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Quinone methides in the chemistry of wood

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ABSTRACT. Modern ideas about the stereoelectronic structure of quinone methides and their reactivity and role as intermediates in the lignification and delignification of wood are treated systematically. A special section is devoted to the method of synthesis of model quinone methides in lignin.

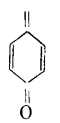
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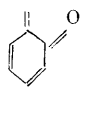
Contents

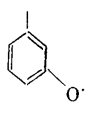
I. Introduction 105
II. Methods of synthesis 105
III. Stereoelectronic structure 108
IV. Chemical reactions 111
V. Quinone methides and the structure of lignin 118
VI. Quinone methides as intermediates in the delignification of wood 120

I. Introduction

The model quinone methods (QM) of lignin are unsaturated cyclic conjugated ketones—derivatives of alkylidenecyclohexadienones; the starting materials for their synthesis are aromatic compounds modelling various structural units of lignin. The involvement of QM in key lignification and delignification reactions is assumed to be generally recognised and this is reflected both in a special review[1] and in familiar monographs.[2–4] Stable QM which are not model compounds of lignin will be mentioned only when needed for comparisons, because the properties of these compounds have already been the subject of a recent review.[5] Endeavouring to achieve a logical description of the data, we shall begin with the properties of the simplest models and shall only then proceed directly to the chemistry of lignin. In conformity with the data accumulated in the literature at the present time, most attention will be devoted to *p*-QM (I); the less stable *o*-QM (II) have been much less investigated. Like the corresponding *m*-quinodimethanes,[6] *m*-QM (III) can apparently exist only as a biradical intermediate with negligible lifetimes. Hitherto their involvement in any kind of reactions of lignin has not been discussed.


(I)


(II)

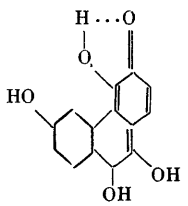

(III)

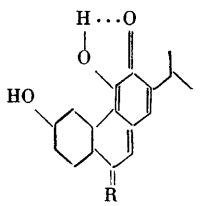
II. Methods of synthesis

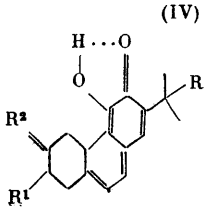
Reliable methods of synthesis of model QM of lignin, which are convenient objects for the study of the mechanisms of lignification and delignification and are synthons for model compounds of lignin, have now been developed.

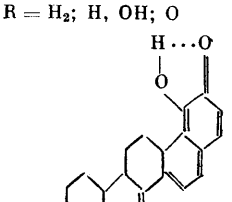
In contrast to the stable sterically hindered QM,[5,7,8] the model *p*-QM of lignin cannot be isolated in a pure form because of their low stability. They can be characterised only in solutions. The sterically hindered QM and QM fused with a benzene ring have no direct bearing on the chemistry of lignin. However, one should note that 10-methyleneanthrone has been isolated from the liquors in the anthraquinone (AQ) pulping of wood, while bianthrone has been detected among the products of the decomposition of the adduct of anthrone and model QM of lignin.[9]

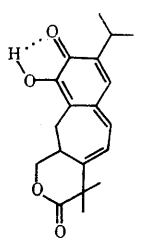
It appears useful to quote examples of stable QM isolated from plants:[10–16]


(IV)


R = H_2; H, OH; O

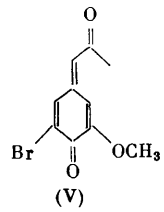

R = H, OH; R^1 = H; R^2 = H_2
R = H, R^1 = OH; R^2 = O


R = H_2, O



In these compounds, the QM system is stabilised both as a result of the lengthening of the conjugation chain and by the intramolecular hydrogen bond. Compound (IV), whose enolic form (a QM) is apparently more stable than the α-keto-isomer, is noteworthy.

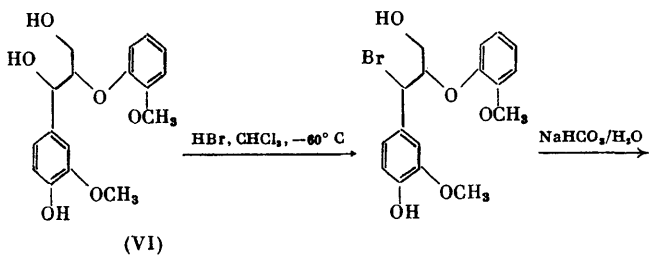
Compound (V) is a rare example of a compound close to the model QM of lignin which has been isolated in a crystalline form; however, its synthesis is poorly reproducible.[17]



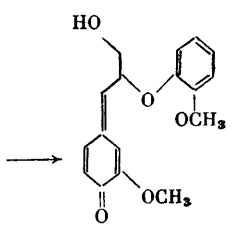
(V)

We shall emphasise two factors. Firstly, there have been numerous studies in which the formation of QM in the course of the processes investigated was postulated. Such publications must be distinguished form the few investigations whose authors dealt with QM directly and the structure of the latter was reliably demonstrated. Secondly, one should treat with caution studies where QM have been identified solely on the basis of electronic absorption spectra. The products of the degradation of these compounds are frequently coloured, which can readily lead to confusion. Thus our experience suggests that Pospisek et al.[18] and Adler and Stenemur[19] could not have obtained all the compounds which they list.

There exist two convenient routes to the synthesis of model QM of lignin: dehydrohalogenation of the corresponding *p*-hydroxybenzyl halide and oxidation of alkylphenols. For example, the method of Johansson and Miksche,[20] whereby fairly complex QM with β-aryloxide substituents have been obtained,[21] leads to success.

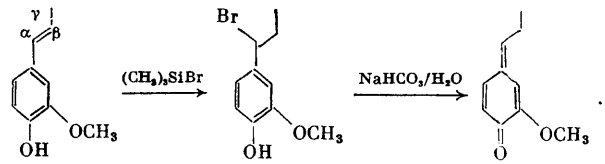


(VI)



(VII)

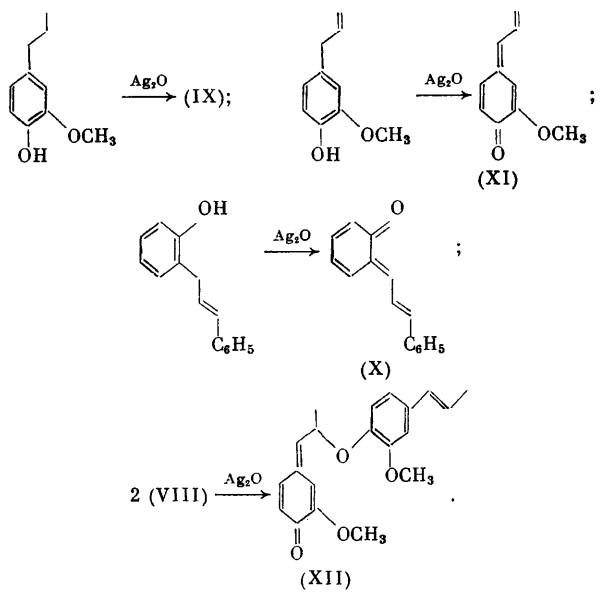
In recent years, this method has lost its importance. Its disadvantage is the use of low temperatures and a reactant such as dry hydrogen bromide, which can give rise to side reactions. In a certain sense, the method of synthesis of QM using bromotrimethylsilane (BTMS) (for its synthesis, see Andrianov[22]) proved to be ideal—this is a "test tube reaction" proceeding at room temperature with total conversion of the initial compound and as a rule an insignificant formation of side products.[23] It involves the formation of the same intermediate bromide as in the case where dry HBr is used.[248] Using bromotrimethylsilane, it is possible to obtain QM not only from *p*-hydroxybenzyl alcohols but also from α-alkenylphenols, for example isoeugenol (VIII):[147]



(VIII) (IX)

QM of the guaiacyl and syringyl series can be readily synthesised by this method; among derivatives of the *p*-hydroxyphenyl series, it has so far been possible to obtain only QM with a β-aryloxide substituent,[24,25] which apparently exerts a "through space" stabilising effect on the mechanism. There is so far no reliable evidence that QM without substituents in the α-position have been obtained.

Another common method of synthesis of QM is oxidation of alkyl- and alkenylphenols by silver oxide:[26–30]



(XII)

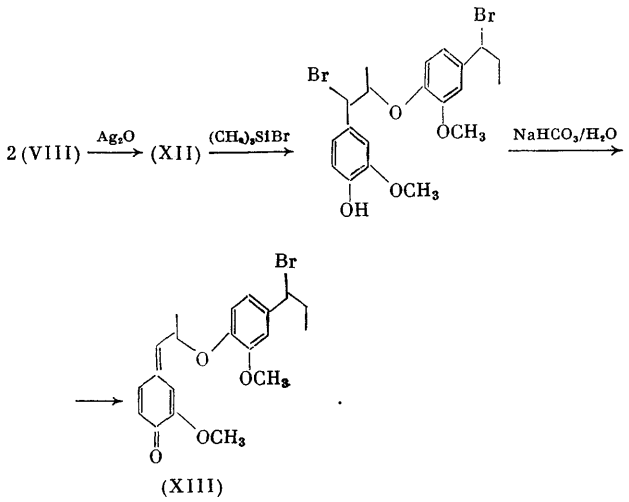
It is assumed that the mechanism of the oxidative conversion of phenols into QM includes either the disproportionation of the corresponding radicals or the formation of an intermediate quinol ether[31] (QM are probable intermediates in the rearrangement of quinol ethers to benzyl ethers[32]).

The formation of QM in the oxidation of phenols is not a "general" reaction; the result of the process depends on the type of oxidant, substrate, and conditions. Thus, contrary to expectations, homovanillic acid affords a product of a completely different type on oxidation with lead tetraacetate.[33] On the other hand, judging from the composition of the secondary products, a QM is formed on oxidation of guaiacylacetone with 2,3-dichloro-5,6-dicyanobenzoquinone.[17] In many cases, oxidation yields a broad spectrum of products.[34–36] We may note that the formation of QM in the oxidation of phenols is regarded as one of the stages of the enzymic degradation of model compounds of lignin and apparently of lignin itself.[37] It is seen from the examples presented above that, depending on the substrate, the reactions of the phenoxyl radicals generated initially may be of different kinds: in one case, they

involve the dehydrogenation of one molecule and in another dimerisation takes place. Thus each method opens up routes of QM of different types.

An important feature of the dimerisation reaction of the phenoxyl radicals derived from α-alkenylphenols is the retention of the steric orientation of the alkenyl substituent in the aryloxide group of the β-aryl ether type QM formed. Previously this reaction was deduced from the analysis of the secondary products formed during processes simulating the initial stages of lignification;[35] this reaction has been recently established directly for the transformation (VIII)→(XII).[38] Thus one can claim confidently that during their lifetime the alkenylphenoxyl radicals do not undergo changes in configuration. Consequently the steric structure of the unsaturated side fragments of lignin must correspond to the stereoisomeric composition of the monomeric alkenylphenols. This conclusion has definite importance for the understanding of the lignification process.

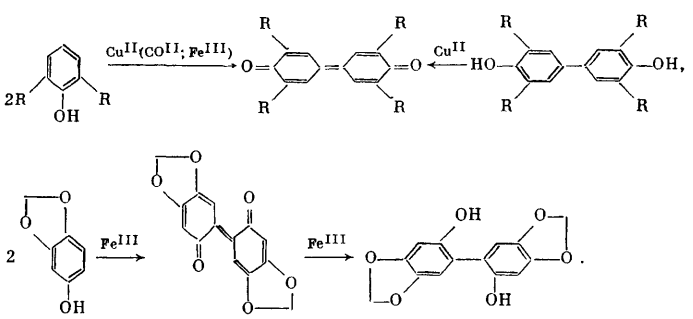
The combination of both methods of synthesis of QM opens a route to the preparation of interesting QM of the type (XIII), which contain a halogen atom in the side chain:[38]



(XIII)

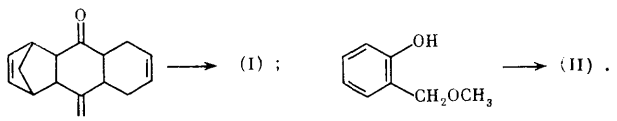
The fact that bromotrimethylsilane does not leave unaffected the multiple bonds of the molecule conjugated with the aromatic ring is used here. The same fact also precludes the employment of bromotrimethylsilane for the synthesis of QM vinylogues from compounds of the type of coniferyl alcohol (we may draw attention to an erroneous study[19] where the opposite was claimed).

The oxidative dimerisation of phenols serves as a familiar preparative method for the synthesis of substituted diphenoquinones—compounds related to QM and differing from the latter by a greater stability:[39–41]



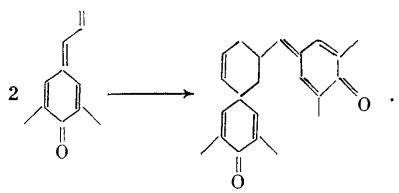
Attention should be drawn to the possibility of the formation of similar structures in lignin, for example, from fragments of the biaryl type.[42]

Individual highly reactive QM, the first members of the *p*-QM (I) [43] and *o*-QM (II) [44,45] homologous series, have been obtained by flash thermolysis:

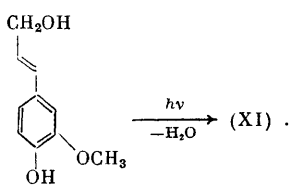


Compounds (I) and (II) remained unchanged in the solid state at a low temperature, but underwent rapid reaction on heating to room temperature or on adding nucleophiles. Flash thermolysis can hardly be used as a general preparative method. We may note that the formation of the unstable QM (II) in the gas phase was detected by photoelectron spectroscopy.[46]

In the series of sterically hindered QM, there is a method for the synthesis of stilbenenquinones by the dimerisation of QM with subsequent disproportionation.[5] In contrast to this, unhindered QM with the α-vinyl substituent are capable of dimerisation of a different type, affording an even more complex QM:[47]



Studies[48,49] in which it was possible to detect the formation of QM vinylogues [of types (XI)] in both aprotic and protic solvents (including water) in the flash photolysis of the corresponding alcohols merit mention:



(XIV)

In hydroxylated media, the QM obtained rapidly undergo nucleophilic addition reactions. The presence of QM was detected in this case only from electronic spectra but, together with the published results mentioned above,[48,49] the detection is convincing. It is striking that only α-vinyl-substituted QM, whose reactivity is reduced compared with the simplest representatives of the series, can be obtained by this method.

The convenient preparative methods described above lead to the formation of typical model QM of lignin in dilute solutions, but the presence of impurities is then inevitable. The target product can be purified by liquid chromatography.[28,50] Hitherto the isolation of model QM of lignin in a pure state under normal conditions has not been reported, although it is possible to concentrate a solution of a QM of the β-aryl type without degradation of the target product.[21,50]

III. Stereoelectronic structure

Hitherto no data have been published on the structure of the quinone methide fragments of the polymeric lignin, but certain significant conclusions can be arrived at by investigating low-molecular-weight objects. Experimental methods, such as X-ray diffraction analysis, which yield detailed information about the molecular geometry, have been applied to certain stable crystalline QM. The introduction of aryl substituents in the α-position in the QM [compounds (XV) [51] and (XVI) [52]] or of *t*-butyl groups in the ring [we may draw attention to the stability of galvinoxyl (XVII) — a free radical containing a QM fragment[53]] as well as fusion with benzene rings [compound (XVIII) [54]] are methods for the stabilisation of the quinone methide system. We may note that the QM are not themselves in any way exotic compounds. It is sufficient to mention that this class includes fluoresceine and alkaline forms of phthaleine dyes.[55] On the other hand, the majority of such systems have no bearing on wood and can be in no sense regarded as model compounds of lignin. An exception is QM with an elongated conjugation chain isolated from plant raw material (see above); one of such substances [compound (XIX)] has been subjected to X-ray diffraction analysis.[11]

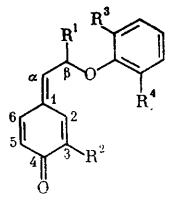
A detailed knowledge of the geometry of the skeletons of the simplest QM is important for the understanding of the physicochemical properties of compounds of this class. QM are quinone derivatives occupying in terms of many properties an intermediate position between benzoquinone (XX) and quinodimethane (XXI). The *para*-substituted compounds (I), (XX), (XXI), etc. belong to the D_{2h} symmetry group, while the corresponding *ortho*- and *meta*-substituted compounds belong to the C_{2v} group. In conformity with this, a classification of the atomic orbitals (AO) constituting the basis of the π-electron system has been put forward.[56] It is significant that, as a consequence of the different symmetries, the orbitals of the lone pairs of the oxygen atom do not mix with the π-system.

