FORMATION, CHARACTERIZATION, AND CHEMICAL REACTIONS

OF

FREE RADICALS IN LIGNIN

BY

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I. INTRODUCTION

1. Pertinent Concerns of Pulp and Paper Industry

The sources of the intrinsic color of wood, the cause of pulp discoloration during pulping, and the origin of brightness reversion of paper have been of major concern to the pulp and paper industry, and yet many problems remain unsolved.

In recent years the worldwide wood shortage and increasing environmental pollution have become additionally important concerns. Under these uncongenial circumstances, the paper industry has been moving towards the manufacture of high-yield pulps in order to obtain a more complete utilization of wood resources. The progressive development of refiner groundwood and thermomechanical pulps seemed to answer a part of the question, however, high-yield pulps as well as the mechanical pulps have the drawback of low brightness and low brightness stability. Their inferior appearances have retarded the use of high-yield and mechanical pulps in high grade papers.

In view of these difficulties, it is imperative to understand the potential chromophoric groups contaminating pulps, and to search out the best practical answer to the water pollution problem by developing bleaching processes that avoid degrading lignin into low molecular weight fragments. This process must achieve both increased brightness with high stability, and reduced detrimental effects on physical and chemical fiber properties.

2. Complexity of Lignin Structure and Color

While wood polysaccharides possess relatively low light

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absorption properties in both the visible and ultraviolet regions of

the spectrum, lignin and some extractives, due to their aromatic

structure, absorb light intensely in the ultraviolet and partly in the

visible region. The absorption in the visible region results in the

yellow-brown color and the low brightness of high-yield and mechanical

pulps. Because the removal of extractives does not change the bright-

ness of high-yield and mechanical pulps significantly, lignin has been

assumed to be the main source of color in high-yield and mechanical

pulps. Hence, in order to understand the potential chromophoric system

in pulps requires a substantial understanding of the structure of

lignin.

Investigations of the chemistry of lignin have shown it to be

a substance of great structural complexity. Its structure is based on

molecular units of the phenylpropane type. The complexity of the

lignin molecules is due in part to the manner in which the C_6-C_3 (C_9)

units are linked to each other and in part to the fact that these

units are not chemically identical (e.g. different in methoxy content),

The molecular structure is further complicated by the variation in

structure of its three main immediate precursors, i.e., p-coumaryl,

coniferyl, and sinapyl alcohols, and from the various mechanisms of

polymerization. It is well known that the isolation of representative

lignin preparations presents formidable difficulties; the chemical

characterization of these preparations is frustrated by their tendency

to undergo secondary reactions of unknown nature. Hence the analytical

determination of functional groups and linkages in lignin is difficult.

The task of devising a satisfactory structural picture of the lignin macromolecule is very laborious. Nevertheless, the problem has been studied by many investigators, sometimes in a straightforward fashion, and sometimes by ingenious analytical methods. The values obtained have been summarized in Fig. 1.[1] Considerable variation in the analytical data from individual analyses are found in practice, and only average values are shown here. The frequency and types of functional groups are readily explained by the theory of lignin structure as proposed by Freudenberg (Fig. 2)[2] and the computer simulation by Glasser (Fig. 3).[3]

3. Basic Chromophoric Structures in Lignin

Because of the complicated structure of lignin, it is a very toilsome task to determine which types of chromophoric systems cause the color of lignin. Based on the literature survey as described in Chapter III in this dissertation, a report from the Wood and Pulp Chromophore Sub-committee of CPPA,[281] several review papers by Gierer,[282] Kringstad,[283] Nakano,[284] and Kondo[275] individually; and the papers presented at the 1972 TAPPI Chromophore Seminar[276] at Raleigh, North Caroliana, four main types of chromophoric groups can be distinguished as follows, and their simple unit structures are depicted in Fig. 4.

I.   Ortho- and para-quinones (Fig. 4 a, b).

II.   Para-quinone methides (Fig. 4c).

III. α-carbonyl groups (Fig. 4d).

IV.   Conjugated double bonds (Fig. 4e).

To remove or modify these chromophoric groups in lignin without impairing the quantity and quality of this polymer is the major goal

Fig. 1 Functional groups and linkages in lignin.[1]

Lig. 2 Freudenberg's formulation for lignin.[2]
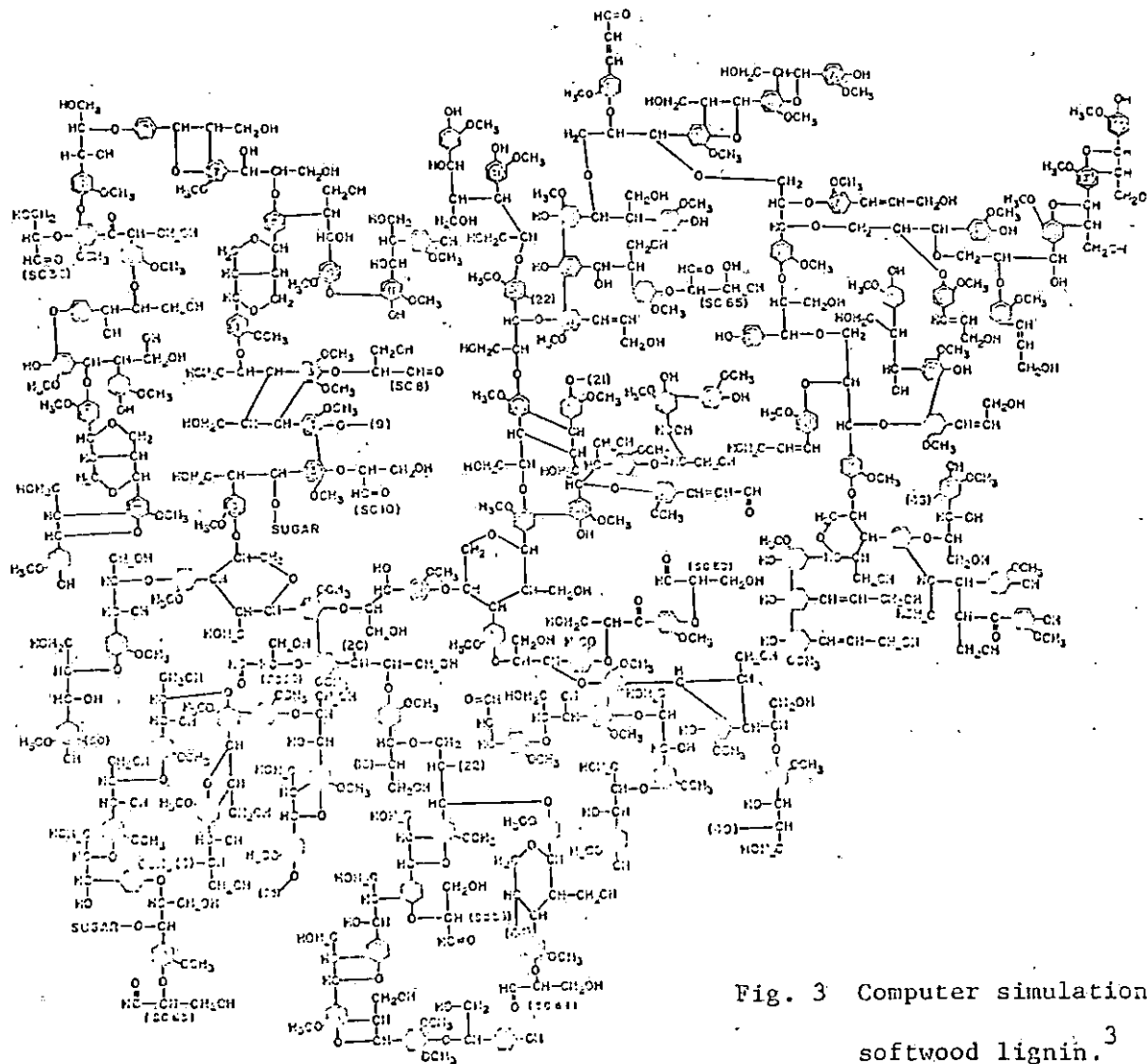
Fig. 3 Computer simulation for softwood lignin.[3]

(a)

(b)

(c)

(d)

(e)
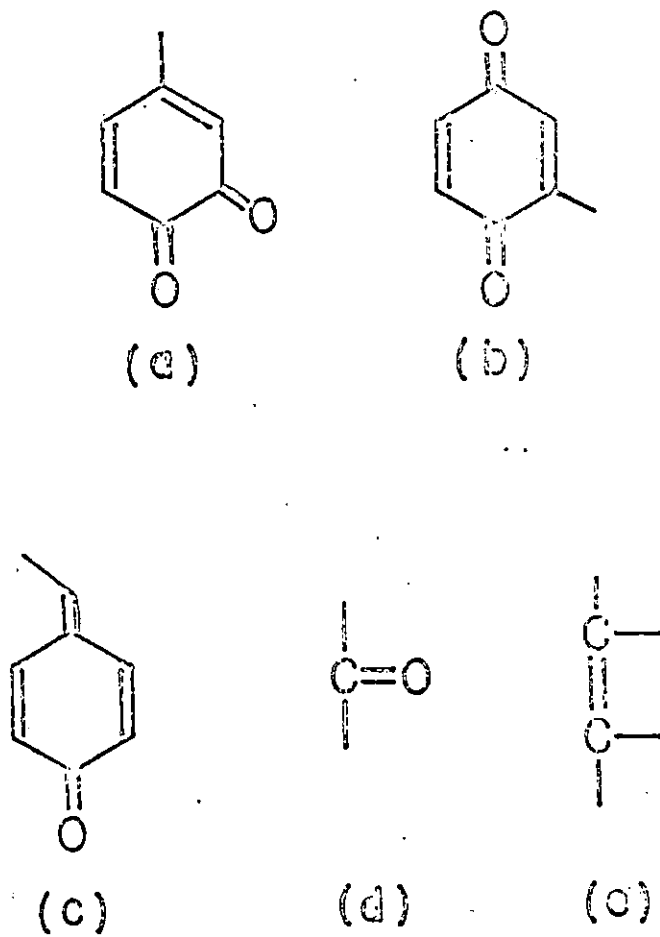
Fig. 4 Basic chromophoric structures in lignin.

of this research. Details are outlined in the following section.

II. OBJECTIVES

The overall objectives of this research were to gain an understanding on the mechanisms of color forming reactions in lignin and high-yield pulps originating from the degradation of the lignin polymer. Both mechanical and photochemical processes were to be used to degrade the lignin. Specific photoreduction reactions would be employed to reduce or remove the lignin chromophores.

The following specific objectives were pursued:

I. Determine the major chromophoric groups in lignin.

II. Characterize the chemical intermediates formed in lignin by mechanical stress and by ultraviolet irradiation; elucidate free radical transformations and secondary reactions which lead to the formation of chromophoric groups in lignin.

III. Establish specific photoreduction reaction mechanisms which lead to the removal or diminution of chromophoric groups in lignin.

IV. Evaluate the light stability of photoreduced lignin-adducts.

V. Demonstrate the feasibility of using photoreduction techniques with high-yield pulps.

III. LITERATURE REVIEW

1. Wood and Pulp Chromophores

1.1 Introduction

Wood is a complex and inhomogeneous macromolecular system made up of cellulose, hemicelluloses, lignin, mineral matter, and extractives. Most woods are relatively light in color, but all contain some coloring components. Within these, knowledge of the nature of chromophoric groups is still meager. Casey[4] claimed that almost every pulp component or reaction product is accused of being the carrier of chromophores. While it is generally conceded that the major contributor of color is the lignin component,[5] it cannot be precluded that cellulose is not contributing also. In some species, the extractives become the controlling factor.[6-9] Color reactions of lignin are a main subject of many textbooks.[10-15]

This review is made in order to obtain information on chromophores in wood and pulp. Emphasis is given to those chromophoric systems that pertain to neutral sulfite, high-yield pulps. Generally, wood has a yellowish, reddish, or brownish shade, which depends on the species[16,17] as well as on the growing conditions, the formation of heartwood, microbiological or physical damage, etc. Superficial consideration indicates that any color of wood is due to some other constituents than either cellulose, hemicelluloses, or lignin; since they are inherently colorless, and since the sapwood of almost all species is practically white.[18,19] Although this is true for some highly colored species[20-22] it is well known that even the whitest

woods change color on exposure to light, suggesting that within the
cellulose, hemicelluloses, and lignin there exists a potentially
colored material or materials. On bright types of woods this is
visualized by an increasing yellowing or darkening upon exposure to
light. In dark colored species, similarly absorbing chromophores are
formed.[23,24] It should be added here that the range of UV light
responsible for discoloration has a wavelength of 3300-4000 Å.[25-29]
Discoloration during light exposure may or may not involve atmos-
pheric oxygen.[30-35] Bleaching of yellowed wood is accomplished by
light of wavelengths above 3850 Å.[26,27,33,36]

Several wood components have been found to be responsible for
the absorption of visible light. A comparison of light absorption
properties of lignin and cellulose[37] has demonstrated that the photo-
chemical reaction is due primarily to chromophoric groups present in
the lignin molecule. On the basis of a general similarity in the
shape of the spectral sensitivity curve of groundwood and the UV
absorption spectrum of lignin, Nolan et al.[38] concluded that lignin
is the primary contributor to the photoinduced yellowing of wood.
Reflectance measurements of thin wood sections have shown that
different spruces have a specific light absorption coefficient of
about 30-60 cm^2/g.[39-41] Norrstrom was able to show that polysaccharides
and materials extractable with dichloromethane contribute, but only in
a minor way, to the light absorption of spruce wood (Picea abies) at
457 nm.[42] He concluded that the color of wood results almost entirely
from chromophoric structures present in lignin. Besides lignin,

resinous extractives can be offenders that cause discoloration on aging. They also affect the bleachability of pulp.[43] Tannins are amorphous substances which range in color from a light yellow to a dark brown.[44] Moreover, all wood contains a small amount of organic coloring substances such as catechins, flavonoids, quinones and leucoanthocyanidins.[44,45] Evidence of this variety can be seen from the results of several studies.[46-52] As reference sources of information on the influence of extractives on color in wood, the short summaries by Kurth[53] and Shriner,[54] and the more extensive monographs of Mayer[55] and Hillis[6] may be cited.

Enzymatic reactions may also contribute to the intrinsic color of wood.[56] Most wood-rotting fungi produce phenol oxidases which have been shown to degrade lignin oxidatively.[57-60] Thereby, demethylation and formation of free radicals and chromophores is observed.[61] However, the mechanisms of their formation have not been studied to any great extent.

1.2 Color in Pulps

In general, color problems encountered in pulps arise either from color already present in wood, or from chemical changes which take place during grinding, cooking, refining and bleaching processes. Based on the literature, much of the color in wood pulps can be attributed to residual lignin and lignin derivatives as well as to the presence of other coloring matters such as quinones, flavones, flavanols, and condensed tannins. Alkaline pulps are generally much darker than other pulps, and this may be due to the presence of more

highly condensed and unsaturated lignin and phenolic materials. However, the nature of the chromophoric systems involved, and the mechanism of their formation require more research. The color of high-yield pulps is much more dependent on the wood species than that of low-yield pulps, because a greater proportion of the lignin and extractives remain.

During the pulping, free radicals have been reported as being formed in lignin. It has been demonstrated by some investigators[62-73] that any solid lignin prepared from wood, including milled-wood lignin, has a natural content of organic free radicals ranging from approximately 0.5×10^{17} to 5×10^{17} spins per gram. Kleinert and Morton[67] found that mechanical breakdown of wood caused a marked increase in the free radical content, and they suggested that stable macroradicals were formed by the cleavage of covalent bonds. Free radical formation was also observed when alkalized wood was rapidly heated to a constant temperature (180-190°C) in the cavity of an ESR spectrometer.[66,67]

Discoloration occurs during grinding, and pulping under acid sulfite, alkaline and semichemical conditions. Condensed lignins are not always highly colored,[74] and a more marked discoloration may be due to the reaction of lignin with minor constituents of the wood or the cooking liquor, such as furfural.[75] Luner et al.[76] have shown that pulping of spruce and birchwood with bisulfite and sulfite cooking liquors of up to pH 10 caused considerable increases in brightness over the whole yield range when compared to the original wood samples. On drying, these pulps lost most of their brightness. This was attributed

to the introduction of potential chromophoric sites as a result of the breakdown of the lignin macromolecule. Azhar and Wayman[77] explained the discoloration on heat ageing with a sulfonic acid-catalyzed condensation of phenolic aryl-α-carbonyl groups with phenolic lignin groups.

The objective in bleaching is the production of a white pulp of stable color obtained at reasonable cost and with a minimum deleterious effect on the physical and chemical properties of the pulp. Two principal reactions take place in bleaching: (1) Solubilization and removal of the colored matter, and (2) changing of the coloring matter to a colorless form which is as stable as possible to light and heat.[78] Two reaction mechanisms compete during bleaching, which are elimination and formation of chromophores.[79] The problem of bleaching high-yield pulps is to obtain high brightness (>80 GE) without dissolving the lignin. This cannot be performed with ordinary bleaching agents such as chlorine, hypochlorite and chlorine dioxide, because these chemicals require the removal of lignous substances.[80] In addition, the brightness of both unbleached and bleached pulp is not permanent, and brightness reversion is accelerated by exposure to light, heat, chemicals and high humidities. The reddening of unbleached sulfite pulps has been shown to involve an oxidation mechanism[81] such as the one occurring in acid peroxide treatment, or in air oxidation in the presence of multivalent ion catalysts such as copper or iron.

Overall, the problem of color in wood and pulp has been studied extensively, but its causes and prevention are still not entirely known. However, a better understanding of chromophoric systems in

pulps can be obtained from knowledge of the reactions of lignin during pulping and photoirradiation.

2. Formation of Potential Chromophoric Groups in Lignin

2.1 Introduction

The constitutional model of lignin[82] gives a broad picture of the reactive groups available in native lignin. These consist of ethers of various types, primary and secondary hydroxyl groups, carbonyl groups, carboxyl and ester functions, ethylene groups, and sulfur-containing groups such as thiols and sulfonic acids introduced as a consequence of kraft or acid sulfite pulping. Since lignin is a phenylpropanoid polymer, there also exist a number of aromatic and phenolic sites and activated aliphatic locations capable of participating in discoloration reactions. Obviously, the complexity of structures of components as well as reactions hinder the studying of potential chromophoric groups in lignin.

Generally, only a small fraction of the lignin can be extracted into water or organic solvents. This would allow convenient investigation of pure and unchanged lignin. Some information can be obtained from studies with model compounds. The degree to which model chromophores are comparable to wood chromophores *in situ* remains however an open question. Fleury and Rapson[83] proposed three criteria which studies with model compounds must meet before their results can be taken in place of those with lignin *in situ*: (1) Similar chemical reactions; (2) Matching extinction coefficients of absorption; (3) Conceivable structure and formation. Because these criteria

cannot be met with certainty, the nature of the chromophores in wood or in lignin can only be speculated upon. Probable chromophoric configuration include aliphatic double bonds conjugated to the aromatic rings, quinone-methides, quinones, chalcone structures, free radicals, and heavy metal complexes with catechol structures.[84]

2.2 Quinones

Of all structural units identified so far, which are present in native softwood lignin[2,85] only coniferaldehyde may explain absorption of visible light. Coniferaldehyde units are present in amounts of about 4% of C-9 units,[86] of which only 1/4 carry free phenolic hydroxyl groups.[87] Earlier reports, that compounds related to coniferaldehyde also absorb light in the visible region, have been traced to the inadvertent presence of coniferaldehyde as an impurity.[88] Pew and Connors[89] reported that phenyl-substituted benzoquinone and coniferaldehyde groups are major contributors to the color of lignin in wood. Quinones may result from the dehydrogenation of guaiacyl-glycerol-β-guaiacyl ethers, and they are orange-yellow in color. The dehydrogenation of α-ethyl-vanillyl alcohol with peroxidase-H_2O_2 has been shown to cause side-chain displacement and formation of a propionaldehyde which converts rapidly into dioxepin by further dehydrogenation.[90]

Other mechanisms have been suggested also, by which quinone structures may be formed during lignification. In recent studies on the photochemical oxidation of lignin or wood, it was shown that photochemically generated phenoxyl radicals of a variety of guaiacyl

derivatives are sensitive to oxygen.[31,32,106,107]   Oxygen or hydroxyl

radicals will add to the phenoxyl radicals to cause demethoxylation

combined with the formation of o-quinoid structures.   Since in lig-

nification of wood, phenoxyl radicals are present together with oxygen

and/or hydroxyl radicals[2] it is possible that demethoxylation may

occur to some degree in a similar reaction, thereby introducing

o-quinone structures in the native lignin molecule.   In a brightness

study of cold soda pulps, Luner[108] proposed a mechanism for the

formation of quinones which is based on free radical attack of lignin

by oxygen.   He emphasized the role that oxygen could play in color

formation of wood and pulp.

Studies of lignin degradation products[151-153] and of dehydro-

genations of model phenols simulating lignification[154-157] or lignin

breakdown[158] have revealed that an important side reaction of the

dehydrogenative coupling process causes the cleavage of aryl-benzyl

carbon-carbon bonds.   This cleavage effects elimination of the

propanoid side chain para to the phenolic hydroxyl group.   It has been

pointed out by several investigators that a product of side-chain

displacement is the 2,6-dimethoxy-1,4-benzoquinone which has been

isolated from studies with lignin model compounds,[156,158,159] with

lignin[161] and with alkali lignin.[162]

Similar eliminations of methoxyl groups leading to o-benzoquinone

structures have also been established.[163,164]   The sequence of

reactions in the dehydrogenation of disyringylmethane by peroxidase-

hydrogen peroxide has been extensively clarified by Connors et al.[163]

The authors concluded that the stepwise oxidative coupling process of disyringylmethane follows the course outlined by Caldwell and Steelink[159] whereby the disyringyl ketone is formed via the corresponding carbinol. The important side-reactions in the second step concern the generation of an o-quinone through demethylation, and of 2,6-dimethoxy-1,4-benzoquinone through side-chain displacement. Continued oxidation of the disyringyl ketone did not lead to products anticipated earlier, but yielded a catechol as well as a complex trimeric quinone incorporating both cerulignone and o-quinone structures. Recently, Harkin and Obst[165] have reported that enzymic phenol oxidation of the lignin model compound 2,4,6-trimethoxy-phenol caused exclusive elimination of a methoxyl group, resulting in a mixture containing mainly 2,6-dimethoxy-1,4-benzoquinone and a little 3,5-dimethoxy-1,2-benzoquinone. They concluded that analogous reactions of guiacyl and syringyl moieties during lignin formation would create quinone structures in wood that could account for some of its color, and some properties of groundwood pulps. In alkalis the p-quinone decomposed slowly and the o-quinone rapidly, yielding intensely colored solutions and pigments. Analogous decomposition of quinoid groups present or formed in lignin during pulping would give rise to strong chromophores that would stain the pulp and discolor spent liquors.

Chlorination of pulp in aqueous medium results in the loss of methoxyl groups (demethylation), leading directly to the formation of substituted o-benzoquinones, according to work by Larson[181] and Hibbert

and his coworkers.[181,182] No evidence to the contrary has been published in the intervening years and, in fact, subsequent studies have provided results which support the conclusion that o-benzoquinone intermediates are formed not only in the chlorination of lignin, but to a measurable degree in nearly all processes involving oxidation of lignin and lignin model compounds.[183,184] Gess and Dence[185] have studied the formation of o-benzoquinones in the reaction of creosol with aqueous chlorine. The creosol (4-hydroxy-3-methoxytoluene) was reacted with chlorine in aqueous dioxane solution under conditions simulating those of the technical pulp chlorination process. Six o-benzoquinones were identified and their yields estimated by vapor phase chromatography after reduction to the corresponding catechol and etherification. The comparatively high yields of 4-chloro-5-methoxyl-o-benzoquinone and their creosol counterparts suggest that the o-quinone was produced by direct oxidation of the parent creosol.

2.3 Metal Complexes

Quinoid compounds are reduced by sodium borohydride to catechols, which form colored complexes with metal ions, especially with ferrous or ferric ions. The presence of catechol groups in lignin has been established by many investigators.[91-96] Demethylation of lignin can be accomplished by acid and alkaline treatments, and this reaction results in the formation of catechol groups. These groups may also be the source of condensations and o-quinone formations. On the basis of color reactions of lignin with ferrous sulfate, it was found that kraft lignins contain about 0.6 catechol units per MeO.[84]

Several authors[84,97-100] have discussed the influence of metal

ions on the color of lignin. On the basis of reactions of catechol

groups with ferrous or ferric ion to form colored complexes, Falkehag

et al.[84] concluded that metal complexes of thiolignins are with the

chromophoric sites. Imsgard et al.[97] mentioned possible chromophores

of ferric complexes with various phenols. The authors reported that

iron presumably as ferric ion, shows an extremely high contribution

to the color of lignosulfonic acids, while the contribution of copper,

manganese and chromium is negligible.[100] Ijima and Nakano[101] recently

reported that the number of sites forming a lignin-iron chelate in pulp

is small. The chelating sites in kraft pulps seem to be completely

saturated with lignin-iron chelates. If additional iron is added to

kraft pulp, the iron is merely absorbed. The color of kraft pulp

is therefore unaffected by the addition or iron. The authors[102] also

reported the types and concentrations of metal ions in lignin, and the

properties of chromophores formed by the metal complexes on the basis

of experiments with purified commercial lignosulfonates and thio-

lignins. The effects of metal ions on the color of lignins were more

prominent in lignosulfonates than in thiolignins, and more significant

in the longer wavelength region (at around 700 nm.). Two types of iron

retention in lignosulfonates were determined: a high content of weakly

bonded iron, and a low content of strongly bonded iron. The former

consists mainly of ferric complexes of phenolic hydroxyl groups and

catechol structures; and the latter shows a higher absorbance

than the former in the visible light region.

Color reactions of lignin with a variety of other inorganic reagents have been studied also. Nakano et al.[103] have shown that the coloration obtained with vanadium pentoxide in phosphoric acid is a consequence of the presence of phenolic hydroxyl groups. Discoloration is probably based on the formation of vanadate esters. The chromogenic action of potassium chlorate in hydrochloric acid is a result of oxidation and quinone formation. In contrast, the color reaction of cobalt thiocyanate with lignin is explained as a π-complex generated by the Co^{2+} ions and the aromatic rings. Color produced by the combinations of ferric sulfate, potassium ferrocyanide and mercuric acetate-ammonium sulfide are said to originate in the carbonyl groups of the hemicellulosic materials and not in lignin itself.[104] Of all the inorganic color reactions, the best known is the Maule reaction which occurs as a consequence of oxidative chlorination.[105,10,11]

2.4 Quinonemethides, Stilbenes and Stilbene-Derivatives

Recently, Leary[109] reported a study of photochemistry of coniferyl alcohol. He found that photolysis of coniferyl alcohol in various solvents does not apparently yield the phenoxy-radical, but give instead a long-lived transient which absorbs near 350 nm. and whose lifetime is unaffected by the presence of atmospheric oxygen. A transient of similar lifetime and spectrum is also observed upon photolysis of the related p-vinyl substituted phenol, isoeugenol in water or in ethanol. He concluded these transient spectra are generated by quinoid methides.

Quinoid structures also contribute to the color of kraft lignin.[110]

Oxygen or the presence of carbohydrates is not a prerequisite for the formation of chromophores in lignin during kraft cooking.[84] It seems quite possible that quinonemethides which have been assumed as intermediates in the alkaline pulping[111-113] could act as oxidative agents. These intermediates could dehydrogenate easily oxidizable species, such as dihydroxydiphenylmethanes, catechols, or p,p'-dihydroxystilbenes. The dehydrogenation of phenolic diphenylmethanes to highly colored quinonemethides has been reported by many investigators.[114-119] The formation of quinonemethides and stilbenequinones was observed in studies of phenol formaldehyde resins.[120-125] The presence of stilbene structures – which may be precursors of stilbene-quinones – in kraft Bjorkman lignin has been suggested by Falkehag.[126] By using spectral analyses, he showed that the ionization $\Delta\epsilon$ curve of reduced kraft lignin possesses peaks at almost identical wavelengths. It seems that peaks of the ionization $\Delta\epsilon$ curve located in the 370-380 nm. region are caused by stilbene structures, and not by carbonyl groups because infrared measurements show that carbonyl groups are either entirely absent, or present in only minor quantities. Falkehag concluded that stilbene structures are formed in kraft Bjorkman lignin by the opening of phenylcoumaran rings.[127,128] Gierer et al.[129-131] have suggested that the mechanism for the alkaline cleavage of the coumaran's hydrofuran ring proceeds via the formation of quinonemethide structures. Enkvist[132] has also shown trans-4,4'-dihydroxy-3,3'-dimethoxystilbene to be present in kraft liquors. Richtzenhain and van Hofe[133] isolated the same stilbene from a spent

sulfite liquor. Other trans-stilbenes without substituents in the
α,α'-positions have also been detected.[111,134,135]

The formation of p,p'- and o,p'-dihydroxystilbene from the
diarylpropanediol (β-1), and the arylcoumaran-dilignol (β-5) under
certain pulping conditions has been demonstrated. These structures
have been estimated to account for 12% of all linkages between
arylpropane units in milled wood lignin of Norway spruce (Picea abies).[136]
The p,p'-dihydroxystilbene arises from the treatment of the β-1
dilignol with acid[137] or alkali,[138] whereas the o,p'-dihydroxystilbene
is produced by reacting the arylcoumaran with kraft liquor at 170°C.[139]
The p,p'-dihydroxystilbene is readily oxidized by atmospheric oxygen
to give a red product to which a stilbene benzoquinone structure has
been assigned.[140] The oxidation reaction is catalyzed by heavy metal
ions, or light, and is considered to be the cause of the reddening
of sulfite pulp.[140,141] The irradiation of stilbenes with UV light
in the presence of oxygen generally leads to the formation of
phenanthrenes.[142] Certain dihydroxystilbenes have the potential of
producing colored stilbenequinones or phenanthraquinones on photo-
chemical oxidation. For instance, the p,p'-dihydroxystilbene is known
to give red products of this type.[141] The o,p'-dihydroxystilbene, in
contrast, does not yield quinones on oxidation with hydrogen peroxide
and cupric ion catalysis, but rather destroys the stilbene.[82] Gierer
et al. have found that α-methyl-o, p'-dihydroxystilbene is a product of
the reaction of dihydrodehydrodiisoeugenol with 2N sodium hydroxide
at 170°C[131] or with neutral sulfite liquor at 180°C.[143] An alkaline

solution of the α-methyl-o,p'-dihydroxystilbene reacts with oxygen to give a colorless cyclized product, the benzofuran.[144]

Nelson and Wallis[145] have recently found that oxidation of the 2,4'-dihydroxy-3,3'-dimethoxystilbene gave a benzofuran and inter-molecularly-coupled products, but no colored stilbenequinone. Irradiation of the stilbene with light (300 nm.) in alkali produced an arylcoumaran by intramolecular cyclization, while similar treatment in ethanol gave a complex mixture of products. The authors concluded from their experiments that o,p'-dihydroxystilbene structures are apparently not important as potential chromophoric groups in degraded lignins.

More recently, Nimz[146] has pointed out that p-hydroxystilbenes are readily oxidized by air to conjugated chromophores of the methyl-enequinone type. Similar behavior can be ascribed to o,p'-dihydroxy-stilbenes as well as phenanthrenes, which may be oxidized further to yield corresponding methylenequinone and phenanthrenequinone systems. Nimz also pointed out that 1,4-diguaiacylbutadiene, which was formed by heating pinoresinol under alkaline conditions,[147] may be oxidized either to the corresponding bismethylenequinone or by cyclization to a phenylnaphthalenedione.

Condensation reactions of lignin have been mentioned in connection with sulfite pulping as being responsible for some formation of color.[186] One potential condensation reaction leading to a chromophore is the formation of a chalcone from vanillin and acetoguaiacone,[187] both of which have been isolated by Enkvist et al.[188] from black liquor.

Meshitsuka and Nakano[189] revealed that chalcones are formed by sulphite

cooking of acetoguaiacone alone or acetoguaiacone plus vanillin.

2.5 Carbonyls and Radicals

The relationships between the contents of chromophoric groups,

molecular weights and color of aqueous solutions of lignosulfonic acid

were studied by Meshitsuka et al.[148] and Iiyama and Nakano.[149] They

concluded that the color of lignosulfonic acids is mainly due to

quinone structures and some conjugated configurations including α–

carbonyl groups. The other chromophoric systems, such as free radicals,

cationic sites and condensed structures, are also expected to

contribute a little to the color of lignosulfonates. The authors

also reported[150] that alcoholic hydroxyl groups have almost no

influence on the color of thiolignin, and that phenolic hydroxyl

groups affect color as much as carbonyl groups do. Methylated and

sodium borohydride-reduced thiolignin is light in color. Radicals

and carbonium ions can be expected to contribute most significantly

to the color of thiolignin. In addition, molecular compounds of

electron donor-acceptor type may also contribute drastically to the

color of lignin.

Kratzl et al.[166,167] have shown that the reaction of oxygen in

alkali with lignin model compounds produced quinones by two reaction

pathways: (1) oxidative coupling of phenolic nuclei to form ortho-

ortho-linked diphenols when the side chain is a saturated alkyl group,

and (2) side chain displacement in model phenols possessing benzyl

alcohol or α-carbonyl groups. In addition to side chain displacement

and oxidative coupling, Eckert et al.[168] proposed at least three other

reaction pathways leading directly to modifications and degradations

of phenolic moieties in lignin. Based on the reaction products, these

inferred pathways are formation of epoxidated quinol structures, and

ring cleavage between the methoxyl bearing ring carbon and either of

the two adjacent ring carbon atoms.

It has been reported that when lignin is dissolved in alkaline

solutions, stable radicals and anions are formed. Some studies have

pointed out that color reactions invariably accompany radical formation

from lignin model compounds, yielding chromophores as end products.[169]

Recently, Sheldon et al.[170] and Clare[171] demonstrated that, at room

temperature, 4-substituted syringyl compounds in aqueous alkali and

air undergo slight degradation to yield the yellow 2,6-dimethoxy-

benzoquinone and a red 3,5-dimethoxy-2-dyhroxybenzoquinone. The

mechanism of this reaction was examined by e.s.r. spectroscopy, and

it appeared that the first step of the reaction consists of the

formation of a phenoxy radical. In a second step, this radical suffers

attack by an oxygen radical to yield a variety of intermediate semi-

quinone radical species, which form red chromophores. The authors

added that side-chain displacement and demethylation were competing

reactions. On the other hand, Leary[32] had discovered that the production

of o-quinones in wood or pulp after UV irradiation would neatly combine

the demethyoxylation and formation of quinones in one step.

Most of the attention given to the reactivity of carbonyl groups

has focused on the color reactions of lignin, where a large number of

characteristic chromogenic reagents[172,173] have proliferated over years. The mechanisms of chromophore formation in high-yield pulps and lignins have been studied by several scientific teams. Lin and Kringstad[174-177] have shown that photoinduced degradation (300-400 nm.) and discoloration of lignin are mainly initiated by the absorption of light by the α-carbonyl groups. It has been suggested that the excited photoirradiated α-carbonyl groups abstract hydrogen from free phenolic units in lignin, thereby generating phenoxy radicals which are intermediates in the degradation and discoloration processes. The authors also found that the photodegradation of non-phenolic lignin models of the phenacylaryl ether type takes place on irradiation with light of wavelengths varying from 300 to 400 nm. In this process phenoxy radicals are formed directly, followed by the formation of color.[178]

The color of wood and its behavior towards reducing agents can be explained by the presence of α-carbonyl groups in wood. Fleury and Rapson[83,179] demonstrated that model compounds of the 2-hydroxy-phenylketone series enhanced light absorption in the visible range when certain substituents (auxochromes) are introduced into the basic conjugated system (chromogene). The reverse, the stepwise removal of auxochromes and chromogenes from an entire chromophore system has been accomplished by a reductive treatment.

3. Conclusions

In summary, we should point out that several chromophoric systems are named in the literature as contributors to lignin's color.

Quinonoid structures appear to be the main culprits of color-forming reactions in lignin. It is clear that these quinones may be derived not only from minor quantities present in the original lignin, but also from chemical reactions that take place during pulping processes. In brief, potential chromophoric groups in wood and pulps may be classified as follows:

Chromophoric functional groups: phenolic hydroxyl groups, double bonds, carbonyl groups, etc.

Chromophoric systems: quinones, quinone methides, biphenyls, etc.

Leuco chromophoric systems: methylenequinones, phenanthrene-quinones, phenylnaphthalenediones, bimethylenequinones, etc.

Intermediates: free radicals

Complexes: chelate structures with metal ions.

Besides studying the formation and reactions of chromophores in wood and pulp, most investigations aim at eliminating or preventing color formation. To decrease the content of chromophores in wood and pulp, four principally different methods are viewed by Rydholm:[190]

(1) Protection of carbonyl and coniferaldehyde groups by reaction with bisulfite to form α-hydroxysulfonate adducts;

(2) Reduction of colored configurations to non-colored leuco bases and similar phenolic structures;

(3) Oxidation of colored configurations with phenolic and quinonoid nature, to carboxyl groups, carbon dioxide, etc.;

(4) Methylation or acetylation of some critical chromophoric groups is conceivable; (cf. ref. 191, 192, 193).

4. General Aspects of Free Radical Chemistry, Photochemistry, Mechanochemistry, and Electron Spin Resonance

This section aims to present a simple overview of free radical chemistry, photochemistry, mechanochemistry, and electron spin resonance (ESR) for the wood chemist or the paper technologist interested in these fields. Neither a comprehensive review nor a physically rigorous development is intended. Appropriate references may be found in the text. The reader who is familiar with these fields may not find much interest in this section, and he may pass immediately to the next chapter.

4.1 Free Radical Chemistry[194-198]

A free radical is best defined as an atom, molecule or complex which contains one or more unpaired electrons. Free radicals can be obtained in a variety of ways. Principally, free radicals are produced by thermal decomposition (thermolysis or pyrolysis), irradiation techniques (using ultraviolet or microwave radiation, X-ray electrons, α-particles, neutrons, X-ray, etc.), mechanical stress, electron transfer reactions, or by electrode reactions.

Although some free radicals are stable enough to be isolated or maintained, most are chemically reactive species and encountered only as intermediates in chemical reactions. Any reaction that involves one or more free radicals as reaction intermediates can be regarded as a free-radical reaction.

Radicals vary in reactivity, and their reactivity like that of other chemical species, is influenced by temperature and by the con-

centration of molecules in their environment. At very low temperatures, even very reactive radicals can be immobilized in highly viscous glasses or crystals and can have very long lives. Reactive radicals are frequently trapped at low temperatures for study by electron spin resonance spectroscopy.

Generally, free radicals undergo five different types of reactions.

