

## Short Communications

## The Free Radical Content in Wood and Lignins

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It is known that any lignin prepared from wood contains significant amounts of organic free radicals of exceptional stability with respect to time and chemical attack.<sup>1-4</sup> Uncertainty exists, however, on the question as to what degree these radicals are originally present in wood protolignin or chemically or mechanically introduced during the isolation procedures. An answer to this question is of interest both with respect to the free radical polymerization reactions involved in the lignification of wood<sup>5</sup> and to the reactivity of lignin. We have carried out some investigations to further explore this question.

*Experimental.* The electron spin resonance spectra were recorded with a Varian E-3 spectrometer. This instrument operates at about 9.5 GHz with a modulation frequency of 100 kHz. Spin concentrations were estimated by comparison with a diphenylpicrylhydrazyl standard, assuming the number of radicals to be proportional to signal height times signal width squared.

*Results.* Table 1 shows the free radical contents of various lignin preparations. These are in reasonable agreement with

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Table 1. Free-radical contents of various lignin preparations and air dry spruce sapwood meal.

Sample	10 <sup>-17</sup> × Spins/g
Milled wood lignin, spruce	0.6
Pew's lignin, spruce	0.9
Spruce decayed by <i>Lenzites trabea</i> (71.4 % weight loss)	1.3
Sweetgum decayed by <i>Poria monticola</i> (78 % weight loss)	3.2
Kraft lignin from softwood	1.0
Methylated kraft lignin from softwood <sup>a</sup>	0.7
Indulin AT	0.9
Air dry spruce sapwood meal	2.0

<sup>a</sup> Methylated with dimethyl sulfate.

values previously reported for similar preparations.<sup>2-4</sup> It is noticeable that although isolated under widely different conditions, softwood lignins have rather similar free radical contents. Somewhat surprising is also the result that air dry spruce sapwood meal has a higher free radical content than all softwood lignins studied here.

It has previously been shown that grinding<sup>6</sup> and exposure to daylight<sup>7</sup> may introduce free radicals in wood. To obtain wood samples free from the influence of these factors one loblolly pine tree and one yellow poplar tree were harvested. In a photographic dark room, "match stick" samples were cut out with a razor blade and transferred to ESR sample tubes. The samples were kept in the dark until the ESR measurements could be carried out, approximately 72 h after the harvesting of the trees.

As shown in Table 2, wood samples prepared in this way have free radical contents which in the case of loblolly pine and yellow poplar heartwood cannot be detected or are in the magnitude of 0.1-0.2 % of the

Table 2. Free radical contents of various fresh wood samples.

Sample	Original samples stored in the dark $10^{-14} \times$ Spins/g	Storage in laboratory light	
		72 h	126 h
		$10^{-14} \times$ Spins/g	$10^{-14} \times$ Spins/g
Loblolly pine, cambium	$\sim 1$	150	400
" sapwood	<sup>a</sup>	4	8
" heartwood	$\sim 1$	20	30
Yellow poplar, cambium	50	90	100
" , sapwood	20	50	60
" , heartwood	<sup>a</sup>	40	200

<sup>a</sup> Not detectable.

radical contents in lignin and wood meal (cf. Table 1). Considering the possibility that these small amounts could have been introduced during sample preparation, these results suggest, in accordance with Rex,<sup>1</sup> that the existence of free radicals in protolignin is highly questionable. Table 2 also shows that on open storage of the equivalent wood samples in daylight, free radicals are formed. Surprisingly fast, radical concentration levels are reached which are comparable to those of the lignin preparations. This is probably due to the influence of light and possibly also fungal attack.

In separate experiments it was found that on dissolving spruce milled wood lignin (MWL) in dioxane, the free radicals disappeared quantitatively. Since MWL is isolated from milled wood by extraction with dioxane, the free radicals normally found in such lignin must have been formed after its isolation and most probably due to the influence of daylight. Based on these findings, the question may be raised if the stable values found for the free radical contents of lignin, really are due to a high degree of stability of the radicals or rather represent steady state concentrations where radicals react, e.g. with air oxygen and new radicals are formed due to the influence of light during storage.