An important source of structural information is provided by calculations with optimisation of the geometry. The first attempt of this kind was apparently undertaken[57] using the MINDO/3 method for calculations relating to the simplest molecule of compound (I). In contrast to the semiempirical quantum-chemical methods, *ab initio* calculations and calculations by the empirical method of atom–atom potentials (AAP) provide more reliable predictions of the geometry. Calculations of both types have been carried out by the present authors[58] for the simplest models (XI) and (XXII). As regards molecular geometry, there is good agreement between the two methods. The distinct alternation of bonds leaves no doubt as to the quinonoid structure of QM.

An extremely interesting feature of asymmetric QM is the predominance of the (*Z*)-isomer in the vast majority of reaction mixtures obtained in the synthesis of these compounds. The (*Z*):(*E*) ratio is usually 2:1 [24,25,59,80] regardless of the mechanism of the synthesis: heterolytic cleavage of bromides or homolytic oxidation of phenol-alcohols. Calculation by the AAP methods, which are known to provide an adequate treatment of non-valence interactions, does not indicate the predominance of either the (*Z*)- or the (*E*)-isomer.[58,60,61] The same result was obtained by the semiempirical calculation using the AM1 method. On the other hand, the *ab initio* calculation in terms of the 3-21G basis set yielded a quantitative estimate of the ratio (*Z*):(*E*) which agreed fully with the experimental ratio.[58] Hence one may conclude that the stereochemistry in the series of QM is regulated not by steric but by electronic factors whose nature has not been elucidated hitherto. In combination, these data suggest that the stereoisomeric composition of QM is usually determined by thermodynamics, i.e. the corresponding synthetic reactions are subject to thermodynamic control. An exception is the case where QM is formed via the recombination of aryloxyl radicals. Such reactions lead to equal amounts of the (*Z*)- and (*E*)-isomers, maintenance of the reaction mixture at room temperature leading to a change in the ratio in the expected direction:[28,38]

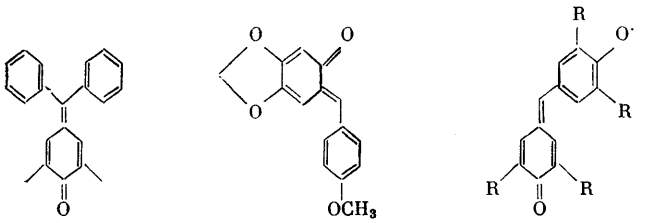


(XI) R = CH=CH$_2$;
(XXII) R = CH$_3$.

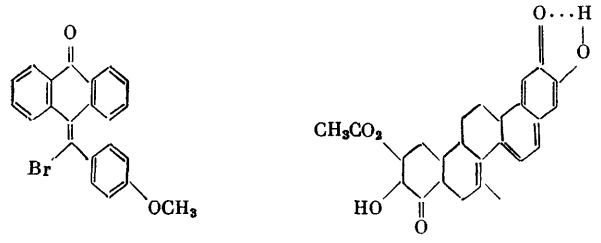


(XXII)

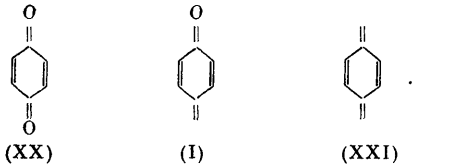
R^1 = H, CH$_3$;
R^2, R^3, R^4 = H, OCH$_3$



(XV) (XVI) (XVII), R = C(CH$_3$)$_3$



(XVIII) (XIX)



(XX) (I) (XXI)

A detailed conformational analysis of the model QM of lignin has been carried out.[58,60–63] It was established by the AAP and AMI methods that the planar conformer of compound (XI) is preferred subject to the stipulation that a second conformer with the ethenyl group displaced from the plane by ~60° should also be present in an appreciable amount.[58] On the other hand, as was to be expected, only the non-planar orientation can be achieved for the α-phenyl

substituent with the same angle of rotation.[63] The β-aryl ether QM (XXIII) have more interesting conformational features especially in connection with the elucidation of the nature of the structural reorganisation of lignin in pulping processes. Clearly, the chemically reversible transformations of the structural units (for example, the conversion of benzyl alcohol units into quinone methide units and conversely) can lead to irreversible changes in the steric structure of the polymer.

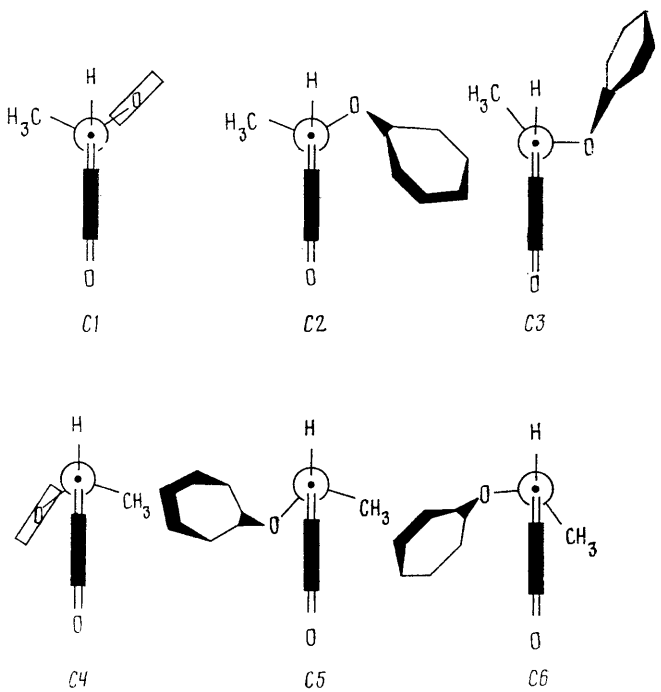
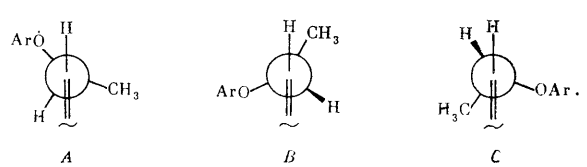


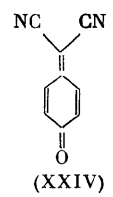
Figure 1. Conformers of the *p*-quinone methide (XXIII, $R^1 = CH_3$): the same conformers occur for other representatives of the series.[62]

Calculations by the AAP method[60–62] for compounds (XXIII) made it possible to identify the set of the possible conformers *C*1–*C*6 (Fig. 1) and to conclude that the conformational lability of the corresponding lignin units is high. The preference for the most favourable conformers *C*2 and *C*5 increases with increase in the steric hindrance of the molecule. Quantitative estimates of the relative energies of the conformers must be treated with caution, bearing in mind the data of Raos and Shevchenko.[64] However, there is no doubt that the ideas concerning the conformational composition of β-aryl ether QM developed previously[24] require revision. It was assumed[24] that three stable conformations are possible for QM (XXIII) ($R^1 = CH_3$, $R^2 = R^3 = OCH_3$): *A*, *B*, and *C*, the conformation *C* being clearly unfavourable owing to steric hindrance:



Using NMR spectroscopy combined with the nuclear Overhauser effect, the authors[24] demonstrated that the H(2) proton of the (*Z*)-isomer is close to the β-methyl group (R^1) and the H^β proton, which constitutes unambiguous demonstration of the existence in solution of the conformer *A*. Nevertheless, the conformation *A* cannot correspond to a potential energy minimum and the same experimental result would have been obtained if the given QM existed as a mixture of the conformers *C*2 (or *C*1) and *C*5 (or *C*4).[62]

The electronic structure of QM and its relation with the reactivity and chromophoric properties of these compounds have attracted attention a fairly long time ago. This was initiated by the simplest calculations using the HMO method.[65,66] Calculations within the framework of better approximations (PPP,[67] CNDO/S [8,28,68–72]) made it possible to reproduce with a high degree of accuracy the electronic absorption spectra of mononuclear QM and to assess the nature of the structural influences. The electronic spectra have long been used for the analysis of QM and large sets of data have been accumulated (for example, see Pospisek and co-workers[18,67] for special studies). However, their main importance at the present time is to serve as a control for quantum-chemical calculations[8,28] and in connection with photochemical problems.[73] The hitherto few attempts at an experimental estimation of the characteristics associated with reactivity have aroused much interest. Thus the first ionisation potentials of QM (II) and (XV), 8.80 eV [46] and 7.72 eV [70] respectively, have been determined by photoelectron spectroscopy. The proton affinity of the simplest QM (I) was found by the method of ion cyclotron resonance as 915 kJ mol^{-1}.[57] An electron affinity of 2.36 eV has been determined for the QM (XXIV) on the basis of not unduly reliable data concerning the position of the band associated with the charge transfer between the QM and hexamethylbenzene.[74] However, we were unable to detect the charge-transfer band for the QM (XI) even in a mixture with donors giving rise to characteristic bands in the presence of benzoquinone.[249] Such behaviour is consistent also with the results of quantum-chemical calculations.[72,75]


(XXIV)

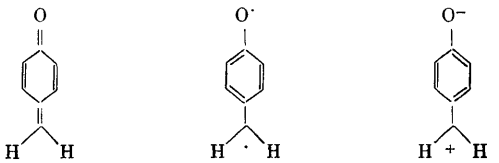
Simplest calculations by the HMO and PPP methods made it possible to establish important features of the electronic structure of QM [5,66,67,76–79] and their protonated forms.[4] The structure of QM and the associated problems of reactivity have now been analysed in fair detail on the basis of a considerable number of semiempirical (CNDO/2, CNDO/S and CNDO/S3, MNDO) [8,28,71–73,75,80–88] and non-empirical[58] calculations.

According to the results of calculations by the CNDO/S3 method,[84] the calcualted energies of the singlet–triplet excitation are too high for the corresponding structures to be regarded as the biradicals (XXV) in the ground state. Only certain excited states can have the biradical character. For planar QM, the energies of such states are unobtainable under the conditions of thermal reactions. The achievement of the biradical state is assisted by the "rotation" of the methylene group out of the plane, but such "rotation" itself requires large energies and the resulting conformation does not correspond to minima on the potential energy surface for the ground state. Thus the biradical forms of the QM (XXV) may play an

appreciable role, in our view, only in photochemical reactions (cf. Burlakov et al.[73]). The non-involvement of the QM biradicals in thermal reactions has also been confirmed by the high regioselectivity of the latter. Mentions concerning the possibility of the existence of QM in a biradical form under normal conditions, which are sometimes encountered, are based on an erroneous interpretation of EPR data during the years when the method only just began to be applied in organic chemistry. In fact solutions of pure QM are diamagnetic.[28]

As regards the zwitter-ionic structures (XXVI),[89] analysis of the bond and atomic valence indices permits the conclusion that such structures (incidentally they have a much higher energy compared with the quinonoid structures) do not correspond to a minimum on the potential energy surface for the ground state.[72,75,84] It is sufficient to say that, after the equalisation of the bond lengths in the ring (with the corresponding lengthening of the C–O and C–C$^{\alpha}$ bonds), the bond alternation does not vanish and there is no significant change in the charge on the C$^{\alpha}$ atom. The electronic[28,71] and ^{13}C NMR spectra[87,90] actually agree well with the quinonoid structures.

Like the biradical structure (XXV), the zwitter-ionic structure (XXVI) can appear only in the vicinity of the saddle point, located an extremely high energy, corresponding to the rotation of the alkylidene group. Therefore, in contrast to Zarubin and Kiryushina,[89] we do not attribute the reactivity of QM for the possibility of their existence in the zwitter-ionic form.



(I) (XXV) (XXVI)

As early as 1983,[72,81] we demonstrated that, as a consequence of the isolated nature of the energy level of the lowest unoccupied molecular orbital (LUMO), the reactions of QM with nucleophiles are usually orbital-controlled. This postulate, which is of key importance for the understanding of the reactivity of QM and which has since been justified by a whole series of empirical and non-empirical calculations,[28,58,71,75,82–87] makes it possible to account for the regioselectivity and the chemoselectivity of numerous reactions involving nucleophilic addition to QM, including those which determine the nature of the pulping processes. The regioselectivity of the orbitally controlled reactions is determined by the contributions of the atomic orbitals to the frontier molecular orbital. For all the QM examined hitherto, the atomic orbital of the C$^{\alpha}$ atom makes the dominant contribution to the LUMO. Only in the case of the QM vinylogue (XI) does another reaction centre, the C$^{\gamma}$ atom, appear with a comparable contribution of its atomic orbitals to the LUMO;[28,58] experimental kinetic data are in full agreement with this assignment.[27]

Many structural influences on the energy of the LUMO of QM have now been elucidated[8,28,71,72,75,81,83] and experimental electrochemical reduction potentials have been obtained for a series of QM in good agreement with calculated data.[28,71,79] Nucleophiles can be in their turn classified in terms of their affinity for QM in conformity with the energies of the highest occupied molecular orbitals.[81,82,89] Such classifications make it possible to estimate reliably the chemoselectivity of nucleophilic addition reactions involving QM. It must be emphasised that there is a small negative charge on the C$^{\alpha}$ reaction centre and the behaviour of QM cannot therefore be explained within the framework of charge control (only the quinonoid tautomers of α-carbonyl-containing phenols are perhaps an exception[83]).

Calculations have now been carried out by the MNDO [87] and CNDO/S3 [71] methods for fairly complex QM of the β-aryl ether type and in the latter case the effect of the conformational isomerism on the electronic structure of the molecules of (*Z*)-(XXIII) ($R^1 = CH_3$, $R^2 = R^3 = OCH_3$) has been determined. This effect is fairly weak, as is, incidentally, also the effect of the appearance of the β-aryloxide substituent itself (which verifies the applicability to lignin of the conclusions obtained from calculations for simplest models). The low-intensity band for the transition involving an intramolecular charge transfer is distinguished by a high conformational sensitivity; the energy of this transition is minimal in the *C*2 and *C*5 conformers, where the two fragments are close to one another.

A similar and more complex and perhaps more important problem is that of a theoretical assessment of the interaction of QM with phenols in neutral and ionised forms. In principle, this reaction is a typical example of the donor–acceptor interaction of a π-acid (QM) and a π-base (phenol) leading to the formation of a covalent chemical bond. Clearly, its mechanism is of interest because interactions of precisely this type determine the nature of many processes leading to the cross-linking and degradation of lignin (see below). It is important to determine whether this reaction proceeds as a classical heterolytic process or whether pre-reaction electron transfer is possible. The point is that the ways in which the heterolytic and radical-ion reactions are influenced are different. A reliable answer to this question can be obtained only by examining the "macroconformations" of the reacting system with variation of the mutual orientation of the reactants and of the distance between them, because the electronic characteristics of the electrophile and the nucleophile change as they approach one another.

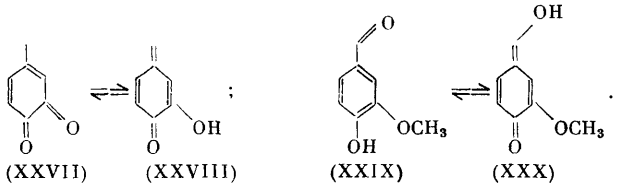
It has been shown[85,86] that the energy of the charge transfer transition in the QM–phenol and QM–phenoxide ion systems is too large for the thermal electron transfer. The addition of phenols to QM is therefore a classical polar reaction regardless of the pH. Another point is that the neighbouring location of the donor and acceptor fragments of the polymer in space makes the polymer sensitive to UV radiation, which is capable of effecting the transition of the system to the chemically excited state with charge separation. On the other hand, in the QM–9,10-anthrahydroquinone dianion (AHQ^{2-}) system the charge transfer energy is low, which indicates a high probability of electron transfer as the first stage of the dark chemical reaction. This difference between the usual phenols and 9,10-anthrahydroquinone makes it possible to explain the significant difference between the influences of the former and the latter on the pulping of wood.[86] We may note that the principal effect of the mutual approach of the reactants is an increase in the energy levels of the LUMO of the QM and that on the whole calculation for the reacting systems confirms the conclusions reached for isolated molecules.