(i)   Radical combination:
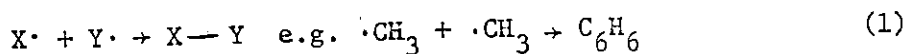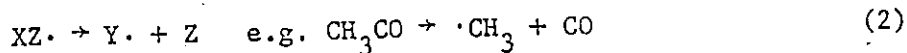
$$X\cdot + Y\cdot \rightarrow X-Y \quad e.g. \quad \cdot CH_3 + \cdot CH_3 \rightarrow C_6H_6 \tag{1}$$

(ii)   Radical fragmentation:

$$XZ\cdot \rightarrow Y\cdot + Z \quad e.g. \quad CH_3CO \rightarrow \cdot CH_3 + CO \tag{2}$$

(iii) Radical transfer:

$$X\cdot + Y - Z \rightarrow X-Y + Z\cdot \quad e.g. \quad CF_3 + CH_4 \rightarrow CF_3H + \cdot CH_3 \tag{3}$$

(iv)   Radical addition:

$$X\cdot + Y = Z \rightarrow X-Y-Z\cdot \quad e.g. \quad CH_3 + CH_2 = CH_2 \rightarrow \tag{4}$$

$$CH_3- CH_2- CH_2\cdot$$

(v)   Radical disproportionation:

$$X\cdot + Y-Z-W\cdot \rightarrow X-Y + Z = W \quad e.g. \quad \cdot CH_3 + CH_3CH_2 \rightarrow \tag{5}$$

$$CH_4 + CH_2 = CH_2$$
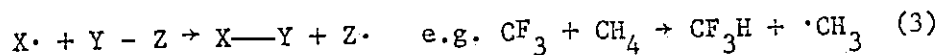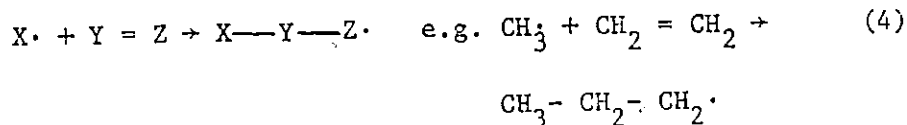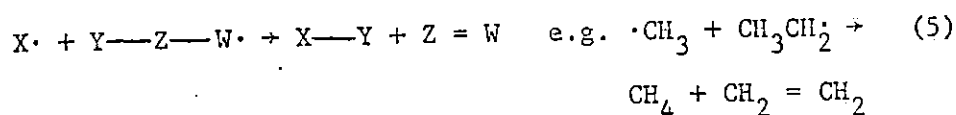
It is obvious that reactions (i) and (v) involve disappearance of radical species. In the other three reactions new radicals replace the initial radicals formed in the reaction process. In other words, reactions (ii), (iii) and (iv) represent chain carrying steps, while (i) and (v) are chain termination processes.

It is obvious that the kinds of reactions in which free radicals actually participate are quite limited. They can be classified either

as radical-propagating reactions or radical-destroying reactions.
In radical-propagating reactions, free radicals react in either a
bimolecular reaction with a substrate molecule or in a unimolecular
process producing other free radicals. Radical-destroying reactions
are bimolecular reactions of two free radicals yielding products that
are not free radicals.

4.2 Photochemistry[199-204]

Photochemistry is the study of the physical processes or chemical
changes which occur in molecules on absorption of visible or ultra-
violet radiation. The regions of the electromagnetic spectrum that are
of interest to photochemistry are the far ultraviolet (100 to 2000 $\overset{o}{A}$),
the near ultraviolet (2000 to 4000 $\overset{o}{A}$), and the visible region (4000 to
8000 $\overset{o}{A}$). As can be seen from Fig. 5 this constitutes a very small
range within the electromagnetic spectrum.

Basic Laws of Photochemistry

Photochemical reactions are governed by four basic laws:

(1) The law of Grotthus and Draper states that only light which
is absorbed by a system can produce a photochemical change.

(2) The law of Stark, Einstein, and Bodenstein states that in
the primary step of a photochemical reaction each quantum
of light absorbed causes activation in one absorbing molecule.

(3) The rule of Warburg states that it is the number of absorbed
photons and not their energy content, that is decisive in
photochemical reactions.

(4) The results of modern organic photochemistry have created
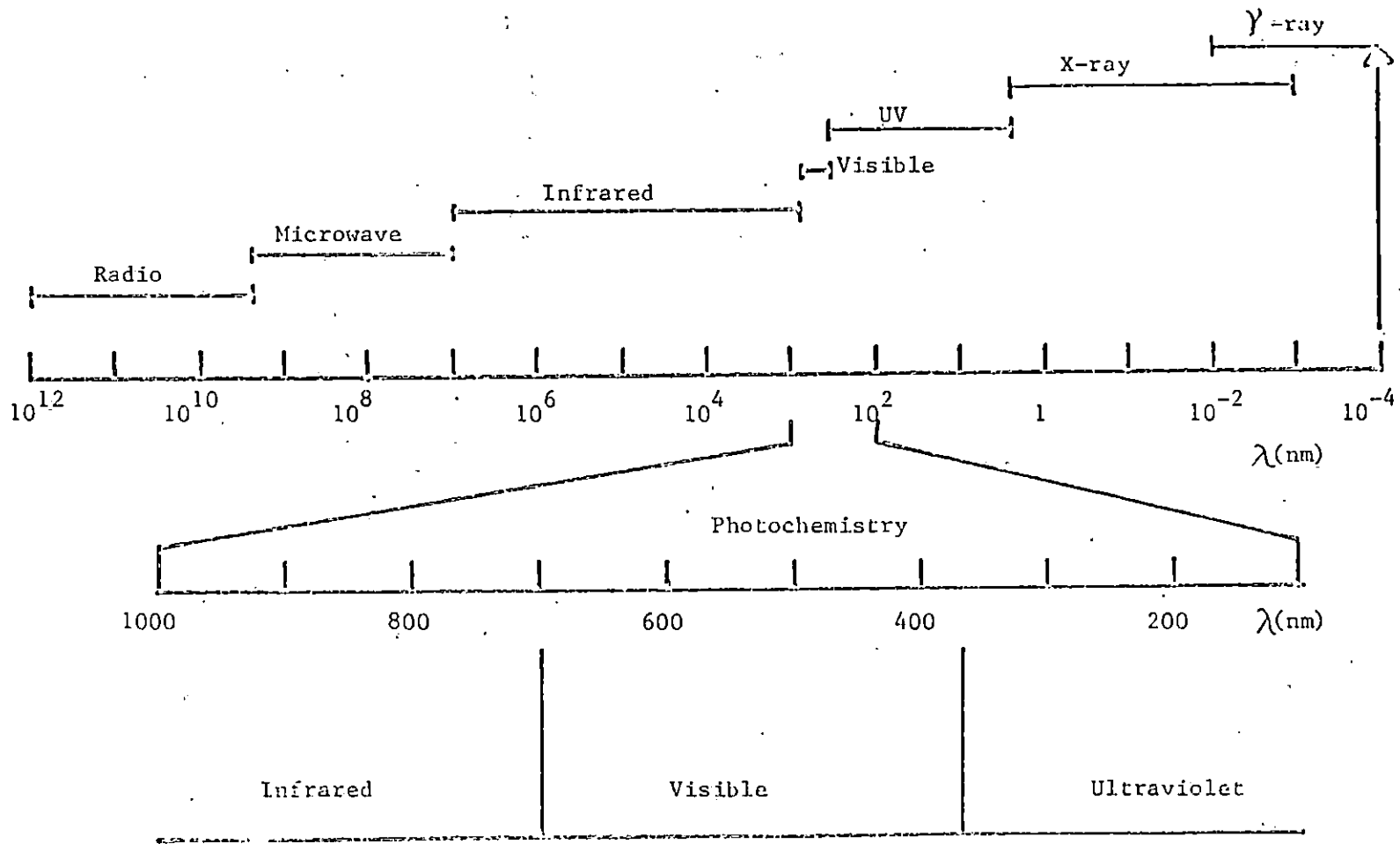
Fig. 5 Spectrum of electromagnetic radiation. Note the tiny portion occupied by the visible region.

a further important rule: The lowest singlet and triplet

states, which can be populated by a molecule by absorption

of each quantum with a certain probability, are the starting

points of most organic photochemical processes.

Relation Among Energies, Wavelengths and Frequencies

The energy required to produce an excited state is obtained by

inspection of the absorption or emission spectrum of the molecule in

question together with the application of the equation

$$E_2 - E_1 = h\gamma \tag{6}$$

where h is Planck's constant, γ is the frequency (sec^{-1}) at which

absorption occurs, and E_2 and E_1 are the energies of a single molecule

in the final and initial states.

The position of an absorption band is often expressed by its

wavelength (λ) in angstroms or its wave number ($\overline{\gamma} = \frac{1}{\lambda}$) in reciprocal

centimeters and its frequency ($\gamma = \frac{c}{\lambda}$) in reciprocal seconds. Hence

equation (1) may be rewritten as

$$E_2 - E_1 = h\overline{\gamma}c = \frac{h \cdot c}{\lambda} \tag{7}$$

According to these relationships, the energies of some typical

wavelengths may be calculated and are given in Table 1.

Photochemical Processes

The presence of the energy from an absorbed photon in the molecule

can manifest itself in several ways. By absorption of light the

molecule is brought into an excited state, electrons from a nonbonding

or bonding molecular orbital being promoted to an antibonding orbital.

This absorption is evidently related to the electronic structure of

Table 1. Energy conversion table

λ $\overset{\circ}{A}$	$\bar{\nu}$ cm^{-1}	$(E_2 - E_1)$	
		Kcal/mole	eV
2,000	50,000	143.0	6.20
2,500	40,000	114.4	4.96
3,000	33,333	95.3	4.13
3,500	28,571	81.7	3.54
4,000	25,000	71.5	3.10
4,500	22,222	63.5	2.76
5,000	20,000	57.2	2.48
5,500	18,182	52.0	2.25
6,000	16,666	47.7	2.07
6,500	15,285	44.0	1.91
7,000	14,286	40.8	1.77

the compound studied; the more easily electrons are promoted, the
smaller the excitation energy and the lower the wavelength of the
light which will be absorbed. As most absorptions obey the Frank-
Condon principle, the state obtained in an absorption is not only
electronically but also vibrationally excited. Since most molecules
have in the ground state a singlet manifold, they will be excited to
the singlet excited state. The molecule may revert to its ground
state by emission of a photon of slightly longer wavelength than that
of the absorbed photon (fluorescence) or by radiationless conversion
or by generation of heat. In some cases, intersystem crossing can
take place, and the molecule will find itself in a higher multiplicity
and hence less energetic level (excited triplet). When the molecule
goes from this more stable state to its ground state, there may still
be an emission, either of a quantum of much longer wavelength than
that of the absorbed radiation (phosphorescence) or of heat. If
the molecule has sufficient energy in the excited state, whether as a
singlet or as a triplet, a bond dissociation may occur at some point in
the molecule, not always on the group involved in the absorption of
the quantum. Hence the dissociation of the molecule, that is, the
cleavage of chemical bonds in a compound under the influence the
light will create free radicals. Since the free radicals formed in most
photochemical reactions are very active and undergo secondary chemical
interactions, various methods of stabilization are necessary to enable
them to be studied analytically.

4.3 Mechanochemistry in General[205-207]

The basic principle underlying the mechano-chemical polymeric

reactions is the scission of carbon-carbon, carbon-oxygen, or other

chemical bonds between atoms, within the backbone of a polymer macro-

molecule under the influence of an applied mechanical stress. The

mechanochemistry of polymers includes processes in which mechanical

stress initiates or accelerates the development of chemical reactions,

or influences them in some other way.

Basically, in the mechanical process, when a polymeric solid or

liquid is subjected to an applied stress, individual macromolecules

deform to try to reach new equilibrium positions. When the resulting

mechanical forces acting on the polymer overcome intramolecular forces

holding the polymer together rupture of primary chemical bonds may

take place. Mechanochemistry thus involves a reaction for which the

activation energy is supplied mechanically. Its consequence is chain

rupture and subsequent formation of macroradicals. The magnitude of

the experienced internal forces, which lead to chain rupture, depend

predominantly on the stress and on the local molecular structure.

Usually the crosslinks or the junction points of entangled molecules

are considered the position of high energy although the maximum might

be midway between entanglements. The reactivity and the fate of

macroradicals in mechanically degraded polymers depends on the parti-

cular environment in which they are formed as well as the structure of

the polymer in question. They can participate in a wide variety of

reactions to form new terminal groups. In the presence of free radical

scavengers such as oxygen, a peroxy compound will result. In an inert atmosphere in the absence of radical scavengers, recombination, disproportionation or other reactions may occur. Occasionally, a radical may react with another polymer molecule and thus lead to the production of branching or cross-linking. All of these reactions will influence the physical, mechanical, and chemical properties of the polymer.

4.4 Electron Spin Resonance[208-213]

Electron spin resonance (ESR; also known as electron paramagnetic resonance, EPR) is a very powerful and sensitive method for detecting, and quantitatively measuring free radicals. It may be fair to say that within the last two decades or so ESR has become one of the more popular and perhaps the single most important experimental approach for research on free radicals.

Principles of ESR Spectroscopy

A free radical (unpaired electron) has a spin and a magnetic movement. It can thus exist in two spin states, which are of equal energy in the absence of an external magnetic field. In the presence of an external field the electron can align itself parallel or anti-parallel to this field. The difference in energy of these orientations is given by the equation:

$$\Delta E = g\beta H \qquad (8)$$

where g is the Landé factor which is a dimensionless proportionality constant of value 2.003, β is the Bohr magneton, and H is the strength of the applied magnetic field in gauss. If radiation is supplied to the sample of frequency γ, such that when the energy of each quantum

equals the difference in energy between the electron states, i.e.,

$$h\gamma = \Delta E = g\beta H \tag{9}$$

resonance occurs.

Characteristics of ESR Spectra

ESR spectra are characterized by four parameters: g-values, hyperfine splittings, line-widths, and intensity. A close study of these parameters enables much detailed structural information about the particular radical to be gleaned.

g-values: The g value is the absolute magnetic field position of the line of an ESR spectrum, as characterized by the equation $h\gamma = g\beta H$. For the free electron the value of g resulting from the electron's spin is 2.00232.

Since the absolute measurement of a g-value requires knowledge of the microwave frequency and the resonant magnetic field, a number of systematic errors can enter, hence, absolute measurements are rarely attempted. Instead one employs standards for which g-values are well known. Table 2 lists the g-values for some of these standards. The unknown g value g_x is

$$g_x = \frac{g_s H_s}{H_x} = \frac{g_s H_s}{H_s - \Delta H} = g_s \left(1 + \frac{\Delta H}{H_s}\right) \tag{10}$$

Here g_s is the g-value of the standard and H_s and H_x are the resonant magnetic fields for standard and unknown, respectively, and

$\Delta H = H_s - H_x$.

As g-value is measured with high accuracy by the position of the center of the spectrum along the base line (measured relative to a

Table 2. Various g-values for standard samples.

Standard sample	g-value
DPPH (α,α'-diphenyl-β-picrylhydrazyl) powder	2.0037
Wurster's blue perchlorate in degassed ethanol	2.0031
Manganous ion (Mn^{2+}) in SrO powder	2.0012
Fremy's salt (Potassium peroxylamine disulfonate)	2.0055
Varian pitch	2.0028
Diphenyl nitroxide	2.0065

standard radical), this parameter has some value in characterizing

the type of radical being observed.

Hyperfine splitting: This is by far the most useful characteristic

of ESR spectra both for elucidating the structure and also the shape

of the radical under study. Although the number of lines of a given

spectrum can be simply calculated, another factor determines the

appearance of the spectrum, namely the spectrum of lines caused by

interaction with each group of magnetic nuclei, known as the splitting

factor or splitting constant α. The value of α is a measure of the

strength of the interaction between the unpaired electron and the

neighboring magnetic nuclei, or a measure of the time which the

electron spends in its vicinity. Hence, a nucleus too distant for

interaction may be considered to have α = 0.

The number of hyperfine lines from a particular nucleus depends

on the nuclear spin, I; this number is given by $(2I + 1)$. For $I = \frac{1}{2}$,

e.g. protons, each nucleus gives rise to two hyperfine lines. The

distance between these two lines is the hyperfine splitting constant α,

as mentioned earlier, which reflects the strength of the nuclear

hyperfine interaction.

Line-widths: The line-width is the distance, in field units, between

the maximum and minimum resolved peaks in the first derivative

representation. The line-width of an ESR absorption is related to the

lifetime of a particular spin state. This lifetime is reduced if

there is rapid interchange of interacting magnetic nuclei. In most

cases, line-width includes a contribution from anisotropy in both the

g-value and the hyperfine splitting and increases with increasing

viscosity and decreasing temperature.

Intensity: The intensity of the spectral signal or, more accurately, the integrated area, is represented by an overall spectral envelope. Experimental and other considerations being equal, signal strength is directly proportional the number of free radicals in the sample.

IV. EXPERIMENTAL SECTION

1. Materials

i.1 Preparation of Wood Meal, Lignin, and Cellulose

The wood and neutral sulfite semichemical pulp samples from sapwood of Douglas-fir trees (Pseudotsuga menziesii) were obtained from the Weyerhaeuser Company's Everett Laboratory at Everett, Washington. Wood meal was prepared by grinding the wood chips in a Wiley mill to pass a one millimeter screen, sieving through a 48 mesh screen, extracting two days with an acetone:water mixture (9:1), drying in air and storing under vacuum over P_2O_5.

Douglas-fir milled wood lignin (MWL) was obtained by milling Douglas-fir wood meal in porcelain mill jars. This apparatus was used with three Roalox porcelain mill jars of 1.3 gallon capacity each, and high carbon chrome steel balls of three-eighths inch average diameter. The charge always consisted of 3500 grams of steel balls and 25 grams of wood meal. The mill was rotated at a constant speed of 60 r.p.m. All the millings were carried out in carbon dioxide in the cold ($2^{o}C$). The resulting product was a fine powder.

The crude MWL was then purified by dissolving it first in 90% acetic acid; precipitating into water; centrifuging and freeze drying from dioxane:water (9:1). The sample was then dissolved in 1,2-dichloroethane:ethanol (2:1) and centrifuged. The supernatent was precipitated into ether and filtered. This precipitate was washed several times with ethyl ether, dissolved again in dioxane:water (9:1), and freeze dried. The MWL obtained was in a powdered form.

42

A lignin-free cellulose sample was obtained by bleaching NSSC pulp (59.44% yield) by the hypochlorite method of Norman and Jenkins.[214]

1.2 Lignin Model Compounds and Chemical Agents

Several lignin model compounds were selected and used in this study. They are depicted in Fig. 5. Model compounds I to VI were available in the laboratory from the previous studies by W. G. Glasser. Compound VII , 4-methyl-o-quinone, was synthesized by oxidation of creosol with sodium metaperiodate as described by Adler and Magnusson.[215]

Some chemical agents employed in this study were reagent grade commercial samples. These are benzoyl chloride, creosol, dimethoxy-benzene, 2-hydroxy-4-methoxybenzophenone, ether, and benzene. Others were ACS certified spectranalyzed grade materials. These are toluene, phenol and dioxane.

2. Methods

2.1 Mechanical Degradation of Wood, Cellulose, and Lignin

Grinding mechanical energy was delivered to the samples in a Norton ball mill as described in a previous section. Samples were collected every 24 hours from the jar and frozen at liquid nitrogen temperature ($77^{\circ}K$) for analytical studies. Owing to the sampling difficulties for steel-ball milling, in some cases, cellulose and lignin were milled in a Pyrex flask with Pyrex beads. The grinding flask with a capacity of one liter, in this case, was charged with 0.5 g of air dried sample and 9 g of Pyrex beads. Milling was carried out in nitrogen, carbon dioxide or in oxygen at ambient temperature by stirring the sample together with glass beads with a stirrer at

(I) $R_1 = CH_3$, $R_2 = H$

(II) $R_1 = C_6H_5CH_2$, $R_2 = H$

(III) $R_1 = CH_3$, $R_2 = Br$

(IV) $R = CH_3$

(V) $R = C_6H_5CH_2$
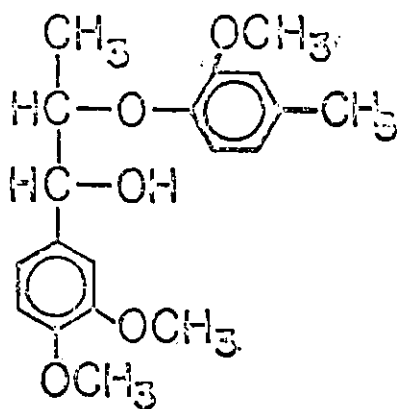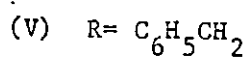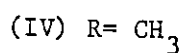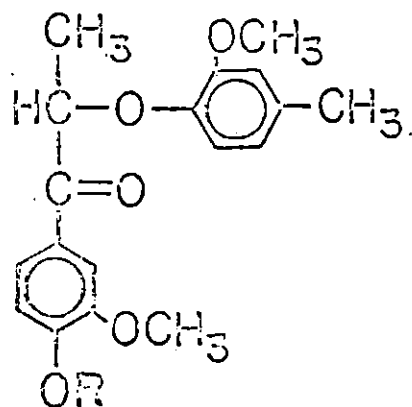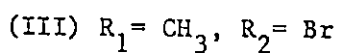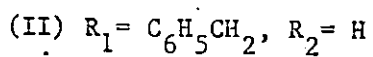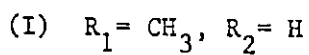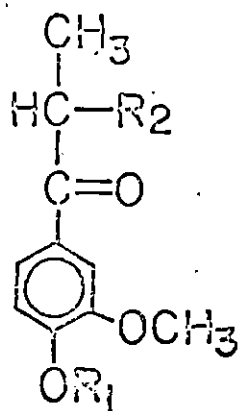
(VI)
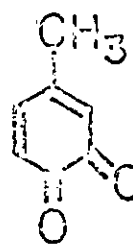
(VII)

Fig. 6 Lignin model compounds.

a constant speed of 700 r.p.m. for three hours. For low temperature

study, the lignin sample was milled in a specially designed Pyrex

flask with a capacity of 30 ml, charged with 0.5 g of air dried sample

and 5 g of Pyrex beads. This flask was vibrated vertically at about

15 cycle/sec in a Dewar flask. Millings were carried out in vacuum,

in liquid nitrogen, or in liquid air (mostly oxygen) at liquid nitrogen

temperature. The achematic diagram of this milling apparatus is

given in Fig. 7. After the samples were milled at this temperature

for 3 hours, liquid nitrogen was introduced into the milling flask,

and the samples were transferred together with liquid nitrogen to ESR

sample tubes (E in Fig. 7), which were inserted into Dewar flasks

filled with liquid nitrogen. Subsequently, the liquid nitrogen in

the ESR sample tubes was pumped away with a vacuum pump, and the

tubes were sealed for ESR measurements.

2.2 Photoirradiation of Lignin

The source of ultraviolet irradiation used was a high-pressure

mercury-xenon compact arc lamp (Conrad Hanovia, Inc., lamp type 901B0011,

200 W) with a lamp housing constructed in the laboratory (Fig. 8).

The relative spectrum energy distribution of the light source, as

given by the manufacturer, is given in Fig. 9. Several kinds of

filters were used, the transmissions of these filters are shown in

Fig. 10.

For irradiation, the prepared samples were placed in a wooden hous-

ing, the inner wall of which was covered with aluminum foil. This hous-

ing had several ventilation openings, and a movable window which can be
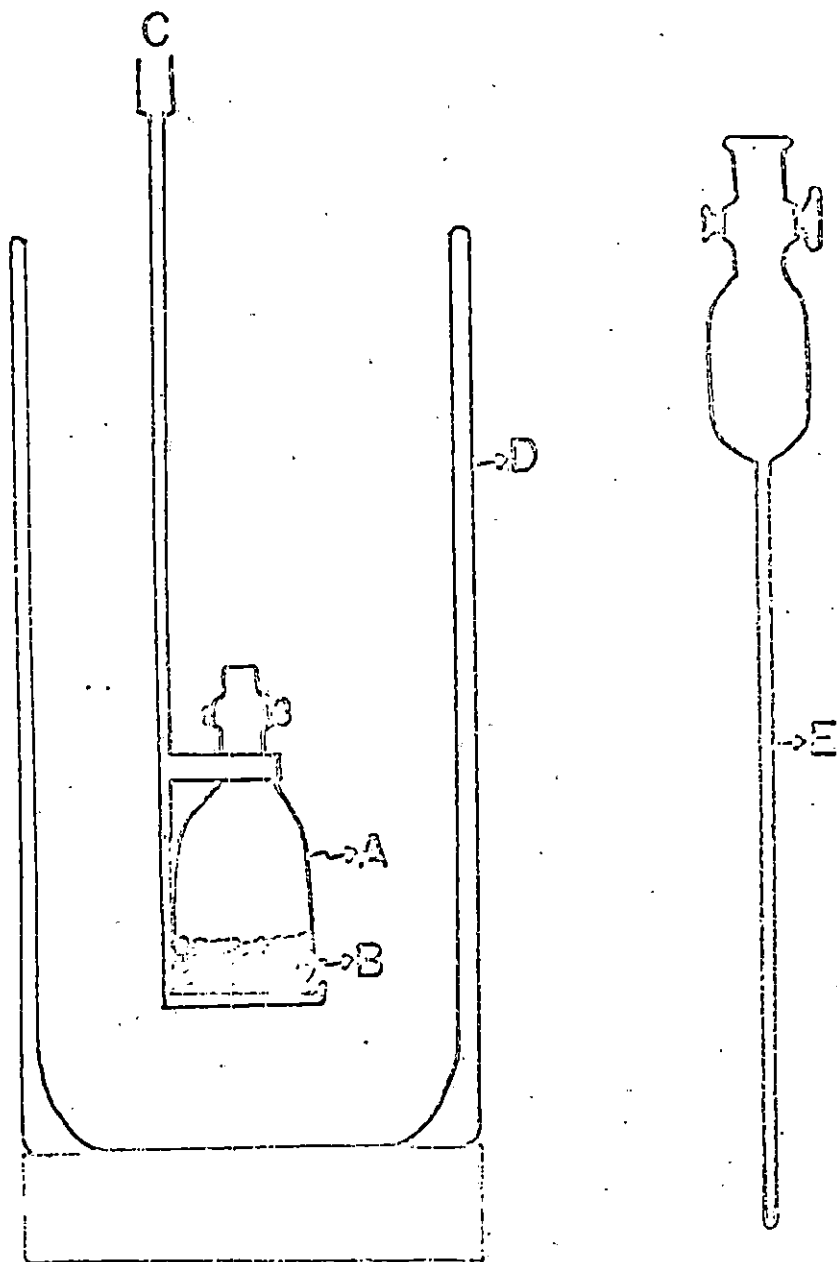
Fig. 7 Schematic sketch of low temperature ball-mill apparatus.
A, glass flask; B, glass beads for milling; C, vibrator connec-
tion; D, Dewar flask containing coolant (liquid nitrogen); E,
ESR sample tube.
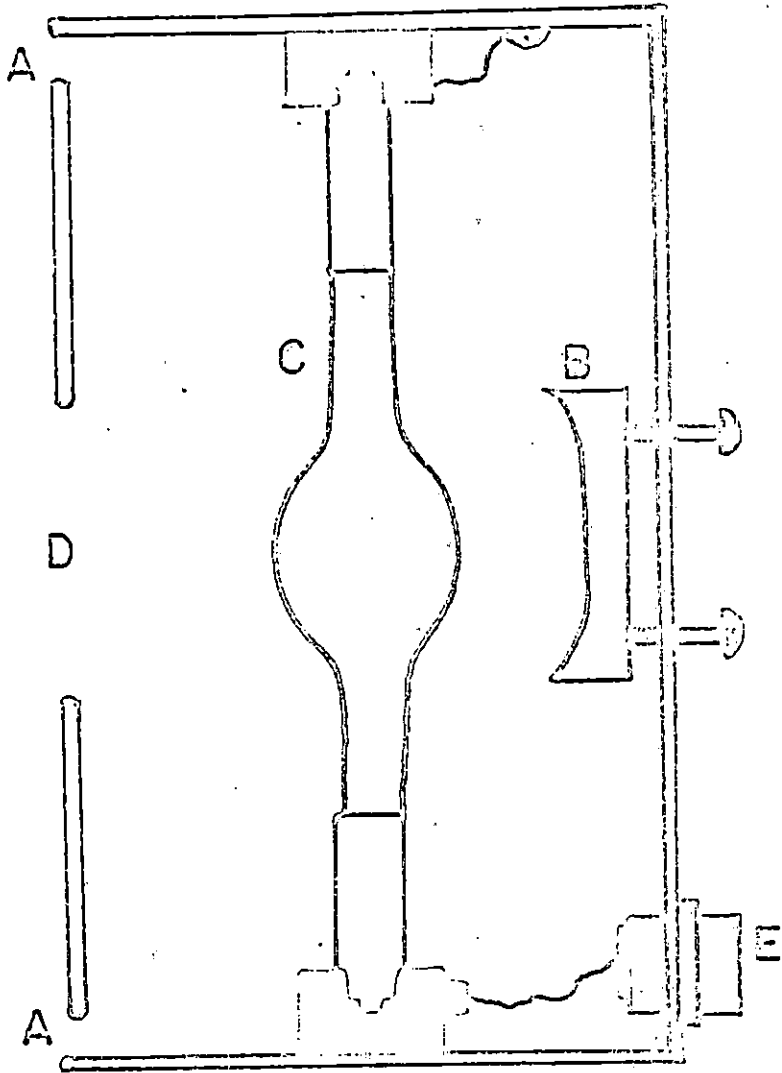
Fig. 8 Lamp housing for the mercury-xenon compact arc lamp.
A, air inlet and outlet; B, mirror; C, lamp; D, window;
E, high voltage connection.

Fig. 9 Spectral distribution of irradiation energy from the mercury-xenon compact arc lamp.
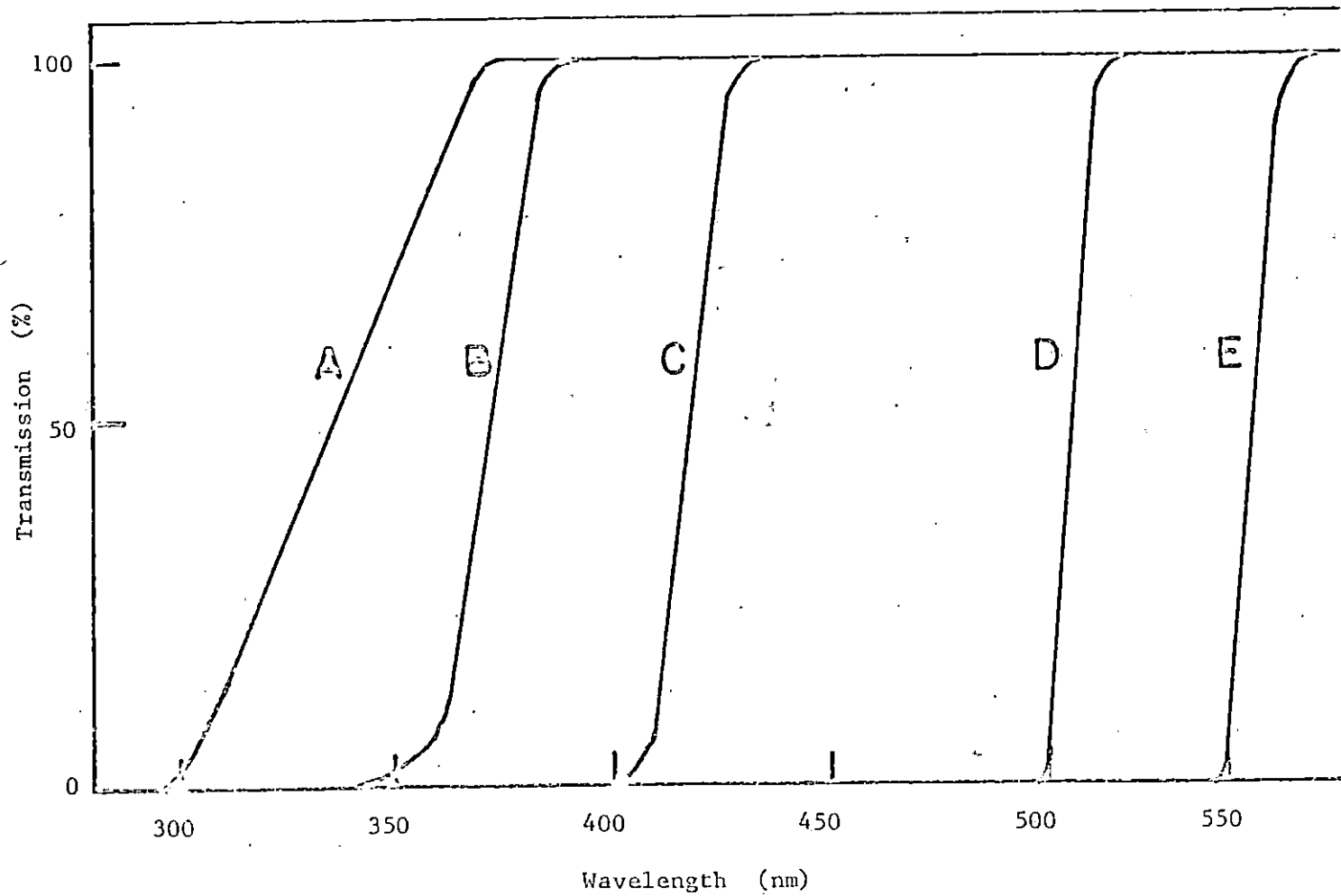
Fig. 10 Transmission curves of sharp-cut-off glass filters. A, indigo; B, green,

C, light-yellow; D, yellow; E, orange.

replaced by a filter. The irradiations were carried out in a well-ventilated hood, hence, heat effects from the light source were made negligible by cooling with an effective air blower.

For ESR studies, lignin or model compounds were packed into a clear fused Suprasil quartz tube (OD 4 mm), which did not produce any signal during the irradiation sequences. The quartz tube containing the samples was evacuated to a constant pressure (10^{-3} mm Hg) and sealed. It was then inserted into a Dewar flask filled with liquid nitrogen, and the flask was inserted into the wooden-housing as mentioned before.

The distance between light source and sample was about 30 cm. The ultraviolet light reached the sample in the quartz tube by passing through a filter (if a filter was used), the two unsilvered quartz walls of a Dewar flask, a liquid nitrogen layer less then 0.5 mm thick, and the quartz wall of the sample tube. The quartz tube containing sample was rotated during the irradiation to ensure uniform irradiation on all surfaces of the sample.

2.3 ESR Measurements

ESR spectra were measured with a Varian E-12 spectrometer operated at X-band with 100 KHz modulation. The g-value was measured by comparison with the pitch provided by the Varian Associates. Free radical concentration was determined by comparing the ESR signal area, which was measured planimetrically, of the observed spectrum with that of the spectrum of 1% α,α'-diphenyl-β-picrylhydrazyl (DPPH) in potassium bromide at the same level of gain and microwave power.

To avoid distortion of the spectra by power saturation, the ESR measurements were carried out at a microwave power of 3 mW. The spectra were measured at about 9400 mc/sec and 3,300 gauss. All spectra were recorded at 77°K by inserting a Dewar flask with a quartz tail into the cavity. For studies at temperatures higher than 77°K, the sample tube was transferred rapidly to the ESR cavity after irradiation at 77°K. The sample temperature was controlled by a standard Varian-temperature accessory (Model-V4257).

2.4 Measurements of Mechanical and Photochemical Degradation

Loss of weight of sample was determined from the initial and final oven-dry weights of milled or photoirradiated samples dried at $105 \pm 3^{\circ}$C for 24 hours.

Change in relative viscosity of samples during milling or photoirradiation was measured in dioxane-water (9:1) solution or in cellosolve solution by using a viscometer. The measurements were carried out in a thermostat at $25.00 \pm 0.05^{\circ}$C. The ultraviolet spectra were obtained with a Hitachi-Perkin-Elmer Model 139 spectro-photometer at room temperature.

The fractions of lignin model compounds after photoirradiation were initially characterized on Sephadex LH-20, fine (Pharmacia Co., Uppsala) using 9:1 dioxane-water for elution. The chromatograms obtained from the analytical columns were recorded by measuring the absorbance, at 280 nm, of the effluent by means of a Unicord II flow-through photometer, manufactured by LKB-Produkter, Stokholm-Bromma, Sweden.

1.5 Photoreduction of Lignin and High-yield Pulps

Lignin dissolved in dioxane-water (9:1) was irradiated with the ultraviolet light of various wavelengths, by using a filtering system, for certain time, and the sample freeze dried. High-yield pulp fibers were suspended in dioxane-water and irradiated under the identical irradiation conditions as was the lignin solution. The treated pulp remaining after filtering of the solvent was washed thoroughly with distilled water, and air-dried. In some cases, 0.05% w/w of UV absorber, 2-hydroxy-4-methoxybenzophenone, was added to the photobleached lignin as a photostabilizer.

V. RESULTS AND DISCUSSION

1. Mechanical Degradation of Wood, Lignin, and Cellulose

1.1 Mechanical Degradation: Ambient Temperature Studies

1.1.1 Naturally occurring free radicals in wood and lignin. Although Rex[65] and Ranby, et al.[64] reported that free radicals did not exist in protolignin, many lignin chemists have detected stable free radicals in isolated lignins. It was suggested[277] that free radicals in lignin may be produced in wood enzymatically, thermally, and chemically during isolation processes.

Stable free radicals actually existed in all lignin containing samples used in this study. As shown in Fig. 11, wood chips and wood meal produced from chips by passing through a Wiley mill, and MWL (all of these samples were stored at ambient temperature for half a year after preparation before tests) exhibited ESR resonance lines with a line-width of 10, 11, and 16 gauss respectively, and all have g values close to 2.003. The concentration of these intrinsic free radicals are in the order of 0.043×10^{17}, 0.976×10^{17}, and 2.446×10^{18} spins/gram respectively for wood chips, wood meal, and MWL. A cellulose sample, however, exhibited no ESR signals even at the highest gain that could be obtained on the instrument used. This implies that, differing from wood chips, wood meal, and MWL, cellulose does not bear any intrinsic free radicals. It is obvious that the ESR signals generated from free radicals in wood chips and wood meal are not derived from the cellulose component. Since the line-shapes and the g-values of the ESR spectra observed from wood chips and wood

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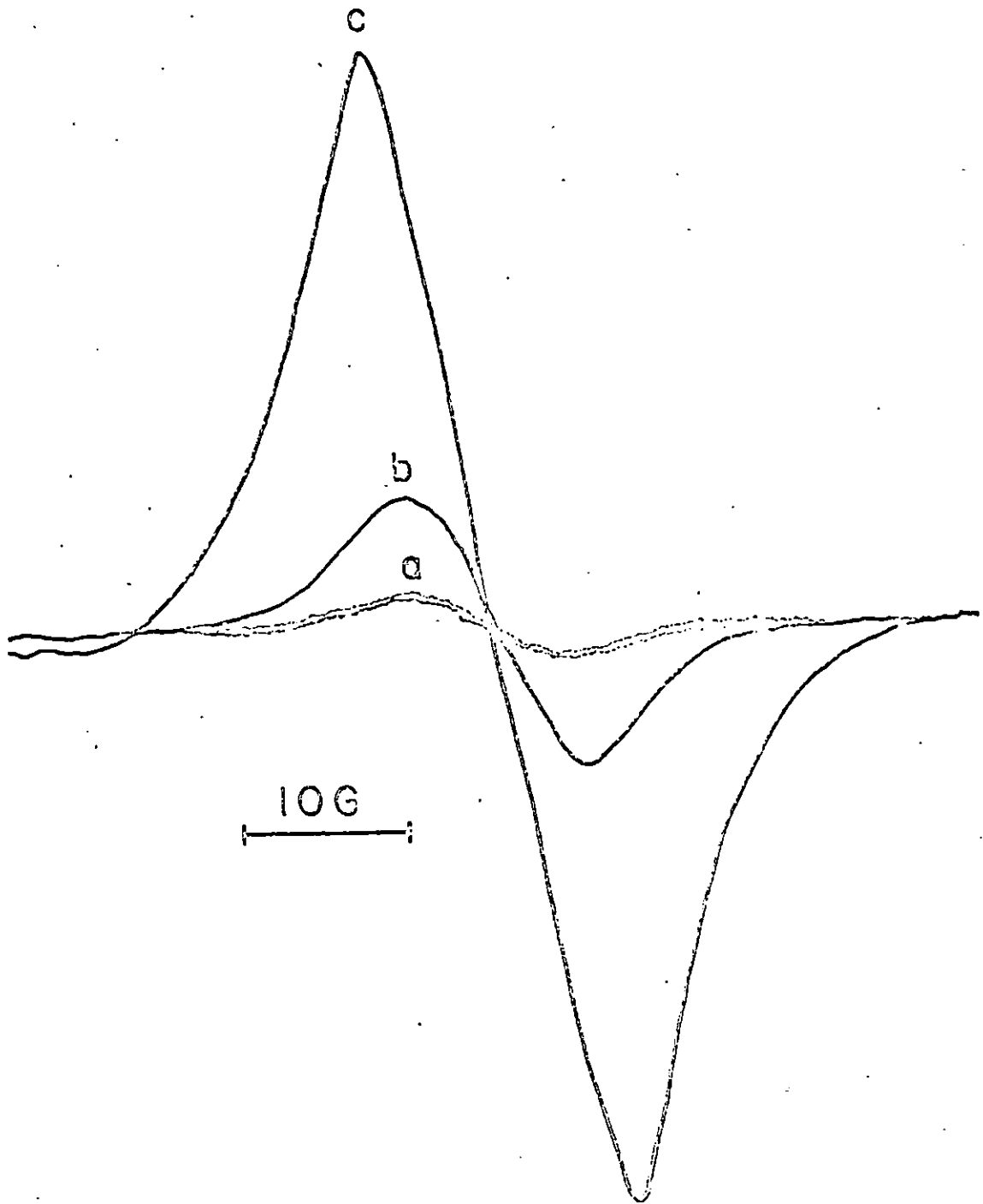
Fig. 11 ESR spectra of intrinsic free radicals in wood chips (a), wood meal (b), and MWL (c). Spectra were recorded at $77^{o}K$.

neal match those from MWL, it is plausible that these signals are derived from intrinsic free radicals originating in the lignin component.

