

HYDROPEROXIDATION IN PHOTOIRRADIATED WOOD SURFACES

David N.-S. Hon

Professor
Wood Chemistry Laboratory
Department of Forest Resources
Clemson University
Clemson, South Carolina 29634-1003

and

William C. Feist

Supervisory Research Chemist
USDA Forest Service
Forest Products Laboratory
Madison, Wisconsin 53705-2398

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ABSTRACT

Wood surfaces are susceptible to photooxidation to produce hydroperoxide. Diffuse reflectance spectroscopy coupled with Fourier transform infrared spectrophotometry (DRIFT) was used to detect hydroperoxide without any sample preparation or damaging the oxidized surfaces. The appearance of a doublet absorption peak at $3,550\text{ cm}^{-1}$, due to the hydroperoxide, was detected from the tangential section of a southern yellow pine, irradiated with lights of $\lambda > 223$ and $\lambda > 300$ nm. More hydroperoxide was detected from the specimens irradiated with the latter light source. Competitive reactions between hydroperoxide formation and decay revealed that at the initial 90 days of irradiation with light of $\lambda > 300$ nm, the rate of formation exceeded the rate of degradation. When the wood was irradiated with light of $\lambda > 223$ nm, most of the hydroperoxide was generated and converted simultaneously into carbonyl groups. This chemical conversion was also observed from the specimen irradiated above 65 C. ESR was used to monitor the formation and decay of the hydroperoxide radical. The kinetics of hydroperoxidation and mechanisms of hydroperoxide formation are discussed.

Keywords: Diffuse reflectance spectroscopy, discoloration, hydroperoxide, southern yellow pine, red oak, radicals, cellulose, hemicelluloses, lignin.

INTRODUCTION

Autoxidation of wood surfaces is a very slow process. However, the rate of oxidation can be accelerated by ultraviolet light, heat, and metal ions (Scott 1965). Of these, ultraviolet light can be singled out as a prevailing factor that contributes to fast oxidation. Several papers (Feist and Hon 1984; Fengel and Wegener 1984; Hon 1991) have dealt with photooxidation of wood, in which degradation of cellulose, hemicelluloses, and lignin was observed. Surface modification by ultraviolet light is also manifested by the ultimate formation of oxygenated species such as carbonyl and carboxyl groups ac-

companied by discoloration (Hon and Chang 1984). The hydroperoxide group that appears at the early state of oxidation is the key functional group that leads to a clear understanding of the primary mechanism of oxidation. Although formation of hydroperoxide products has been identified (Hon et al. 1982), no detailed study has been reported on the formation and decay of such products. Such a situation is not really surprising since hydroperoxide usually appears at a low stationary concentration, and analytical techniques were limited to chemical titration in solutions and conventional dispersive IR spectroscopy.

Chemical titrations provide high sensitivity but are nonspecific. Dispersive IR spectrometry is more informative on the structure of hydroperoxide, but the energy levels are generally not sensitive enough to detect hydroperoxide. Fortunately, the recent commercial appearance of Fourier transform infrared (FTIR) spectroscopy has alleviated this problem (Griffiths 1975; Hon 1986). In FTIR, an interferometer is utilized instead of the prisms and slits used in the conventional dispersive IR spectrometry with the advantage that all wavelengths can be scanned simultaneously. Since each FTIR scan takes only 1.5 sec, it is practical to make repeated scans, which has the effect of increasing the signal-to-noise ratio and hence the sensitivity of the techniques. Diffuse reflectance (DR) spectroscopy is used to study the reflection and absorption of chemical groups at a surface without any sample preparation or modification of the surface of the material. It is essentially a nondestructive technique. Hence, the combined operation of FTIR and DR spectroscopy, the so-called DRIFT operation, has provided a beneficial tool to analyze and characterize the hydroperoxide group generated on wood surfaces.

