89%) was isolated: nmr τ 8.71 (s, 9 H), 7.71 (s, 3 H), 2.98 (d, 2 H, J = 8 Hz), 2.77 (d, 2 H, J = 8 Hz); mass spectrum m/e (rel intensity) 39 (21), 40 (21), 41 (42), 77 (16), 91 (26), 93 (26), 105 (50), 133 (100), 148 (20, M^+).

Anal. (flash distilled, 14 mm). Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.26; H, 10.86.

Registry No.—Lithium, 7439-93-2; ammonia, 7664-41-7; *p*-isopropylbenzaldehyde, 122-03-2; *p*-cymene, 99-87-6; *p-tert*-butyltoluene, 98-51-1; *p-tert*-butyl benzaldehyde, 939-97-9.

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The Origin of the Paramagnetic Species in Lignin Solutions. Autoreduction of 2,6-Dimethoxybenzoquinone and Related Quinones to Radical Anions in Alkaline Solution

J. D. FITZPATRICK AND CORNELIUS STEELINK*[1]

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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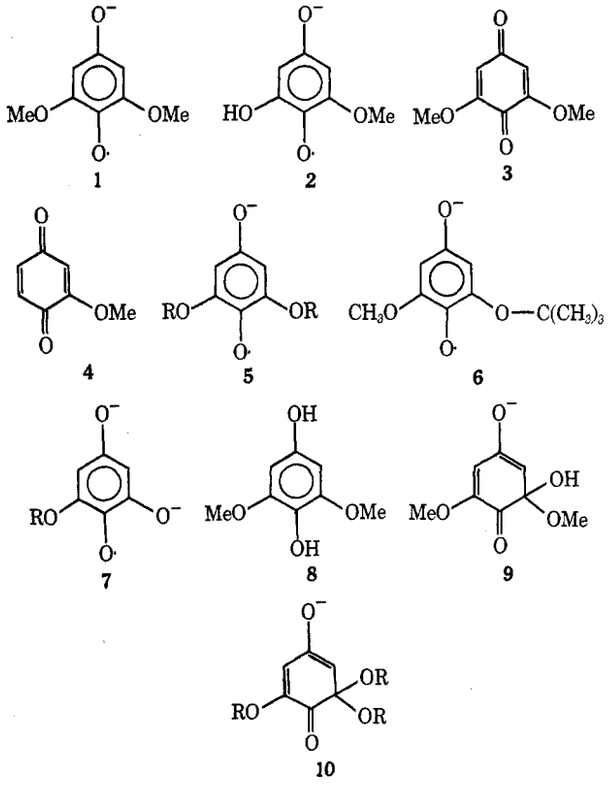
The lignin model compound, 2,6-dimethoxybenzoquinone (**3**), is spontaneously reduced to stable semiquinone radical anions by alkaline solutions of water or alcohol. This behavior parallels that of hardwood lignins. Rapid replacement of the methoxyl groups by alkoxide ion occurs in alkanolic solvents; steric factors play an important role in this exchange. The primary reaction intermediate appears to be a cyclohexadienone adduct of quinone and nucleophile; its concentration is rate determining. A mechanism for the reaction is proposed.

Lignin, the ubiquitous component of terrestrial plants, has been shown to be paramagnetic.[2-5] The paramagnetism of lignin preparations increases with extent of chemical and enzymatic degradation.[5] Hardwood lignins, which contain a high proportion of 3,5-dimethoxy-4-hydroxyphenyl elements, have a higher spin content than analogous softwood lignins (whose chief structural elements are 4-hydroxy-3-methoxyphenyl groups). Alkali lignins show the highest radical content of all preparations.

When hardwood lignin preparations are dissolved in dilute aqueous base, a paramagnetic species is formed. This has been identified as 2,6-dimethoxy-*p*-benzosemiquinone (**1**).[6] In strong base, a second radical (**2**) appears.[6] All commercial hardwood lignins, such as kraft and Meadol, yield **1** and **2**. Brauns native and Bjorkman hardwood lignins yield low concentrations of **1**, as does Indulin (predominantly a softwood product).