1.1.2 Mechano-radicals produced by steel-ball milling. When wood meal was milled with a steel-ball mill in carbon dioxide at $2^{o}C$, free radicals were generated in the sample and were detected by ESR spectroscopy. The radicals were exhibited as a singlet ESR resonance line with a line-width of 15 gauss, having a g-value of 2.003. Since the line-shape and line-width together with the g-value conform to those from lignin, it is believed that free radicals were produced in the lignin component of the wood meal.

From further study of the effect of milling time on the formation of free radicals in the lignin of wood meal, a number of features are of interest. The results are shown in Figure 12. They are based on data obtained from millings carried out in February of 1976; and in February of 1977. Three samples each were collected from the first milling, and 12 samples each from the latter. The experimental data indicate that concentration of free radicals produced during milling was reproducible, and no experimental artifact.

Fig. 12 suggests that free radicals were produced at a high rate during the early stages of ball-milling, with the maximum amount being recorded on the fourth day. This period of radical build-up is followed by a decline on the fifth day of milling, and levelling off for further milling periods.

Since the milling was carried out at $2^{o}C$, it is believed that formation and decay of mechano-radicals occurred synchronously during the course of the milling. It is plausible that during the first four
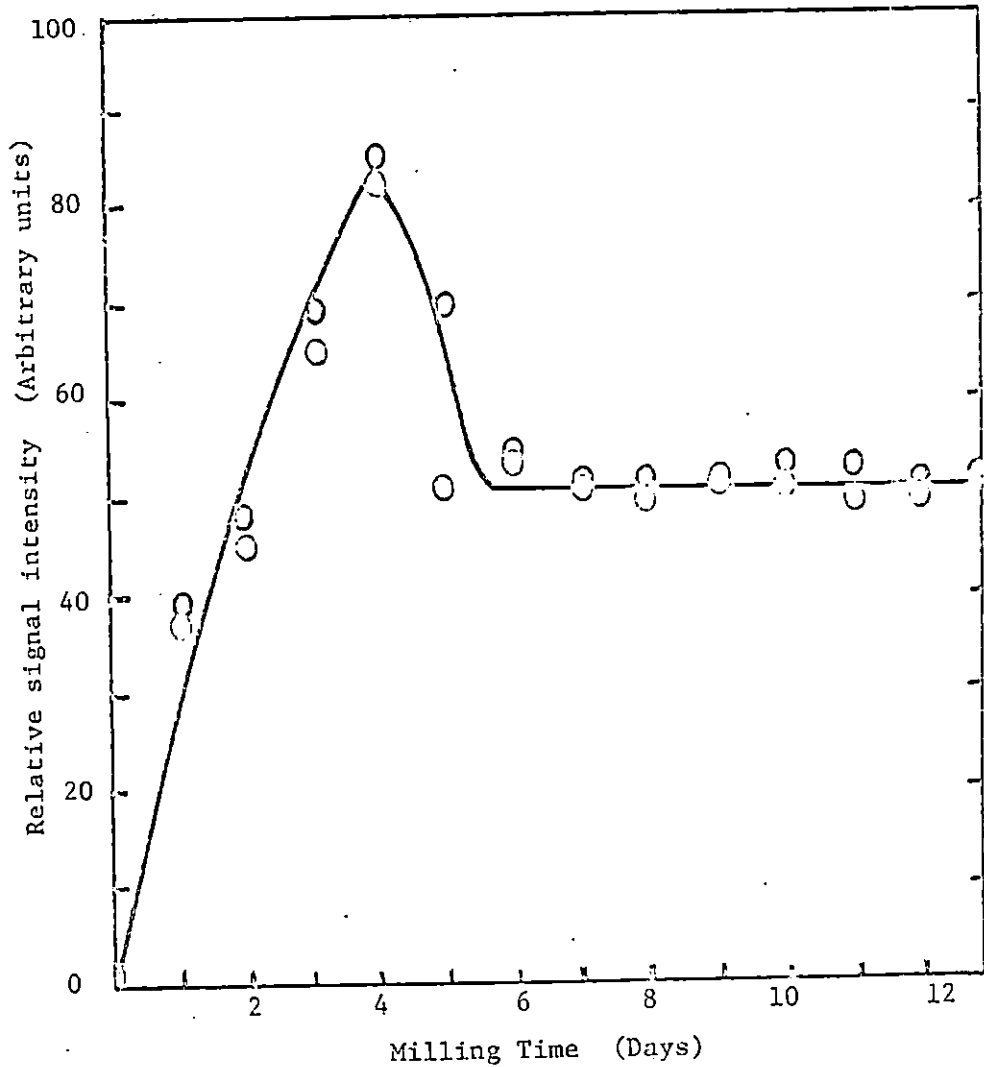
Fig. 12 Accumulation of free radicals in wood meal milled
with steel balls in carbon dioxide at $2^{o}C$. Data obtained from two
sets of experiments: (O), milled in February of 1976; (◌),
milled in February of 1977.

days of milling, most of the lignin mechano-radicals formed were trapped in a rather rigid and stable matrix which restricted their mobility. Consequently, the rates of formation and accumulation were greater than the rate of decay of mechano-radicals. However, it seems that beyond the fourth day of milling, the rate of decay of mechano-radicals increased and exceeded the rate of formation, resulting in the decrease of mechano-radical concentration. The rates of formation and decay of mechano-radicals reached equilibrium after about six days of milling.

It would be interesting to find if the concentration of mechano-radicals in lignin is consequently controlled by the particle size of the wood meal. Unfortunately, it was not possible to determine the size of milled wood particles because of the tendency to agglomerate to large aggregates. Yet from the pictures of scanning electron microscopy (SEM), as shown in Fig. 13, it is apparent that the particle size was reduced drastically in the fourth day of milling; beyond this period, the reduction of particle size was insignificant. On comparison of the ESR and SEM studies, it was revealed that the trends of mechano-radical formation and particle size reduction are seen to parallel one another.

1.1.3 Mechano-radicals produced by glass-bead milling. In order to procure information on the progression of mechano-radicals produced in the lignin and cellulosic components of wood, a glass-bead milling was performed.

When wood meal, cellulose, and MWL were milled in carbon dioxide at $0 \sim 2^{\circ}C$ for 3 hrs, ESR spectra of these samples were detected at $77^{\circ}K$. They are shown in Fig. 14. ESR spectrum of cellulose exhibited a poorly resolved multiplet signal. Such an observation indicates that mechano-

(a)

(b)

Fig. 13 Change of particle size of wood during milling. Milling time: (a), before milling; (b), 1 day; (c), 2 days; (d), 3 days; (e), 4 days; (f), 5 days; (g), 9 days; (h), 13 days. Magnification: x 100.
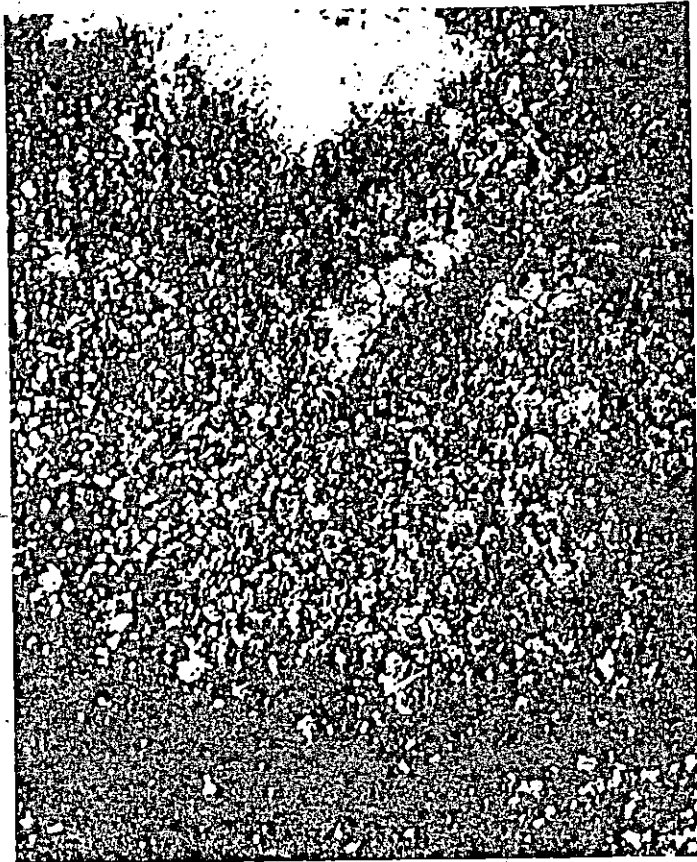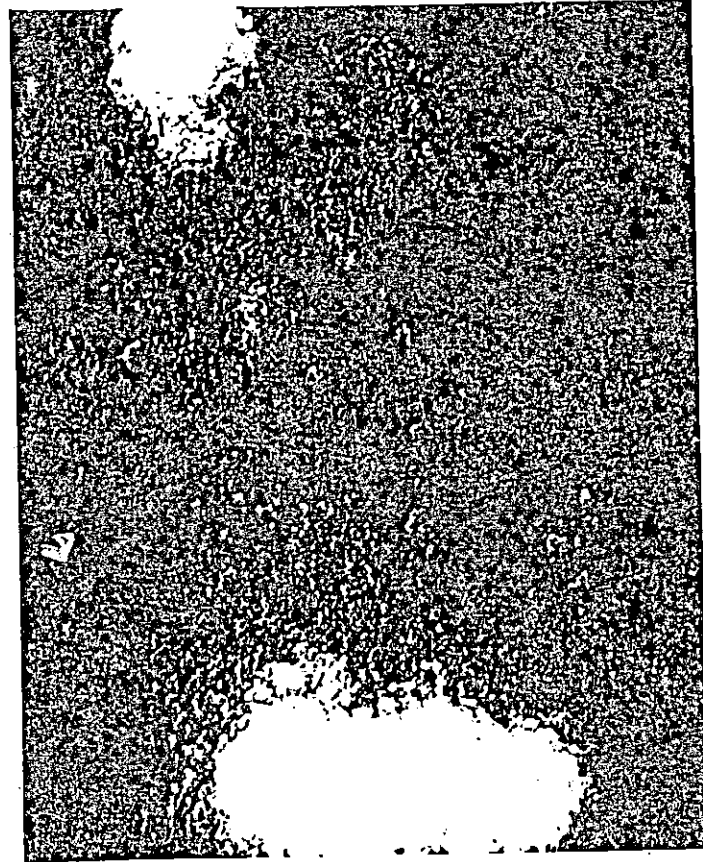
(c)   (d)

Fig. 13 Continued.
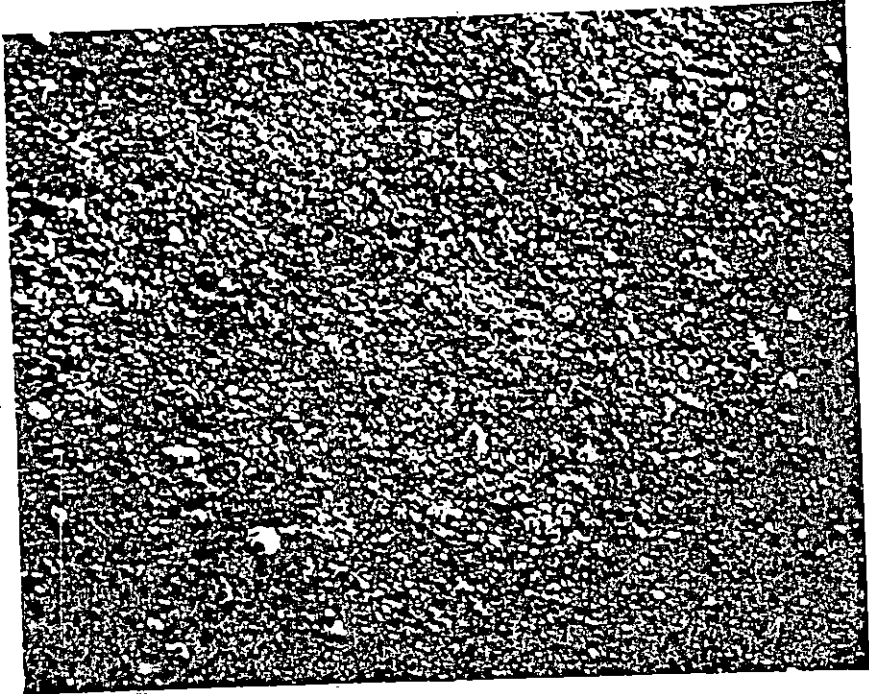
(f)
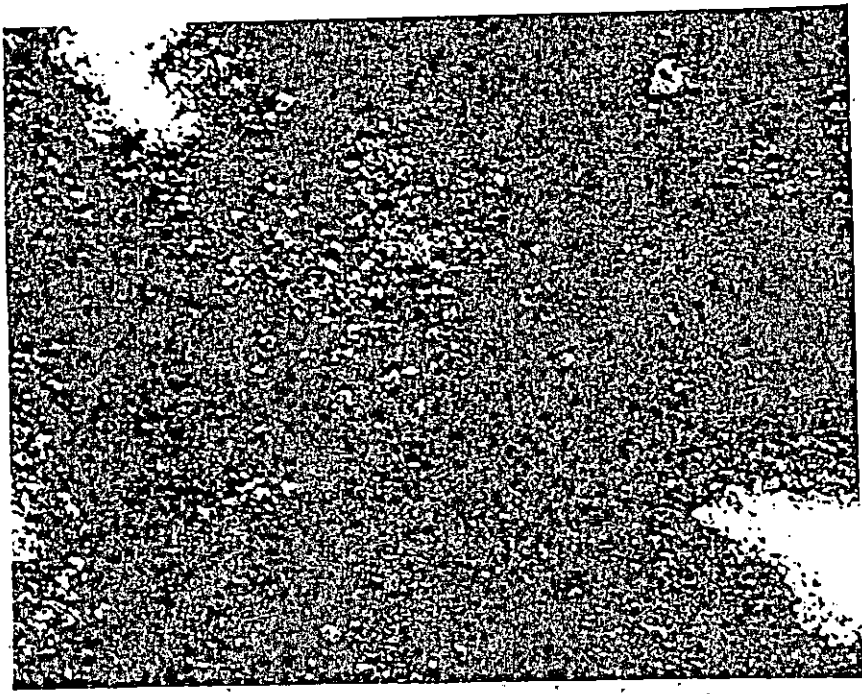
(e)
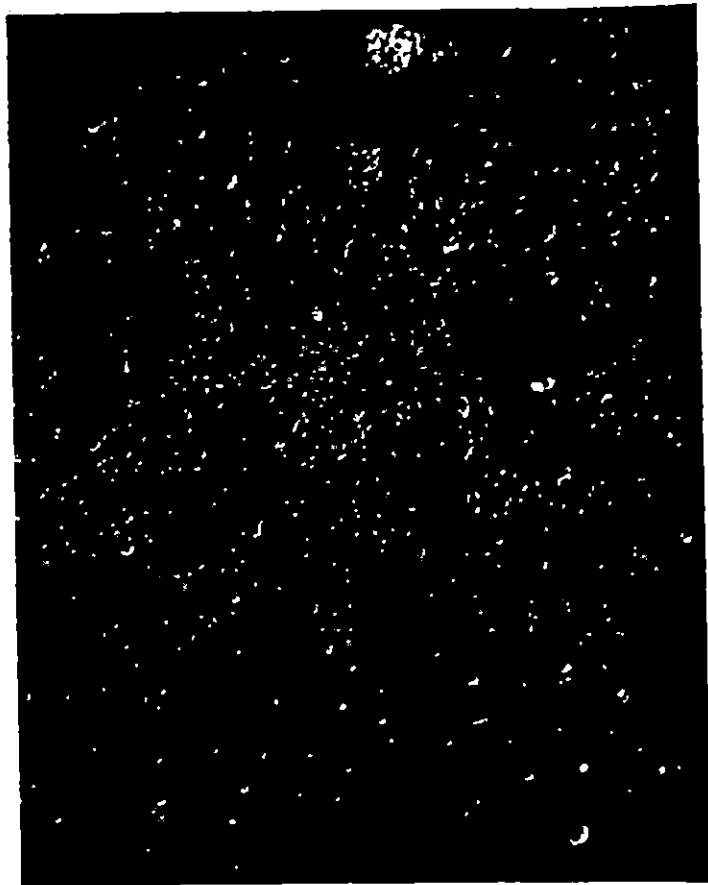
(g)   (h)

Fig. 13 Continued.
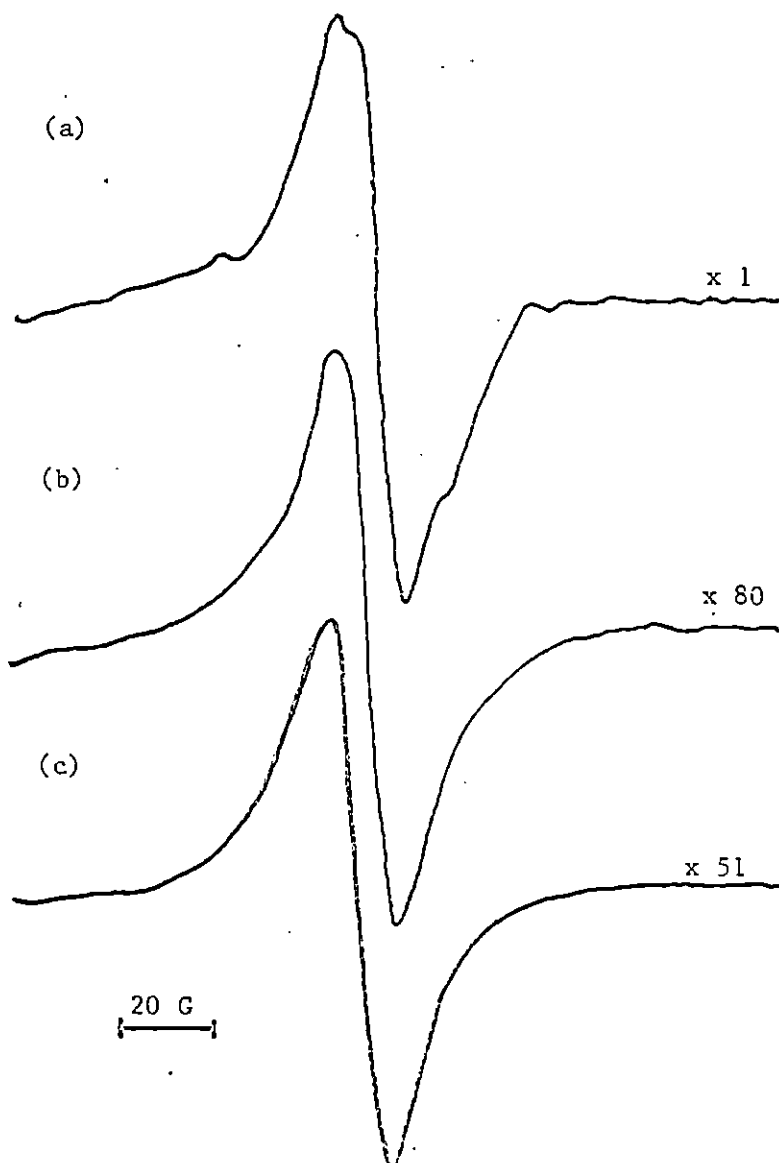
Fig. 14 ESR spectra of cellulose (a), MWL (b), and wood meal (c) milled with glass beads for 3 hrs in nitrogen at ambient temperature. Spectra were recorded at 77°K. Multiplication number represents the ESR relative signal intensity.

radicals were produced in cellulose by mechanical stress, inasmuch as no ESR signal was observed before milling. However, the relative signal intensity was very weak as compared with those from MWL and wood meal samples. Both lignin and wood meal exhibited a singlet signal with a g-value of 2.003. Among these three samples lignin exhibited the strongest signal whereas the signal of cellulose was the weakest.

When these samples were milled in the presence of nitrogen or oxygen, similar singlet signals were detected from all samples. Essentially there is no significant effect on mechano-radical concentration when they were milled in either carbon dioxide or in nitrogen. However, ESR signals of all samples milled in the presence of oxygen were reduced to about 60% of those milled in the presence of carbon dioxide or nitrogen. In addition, the line widths of the signals were broadened, suggesting that oxygen-radical collisions occurred which contribute to the magnetic relaxation of free radicals.[216] The results are tabulated in Table 3. A similar effect was observed for photoinduced free radicals in lignin.[217]

As indicated from these findings, it is apparent that mechano-radicals are produced in wood during the milling process, i.e., by mechanical stress. The low concentration of free radicals in milled cellulose was observed. This may be because the labile cellulosic free radicals underwent secondary reactions before their ESR signals can be detected, whereas relatively stable free radicals were produced in lignin. Hence, a higher concentration of free radicals of lignin was observed.

It should be mentioned here that experiments in which the tested sample was replaced with powdered Pyrex glass showed that Pyrex beads

Table 3. Comparison of ESR spectra of wood meal, cellulose and lignin[#]

Sample	Atmosphere	ESR spectrum		
		Line	Line-width gauss	Relative intensity[##]
Wood meal	N_2	Singlet	11	50.0
	O_2	Singlet	13	30.6
	CO_2	Singlet	11	51.0
Cellulose	N_2	Multiplet	18	1.0
	O_2	Multiplet	22	0.4
	CO_2	Multiplet	18	1.0
Lignin	N_2	Singlet	15	78.0
	O_2	Singlet	18	49.0
	CO_2	Singlet	16	80.0

[#] Samples were milled with a glass-bead mill in carbon dioxide at
   2°C for 3 hr.

[##] Calculations based on the value of cellulose milled in nitrogen.

were not responsible for the ESR signal.

1.1.4 Decay of mechano-radicals in wood and lignin at ambient temperature.
Free radicals formed in lignin are capable of undergoing secondary
reactions, implying that free radicals formed in the system are highly
reactive. Decay of these free radicals was studied.

When the wood meal, after ball-milling for a certain period at $2^{o}C$,
was allowed to stand at ambient temperature in nitrogen or in carbon
dioxide for several days, the concentration of mechano-radicals decreased.
The results are shown in Fig. 15. These results indicate that whether
free radicals were produced on the 1st, 4th, or 10th day of milling,
the rate of decline in concentration was the same. It is obvious that
some portion of free radicals formed in lignin are not stable within
the first two days of storage at ambient temperature. After two days
elapsed, the surviving free radicals were relatively stable. The
difference in stability or reactivity of mechano-radicals formed in
lignin may be attributed in part to differences in radical structures;
another possible explanation is that even among identical mechano-
radicals, some remain more mobile within their immediate environment
that others; this restriction in mobility may result from polymer
rigidity or from steric effects. Hence, the more mobile or accessible
mechano-radicals were decayed more rapidly at ambient temperature than
the rest. It is noticed that after lignin was milled and stored at
ambient temperature for about 4 days, different concentration levels of
stable mechano-radicals were observed as shown in Fig. 15. This
indicates that certain stable mechano-radicals were being activated by
mechanical energy causing them to undergo decay reactions. Such
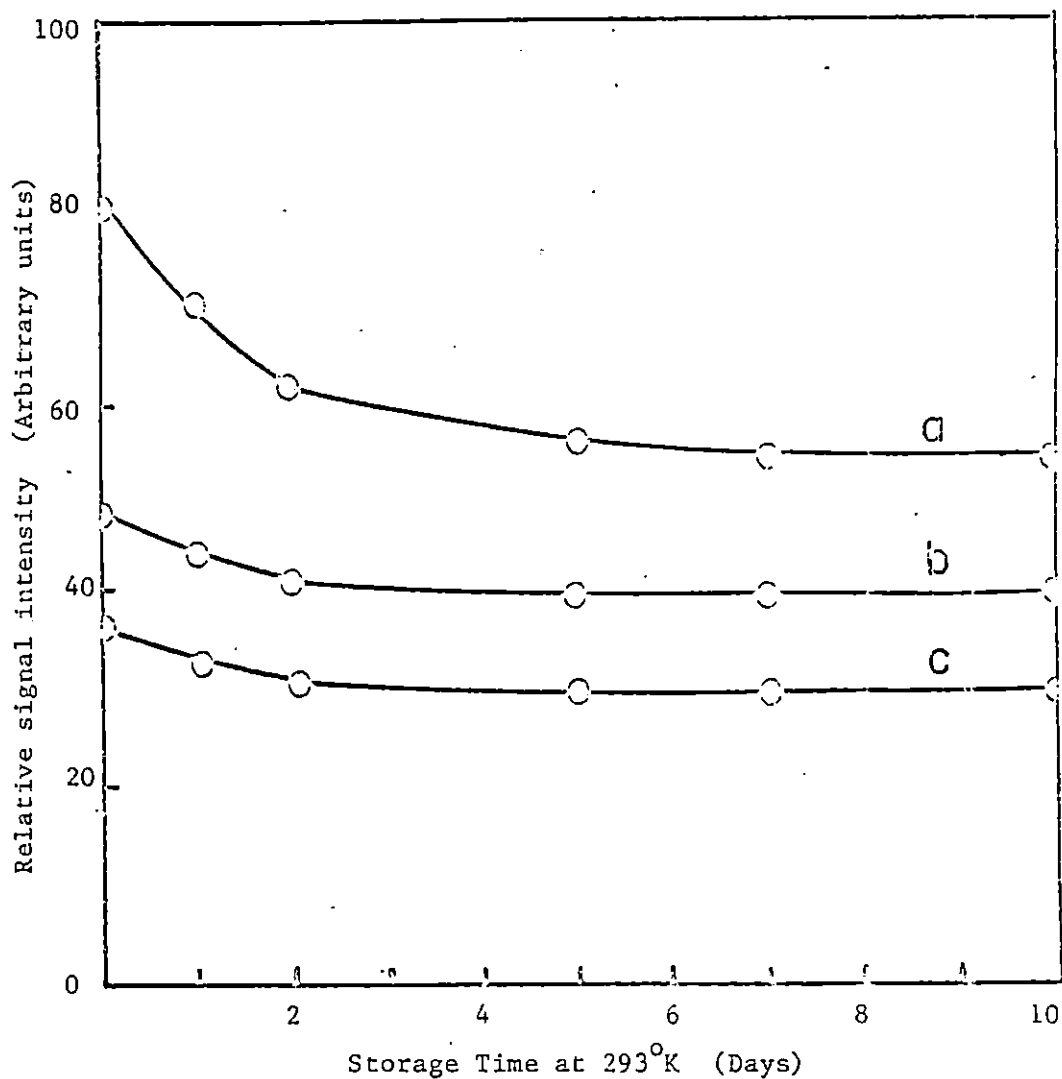
Fig. 15 Decay curves of ESR spectra of wood meal milled with steel balls in carbon dioxide at 2^OC for (a) 4 days; (b) 10 days; (c) 1 day.

reactions did not occur if the mechanical energy supplied was terminated.

It should be mentioned here that there is a possibility that the subsequent reactions of free radicals with the small amount of oxygen contaminating the nitrogen and carbon dioxide accelerated the decay of free radicals because they are very active toward the oxygen molecule as described below.

When oxygen was introduced into the sample tube, containing the ball-milled sample, at $77^{\circ}K$, variation of ESR spectra was not observed. However, when oxygen was introduced at ambient temperature and cooled to $77^{\circ}K$ for measurement, the variation of ESR spectra observed is clearly indicated, that is, the relative signal intensity of the spectrum was decreased to 60% of its original value. Based on this observation, we consider that free radicals formed in lignin must be very sensitive to oxygen, and it appears likely that peroxy radicals are subsequently formed. However, peroxy radicals were not detected in this study. This may be due to the fact that ESR lines of such a species are weak and masked by the stronger resonance lines of ligninic mechano-radicals, or the peroxy radicals are too active and undergo secondary reactions at ambient temperature before their signals could be detected at $77^{\circ}K$.

In addition the fact that the spectra were not changed when oxygen was introduced at $77^{\circ}K$ may be attributed to the low diffusion and reactivity of oxygen at-this low temperature. It should be noted here that the formation of peroxy radicals, however, was detected when sample was milled at $77^{\circ}K$. Details will be described in a subsequent section.

1.1.5 <u>Reaction</u> <u>of</u> <u>mechano-radicals</u> <u>with</u> <u>oxygen</u> <u>and</u> <u>radical</u> <u>scavengers</u>.

As mentioned in a previous section, formation of mechano-radicals in lignin during the milling process was not influenced by the presence of nitrogen and carbon dioxide, but free radicals underwent secondary reactions rapidly when in contact with oxygen.

When wood meal and MWL were milled in the presence of oxygen or other radical scavengers, secondary reactions were also observed.

When wood meal was milled in a stream of nitrogen, carbon dioxide, and oxygen, the ESR spectra observed indicate secondary reactions. This is illustrated in Fig. 16. When the milling was carried out in nitrogen or carbon dioxide the ESR spectra indicated the same magnitude of relative signal intensity, however, when the milling was carried out in oxygen, the relative signal intensity of the spectrum observed was very weak. This indicated that unstable mechano-radicals once formed in the system reacted rapidly with oxygen, leading to the termination of free radicals. Thus the ESR signal detected in oxygen was weaker than that produced in the inert atmosphere. This phenomenon was also observed in MWL when it was milled in oxygen.

The secondary reaction of mechano-radicals was also confirmed by introducing 1% w/w of radical scavengers into the milling system. When toluene and phenol were used as radical scavengers, the ESR signal generated from free radicals in lignin was greatly decreased even if milling was done in nitrogen or carbon dioxide. These ESR spectra are also shown in Fig. 16. Between the two scavengers used, toluene reacted with ligninic mechano-radicals more rapidly than
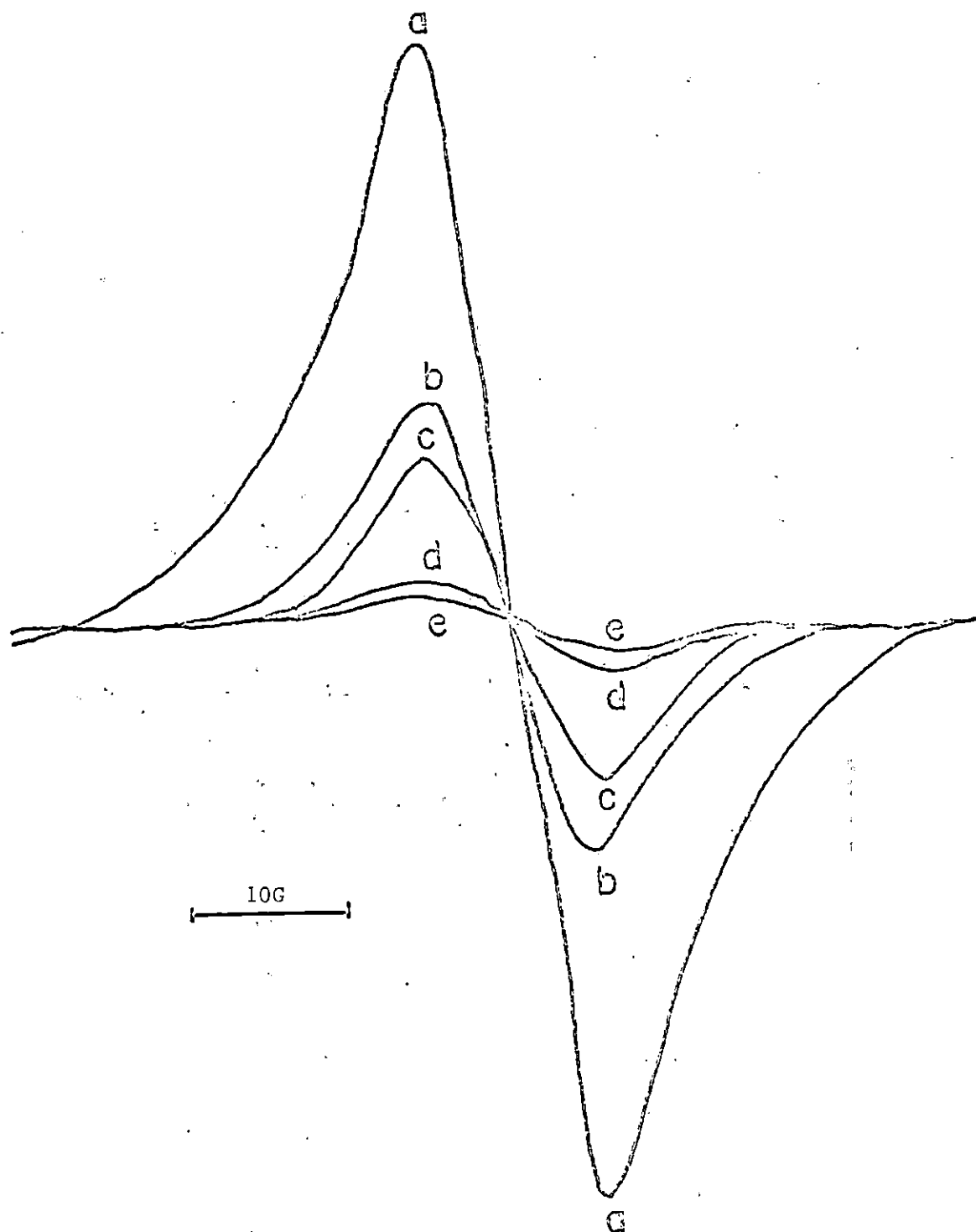
Fig. 16 ESR spectra of wood meal, milled with glass beads with radical scavengers for 3 hrs at ambient temperature. (a), control; (b), phenol in carbon dioxide; (c), oxygen; (d), toluene in carbon dioxide; (e), toluene in oxygen.

phenol in nitrogen, and the rate of reaction was slightly enhanced in oxygen. Hence, it is clear that ligninic free radicals are very sensitive to oxygen and toluene and phenol. Secondary reactions were accelerated by these additives, and free radicals were stabilized or terminated.

1.1.6 <u>Change of viscosity and loss of weight of lignin after milling</u>.

It has already been demonstrated that mechano-radicals were produced in lignin by means of mechanical stress, implying that lignin was mechanically fractured leading to the formation of mechano-radicals.

Mechanical degradation of lignin was further confirmed by the studies of change of viscosity and loss of weight after lignin was milled. For comparison, change of viscosity of cellulose was also studied.

Fig. 17 shows the effect of mechanical stress on lignin and cellulose during the glass-bead milling at ambient temperature (for original experimental data, see APPENDIX I). It is obvious that when milling was carried out in nitrogen, the viscosity of either lignin or cellulose decreased rapidly in the initial stages of milling; but after 5 hrs, the rate of change gradually diminished. Further, when milling was carried out in the presence of oxygen, the viscosity of both lignin and cellulose was much more reduced than when milling occurred in nitrogen. This can be attributed to the fact that the transient mechano-radicals were intercepted and stabilized by oxygen to form peroxy elements; where in the absence of oxygen, the mechanical reaction may have caused polymer branching and cross-linking.

From these viscosity measurements, it is noted that regardless of
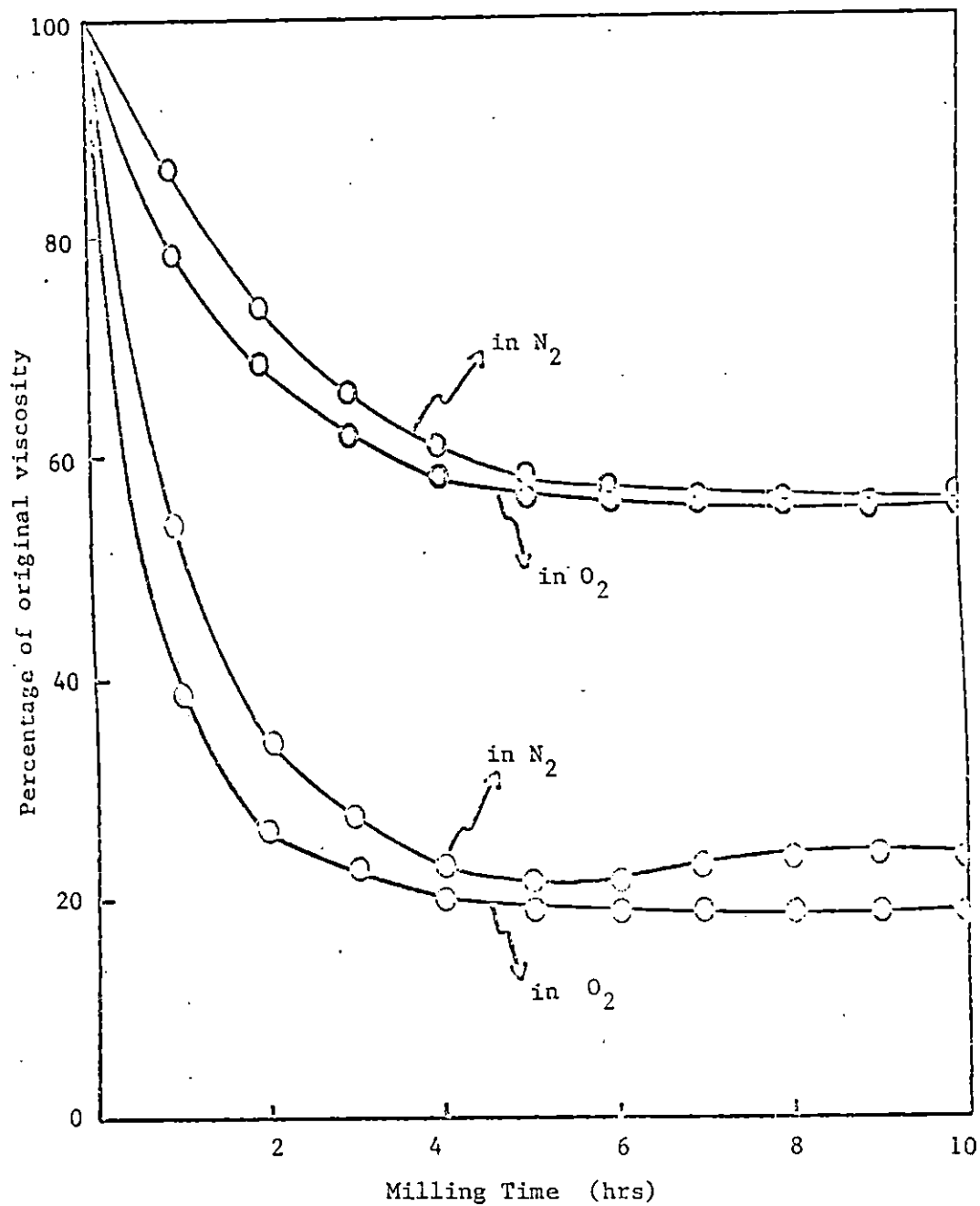
Fig. 17 Decrease of relative viscosity of cellulose (0) and MWL (0)
during glass-bead milling at ambient temperature.

atmospheric conditions (in oxygen or in nitrogen), the magnitude of
viscosity reduction was greater for lignin than for cellulose. This
implies that lignin suffered more severve degradation than cellulose
under identical milling conditions. It is also indicative of lignin's
superior performance as an absorber of compressing forces; a role, it
was originally designed for by nature.

