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On Formation of Anthrasemiquinone in the Conditions of Wood Alkaline Pulping*

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Electron spin resonance (ESR) and electronic absorbance spectral experiments demonstrate that reversible temperature variation of anion-radical concentration in the system anthraquinone (AQ) — anthrasemiquinone (AS) — anthrahydroquinone (AHQ) in aqueous alkali is a property of that system and not of the more complicated catalyst-wood system. Lignin model compounds present in low concentrations have no influence on this variation. A raise of radical concentration is accompanied by a change of the solution colour from red into yellow. In pulping conditions AQ can be reduced either by the hydrocarbon or by the lignin component of wood, probably also by numerous organic compounds and even by the alkali itself. As a result of this process, an AQ-AS-AHQ system is being formed.

INTRODUCTION

9,10-Anthraquinone is a widely used catalyst of wood alkaline pulping. Figure 1 illustrates the generally accepted overall mechanism of its action. But nowadays, about fifteen years after the discovery of the catalytic pulping process, thorough studies of the mechanism resulted in many more questions than answers. The most important open question seems to be the proportion of heterolytic and homolytic reactions in delignification processes.[1,2] The behaviour of the system anthraquinone (AQ) — anthrasemiquinone ($AS^{\cdot -}$) — anthrahydroquinone (di)anion ($AHQ^{=}$) is of interest in relation to this general problem.

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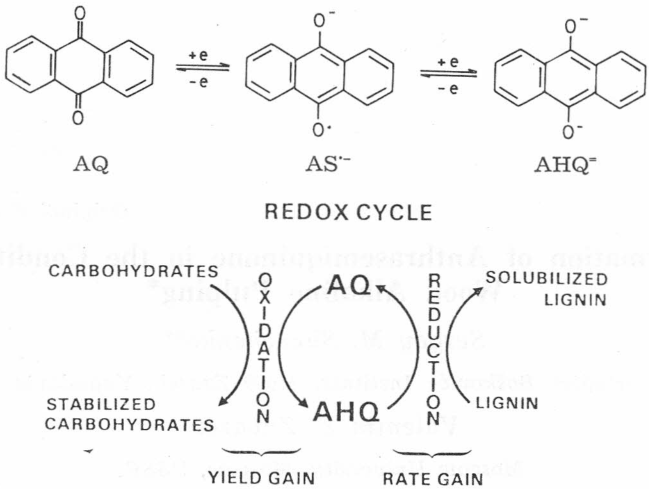


Figure 1. A redox cycle proposal for explaining the catalytic action of AQ during alkaline wood pulping.[2]

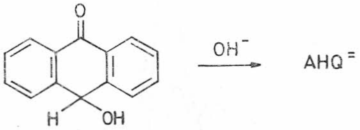
The reduction of AQ in aqueous alkaline solution is an important part of the redox-cycle of catalytic pulping. To understand the mechanism of this process, it is necessary to find out the paths of formation of the catalyst. Until now it was neither clear which compounds present in pulping liquor may reduce AQ, thus forming the system under consideration, nor what is the influence of such compounds on AS concentration.

The system AQ-AS$^{\cdot-}$-AHQ$^{=}$ was studied several times, though only in the presence of wood components or other reducing agents.[3–6] But, it is clear that if we are trying to explain the interaction of the reduced catalyst with wood, the pure system has to be examined first. The most important problem related to equilibria in AQ-AS$^{\cdot-}$-AHQ$^{=}$ system seems to be its interaction with lignin electron acceptors. High stability of AS$^{\cdot-}$ offers a possibility of using it as an indicator of radical processes. Addition of a lignin model compound to AQ-AS$^{\cdot-}$-AHQ$^{=}$ system might lead to accumulation of AS$^{\cdot-}$ or, conversely, to a decrease of AS$^{\cdot-}$ concentration because of its specific reaction with electron acceptor.

The aims of the present investigation were: to clarify the reasons and the character of the dependence of the radical concentration on temperature, to determine the influence of lignin model compounds on the equilibrium in the system AQ-AS$^{\cdot-}$-AHQ$^{=}$, and to find out the source of reductants of AQ in pulping systems.