We have found that hot water extracts of commercial alkali lignins contain appreciable amounts of 2,6-dimethoxyquinone (**3**) and small quantities of vanillin, syringaldehyde, and polymeric material. No 2-methoxybenzoquinone (**4**) was found. Native hardwood lignins do not yield any of the above with hot water. However, when refluxed with 1.0 M NaOH in air, they form vanillin, syringaldehyde, and traces of **3**. Since **3** appears to be the sole structural precursor of the paramagnetic species (apparently formed during a Dakin-type cleavage of native lignin during the pulping process),[7] we decided to investigate its behavior in a variety of basic solvents. The behavior of **3** may have relevance for other systems. Redox reactions of **3** have been implicated in plant resistance to fungal attack;[8a] its formation in plants may have arisen by a Dakin cleavage of lignin during attack by oxidases and peroxide.[8b]



1 2 3 4 5 6 7 8 9 10

Results

Reduction of Quinone 3 in Alkanolic Solvents.—When 10^{-3} M solutions of **3** were mixed with anhydrous alkanols and sodium ethoxide, strong esr signals were observed for 2,6-dialkoxybenzosemiquinones (**5**). Sec-

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(6) J. D. Fitzpatrick and Cornelius Steelink, *Tetrahedron Lett.*, 5041 (1969).

(7) K. Kratzl, W. Schafer, P. Claus, J. Gratzl, and P. Schilling, *Monatsh. Chem.*, **98**, 891 (1967).

(8) (a) M. E. Mace and T. T. Hebert, *Phytopathology*, **53**, 692 (1967); (b) E. S. Caldwell and C. Steelink, *Biochim. Biophys. Acta*, **184**, 420 (1969).

TABLE I

HYPERFINE SPLITTING CONSTANTS (IN GAUSS) OF SEMIQUINONE ANIONS

Semiquinone	Solvent	Base	A^H_{OR}	A^H_{ring}
2,6-Dimethoxy-*p*-benzosemiquinone (1)	Anhydrous methyl alcohol	0.1 *M* NaOMe	0.75	1.50
2,6-Dimethoxy-*p*-benzosemiquinone (1)	50% *tert*-butyl alcohol in water	0.1 *M* NaOH	0.77	1.50
2,6-Diethoxy-*p*-benzosemiquinone (5)	Anhydrous ethyl alcohol	0.1 *M* NaOEt	0.80	1.60
2,6-Diethoxy-*p*-benzosemiquinone (5)	Anhydrous ethyl alcohol	0.1 *M* NaOH	0.87	1.50
2,6-Diethoxy-*p*-benzosemiquinone (5)	80% Ethyl alcohol–20% water	0.1 *M* NaOH	0.90	1.46
2,6-Diethoxy-*p*-benzosemiquinone (5)	50% Ethyl alcohol–50% water	0.1 *M* NaOH	0.94	1.42
2,6-Diethoxy-*p*-benzosemiquinone (5)	25% Ethyl alcohol–75% water	0.1 *M* NaOH	0.96	1.41
2,6-Diethoxy-*p*-benzosemiquinone (5)	10% Ethyl alcohol–90% water	0.1 *M* NaOH	0.97	1.38
2-Hydroxy-6-ethoxy-*p*-benzosemiquinone (7)	Anhydrous ethyl alcohol	1.0 *M* NaOEt	0.68	2.80, 0.6[a]
2,6-Diisopropyl-*p*-benzosemiquinone (5)	Anhydrous isopropyl alcohol	0.1 *M* NaO-*i*-Pr	0.45	1.65
2,6-Diisopropyl-*p*-benzosemiquinone (5)	50% Isopropyl alcohol–50% water	0.1 *M* NaOH	0.50	1.40
2-Hydroxy-6-isopropoxy-*p*-benzosemiquinone (7)	Anhydrous isopropyl alcohol	1.0 *M* NaO-*i*-Pr	0.40	2.90, 0.15[a]
2-Hydroxy-6-methoxy-*p*-benzosemiquinone (2)	Anhydrous *tert*-butyl alcohol	0.1 *M* NaO-*tert*-Bu	0.60	2.90, 0.28[a]
p-Benzosemiquinone[b]	Anhydrous methyl alcohol	0.1 *M* NaOH		2.40
2-Methoxy-*p*-benzosemiquinone[c]	Water	pH 9.18 buffer	0.85	3.65, 1.95, 0.54