Moreover, after lignin was milled for 10 hrs in the presence of
oxygen, carbon dioxide, or nitrogen, weight loss was determined by
extraction with a benzene-ether (1:1) solution overnight. Results are
shown in Fig. 4. It was found that a small part of the lignin was
extractable with benzene-ether. When lignin was milled in the presence
of nitrogen as well as in carbon dioxide, the loss of weight of lignin
was less than 0.6% in both cases, whereas in the presence of oxygen, the
loss was 1.8%.

1.2 Mechanical Degradation: Low Temperature Studies

1.2.1 Milling of lignin at 77°K.
When the lignin sample was milled with
glass-bead at 77°K in vacuum for 3 hrs, a poorly resolved multiplet ESR
signal was observed, as shown in Fig. 18a, instead of the singlet
spectrum observed from the sample milled at ambient temperature. It is
assumed that other transient mechano-radicals, which decayed rapidly
at 2°C, were trapped at 77°K, but their ESR signals were superimposed
by a stronger singlet signal, hence, only a diffuse spectrum could be
detected.

When oxygen was introduced into the sample at 77°K for 60 min, the
multiplet spectrum was converted into a singlet spectrum with a small
side-peak at the lower magnetic field, but the overall intensity of the

Table 4. Weight loss of lignin after extraction with benzene-ether[#]

Milling atmosphere	Before extraction	After extraction	Loss of weight (%)
	mg.	mg	
Nitrogen	500.0	497.60	0.48
Carbon dioxide	500.0	497.08	0.58
Oxygen	500.0	490.90	1.82

Samples were milled with a glass-bead mill at $2^{\circ}C$ for 10 hrs.
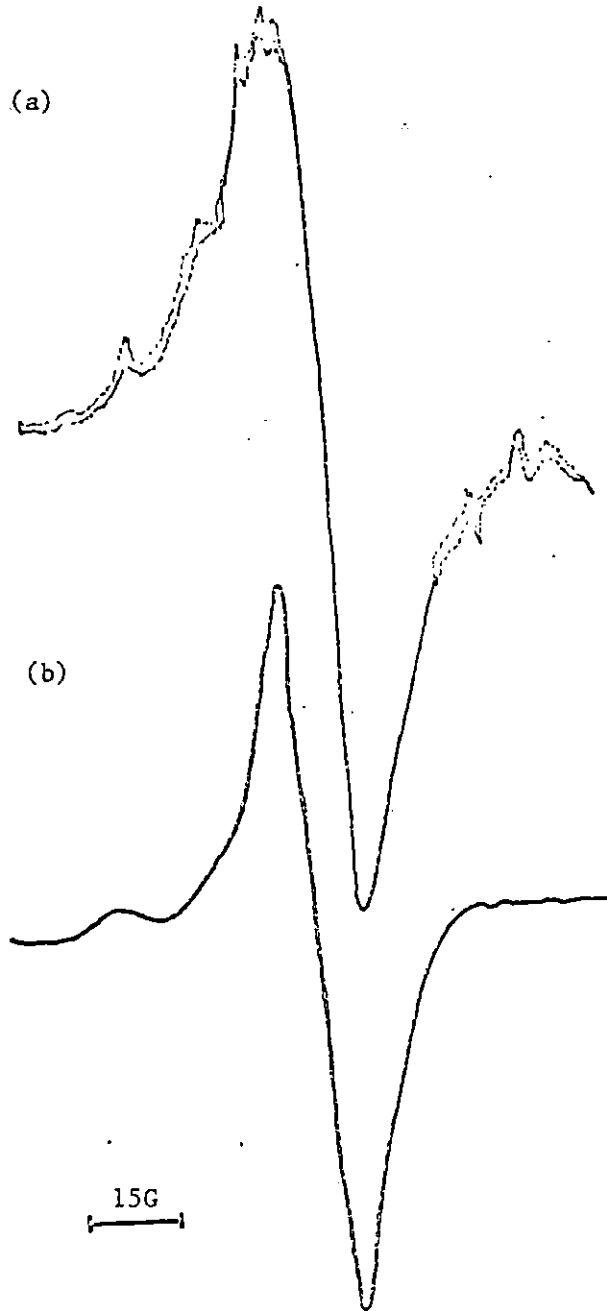
Fig. 18 ESR spectra of MWL milled at 77°K. (a), in vacuum;
(b), after oxygen was admitted to the sample for 60 mins at
77°K.

signals was unaltered. The g-value of the small side peak and the principal line are 2.007 and 2.003 respectively. 2.007 is the g// value reported for peroxide radicals.[219] In order to learn whether the 2.007 side peak represents indeed a peroxide radical, the experiment was repeated in liquid nitrogen.

When a lignin sample was milled in liquid nitrogen at $77^{\circ}K$, which was subsequently pumped off after milling, a different ESR spectrum was observed, as shown in Fig. 19. The spectrum displayed definite symmetric properties, representing the powder pattern of an axially symmetric ESR peaks.[218] The g-value of g// and g⊥ are 2.007 and 2.034, respectively ($\bar{g}$ = 2.021). These values are very close to those of the peroxy radicals formed in photoirradiated polymers.[219] Hence, it is apparent that transient mechano-radicals are capable of reacting rapidly with oxygen molecules even at $77^{\circ}K$. Thereby, peroxy radicals are formed. This result is surprising in so far as the experiment was carried out in liquid nitrogen. However, it must be recognized that it is extremely difficult that liquid nitrogen is purified and completely freed from all traces of oxygen. Thus, peroxide radicals are formed from mechano-radicals and traces of oxygen even at conditions of $77^{\circ}K$. Further, when lignin was milled in liquid air at $77^{\circ}K$, a similar ESR signal was obtained but the magnitude of the intensity increased several fold.

Evidently certain transient mechano-radicals produced in lignin were trapped at $77^{\circ}K$. They seem to be able to interact with oxygen molecules to form peroxy radicals even at this low temperature. As previously indicated oxygen did not react with mechano-radicals at $77^{\circ}K$ after milling the lignin at ambient temperature because of the low

20G
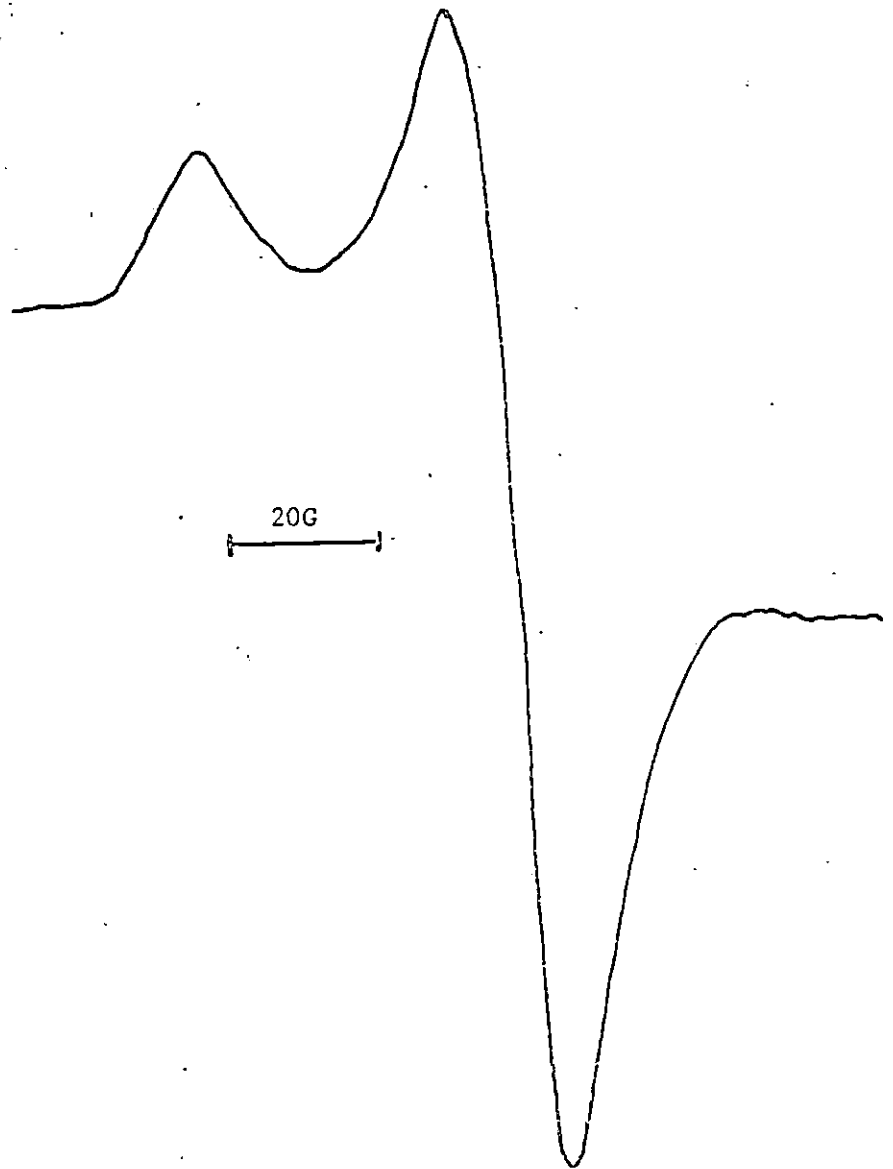
Fig. 19 ESR spectrum of MWL milled in liquid nitrogen at $77^{O}K$.

diffusion and reactivity of oxygen at this low temperature. From this study, it is evident that oxygen present in the milling system was activated by mechanical energy; and the probability that it will trap transient mechano-radicals generated at the newly formed surface of lignin is high.

In order to obtain more information on the mechanical rupture of lignin, several model compounds were used in the identical milling conditions at $77^{\circ}K$. No ESR signals were obtained from benzene, toluene, isoeugenol, vanillin, guaiacol, 1,4-dimethoxybenzene, creosol, glycerol aryl ether, or benzil, demonstrating that side-chain rupture did not occur in low molecular weight compounds. The formation of mechano-radicals in lignin is due to the chain scission of the macromolecules.

1.2.2 Decay of mechano-radicals produced at $77^{\circ}K$. When lignin was milled in liquid nitrogen or liquid air for 3 hrs at $77^{\circ}K$, an asymmetric spectrum derived from peroxy radicals was observed, as shown in Fig. 19. After the milling, the sample was allowed to warm to $298^{\circ}K$ for a certain time and recorded again at $77^{\circ}K$. This warm-up process caused a change in the ESR signal. By studying the change of the line-shape of ESR spectrum, an asymmetric spectrum derived not only from the peroxy radicals was revealed, another type of stable mechano-radical which generated a singlet spectrum also existed. The decay curves of the signals of peroxy and other radicals are shown in Fig. 20. Apparently the peroxy radicals were very unstable at $298^{\circ}K$, they decayed almost to zero within 7 min, where the mechano-radicals which generated a singlet signal were rather stable at this temperature. They decayed very slowly
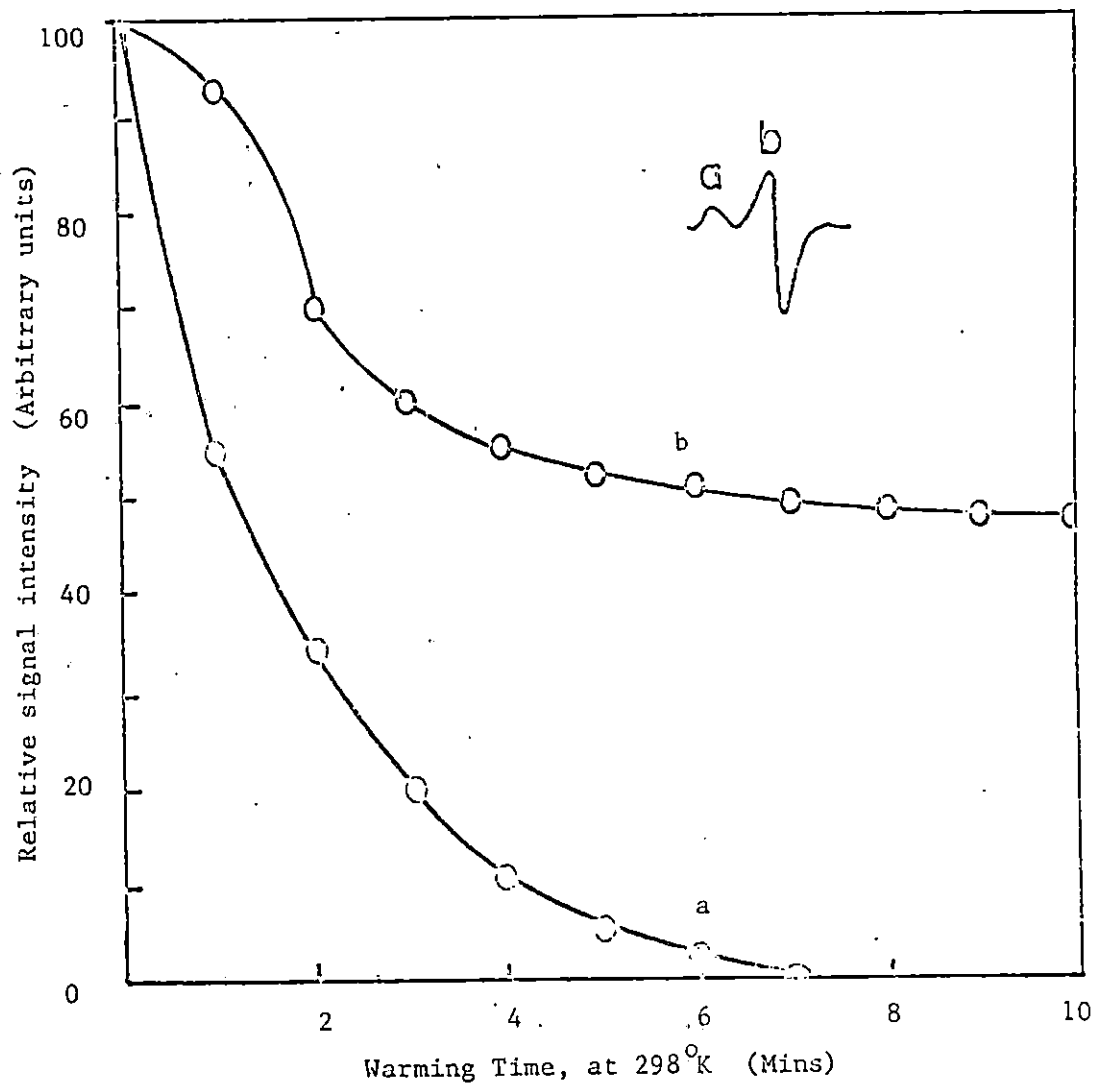
Fig. 20 Decay curves of lignin mechano-radicals (b) and peroxy radicals (a) in MWL after milling at 77°K.

after 10 min of warming.

Interesting and striking features were observed in another phase of the decay experiment which dealt with the temperature dependence of radical concentration. After lignin had been milled in vacuum at 77°K, the temperature of the sample was allowed to raise slowly. It was found that the loss of mechano-radicals was abnormal compared to the regular decaying pattern. Usually free radicals are destroyed as the temperature raises. Alternately, in the case of lignin mechano-radicals, when the temperature was raised, the concentration of mechano-radicals increased in the temperature range between 120-150°K. This implied that certain new mechano-radicals were created by the warming at the temperature of this range. Further, this anomalous decaying behavior was also observed from lignin milled in the presence of liquid air (mostly oxygen) at 77°K, but the increase in its concentration was highest at temperatures between 150-200°K. These unusual decay curves are shown in Fig. 21. It is unlikely that chemical bonds were broken by the thermal energy at such low temperatures. This phenomenon should be attributed to certain factors associated with the milling process as discussed below.

First of all it was found that lignin powder from milling possessed strong static or electrical charges. It could hardly be removed from the glass wall of milling flask. Mechanical destruction is always accompanied by friction, which produce electric charges. This electricity is known as triboelectricity in polymer systems. Coexistence of this charge with mechano-radicals is commonly observed when polymers are subjected to mechanical degradation. Therefore, it is not
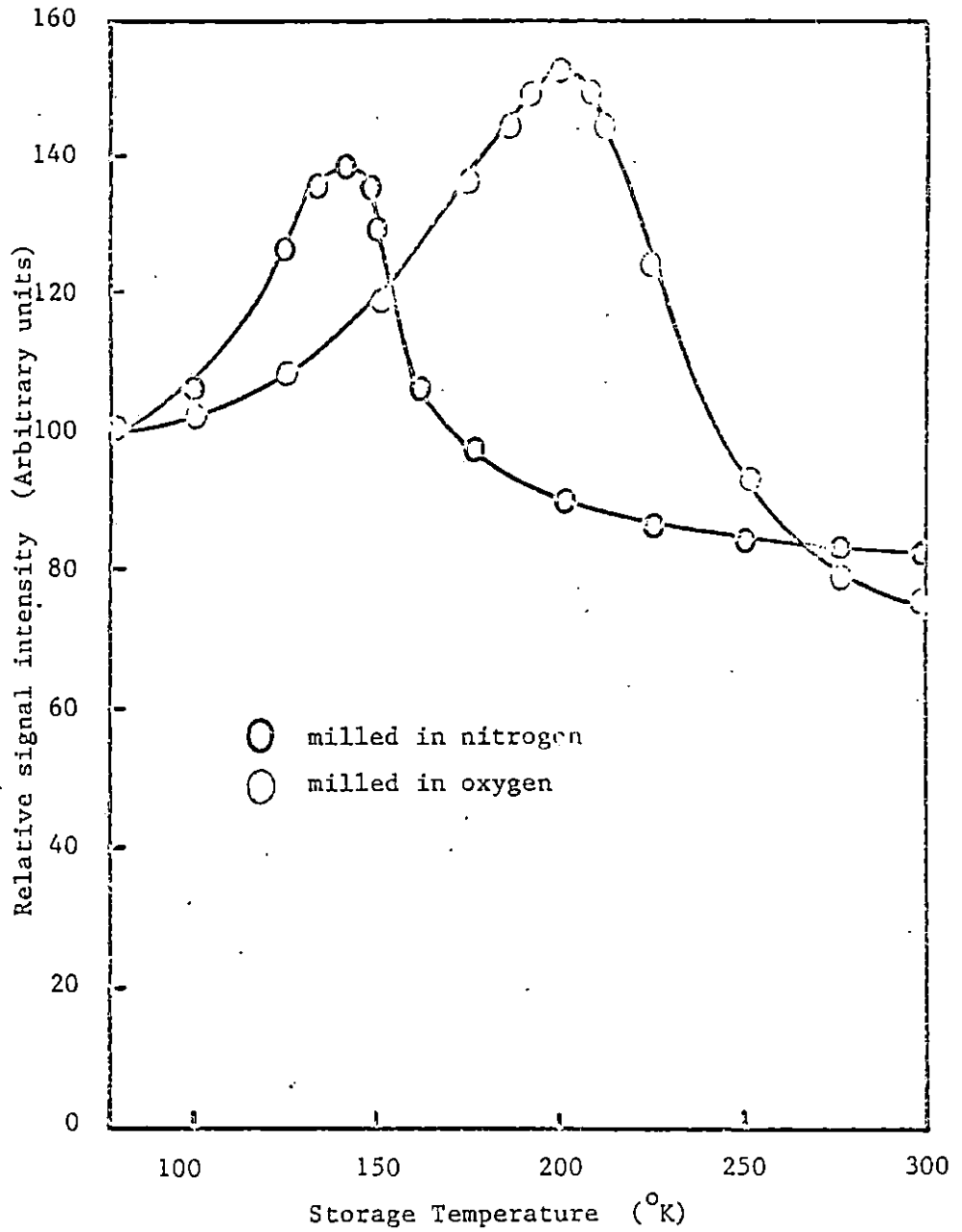
Fig. 21   Changes of ESR relative signal intensity of MWL milled at 77°K.

surprising that lignin is electrically charged after milling.

It is known that radicals have a rather large electron affinity, and a number of radicals are able to trap electrons to form anions, if there is an excess charge available.[220] By raising the temperature of the milled sample, the electrical charge was released and mechano-radicals were regenerated again. This is the cause of the augmentation of mechano-radicals upon heating. Moreover, when oxygen was present, the released charge was attracted by the oxygen to form O_2^-, it then reacted with the radical to peroxy radical and released an electron which subsequently leaked to the electrical ground. When the temperature was above $150°K$ in the vacuum, or $200°K$ in oxygen, mechano-radicals apparently decayed, and the excess charges were leaked to earth.

It should be mentioned that when lignin samples were milled in vacuum or in the presence of oxygen, the abnormal decay behavior of mechano-radicals differed with regard to the environment in which they were generated. This can be explained with the difference in reactivity of mechano-radicals towards thermal energy applied to the system during warming. When the temperature raised from $77°K$ after milling in vacuum, the anions inclined to release excess electrons due to the high reactivity of certain mechano-radicals. Some mechano-radicals were regenerated in such a way, but they probably could not survive at a high temperature ($>150°K$); when the milling was carried out in oxygen, the newly regenerated mechano-radicals were trapped by oxygen to produce peroxy radicals. As shown in Fig. 22, the new radical species created by the warming in oxygen was attributed to the peroxy radicals.

1.3 Mechanisms of Mechano-radical Formation and Decay in Lignin
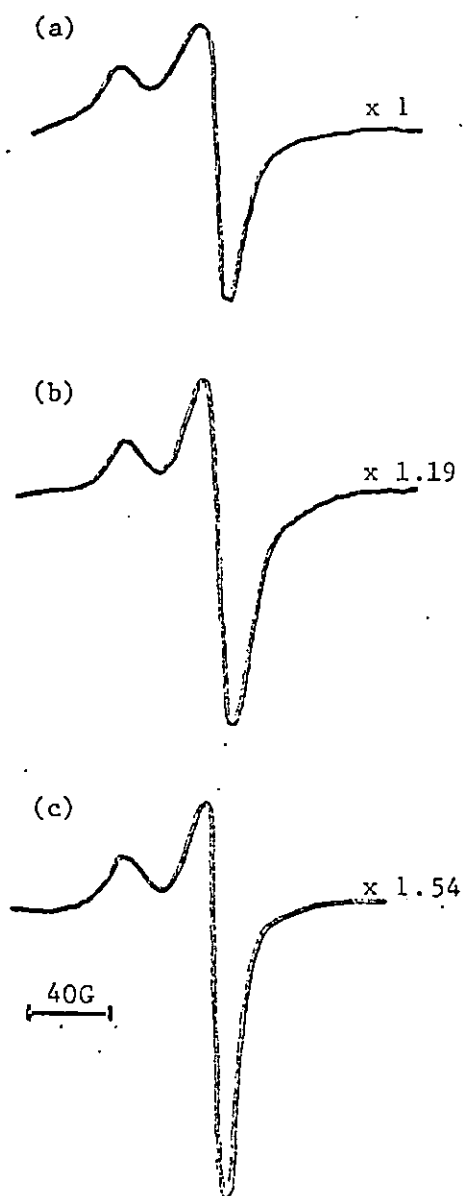
Fig. 22 Changes in the ESR line-shape and relative signal
intensity of MWL upon warming from $77^{\circ}K$ (a) to $150^{\circ}K$ (b), and
$200^{\circ}K$ (c). Multiplication number represents the ESR relative
signal intensity.

Based on experimental results, it is clear that mechanical treatment of wood meal, cellulose and MWL by grinding in a ball mill causes degradation. Free radicals were formed in the interim. In other words, the mechanical energy available in ball milling of wood is sufficient to rupture covalent bonds. This observation also agrees with the previous results on milling wood materials.[63,65,66,221-223]

In order to elucidate the overall mechanisms taking place during mechanical treatment, experiments should be carried out at the temperature of liquid nitrogen (77°K). At this temperature transient mechano-radicals can be trapped. These radicals can subsequently be monitored by means of ESR studies. If the experiments were carried out at ambient temperature, only stable mechano-radicals can be detected and studied. Hence, only an incomplete picture of mechanisms can be obtained.

Comparing the three milled samples, namely, wood meal, cellulose, and MWL, it is apparent that lignin suffered more degradation than cellulose. The structures of these polymers are entirely different, whereas cellulose structure is a linear polymer, lignin is a three dimensional cross-linked polymer. As described earlier, when a polymer molecule is subjected to an applied stress, the junction points of entangled molecules or cross-links are considered the position of high energy storage. Accordingly, during the milling process cross-linked positions in lignin are preferentially cleaved and activated. It is also possible that as a result of energy redistribution the chemical bonds connecting the cross-links with side groups and atoms are weakened.

Cellulose is a linear polymer linked by (1→4) glycosidic bonds.

Under the influence of mechanical stress, glycosidic bonds are broken
and activated. When these bonds break, alkoxy type free radicals will
be produced, and exhibit a singlet ESR signal.[224] As from the ESR
studies, beside a singlet signal ($\Delta H_{msl} = 22G$), several side peaks were
observed also. This implies that the cleavage of bonds other than
glycosidic bonds also took place, as shown in eqs. 11 and 12 :

$$R_{cell}-0-R_{cell} \xrightarrow[\text{energy}]{\text{Mechanical}} R_{cell}-0\cdot + R_{cell}\cdot \qquad (11)$$

$$R_{cell}-H \xrightarrow[\text{energy}]{\text{Mechanical}} \text{Free radicals} \qquad (12)$$
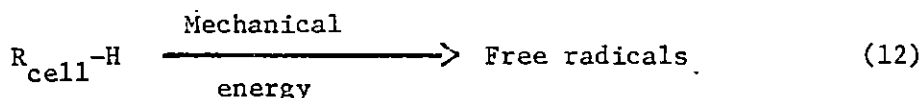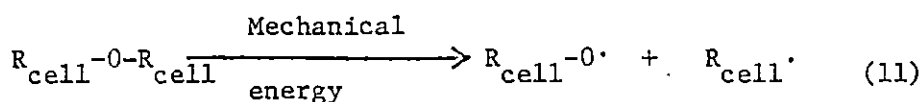
Since the ESR signals detected from cellulose are much smaller
than those from lignin, it is plausible to consider that the mechanical
degradation of cellulose is much less severe than lignin. This supposi-
tion was also supported by the viscosity studies. Details of mechanisms
will not be considered here.

Inspection of structural formulation readily reveals that lignin
is principally linked with carbon-carbon and carbon-oxygen (i.e., ether
linkage) bonds. Accordingly, when mechanical stress is applied to
the lignin molecules, the ruptures of these carbon-carbon and carbon-
oxygen bonds are occurred randomly, hence, mechano-radicals are
generated.

ESR findings revealed that a singlet signal with a g-value of
2.003 was predominant in lignin after milling regardless of the milling
conditions. The only possibility of producing singlet spectrum is by

cleaving carbon-oxygen bonds, that is ether linkages in lignin structure. The cleavage of carbon-carbon bonds in lignin gives rise to complicated ESR signals due to the many protons in its environment. This was not observed in this study. Hence, the singlet signal observed from milled lignin was attributed to the phenoxy radicals on the grounds of the cleavage of ether bonds as shown in eq. 13 .

$$R_{lig}-0-R_{lig} \xrightarrow[\text{energy}]{\text{Mechanical}} R_{lig}-0\cdot \; + \; R_{lig}\cdot \quad (13)$$
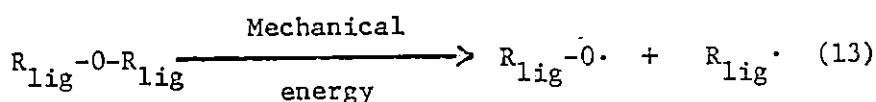
It is well known that phenoxy radicals generate singlet ESR signals as is apparent in many polymers.[225,226] The singlet spectrum observed from lignin in this study is very similar to that found by Kleinert,[66] Kringstad and Lin,[106] and Hon.[217]

Simultaneously, after the cleavage of ether bonds, radical pairs were formed. The ESR signal of this radical pair was superimposed with the singlet signal of phenoxy radical, and hence only a diffuse multiplet spectrum was observed as shown in Fig. 18a, when lignin was milled in vacuum at 77°K. The radical pairs were very labile and decayed rapidly at 298°K whereas the phenoxy radicals were rather stable at such temperature.

Since the phenoxy radical was found to be stabilized by the strongly delocalized unpaired electron,[227] and the temperature at which the sample was milled and the ESR measurement performed was appreciably lower than the glass transition temperature of lignin,[228] the phenoxy

radicals detected in this experiment are fairly stable at ambient temperature.

It is worth mentioning here that in addition to phenoxy radicals, alkoxy radicals, which also exhibit a singlet signal, can be produced when chemical bonds are broken in the lignin-carbohydrate complex,[229-231] as shown below:

$$R_{cell} - O - R_{lig} \xrightarrow{\text{M.E.}} R_{cell} - O \cdot + R_{lig} \cdot \tag{14}$$

$$R_{cell} - O - R_{lig} \xrightarrow{\text{M.E.}} R_{cell} \cdot + R_{lig} - O \cdot \tag{15}$$
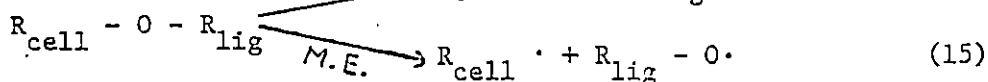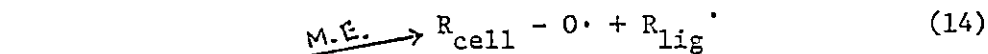
Since isolated lignin may be contaminated with about 2-5% of carbohydrate,[230] this would not influence greatly the overall ESR signals, detail of the signals generated from carbohydrate will not be taken into account here.

Besides this stable phenoxy radical, as studied from the decay behavior of free radicals in lignin, it was noted that another type of free radical, which also generated a singlet spectrum, is rather unstable at ambient temperature. It has been known, based on the lignin structure, that there are two types of aromatic structure, i.e., uncondensed (VIII) and condensed (IX) phenyl groups, in lignin.

(VIII)   (IX)
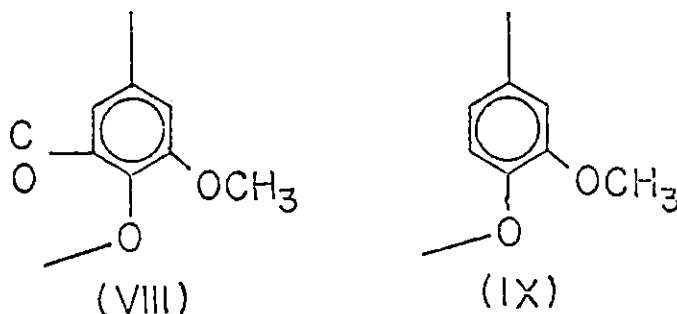
The distribution of each in the lignin molecule is approximately 50%.
When ether bonds in (VIII) and (IX) were ruptured by mechanical energy,
phenoxy radicals were produced. Due to steric reasons, the phenoxy
radical of (VIII) possesses a higher degree of stability than that of
the phenoxy radical of (IX). It is likely that the singlet signal,
which was rather unstable at ambient temperature, was derived from the
uncondensed phenoxy radical. The other possibility for formation
of unstable mechano-radicals contributing to the singlet signal is due
to the cleavage of aliphatic type ether to create alkoxy radicals
but this was unlikely. These free radicals are not as stable as the
phenoxy radical since the latter is stabilized by its resonance
structures, that is, the unpaired electron can be delocalized at the
ortho- and para-positions of the benzene ring, where the alkoxy
radicals are unable to delocalize.

Since these radicals decay in nitrogen and carbon dioxide, it is
to be expected that the recombination reaction will be the normal fate
of the radical unless some other reaction intervenes. However, it is
to be noted that radical recombination reactions need not necessarily
be those derived from a single chain to give no detectable degradation.
Occasionally, a radical may react with another polymer molecule, and
thus lead to the production of some degree of branching or cross-
linking.

In some instances, chain transfer may occur resulting in the
location of the free radical in a terminal position on the polymer
chain. Further, as disproportionation is also the usual termination

process, the termination of two radical containing fragments will yield one polymer chain terminated by a double bond, and one with saturated end groups.

Accordingly, the overall reaction mechanisms can be envisaged as the following schemes:

I. Radical combination:
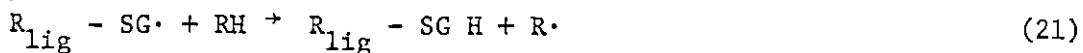
$$R\cdot + R\cdot \rightarrow R - R \tag{16}$$

$$R - O\cdot + R\cdot \rightarrow R - O - R \tag{17}$$

$$R - O\cdot + R - O\cdot \rightarrow R - O - O - R \tag{18}$$

II. Radical fragmentation:

$$R_{lig} - SG\cdot \rightarrow R_{lig}\cdot + S=G \tag{19}$$

III. Radical transfer:

$$R_{lig}\cdot + RH \rightarrow R_{lig}H + R\cdot \tag{20}$$

$$R_{lig} - SG\cdot + RH \rightarrow R_{lig} - SG\,H + R\cdot \tag{21}$$

IV. Radical addition:

$$R_{lig}\cdot + R_{lig} - S=G \rightarrow (R_{lig})_2 - SG\cdot \tag{22}$$

$$R_{lig} - SG\cdot + R_{lig} - S=G \rightarrow R_{lig} - \underset{\underset{\underset{\underset{R_{lig}}{|}}{G}}{\overset{\displaystyle SG\cdot}{|}}}{S} \tag{23}$$

V. Radical disproportionation

$$R_{lig}\cdot + R_{lig} - SG\cdot \rightarrow R_{lig}H + R_{lig} - S=G \tag{24}$$
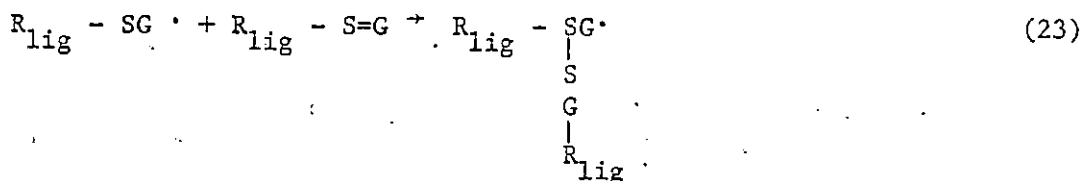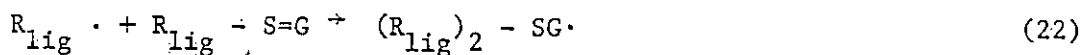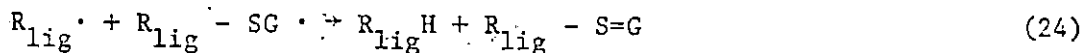
where R represents lignin or cellulose molecule, SG and S=G represent saturated side group and unsaturated side group, respectively.

It has been demonstrated that the presence of oxygen and other radical scavengers will accelerate secondary reactions and stabilize

the free radical at their degraded sites, ultimately leading to a decrease in the free radical concentration.

Free radicals react with molecular oxygen to give peroxy radicals (ROO·) and these radicals are capable of initiating oxidative processes as shown below:[217]

Initiation $R - O - R \rightarrow R - O\cdot + R\cdot$ (11,13)

Propagation $R\cdot + O_2 \rightarrow RO_2\cdot$ (25)

              $RO_2\cdot + RH \rightarrow ROOH + R\cdot$ (26)

Termination $R\cdot + R\cdot \rightarrow$ inert product   (16)

              $R\cdot + RO_2 \rightarrow$ inert product   (27)

              $RO_2\cdot + RO_2\cdot \rightarrow$ inert product   (28)
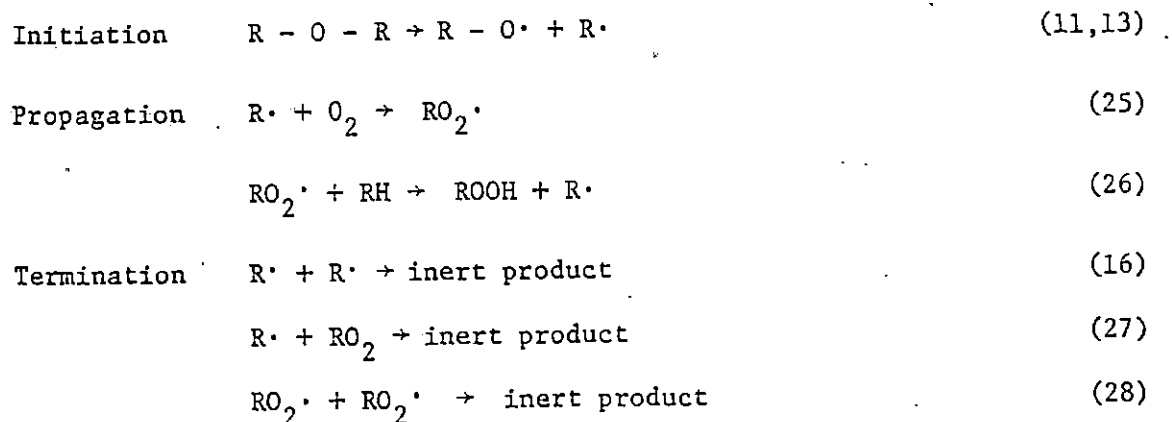
where R represents lignin or cellulose molecule.

It should be stressed the importance of oxygen during the milling at $77^{\circ}K$. As demonstrated in a preceding experiment, an anomalous decay behavior of mechano-radicals was observed when the temperature of milled sample was raised above $120^{\circ}K$. We postulate that this phenomenon was due to the charge from triboelectricity in the polymer. Mechano-radicals are able to trap electrons from the excess charge of triboelectricity. This charge was released from mechano-radicals when the temperature was raised above $120^{\circ}K$. Molecular oxygen was able to trap the labile mechano-radicals at the range of $150-200^{\circ}K$ to produce peroxy radicals, and these peroxy radicals readily underwent secondary reactions above $200^{\circ}K$.