TEMPERATURE JUMP OF AS$^{\cdot-}$ CONCENTRATION

It has been reported that the fraction of AS$^{\cdot-}$ in the AQ-AS$^{\cdot-}$-AHQ$^{=}$ system increases with temperature.[4–6] However, all the experiments on which those conclusions are based have two serious flaws apparently unnoticed by the authors. First as mentioned above, the systems under consideration always included an extra component of wood constituent, whose influence was not exactly known. Second, it has been shown that determinations of radical concentration under variable temperature conditions may be incorrect in the case of aqueous solutions.[7] Therefore, in preliminary experiments we prepared the AQ-$AS^{\cdot -}$-$AHQ^{=}$ system by dissolution of 10-hydroxyanthrone (*1*) in 1 M aqueous NaOH in evacuated sealed ampules used in ESR experiments later.



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In this series of experiments, only relative temperature variations of $AS^{\cdot -}$ concentration were measured by simple comparison of line intensities in high resolution ESR spectra. After dissolving *1* at 25 °C, a transparent red solution formed which gave a distinct $AS^{\cdot -}$ spectrum of constant line intensities. After stationary concentration of $AS^{\cdot -}$ at 25 °C was reached, the samples were heated to 96 °C, then cooled immediately, and after 0.5 minutes the ESR spectrum was recorded. This approach was chosen to exclude the apparent effect of temperature rise of a radical concentration which is characteristic of aqueous solutions.[7]

The heating of a $7 \cdot 10^{-4}$ M AQ-$AS^{\cdot -}$-$AHQ^{=}$ solution for not less than 3 minutes resulted in a reversible 3—4 fold rise of $AS^{\cdot -}$ concentration, the latter being reduced to the initial value at 25 °C for a period of 10 minutes. The total concentration of the catalyst was within the limits typical of wood pulping. A 10 fold increase of total concentration led to suppression of the effect: only a 1.5 fold rise of $AS^{\cdot -}$ concentration was observed in that case.

Addition of AQ in 20 M excess to *1* does not influence the results. Oxygen, being present in amounts which cannot change appreciably the $AHQ^{=}$ concentration (residual pressure up to 10^2 Pa), has no effect, either. Admitting air to the system results in a decrease of $AS^{\cdot -}$ concentration and the intensity of solution coloration, *i. e.* in a parallel oxidation of $AS^{\cdot -}$ and $AHQ^{=}$.

Reversible temperature variations of ESR spectrum are accompanied by corresponding variations in the absorbtion spectrum (Figure 2, compare[8]). The latter obviously correspond to the rise of the AS part of the mixture, 746—756 nm band corresponding strictly to $AS^{\cdot -}$ absorbtion. The AQ-$AS^{\cdot -}$-$AHQ^{=}$ system may be regarded as thermoindicator because of the characteristic reversible colour transitions from red at 25 °C to yellow at 96 °C. The colour change in AQ-$AS^{\cdot -}$-$AHQ^{=}$ system does not mean disappearance of one of the components. Thus, the yellow solution is not a solution of $AS^{\cdot -}$ only, but a solution with a relatively high $AS^{\cdot -}$ concentration. It has to be noted that the room temperature spectrum presented in Figure 2 does not coincide completely with the spectrum given by Anne and Moiroux[9] for the product of electrochemical reduction of AQ. The difference may be ascribed to solvent effect.

THE CATALYST AND *p*-QUINONEMETHIDES

It seems possible that in the initial stage the interaction between the reduced form of the catalyst and lignin proceeds as an electron transfer reaction, with *p*-quinonemethides being electron acceptors.[10,11] Actually, $AS^{\cdot -}$