In this paper, the usefulness of a diffuse reflectance spectroscopy coupled with Fourier transform infrared spectroscopy to identify hydroperoxide product is demonstrated. The formation and decay of hydroperoxide are monitored by means of electron spin resonance spectroscopy.

MATERIALS AND METHODS

Southern yellow pine (*Pinus* spp.) and red oak (*Quercus* spp. *Erythrobalanus*) were used as the wood materials. For DRIFT examination, specimens with microtomed transverse, radial, and tangential surfaces with dimensions of 1 × 1 × 1 inches were prepared for ultraviolet light irradiation. For ESR study, specimens with dimensions of 30 mm × 2 mm × 100 μm were prepared.

For DRIFT study, wood specimens were irradiated with a high-pressure quartz xenon-compact mercury lamp with a lowest wavelength

of 223 nm. A pyrex filter that cut off wavelengths shorter than 300 nm was also used. The distance between the light source and specimens was 50 cm, and the irradiation was conducted in a chamber with a temperature controller. A Nicolet 20 DX FTIR spectrometer was used to obtain 2 cm⁻¹ resolution spectra over the 4,000 to 400 cm⁻¹ region. The spectrometer was equipped with a liquid-nitrogen-cadmium telluride (MCT) detector. The sample chamber was allowed to come to equilibrium with a continuous nitrogen purge prior to data collection. A Harrick diffuse reflectance accessory, which can be placed inside and removed from the sample chamber, was used. The irradiated specimens were placed in the sample holder in the center of the diffuse reflectance accessory and scanned 500 times.

For ESR study, the wood specimen was inserted into a quartz sample tube, which was then inserted into a Dewar filled with liquid nitrogen, and irradiated with ultraviolet light. A Varian E-12 X-band ESR spectrophotometer was used to detect the formation and decay of free radicals generated on the wood surfaces. To avoid distortion of the ESR spectra by power saturation, the ESR measurements were carried out at a microwave power of 2 mW. All spectra were measured at 77 K (-196 C).

RESULTS AND DISCUSSION

DRIFT spectra of photoirradiated wood surfaces

When specimens of southern yellow pine and red oak were irradiated with ultraviolet lights with wavelengths of $\lambda > 223$ nm and $\lambda > 300$ nm, changes in infrared spectra, indicating changes in chemical and functional groups, were observed. Typical FTIR spectra of a non-photoirradiated (A) and a photoirradiated southern yellow pine (B) are shown in Fig. 1. It is of particular interest to notice the changes in the absorption regions 1,100-1,200 cm⁻¹, 1,510-1,610 cm⁻¹, 1,720 cm⁻¹, and 3,550 cm⁻¹, due to the C-O-C bridge of cellulose, aromaticity of lignin, carbonyl and hydroperoxide functional groups, respectively (Chan and

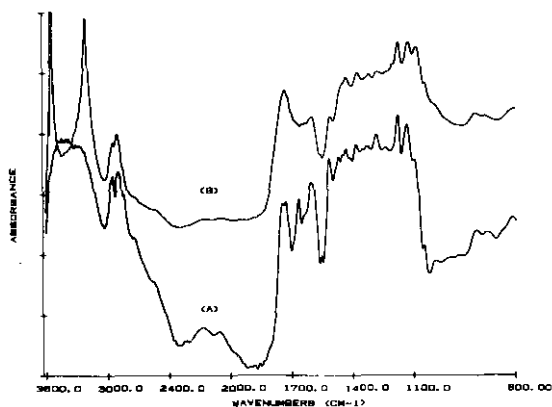


FIG. 1. FTIR spectra of a tangential surface of southern yellow pine. A, control specimen; B, specimen photoirradiated for 60 days.