Based on these findings, the following mechanisms are postulated:

At 77^OK after milling <u>in vacuum</u>:
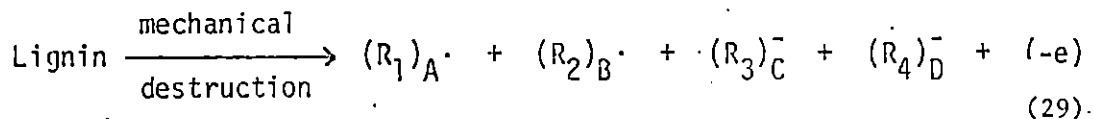
$$\text{Lignin} \xrightarrow[\text{destruction}]{\text{mechanical}} (R_1)_A{\cdot} \ + \ (R_2)_B{\cdot} \ + \ (R_3)_C^- \ + \ (R_4)_D^- \ + \ (\text{-e}) \tag{29}$$

After the heat treatments in the temperature range $120\text{-}150^O$K:

$$(R_3)_C^- \xrightarrow{\Delta} (R_3)_C{\cdot} \ + \ (\text{-e}) \tag{30}$$

INCREASE ESR INTENSITY

$$(R_4)_D^- \xrightarrow{\Delta} (R_4)_D{\cdot} \ + \ (\text{-e}) \tag{31}$$
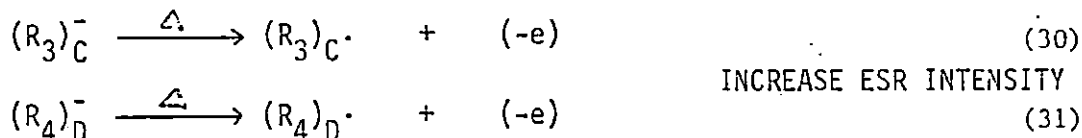
Heat treatment at the temperatures above 150^OK:
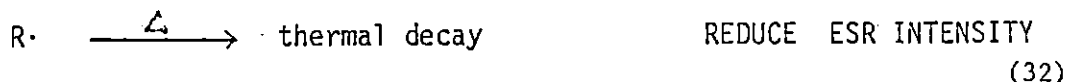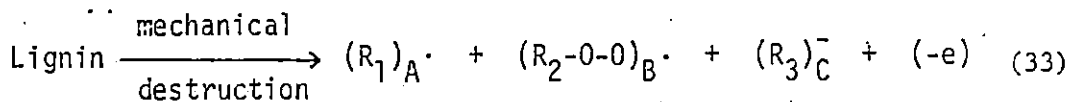
$$R{\cdot} \ \xrightarrow{\Delta} \ \text{thermal decay} \tag{32}$$

REDUCE ESR INTENSITY

At 77^OK after milling <u>in oxygen</u>:

$$\text{Lignin} \xrightarrow[\text{destruction}]{\text{mechanical}} (R_1)_A{\cdot} \ + \ (R_2\text{-0-0})_B{\cdot} \ + \ (R_3)_C^- \ + \ (\text{-e}) \tag{33}$$

$$O_2 \ + \ (\text{-e}) \longrightarrow O_2^- \tag{34}$$

After the heat treatments in the temperature range $150\text{-}200^O$K:

$$(R_1)_A{\cdot} \ + \ O_2^- \xrightarrow{\Delta} (R_1\text{-0-0})_A{\cdot} \ + \ (\text{-e}) \tag{35}$$

INCREASE

$$(R_3)_C^- \xrightarrow{\Delta} (R_3)_C{\cdot} \ + \ (\text{-e}) \tag{30}$$

E S R

$$(R_3)_C{\cdot} \ + \ O_2^- \xrightarrow{\Delta} (R_3\text{-0-0})_C{\cdot} \ + \ (\text{-e}) \tag{36}$$

INTENSITY
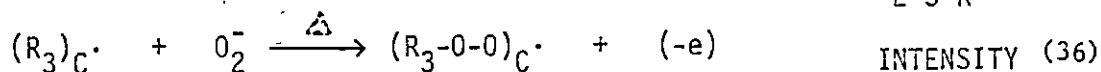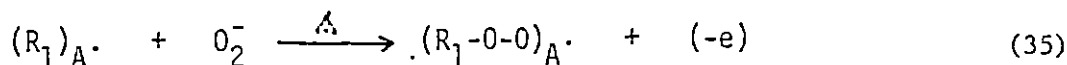
Heat treatment at the temperature above 200^OK:

$$R\text{-0-0}{\cdot} \ \xrightarrow{\Delta} \ \text{thermal decay} \tag{32}$$

REDUCE ESR INTENSITY
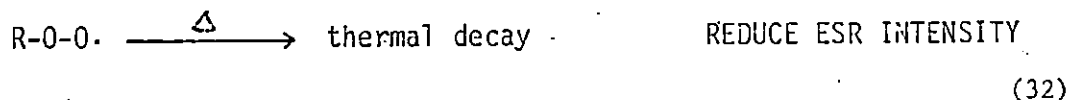
The termination of peroxy radicals, the formation of hydroperoxide, as well as the decomposition of hydroperoxide within lignin molecule

has several important consequences which may lead to the formation of chromophoric groups in lignin.

There are several possible pathways leading to the termination of peroxy radicals. One possibility is that peroxy radicals were capable of abstracting hydrogen atoms from lignin molecules to produce polymer hydroperoxide, as shown in eqs. 37 and 38.

$$R_{lig} - O_2 \cdot + R_{lig}H \rightarrow R_{lig} - O_2H + R_{lig} \cdot \tag{37}$$

$$R_{lig} - O_2 \cdot + R_{lig} - OH \rightarrow R_{lig} - O_2H + R_{lig} - O \cdot \tag{38}$$
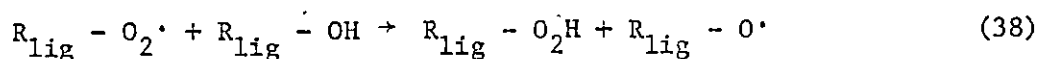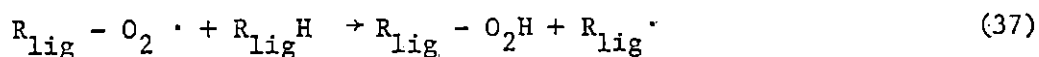
It is known that phenol readily donates protons to free radicals, and in secondary alcohols the hydroxyl group exerts a moderately activating effect upon the geminal C-H bond. Consequently, peroxy radicals formed in lignin abstracted these types of hydrogen perferentially.

The other possibility of a termination reaction is that peroxide radicals combined with carbon radicals in lignin. The combination with oxygen (alkoxy) radicals, and peroxy-peroxy coupling are also possible but the resulting trioxide as well as tetraoxide intermediates, respectively, were very unstable above $243^{\circ}K$[232] and $100^{\circ}K$.[233]

The decomposition of peroxy radicals may lead to the formation of double bonds and carbonyl groups in lignin which certainly will influence the color of the polymer. The reactions are illustrated as follows:[234,235]
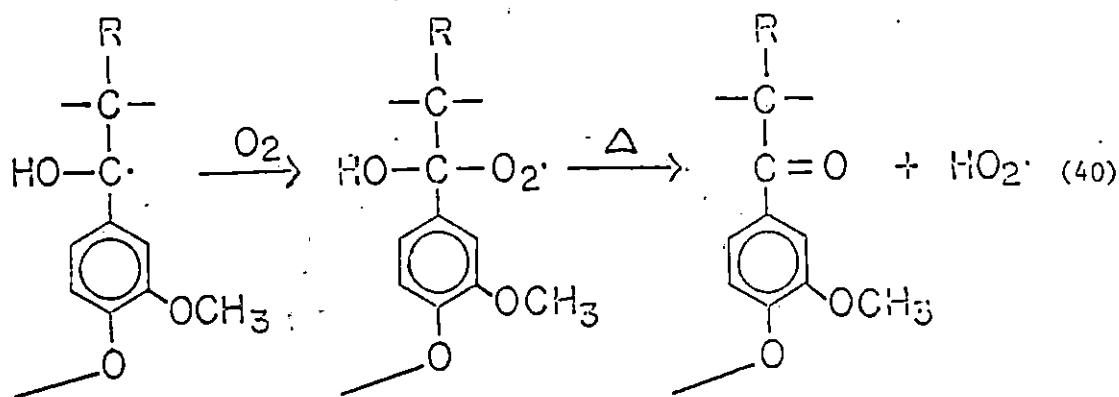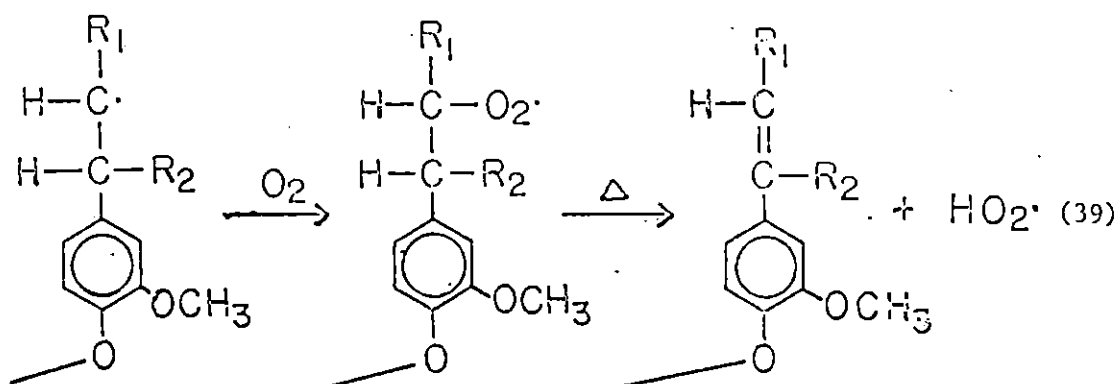
Further, it is known that peroxy compounds are not stable at ambient conditions, they may be stabilized with the formation of oxygen-containing end groups and the detachment of the hydroxy groups as in eq. 41.

$$R-O-O-H \xrightarrow{\Delta} R-O^{\cdot} + {}^{\cdot}OH \tag{41}$$

These groups have demonstrated the ability to initiate demethoxylation of lignin[236] which would create o- and p-quinonoid structures in the polymer to cause discoloration reaction, as shown in eqs. 42 and 43.

$$(42)$$

$$(43)$$
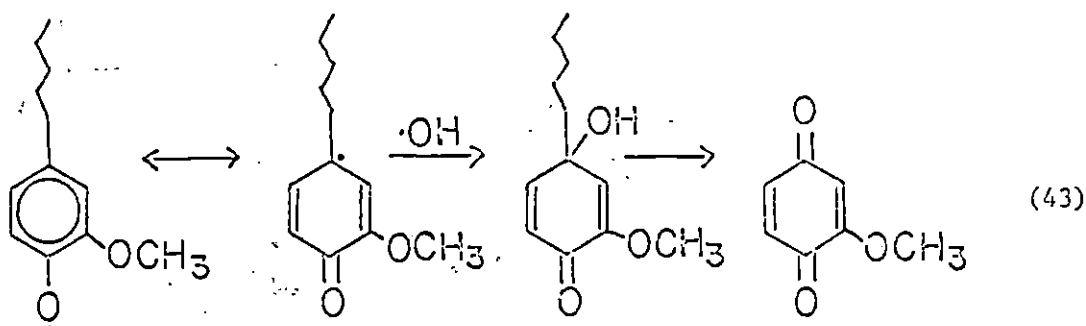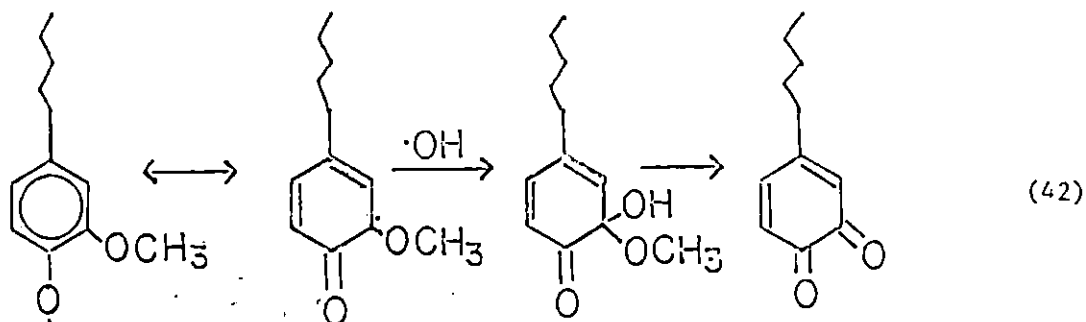
Although oxidation of cellulose is well established,[217,237] the oxidative process shown above is taking place predominately in the lignin polymer, because few free radicals are detected in cellulose.

In addition, in the attack on saturated groups in lignin by ROO· radicals, branching and crosslinking may result.

Mechano-radicals formed in lignin reacted with radical scavengers, namely, toluene and phenol, and they are stabilized. It is known that toluene[238,278] and phenol[239-240] are capable of reacting with free radicals by donating their protons with the formation of stable products. Simply, benzyl and phenoxy radicals were produced.

Accordingly, toluene and phenol react thus:

$$R_{lig} - O\cdot + XH \rightarrow R_{lig} - OH + X\cdot \tag{44}$$

$$R_{lig}\cdot + XH \rightarrow R_{lig}H + X\cdot \tag{45}$$
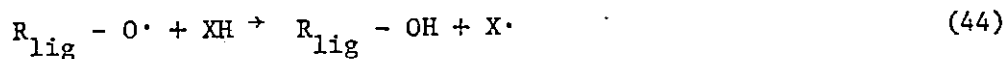
where XH represents radical scavenger, and X· represents the benzyl radical or the phenoxy radical. The benzyl and phenoxy radicals subsequently reacted with a second polymeric radical or dimerized:

$$X\cdot + R_{lig} \rightarrow R_{lig} - X \tag{46}$$

$$X\cdot + R_{lig} - O\cdot \rightarrow R_{lig} - O - X \tag{47}$$

$$X\cdot + X\cdot \rightarrow X - X \tag{48}$$
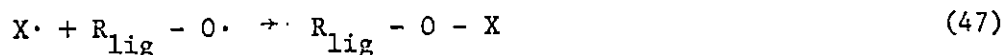
Since lignin is a three dimensional network polymer, the parts of the polymer chain on either side of the cleavage are diffusion limited. Because of the rigidity of the solid matrix, recombination reactions seem to proceed with difficulty. The recombination of cellulosic and ligninic free radicals to form lignin-carbohydrate complex is very unlikely. In fact, several experiments aimed at producing artifact lignin-carbohydrate complex by the milling process totally failed.[241-243]

Based on these facts, it is conceivable that the secondary reactions of mechano-radicals, and the oxidation process in lignin will lead to the formation of chromophoric groups which darken the lignin polymer.

Finally, it should be recalled that when lignin was milled in the presence of oxygen, it was possible to remove benzene-ether soluble low molecular weight compounds from the lignin polymer. This resulted in the loss of weight of lignin after extraction. Since peroxy

radicals were formed in this milling system, it is believed that extractable compounds were formed via peroxy radical route.

As mentioned, phenoxy radicals were formed in lignin after milling. These radicals are stabilized by resonance, and the odd electron is distributed over the oxygen atom and all carbon atoms of the aromatic ring. The highest spin density is found on oxygen and at the C_1 position.[244] Accordingly, molecular oxygen preferentially attacked the C_1 position to produce peroxy radicals. According to the study of Horswill and Ingold,[245,246] three types of reactions take place between phenoxy radicals and peroxy radicals, namely, (i) phenoxy-peroxy coupling, (ii) phenoxy-phenoxy coupling at the C_1 position, and (iii) phenoxy-phenoxy coupling through the oxygen of one radical and the C_1 position of the second radical. If these reactions are applicable to the lignin polymer, there is no doubt that p-, and o-quinones were the main chromophoric groups produced in lignin after milling, and the p-quinonoid moiety, a fragment from lignin polymer, was the component that could be extracted by benzene-ether solvent.

It should also be borne in mind that if the p-quinone was not removed from lignin after milling, this reactive compound will be recondensed to the parent lignin polymer to produce a polymeric chromophoric system in lignin.

2. Photodegradation of Lignin

2.1 Degradation and Discoloration of Solid Lignin Irradiated with Ultraviolet Light

When solid lignin (MWL) was irradiated with different lights, namely, wavelength $\lambda > 2600$ Å, $\lambda > 3000$ Å, $\lambda > 3500$ Å, $\lambda > 4000$ Å, and $\lambda > 5000$ Å, in oxygen for 30 hrs, a change of absorption in the ultraviolet spectra was found as shown in Fig. 23. It is obvious that when $\lambda > 2600$ Å and $\lambda > 3000$ Å were employed, the absorption peak at 280 nm attributed to the aromatic ring decreased, but the absorptions at 350 nm and beyond 400 nm were conversely increased. When light $\lambda > 3500$ Å was employed the peaks at 280 nm and 350 nm did not change, but the absorption region beyond 400 nm decreased. Similar results were also obtained from samples irradiated in a nitrogen atmosphere but the adverse effect was less than that irradiated in oxygen.

Moreover, it is noticed that while the color of lignin was changed from pale yellow to light brown when it was irradiated in vacuum with light $\lambda < 3500$ Å; no significant change was observed by human eyes with lights $\lambda > 3500$ Å. When solid lignin was irradiated with lights $\lambda < 3500$ Å in oxygen, it was discolored to a red-brown color.

These findings indicate that irradiation with light of $\lambda < 3500$ Å has an adverse effect on the molecule in terms of color build-up, or the formation of chromophoric groups contributing to the discoloration of lignin. This adverse effect was accelerated by the presence of oxygen. However, no adverse effect was observed when the sample was irradiated with lights $\lambda > 3500$ Å, yet a photobleaching effect was recognized by using longer wavelengths.
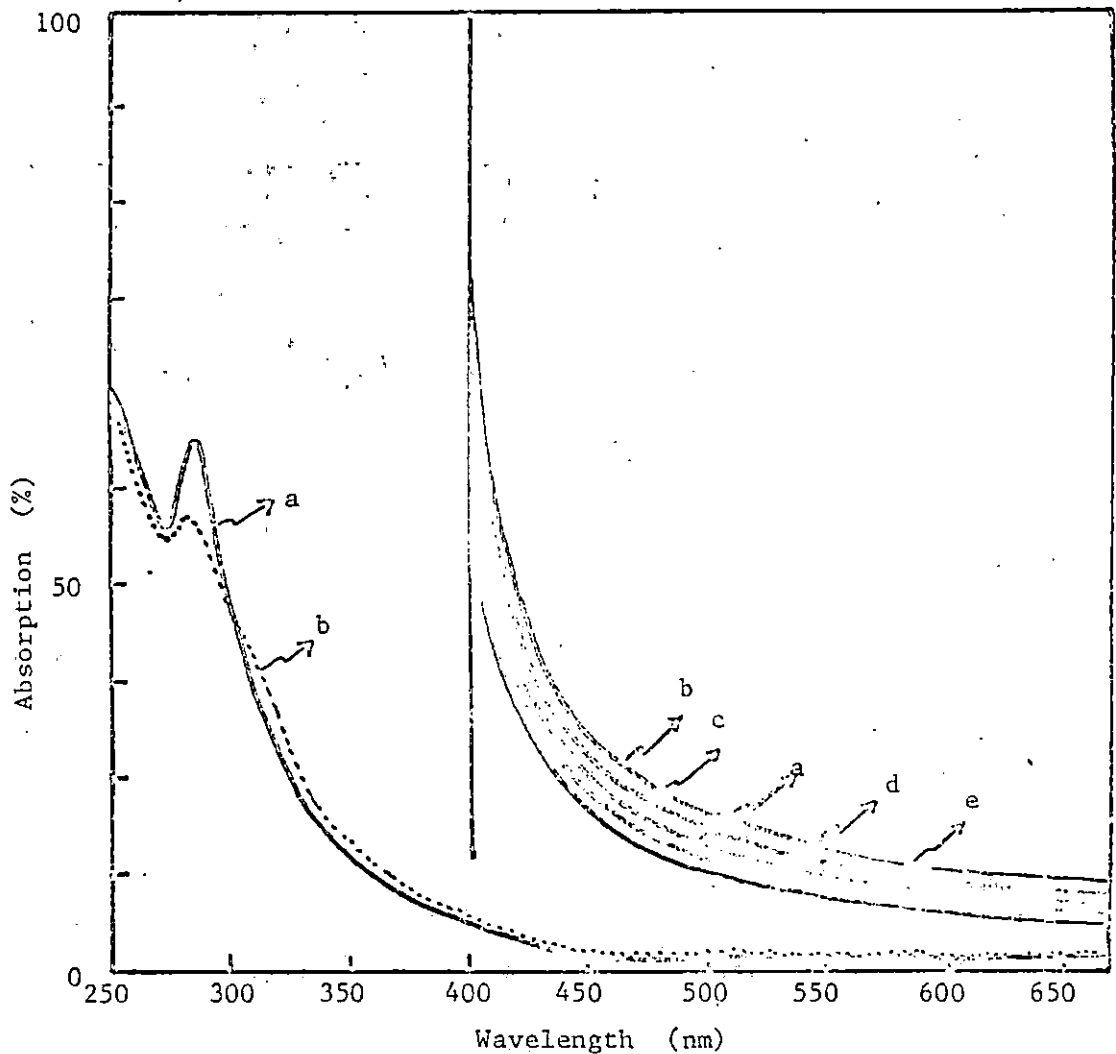
Fig. 23 Ultraviolet absorption spectra of MWL solution after irradiation of the solid sample with different lights. (a), control; (b), $\lambda > 2600$ Å; (c), $\lambda > 3000$ Å; (d), $\lambda > 3500$ Å; (e), $\lambda > 4000$ Å. The vertical scale in the visible region is expanded 18 times.

2.2 Loss of Weight of Lignin Upon Photoirradiation

After lignin was irradiated at different wavelengths in vacuum

and in oxygen for 30 hr, weight loss of lignin was studied. Results

are shown in Table 5. It is clear that immediately after photoirradia-

tion, weight loss of lignin was insignificant, except if irradiation

was performed with light of $\lambda > 2600$ Å. However, it was noted that

irradiation increased the amount of benzene-ether soluble fractions

from 8.9% to 14.6% when irradiation was carried out with light of

$\lambda < 3500$ Å in the presence of oxygen. This indicates that fragmentation

of lignin and cleavage of interunit bonds may create small molecular

weight compounds.

2.3 Change of Viscosity of Lignin After Photoirradiation

After lignin was dissolved completely in cellosolve (30 mg/100cc),

it was irradiated with light of $\lambda > 2600$ Å and $\lambda > 3000$ Å in vacuum and

in oxygen. Patterns of change of viscosity are of interest. For

both irradiation regions, little change of viscosity was observed when

the lignin solution was irradiated in vacuum, as shown in Fig. 24 (for

original experimental data, see APPENDIX II). However, when irradiation

were carried out in oxygen, change of viscosity was discernible.

When the lignin solution was irradiated with light $\lambda > 3000$ Å,

there was no change of viscosity in the initial hour, but an obvious

change was observed between 2-3 hrs of irradiation. When oxygen was

present, the viscosity was increased to its maximum, then decreased

monotonously. When lignin was irradiated with light of $\lambda > 2600$ Å, an

increase of viscosity was observed at the very beginning but its

Table 5. Weight loss of lignin after photoirradiation[#]

Wavelength $\overset{o}{A}$	Irradiation atmosphere	Original weight, mg	Loss of weight	
			Weight I[##] mg	Weight II[###] mg
$\lambda > 2600$	vacuum	100.0	98.5	90.2
	oxygen	100.0	93.0	85.4
$\lambda > 3000$	vacuum	100.0	99.3	94.7
	oxygen	100.0	97.4	91.1
$\lambda > 3500$	vacuum	100.0	99.9	99.4
	oxygen	100.0	99.8	99.3
$\lambda > 4000$	vacuum	100.0	100.0	100.0
	oxygen	100.0	100.0	99.9
$\lambda > 5000$	vacuum	100.0	100.0	100.0
	oxygen	100.0	100.0	100.0

Irradiated at ambient temperature for 30 hr.

Weight of sample after photoirradiation.

Weight of irradiated sample after extraction with benzene : ether solvent.
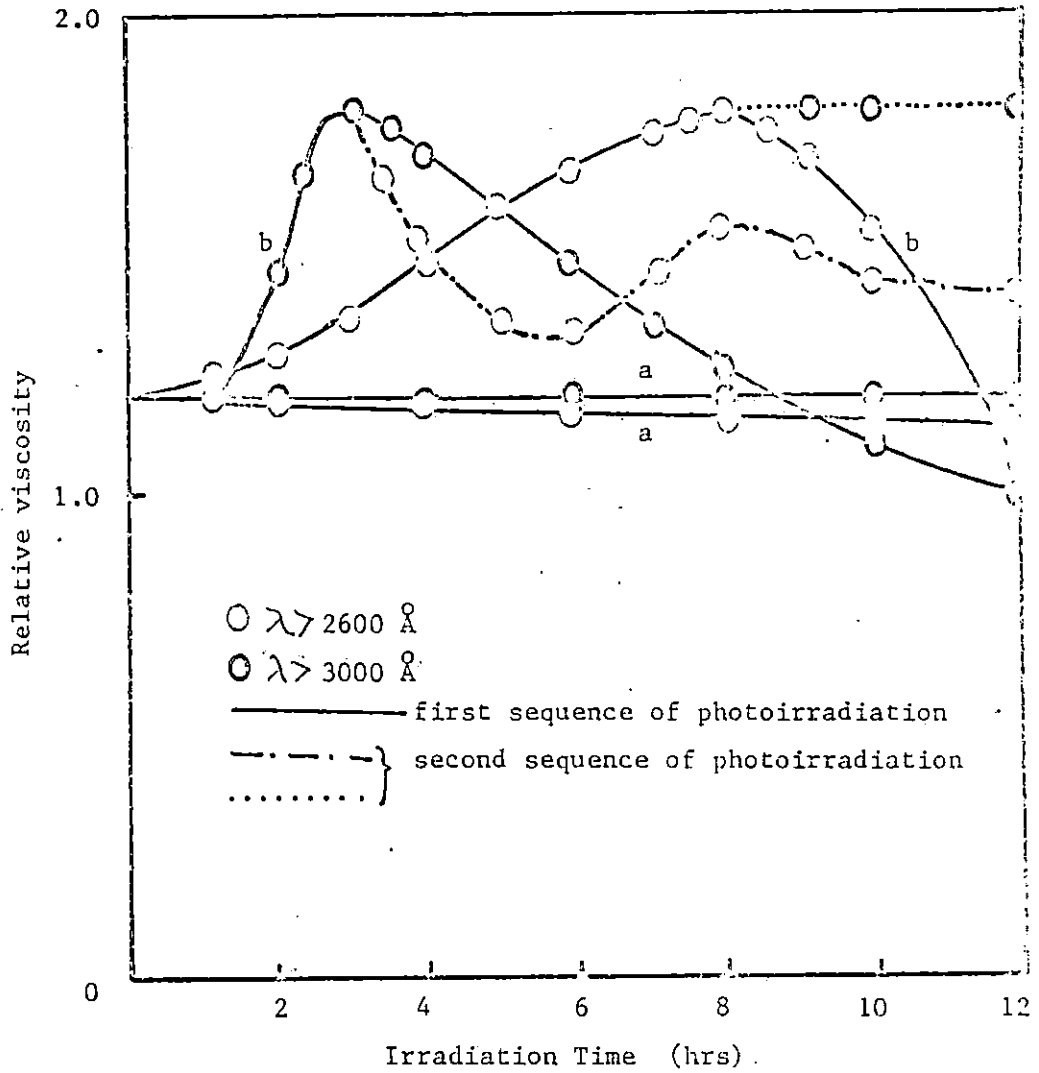
Fig. 24 Change of relative viscosity of MWL irradiated with

lights (0) $\lambda > 2600$ Å and (0) $\lambda > 3000$ Å in (a) vacuum, and (b) oxygen.

rate was slow. The viscosity reached a maximum after 8 hrs of irradiation and then followed a decrease in viscosity.

It is plausible to consider that during the irradiations, cross-linking or branching took place in lignin which resulted in the increase of viscosity. In the case of irradiation with light of $\lambda > 3000 \overset{o}{A}$, this phenomenon was observed after irradiation of 2~3 hrs, then further degradation took place; in the case of with light of $\lambda > 2600 \overset{o}{A}$, crosslinking or branching reaction took place in the initial 2~3 hrs, due to the light component $\lambda > 3000 \overset{o}{A}$, but the chemical constituents of this crosslinked portion were not resistant to light of $\lambda > 2600 \overset{o}{A}$ and underwent decomposition; another type of crosslinking or branching reaction took place thereafter, which degraded after 8 hrs of irradiation.

In order to obtain information on the photostability of the photo-crosslinked portion of lignin, a reirradiation process was employed. After the lignin solution was irradiated with light of $\lambda > 3000 \overset{o}{A}$ for 3 hrs in oxygen (its viscosity reached its maximum), radiation was con-tinued with light of $\lambda > 2600 \overset{o}{A}$, in this sequence, the viscosity decreased sharply for 2 hrs, and increased again by prolonged irradi-ation. After the lignin solution was irradiated with light of $\lambda > 2600 \overset{o}{A}$ for 8 hr in oxygen (its viscosity reached its maximum), then continuously reirradiated with light of $\lambda > 3000 \overset{o}{A}$, the viscosity was not changed. These results are illustrated in Fig. 24.

It must be concluded that although crosslinking or branching react-ions were induced by light, the chemical constituents of these products differed if different lights were used. The crosslinking or branching

reaction induced with light of $\lambda > 3000$ Å was not resistant to irradiation with light of $\lambda > 2600$ Å; whereas that induced with light of $\lambda > 2600$ Å was resistant to light of $\lambda > 3000$ Å.

The viscosity of lignin celloslove solution was not changed when it was irradiated with light $\lambda > 3500$ Å either in the presence of oxygen or in vacuum.

2.4 Formation of Free Radicals in Photoirradiated Lignin

When lignin (MWL) was irradiated with light of $\lambda > 2600$ Å for 60 min at $77^{\circ}K$, a typical ESR spectrum was observed, as shown in Fig. 25. It is evident that a singlet signal with a line-width of 14 gauss located at the center was predominant; several side peaks appeared in the lower magnetic field, that is left of the principal line. The principal singlet signal has a g-value of 2.003. Its relative intensity was 5.3-fold more intense than the singlet spectrum derived from the intrinsic free radicals in lignin, and the overall concentration of free radicals was 0.512×10^{17} spins per gram.

When the sample was irradiated at ambient temperature under the identical experimental conditions, and measured at $77^{\circ}K$, only a singlet spectrum ($\Delta H_{ms1} = 10$ G) was observed. Free radicals generating the side peaks of the signal shown in Fig. 25 were very labile at ambient temperature. They survived at $77^{\circ}K$, but rapidly underwent secondary reaction at ambient temperature. This also indicated that the signal shown in Fig. 25 was not derived from a single free radical species, it was superimposed with at least two types of free radicals.

Change of the line shape also can be studied by means of micro-wave power saturation effect if the signals observed originated from
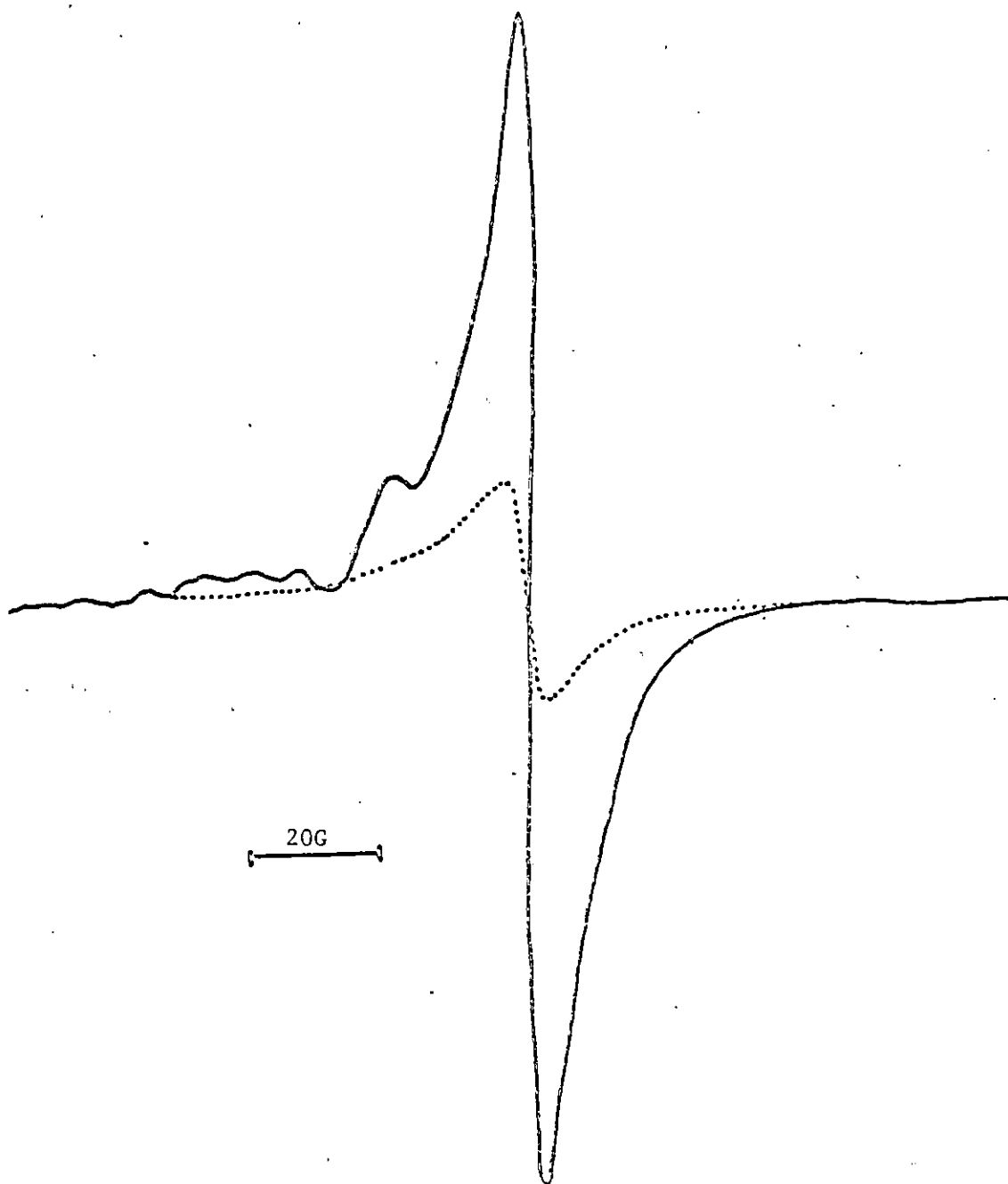
Fig. 25 ESR spectra of MWL irradiated with ultraviolet light at
77°K. Dotted line signal was the intrinsic free radicals in MWL.
Spectra were recorded at 77°K.

several kinds of free radical species. Fig. 26 shows the behavior

of the signals subjected to power saturation. Obviously, the side

peaks of the signals detected at 77°K saturated more easily than

the principal line; when the microwave power was reduced, the intensity

of the side peak was increased while the principal singlet signal remain-

ed unaffected. Deformation of the spectrum due to power saturation

probably occured at the power level of 40 mW. It is evident that

several kinds of free radicals contributing to individual peaks were

produced in lignin at 77°K.

The effect of irradiation time on the ESR signal intensity

corresponding to free radicals produced in lignin is shown in Fig. 27.

Free radicals appeared to be formed rapidly during the first 4 hrs

of irradiation at 77°K. More free radicals were produced and trapped

when lignin was irradiated at 77°K.

It is noteworthy to mention here that the singlet components

derived from the intrinsic free radicals of lignin and those derived

from free radicals of photoirradiated lignin are quite different in

nature, since the line-widths between them are varied. They are 10

and 14 gauss respectively for un-irradiated and irradiated lignins,

although their g-values are close to the value of 2.003.

2.5 Behavior of Lignin's Free Radicals at 77°K

Although ESR signals are detectable at 77°K in photoirradiated

lignin, it is necessary to pinpoint whether these free radicals are

stable at this temperature. Hence, the sample after irradiation with

light of $\lambda > 2600$ Å for 60 min at 77^{b}K was allowed to stand at that

temperature. The intensities of the ESR spectra were checked for some
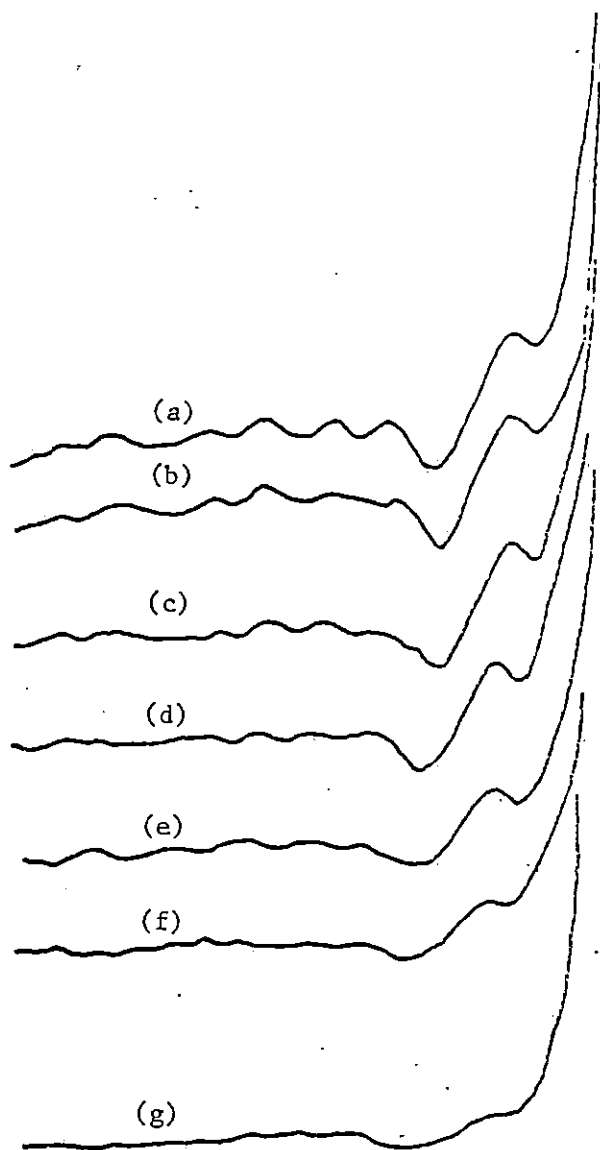
Fig. 26 Power saturation of ESR spectra of MWL irradiated with
ultraviolet light at 77°K. Microwave power (mW): (a), 5; (b),
10; (c), 15; (d), 20; (e), 30; (f), 35; (g), 40.
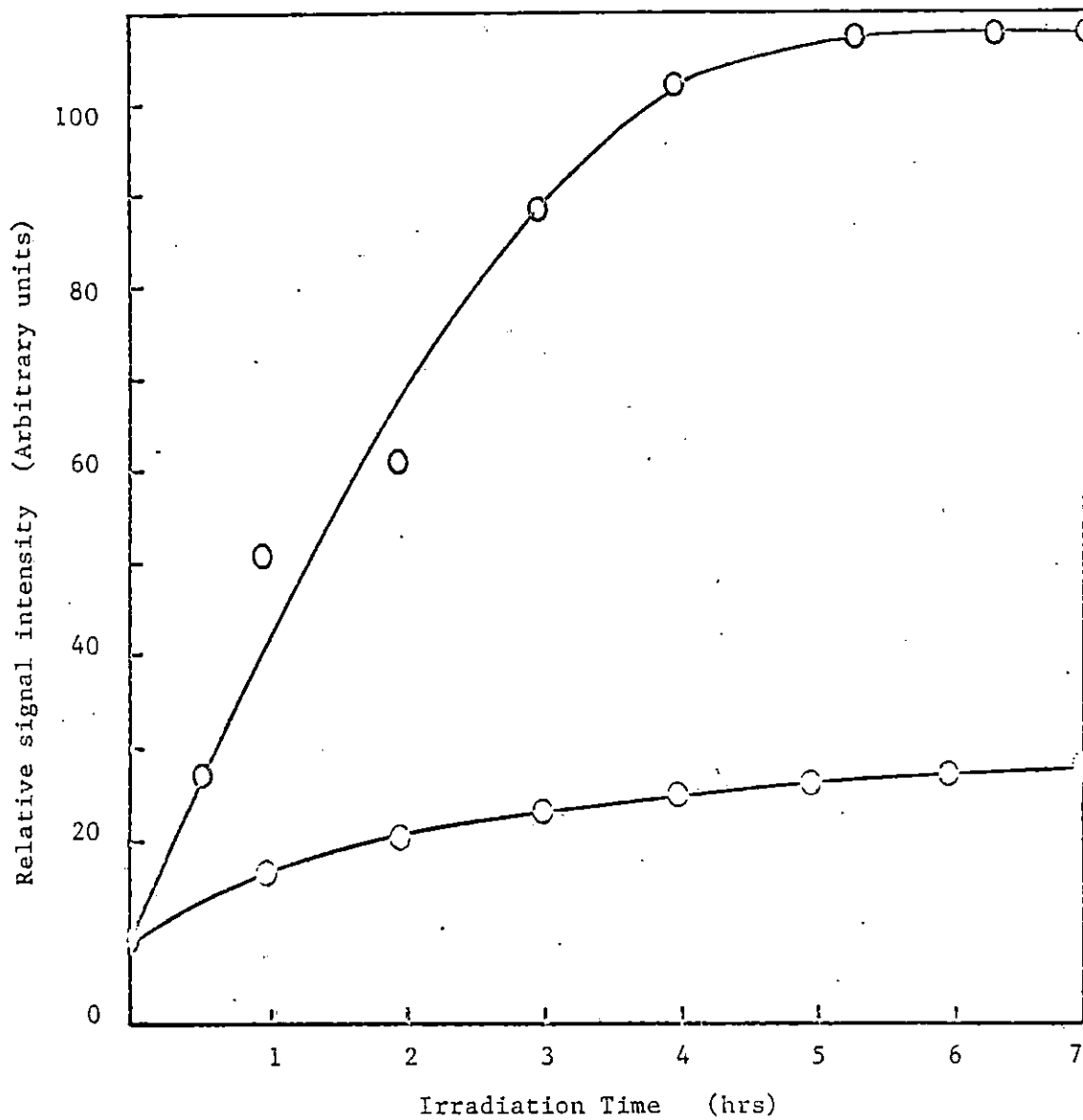
Fig. 27 Rate of formation of free radicals in MWL irradiated with
ultraviolet light at $77^{\circ}K$ (0) and at ambient temperature (0).

time after the start of the first observation immediately after irradiation.