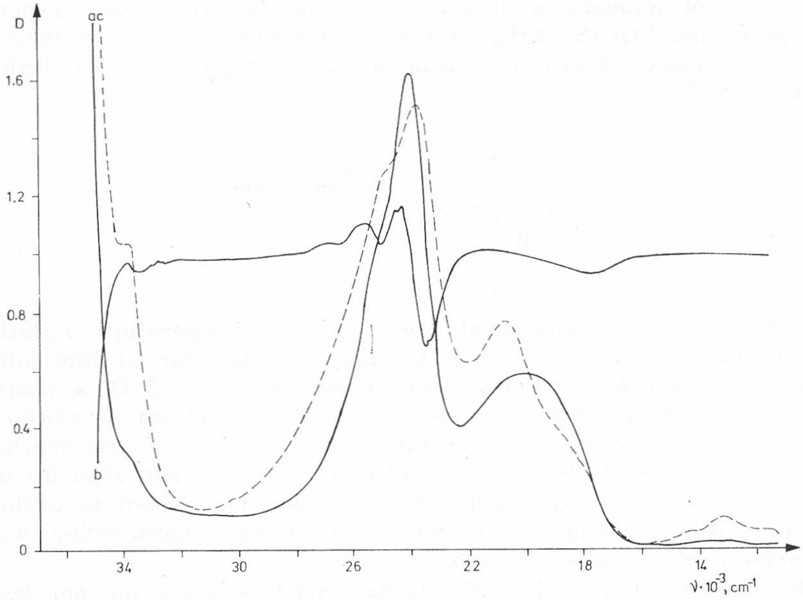
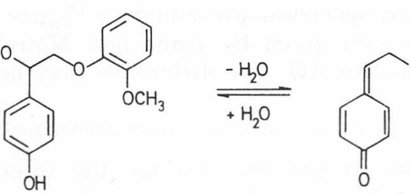
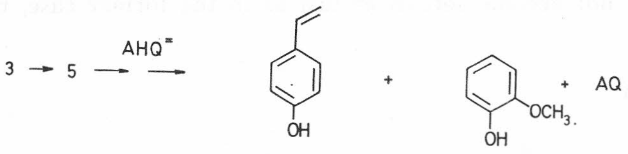


Figure 2. Reversible temperature variations of the electron absorbance spectrum of $AS^{\cdot -}$-$AHQ^{=}$; a) 25 °C, λ_{max} (lg ε); 262 (4.27), 416 (3.96), 499 (3.51), 746 (1.82) nm; b) 25 °C, first derivative of the spectrum; c) 96 °C, λ_{max} (lg ε); 262 (3.97), 282 (4.15), 420 (3.91), 480 (3.62), 756 (2.73) nm. Evacuated cuvette, $1.86 \cdot 10^{-4}$ M solution of *1* in 1 M aqueous NaOH.

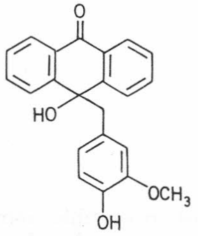
formation from AQ and $AHQ^{=}$ in aqueous alkali is a reduction of such a type. We heated a $7 \cdot 10^{-4}$ M solution of AQ-$AS^{\cdot -}$-$AHQ^{=}$ (prepared from *1*) in 1 M aqueous NaOH with such additives as 4-hydroxy-3-methoxyphenylmethanol (*2*) and 1-(4-hydroxyphenyl)-2-(2-methoxyphenoxy)ethanol (*3*), in a concentration of 0.05 M, which form the related *p*-quinonemethides (*4* and *5*, correspondingly) on being heated in aqueous alkali.[12]



The presence of these compounds had no influence on characteristic temperature variations of ESR spectra (3 minutes, 96 °C). In the case of compound *3*, prolonged heating to 1 hour resulted in an irreversible reduction of $AS^{\cdot -}$ concentration and also in decoloration of the solution, *i. e.* in changes undoubtedly connected with an irreversible chemical reaction. The character of such a reaction is well known: it is reductive splitting of *β*-aryletheric bond proceeding *via* *p*-quinonemethide intermediate.[12]



Interaction between reduced AQ and *p*-quinonemethides was studied by using simpler compounds, able to form unsplittable *p*-quinonemthides (*4* is an example).[13,14] Such intermediates may appear also in lignin during alkaline pulping of wood, and it is not quite clear, whether these compounds can irreversibly bind AHQ. Some conclusions may be made on the basis of the data of Dimmel and Shepard[13], but we have also studied the behaviour of simple adduct of *2* and $AHQ^{=}$ (*6*, $7 \cdot 10^{-4}$ M in aqueous NaOH).