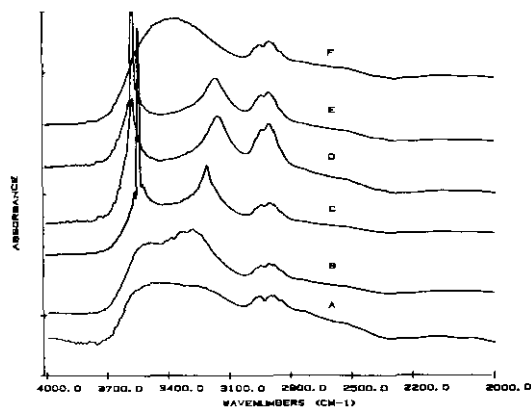


FIG. 2. The change in FTIR spectra of a tangential surface of southern yellow pine irradiated with ultraviolet light. Irradiation time: A, control; B, 30 days; C, 60 days; D, 90 days; E, 120 days; F, 150 days.

Coxon 1987; Hon 1991; Morohoshi 1991). The magnitude of reduction was greater for specimens irradiated with $\lambda > 223$ nm. The reduction of the absorbance band 1,110–1,200 cm^{-1} was observed for specimens irradiated with $\lambda > 223$ nm. However, with the irradiation of light $\lambda > 300$ nm, this change can be seen only from the radial and tangential surfaces of red oak and tangential surface of yellow pine. Hydroperoxide could be detected only on the tangential surface of southern yellow pine with both lights, and the magnitude was larger for the specimens irradiated with the light of $\lambda > 300$ nm. These variations manifested the non-uniform distribution of wood chemical components on the wood surfaces. The degree of interaction between these components at different locations in the cell walls and with different light energies produced different oxidized products. Some chemicals distributed at the tangential surfaces of the southern yellow pine were inclined to react with light and oxygen readily to produce a high amount of hydroperoxide product.

Formation of hydroperoxide in photoirradiated wood surface

The rate of hydroperoxide formation as a function of irradiation time, for up to 150 days, was studied. An array of DRIFT spectra re-

corded for specimens irradiated with light of $\lambda > 300$ nm is shown in Fig. 2. It is obvious that no absorption band located at 3,500 cm^{-1} , which is due to the hydroperoxide functionality, was observed for control specimens (Fig. 2A). For the specimen that had been irradiated for 60 days, two peaks with a broad absorption band at 3,500 cm^{-1} can be seen, and the absorption band increased its intensity when the specimen was further irradiated for 120 days. However, it is of interest to note that when the specimen was irradiated for more than 150 days, the absorption band due to the hydroperoxide disappeared, indicating the deterioration of the functional group. The overall changes in absorption intensity of 3,550 cm^{-1} as a function of irradiation time are illustrated in Fig. 3. The figure also illustrates a peculiar behavior of change in absorption intensity at peak 3,550 cm^{-1} for the specimens irradiated with light of $\lambda > 223$ nm. The absorption intensity of peak 3,550 cm^{-1} increased during the initial 45 days of irradiation and decreased in the next 30 days of irradiation. The intensity increased gradually again after 90 days of irradiation and decreased again after 120 days of irradiation. The overall intensity of hydroperoxide from these specimens were much weaker than that obtained from specimens irradiated with light of $\lambda > 300$ nm. During the

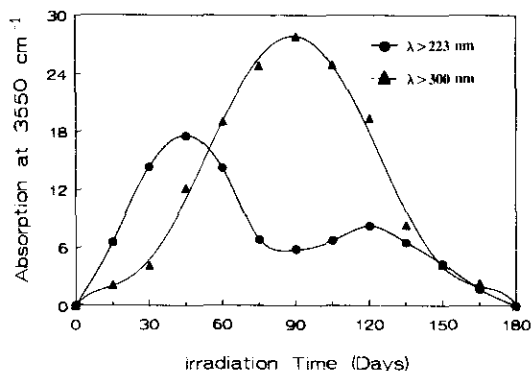


FIG. 3. Changes in hydroperoxide FTIR absorption peaks of the specimen irradiated with ultraviolet lights as a function of irradiation time.