Over short distances, electron transfer can be only a radical-ion stage of the addition reaction (it is important that the barriers to such polar reactions vary in parallel with the charge transfer energies). At the same time, one can imagine also the direct degradation of lignin by electron transfer from AHQ^{2-} or the radical-anion $AHQ^{\cdot-}$ to the QM.[92,93] As a result of such a process, a new species is generated from the QM — the *p*-hydroxybenzyl radical-anion, which has the properties of a nucleophile and a base,

dimerising rapidly with formation of the $C^{\alpha}-C^{\alpha'}$ bond in the case of sterically hindered QM.[5,94] The possibility of dimerisation is explained by the fact that the negative charge in this structurally benzenoid system is located on the oxygen atom, while the spin density is concentrated on the C^{α} atom, which has a negligible charge, as in the case of the QM itself.[75] Contrary to the hypothesis of Dimmel and Shepard,[92] the direct two-electron reduction of the QM (or the one-electron reduction of the radical-anion) with formation of the corresponding dianion is virtually ruled out because of the inability of the latter to exist independently.[75]

It has been shown experimentally that the electrochemical reduction of model lignin QM of the β-aryl ether type leads to the reductive cleavage of the β-aryl ether bond.[95] The radical-anion obtained from such a QM is unstable and the principal route to its degradation is in fact the cleavage of the β-aryl ether bond. In the presence of 9,10-anthraquinone (AQ), the phenomenon of electrocatalysis is observed, i.e. electron transfer from AHQ^{-} to the QM.[95] This phenomenon is characteristic only of QM whose radical-anions are capable of rapid decomposition via the cleavage of the β-aryl ether bond: other model QM are also reduced irreversibly, but electrocatalysis in the presence of 9,10-anthraquinone does not occur.[91] An attempt has been made[88] to assess theoretically the energetics of electron transfer to QM from both reduced forms of 9,10-anthraquinone — AHQ^{2-} and AHQ^{-}. It was found that the reaction should be highly exotheric for the dianion, while for the radical-anion the difference between the energies of the initial compounds and products is low. This, however, did not enable the authors to reach a definite conclusion whether the first or second process was preferred; we may note that the very attempt at a calculation for the energetics of reactions with participation of ions without taking into account solvation is incorrect.

In conclusion we may mention that the prototropic (phenol–quinonoid) tautomerism of QM has been the subject of a theoretical study in recent years. In connection with the problem of the physiological activity of dopamine, a non-empirical calculation (STO-3G) has been carried out with complete optimisation of the geometry of the tautomers (XXVII) and (XXVIII):[96]



(XXVII) (XXVIII) (XXIX) (XXX)

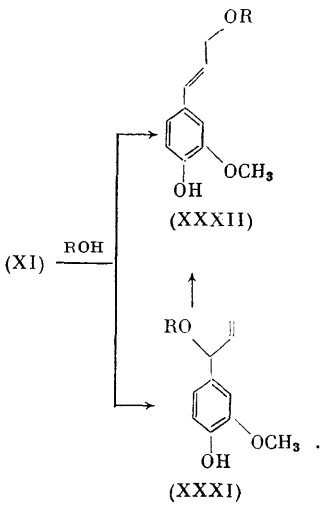
The appreciable energy difference in favour of the *o*-quinone (XXVII) and the large dipole moment of the latter, ensuring stabilisaiton in solution, led the authors to the conclusion that the fraction of the QM (XXVIII) is negligible. The situation is the same also as regards the tautomerism of *p*-hydroxycarbonyl compounds, for example (XXIX)⇌(XXX): for typical model compounds of lignin, the equilibrium is always displaced towards the phenol.[83] Nevertheless the possibility of tautomerism must be taken into account in estimating the reactivity of model compounds of lignin in conformity with the Curtin–Hammett principle.

IV. Chemical reactions

There is no doubt that in the chemistry of wood nucleophilic addition, in which these compounds play the role of substrates, is of greatest importance among the reactions of QM. The addition of water, alcohols, and phenols to QM is of interest in connection with the analysis of the lignification process and hence also of the primary structure of lignin. Another (hitherto completely undeveloped) applied aspect of this reaction is that of the chemistry of organic solvent pulping of wood in alcohols and water–alcohol mixtures.

The kinetics of the addition of hydroxylated compounds to QM have been investigated[49,97–101] using a fairly wide set of reagents but for an extremely limited number of QM. The interpretation of the results and the conclusions about the mechanism of the addition reaction reached in some of the publications[49,98,99] must be treated with caution, since the products were not identified. On the other hand, the quantitative data concerning the stability of QM in various media (in particular as a function of pH) are of undoubted interest. In aqueous solutions, the rate of reaction of the QM (XI) increases with both decrease and increase in pH, the nature of the kinetic curves agreeing with the expected change in mechanism (the primary step is the addition of a proton at low pH and the addition of a hydroxide anion at high pH; in neutral media, one can postulate a concerted nucleophilic and electrophilic attack by water molecules).[49]

Compared with the data of Hemmingson and Leary,[49] the conclusion that the reactivity of QM is low in relation to the SH^{-} and OH^{-} ions, based on the fact that solutions of QM in solvents immiscible with water are stable in contact with aqueous NaOH and Na_2S solutions, appears paradoxical.[102] In fact Ralph's interpretation[102] is erroneous; the observed behaviour apparently arises simply from the heterophase nature of the systems considered.



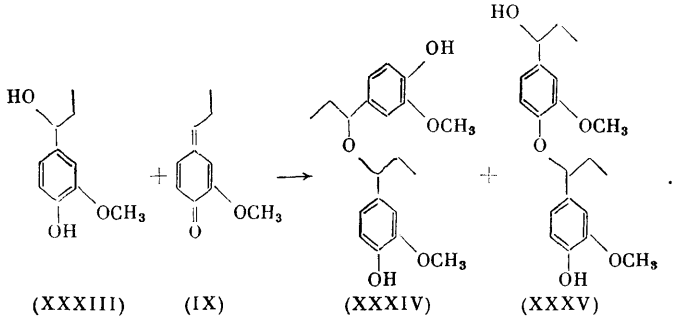
(XXXII) (XI) ROH (XXXI)

The fact that the mechanisms of the addition reactions in neutral and alkaline media are different explains also the characteristic "contradiction" between the theory and experiment in the treatment of structural influences on the reactivity of QM. It is not difficult to understand why the appearance of methoxy-groups in the ring lowers the rate of addition;[49] the reason lies in the electron-donating effect of the substituent. On the other hand, an increase in the length of the conjugation chain lowers the energy level of the LUMO, which should entail an increase in the reactivity in one-electron reduction and orbital-controlled nucleophilic addition reactions.[28] Electrochemical data have shown that such is entirely the case in the reduction reaction. As regards addition, one can confidently assume that this also applies under pulping conditions, where highly nucleophilic ions behave as active agents. On the other hand, in a neutral medium the rate of addition of hydroxylated compounds

falls sharply on passing from QM to their vinylogues.[29,100] Hence it follows that in a neutral medium the reaction mechanism involves the protonation of the carbonyl group as the first stage and not attack on the C^{α} atom. In general, one may conclude that the reactivity of QM in a neutral medium varies in opposition to their stability (an increase in stability may be achieved both by introducing electron-donating substituents and by increasing the conjugation chain length).

Analysis of the orders of the reactions of QM with various hydroxylated compounds in a neutral medium leads to the conclusion that a complex, possibly concerted addition mechanism operates,[99] but kinetic data alone are insufficient for any reliable conclusion. According to Leary et al.,[99] acids add faster than alcohols and only in the former case can one trace the parallel variation of the rate of reaction and the pK_a. In the latter case, a distinct dependence of the rate of addition on steric factors is observed (see also Apushkinskii et al.[100]). Water adds to QM fairly slowly; a sharp acceleration of the process is achieved by adding an acid catalyst.[101] The introduction of type (XI) QM vinylogues into the reaction usually leads to a mixture of 1,6- and 1,8-adducts.[27,49,97] Kinetic control of the addition reactions of both neutral hydroxy-compounds and their ionised forms (OH, OCH_3^-) leads to the preferential formation of the thermodynamically less stable product (XXXI); in an acid medium, equilibrium is readily established and the fraction of the product (XXXII) increases.[27,97] We may note that reduction by lithium tetrahydroaluminate, which in terms of its mechanism is also a nucleophilic addition reaction, affords similarly a mixture of the 1,6- and 1,8-hydrogenation products with the former predominating.[29]

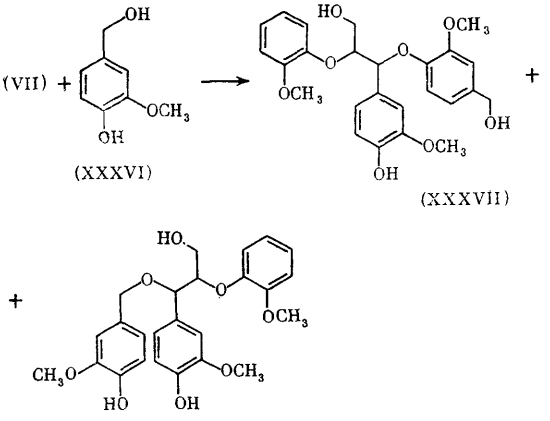
An important factor determining the results of the competitive addition of hydroxy-compounds to QM is the stability of the product. For example, under lignification conditions, the rate of hydrolysis of β-aryl ethers can exceed by a factor of 400 the rate of hydrolysis of β-alkyl ethers.[103] This is an additional factor (together with the higher rate of addition of alcohols to QM compared with phenols), which explains why the reactions of the model lignin QM with vanillyl[104] and dihydroconiferyl[103] alcohols afford dialkyl and not alkyl aryl ethers. The addition of phenols to QM in an anhydrous medium makes it possible to obtain α-aryl ethers,[100,101,105] but in aqueous solution containing an alcohol and a phenol, the alcohol addition product is formed exclusively according to Hemmingson and Leary.[104] We may note, incidentally, that the main factor is undoubtedly kinetic: according to our data, the rate of addition of alcohols to QM is much higher than that of phenols.[100] We have established by ^1H NMR spectrscopy that in an anhydrous medium guaiacylpropanol (XXXIII) adds to the corresponding QM (IX) with the preferential formation of the product (XXXIV).



(XXXIII) (IX) (XXXIV) (XXXV)

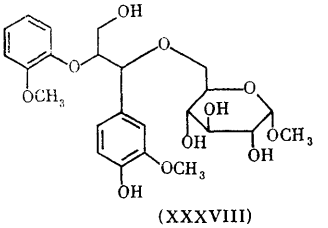
The alternative product (XXXV) is formed in an insignificant amount, corresponding to the ratio of the rates of reaction of phenol and isopropyl alcohol with the QM (IX). Taken together, these data show that the fraction of benzyl ether linkages of the type $C^{\alpha}-O-C^{\alpha}$ and $C^{\alpha}-O-C^{\gamma}$ in native lignin must be much higher than the fraction of the α-aryl *p*-hydroxybenzyl ether fragments.[1,103]

On the other hand, according to Brunow et al.,[101] the product of the addition of vanillyl alcohol (XXXVI) to the β-aryl ether type QM (VII) is predominantly the *erythro*-benzyl aryl ether (XXXVII) in both non-aqueous and neutral aqueous organic media. Incidentally this conclusion is based on the composition of the products isolated from the reaction mixture by column chromatography in a fairly low yield.



(XXXVI) (XXXVII)

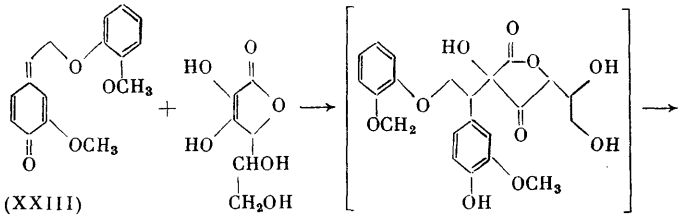
The addition of sugars and related compounds to QM has been investigated in connection with the problem of the formation of lignocarbohydrate linkages. It was shown that D-glucose, methyl α-D-glucoside, and D-glucuronic acid react with β-aryl ether type QM via the C^{α} atom with formation of the corresponding ethers and esters, for example, (XXXVIII).[106–109] It is significant that the nucleophile competing with sugars *in vivo* (water) suppresses to an appreciable extent the interaction of QM with glucose but not with glucuronic acid.



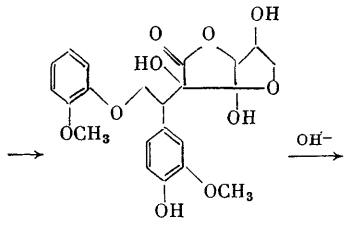
(XXXVIII)

Yet another interesting aspect of reactions of this type is associated with the delignification of wood. It has been found that reducing sugars and their derivatives are capable of cleaving β-aryl ether linkages in phenolic model compounds of lignin under the conditions of alkaline pulping.[110–112] The stability of the methylated models supports the view that this reaction proceeds via a QM intermediate, while the high reactivity of ascorbic acid and at the same time the inactivity of non-reducing sugars are evidence for the involvement of the enediol form of the cleaving agent. Indeed, under neutral conditions, the reaction of the QM (XXIII) with ascorbic acid afforded the adduct (XXXIX), which on heating in

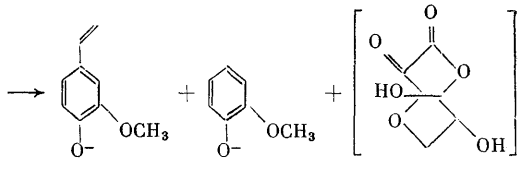
aqueous alkali gave rise to the products of the cleavage of the β-aryl ether—guaiacol and vinylguaiacol:[110]



(XXIII)

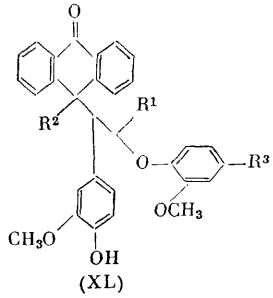


(XXXIX)



It is easy to note the close analogy between the mechanism of this reaction and the heterolytic mechanism of the action of anthrahydroquinone.[9] The difference between the structures of the adducts (XXXVIII) and (XXXIX) is noteworthy: the $C^{\alpha}(QM)-O-C$ linkage is formed in the former case and the $C^{\alpha}(QM)-C$ linkage is formed in the latter. The NMR spectra published in the literature[108,110] give rise to no doubts about the assignment of the structures, but we believe that the interpretation from a single standpoint of the mechanism of the interaction of QM with carbohydrates and related compounds requires further accumulation of experimental data. At any rate, it can now be postulated that, together with ether and ester linkages between components of the lignocarbohydrate complex (LCC), there are also carbon–carbon bonds which are readily hydrolysable in alkaline solutions.

In recent years studies on nucleophilic addition to QM received a fresh stimulus in connection with the investigation of the mechanism of the anthraquinone pulping of wood. In connection with this problem, the range of nucleophiles has expanded, which led to new fundamentally important results. The adducts (XL) of anthrahydroquinone and related compounds with model lignin QM[9,113–124] and lignin itself (under the conditions of the formation of QM *in situ* [113,125]) were obtained under mild conditions.



(XL)

$R^1 = H, CH_3, CH_2OH$; $R^2 = H, OH, CH_3\ C_6H_5$; $R^3 = H$, lignin.