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At 25 °C a pale yellow solution of *6* demonstrated only a weak ESR signal of $AS^{\cdot -}$. However, 0.5 minute heating at 96 °C led to a 17 fold raise of the signal intensity. Decreasing the temperature to 25 °C, we obtained a pink solution with a 6 times stronger ESR signal than initially. Later, this solution demonstrated reversible colour and ESR signal variations identical with variations characteristic of the AQ-$AS^{\cdot -}$-$AHQ^{=}$ system.

AQ AS AN OXIDANT IN AQUEOUS ALKALINE MEDIA

The equilibrium in AQ-$AS^{\cdot -}$-$AHQ^{=}$ system establishes quickly and, as we have shown, is practically not influenced by additives. Therefore, the ESR signal of $AS^{\cdot -}$ may be used to detect the reduction of AQ in aqueous alkaline media. We examined quantitavely the behaviour of the catalyst in the presence of wood hydrocarbons which are considered in the literature as the only reductants of AQ. It is essential that we used a special techniques (see experimental part) of quantitative measurements, avoiding artificial effects characteristic of aqueous solutions.[7]

An evacuated ampule filled with alkaline spruce chips extract was heated in ESR spectrometer cell. We observed the appearance of $AS^{\cdot -}$ above

70 °C. Once appeared, $AS^{\cdot-}$ is present in a stationary concentration which is characteristic of every temperature value. The concentration smoothly and reversibly rises with temperature in the range of 25—170 °C (Figure 3). It has to be noted that we did not observe any decrease of $AS^{\cdot-}$ concentration (compare[4]). Heating the same concentration of AQ in a sealed, but not evacuated, ampule has shown the same behaviour. The only, but essential difference, is the fact that in the latter case stationary concentration of $AS^{\cdot-}$ at 170 °C did not become settled as fast as in the former case, but 10 minutes later.

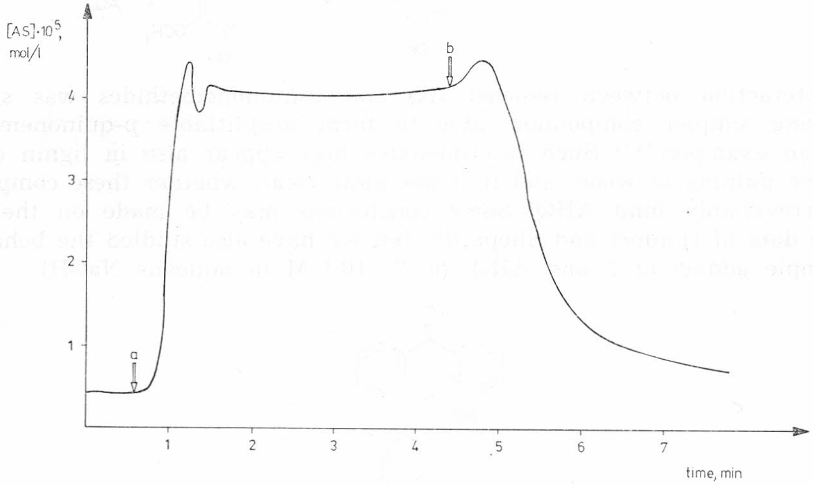


Figure 3. Typical kinetic cycle of reversible temperature variations of the $AS^{\cdot-}$ concentration. The arrows indicate moments of sample temperature rise (a) from 25 to 170 °C and decrease (b) from 170 to 25 °C. Evacuated ampule, AQ (1 mg) in 0.01 ml of 1 M aqueous NaOH extract of spruce chips; ESR technique.

Lignin model compound *2*, the corresponding aldehyde (vanyllin) and even methanol (20 M excess to AQ) also reduce AQ within a few minutes at temperatures higher than 100 °C in aqueous alkali. In such conditions we observed an intensive ESR signal of $AS^{\cdot-}$ and yellow coloration; at 25 °C the colour changed to red. We observed an analogous process using 50% in 1 M NaOH of both methanol and 1,4-dioxane (methanol without an alkali does not reduce AQ even at 170 °C). In the latter case, high stationary concentration of $AS^{\cdot-}$ ($1.5 \cdot 10^{-4}$ M) became settled in 5 minutes at 170 °C; it is essential that it does not decrease after cooling, the colour of the solution being still yellow. It seems that $AS^{\cdot-}$ anion radical is strongly stabilized in alkaline aqueous-dioxane media.