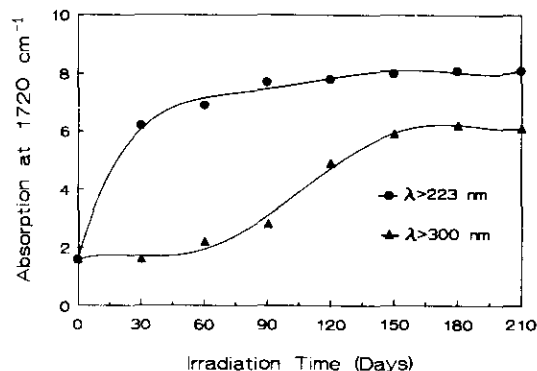


FIG. 4. Changes in carbonyl FTIR absorption peaks of the specimen irradiated with ultraviolet lights as a function of irradiation time.

same period of ultraviolet irradiation, a rapid increase in the absorption peak at $1,720\text{ cm}^{-1}$ of wood specimens being irradiated was observed for both lights, as shown in Fig. 4. This suggests that carbonyl groups are generated at the oxidized surfaces. The specimens irradiated with light of $\lambda > 223\text{ nm}$ exhibited a stronger absorption peak than those with light of $\lambda > 300\text{ nm}$, and the rate of formation of carbonyl groups was much faster for the specimens irradiated with the shorter wavelength.

An induction period seemed to be required for specimens irradiated with the longer wavelength. By comparing Figs. 3 and 4, the correlation between the changes in the peak absorptions at $3,550\text{ cm}^{-1}$ and $1,720\text{ cm}^{-1}$ is seen.

It is apparent that the reduction of peak absorbance at $3,550\text{ cm}^{-1}$ has contributed to the increase of peak absorbance at $1,720\text{ cm}^{-1}$, especially for specimens irradiated with light of $\lambda > 300\text{ nm}$. Hence, the destruction of hydroperoxide is likely contributing to the generation of carbonyl groups. Although only a lesser amount of hydroperoxide was detected from the specimens irradiated with light of $\lambda > 223\text{ nm}$ (Fig. 3), higher amounts of carbonyl groups were generated. This indicates that most of the carbonyl groups detected in the specimens were generated by light directly. During irradiation, it is also very likely that hydroperoxide generated was decomposed instantly to carbonyl groups. The instability of hydro-

peroxide in light of $\lambda > 223\text{ nm}$ will be discussed in a subsequent section. This also suggested that the carbonyl groups formed in the specimens irradiated with light of $\lambda > 300\text{ nm}$ are most likely due to the conversion of hydroperoxide.

Stability of hydroperoxide

It has been reported that hydroperoxide is very unstable against heat and light (Hon 1979; Hon and Glasser 1979). As discussed earlier, a more intense hydroperoxide signal was observed from the specimens irradiated with light of $\lambda > 300\text{ nm}$, suggesting that hydroperoxide initially generated from the specimens irradiated with light of $\lambda > 223\text{ nm}$ was simultaneously decomposed by the same light and converted to carbonyl groups. This explains the observation that fewer hydroperoxide and more carbonyl groups were observed from the specimens irradiated with light of $\lambda > 223\text{ nm}$. The stability of hydroperoxide was also examined with specimens irradiated with $\lambda > 300\text{ nm}$ for 60 days at temperatures ranging from 30 to 90 C. The stability of hydroperoxide was examined in terms of the IR absorption peak at $3,550\text{ cm}^{-1}$. The results are summarized in Fig. 5. It is obvious that photo-induced hydroperoxide was stable below 65 C; above this temperature, it decomposed rapidly. For the specimens irradiated at 80 C, only a weak and broad signal was observed.

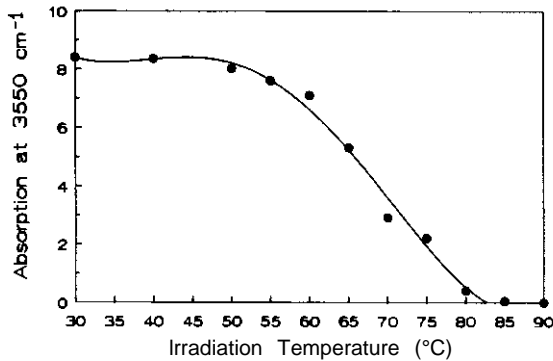


FIG. 5.