[a] Ring protons not specifically assigned. [b] Included in table as a reference compound. [c] Prepared by dissolving 2-methoxybenzoquinone in buffer. Unstable at higher pH values.

ondary radicals of type **7** appeared soon after mixing in 0.1–1.0 *M* NaOR. The exception to this group of alkanols was *tert*-butyl alcohol; in this case, there was evidence for the transitory existence of radical **6**, which rapidly gave way to radical **2**. At higher concentrations of NaOR, only the secondary radical **7** was observed. Again, the exception was encountered with *tert*-butyl alcohol, which showed only radical **2**. Thus, complete and fast alkoxy exchange occurred within all systems except *tert*-butyl alcohol. The esr results are summarized in Table I.

When NaOH was substituted for the NaOR in the alkanol solvents, only radicals of type **5** were observed for all alcohols except *tert*-butyl alcohol. In the latter case, only radical **1** was observed, indicating that no ether exchange had occurred. The coupling constants for **1** agreed with those reported by Hewgill.[9]

To assess the effect of solvent type on the exchange reaction, we used a variety of aqueous alcohol mixtures. In 50% water–alcohol, quinone **3** yielded radical **5**, identical with that found in 100% alcohol (with the exception of *tert*-butyl alcohol, which gives radical **1**). In this solvent system, complete ether exchange occurred. In an attempt to find the lower limit of alcohol content at which exchange did not occur, we used successively more dilute alcoholic solutions in water. Even at 10% ethanol in water, complete exchange of OEt with OMe took place.

Further studies showed that each alcohol exhibited a threshold value or minimum concentration at which the OR–OMe exchange would occur. This is illustrated in Figure 1. For primary alcohols, a 5% solution of alcohol in water exhibits the presence of both radicals **1** and **5**, a concentration at which partial exchange occurs. With secondary and tertiary alcohols, no exchange was observed and only radical **1** was present.

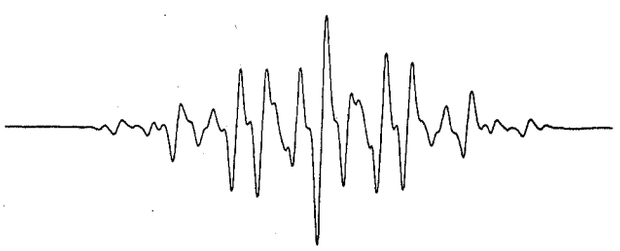


Figure 1.—Esr spectrum of 2,6-dimethoxybenzoquinone in 5% ethanol and 0.10 *M* NaOH. Both radicals **1** and **5** are present.

The effect of solvent polarity on the coupling constants was pronounced. With increasing polarity, there was a regular decrease of the ring proton coupling and an increase of the alkoxyl proton constants. Apparently, semiquinone **5** underwent asymmetric solvation (or hydrogen bonding) to a considerably larger extent than alkyl-substituted benzosemiquinone anions.[10]

In the above reactions, the principal nucleophile appears to be an alkoxide ion, even though the concentration of water and OH^- is much greater. This is not unexpected, since the equilibrium

$$ROH + OH^- \rightleftharpoons RO^- + H_2O$$

(9) F. R. Hewgill and L. R. Mullins, *J. Chem. Soc. B*, 1155 (1969).

(10) T. A. Claxton and D. McWilliams, *Trans. Faraday Soc.*, **64**, 2593 (1968).

contains appreciable amounts of alkoxide ion even at 5% alcohol concentration. A simple calculation[11] for a 5% aqueous solution of a typical alcohol shows that more than 10^{-2} M alkoxide is present in solutions containing 0.1 M NaOH.

