measurements were conducted again at -196°C , to examine any changes in the ESR signal pattern and intensity. An identical singlet ESR signal was detected from specimens treated with sulfur dioxide and nitric oxide. This suggested that stable phenoxy radicals in wood were not sensitive enough to react with sulfur dioxide and nitric oxide.

Reaction of photoinduced wood free radicals with active gases

When a wood specimen was irradiated with ultraviolet light at -196°C , it exhibited a multiplet signal (Fig. 3), as discussed earlier. Sulfur dioxide was then condensed into the sample tube at -50°C for 5 min and pumped away. An ESR measurement was performed again at

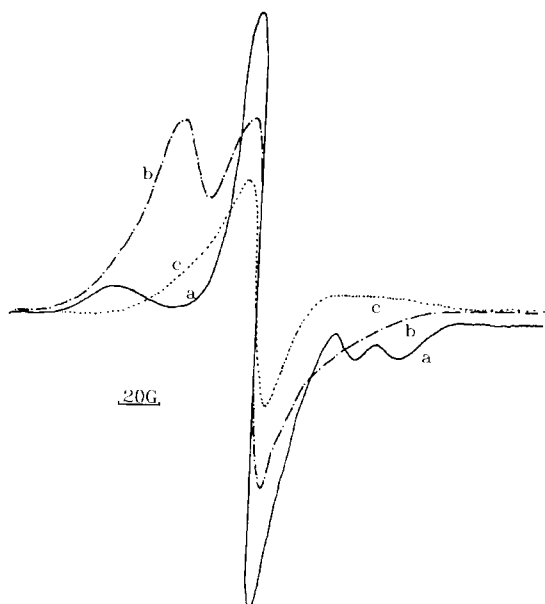


FIG. 3. Changes in ESR signal of wood irradiated with ultraviolet light at -196°C . (a) Original signal recorded at -196°C ; (b), recorded at -196°C after SO_2 was introduced into the irradiated specimen at -50°C for 5 min; (c) recorded at -196°C after specimen in (b) was warmed to 25°C for 60 sec.

-196°C , and the multiplet signal was transformed into an asymmetric singlet signal, which had a g_{\parallel} of 2.019 and a g_{\perp} of 2.002. The average of the g values was 2.010. These are likely due to the sulfonyl and sulfite radicals (Ueda et al. 1963). It is clear that photoinduced free radicals were able to react with sulfur dioxide to create sulfonyl and sulfite radicals. When the specimen was warmed to 25°C for 60 sec, and recorded again at -196°C , the asymmetric signal was further transformed into a singlet signal with a line width of 15 gauss. This suggested that sulfonyl and sulfite radicals were unstable and decayed rapidly at 25°C . The singlet signal having a g value of 2.003 was contributed from the phenoxy radicals. They were inert towards sulfur dioxide. The formation of sulfonyl groups at the wood surface exposed to sulfur dioxide and light had been substantiated by a Fourier transform infrared spectroscopic study (Hon and Chao 1989).

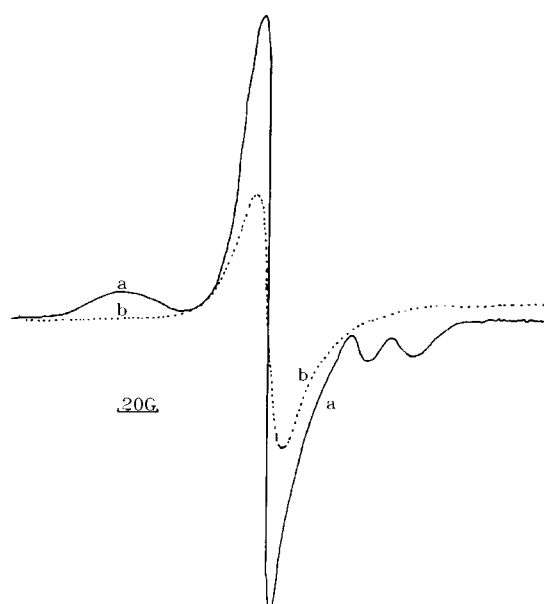


FIG. 4. Changes in ESR signal of wood irradiated with ultraviolet light at -196°C . (a) Original signal recorded at -196°C ; (b), recorded at -196°C after NO was introduced into the irradiated specimen at -155°C for 5 min.

After a wood specimen was irradiated with ultraviolet light at -196°C , nitric oxide was introduced into the sample tube at -155°C . It is interesting to note that the multiplet signal of wood free radicals disappeared and only a singlet signal with reduced intensity was detected (Fig. 4). When the sample was warmed to 25°C for 60 sec, the singlet signal remained unchanged. This suggested that carbon radicals, which contributed to the side peaks, and a portion of alkoxy radicals, which contributed to a part of the centered singlet signal, reacted rapidly with nitric oxide to produce nonparamagnetic products that could not be detected by ESR. The center singlet signal due to the phenoxy radicals was inert toward nitric oxide.