ESR studies of hydroperoxy radicals in wood

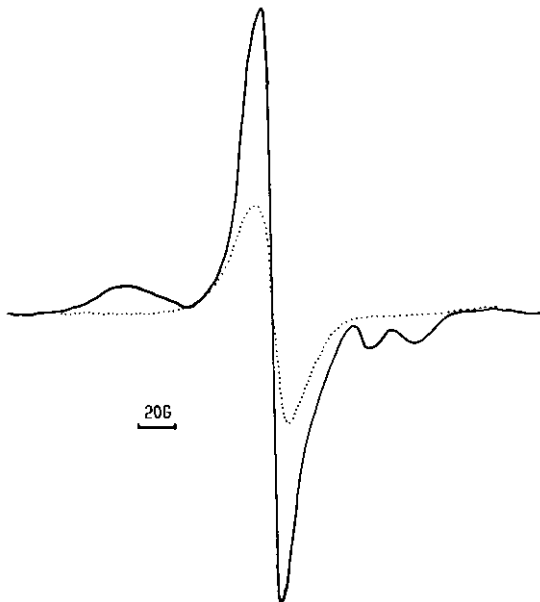


FIG. 6. ESR spectra of southern yellow pine irradiated with ultraviolet light in vacuum for 60 mins at 77 K. The singlet signal (----) was observed after the irradiated specimen was warmed to ambient temperature for 60 sec. All spectra were recorded at 77 K.

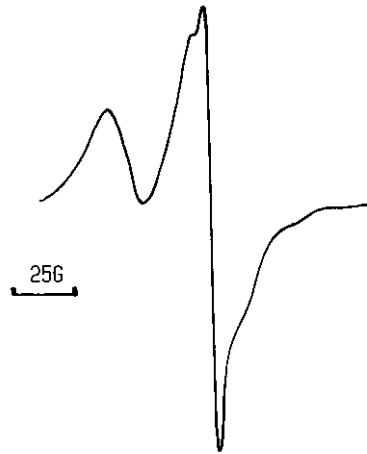


FIG. 7. A typical ESR spectrum of peroxy radicals in photoirradiated southern yellow pine.

with a strong singlet signal with a line width of 15 gauss in the center was observed (Fig. 6). When the irradiated specimen was warmed from -196 C to ambient temperature and held at that temperature for 60 sec, this multiplet ESR signal was converted into a singlet signal, indicating that free radicals contributing to the side peaks decayed rapidly at ambient temperature, whereas the stable free radicals contributing to the singlet signal remained unchanged. Based on our previous studies (Hon 1983, 1987), it is apparent that the unstable free radicals were generated in cellulose, whereas the stable free radicals were phenoxy radicals generated in lignin. When the specimens were irradiated in the presence of liquid oxygen at -196 C for 60 mins, an asymmetric singlet signal with an average g -value of 2.0023 was observed (Fig. 7). Because of the similarity of the ESR pattern as well as the g -value to those from hydroperoxy radicals formed in cellulose and lignin, it is believed that photo-induced free radicals generated in wood are capable of reacting with oxygen molecules to produce hydroperoxy radicals. When the irradiated specimen was warmed to ambient temperature, the asymmetric singlet signal of hydroperoxide was rapidly transformed into a singlet signal, signifying the instability of hydroperoxide radicals at ambient temperature.