Reduction of Quinone 3 in Aqueous Base. A. Esr Spectra.—When quinone **3** was dissolved in aqueous base, an esr signal was generated. The signal reached a maximum intensity slowly (1–24 hr) depending on pH, and then decayed. At high pH values, a new signal emerged, that of radical **2**. The maximum concentration of semiquinone anion was 10 mol % of the original quinone, as measured against a standard solution of 2,2,6,6-tetramethylpiperidine-1-oxyl. This behavior of quinone **3** parallels that of hardwood lignins in aqueous base.

The intensity of the esr signal is pH dependent. Radicals were generated at pH values as low as 9. At pH 10 and 1×10^{-3} M quinone, there appears to be an incubation period of about 10 min before radical **1** signal appears.[12] Thereafter, a slow increase in radical concentration occurs until a maximum is reached. This is followed by a slow decay. At higher pH, the primary radical is supplanted by a secondary radical **2** whose concentration is usually greater than that of the primary radical. Thus, at pH 12.45, radical **1** reached its maximum concentration in 1.0 hr; radical **2** reached its maximum concentration in 4.0 hr. The secondary radical **2** has a longer half-life than the primary. The entire time sequence is shortened at higher pH. At pH 14, the primary radical is not even observed.

The color of the quinone solution changed dramatically when mixed with base. The yellow color of the quinone was instantly discharged on contact with base. Thereafter, the sequence of color changes was colorless–pink–red. At the end of 24 hr, the solution was red-brown. Only 2% of the original quinone **3** was recovered from the red-brown reaction mixture.

The formation of primary and secondary radical species from hydroquinones has been detected by esr spectroscopy.[13,14] The kinetics of formation of radical species from unsubstituted benzoquinone has been studied by optical spectroscopy;[15,16] these studies were based on flow techniques for rapid reactions. Our system appeared to behave by a different mechanism, and take place at a much slower rate. Therefore, our measurements (see below) were made in a static system.

B. Optical Spectra.—In the above, it was shown that hydroxide ion (or alkoxide ion) causes the reduction of quinones as well as displacing the methoxyl group from the ring. To further elucidate the mechanism of this reaction, we found it necessary to examine some of the species in the reaction mixture by ultraviolet and visible spectrophotometry. These studies were restricted to aqueous solutions, since a few observations in ethanolic solution indicated similar behavior to aqueous solutions.

When quinone **3** (1×10^{-3} M) was mixed with pH 11 aqueous buffer solution, and the reaction was scanned by ultraviolet spectrophotometry over a period of 3 hr, a set of spectra was obtained as shown in Figure 2. At higher pH values, similar sets of spectra were obtained. In these cases, the 245 nm band was much more intense with respect to the 210 and 300 nm bands, as well as in absolute intensity. The 300 nm band was shifted toward higher wavelengths at higher pH values.

The existence of two isobestic points (at 227 and 278 nm) indicated that a single product, or a number of products with identical chromophores, were formed from the decay of the 245 nm band. Since the reduction of quinone **3** could yield semiquinone anion radicals, hydroquinone anions, and dianions, as well as the quinone itself, we decided to determine the absorption maxima of some of these species. The maxima are recorded in Table II.

TABLE II
ABSORPTION MAXIMA OF VARIOUS COMPOUNDS IN WATER SOLUTION

Compd	λ_{max}, nm	ϵ
2,6-Dimethoxybenzosemiquinone	210	(110)[a]
(in pH 12, buffer)	315	(40)[a]
	430	(5.8)[a]
	550	(0.90)[a]
2,6-Dimethoxyquinone	288	8.9×10^3
	395	3.8×10^2
2,6-Dimethoxyhydroquinone	284	3.9×10^3
2,6-Dimethoxyhydroquinone dianion (in 0.01 M NaOH and $Na_2S_2O_4$)	210	1.4×10^4
	318	4.0×10^3

[a] Relative intensities.