Interaction of sulfonyl radicals with nitric oxide

When the photoirradiated wood with sulfonyl and sulfite radicals was warmed to -155°C and nitric oxide was introduced into the sample tube for 5 min and pumped away, the

line-shapes of ESR signals of sulfonyl and sulfite radicals remained unchanged. However, the total signal intensity was reduced. This implied that sulfonyl and sulfite radicals had not reacted with nitric oxide. However, certain wood free radicals reacted with nitric oxide that resulted in a reduction of signal intensity. This also suggested that certain free radicals in wood were inactive towards sulfur dioxide but were reactive toward nitric oxide.

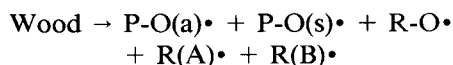
Interaction of nitric oxide-treated wood with sulfur dioxide

When the photoinduced wood free radicals were reacted with nitric oxide, nonparamagnetic products were formed, and only a singlet signal was detected at -155°C . When this specimen was warmed to -50°C and sulfur dioxide was introduced into the sample tube for 5 min and pumped away, the singlet signal remained unchanged. This suggested that all photoinduced free radicals, except phenoxy radicals, reacted with nitric oxide. No excess amount of free radicals was available to react with sulfur oxide.

These experiments demonstrate that all photoinduced wood free radicals were reactive with nitric oxide to form nonradical products, and only a partial amount of photoinduced free radicals was reactive with sulfur dioxide to produce sulfonyl and sulfite radicals. Phenoxy radicals were not reactive toward sulfur dioxide and nitric oxide.

Mechanisms of reactions among photoinduced free radicals, sulfur dioxide, and nitric oxide

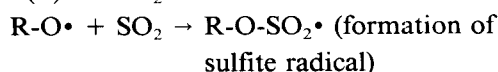
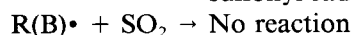
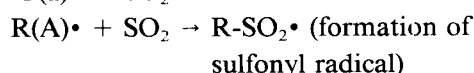
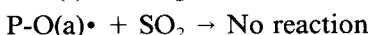
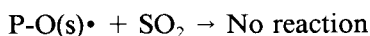
On the basis of ESR studies, valuable information is provided on the reactivity of photoinduced free radicals in wood with or without the presence of sulfur dioxide and nitric oxide. These studies also shed light on the selectivity of the reactions among photoinduced free radicals, sulfur dioxide, and nitric oxide. The following mechanisms can be deduced: Formation of free radicals in wood at -196°C by ultraviolet light:



where $\text{P-O(a)}\cdot$, $\text{P-O(s)}\cdot$, $\text{R-O}\cdot$, $\text{R(A)}\cdot$ and $\text{R(B)}\cdot$ were active phenoxy radicals, stable phenoxy radicals, alkoxy radicals, group A carbon radicals, and group B carbon radicals, respectively.

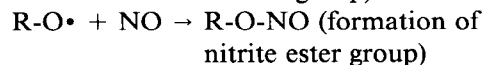
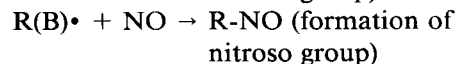
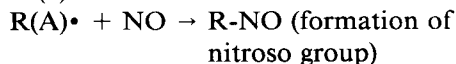
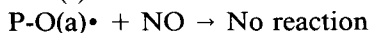
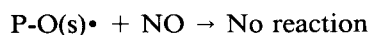
At 25°C , $\text{P-O(a)}\cdot$, $\text{R(A)}\cdot$ and $\text{R(B)}\cdot$ decayed rapidly and stabilized, whereas $\text{P-O(s)}\cdot$ remained stable.

When photoinduced wood free radicals were exposed to sulfur dioxide:



Sulfonyl and sulfite radicals were unstable at 25°C . They are likely to convert into sulfinic acid and sulfonate ester.

When photoinduced wood free radicals were exposed to nitric oxide:



The R(B) group was more reactive with nitric oxide than sulfur dioxide.

CONCLUSIONS

Phenoxy, alkoxy, and carbon radicals were generated on wood surface when irradiated with ultraviolet light. Phenoxy radicals were quite stable at 25°C , whereas alkoxy and carbon radicals decayed rapidly at that temperature. Phenoxy radicals were also inert toward sulfur dioxide and nitric oxide. All carbon radicals or alkoxy radicals were capable of reacting with