Such compounds (R^2 = OH) readily undergo the Grob heterolytic fragmentation in aqueous alkali, which results in the cleavage of the β-aryl ether bond and the regeneration of anthraquinone.[9] The high regio- and stereo-selectivities of the addition are striking: in the case of model compounds, a single adduct is formed as the *threo*-isomer (R^2 = H, OH),[114,118] while for lignin the formation of the *threo*-isomer is preferred.[113] Sterically hindered derivatives of anthrone give rise to a mixture of the *threo*- and *erythro*-adducts (XL, $R^2 = CH_3, C_6H_5$), under the conditions of kinetic control the *threo*-isomer being formed preferentially; an increase in the reaction time in an aqueous alkaline solution leads to an increase in the fraction of the *erythro*-isomer, which, however, rarely reaches one half.[119,122] Such behaviour indicates the reversibility of the addition and the ease of the dissociation of the adducts in aqueous alkali. This is also indicated by other data.[126,127]

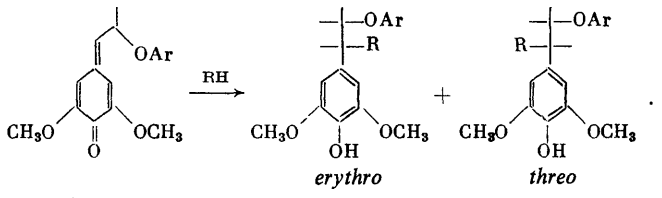
α-Aryl ethers are known to be readily converted into QM in aqueous alkali even at room temperature.[128] Therefore the introduction of dehydrodiisoeugenol and related compounds into the reaction with anthrone and anthrahydroquinone under these conditions leads to the formation of the corresponding adducts, but in the given instance with a distinct preference for the *erythro*-isomer.[115] We may note incidentally that in the case of β-aryl models containing the hydroxymethyl group the splitting off of formaldehyde is so fast that the formation of the corresponding product (stilbene) predominates over the formation of the adduct.[115]

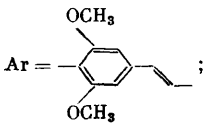
Other nucleophiles, such as amines[23] and water (in dioxane),[129] afford *threo*-adducts preferentially. Such stereoselectivity is actually the property of the QM themselves: in an acid medium, where the reaction probably proceeds via a carbonium ion, selectivity falls sharply.[23,114,129] The regioselectivity of the addition to QM can be logically accounted for within the framework of ideas about orbital control (see above) but as regards stereoselectivity the situation is more complex. In principle, in this case one might begin with modern ideas about the hindrance of reaction centres[130] and the conformational composition of the QM attributed to them by Ralph and Adams.[24] The trouble is that the ideas of Ralph and Adams (see also Chum et al.[50]) are most probably erroneous (see above). The stereochemistry of the formation of the adducts therefore still awaits its elucidation. It has been shown that the action of *erythro*-phenol-alcohols with bromotrimethylsilane[23] gives rise exclusively to the *threo*-bromo-derivative, which is converted into a 1 : 1 mixture of *erythro*- and *threo*-derivatives in 0.5 h.[102] On this basis, the author[102] put forward the hypothesis that S_N2 substitution takes place in this case. It is much more likely that the reaction proceeds via a carbonium ion.[248] The related reaction of acetyl halides with *p*-hydroxybenzyl alcohols, affording *p*-acetoxy-α-halo-derivatives in a quantitative yield under mild conditions, is known.[131] We may note that the latter derivatives are convenient synthons for the generation of QM *in situ* in an alkaline medium.[123,124,132]

General rules which would make it possible to predict the stereochemistry of the product of the addition to QM do not exist. Nevertheless, this question is important if only because of its relation with the stereoisomeric composition of the lignin chains, since the lignification process proceeds with participation of QM as intermediates. It is therefore significant that, according to Nakatusbo and Sato[21] and Dyall and Winstein,[29] the addition of water to the QM (VII) gives rise to the ratio *threo*:*erythro* = 7 : 3 in dixoane and 1 : 1 on catalysis by HCl. At the same time, carboxylic acids afford predominantly the *erythro*-diastereoisomers in their reactions with QM.[21,26,129] Kinetic data[99] make it possible to postulate a trimolecular reaction in the latter case and to relate the

anomalous stereoselectivity to the specific formation of intermolecular hydrogen bonds in a pre-reaction complex;[23,133] incidentally, such explanations have not been supported by serious evidence. The involvement of hydrogen bonds in the transition state has been discussed also in an attempt to account for the preferential formation of the *threo*-isomer in the reaction of QM with water.[21]

We may draw attention to the fact that the conclusion that one of the stereoisomers is slightly preferred is frequently reached by comparing their final yields (see, for example, Zanarotti[26]). Naturally, such results are unreliable: the correct procedure involves the analysis of spectroscopic data for the reaction mixtures. In this connection, it is not clear whether a slightly greater amount of the *erythro*-isomer is really formed in the addition of water in the presence of HCl to the β-aryl ether QM in the case of the syringyl derivatives while for guaiacyl QM the isomers are present in equal proportions.[26] The conclusion that the *erythro*-adducts of a whole series of nucleophiles are preferred under the conditions of acid and base catalysis[26] appears reliable, since the preference is fairly distinct:

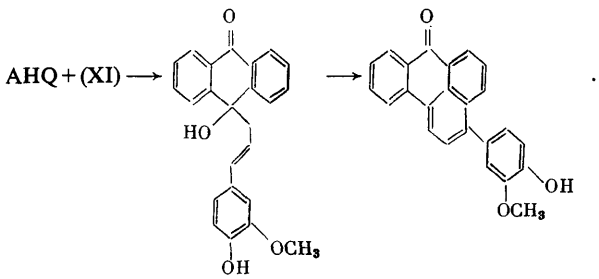




R=OCH_3, CH_3COO, C_6H_5O, $(CH_3CO_2)_2CH$, 2,4,6-$(CH_3O)_3C_6H_2$.

It may be that the discrepancy between data for the stereoisomeric composition of the products of the nucleophilic addition to QM depends on whether thermodynamic or kinetic control operates in the course of the reaction (this depends on the reactants and to a greater extent on the conditions).

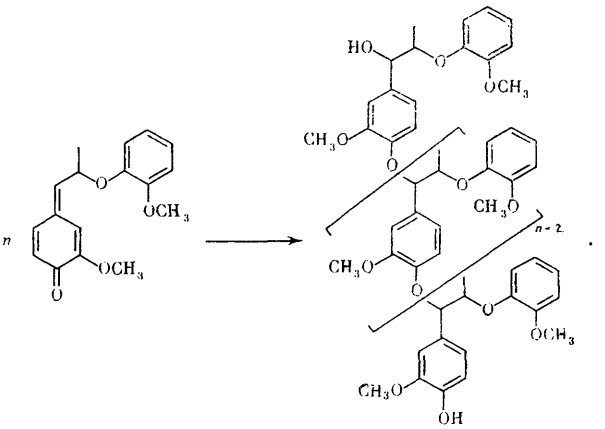
The addition of anthrone and anthrahydroquinone to QM vinylogues takes place with formation of the C(10)–C$^{\gamma}$(QM) bond;[116,125] under pulping conditions, such products are irreversibly converted into condensed systems:[9]



We may note further that in the reaction of anthrahydroquinone with QM there is a possibility of the formation also of a small amount of the product of hydroxyalkaltion in the β-position in the aromatic ring; such substances have been found also in the anthraquinone pulping liquors.[9,123]

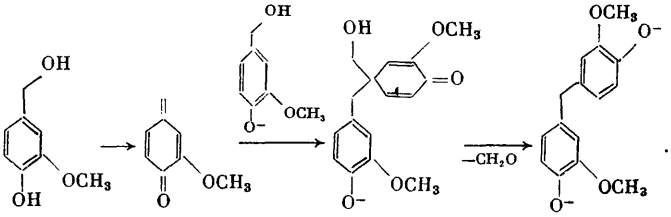
It has been recently shown in relation to the addition of primary amines that the reactivities of (*E*)- and (*Z*)-QM are different: for the (*Z*)-isomer, the addition is 1.4 times faster.[59] This observation throws new light on the significance of the studies on the stereochemistry of QM described above.

It is well known that a convenient method of modelling lignin as a polymer involves the use of a dehydropolymer, in the formation of which QM intermediates apparently play a role (see below). A different type of a model regular polymer can be obtained directly from QM by polymerisation initiated by a base or electrochemically:[50,102]



In terms of its mechanism, such polymerisation also represents nucleophilic addition. In the presence of alkali metal cations, the addition reaction is controlled kinetically and the *threo*-isomer is formed preferentially; in the presence of bulky tetraalkylammonium cations, thermodynamic control operates and preferential formation of the more stable *erthro*-product is observed (the possible explanation of this reaction is provided by the difference between the degrees of chelation of the cations).[50] A polymer, in all probability with a different structure, is formed on oxidation of guaiacylacetone derived from the corresponding QM.[17]

Under the conditions of alkaline pulping, *p*-hydroxybenzyl alcohols, which are capable of forming QM, readily undergo self-condensation with formation of oligomeric products.[104,126,134] This process, which simulates one of the possible pathways leading to the cross-linking of lignin, apparently also takes place as nucleophilic addition to QM *in situ*, for example:



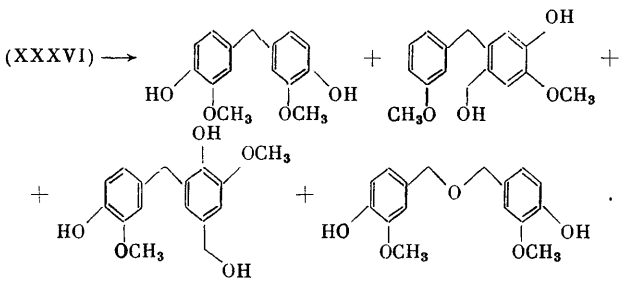
(XXXVI)

Similar reactions may be observed also in the generation of QM in another way, for example from sulphones.[135]

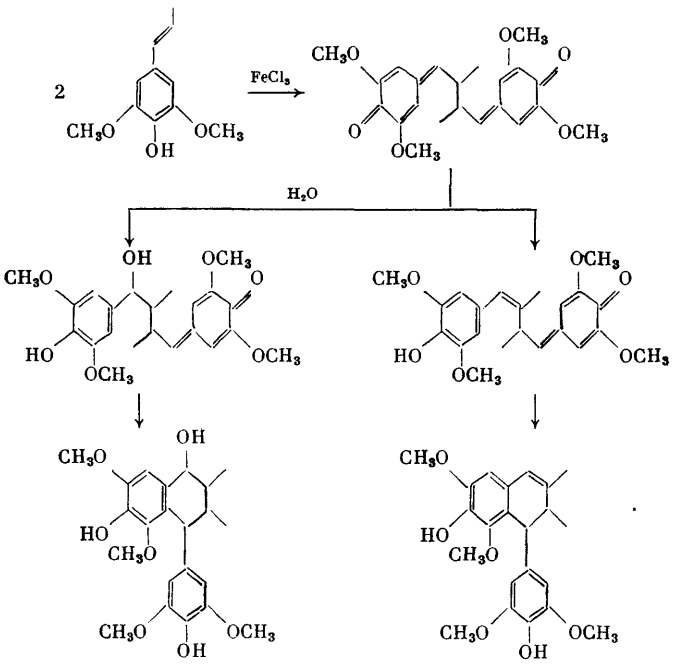
In the presence of anthrahydroquinone, this reaction is suppressed[136] and the formation of bibenzyl derivatives is observed—these may be the products of the "head to head" dimerisation of the radical-anions formed from the QM.[126]

We may draw attention to the fact that processes similar to alkaline oligomerisation take place also in neutral aqueous or

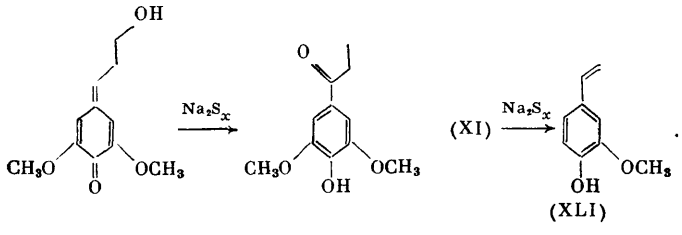
aqueous alcoholic media[104] as well as in the solid phase on silica gel[137] (simulation of the heterogeneous medium in plants), constituting therefore one of the possible lignification pathways:



An interesting example of intramolecular cross-linking has been described[34] (the reaction mechanism has not been reliably demonstrated by the hypotheses put forward are well founded):

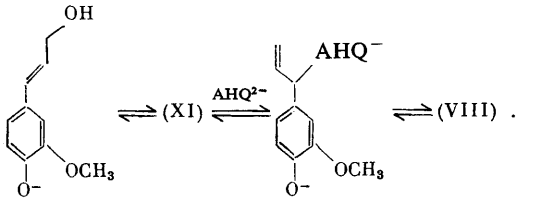


Depending on the nucleophile, the addition may be the first stage of a more complex process. Whereas sodium sulphide affords the corresponding thiol in the reaction with QM, the reaction of QM with sodium polysulphide in aqueous solution affords oxidation products even at room temperature; in the latter case the additon is merely the first undetected stage:[138]

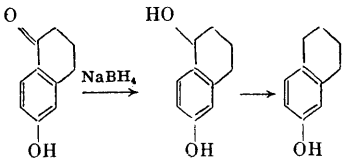


Dimethyl sulphoxide reacts similarly with QM.[132]

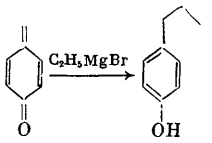
The QM reduction reactions have also been frequently discussed. On the basis of the dynamics of the accumulation of coniferyl alcohol (XIV) and isoeugenol (VIII) during anthraquinone pulping, it has been suggested that compound (VIII) is actually obtained in the pulping process from compound (XIV) by direct reduction of the latter to a QM:[139]



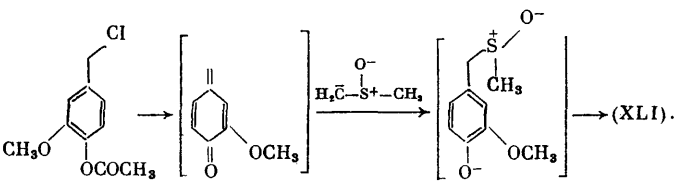
The increase of the fraction of isoeugenol among the coniferyl alcohol reaction products in aqueous alkali after the addition of anthrahydroquinone agrees in principle with this hypothesis.[140,141] However, the interaction of vanillyl alcohol (XXXVI) and apocynol (XLII) with anthrahydroquinone on heating in aqueous alkali leads not to the reduction of the corresponding QM [142] but to the formation, as shown in the first example, of adducts.[136] Apparently the hydride transfer reactions are nevertheless not characteristic of anthrahydroquinone. Reagents such as lithium tetrahydroaluminate and sodium tetrahydroborate can naturally reduce the QM directly.[26,27,29] This apparently constitutes the mechanism of the familiar reaction of alkyl hydroxyphenyl ketones with sodium tetrahydroborate:[142,143]



The use of organometallic compounds as nucleophiles makes it possible to obtain alkylphenols with a lengthened chain via QM:[43]

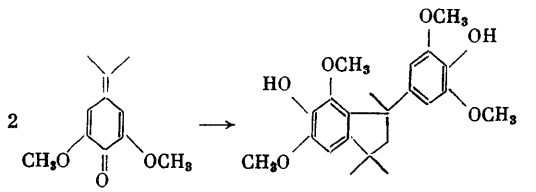


An increase in the length of the chain can be achieved also by the nucleophilic addition of the dimsyl anion (generated from dimethyl sulphoxide and sodium hydride) to QM:[132]

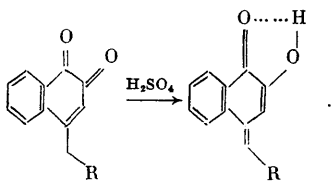


We may note that the difficulty of experiments with unstable compounds such as QM sometimes gives rise to doubts about the reliability of the results. This applies to many reports of the formation of "head to head" QM dimerisation products, for example that of Leray and Thomas.[144] The mechanism of the QM dimerisation reactions, similar to the reaction on treatment with

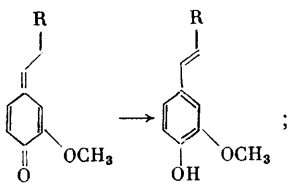
triethylammonium acetate presented below, is frequently osbscure and hardly represents the direct coupling of two QM molecules:[145]



Tautomeric transformations constitute a special type of reactions of QM. We mentioned above that the phenol–quinonoid tautomerism is usually manifested only in the case of sterically hindered compounds; for typical model compounds of lignin, aromatisation is the driving force of the rearrangement and the QM are usually transformed irreversibly into related phenols but not conversely. Condensed systems are an exception. Thus on treatment with a catalyst, 4-benzyl- and 4-alkyl-1,2-naphthoquinones are converted into QM:[146]

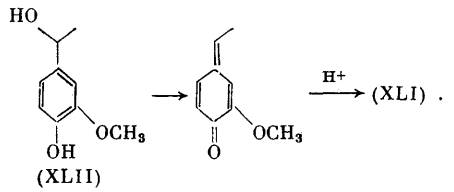


A typical rearrangement of QM is their irreversible stereoselective conversion into (*E*)-α-alkenylphenols, for example:[100,147]

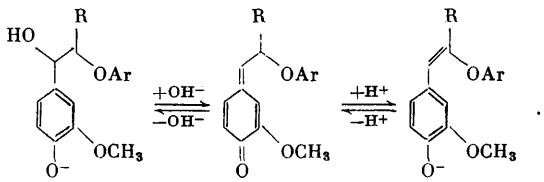


R = H, CH_3, C_6H_5, CH_2Br.