In Fig. 1 it is shown for three different lignin preparations that on storage in the dark, significant reductions in the free radical contents may occur even after a relatively short period of time. Based on these data it is concluded that at least part of the free radicals in lignin preparations are not stable. This indicates that

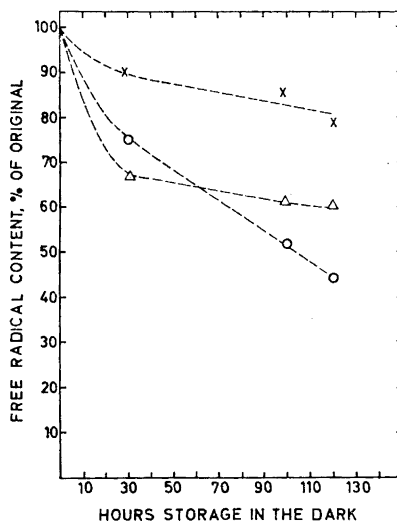


Fig. 1. Free radical content of various lignin preparations as a function of time of storage in the dark.

× Indulin AT (Kraft lignin); O Sweetgum decayed by *Poria monticola* (78 % weight loss); Δ Spruce decayed by *Lenzites trabea* (71.4 % weight loss).

a continuous change in the chemical structure of such lignins takes place on storage in daylight. The observations demonstrate the importance of excluding the influence of daylight for reliable free radical studies of lignin and wood.

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## Electron Spin Resonance Studies of the Nitroxide Radicals Formed in the Reaction between Nitrogen Dioxide and Dimethyl Sulphoxide

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Previous electron spin resonance (ESR) studies have demonstrated that free radicals are formed in solutions containing nitrogen dioxide  $\text{NO}_2$ , and a variety of different organic substances.<sup>1-3</sup> Thus, the radicals observed with compounds containing the groups  $-\text{CH}_2-\text{CO}-$ ,  $>\text{C}=\text{CH}-\text{CO}-$ , or  $-\text{CO}-\text{CH}_2-\text{CO}-$  were found to be  $\alpha$ -iminoxy and 2-iminoxy-1,3-dioxo radicals, respectively.<sup>2</sup> Identical radicals were also obtained in the reaction between 1,3-dioxo compounds and tetranitromethane.<sup>4</sup> The radicals formed when  $\text{NO}_2$  reacts with methyl methacrylate have been considered to be nitroxide radicals.<sup>2,5</sup> The structure of the radicals observed in

solutions of  $\text{NO}_2$  and a variety of olefinic substances seems not to be completely understood, even if there is strong evidence for the formation of an  $\text{NO}_2$ -olefin  $\pi$ -complex.<sup>3</sup>

This note describes the ESR-spectra of the radicals formed in the light induced reaction between  $\text{NO}_2$  and dimethyl sulphoxide. After bubbling  $\text{NO}_2$  through dimethyl sulphoxide for about one minute, the sample was irradiated *in situ* in the ESR-cavity with UV light. Almost immediately, radicals appeared which exhibited the spectrum shown in Fig. 1a. Of the six main groups present the two outer groups were split into quartets (1:3:3:1) without any overlaps. The four central groups also showed a quartet splitting but in this case there was overlap from further lines. An experiment performed with Fremy's radical as an internal standard gave a  $g$ -value equal to 2.0059 for the observed radical.

The radicals could also be produced when dimethyl sulphoxide was diluted by solvents such as benzene, chloroform, or  $\text{H}_2\text{O}$ , prior to bubbling with  $\text{NO}_2$ . No radicals could be detected when dimethyl sulphoxide was replaced by dimethyl sulphone, or when  $\text{NO}_2$  was replaced by tetranitromethane; nor could any radicals be detected when  $\text{NO}_2$  was replaced by  $\text{NO}$  purified from  $\text{NO}_2$  by bubbling through an alkaline water solution.

When the radicals were prepared from dimethyl sulphoxide- $d_6$  the spectrum shown

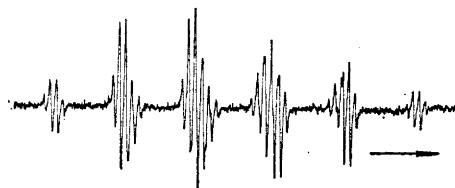


Fig. 1a. ESR spectrum of the radicals formed in the reaction between  $\text{NO}_2$  and dimethyl sulphoxide.

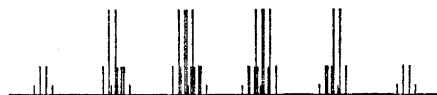


Fig. 1b. Reconstruction of the spectrum of Fig. 1a.