Not only different organic compounds, but also hydroxide ion can reduce AQ, but at more elevated temperatures. We observed the appearance of $AS^{\cdot-}$ (in small concentrations) on heating AQ with aqueous alkali when specially purified reagents were used. The application of impure, technical alkali and water greatly intensifies this effect, probably because of the action of metal cations which can change their oxidation states.

DISCUSSION

The increase of $AS^{\cdot -}$ concentration in AQ-$AS^{\cdot -}$-$AHQ^{=}$ system on heating in aqueous alkaline solution is a property of the catalyst but not only of interacting catalyst-wood system. The limits of variations of its concentration in this system are evaluated now at the temperature range of 25—96 °C, and the next problem is the influence of different organic species on this process. Since initial compound *1* is a reduced form of AQ, its dissolution in aqueous alkali must yield $AHQ^{=}$ only. We ascribe the appearance of $AS^{\cdot -}$ to the interaction with residual oxygen in the ampule and to possible admixture of an oxidation product in a sample of *1*. Reversible rise of $AS^{\cdot -}$ concentration with temperature proves that AQ is also present in the system, but probably in an amount comparable with that which can be dissolved in the volume of aqueous alkali used. Of course, a great excess of reducing agent may influence the position of the equilibrium (the experiment with aqueous dioxane presents an example of such an influence), but lignin model compounds present in the usual amounts have no observable effect. It is interesting that an amount of AQ in the ampule has no influence on temperature increase of $AS^{\cdot -}$ concentration. This indicates that only a negligible amount of AQ dissolved in aqueous alkali participates in AQ-$AS^{\cdot -}$-$AHQ^{=}$ equilibrium.

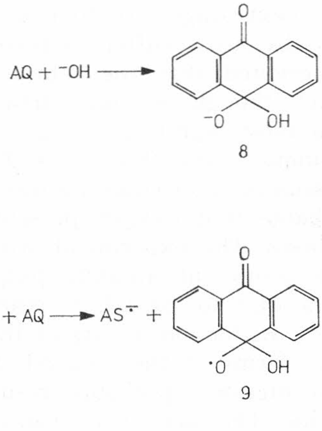
It turned out that controlling $AS^{\cdot -}$ concentration we cannot follow the interaction between lignin *p*-quinonemethides and the reduced catalyst. It seems possible that the position of the equilibrium AQ-$AS^{\cdot -}$-$AHQ^{=}$ itself has no relation to the rate of this process, and consequently to the rate of delignification.

Simple experiments with compound *6* have proved that at elevated temperatures molecular products of the interaction between *p*-quinonemethides and the catalyst can dissociate rapidly in alkaline solution. This does not mean without fail that a dissociation is homolytic; more likely that $AS^{\cdot -}$ appears at the next stage. Another product of dissociation, the unstable intermediate *4*, obviously suffers irreversible chemical transformation. It is generally accepted that the source of AQ reductant is the hydrocarbon part of wood,[12] though possible participation of the lignin part was also mentioned.[6] The most significant result concerning AQ reduction by hydrocarbons is the kinetic curve (Figure 3). The shape of this curve is in concordance with the assumption of chain radical oxidation of hydrocarbons in solution. It seems probable that oxygen present in the pulping mixture also takes part in the process. The experiment with an unevacuated sample demonstrated that in the course of alkaline pulping the initially present oxygen quickly disappears due to oxidation reactions, the catalyst being a transmitter of an oxidant. Reduction of AQ at the initial stage of pulping, with generation of soluble forms of the catalyst, followed by its extension through the volume of a digester, probably results in fast conversion of oxygen to hydrogen peroxide. The latter itself can accelerate delignification.[15] The catalyst can transfer an oxidant not only to hydrocarbon, but also to the lignin part of wood, so it is possible for oxidized lignin fragments to accumulate during »reductive« AQ pulping. The important role of quinoid catalysts in biological systems is often connected with their participation in the generation of active oxygen species, and non-physiological functions of quinones are essentially similar to those in physiological processes.[16]

The data presented here prove that the source of reductant in AQ pulping is not only the hydrocarbon part of wood, but also alcohols, alcoholic groups of lignin, and even aqueous alkali itself. This result is essential, at least for an understanding of AQ alkaline pulping in alcoholic media.[17] But now it seems that such a strong oxidant as AQ can be reduced at elevated temperatures practically by every lignin or hydrocarbon subunit (only relative rate and interphase problems are questionable). Multisource reduction of AQ enables the catalyst to transform into its reduced form at an early stage of pulping, irrespective of the rate of hydrocarbon dissolution.