This reaction was observed previously only under the conditions of acid–base catalysis (the involvement of water was postulated at the neutral pH).[145,148,149] Thus, whereas primary and secondary amines add readily, like ammonia, to QM, treatment with tertiary amines actually leads to isomerisation.[148] Incidently, it has been found that this isomerisation also proceeds in a neutral solvent at a rate comparable to the rates of addition of alcohols and phenols (in equimolar amounts).[100,147] It is of interest to note that conversion into alkenylphenols is in essence the only pathway to the degradation of the simplest model lignin QM in the absence of other reagents.[147] Such a reaction provides a method of synthesis of stereoisomerically pure alkenylphenols, which can be in their turn quantitatively converted into the initial QM (see above). QM can isomerise also under pupling conditions. According to kinetic data, *p*-hydroxybenzyl alcohols with β-aryl ether substituents are in fact converted in this way into enol ethers.[150,151] An example of the simplest model experiment is provided by the heating of an equimolar mixture of apocynol (XLII) with anthrahydroquinone-monosulphonate in aqueous 1 M NaOH (137 °C, 1 h).[142] The expected products ethylguaiacyl (the QM reduction product) and vinylguaiacyl (XLI) (the QM isomerisation product) were isolated:



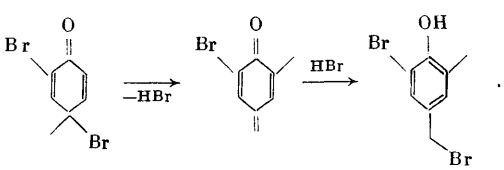
The authors[142,152] postulate the following equilibrium under pulping conditions:



This is supported by the similarity of the cleavage products in the anthraquinone pulping of phenol-alcohols and the corresponding enol ethers and also the (*E,Z*)-isomerisation of the latter under these conditions.

It is of interest to note that the conversion of many model compounds of lignin into isoeugenol (VIII) via a QM intermediate is achieved with formation of precisely the (*E*)-isomer;[138] the cleavage of the β-aryl ether linkage with participation of anthrahydroquinone[122] or anthrone[120] also belongs to reactions of this class. The factors which determine the stereochemistry of the product have no bearing on the stereochemistry of the intermediate adduct despite the views of the author.[122]

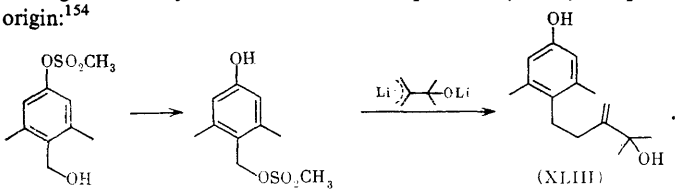
QM are capable of acting as isomerisation intermediates but this time of a completely different kind[153] (cf. Brunow and Sumelius[32]):



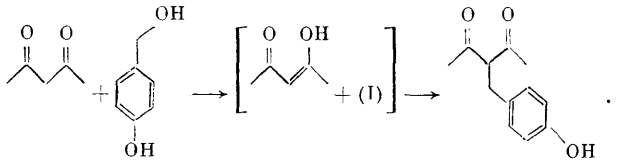
In recent years, there has been a growth of interest in organic chemistry in QM as promising synthons.[5,26,27,132,154–158] We should like to draw attention to studies unrelated to the chemistry of wood; the use of their results may lead to the discovery of new procedures for the specific transformation of lignin.

The high electron affinity of QM is responsible for the possibility of their copolymerisation with electron-donating monomers. Thus the 1,6-addition of styrene to α,α-dicyanoquinone methide takes place readily with formation of a linear regular copolymer.[74] The characteristic addition reactions make it possible to use QM in the synthesis of lignans and neolignans[26,27,159–161] and numerous compounds with *p*-hydroxybenzyl groups. It is most convenient to use QM *in situ*, whereupon *p*-hydroxybenzyl alcohols or, what is much more convenient, their derivatives, which are capable of readily affording QM under the reaction conditions, enter into the reaction directly. Such derivative may be esters,[27,162] halides,[23,123,126,132,163] methanesulphonates,[154] benzenesulphonates,[164] aminophenols,[163,165] etc.[52,166]

As an exotic example, we may quote the following reaction leading to the synthesis of a natural product (XLIII) of plant origin:[154]

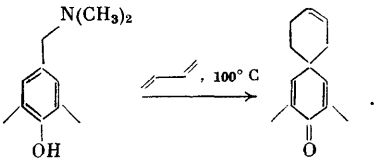


The possibility of the formation of a QM as an intermediate has been used also in the development of a method for the removal of a protecting group in the series of benzyl ethers.[131] *p*-Hydroxybenzylation of the readily enolisable 1,3-diketones takes place on heating in water (it is striking that benzyl alcohol, which is incapable of being converted into a QM, does not enter into this reaction):[155]



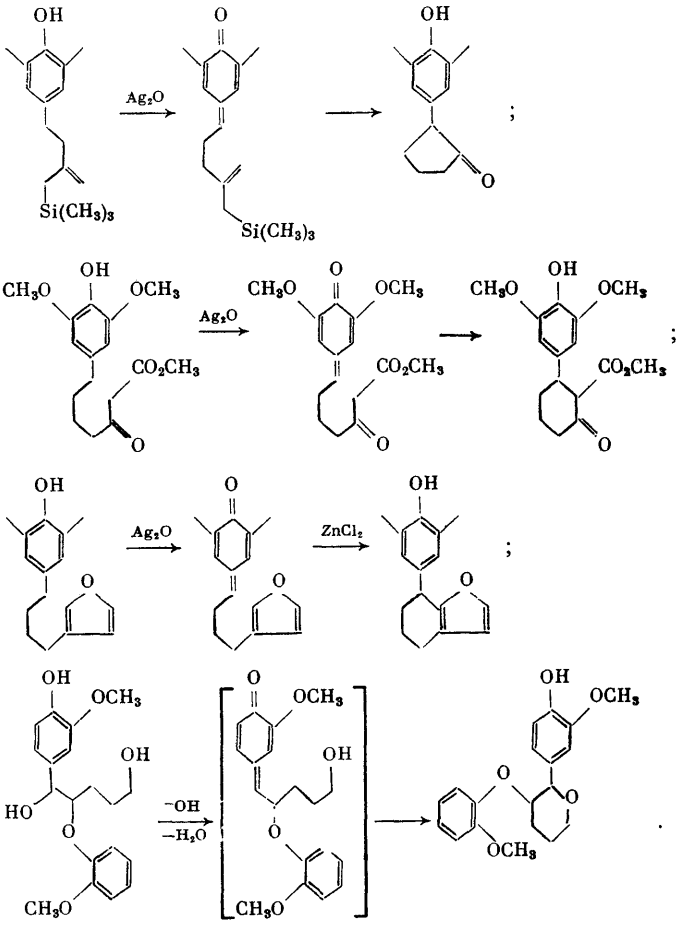
In the case of QM vinylogues, similar reactions with acetylacetone and nitroethane afford mixtures of regioisomers.[27] There is a reaction, involving intramolecular addition to the C^{α} atom, which leads to various carbocycles and heterocycles[111,167,168] (examples are given in Scheme 1).

QM can also enter into cycloaddition reactions as dienophiles and dienes. Attention should be drawn to the fact that the Diels–Alder reaction makes it possible to use specific trapping agents for QM and gives rise to prospects of obtaining unusual lignin derivatives. The following reaction may serve as an example of the use of butadiene as a trapping agent for *p*-QM formed *in situ*:[165]

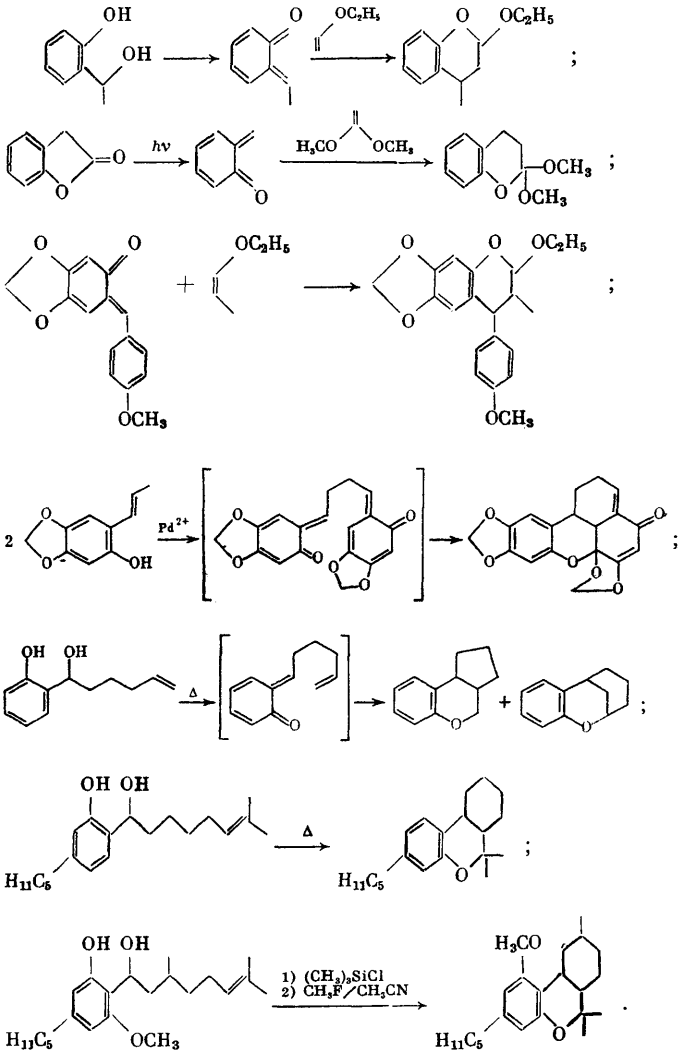


Addition to the exocyclic double bond of the QM takes place according to the idea of the orbital control of the reaction. Examples of reactions with participation of *o*-QM, also preferentially *in situ*,[30,52,166,169–175] are given in Scheme 2.

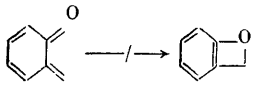
Scheme 1



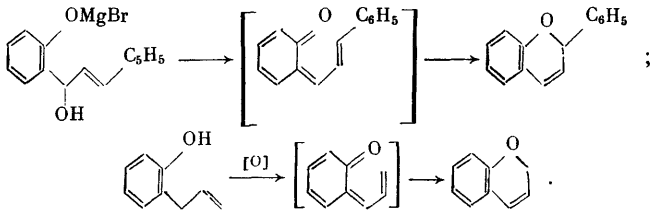
Scheme 2



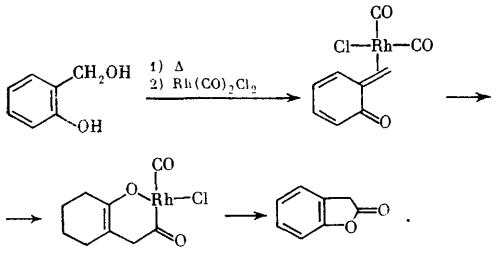
These examples refer to intramolecular cycloaddition. We may note that direct cyclisation with formation of oxetans is not characteristic of *o*-QM, in contrast to, for example, *o*-quinodimethanes:[56]



On the other hand, examples of the formation of a six-membered ring are known:[30,176]



An intermolecular cycloaddition reaction, leading to trimers, has also been noted for the simplest *o*-QM.[44,45,173,175,177] An interesting example of a reaction of QM, proceeding via an organometallic complex, which was not isolated, has been described:[178]



The properties of *o*-QM as dienes are such that the [4 + 2]-cycloaddition reaction with dienophiles having an enhanced electron density at the multiple bond, such as keten acetals and vinyl ethers, is preferred; the reactions with alkenes having weak electron-donating let alone electron-accepting substituents, do not take place quite so readily.[172]

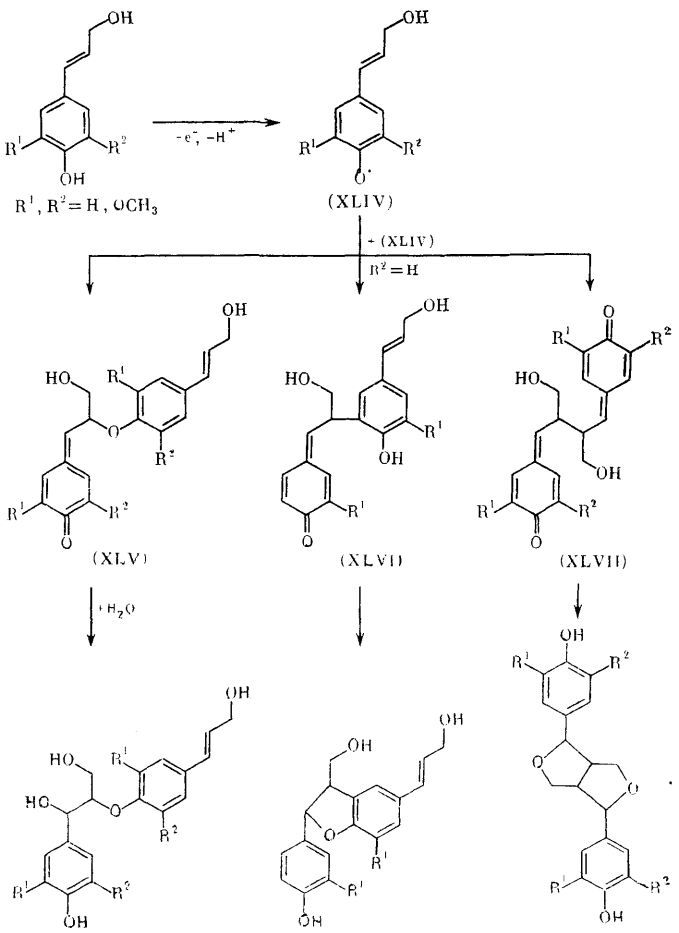
V. Quinone methides and the structure of lignin

The biosynthesis of lignin is traditionally represented as a dehydrogenation polymerisation process, during which QM, playing the role of intermediates, are formed. These views arose as a result of a considerable number of early studies and have been reflected in familiar monographs.[2,3,179] In the 1950's–1960's, it was sometimes reported that the formation of QM had been detected directly in processes modelling lignification;[1] these reports appear doubtful nowadays. The idea that QM intermediates participate in lignification processes is based mainly on the analysis of oligomeric products of model experiments on the oxidative polymerisation of compounds considered as lignin precursors.

According to Freudenberg and Neish,[179] lignin is formed via the stage involving the dehydrogenation of low-molecular-weight precursors with formation of the corresponding radicals whose dimerisation actually constitutes the first stage of the polymerisation. The rules governing the recombination of aryloxyl radicals are well known. This process leads to the formation of QM dimers, whose structure is determined by the selectivity of the dimerisation reaction. *p*-Hydroxyphenylallyl alcohols have been considered as the main lignin precursors. This agrees well not only with the available information about the structure of native lignin but also with the latest data on the ionisation potentials of the possible precursors:[180] indeed, phenols with an α-unsaturated side chain should in fact exhibit the highest reactivity in oxidation in neutral and weakly acid media; this preference is very pronounced. The regioselectivity of the dimerisation is consistent with the familiar distribution of spin density in the radicals (XLIV),[181,182] which is manifested by the formation of the dimers (VIII) and (XLV)–(XLVII) (in the form of racemic mixtures).[34,183] We should warn, incidentally, against attempts to relate directly the spin density to the fraction of particular structures in the polymer. The latter is to a large extent determined by steric factors and the relative stabilities of the products.[181]

The QM (XLV)–(XLVII) are converted into phenolic dilignols as a result of a nucleophilic addition reaction (the reaction with water affords β-aryl ether structures; an intramolecular reaction gives rise to cyclic systems). Examples of the possible processes are given in Scheme 3.[1,184,185]

Scheme 3



Subsequent growth of the macromolecule involves the oxidation of the dilignols to the corresponding radicals and the reactions of the latter with one another and with other radicals. This can also result in the formation of QM.[183] According to Forss and Fremer,[184] the

macromolecule is formed from the dilignols via the following stages (only the stages with participation of QM are listed):

dehydrogenation of oligolignols, which subsequently react with one another and with monolignols, affording biaryl derivatives, diaryl ethers, and QM;

the addition of phenols to QM, in which oligomeric lignols participate without losing a hydrogen atom;

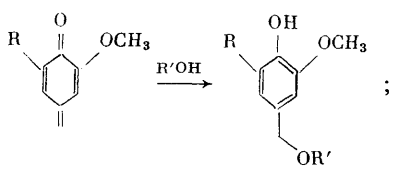
addition of carbohydrates to QM, which results in the formation of lignocarbohydrate linkages;

polymerisation of QM leading to linear aryl benzyl ethers.