There is no appreciable change of the ESR signals at 77°K within the first few hours but the change was perceptible when the sample was stored for 12 hrs or longer. The principal lines of the ESR increase, while the side peaks decrease as shown in Fig. 28. When the storage time was prolonged to 24 hrs, the intensity of the principal line increased to 142% whereas the side peaks were reduced to 52% of their original values. This phenomenon continued but slowed down after 72 hrs of storage. It is important to note here that the overall intensity of the spectra were not altered during this storage period. Based on this fact, it is reasonable to consider that free radical transformation occurred even at 77°K. In other words, some labile free radicals are too labile and attacked other molecules in their vicinity, and the labile free radicals were terminated. Simultaneously, new radical sites were produced. Inasmuch as this is a 1:1 basic transformation reaction, a large change in overall intensity of the ESR, that is, free radical concentration was not observed.

2.6 Behavior of Lignin's Free Radicals at 298°K

After lignin was irradiated at 77°K with light of $\lambda > 2600$ A, and warmed to 298°K, the behavior of free radicals was quite different from that observed at 77°K. As shown in Fig. 28, it is apparent that when the sample was warmed at 293°K for 10 sec and recorded again at 77°K, ESR intensities of the principal line and side peaks decayed rapidly. Signals of the side peaks decayed to almost zero within 25
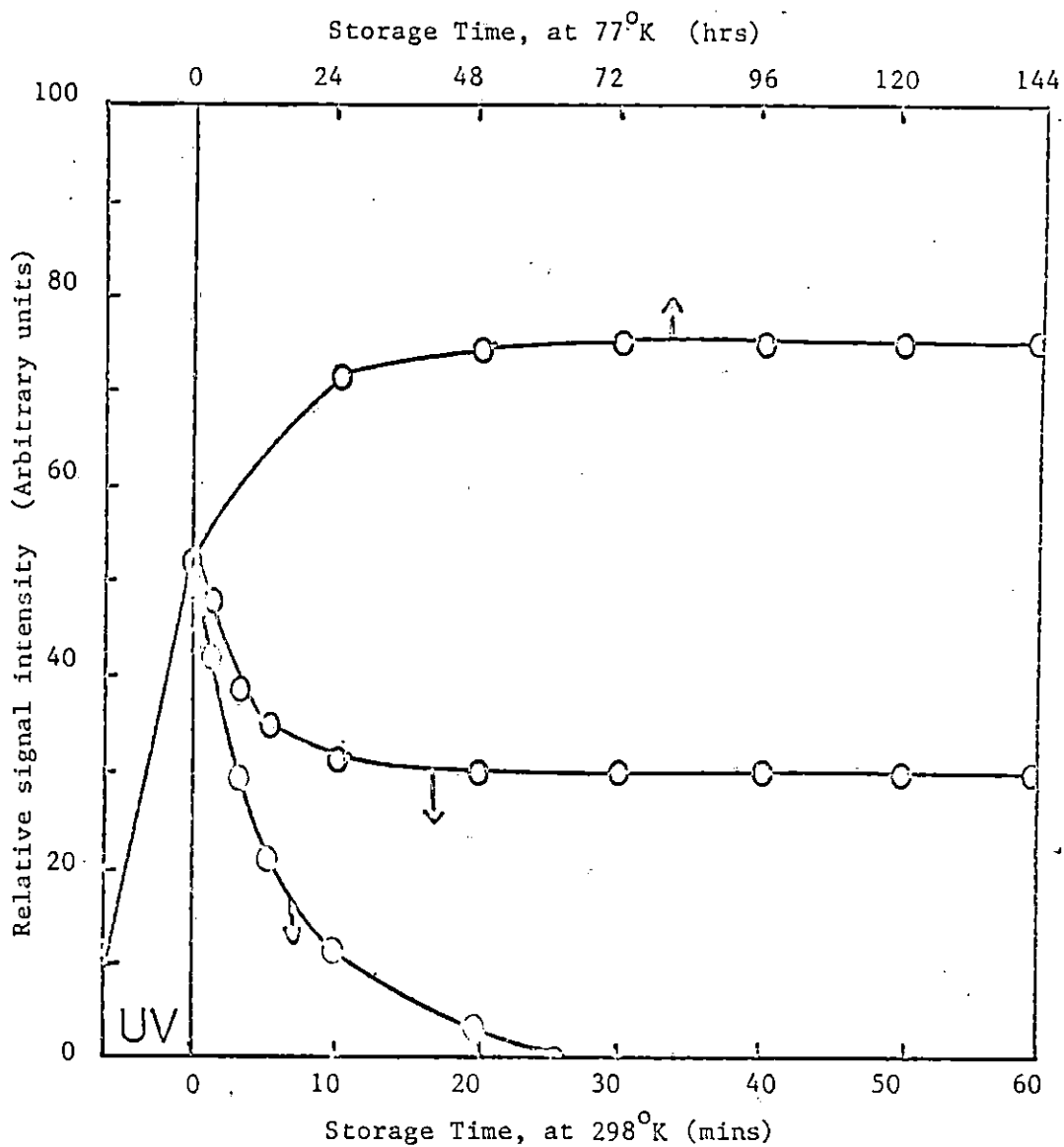
Fig. 28 Radical transformation and decay of MWL free radicals at
77°K and 298°K. Decay curves: (0), principal line; (C), side peaks.

mins whereas the singlet signal remained constant after 14 mins of warming. From the variation of the line shapes, it is recognized that free radicals which contributed to the side peak components were quite labile as regards thermal energy. They decayed rapidly. Again, this finding indicates that at least two kinds of free radicals contributing to the singlet and side peak components were trapped at $77^{\circ}K$; one type of free radical was unstable, and decayed when heat is applied, the other type of free radical was stable and remained almost unchanged even after a prolonged warming time.

Further, by comparison with the instrinsic free radicals; i.e., 0.08×10^{17} spins/gram, in lignin, it is noticed that twice as many free radicals produced in photoirradiated lignin (i.e., 0.16×10^{17} spins/gram) were stable at $293^{\circ}K$, whereas 0.264×10^{17} spin/gram of free radicals were unstable at $293^{\circ}K$.

2.7 <u>ESR</u> <u>Studies</u> <u>of</u> <u>Lignin</u> <u>Model</u> <u>Compounds</u> <u>Irradiated</u> <u>with</u> <u>Ultraviolet</u> <u>Light</u>

Because of the complexity of lignin structure, it is extremely hard to determine free radical sites formed in lignin by ultraviolet light. In order to gain information on this enigma, certain model compounds were used.

As shown in Fig. 1 it is known that lignin contains about 0.06/ OCH_3 carbonyl group (mainly in nonphenolic units). These groups may have been formed by various uncontrolled reactions during the biosynthesis or the isolation of lignin. It has been suggested that peroxy radicals formed in lignin may decompose to produce carbonyl groups.

The formation or introduction of carbonyl groups into lignin results in a shift of the absorption band toward longer wavelengths (300-400 nm). In addition, carbonyl groups, when exposed to light are easily excited to singlet or triplet state which could subsequently lead to a number of photochemical reactions. Hence, certain lignin model compounds containing α-carbonyl groups were selected. The role of carbonyl groups in photodegradation of lignin was studied.

When phenolic model compounds bearing α-carbonyl groups were irradiated with light, only a strong singlet signal (ΔH_{msl} = 16 G) with a g-value of 2.003 was observed. This singlet signal was derived from phenoxy radicals. In order to prevent the singlet signal from obliterating signals of other primary free radicals, free phenolic hydroxy groups were blocked by derivatization, those derivatives used in this work are illustrated in Fig. 6.

When all of these model compounds were irradiated with light of λ > 2600 Å at 77°K for 60 min in vacuum, prominent ESR spectra were observed. The numerical parameters of the spectra are shown in Table 6.

The ESR spectrum of model compound I observed at 77°K after photoirradiation is shown in Fig. 29. A poorly resolved seven-line spectrum was detected. A similar spectrum was obtained from model compound II. Since the intensity ratio of the spectrum is not the expected ratio for interaction of an electron with six equivalent protons, it is believed that the spectrum observed, as shown in Fig. 29, is not a single signal originating from a single radical species,

Table 6. ESR spectra of photoirradiated lignin model compounds.[#]

Compound[##]	ESR	
	77°K	298°K
I	7-line	singlet
II	7-line	singlet
III	5-line	none
IV	5-line	singlet
V	5-line	singlet
VI	5-line(weak)	singlet(weak)
Benzyol chloride	singlet	singlet

[#] Irradiated with the ultraviolet light at 77°K for 60 min.

[##] Structure of the model compound was shown in Fig. 6.
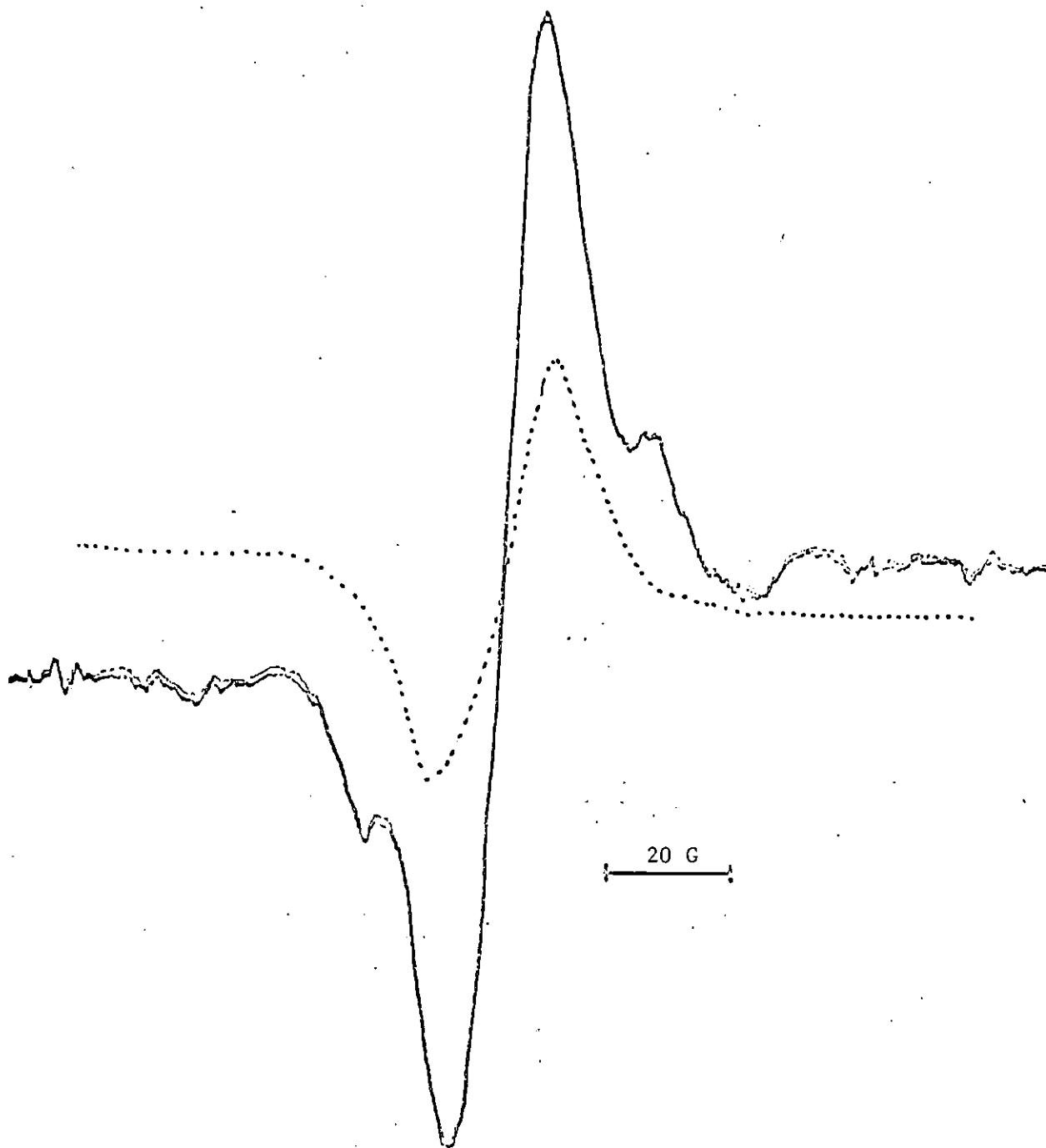
Fig. 29   ESR spectrum of lignin model compound I   irradiated at
77°K for 60 mins.   Dotted line signal was obtained after the
irradiated sample was warmed to 298°K for 3 mins.   Spectra were
recorded at 77°K.

but is a superposition of several signals which may be attributed to several radical species. When the sample was allowed to warm to $298^{\circ}K$ for 3 mins and its spectrum recorded again at $77^{\circ}K$, the seven-line spectrum was converted into a singlet signal with a line-width of 11 gauss. The g-value is 2.006.

It is known that carbon-carbon bonds adjacent to carbonyl groups are prone to dissociate in a photochemical reaction. This reaction is referred to as the Norrish type 1 reaction.[247] Accordingly, the model compounds I and II likely undergo this type of reaction (eq. 49).

$$\text{(I)} \qquad \qquad \text{(X)} \qquad \qquad \text{(49)}$$
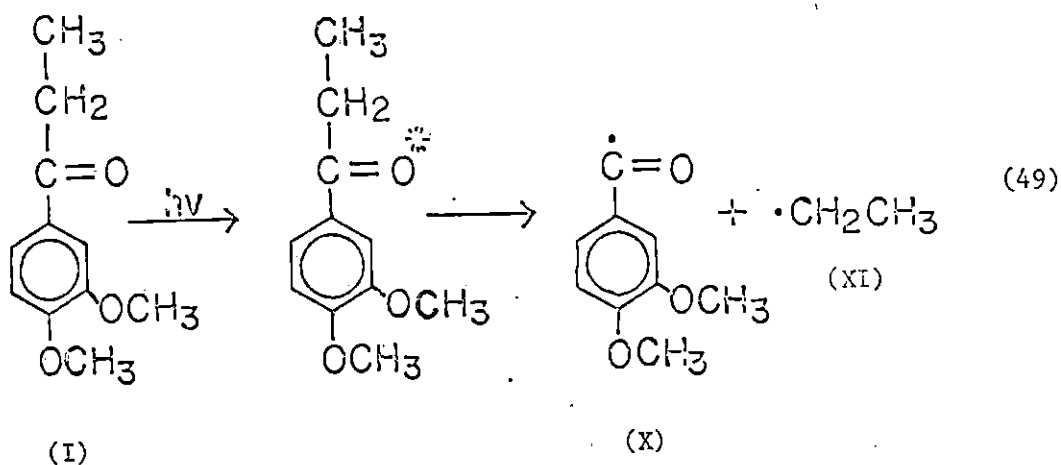
In this reaction, ethyl radicals XI would give rise to a seven-line spectrum, where acyl radicals (benzoyl radical) X would give rise to a singlet spectrum. The experimental results exactly corroborated this reaction pathway.

When benzyl chloride XII was irradiated under the identical conditions, a singlet spectrum (ΔH_{msl} = 10G) with a g-value of 2.006 was detected. This is expected because the carbon-halogen bond is

weakened by photoirradiation, when benzoyl chloride was irradiated with light, C-Cl bonds were cleaved and benzoyl radicals XI were produced (Eq. 50). The g-value is also in agreement with the literature data.[279]

(XII)   (X)   (50)
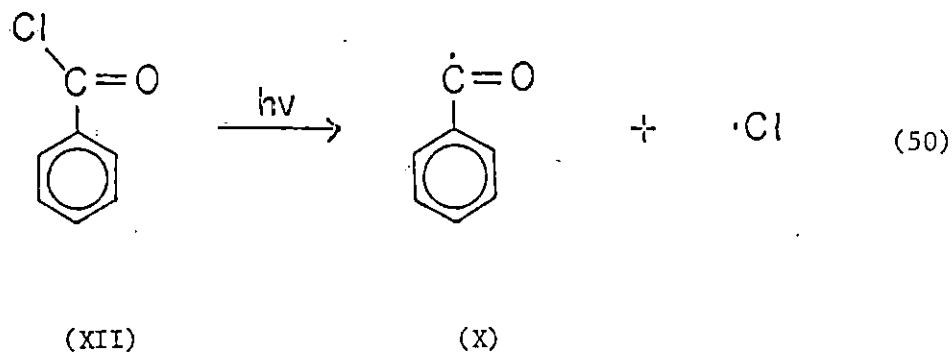
The line shapes as well as the g-values of the singlet spectra from benzoyl chloride and model compounds I and II are identical, indicating that the singlet spectrum was derived from benzoyl radicals. Hence, model compounds I and II underwent Norrish type 1 process by the action of light.

The β-0-4 linkage (Aryl-β-ether) is a frequently occuring one in lignin. The influence of light on this linkage adjacent to carbonyl groups is not known. Because this structure is an important linkage in lignin, several model compounds, i.e., compounds IV and V were studied to elucidate the role of carbonyl groups and their influence on the light stability of the ether bonds adjacent to them.

When model compound IV was irradiated at 77°K, a prominent five line spectrum was observed as shown in Fig. 30. If the sample irradiated was warmed to 298°K for 3 mins and recorded again at 77°K, the five-line spectrum was changed to a singlet signal with a line-width

20 G
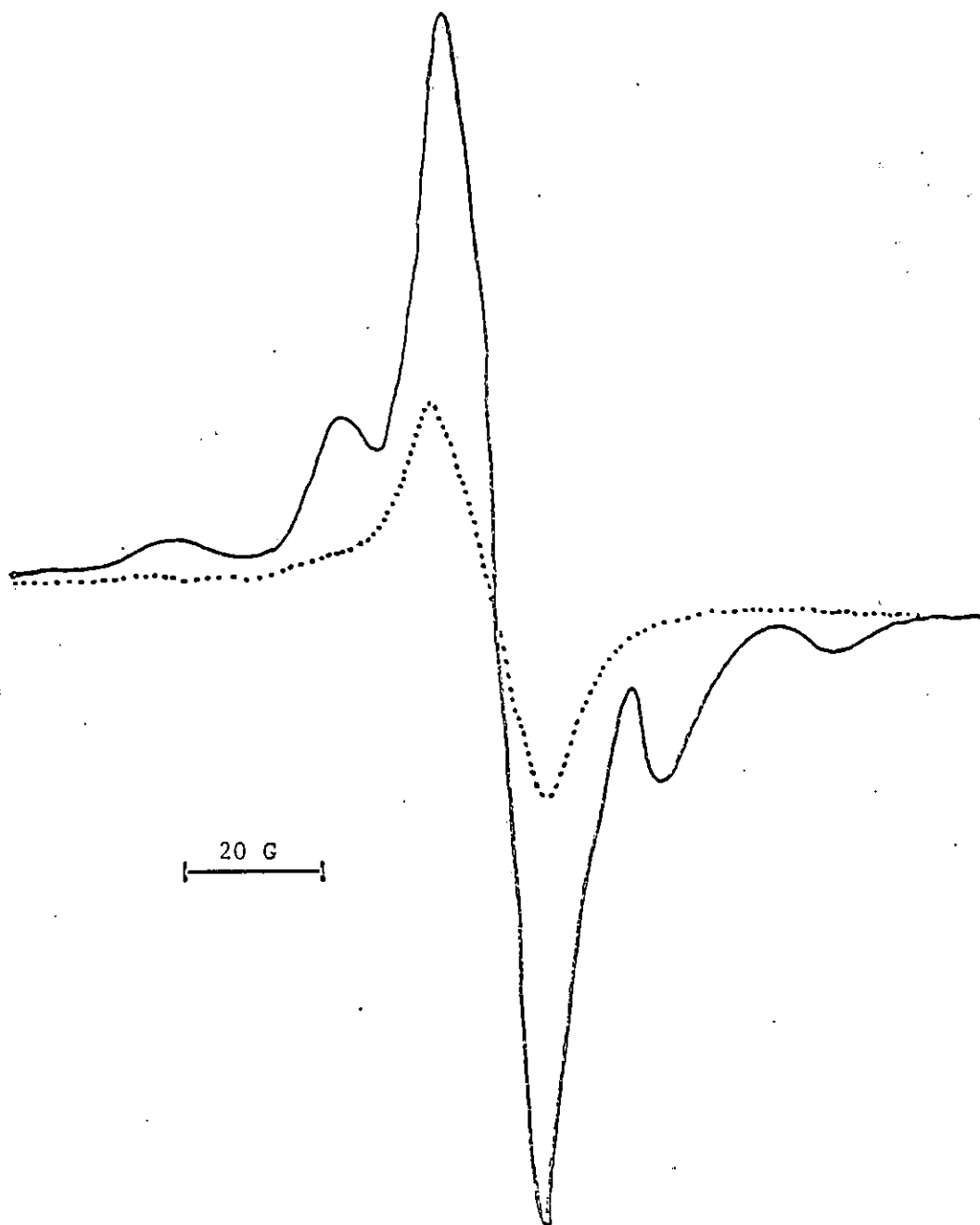
Fig.30. ESR spectra of model compound IV irradiated with ultraviolet
light at 77°K for 60 mins. The dotted line signal was obtained
after the irradiated sample was warmed to 298°K for 3 mins. Spectra
were recorded at 77°K.

of 15 gauss, and a g-value of 2.003. Since the g-value is lower than that of benzoyl radicals (g = 2.006), and matches the value of phenoxy radicals (g = 2.003), the Norrish type 1 reaction apparently does not occur in these compounds, and is replaced by cleavage of ether bonds took place. Similar results were also obtained from compound V .

In pursuance to clarifying the reaction mechanism, a different model compound III was irradiated under the identical conditions described above. An analogous prominent five-line spectrum was observed as shown in Fig. 31. However, when this sample was subsequently warmed to $298^{\circ}K$ for 3 mins and recorded again at $77^{\circ}K$, all signals disappeared. Apparently the five-line signals were derived from free radicals XIII by cleavage of the C-Br bonds as shown in Eq. 51.

$$(51)$$

(III)   (XIII)
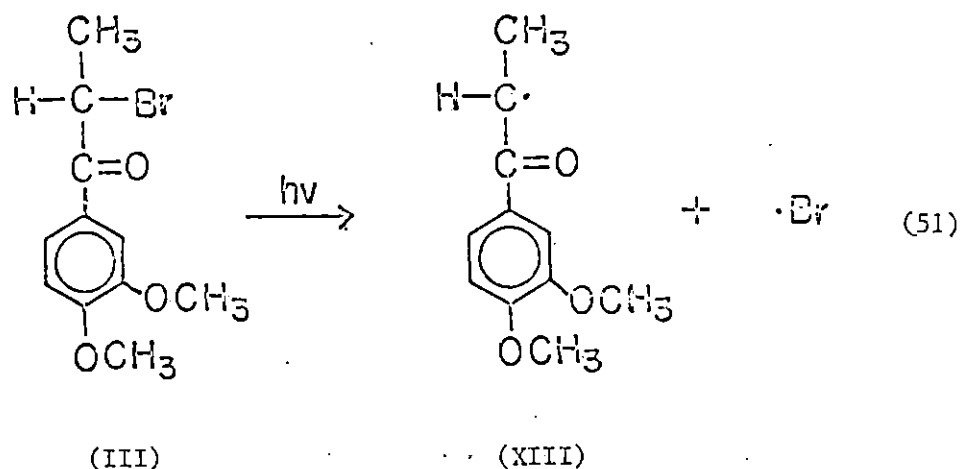
From these findings, it is clear that the singlet signals from compounds IV and V were derived from phenoxy radicals due to the cleavage of ether bond at the β-position. This reaction may be set forth as follows (eq. 52):
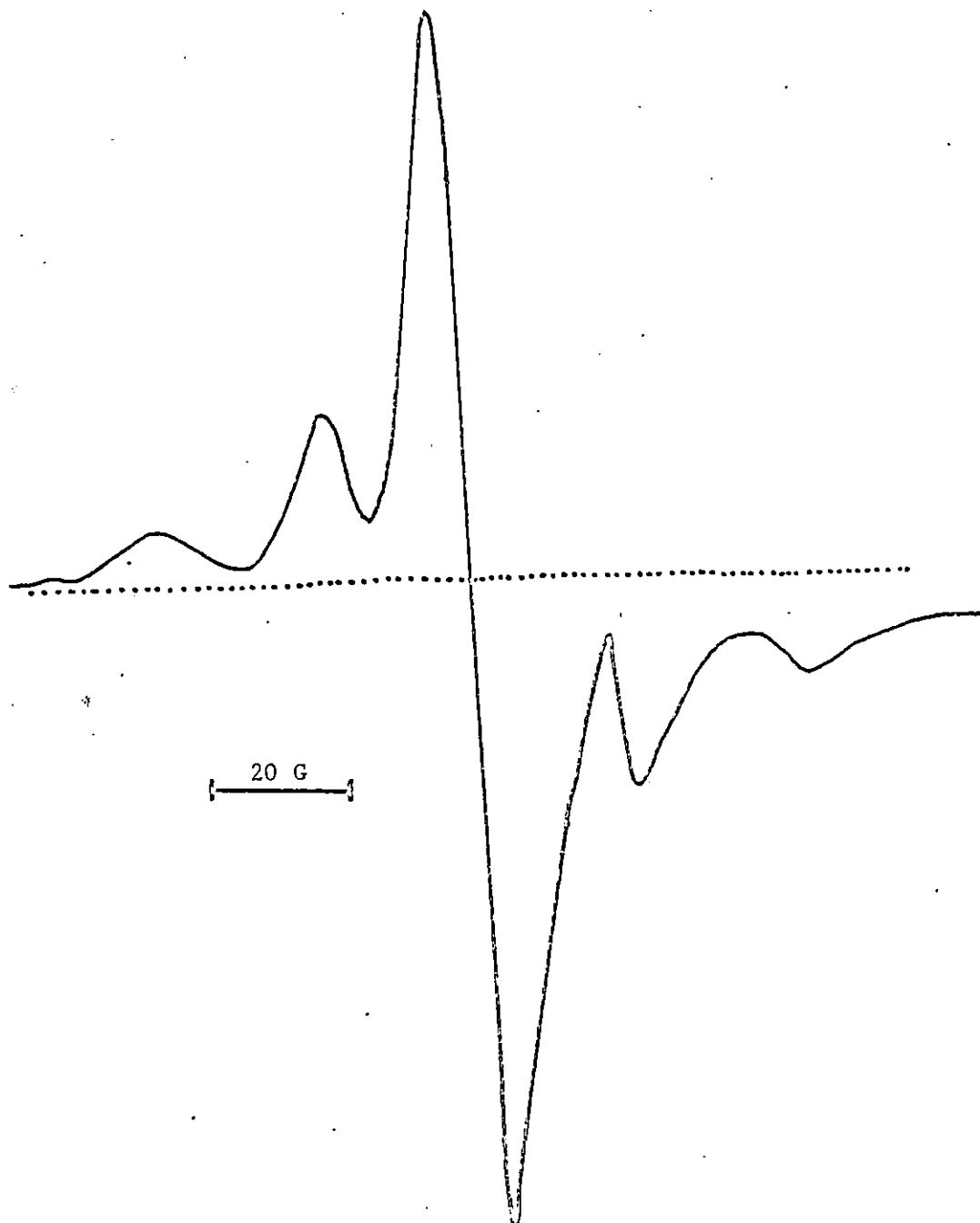
Fig. 31 ESR spectra of model compound III irradiated with
ultraviolet light at 77°K for 60 mins. The dotted line signal
was obtained after the irradiated sample was warmed to 298°K
for 3 min. Spectra were recorded at 77°K.

$$(52)$$

(IV)   (XIII)   (XIV)
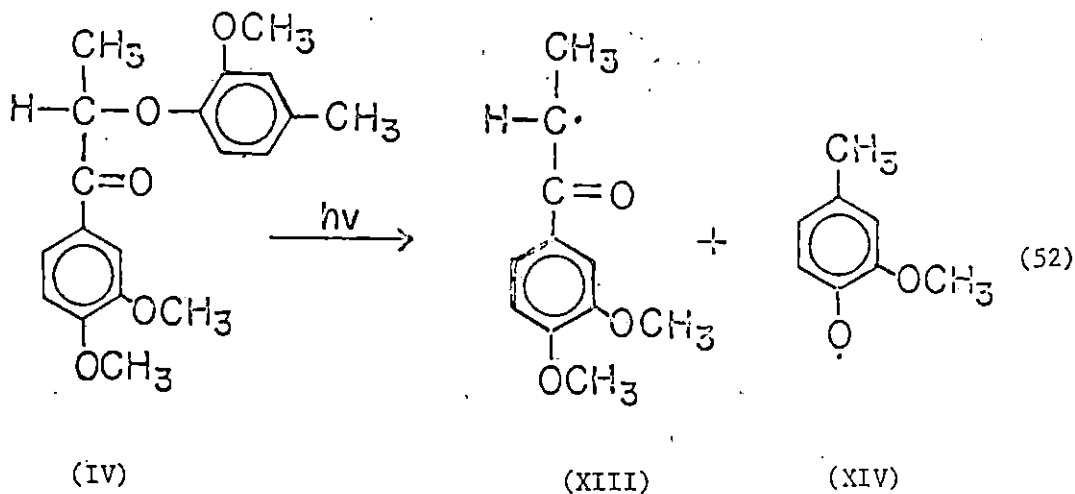
The radical pair XIII simultaneously formed were attributed to the five-line component of the spectrum. Since no aryl-β-ether bond was present in the compound III, no phenyl radical was detected from it.

Additional support for this mechanism was obtained from a gel-filtration study. The results are shown in Fig. 32. Since the elution volumes of fragments from photoirradiated model compound IV were identical with those of propioguaiacone (model compound I) and creosol, it appears likely that the β-0-4 linkage of compound IV was cleaved, resulting in the formation of compound I and creosol.

It should be noted that when all the model compounds discussed above, were irradiated with light of $\lambda > 3000$ Å instead of $\lambda > 2600$ Å, similar results were obtained. However, the intensity of the ESR signals was weaker for the 3000 Å experiment than for the 2600 Å experiment. This difference is due to the higher energy supplied to the system at the latter wavelength.

When model compound VII, which possesses a benzylic alcohol group at the α-position of the phenylpropane unit, was irradiated with light
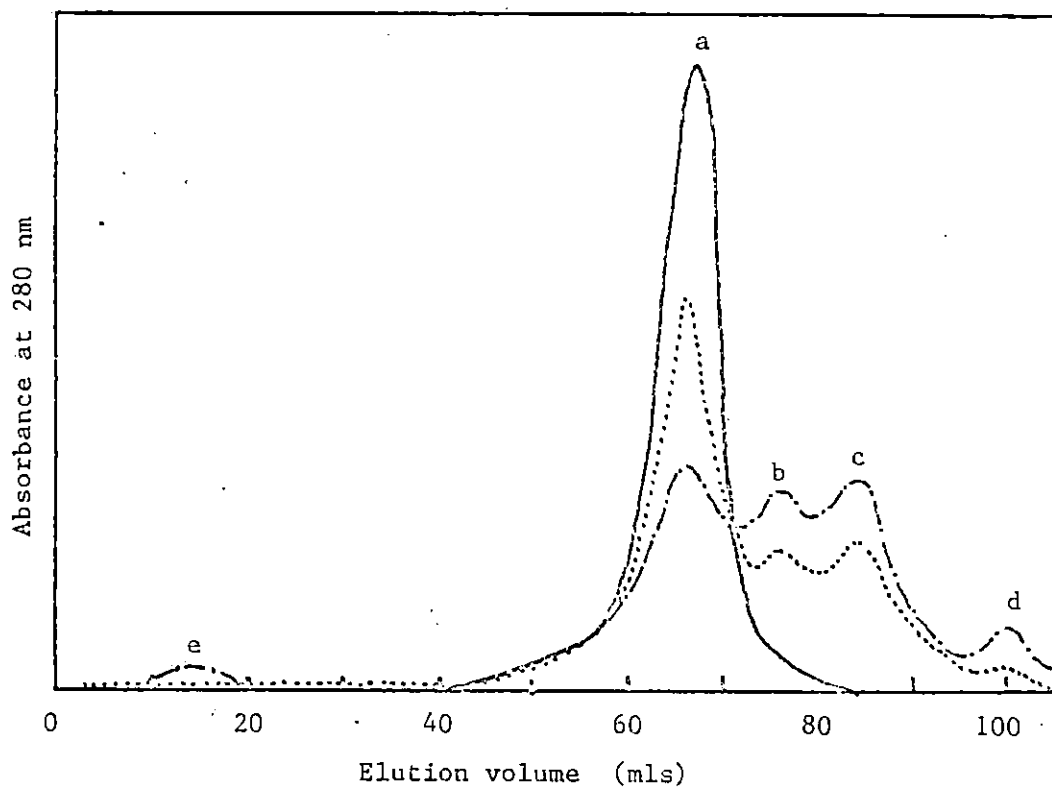
Fig. 32 Elution of lignin model compound IV from Sephadex HL-20 after photoirradiation. Irradiation time: Control (———), 60 mins (·········), 300 mins (–·–·–·–). Identification: (a) Compound (IV), (b) Compound (I), (c) Creosol, (d) and (e) unidentified compounds.

of $\lambda > 2600$ Å at 77°K for 60 min, a diffuse and weak five-line spectrum was detected. When this irradiated sample was warmed to 298°K, only a singlet signal with a line-width of 16 gauss was observed. This suggests that the β-0-4 aryl-ether linkage was cleaved by light. Since the intensity of the spectrum of this compound is only 22 and 27% of that obtained from compounds IV and V, respectively, photodegradation of model compound VI with a benzylic alcohol group is less efficient than irradiation of those with a carbonyl group at the same position.

When 0.05% (w/w) of compound I was mixed with compound VI and irradiated with light at 77°K, a prominent five-line spectrum was observed. This indicates that the ether linkage of compound VI was cleaved following absorption and transfer of energy by compound I. Hence, this fact suggested that compound I functioned as a photosenzitizer and accelerated the photochemical reaction.

These lignin model compound studies shed light on understanding the photodegradation process of the lignin macromolecule. Several important facts were elicited. They are:

(1) Phenoxy radicals were readily produced from free phenolic hydroxy groups by the action of light.

(2) Carbon-carbon bonds adjacent to α-carbonyl groups were photodissociated via the Norrish type 1 reaction.

(3) The Norrish type 1 reaction did not occur efficiently in those compounds with ether bonds adjacent to α-carbonyl group. Photodissociation took place at the ether bond.

(4) Compounds bearing benzyl alcohol groups are not susceptible to photodissociation except when photosensitizers are present.

(5) α-carbonyl groups functioned as photosensitizers in the photodegradation of lignin.

2.8 Mechanisms of Formation of Free Radicals and Chromophoric Groups in Photoirradiated Lignin

Since photodegradation of lignin was small at wavelengths beyond $\lambda > 3500$ Å, the following discussion will be confined to the reactions taking place at wavelengths shorter than 3500 Å.

ESR studies revealed that phenoxy radicals were readily produced from lignin upon photoirradiation. The process preferentially took place at lignin's free phenolic hydroxy groups in lignin (eqs. 53 and 54).

$$\text{(structure with OCH}_3\text{, OH)} \xrightarrow{\text{h}\nu} \text{(phenoxy radical with OCH}_3\text{, O·)} + (\cdot H) \quad (53)$$

$$\text{(structure with OCH}_3\text{, OH)} + X \xrightarrow{\text{h}\nu} \text{(O}\cdots\text{H}\cdots\text{X)} \longrightarrow \text{(O·)} + (HX\cdot) \quad (54)$$
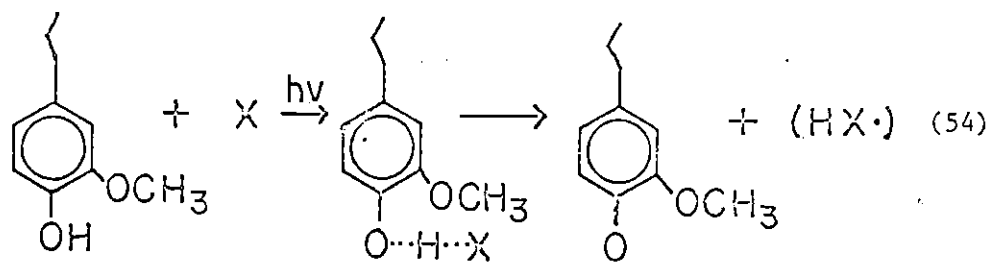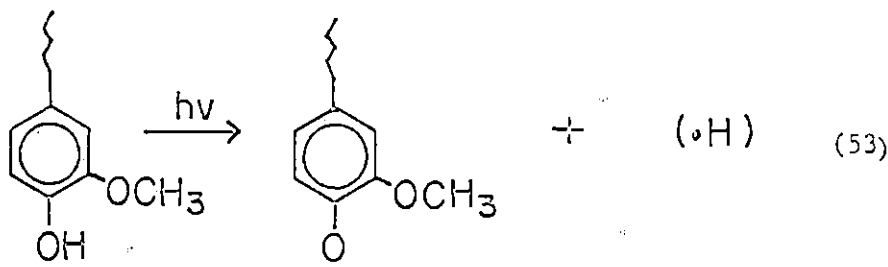
X: chromophoric groups; proton acceptors

Phenolic hydroxyl groups may absorb light directly to produce phenoxy radicals (eq. 53). They may also be produced when hydrogen atoms are abstracted by other functional groups present in lignin, where they are in the excited state after absorbing light (eq. 54). As mentioned earlier, α-carbonyl groups were present in lignin. They

function as sensitizers to accelerate the formation of phenoxy

radicals in lignin. Electronically excited carbonyl groups have long

been known to be voracious hydrogen atom abstractors, and phenols

are good hydrogen donors for photo-excited carbonyl compounds. Hence,

phenolic hydroxy groups may feasibly transfer their protons to the

oxygen atoms of the excited carbonyl groups, consequently, leading

to the formation of phenoxy radicals (eq. 55).