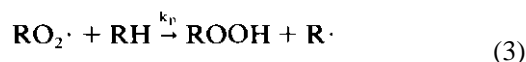
Mechanism of hydroperoxidation and formation decomposition

Kinetic of initiated oxidation. – It has been known for a long time that chemical reaction between atmospheric oxygen and organic components at wood surfaces at ambient temperature is a very slow process. However, the rate can be enhanced by metal ions and light. In common with other radical chain reactions in polymers, photooxidation of wood surfaces can be divided into three separate processes: initiation, propagation, and termination, as indicated below:

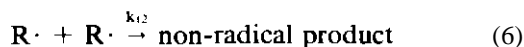
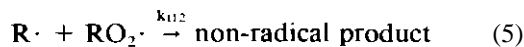
Initiation:



Propagation:



Termination:



where RH represents chemical components, such as cellulose, hemicelluloses, and lignin, at the wood surface.

From these mechanisms, the rate of oxidation can be illustrated as follows:

$$\frac{d[O_2]}{dt} = k_p[R\cdot][O_2] \quad (7)$$

Using the usual steady-state assumptions, the rate of chain initiation can be illustrated as follows:

$$R_1 = k_{i1}[ROO\cdot]^2 + 2k_{i12}[R\cdot][ROO\cdot] + k_{i2}[R\cdot]^2 \quad (8)$$

If k_{i12} is equal to $(k_{i1}k_{i2})^{1/2}$, Eq. (8) can be derivatized into Eq. (9):

$$R_1 = (k_{i1}[ROO\cdot] + k_{i2}[R\cdot])^2 \quad (9)$$

At the initiation stage, if $R\cdot$ or $ROO\cdot$ is the only product or both are formed, the rate of oxidation can be illustrated in Eqs. (10), (11) and (12), respectively.

$$\frac{d[O_2]}{dt} = \frac{k_o[O_2]R_1^{1/2}(k_p[RH] + k_{i1}^{1/2}R_1^{1/2})}{k_p k_{i2}^{1/2}[RH] + k_o k_{i1}^{1/2}[O_2] + (k_{i1}k_{i2}R_1)^{1/2}} \quad (10)$$

$$\frac{d[O_2]}{dt} = \frac{k_o k_p [O_2][RH]R_1^{1/2}}{k_p k_{i2}^{1/2}[RH] + k_o k_{i1}^{1/2}[O_2] + (k_{i1}k_{i2}R_1)^{1/2}} \quad (11)$$

$$\frac{d[O_2]}{dt} = \frac{k_o[O_2]R_1^{1/2}(2k_p[RH] + k_{i1}^{1/2}R_1^{1/2})}{k_p k_{i2}^{1/2}[RH] + k_o k_{i1}^{1/2}[O_2] + (k_{i1}k_{i2}R_1)^{1/2}} \quad (12)$$

If the system is rich in oxygen, then the rate of oxidation becomes:

$$\frac{d[O_2]}{dt} = k_p[RH]\left(\frac{R_1}{k_{i2}}\right)^{1/2} \quad (13)$$

If the system is low in oxygen, then the rate of oxidation becomes:

$$\frac{d[O_2]}{dt} = k_p[O_2]\left(\frac{R_1}{k_{i2}}\right)^{1/2} \quad (14)$$

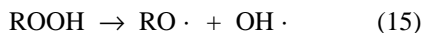
Formation mechanisms. – When wood is irradiated with ultraviolet light, free radicals are generated at the surfaces due to the dehydrogenation, dehydroxylation, dehydroxymethylation, demethoxylation, and chain scission that occurs in cellulose, hemicellulose, and lignin distributed at the wood surface (Eq. 1) (Hon 1991). The presence of oxygen in the system provides the opportunity for oxygen molecules to react with free radicals in wood to generate hydroperoxy radicals (Eq. 2), which in turn abstract protons to produce hydroperoxides (Eq. 3). This can be seen from the transformation of a multiplet signal of ESR, due to the various carbon radicals, to an asymmetric singlet signal, due to the hydroperoxy radicals. Singlet oxygen, resulting from the interaction of ultraviolet light and molecular oxygen, and its subsequent attack on wood surfaces have been proved as another possible initiation route for hydroperoxide formation (Hon et al. 1982).