Two mutually complementing models of lignification exist—bulk and endwise models; the true process can be only of a mixed kind.[184]

We emphasise that the existing ideas about lignification should be regarded merely as a hypothesis but a hypothesis which is fairly logical and which works well. Within its framework, QM play an unusually great role as intermediates. Thus about 70% of the interunit bonds in conifer lignin are formed as a result of β-coupling[185] and any radical reaction involving the β-position yields an intermediate QM which is subsequently converted into a more stable system. Among the characteristics of the reactions of QM, nucleophilic addition to the C^{α} atom is the most important reaction (if not the only one) for lignification.[1] Plant tissues contain simultaneously a multiplicity of compounds capable of acting as nucleophiles (water, carbohydrates, uronic acids, and alcoholic and phenolic groups of the lignin being formed). Nucleophilic addition ensures the formation of typical lignin structures: *p*-hydroxybenzyl alcohols, ethers, and esters. Therefore studies on the kinetics and mechanisms of the above reaction are of primary importance for the understanding of the structure of wood: thus whatever nucleophile adds preferentially to the QM, it determines the frequency of various types of benzyl structures in the final polymer.

The situation as regards the relative nucleophilicities of the solution components in the wood cell is fairly complex. We have already mentioned the mixed order of the addition reaction, indicating its complex mechanism. The dependence of the rate of reaction on the pK_a of the hydroxy-compound[179] seemingly shows that the addition of acids should proceed more readily and hence that one should expect a higher content of ester linkages in the lignocarbohydrate complex compared with ether linkages.[2] At the same time, it has been noted[186] that without a catalyst coumaric and ferulic acids react fairly slowly with QM (in the presence of tetrabutylammonium hydroxide, esters are formed instantaneously and quantitatively). The experiments on the competitive addition of nucleophiles such as ethanol, water, and acetic acid[98] showed that the reaction of a model QM with their isoequimolar mixture afford predominantly benzyl ethyl ether:

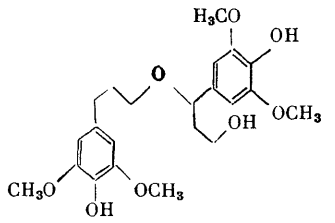


;

R = $C(CH_3)_3$, R′ = H, C_2H_5, CH_3CO.

At a higher pH (4–6), the concentration of the more nucleophilic CH_3COO^- ion increases and benzyl acetate becomes the main product, although benzyl ethyl ether is formed in appreciable amounts. In an alkaline medium, the presence of the strong nucleophiles HO^- and $C_2H_5O^-$ again leads to a low yield of the ester. One may conclude that in the neutral or weakly acid medium, characteristic of plant tissues, ester type lignocarbohydrate linkages are formed most readily, although a considerable proportion of ether linkages should be present together with the latter. It is significant that, by virtue of its weaker nucleophilic properties, water does not interfere with the formation of the lignocarbohydrate complex. However, an excess of water in the presence of a deficiency of other nucleophiles makes the formation of linear chains with α-alcoholic groups the main reaction pathway of primary QM; we may note that similar structures arise also in the hydrolysis of benzyl ether linkages, which takes place readily.[179]

The nucleophilic addition of lignin fragments to QM with participation of alcoholic, phenolic, and carboxylic acid groups of the former should be regarded as one of the important routes to the formation of lignin.[1,101,183] Unfortunately, the instability of the $C^{\alpha}-O-C^{\gamma}$ and $C^{\alpha}-O-C(4)$ bonds formed gives rise to serious difficulties in securing evidence for their presence in the native polymer; early studies devoted to the formation of such bonds require additional tests. However, the isolation of the dimer (XLVIII) from the products of the hydrogenolysis of lignin[1] appears to constitute convincing evidence for this; the presence of bonds of this kind agrees also with the familiar results of computer simulation of the biosynthesis lignin.[187]

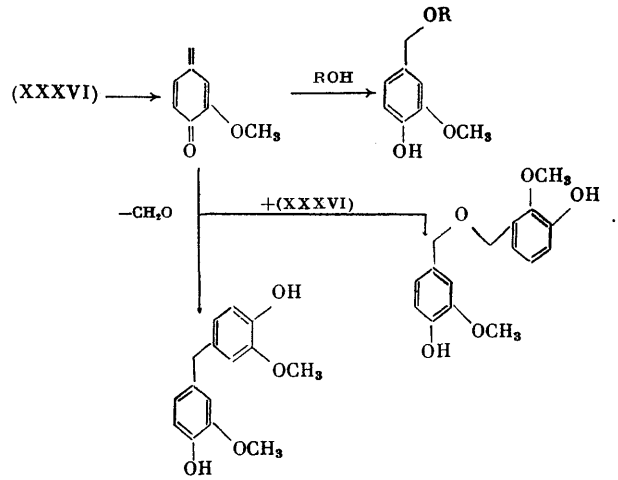


(XLVIII)

Model QM combine with glucuronic acid[107] and glucose[107,183] (see above). This reaction proceeds also in the presence of water. Such processes can be regarded as simulation of the formation of the lignocarbohydrate complex. However, bearing in mind the competition by water and other nucleophiles, the formation of an appreciable amount of the lignocarbohydrate linkages in this way requires a fairly high concentration of carbohydrates near the QM at the instant of their formation or the fixation of the quinone methide structure in the vicinity of the carbohydrates of the cell wall. The latter is fairly probable since it is believed that the dehydrogenation polymerisation of monolignols takes place in the outer cell membrane in the vicinity of the carbohydrates of the cell wall, which contains in addition a relatively small amount of free water.[183]

The view that the reactions of QM during lignification are irreversible and that the structure of native lignin is therefore directly determined by the nature of the reactions of the primary QM was widely held previously.[2,179,185] Hence follows, for example, the misunderstanding arising on comparing the frequency of the lignocarbohydrate linkages and the number of carbon fragments capable of reacting with QM. It was found later that not only under severe pulping conditions but also directly in plant tissues there is a possibility of the formation of "secondary" QM.[188,189] If this is so, then the autodegradation and secondary structure formation processes can lead in the course of time to appreciable changes in the frequency with which interunit bonds of different types are encountered (we have in mind both the ways in which the lignin subunits are joined together and the lignocarbohydrate linkages).

This possibility is supported by convincing experiments on model compounds. Thus in neutral and weakly acid aqueous media, vanillyl alcohol (XXXVI) forms α-ether linkages with aliphatic alcohols and glucose (the half-reaction time for 10% ethanol is 2.7 years).[188] The involvement of QM in this process is confirmed if only by the fact that veratryl alcohol is converted into an ether much more slowly under the same conditions. The self-condensation of vanillyl alcohol can serve as the simplest model of the secondary cross-linking of lignin. Under lignification conditions, this process also takes place[1] with the exclusive formation of dibenzyl and not aryl benzyl ether. Further self-condensation of lignin over a period of time with formation of diarylmethane structures is also possible.



Model studies together with the analysis of the composition of the lignins and dehydropolymers isolated suggests the important role of QM both in the initial stage of lignification and in the course of the wood ageing processes.[1] In the early stage, the competition by the nucleophile for the "primary" QM determines the ratio of the structural units with a free and etherified α-hydroxyls. It has been suggested that, owing to the presence of a large amount of water during lignification, the "primary" lignin contains many benzyl alcohol groups and resembles Feudenberg's dehydropolymers.[1] After a time, re-etherification and the formation of stable *p*-hydroxybenzyl ether structures (the lignocarbohydrate linkages and the $C^{\alpha}-O-C^{\gamma}$ linkage) take place. Such development of the lignification process agrees with the model[187] proposed as a result of computer simulation using data for the compositions of the lignins isolated.

The question of the relation between the colour of lignins and the presence of quinone methide structures in them is interesting and hitherto has been little elucidated. Its practical importance is evident, since a correct answer to it may lead to novel procedures for combating the yellowing of cellulose.

It is believed that, together with qinonoid structures, stilbenequinones, conjugated bis-*p*-quinone methides, and hydroxyaryl-substituted QM are included among the chromophoric systems of the residual lignin.[190−192] It must be emphasised that these are only hypotheses based on the results of model experiments and not on the analysis of the lignins themselves after chemical processing of wood (the assignment of the structures in the latter case is not unambiguous). The formation of stable QM structures in the self-condensation and subsequent oxidation in air of a number of model compounds of lignins has been postulated[193−195] on the basis of the spectroscopic characteristics of the products. Even these data, obtained on simple models, do not appear to be reliable. On the other hand, the presence of such systems both in the bulk of cellulose and in treated liquors is fairly likely. The conjugated and shielded QM are stable and are usually brightly coloured — both as a result of conjugation and as a consequence of the possibility of intramolecular charge transfer in systems of this kind.[63,68,196] The latter effect should be manifested particularly strikingly in the presence of alkali when the electron-donating phenolic groups are ionised.

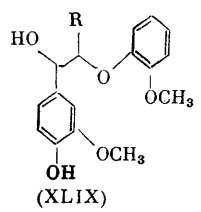
VI. Quinone methides as intermediates in the delignification of wood

Although it has not so far been possible to detect the presence of quinone methide structures under the conditions of the pulping of wood, nevertheless this does not by itself justify a sceptical attitude to the proposed mechanisms of the pulping reactions with participation of QM. In principle, such a situation arises for the majority of intermediates: if they are indeed highly reactive, then their stationary concentration is low; the study of intermediates always requires special methods and conditions different from those which obtain when the relevant reactions are carried out.

It is remarkable that QM give rise to identical problems in the chemistry of wood and in bioorganic chemistry. Thus hypotheses that many biological processes take place with participation of these intermediates and that one is dealing with compounds very similar to model QM of lignin have long been put forward.[17,197−204] It has been suggested that the formation of QM can explain the reactivity of many flavonoids.[205]

The conclusion that many key pulping reactions take place via QM is based on numerous experiments performed on model compounds. As early as the beginning of the 1960's, the results of kinetic studies on the hydrosulphide and hydrosulphite treatment of vanillyl alcohol (XXXVI) suggested that these processes proceed via a QM intermediate whose formation is the rate-limiting stage; this has received additional confirmation from the marked retardation of the reaction in alkaline and neutral media on alkylation of the phenolic hydroxyl.[206,207] It was also established that the formation of QM determines the rate of degradation of the benzyl ether linkages[208] (the blocking of the phenolic hydroxyl stabilises such linkages, in particular the lignocarbohydrate linkages[106]).

Subsequently these views were confirmed by kinetic experiments on more complex models[111,209−212] and it is at present regarded as established for example, that the stage determining the rate of the alkaline degradation of β-aryl ethers (XLIX) is the formation of QM. The situation is similar also as regards the corresponding syringyl analogues but with the difference that the presence of two electron-donating methoxy-groups (incidentally such groups stabilise the QM) promotes a faster elimination of the α-hydroxy-group.[212]



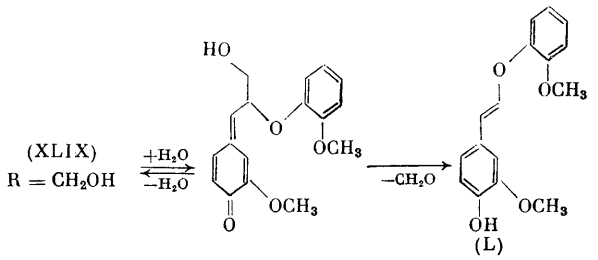
(XLIX)

R = H, CH_3, CH_2OH.

In experiments on model compounds, it was shown that the conversion of the initial *p*-hydroxybenzyl alcohol into a QM is the rate-limiting stage both in the cleavage of β-aryl ethers under the conditions of sulphate pulping and in condensation processes.[210,213] This is why the given reaction is of first order with respect to the initial alcohol and its rate is independent of the concentration of the OH^- and SH^- ions (at pH ⩾ 12 when the phenolic groups are fully ionised and at a SH^- concentration sufficient to capture all the QM intermediates). These data are part of the experimental evidence for the quinone methide mechanism of the cleavage of β-aryl ether linkages. An additional confirmation of this mechanism comes from the fact that β-aryl ethers without a free phenolic hydroxyl are cleaved more slowly.[214–216] However, the mechanism of degradation in the case of models containing two syringyl nuclei has not been ultimately elucidated and is apparently more complex than in the case of the guaiacyl–guaiacyl and syringyl–guaiacyl models; it is sufficient to say that the transition from the β-guaiacoxide to the β-syringoxide substituent accelerates the cleavage[212] (cf. Miksche[209]).

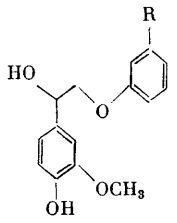
The most important experiment demonstrating the formation of QM during pulping was carried out by Miksche and co-workers.[20,213] They kept the stereoisomerically pure model (XLIX, R = CH_3) in 0.1 M aqueous NaOH at 100–120 °C for several hours. A considerble proportion of the initial compound was then recovered from the reaction without change in its chemical structure but in the form of a 1 : 1 mixture of the *threo*- and *erythro*-stereoisomers. Only the reversible formation of a planar intermediate could lead to such a result. Bearing in mind that the reaction proceeds in alkali and the formation of a carbonium ion is therefore ruled out, one can assume that under the conditions specified *p*-hydroxybenzyl alcohol give rise to QM at an appreciable rate and the latter combine in their turn with a OH^- anion to reform the initial compound; thus a stationary concentration of QM exists in the solution.[128]

These data have been confirmed in principle also in another study,[102] where the behaviour of the more representative model (XLIX, R = CH_2OH) was investgiated and 79% of the initial compound in the form of an *erthro*:*threo* = 3:1 mixture was recovered from the pure *erythro*-isomer. It was found that, under similar conditions (125 °C, 1.5 h), both in the presence of pure NaOH and in the presence of Na_2S the starting material is recovered to the extent of 50–60% having isomerised to the extent of 5–10%; the vinyl ether (L) is then formed as a reaction product in an appreciable amount (15–30%). Hence follows the following reactivity sequence: (HO^- > HS^-) ≃ retroaldol condensation (i.e. the elimination of formaldehyde).[102]



In our view, the results of these experiments (if they are confirmed) indicate something else, namely that, under the conditions of alkaline pulping, the conversion of the β-aryl ether structures of the type considered into vinyl ether structures is the main reaction pathway. However, one should refrain in this case from making assessments of the reactivity of the kind which refer in principle to chemical reaction kinetics: it is extremely likely that the process is thermodynamically controlled. A strikingly low degree of isomerisation has been quoted by Ralph:[102] it can be either a result of the virtually complete conversion of the QM formed into a vinyl ether or can be eividence of a low degree of conversion of the initial β-aryl ether into the QM. Overall, these results conflict with modern ideas and clearly require additional tests.

Whereas the hypothesis that the pulping reactions of *p*-hydroxybenzyl alcohol groups proceed via QM itself belongs to the class of generally accepted ideas, makes it possible to explain the entire set of experimental data, and is hardly criticised, the answer to the question of the rate-limiting stage in the cleavage of β-aryl ether structures is far from being unambiguous. In the study of the cleavage of the model (LI) under the conditions of alkaline pulping, a distinct dependence of the rate of the process on the substituent R was obtained.[217] This is possible only when the slow stage in the overall mechanism is the direct decomposition of the β-aryl ether linkage. On the other hand, in the formation of vinyl ethers from similar models the rate-limiting stage is in fact the formation of the QM.[217]



(LI)

The rapid and slow stages can apparently change depending on the models and the types of pulping. Thus under the conditions of sulphate and anthraquinone pulping of wood, the influence of the substituent R is no longer felt but a distinct dependence of the rate of cleavage on the substituent in the phenolic ring (QM precursor) is observed.[218] Here the slow stage is clearly the formation of the QM; the reason for the change in the rate-limiting stage is clear from Fig. 2.