The spectrum of radical **1** was obtained by two methods. (1) A solution of hydroquinone **8** in base was oxidized with oxygen. The rates of increase in signal intensity of the esr spectrum were compared with the increase of peaks in the optical spectrum, run under identical conditions. (2) Equimolar mixtures of quinone **3** and hydroquinone **8** were placed in aqueous base. A very strong stable spectrum was observed in the optical and esr regions. Peaks at 550 (weak), 427, 317 (broad), and 210 nm were recorded and are in accordance with values reported for similar systems.[17,18] The anion of hydroquinone **8** was prepared in basic solution containing sodium hydrosulfite. It was noted (Table II) that the broad peak at 317 nm could arise from all three species: **1**, **3**, and **8** anions.

It is obvious that the 245 nm band is not characteristic of any of the compounds listed in Table II. A first-order plot was obtained for the decay of this band over a 3-hr period. The rate constant was independent of pH over a broad range (Table III). At pH values above 13, however, the constant did increase slightly. When the concentration of quinone was varied over a twofold range, rate data were obtained which were consistent with first-order kinetics. At pH values of 10 or less, the reaction was too slow to permit

(11) E. J. King, "Acid Base Equilibria," Topic 15 in the International Encyclopedia of Physical Chemistry and Chemical Physics, Macmillan, New York, N. Y., 1965, p 284.

(12) This may be due to scavenging of the initially formed radical by dissolved oxygen which had not been completely removed.

(13) J. Pilar, I. Buben, and J. Pospisil, *Tetrahedron Lett.*, 4303 (1968).

(14) T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1488 (1965).

(15) M. Eigen and P. Matthies, *Chem. Ber.*, **94**, 3309 (1961).

(16) M. Sasaki, *Nippon Kagaku Zasshi*, **90**, 1231 (1969).

(17) Y. Harada and H. Inokuchi, *Mol. Phys.*, **8**, 265 (1963).

(18) H. Diebler, M. Eigen, and P. Mathies, *Z. Electrochem.*, **65**, 634 (1961).