(55)

(XV)
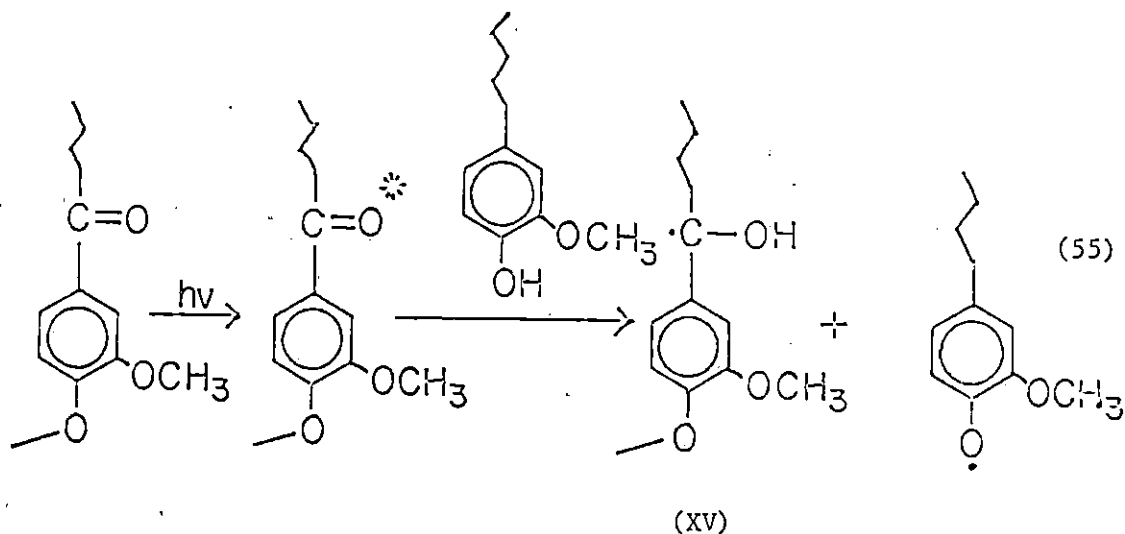
The benzyhydroxy radicals XV may oxidize in air (oxygen) and

be converted back to carbonyl groups, and undergo further photoreactions.

The second way to produce phenoxy radicals is indirectly from

Norrish type 1 cleavage reaction. Acyl radicals produced after the

α-cleavage may abstract hydrogen from free phenolic hydroxy groups

to form an aldehyde, phenoxy radicals being produced concurrently

(eq. 56).
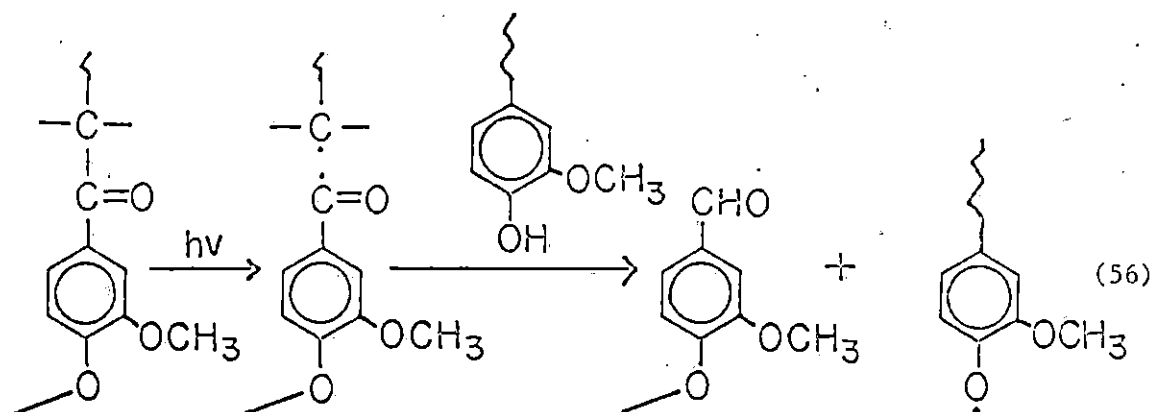
As demonstrated earlier, photo-excited carbonyl groups in lignin chemically functioned depending on their location. Norrish type 1 cleavage occurred in carbonyl compounds having adjacent free aliphatic side chains; this reaction did not occur if ether bonds were adjacent to the carbonyl groups. It is believed that carbonyl groups initially absorbed light to produce an excited state, before they have enough energy for α-cleavage, they then transferred their energy to the ether moiety and the ether linkage was cleaved followed by the formation of phenoxy radicals (eq. 57).

(57)
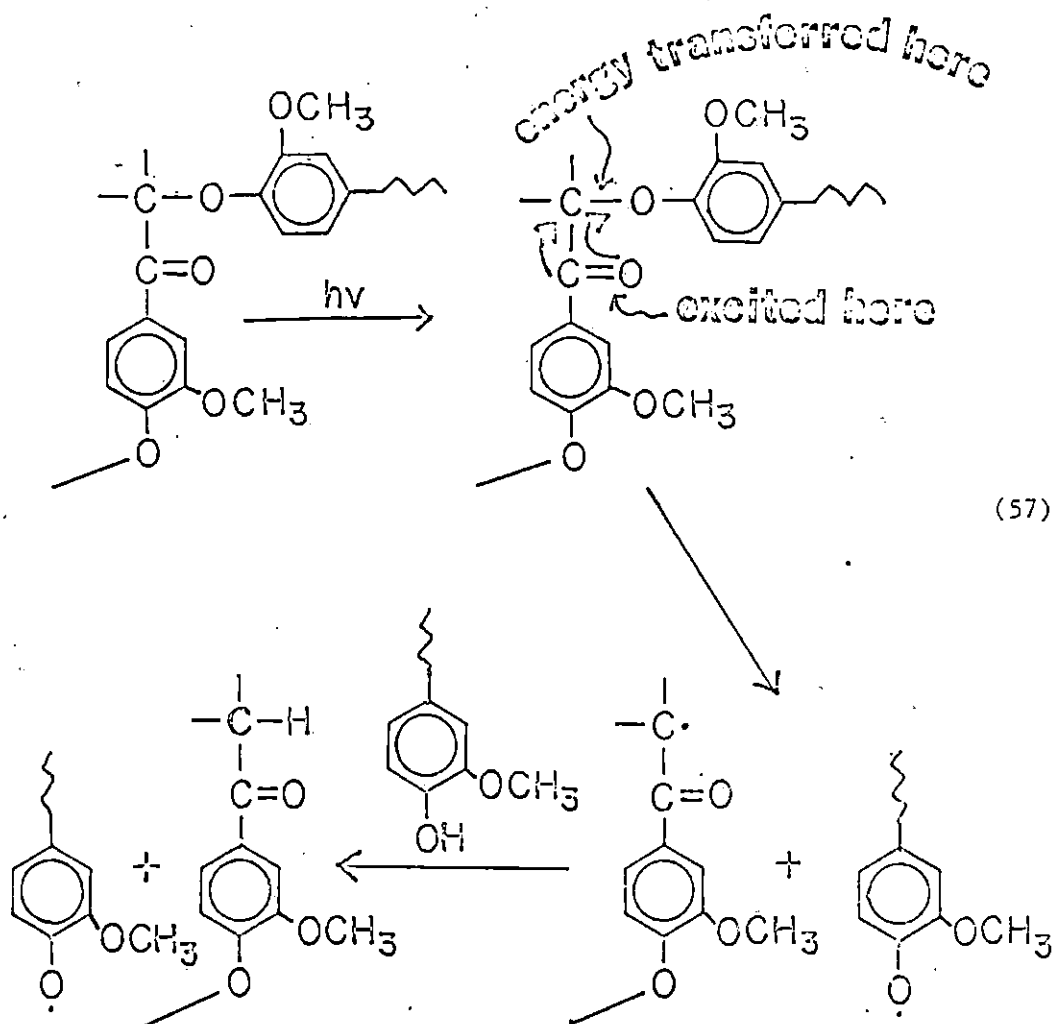
In addition, phenoxy radicals can be formed by dehydrogenation of condensed type phenols with other uncondensed type phenols of higher potential. For instance,

$$\text{(structures)} \qquad (58)$$
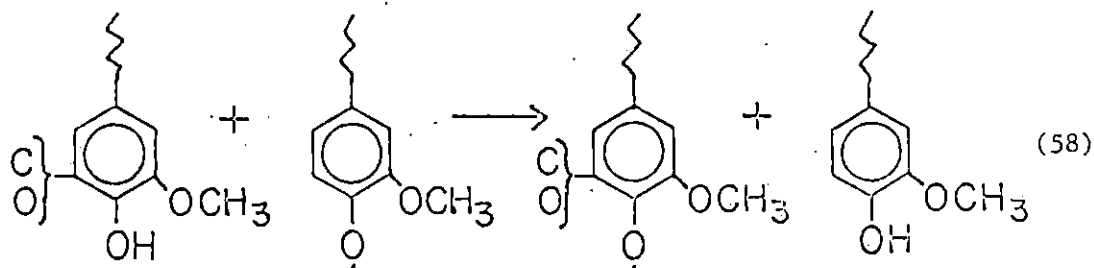
It is notable that phenoxy radicals are the major intermediate formed in photoirradiated lignin.

Although phenoxy radicals are rather stable intermediates, they are capable of being excited by light, or reacting with oxygen.

First of all, phenoxy radicals may be excited by light and induce demethylation of the guaiacyl unit of lignin to produce o-quinonoid structure (eq. 59).

$$\text{(structures)} \qquad + \qquad \cdot CH_3 \qquad (59)$$
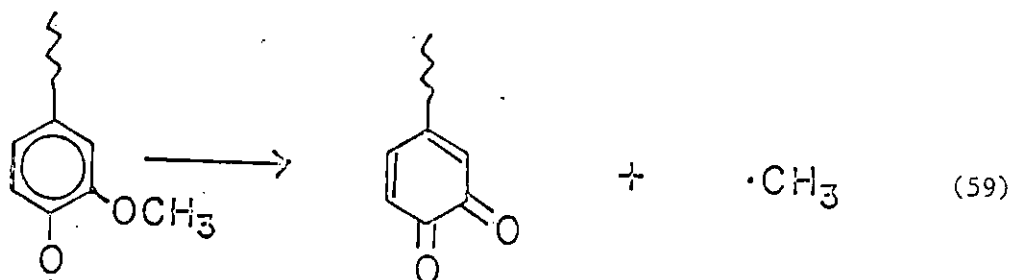
It has been reported that methoxy content of lignin decreased from 15.6% to 10.45% after photoirradiation.[250] It has been suggested that o-quinone is the end-product of the reaction.[35]

In the presence of oxygen, demethoxylation may also occur, as shown in eq. 60, o-quinone was also formed.

(60)
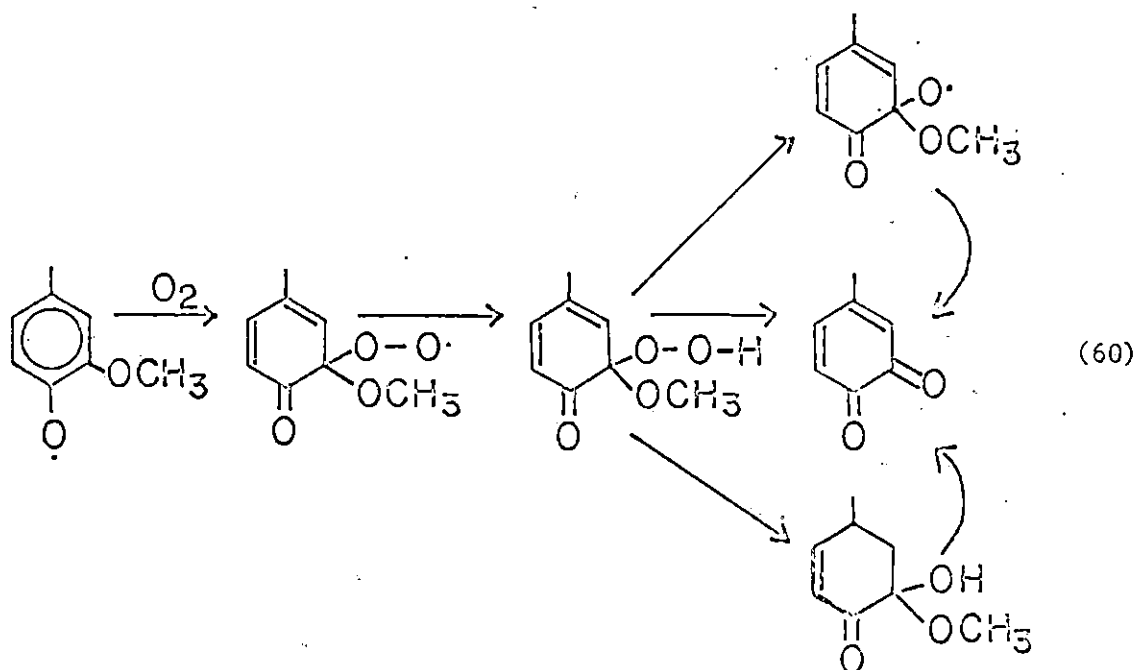
In addition phenoxy radicals may also react directly with oxygen to create o-quinonoid structures in lignin (eqs. 61 and 62).

(61)

(62)
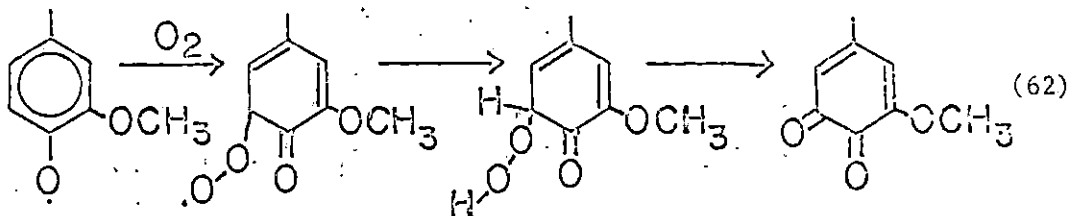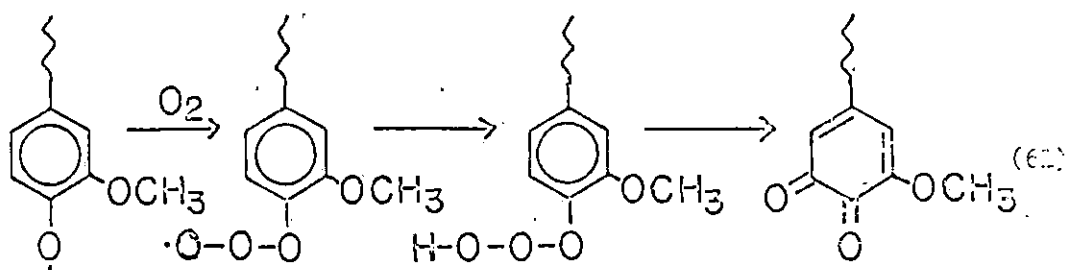
There is another possible way to produce p-quinone when oxygen is present in the irradiation system. This reaction may be described as follows (eq. 63):

$$(63)$$
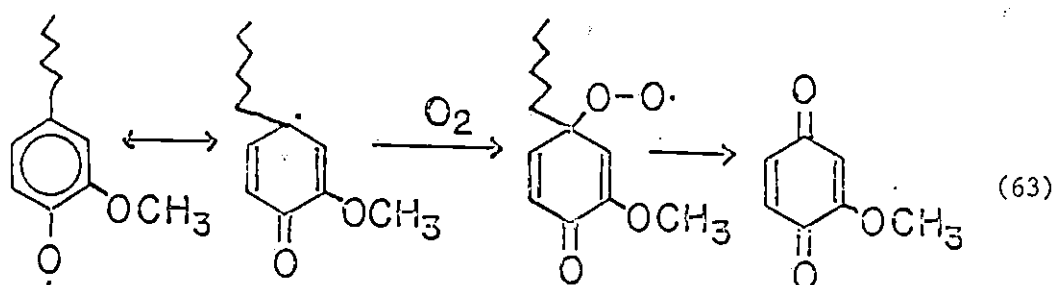
3. Formation of Quinonoid Structures in Lignin

Phenoxy radicals were the preponderant intermediate formed in lignin during either milling or photoirradiation. Due to the high probability of these free radicals reacting in light and with oxygen, it has been proposed that quinonoid type structures were built up in the lignin macromolecule. Details of the pathways leading the phenoxy radicals to form quinonoid structures are considered here.

3.1 Phenolic Coupling Reactions: Overall View

Because of the π-electron system of the phenylpropane unit of lignin, the unpaired electron created on the phenolic oxygen is immediately distributed by mesomerism throughout the molecule, the free radical thereby being stabilized.[251] It is known that if the side chain of the phenylpropane unit does not possess any styrene type conjugated bonds, the spin density is nearly 50% higher in the

C_1 (para-) than in the C_3 or C_5 (ortho position of the phenolic hydroxy group) position. This bears out the observation that C_1 coupling seems to predominate when in competition with ortho coupling.[252] Of course, this reaction depends on the configuration of the structure.

From these facts, it is entirely reasonable to assume that, once formed, phenoxy radicals, unless sterically hindered, will couple together with the intermediates in the system by C-C and C-O bonds, exclusively at positions ortho- and para to the phenolic hydroxy group. The mechanisms of these reactions are complicated. It would seem likely that quinonoid structures are formed.

3.2 Formation of Quinonoid Structures in Lignin During Mechanical Degradation

After milling in oxygen, a small part of lignin can be extracted with benzene-ether. The concentration of the extract was too low to be detected by ultraviolet spectroscopy but it was recognized that the condensed extract absorbed at 280 nm when it was eluted through a sephedex-gel filtration column. It is more likely that the extraction contained compounds with phenyl functional groups, and the p-quinone should be the most prominent one if we consider that peroxide radicals were formed at the C_1 (para) position with a side-chain containing benzyl alcohol group. Elimination of the side chain will produce p-quinonoid structures as shown in eq. 64.

Besides this, it should be pointed out that o-quinones were also created during the milling in the presence of oxygen. However, since the o-quinone moiety had to be incorporated in the high molecular

(64)
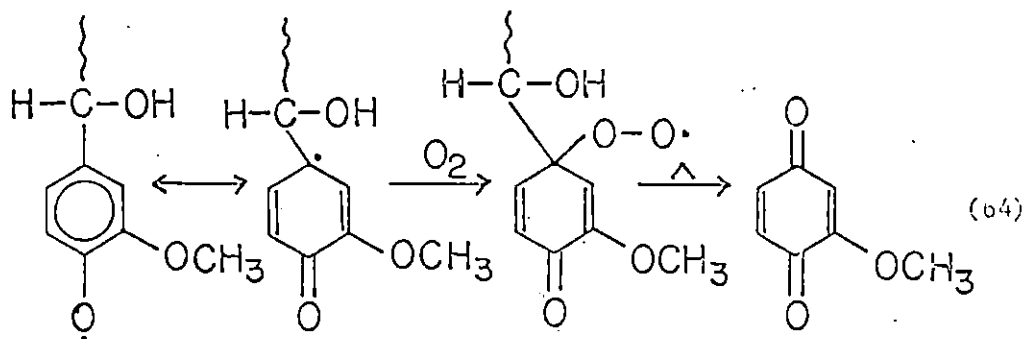
compound of lignin, it was susceptable to extraction with benzene-ether.

In addition, α-carbonyl groups and ethylenic double bonds may also be formed as described earlier in this text, and by others.[253]

Finally, it should be mentioned here that if the p-quinone moiety in low molecular weight compounds was not removed from the lignin polymer after milling, it would be able to recondense to the parent lignin polymer to produce a phenyl ether type quinonoid structure.[252] The possible reaction sites of this condensation on p-quinone are illustrated by the arrows as shown below.[244,252]
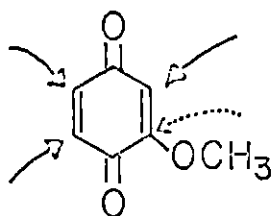
For example, one of the reactions is shown in eq. 65.

3.3 Formation of Quinonoid Structures in Lignin During Ultraviolet Degradation

Phenoxy radicals produced in lignin during the photoirradiation process lead to the formation of o-quinonoid structures rather than

$$(65)$$
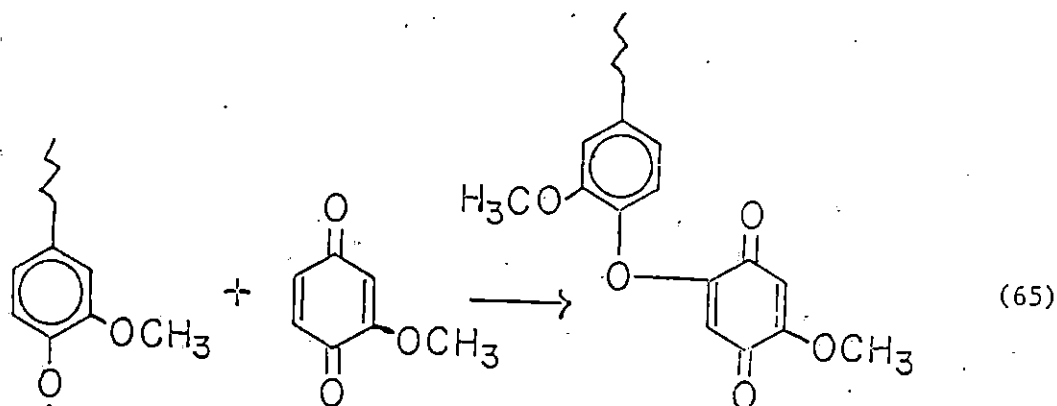
p-quinonoid structures according to the model compound studies discussed above.

Because of the difficulty in isolating o-quinone compounds from the lignin macromolecule, indirect information was obtained by use of lignin model compound studies.

When creosol (4-methyl-guaiacol) was irradiated with light of $\lambda > 2600$ A. in vacuum or in oxygen, the colorless solution was converted to a deep yellow color; the change of its absorption in the visible region during photoirradiation periods was evident, especially when it was irradiated in the presence of oxygen. The changes in the visible spectra are shown in Fig. 33. Absorbance of visible light between 520–600 nm was significantly increased as a function of irradiation time. It is known that o-quinone absorbs light in this region,[286] hence, it is believed that such chromophoric groups were formed under the influence of light. The reaction mechanism is postulated as follows (eq. 66).
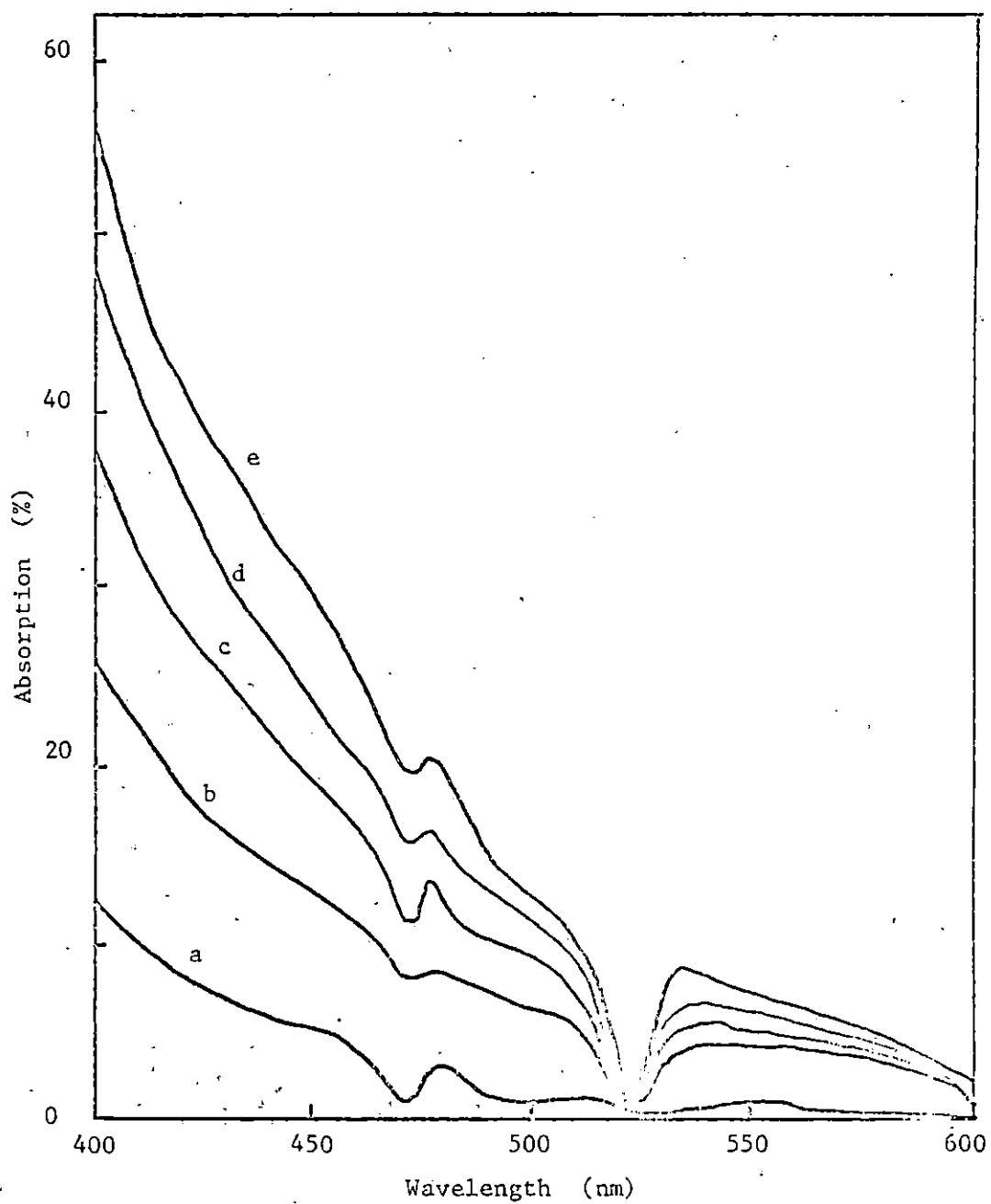
Fig. 33 Discoloration of creosol irradiated with ultraviolet light in the current of oxygen. Irradiation time: (a), control; (b), 30 min; (c), 60 min; (d), 90 min; (e), 120 min.

$$\text{CH}_3\text{-C}_6\text{H}_3(\text{OCH}_3)(\text{OH}) \xrightarrow[\text{O}_2]{hv} \text{4-methyl-o-quinone} + \text{CH}_3\text{OH} \qquad (66)$$
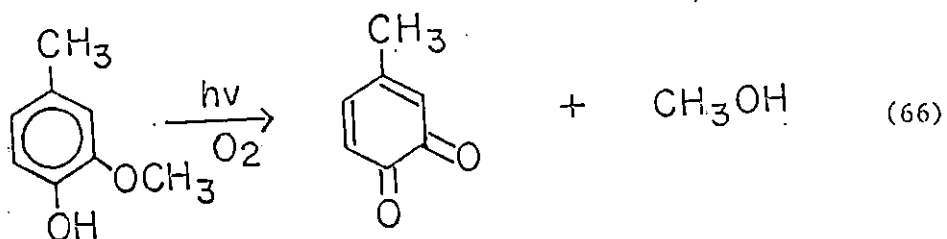
The formation of 4-methyl-o-quinone from creosol after photo-irradiation was confirmed from the TLC experiments. The TLC chromatograms are shown in Fig. 34. The R_f value of oxidized creosol had the identical R_f value as 4-methyl-o-quinone.

Moreover, when anisole was irradiated in vacuum at 77°K for 60 min, a multiplet ESR spectrum was observed as shown in Fig. 35. When the sample irradiated was warmed to 273°K for 3 min and recorded again at 77°K, only a singlet spectrum was observed, indicating that a four-line component (illustrated with arrows in Fig. 35) with a splitting constant of 22.8 gauss decayed. This signal is derived from the methyl radical.[285] Accordingly, demethylation occurred when anisole was irradiated with ultraviolet light.

Based on these lignin model compound studies, we conclude that the o-quinonoid moiety is formed in the lignin macromolecule when irradiated with ultraviolet light.

On the whole, it is apparent that quinonoid moieties formed in lignin were the major chromophoric groups in lignin, being formed during the milling as well as the photoirradiation process. P-quinonoid type structures were predominantly formed during milling; where o-quinonoid type structures were predominately formed during
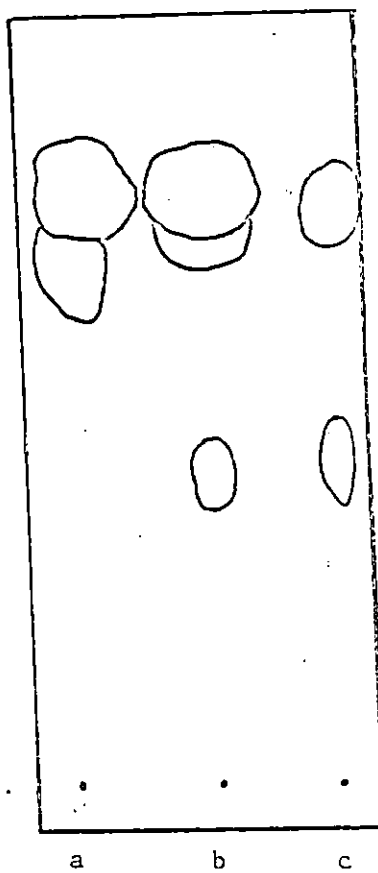
Fig. 34 Chromatograms (TLC) of creosol (a), photooxidized creosol (b) and 0-quinone (c). Developer: benzene:dioxane:acetic anhydride (18: 4:0.8).
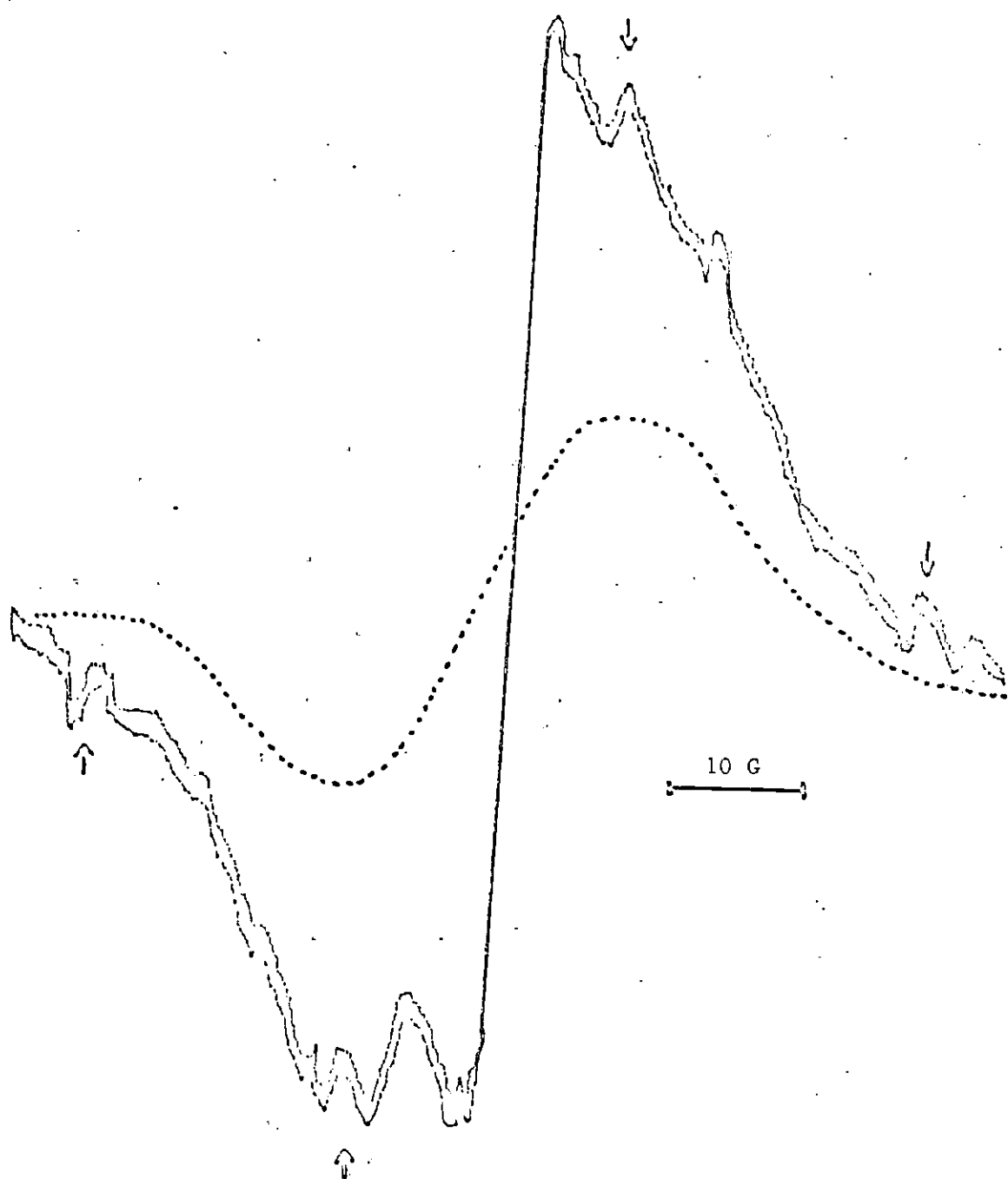
Fig. 35 ESR spectra of anisole irradiated with ultraviolet light
at 77°K for 60 min. The dotted line signal was obtained after
warming the sample to 298°K for 3 min. Spectra were recorded at
77°K.

the photoirradiation process.

4. Photoreduction of Lignin

The color of lignin, as seen by human-eye is due to the light from
the visible region of the absorption spectrum (400-750 nm). As demon-
strated, the greater part of the visible spectral emissions of lignin
originated from the o-quinonoid moieties. It has also been shown that
light of $\lambda > 3500$ Å is not capable of degrading lignin. If such a
longer wavelength shines on lignin, the quinonoid moiety of lignin may
be excited by light and undergo photochemical reaction; quinonoid
structures hence can be modified or eliminated without damaging the
lignin. It is also known that lignin contains stable phenoxy radicals,
and these free radicals may also contribute to the color of lignin since
phenoxy radicals always exhibit absorption in the visible region of
500-600 nm.[197] Again, if a light with wavelength in this region was
employed to irradiate, these free radicals may be excited and destroyed.
Theoretically, the elimination or destroying of quinonoid moieties
and free radicals in lignin will certainly remove most of the color of
lignin. The following results were obtained based on this theory.

4.1 Elimination of Intrinsic Free Radicals in Lignin

Stable phenoxy radicals always exhibit color. In order to
elucidate the effect of light on these free radicals related to the
color reversion of lignin, ESR spectroscopy was used to monitor the
change of free radical concentration. When dry lignins were irradiated
for 60 minutes at different wavelengths the results shown in Fig. 36
were obtained. The relative signal intensities of the ESR signals,
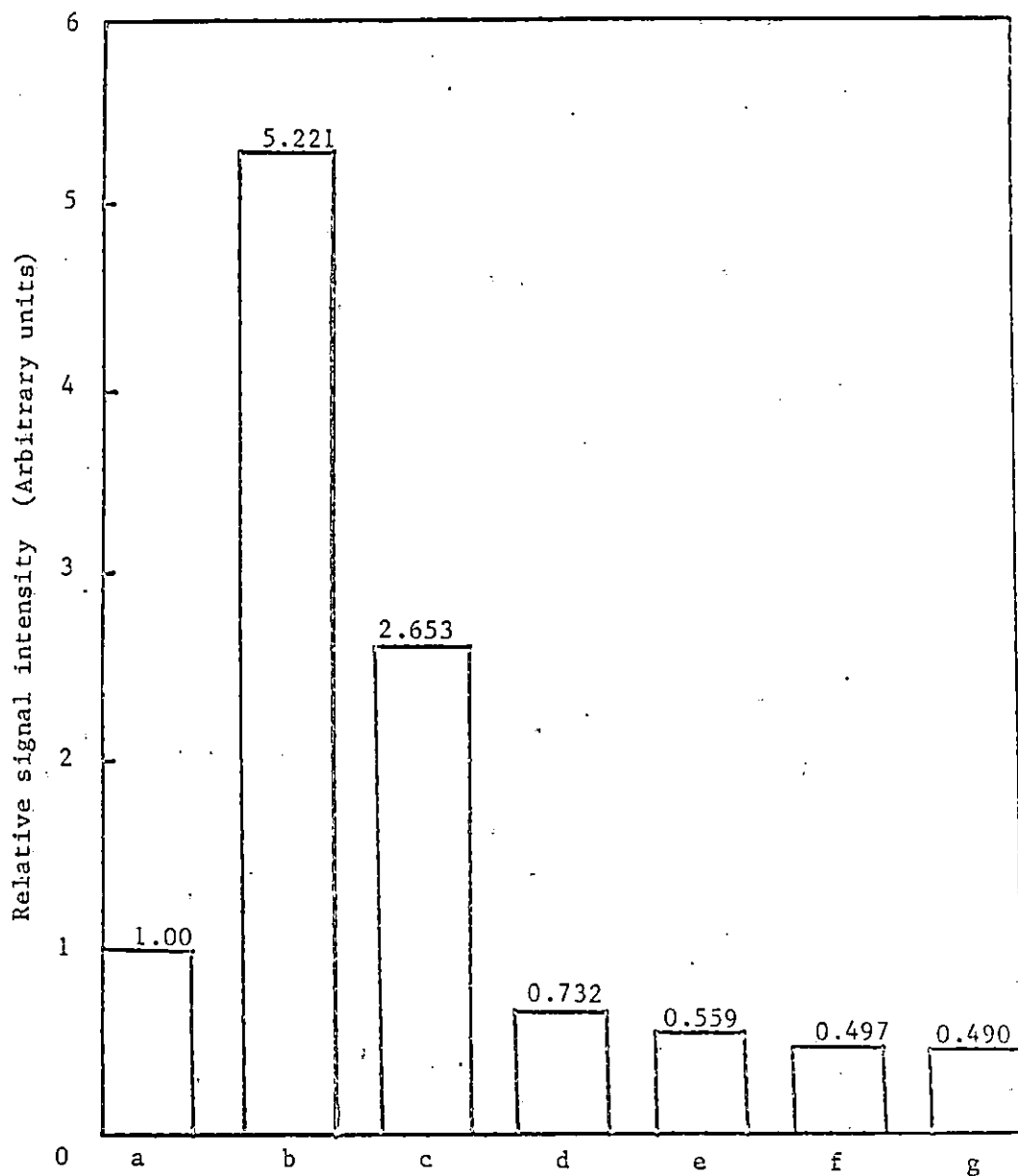
Fig.36 Photo-induced and photo-decayed free radicals in MWL by different lights. Wavelength: (a), control; (b), $\lambda > 2600$ Å; (c), $\lambda > 3000$ Å; (d), $\lambda > 3500$ Å; (e), $\lambda > 4000$ Å; (f), $\lambda > 5000$ Å; (g), $\lambda > 5400$ Å.

which are proportional to the concentration of free radicals, in lignin

increased when wavelength λ < 3500 Å were used. Concentration of free

radicals were increased 5.2 and 2.7 fold with light of λ > 2600 Å and

λ > 3000 Å, respectively. When light of λ > 3500 Å was used, concen-

tration of free radicals was decreased. It was found that approximately

50% of the free radicals were destroyed with light λ > 4000 Å. The trends

of free radicals to increase or decrease in lignin at different wave-

lengths were corroborated with the variation of lignin absorption

spectrum after irradiation with light of different wavelengths as

discussed previously (Fig. 23). When irradiation of lignin with light

of λ > 4000 Å was prolonged for 30 hr, the free radicals could not be

removed completely, and the irradiated lignin remained light brown color.