Yet another question is important: how many QM precursor structures are present in native lignin and is their number sufficient for QM to play the appreciable role attributed to them? A large proportion of the phenolic hydroxyls in structures of the arylglycerol–β-aryl ether type have been converted into ether groups.[138,185] The fraction of *p*-hydroxybenzyl alcohol groups in the lignin of ground pine wood is estimated as 0.06 per methoxy-group[3] (p. 167, see also Veeramani[219]), but it is difficult to estimate the reliability of these data. However, we may note that *p*-hydroxybenzyl ethers, which can be readily converted into QM, may also serve as QM precursors[138,150] and the rupture of only a small number of weak bonds may be sufficient for the degradation of the polymer, facilitating its dissolution. Furthermore, the fraction of QM precursor structures increases during pulping as the α- and β-aryl ether linkages are cleaved and phenolic hydoxyls are thereby liberated. The new phenolic units are capable in their turn of being cleaved via the quinone methide mechanism and such cleavage of units can proceed until a subunit of a different type is encountered (lignin piling[216]). Gierer[220] noted that the delignification in the course of traditional pulping of wood proceeds exclusively via nucleophilic reactions, while in the bleaching of bulk cellulose electrophilic reactions take place initially and may then be

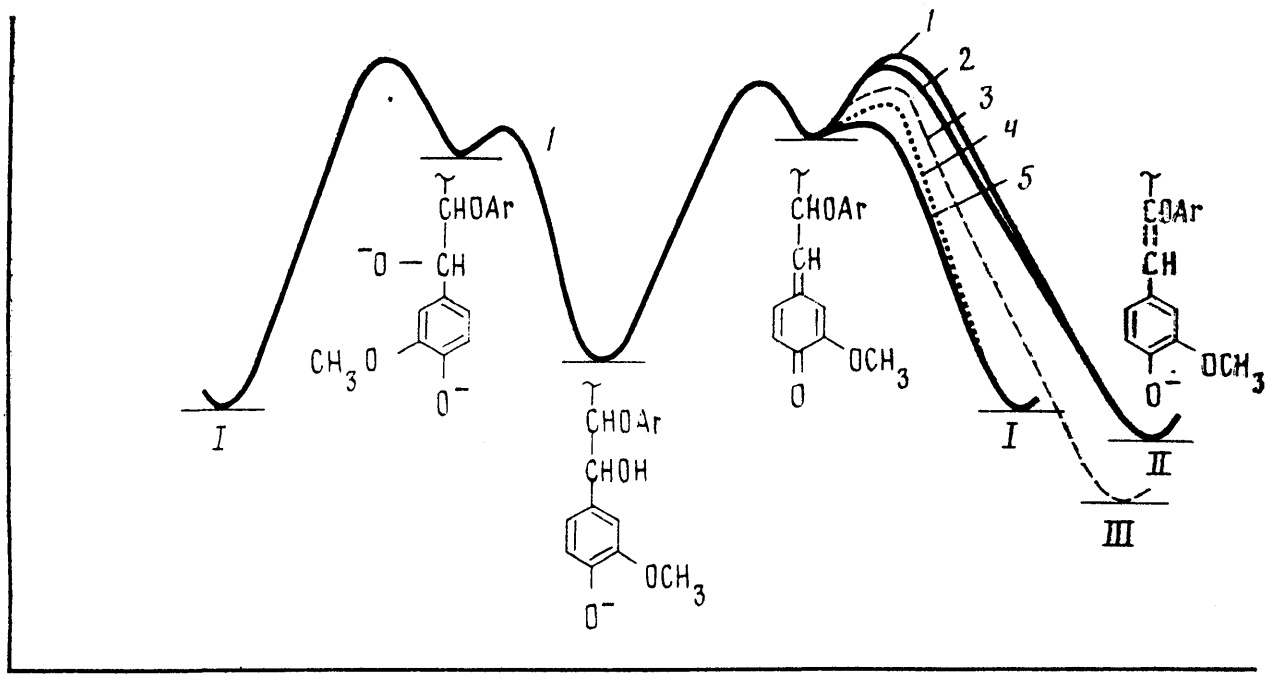
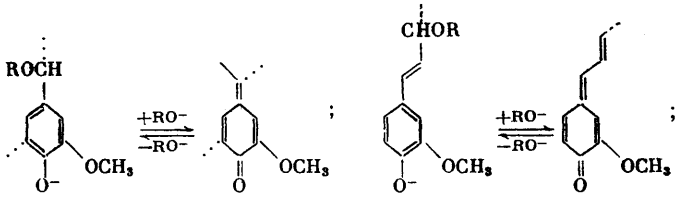


Figure 2. Proposed energy diagram for the reaction of terminal phenolic units of lignin:[218] (I) fragments (dissociation of the β-ether linkage); (II) vinyl ether; (III) condensation products; (*1*) OH^-; (*2*) terminal CH_2OH group, elimination of CH_2O; (*3*) ArO^-; (*4*) SH^-; (*5*) AHQ^{2-}.

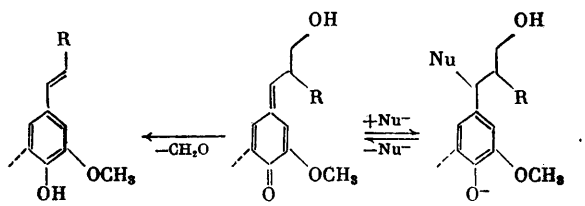
followed by nucleophilic processes. The active agent in pulping consists of nucleophiles (SO_2 and OH^-, SH^-, HSO_3^-, SO_3^{2-}, AHQ^{2-}, and AHQ^-). According to current ideas, these agents do not destructure lignin via direct substitution reactions. In the first stage, they react with electrophilic substrates, which also include QM. The latter are known to be formed via the elimination of an α-substituent or, in the case of conjugated systems, a γ-substituent. This process may proceed at any pH. A reaction of this kind at high pH is illustrated by the following scheme:



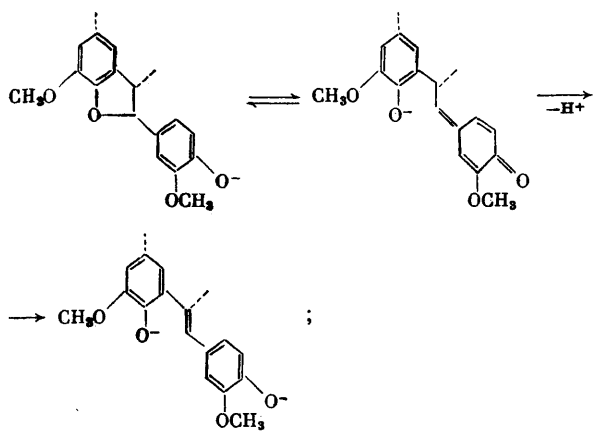
R = H, Alk, Ar.

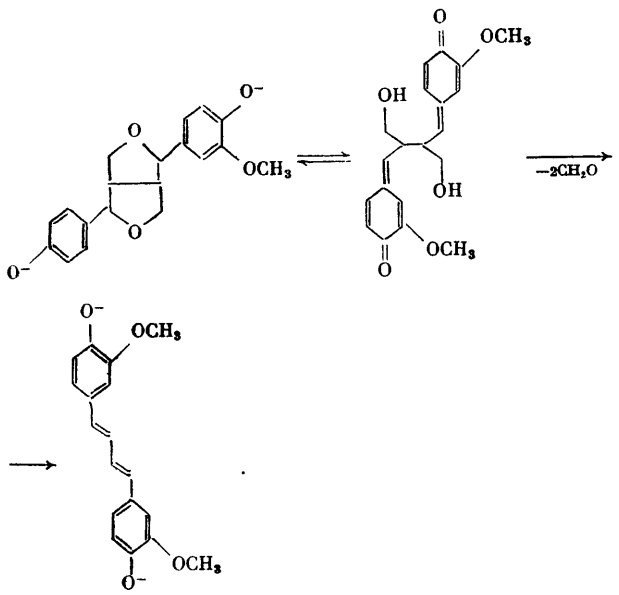
In a familiar review,[220] similar schemes refer also to the reactions of lignin in acid media; this is erroneous, since in the latter case one should refer to the formation of the corresponding α-carbonium ions.

When several nucleophiles are present in solution, they compete with one another, attacking the substrate, and the nature of the reaction of lignin in different types of pulping is determined to a large extent by the relative nucleophilicities of the components of the liquor, their concentration, and also the properties of the corresponding α-substituents as leaving groups (we recall that the formation of the QM is reversible). Another competing reaction leading to aromatisation is the elimination of formaldehyde with formation of the more stable styryl structures.[111,141,221,222]



The stilbene and diarylbutadiene structures are formed from coumaran and pinoresinol lignin fragments:

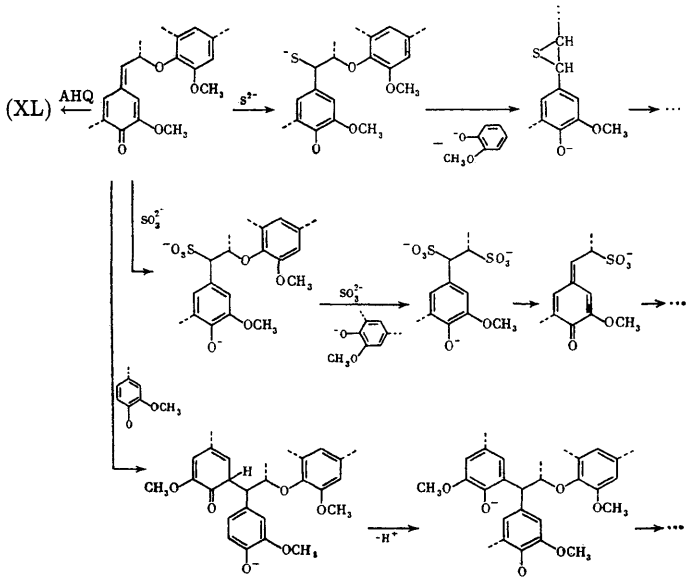




Since similar processes are inhibited on blocking the phenolic hydroxyl, one may conclude that the formation of the QM intermediate is essential for the reaction of the given type;[223,224] it is probably in fact the rate-limiting stage in the formation of vinyl ethers.[111]

According to existing ideas, the pulping reagents are strong nucleophiles which effectively capture the QM with formation of adducts, which rapidly and irreversibly decompose with the dissociation of β-aryl ether linkages. Such cleavage represents in essence a redox process. In broad outline, the mechanism of the heterolytic addition–cleavage is the same for sulphate,[140,216,225] sulphite,[226–228] and anthraquinone[9,229] pulping as well as the pulping in the presence of low-molecular-weight phenols[230,231] (Scheme 4).

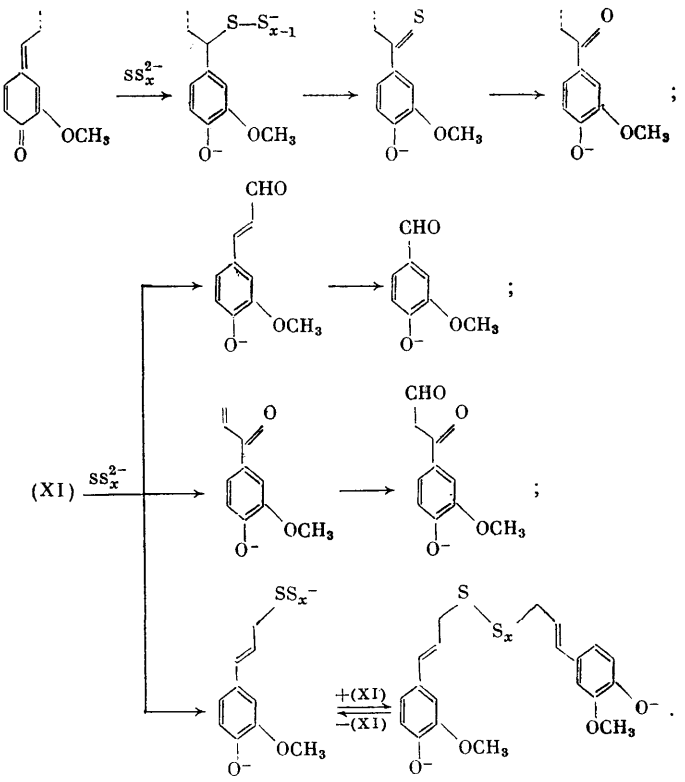
Scheme 4



We may note that similar products of the addition to *o*-QM under pulping conditions are formed also from *o*-hydroxybenzyl alcohol structures.[232] The cleavage of the β-aryl ethers via intramolecular attack on the ionised α-substituent is in principle possible both in the case of α-alcohols and α-thiols. However, the pK values for the ionisation of benzyl alcohols are much higher than for thiols. Therefore it appears that the fragmentation of the phenol-alcohol units is more effective in the sulphate pulping than in the soda pulping.[121]

Other complex processes also take place at the same time. Thus the formation of a number of products from model compounds of lignin under the conditions of sulphate pulping has been explained by the mechanisms presented in Scheme 5, which apparently operate in the course of the reactions of wood itself.[138,141]

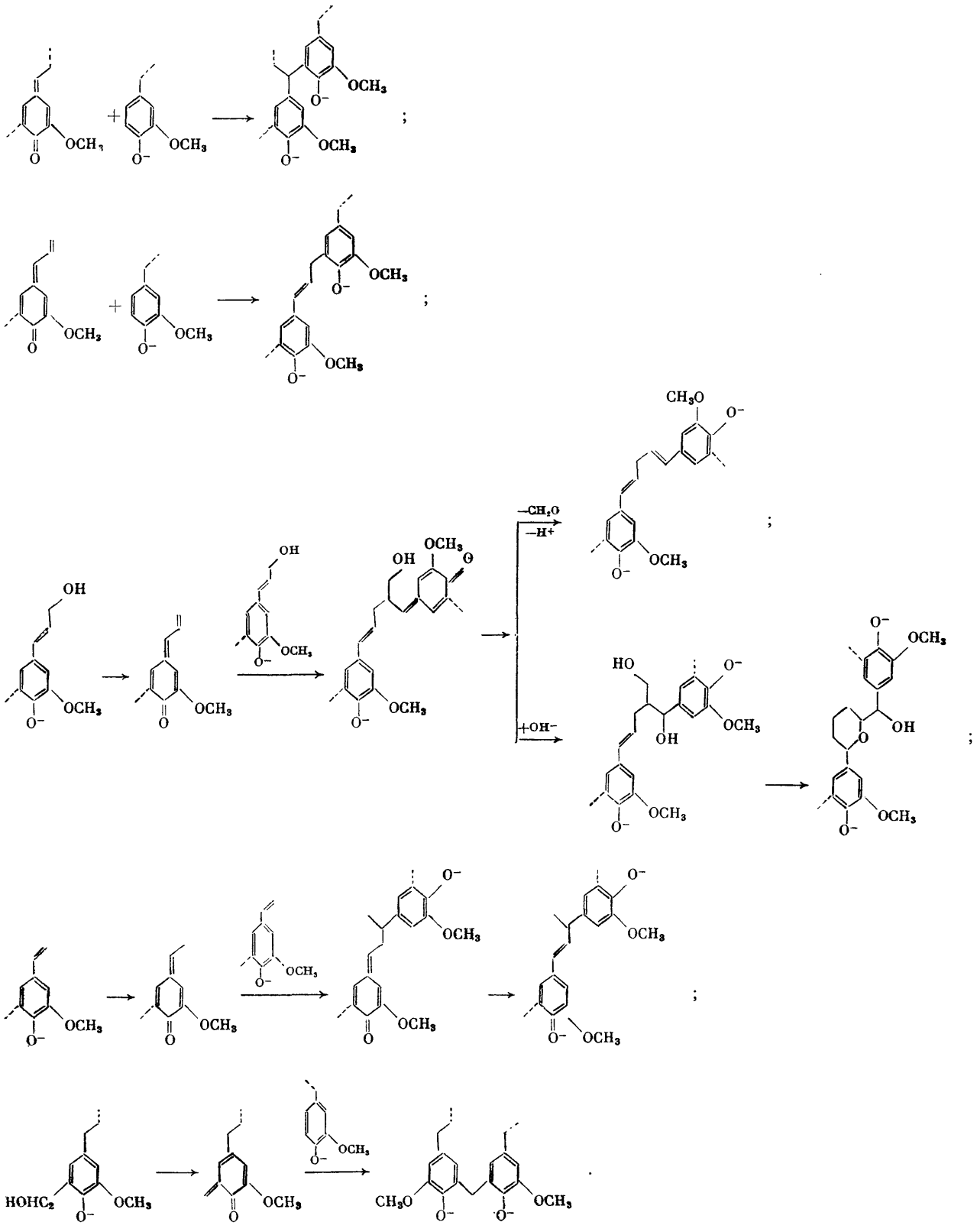
Scheme 5



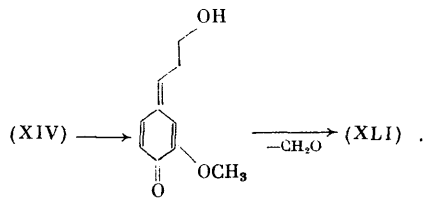
These reactions constitute polysulphide oxidation and in the case of the QM (XI) the initial stage is 1,6- or 1,8-addition. Clearly in polysulphide pulping their role should increase.