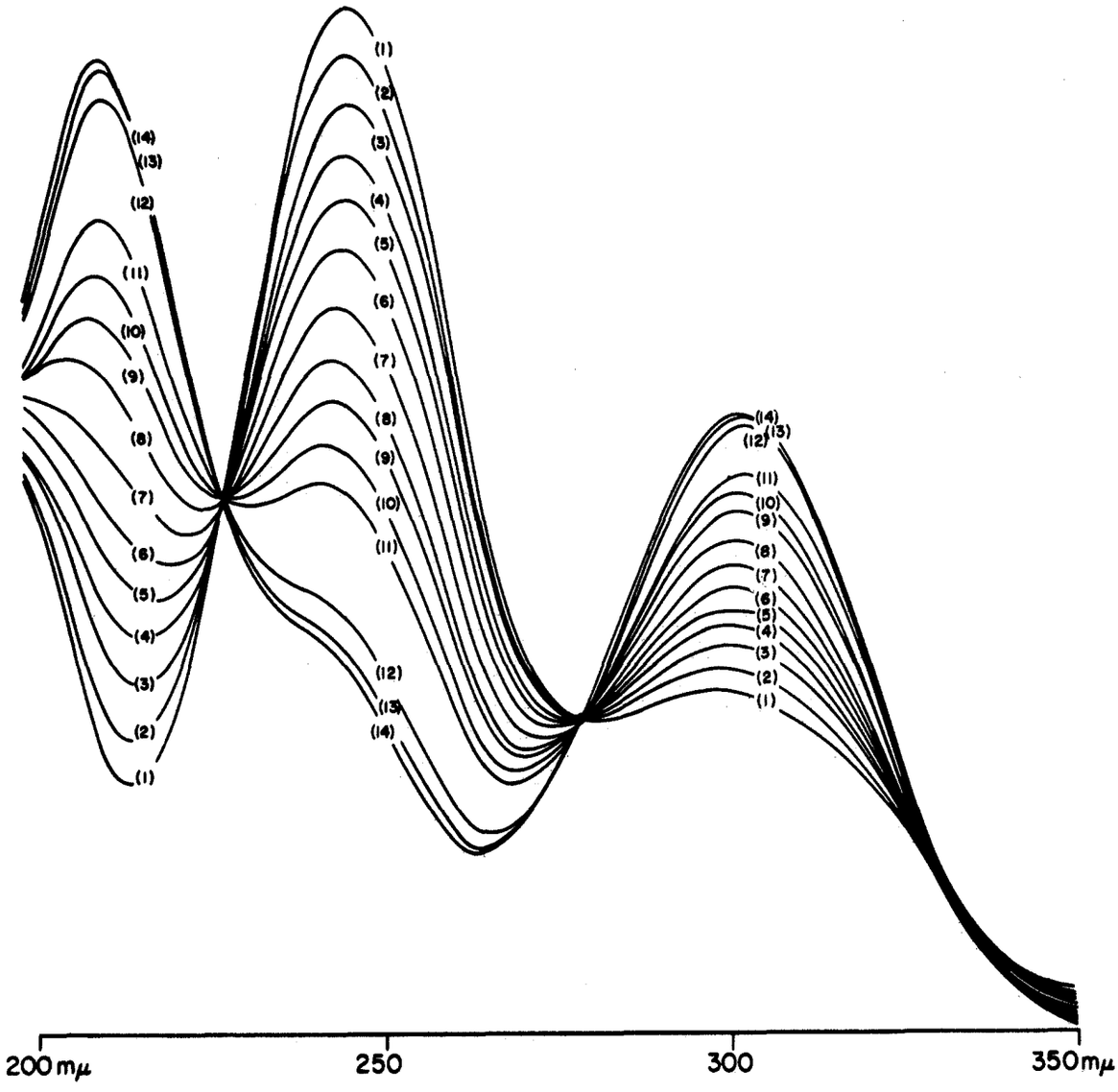


Figure 2.—Ultraviolet absorption spectrum of 2,6-dimethoxybenzoquinone (1×10^{-3} *M*) in 0.01 *M* NaOH. Time after mixing quinone **3** and base: (1) 2 min, (2) 7 min, (3) 12 min, (4) 17 min, (5) 22 min, (6) 28 min, (7) 37 min, (8) 47 min, (9) 57 min, (10) 67 min, (11) 77 min, (12) 137 min, (13) 177 min, (14) 197 min.

TABLE III
FIRST-ORDER RATE CONSTANTS

Species	Initial concn of quinone, *M*	Solvent	*k*, min^{-1}
245 nm band (decay)	7.5×10^{-4}	pH 12, buffer	0.022
	5×10^{-4}	pH 12, buffer	0.022
	1×10^{-3}	0.01 *M* NaOH	0.015
	1×10^{-3}	0.001 *M* NaOH	0.012
Radical **1** (formation)	1×10^{-3}	pH 9.18, buffer	0.011
	1×10^{-3}	0.01 *M* NaOH	0.008
	1×10^{-3}	pH 12.45	0.006

detectable changes over a 30-min scan, although small esr signals were present. At low pH values, the quinone spectrum was dominant.

During the decrease of the 245 nm band, increases were observed for bands at 210, 280–315, and 500 nm. These bands could represent one or more phenolate anions, dianions, or radical anions. They did not lend themselves to ready kinetic analysis.

On the basis of its spectral characteristics, we assigned the structure **9** to the species absorbing at 245 nm. Adducts such as **9** have been reported for quinones;[15,19] cyclohexadienone compounds have absorption maxima in this spectral region.[20-23]

The 210 nm band could represent phenolate anion or anion radical; the broad band at 280–315 nm could contain contributions from phenolate anion, radical anion, and quinone. The band at 550 nm probably represents decay products of the semiquinone radical. None of these bands lent themselves readily to kinetic analysis.

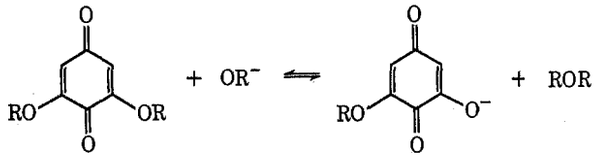
When esr measurements were taken of this reaction sequence under conditions identical with those monitored by optical spectroscopy, a first-order increase in radical species was obtained. The first-order rate for

(19) C. A. Bishop and L. K. J. Tong, *J. Amer. Chem. Soc.*, **87**, 50 (1965).
(20) H. W. Wanzlick and U. Jahnke, *Chem. Ber.*, **101**, 3744 (1968).
(21) C. J. R. Adderley and F. R. Hewgill, *J. Chem. Soc. C*, 2771 (1968).
(22) H. Musso and D. Maassen, *Justus Liebigs Ann. Chem.*, **689**, 94 (1965).
(23) H. Musso and D. Bormann, *Chem. Ber.*, **98**, 2774 (1965).