These experimental findings revealed that free radicals can only be

partially removed by long wavelength irradiation. Visibly, the color

of lignin remains unchanged on such treatment.

4.2   Elimination of o-quinonoid Moiety From Lignin

Decrease of total visible absorption in lignin was observed when

lignin was irradiated with light of λ > 3500 Å (Fig. 23). This was due

to the photo-elimination of free radicals in lignin as mentioned above

(Fig. 36). The other possibility was that o-quinonoid moiety present in

lignin was photo-eliminated. O-quinonoid moieties are very sensitive

to light,[254] being excited by light to form biradicals, and undergo a

coupling reaction. The chromophoric system could hence be destroyed.

The mechanisms of the photo-elimination of o-quinone in lignin were

not fully elucidated in this study. However, based on the knowledge of

photochemistry of quinones coupled with the proposed structures of

lignin, several modes of photo-elimination of chromophoric groups in lignin were postulated.

As shown in Fig. 1 lignin contains a certain amount of aldehyde groups and double bonds. They may contribute to color in lignin. In the presence of light, aldehyde groups and double bonds may react with o-quinone to destroy the chromophoric system. The reaction mechanisms were postulated as follows:

(a) Photoaddition of aldehydes to o-quinones in lignin (eq. 67).
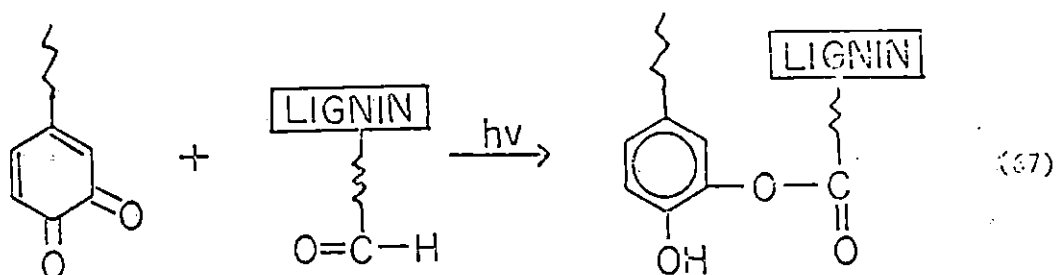
This type of reaction was found when o-quinone reacted with aliphatic and aromatic saturated and unsaturated aldehydes under the influence of light.[255,257]

(b) Photochemical cycloaddition of o-quinones to double bonds in lignin (eq. 68).
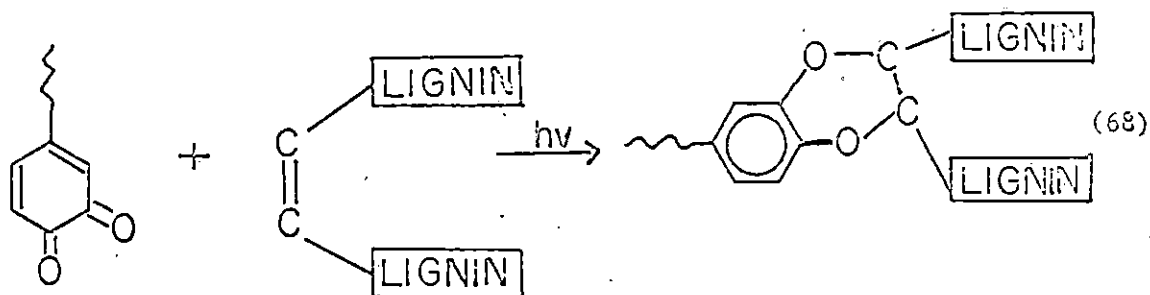
Similar reactions were found by Schonberg and Mustafa[258,259] in that aromatic substituted ethylene (e.g., styrene, stilbene, triphenylethylene) undergo an addition reaction with o-quinone under the influence of light.

Nevertheless, as observed from Fig. 23, chromophoric groups in the dry lignin were not completely removed by light. This may be due to the fact that lignin is a three-dimensional highly branched polymer, this structural configuration highly restricts the mobility of the molecules. Accordingly, the probability that quinonoid moieties excited by light react with aldehyde groups and double bonds is very small.

In order to overcome this obstacle several photoreduction agents were carefully selected to remove the color of lignin. Significant results were obtained. The following irradiations were performed on solution of lignin, rather than the dry powder.

Fig. 37 demonstrated the change of absorption spectrum of a lignin solution (dissolved in dioxane-water in the ratio of 9:1) irradiated with light of $\lambda > 3500$ Å as a function of irradiation time. It should be mentioned here that the absorption spectrum of lignin solution was not changed when sample was allowed to stand at ambient conditions for a long time. When the lignin solution was irradiated with light of $\lambda > 3500$ Å, however, significant reduction of absorption intensity was recognized.

Absorption beyond 500 nm was almost reduced to zero when the irradiation time was 120 min. This indicated that photoreduction took place. After removing the dioxane-water from lignin solution by a rotary evaporator or by freeze-drying, a white lignin powder was
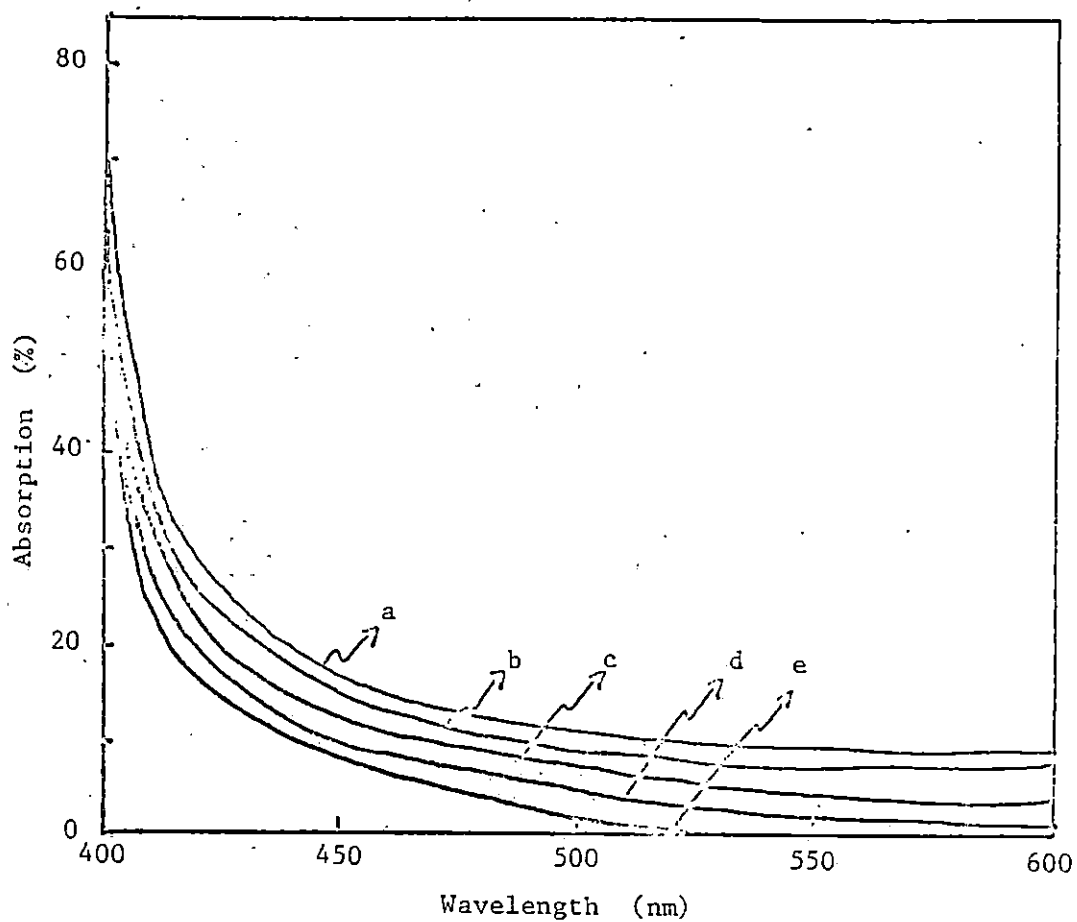
Fig. 37 Photoreduction of MWL solution irradiated with ultraviolet light ($\lambda >$ 3500 Å). Irradiation time: (a), control; (b), 30 min; (c), 60 min; (d), 90 min; (e), 120 min.

obtained.

In order to glean more information on the photoreduction
mechanisms, model compound, 4-methyl-o-quinone was subjected to an
identical irradiation experiment, the results are shown in Fig. 38.

Apparently, when the 4-methyl-o-quinone, a deep red crystalline
substance, was irradiated in the presence of dioxane-water (9:1) for
30 min, reduction of absorption intensity was observed. When the
irradiation time was prolonged to 120 min, the absorption region between
550-600 nm was almost reduced to zero. The photoreduced product
obtained was a yellow crystal.

Reaction of o-quinone and dioxane under the influence of light
should be via a free radical process. Schematic ESR studies on the
intermediates involved in this system were conducted.

When dioxane-water (9:1) solid solution was irradiated with light
of $\lambda >$ 3500 $\overset{o}{A}$ at 77°K, no ESR signal was detected, indicating that no
free radicals were produced in the system. This is because dioxane
and water only absorb light of wavelength shorter than 2000 $\overset{o}{A}$.[260-262]
When 0.01 %   of 4-methyl-o-quinone was added to dioxane-water,
followed by photoirradiation under the identical conditions as the
lignin solution, a five-line ESR spectrum was observed as shown in
Fig. 39. When the sample irradiated was warmed to 298°K for 3 min
and recorded again at 77°K only a singlet spectrum was observed.
Accordingly, the changes of ESR spectrum indicated that the five-line
spectrum was superimposed with a singlet and a four-line component.
The singlet signal was derived from the aroxy radicals in o-quinone;
and the four-line signal was assigned to dioxanyl radicals.
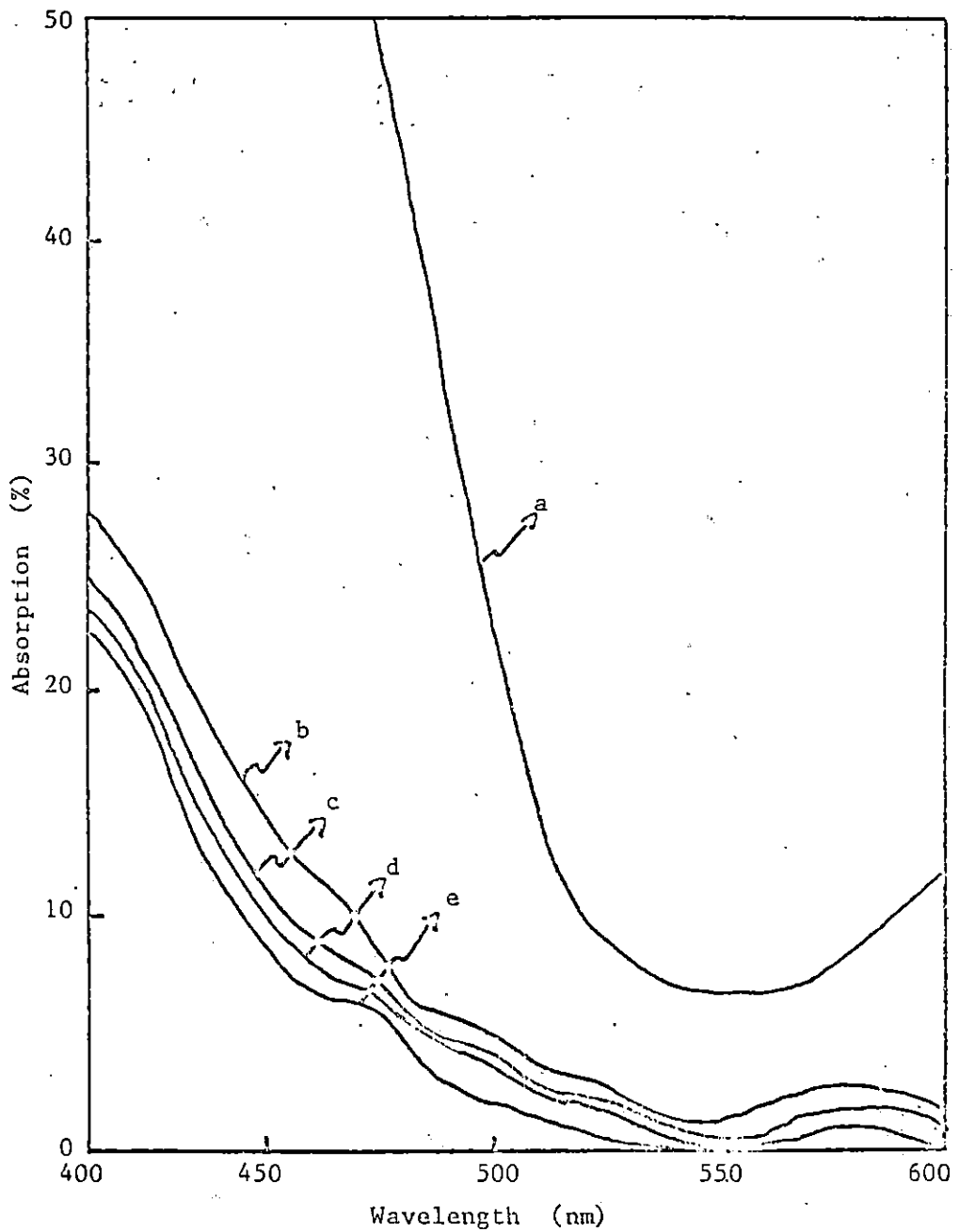
Fig. 38 Photoreduction of 4-methyl-o-quinone in dioxane solution
irradiated with ultraviolet light ($\lambda > 3500$ Å). Irradiation
time: (a), control; (b), 30 min; (c), 60 min; (d), 90 min;
(e), 120 min.
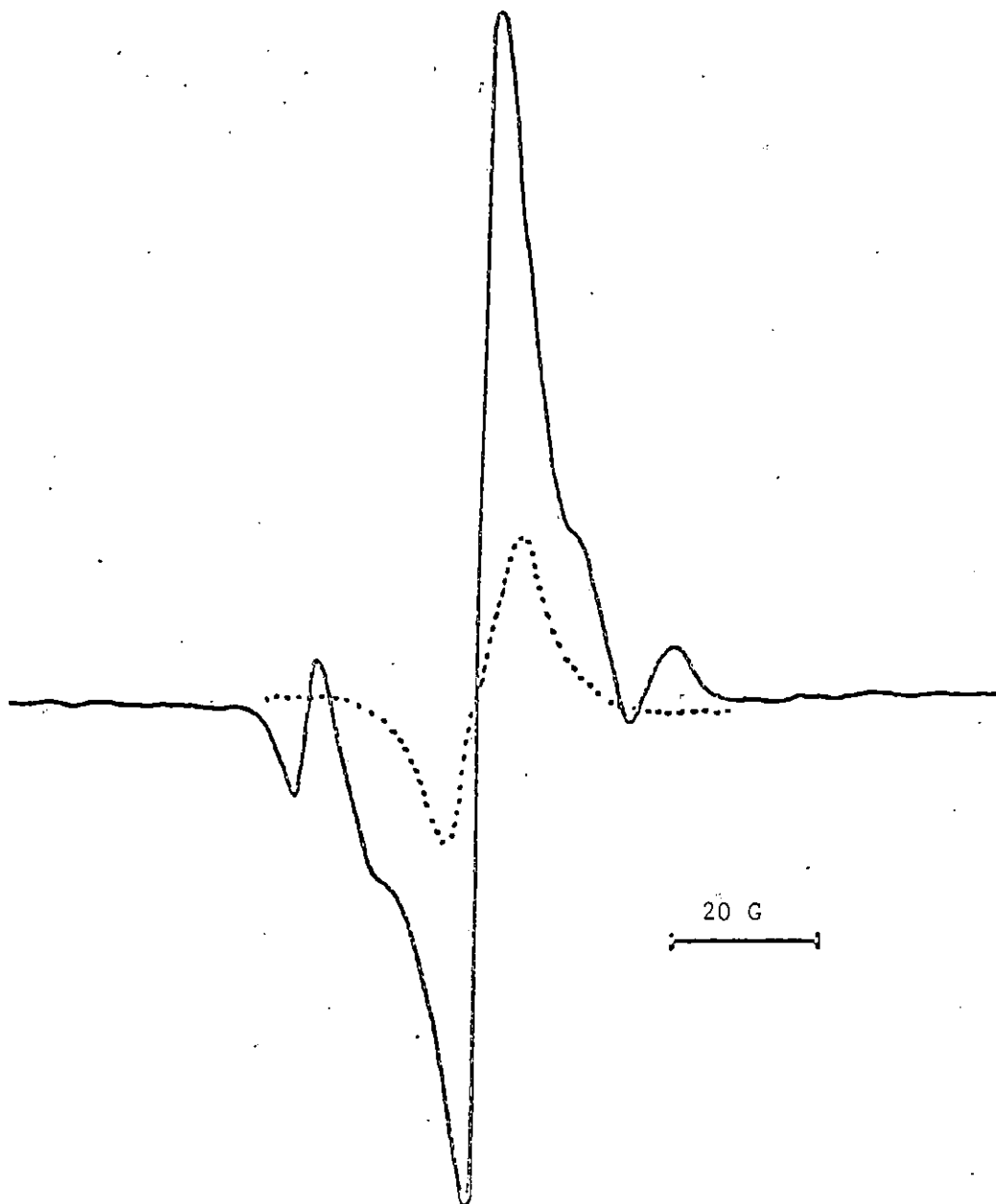
Fig. 39   ESR spectra of dioxane, in the presence of 0.01% 4-methyl-o-quinone, irradiated with ultraviolet light ($\lambda > 3500$ Å) for 60 min at 77°K. The dotted line signal was obtained when the sample was warmed to 298°K for 3 min. Spectra were recorded at 77°K.

The ESR signal as well as the splitting constant of the four-line was quite in line with the literature value of dioxanyl radicals.[263,264]

It is known that dioxane (ether) possesses a potentially reactive C-H bond in the α-position to the ether linkage,[265,266] and it has been suggested that the inductive effect of the oxygen in the dioxane (ether) molecule facilitates the abstraction of the hydrogen atom from the α-position to give the derived dioxanyl radicals.[265,280]

In this case, o-quinone may serve as a photoinitiator and abstract a hydrogen from dioxane; the dioxanyl radicals thus formed may react with the other pair of aroxy radicals in o-quinones. This reaction similarly occurred in the lignin polymer. The mechanism proposed for this reaction (eqs. 69 and 70) is:
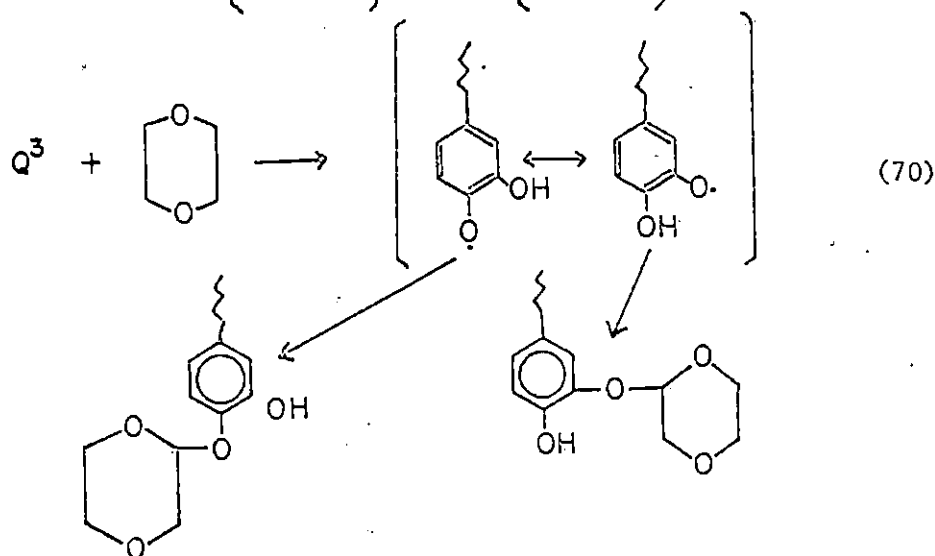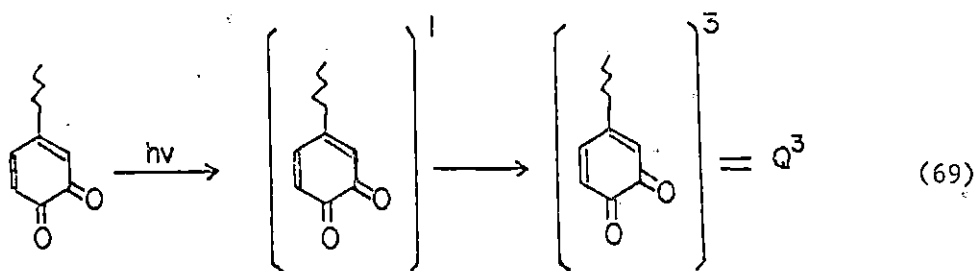
Although we have demonstrated that the o-quinonoid moiety is the major chromophoric group in lignin, it can be photoreduced with dioxane. It should be borne in mind that lignin contains carbonyl groups and ethylenic double bonds. They may function as photoinitiators to induce the photoreduction just described above. Hence, the other possible photoreduction mechanisms of chromophoric groups in lignin by dioxane were postulated as follows (eqs. 71, 72, 73):

(71)

(72)

(73)
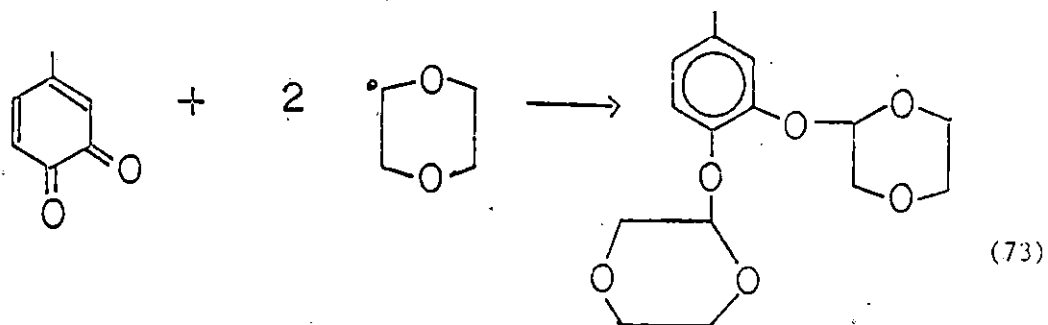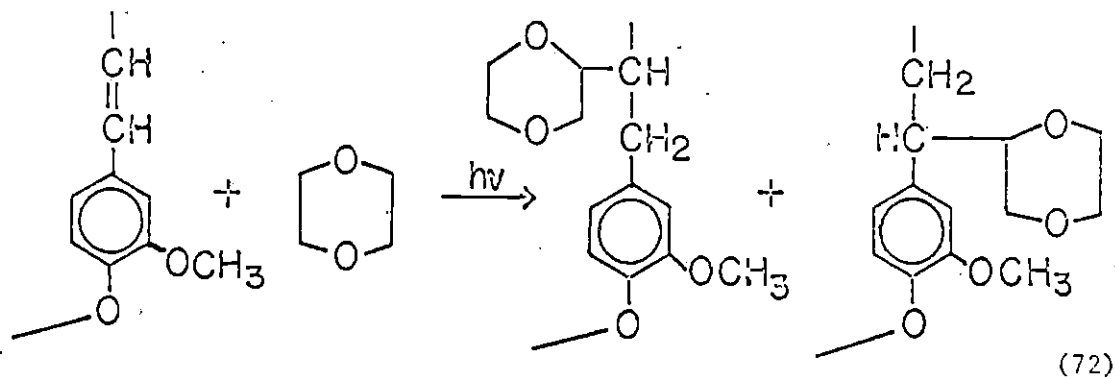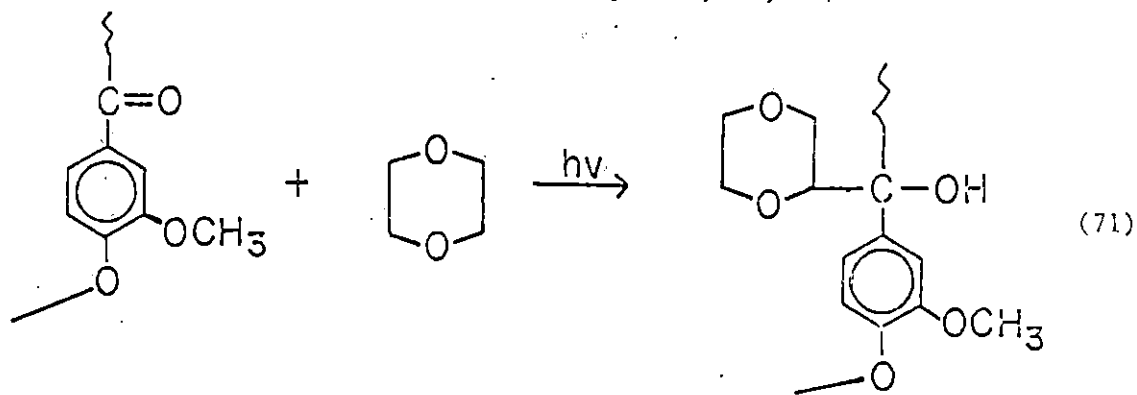
The photoreactions of dioxane and carbonyl compounds and double bonds have been demonstrated by many investigators.[255-259]

Based on these findings, it is believed that the concerted photoreduction of quinones, carbonyl groups (including aldehydes) and double bonds in lignin with dioxane was the major reaction that converted light brown colored lignin to snow-white lignin.

4.3 Stabilization of Photoreduced Lignin by UV Absorber

Color reversion is always a serious problem on lignin and high-yield pulps. The understanding of whether photoreduced lignin also undergoes color reversion seems to be mandatory.

In practice, polymers are usually protected against photooxidation by the addition of stabilizer. In this study, 2-hydroxy-4-methoxy-benzophenone (0.05% W/W) was added to photoreduced lignin as a UV absorber. The UV absorbers are believed to operate by a mechanism in which the stabilizer prevents the light from reaching chromophoric groups. The harmful radiation is directly absorbed by the stabilizer then harmlessly dissipated.

When the photoreduced lignin was placed in a room at ambient temperature (without direct irradiation of light), the color of lignin was not changed during 10 months' storage. However, when the sample was irradiated with sunlight directly for only 3 months, a change in color of the photoreduced lignin was recognized.

When the UV absorber, 2-hydroxy-4-methoxy-benzophenone (HMB), was added to the photoreduced lignin, the color reversion was not observed in 6 months of irradiation by sunlight.

4.4 Application of Photoreducing Methods to High-Yield Pulps

It is important to explore whether the photoreducing methods are applicable to high-yield pulps. Similar reaction was carried out by suspending high-yield pulps in dioxane-water (9:1) overnight; followed by irradiation with light of $\lambda > 3500 \overset{o}{A}$ for 30 min. The light-brown colored high-yield pulp was reduced to a pale-yellow colored pulp. This implied that the photoreduction method is applicable to high-yield pulps. However, it should be mentioned here that high-yield pulp suffered a serious color reversion problem after it was stored in a room at ambient conditions for about six months. Apparently, further study in optimization reaction conditions for completely reducing chromophoric groups as well as stabilization of photoreduced high-yield pulps is necessary.

VI. CONCLUSIONS

New information on the mechanisms of color formation and removal in lignin was obtained experimentally. These findings may be summarized as follows.

1. Degradation of Lignin by Mechanical Processing

Wood, cellulose, and lignin were degraded by mechanical stress. Decrease of viscosity and loss of weight of the lignin milled at ambient conditions revealing the overt effect on lignin by mechanical stress are interpreted in terms of free-radical reactions. ESR studies indicated that chemical bonds were cleaved in wood, cellulose, and lignin, and the lignin suffered the most severe degradation. Several types of mechano-radicals were produced in lignin during the mechanical processing. Among these, phenoxy radicals (aroxy radicals) were rather stable, where carbon-radicals were labile at ambient conditions. Condensed phenoxy radicals were relatively more stable than the uncondensed type phenoxy radicals. The transient mechano-carbon-radicals reacted readily with oxygen molecules to produce peroxy radicals. Termination and decomposition reactions of these labile free radicals lead ultimately to the formation of p-quinones (major), o-quinone, carbonyl groups and double bonds in lignin macromolecules.

2. Photodegradation of Lignin by Ultraviolet Light

Change of viscosity and loss of weight of photoirradiated lignin were observed when the polymer was irradiated with light shorter than 3500 Å; photodegradation of lignin was not observed when it was

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irradiated with light of longer than 3500 $\overset{o}{A}$. Incomplete photo-
elimination of free radicals, and incomplete photoreduction of lignin
were recognized when the light greater than 4000 $\overset{o}{A}$ was used.

Phenoxy radicals were the predominant intermediates formed in
photoirradiated lignin. Elimination of free side-chains of phenyl-
propane units took effect in α-carbonyl group bearing molecules
by way of Norrish type 1 cleavage. Although ether is non-absorbing
in far ultraviolet, β-0-4 ether linkages adjacent to α-carbonyl
groups were adequately cleaved by obtaining photon energy which was
transferred from excited α-carbonyl groups. The α-carbonyl groups
also functioned as photosensitizers accelerating photochemical
reactions of lignin. Simply, the photoactivated carbonyl groups may
abstract hydrogen atoms from phenolic hydroxy groups, benzylic alcohols,
and other sources. The newly formed radicals may undergo further
reactions creating chromophoric groups in lignin. 0-quinones were
the major chromophoric groups formed in photoirradiated lignin.

3. Photoreduction of Chromophoric Groups in Lignin

Potential chromophoric groups and free radicals in lignin can
be partially removed by using ultraviolet light greater than 4000 $\overset{o}{A}$.
Chromophoric groups can be completely removed by irradiation of lignin
in dioxane-water with long wavelength (i.e., $\lambda > 3500$ $\overset{o}{A}$). 0-quinones
(major), carbonyl groups, aldehydes, and double bonds were trapped or
blocked by dioxanyl free radicals. Chromophoric systems were hence
effectively destroyed in lignin macromolecules.

4. Light Stability of Photoreduced Lignin

Photoreduced lignin was quite stable at ambient conditions.

Color reversion of this modified lignin occurred when the sample was

irradiated with sunlight directly for 3 months. This adverse effect

can be precluded by adding 0.05 W/W% of UV absorber, 2-hydroxy-4-

methoxy-benzoquinone, into the system.

5. Photoreducibility of High-yield Pulps

Photoreduction method of lignin is applicable to high-yield

pulps. Color reversion of reduced high-yield pulp was more serious

than in reduced lignin due to the incomplete removal of chromophoric

groups. Further studies on controlling the photoreduction techniques

of high-yield pulps seem to be indicated.

VII. RECOMMENDATIONS

1) Transient mechano-radicals are created in wood, cellulose, and lignin. Before these mechano-radicals undergo secondary reactions leading to chromophoric group formation, they may be trapped by certain scavengers during mechanical processing to avoid the color-forming reactions. Hence, certain adequate scavengers should be selected. Radical scavengers selected should be highly light-resistnat. Those scavengers which absorb light between 290 to 350 nm are not recommended. Long-chain scavengers are highly recommended because their flexibility will modify the rigid structure of lignin.

2) On photoreduction of high-yield pulps one should consider the action of light on cellulose, hemicellulose, lignin, and extractives. The photochemistry of cellulose,[267-270] and hemicellulose[271-274] are well documented. Photochemistry of lignin is described in this text. Information is unavailable on the photochemistry of extractives. This field should be explored.

3) Optimal experimental conditions for photoreduction of high-yield pulps should be examined. Penetration of photoreducing agents into the cellulose fiber is the most important subject. The need for swelling the cellulosic fiber should be stressed.

4) Photoreduction by agents other than dioxane should be attempted based on the chemistry and economic viewpoints. Toxicity, economic feasibility, and availability of the reducing agents must be considered. Certainly, agents which absorb light between 290-350 nm are not recommended.

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5) Physical, mechanical, and chemical properties of photoreduced high-yield pulps should be examined. These properties greatly depend on the photoreducing conditions and the photoreducing agents introduced.

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APPENDIX 1. DECREASE OF RELATIVE VISCOSITY OF CELLULOSE DURING GLASS BEAD MILLING AT AMBIENT TEMPERATURE.

Milling time, hr	Milled in Oxygen				Milled in Nitrogen			
	t_o	t	η_r	%	t_o	t	η_r	%
0	174	642.1	3.69	100.0	174	642.1	3.69	100.0
1	174	501.1	2.88	78.0	174	558.5	3.21	87.0
2	174	436.7	2.51	68.0	174	468.1	2.69	72.9
3	174	403.7	2.32	62.9	174	422.8	2.43	65.9
4	174	365.4	2.10	56.9	174	391.5	2.25	61.0
5	174	360.2	2.07	56.1	174	372.4	2.14	58.0
6	174	351.5	2.02	54.7	174	365.4	2.10	56.9
7	174	351.5	2.02	54.7	174	360.2	2.07	56.1
8	174	351.5	2.02	54.7	174	360.2	2.07	56.1
9	174	351.5	2.02	54.7	174	360.2	2.07	56.1
10	174	351.5	2.02	54.7	174	360.2	2.07	56.1

NOTE: Concentration of cellulose solution was 0.5 g/100 c.c.

Efflux time of cuen solvent = t_o.

Efflux time of cellulose solution = t.

Relative viscosity (η_r) = t/t_o.

Percentage of original relative viscosity = %.

APPENDIX 1A. DECREASE OF RELATIVE VISCOSITY OF LIGNIN DURING GLASS BEAD MILLING
AT AMBIENT TEMPERATURE.

Milling time, hr	Milled in Oxygen				Milled in Nitrogen			
	t_o	t	η_r	%	t_o	t	η_r	%
0	121.9	146.3	1.20	100.0	121.9	146.3	1.20	100.0
1	121.9	57.3	0.47	39.2	121.9	78.0	0.64	53.3
2	121.9	37.8	0.31	25.8	121.9	50.0	0.41	34.2
3	121.9	34.1	0.28	23.3	121.9	39.0	0.32	26.7
4	121.9	29.2	0.24	20.0	121.9	34.1	0.28	23.3
5	121.9	28.0	0.23	19.2	121.9	31.7	0.26	21.7
6	121.9	28.0	0.23	19.2	121.9	31.7	0.26	21.7
7	121.9	28.0	0.23	19.2	121.9	34.1	0.28	23.3
8	121.9	28.0	0.23	19.2	121.9	34.1	0.28	23.3
9	121.9	28.0	0.23	19.2	121.9	34.1	0.28	23.3
10	121.9	28.0	0.23	19.2	121.9	34.1	0.28	23.3

NOTE: Concentration of lignin solution was 0.4 g/100 c.c.

Efflux time of cellosolve = t_o.

Efflux time of lignin solution = t.

Relative viscosity (η_r) = t/t_o.

Percentage of original relative viscosity = %.

APPENDIX 2. CHANGE OF RELATIVE VISCOSITY OF MWL IRRADIATED WITH ULTRAVIOLET LIGHT.

Irradiation time, hr	Irradiated in Oxygen		Irradiated in Nitrogen	
	η_{rA}	η_{rB}	η_{rA}	η_{rB}
0	1.20	1.20	1.20	1.20
1.0	1.24	1.20	1.20	1.20
2.0	1.28	1.45	1.19	1.20
2.5	----	1.64	----	----
3.0	1.36	1.79	----	----
3.5	----	1.75	----	----
4.0	1.46	1.70	1.18	1.20
5.0	1.59	1.59	----	----
6.0	1.67	1.43	1.17	1.20
7.0	1.74	1.33	----	----
7.5	1.77	----	----	----
8.0	1.78	1.26	1.16	1.20
8.5	1.74	----	----	----
9.0	1.70	----	----	----
10.0	1.53	1.11	1.15	1.20
11.0	----	----	----	----
12.0	1.03	0.90	1.14	1.20

NOTE: Relative viscosity (η_r) = t/t_o; efflux time of cellosolve solvent is 121.9 sec.

η_{rA} was obtained after irradiation with light $\lambda > 2600$ Å;

η_{rB} was obtained after irradiation with light $\lambda > 3000$ Å.

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FORMATION, CHARACTERIZATION, AND CHEMICAL REACTIONS OF

FREE RADICALS IN LIGNIN

BY

Nyok-Sai Hon

ABSTRACT

Free radicals are produced in lignin during mechanical treatment and irradiation with light of various wavelengths.

During mechanical treatment, the lignin macromolecule is degraded severely as revealed by ESR and viscosity measurements. Several types of mechano-radicals are produced in lignin during the mechanical process. Among these the phenoxy radicals are rather stable, where carbon-radicals are labile at ambient conditions. Transient mechano-radicals reacted readily with oxygen molecules to produce peroxy radicals even at $77^{\circ}K$, but they decayed rapidly at ambient temperature.

Photodegradation of lignin was observed when macromolecule was irradiated with light of $\lambda < 3500 \overset{o}{A}$ as revealed by ESR, viscosity, and weight loss. Phenoxy radicals are the predominant intermediates in the photoirradiated lignin as shown by ESR studies. Elimination of side chains of lignin phenyl propane units took effect in $\measuredangle$-carbonyl group bearing molecules. By contrast, β aryl ether substituents adjacent to $\measuredangle$-carbonyl groups caused ether cleavage under identical conditions of photoirradiation. This is attributed to energy transferred from excited $\measuredangle$-carbonyl groups to the ether bonds. The $\measuredangle$-carbonyl groups also functioned as photosensitizers accelerating photochemical reactions of

lignin.

Termination and decomposition reactions of mechano-radicals and
photoinduced free radicals in lignin ultimately lead to the formation
of para- and ortho-quinones, carbonyl groups, and double bonds which
cause the color of lignin.

These potential choromophoric groups can be partially removed from
lignin by using ultraviolet light of $\lambda > 4000$ Å; and they can be comple-
tely removed by irradiation of lignin in the presence of dioxane-water
with light of $\lambda > 3500$ Å. Experimental findings suggest that chromo-
phoric groups in lignin were being trapped or blocked by dioxanyl
radicals resulting in brightening. However, the photoreduced lignin-
adduct suffered color reversion. This adverse effect can be prevented
by using 2-hydroxy-4-methoxy-benzophenone as a photostabilizer.

The feasibility of applying photoreduction techniques to high-
yield pulps was demonstrated. However, optimal experimental conditions
for photoreduction of lignin in high-yield pulps have not been estab-
lished yet.