In the absence of strong nucleophiles (soda pulping), the elimination of terminal hydroxymethyl groups with conversion of the native β-aryl ether structures into the β-aryloxystyryl structures (more stable in alkali) predominates.[216] This reaction naturally does not belong to the class of fragmentation reactions. On the contrary, it produces formaldehyde, which is in principle capable of cross-linking phenols. The elimination of formaldehyde from various fragments of lignin represents generally speaking a process which can be fairly readily achieved and the formation of QM as intermediates

Scheme 6



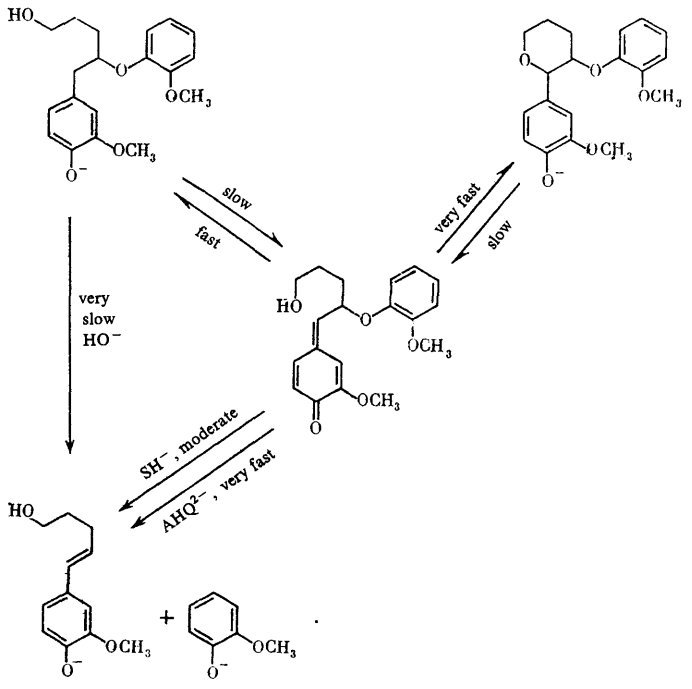
actually facilitates it. Thus the following mechanism has been postulated for the simple coniferyl alcohol (XIV) model:[141,233]



The relative importance of various routes to the rearomatisation of the QM is determined by the basicity and nucleophilicity of the reagents. Competitive experiments made it possible to establish the following series based on the rates of the reactions considered: the formation of QM $\ll$ elimination of CH_2O < addition of carbanions to QM < addition of SH^- to QM.[210]

When the structure of the lignin fragment does not lead to the chain degradation pathway, the addition of a low-molecular-weight nucleophile nevertheless assists the delignification process, retarding (although not blocking completely) the condensation of lignin and preventing the formation of stable styrene structures.[216,234] One of the important routes to such condensation involves the addition of phenolic fragments of lignin to QM, which takes place readily in an alkaline medium[104,138,141,216,220,232,233,235,236] (Scheme 6).

A remarkable example of a model system of competing pulping reactions has been described:[111]



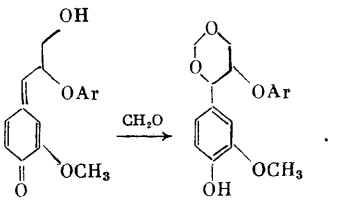
In the case represented, the nucleophilic addition of pulping agents competes with intramolecular addition and the efficiency of the suppression of the latter by the introduction of anthrahydroquinone demonstrates the unique properties of this nucleophile. Striking examples of the suppression of the self-condensation of *p*-hydroxybenzyl alcohols and dioxane-lignin by this reagent as well as other strong nucleophiles as reductants are also known.[126,135,237]

We may note that the corresponding bibenzyls have been detected among the products of the self-condensation of model alcohols in the presence of anthrahydroquinone.[126] In principle, these compounds can be the products of the dimerisation of the radical-anions produced by electron transfer to the QM,[238] but an unambiguous conclusion concerning their origin is so far impossible. Bearing in mind the theoretical considerations described above, the hypothesis[238,239] of the possibility of electron transfer to the QM from arylate anions or carbohydrates under the pulping conditions appears unconvincing.

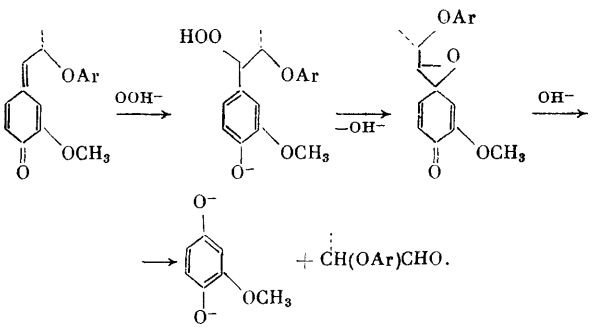
It is of interest to note that heating of *p*-hydroxybenzyl alcohols in aqueous alcoholic mixtures affords, together with their self-condensation products, also etherification products which are most probably produced via QM.[104,188] It appears that such processes can occur in the course of organic solvent pulping.

Evidently the influence of phenols on the pulping process should depend on their molecular weight: the interaction of lignin QM with low-molecular-weight phenols leads to cross-linking accompanied by the rupture of the chain (the overall effect is positive), while the addition of high-molecular-weight fragments of lignin prevents the delignification process. Low-molecular-weight phenols, for example coniferyl alcohol (XIV), which can themselves be readily converted into QM condensing with lignin under pulping conditions, are an exception. As already mentioned, the presence of powerful nucleophiles (for example, SH^- and AHQ^{2-}) in the pulping liquor hinders condensation processes of different types.[136,237,240] We emphasise that the final result of the "fight for QM" depends not only on the nucleophilicity of the reagents but also on the rates of the subsequent irreversible reactions—cleavage or condensation.

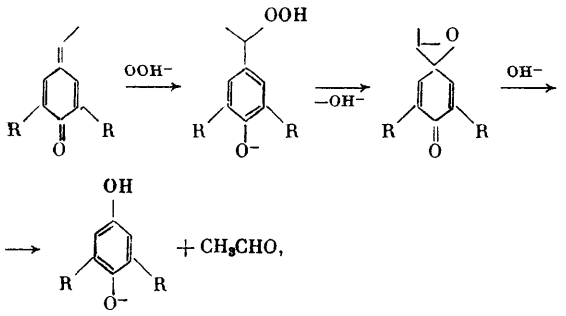
We may also note the following reaction as an interesting example of condensation with participation of QM and low-molecular-weight lignin degradation products:[241]



Unusual reactions with participation of QM may occur in oxidative delignification, where both electrophiles (for example, O_2) and nucleophiles (for example, OOH^-) function as active agents. The addition of the peroxide ion can lead to the rupture of the lignin chain:[233,241]

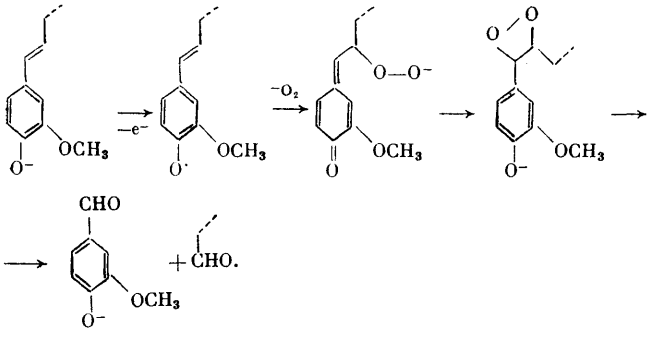


The following reactions were observed in a model experiment:[241,242]



R = C(CH$_3$).

The oxidation of conjugated phenols leads to the dissociation of the $C^{\alpha}-C^{\beta}$ bond, the intramolecular nucleophilic addition to QM being an important stage of the process:[233,241–243]

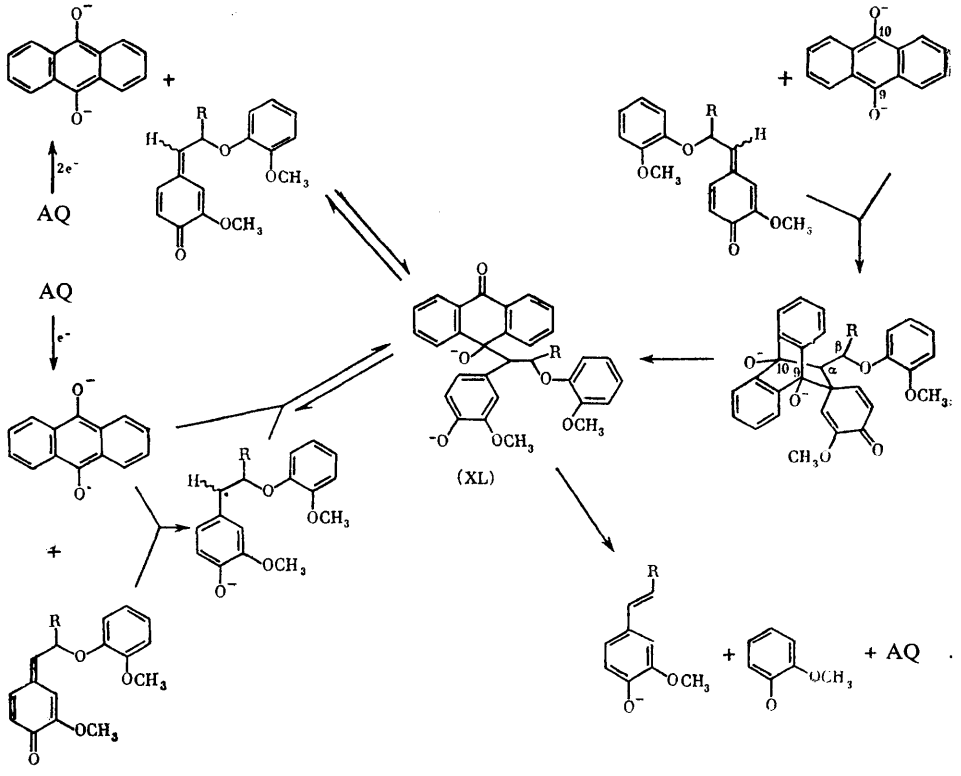


We have already noted that there is a close similarlity between the mechanisms of pulping involving strong nucleophiles (the fact that the addition of anthraquinone exerts a greater effect on the soda pulping of wood than on the sulphate pulping has in fact been explained by the competition between the related reagents[9]). The results of studies of the anthraquinone pulping carried out in recent years are therefore of special interest. Together with the observation of the characteristic features of the process involving anthraquinone as such, they made it possible to re-examine the properties of lignin and its reactivities in various technological processes.[9]

Above we discussed in detail various aspects of the reactions of model lignin QM with derivatives of anthracene such as anthrahydroquinone and anthrone. The "classical" mechanism of the cleavage of phenolic β-aryl ether subunits of lignin in the course of pulping involves the formation of the adduct (XL), which then undergoes Grob fragmentation. Such ideas are based on the isolation of the adduct under mild conditions; the adduct decomposes via the postulated mechanism on heating in aqueous alkali. However, this does not yet rule out the possibility of other reaction pathways.

Anthranol and anthrahydroquinone may be regarded as effective trapping agents for QM. The reasons for their high affinity for QM and the associated ability of these compounds to cleave the β-aryl ether linkages of lignin have been interpreted within the framework of different theories. The interaction of the above reagents with QM can be quite logically explained within the framework of the theory of hard and soft acids and bases:[9,89] in this approach, the anions behave as nucleophiles attacking the electrophilic substrate and the key stage of the process is the formation of an adduct of the type (XL) (Scheme 7).

Scheme 7



It has been suggested[142] that the oxidation-reduction interaction of anthrahydroquinone with QM can proceed via the formation of a charge-transfer π-complex and that the anthraquinone–AHQ^{2-} system as it were "creeps" along the surface of the gel-like lignin polymers and hemicelluloses supplying or abstracting electrons. Dimmel and co-workers[92,93,95,111,238,239,244] proposed a likely one-electron transfer theory in which the key stage ensuring cleavage is electron transfer to QM.

Finally, Ralph[102] recently put forward the hypothesis (with a reference to a private communication by Suckling) that the primary stage of the reaction of the reduced form of the catalyst with the lignin QM may be the Diels–Alder reaction. This hypothesis is least well founded. However, it is significant that all three mechanisms can involve the formation of the "key" adduct (XL), admittedly via different pathways, so that it is so far not clear whether we are justified in regarding all the above pathways as alternative pathways. On the other hand, it is useful to formulate a fundamental question the answer to which would make it possible to understand whether there is any point in considering a charge-transfer mechanism as an alternative to the "classical" mechanisms. This question refers precisely to the properties of QM and can be written as follows: what is faster under the pulping conditions — the decomposition of the corresponding radical-anion or the coupling of the latter to anthrahydroquinone? Only in the former case can the specific features of the one-electron reactions be manifested significantly (although, as we have already mentioned, in the latter case also the demonstration of the existence of a one-electron stage might affect the choice of procedures for intensifying the catalytic process).

Dimmel et al.[95] drew attention to the fact that the reductive cleavage of β-aryl ether QM with participation of the reduced forms of anthraquinone, but without the formation of an adduct, is observed in electrochemical experiments. However, it is not clear how likely in general the formation of an adduct is under the conditions of the electrochemical carried out by Dimmel et al.[95] Furthermore, as a consequence of the dependence of the rates of formation of the adduct and of the electron transfer on the temperature and the solvent, the legitimacy of the extrapolation of the results of Dimmel et al.[95] to the pulping process is not evident. We may note that experiments do not provide an answer to the following question either: is the dianion AHQ^{2-} or the radical-anion $AHQ^{\cdot-}$ more likely as the electron donor? The rapid disproportionation of $AHQ^{\cdot-}$ usually leads to the simultaneous formation of AHQ^{2-} and Dimmel et al.[95] dealt with a mixture of reduced forms of anthraquinone at least in preparative experiments (cf. Shevchenko et al.[127]).

In our view, the mechanism of electron transfer catalysis is quite likely, but it is very difficult to demonstrate it reliably and so far there is no such evidence. This is a fairly common situation; electron transfer processes do not constitute any kind of exception but the assignment of any reactions to the given class is based on a set of indirect evidence and is frequently liable to be controversial. Apparently in the given case one should use photostimulation, but so far such experiments have not been carried out. The hypothesis is supported by the catalytic activity of bulky organometallic complexes.[245]

One should not imagine that the situation is one where the operation of an electron transfer mechanism necessarily implies that the reduced form of the catalyst is able to "bombard" lignin readily with electrons from a large distance. Outer-sphere electron transfer is known to constitute the least favourable pathway in the reaction between two compounds: the two reagents should react regardless of any advantages which the electronic interaction between them could afford. Polar and inner-sphere processes are in most cases preferable as regards energy.[246] The phenomenon of autocatalysis observed by Dimmel et al.[95] does not in any way conflict with this: it nevertheless implies that the electron transfer to QM in solution takes place more readily than from the electrode surface. This does not imply that the mutual approach of the reactants is not necessary for the process to occur. Naturaly tunnelling over a large distance is possible,[247] but, for reasons already stated, its probability must be much lower than the probability of more complex mechanisms involving, for example, the formation of pre-reaction charge-transfer complexes. Such mechanisms with chemical stages are characteristic of electron transfer reactions.[246]

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