From both initiation routes, the presence of hydroperoxide was detectable by DRIFT and by chemical titration (Hon et al. 1982).

Like any other radical species, the hydroperoxy radical will terminate itself by reaction with other radical species available in the environment (Eqs. 4–6). It appears that at the initial stage of oxidation, the rate of propagation is much larger than the rate of termination. Hence, the accumulation of DRIFT signal can be observed prior to 90 days of irradiation for the specimens irradiated with light of $\lambda > 300$ nm. However, as the irradiation time was prolonged, the rate of termination or decay was larger than the rate of propagation, leading to the reduction of DRIFT signal intensity.

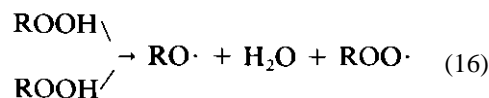
The energy of light quanta of wavelength below 320 nm is sufficient to cleave RO-OH and R-OOH bonds, but not ROO-H bonds, which have dissociation energies of 42, 70 and 90 kcal/mol, respectively (Benson 1965). Hence, the photolysis of RO-OH and R-OOH predominate in the decomposition reaction. However, ROO-H can be cleaved by light of $\lambda > 223$ nm. It should also be borne in mind that the decomposition of hydroperoxides can also be induced by raising the temperature.

During the photoirradiation of wood, it is clear that there are competitive reactions between the formation and decomposition of hydroperoxide, especially with the light of $\lambda > 223$ nm. The overall rate of decomposition appeared to be larger than the rate of formation. It is quite different with the light of $\lambda > 300$ nm. Initially, the concentration of hydroperoxide that formed at the wood surface was small. In the presence of ultraviolet light, it decomposed by a monomolecular mechanism:



The decomposition of one hydroperoxide molecule generates two radicals. Both can initiate photooxidation and generate one new hydroperoxide each (more as a chain reaction is initiated). Therefore, hydroperoxide is produced faster than it decomposes and starts to

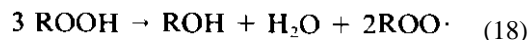
accumulate. As more hydroperoxide is produced, it tends to decompose by a bimolecular mechanism:



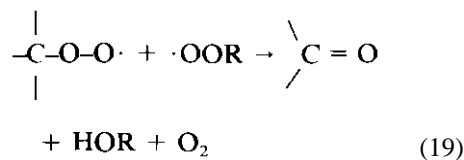
As two molecules are decomposed, only two radicals are generated; and the rate of production thus decreases compared with the rate of destruction. At higher local concentrations, induced decomposition also occurs:



and the overall reaction (16) + (17) becomes:



This also contributes to a rapid decrease of hydroperoxides. Moreover, at high local concentrations, hydroperoxy radicals produced close together are more likely to recombine than to propagate a chain reaction:



CONCLUSIONS

The hydroperoxidation of wood surfaces can be readily detected by using the DRIFT technique without any sample preparation and destroying the surface. The ESR technique also provided valuable information on the free radical formation mechanism that explains the formation of hydroperoxide. Experimental results revealed that hydroperoxide can be detected only on the tangential surface of southern yellow pine with lights of $\lambda > 223$ nm and $\lambda > 300$ nm, and the magnitude was larger with the latter light. No hydroperoxide was detected from red oak. Results also proved that free radicals generated in wood react readily with oxygen molecules to produce hydroperoxide. More hydroperoxide was detected from the specimens irradiated with light of $\lambda > 300$ nm; however, most of the hydroperoxides gen-

erated from the specimens irradiated with light of $\lambda > 223$ nm were decomposed rapidly to produce carbonyl groups. Hence, more carbonyl groups were detected from the specimens irradiated with the latter light source. A competitive reaction between formation and destruction of hydroperoxide appears to be occurring during the photoirradiation, and the hydroperoxide is unstable above 65 C.

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