Many organic compounds can reduce AQ in pulping conditions. Therefore, all studies of a mechanism of AQ pulping in aqueous-organic media may lead to erroneous conclusions. The puzzling result of Poppius[18] can be mentioned as an example. This investigation resulted in a strange stoichiometry of β-aryl ether cleavage by $AHQ^{=}$: one mole of the latter seemed to cleave 4—5 moles of the lignin model. But an alkaline aqueous-dioxane solution was used in this study. 1,4-Dioxane, as it was shown, takes the place of reductant, transforming AQ (one of the products of β-aryl ether cleavage, see above) to $AS^{\cdot -}$, which can also take part in subsequent reductive cleavage reactions, directly or as a source of $AHQ^{=}$. Results obtained in such conditions have no relation to real stoichiometry of the reaction between $AHQ^{=}$ and β-aryl ether.

Until now it was known that only quinones having free α-positions react with hydroxide ions in water resulting in the formation of semiquinone anion-radical; it was mentioned that AQ forms no $AS^{\cdot -}$ with aqueous alkali.[19] But the heating changes AQ chemical reactivity, and it is possible that at elevated temperatures AQ can react even with hydroxide ion, according to the proposed mechanism[20]:



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$$9 + 9 \longrightarrow 2\,AQ + H_2O_2$$

However, since it is difficult to purify an alkali, the low intensity signal of $AS^{\cdot -}$ in »pure aqueous alkali« may in fact be a consequence of the interaction of AQ with some minor admixtures.

EXPERIMENTAL

All the measurements were performed using evacuated systems (residual air pressure less than 0.1 Pa). Electron absorbtion spectra were recored on a Specord M40 (GDR) spectrometer with thermostat and quartz cuvette. In ESR experiments Varian E109 and especially modified RE 1307 (USSR) spectrometers were used. In all the conditions full ESR spectra were recorded, corresponding exactly to the spectrum of $AS^{\cdot -}$ (compare[3-5]). No other radicals were observed.

Experiments With a Reduced Form of AQ

In the first series of experiments the simplest way was used to avoid artificial effects characteristic of aueous solutions. All the ESR measurements were performed at the same temperature (25 °C), hot samples being cooled and placed in the spectrometer cell. The time between the end of heating and the spectrum recording was 0.5 minutes. Aqueous solution of 1 M NaOH was placed in the bottom part of a molibdenum glass ampule (Figure 4a), compopund *1* being placed into the bubble at the top of the ampule in solid form (initially as a dilute benzene solution, the solvent was evaporated later). The ampule was evacuated using the standard degassing technique, and sealed. The two components were mixed, yielding a transparent red solution of the reduced form of AQ. The excess of solution was placed into the bubble, and the rest was sealed anew, so as to have a minimal free volume in the final thin ampule.

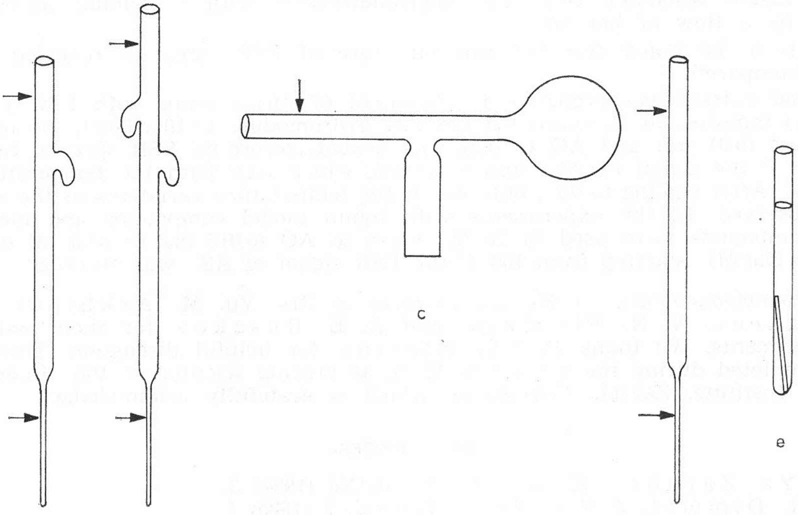

Figure 4. Vessels used in measurements: a) *1* only, ESR b) *1* with lignin models, ESR; c) *1* only, electron absorbance; d) AQ with wood extract and various organic compounds, ESR; e) the latter in microthermostat with paraffin oil. Arrows indicate the places of sealing.

After fixing the stationary concentration of the radical at 25 °C, the sample was heated outside the spectrometer on a water bath. Quantitative estimations were based on measurement of line intensities in ESR spectrum. A contour of the spectrum varied with the temperature (compare[4]), but all the spectra recorded at 25 °C were identical. Special experiments were performed to prove that the observable temperature jump of $AS^{\cdot -}$ concentration was not connected with the type of glass or any admixtures in alkali and water.

The solution of compound *6* was prepared in the same manner. For the experiments with lignin model compounds, the ampules with two bubbles were used (Figure 4b).

Electron absorbance spectra were recorded using a special quartz cuvette (Figure 4c). The alkaline solution was placed into the buble, and compound *1* as a solid into the cuvette itself. The treatment was very similar to the preparation of ESR samples. In the course of measurements the cuvette was placed in the thermostat inside the spectrometer.

Experiments With AQ

Molybdenum glass ampules (Figure 4d) were used in these experiments. AQ, and then the aqueous alkaline solution were placed into the bottom of the ampule, which was then evacuated and sealed. Absolute concentrations of $AS^{\cdot -}$ were measured using the nomogram technique of integration of the rough ESR signal. Measurements were performed for the samples placed in ESR spectrometer cell. A special technique was implemented to prevent temperature variation of ESR signal due to the change of resonator quality. A small evacuated ampule was placed into a quartz tube with liquid paraffin (Figure 4e) which played the role of microthermostat. Liquid paraffin compensate temperature variation of water properties described in ref. 7, the overal effect being the intensity of ESR signal corresponding to the actual concentration of a radical in aqueous solution. All the measurements at different temperatures were performed for the samples placed inside resonator cell. The microthermostat with a sample inside was heated by a flow of hot air.

It is to be noted that the fine structure of ESR signal is revealed up to 160 °C (compare[4]).

Wood extract was prepared by treatment of spruce chips with 1 M aqueous NaOH (5 minutes, 70 °C, evacuated ampule, hydromodule 1 : 10). Then, the mixture of extract (0.01 ml) and AQ (1 mg) was heated, recording ESR spectra. Starting from 70 °C the signal of $AS^{\cdot -}$ was observed, which rose with the temperature up to 170 °C. After cooling to 25 °, only reversible temperature variations of the spectra were observed. In the experiments with lignin model compounds and methanol these compounds were used in 20 M excess to AQ (0.015 mg in 0.03 ml of 1 M aqueous NaOH). Starting from 100 °C the ESR signal of $AS^{\cdot -}$ was observed.

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SAŽETAK

O nastajanju antrasemikinona u alkalnoj drvenoj pulpi

Sergej M. Ševčenko, Valentin E. Zubarev i Andrej P. Rudenko

Elektronska spinska rezonancija (ESR) i elektronski apsorpcijski spektri pokazuju da je reverzibilna temperaturna promjena koncentracije anion-radikala u sitemu antrakinon (AQ) + antrasemikinon (AS) + antrahidrokinon (AHQ) u vodenoj lužini svojstvo toga sustava, a ne mnogo složenijeg sistema katalizator — drvo. Ligninski modelni spojevi prisutni u niskim koncentracijama ne utječu na tu promjenu. Porast koncentracije radikala popraćen je promjenom boje otopine od crvene u žutu. U alkalnoj drvenoj pulpi AQ se može reducirati bilo ugljikovodičnom ili ligninskom komponentom drva, vjerojatno također brojnim organskim spojevima ili čak samom lužinom. Kao rezultat tog procesa nastaje sustav AQ—AS—AHQ.