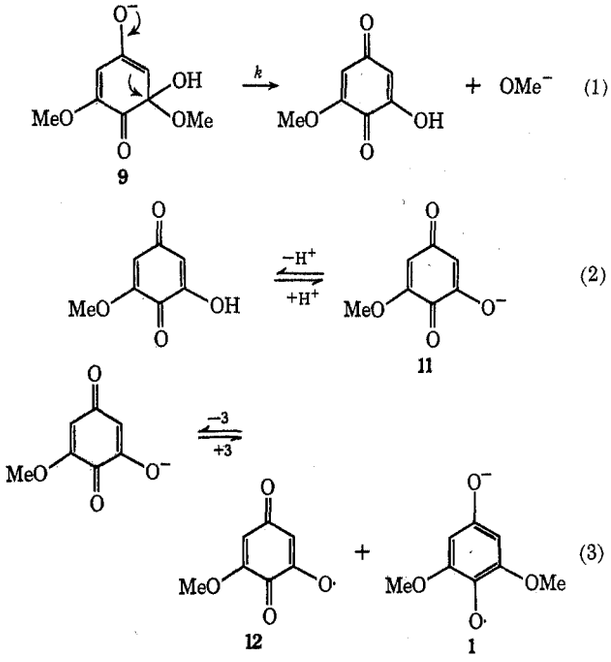
the increase of radical **1** approximated that of the 245 nm band.

Discussion

These results indicate that the formation of semiquinone radicals of types **1** and **5** is preceded by a rapid equilibrium between quinone **3** and OH^- (or OR^-) and adducts such as **9**[16] or **10**.[9] In most alkanolic solvents, replacement of both methoxyl groups from **3** occurs rapidly to yield adduct **10** with the exception of attack by bulky nucleophiles. At very high concentrations of OR^-, direct attack on the OR group may compete with nuclear attack.



To account for the appearance of radical **1** from quinone **3**, we propose the following mechanism in which the decomposition of adduct **9** (or **10**) is rate controlling. This is similar to a mechanism proposed by Eigen[15] for unsubstituted benzoquinone, but differs in the identity of the rate-controlling species.



The compounds **11** and **12** absorb in the 500–550 nm region and their presence would account for the simultaneous appearance of red substances with the appearance of radical species. Radical **12** would decay rapidly; radical **1** is stable. Equilibria 2 and 3 would be expected to form high concentration of products.

This reaction is considerably slower than that reported for the unsubstituted benzoquinone.[15] This may be due to the inability of **9** to enolize rapidly to a reducing species, as was the case for the Eigen and Mathies[15] intermediate.

Conclusion

This quinone–base system appears to be a reasonable model for the behavior of hardwood lignins under basic conditions. Quinone **3** arises from the oxidative degradation of 3,5-dimethoxy-4-hydroxyphenyl moieties in lignin. Quinone **4** would be expected to arise from the degradation of the 4-hydroxy-3-methoxyphenyl moieties, which are also present in hardwood lignins. However, its absence from the reaction mixtures and esr spectra is not unexpected, due to its known instability in aqueous alkaline media.[24,25]

One might predict that a variety of substituted quinones could be found in commercial hardwood lignin solutions, whose structures would depend on the nucleophiles present in the alkaline solutions. Certain applications of the paramagnetic character of lignin preparations, such as potential radical initiators, have already been suggested.[26] The role of alkoxy-substituted quinones in disease resistance of plants may be due to the spontaneous generation of radical intermediates under mildly basic conditions. The activity of the carcinostatic antibiotic Mitomycin C (a substituted benzoquinone) also appears to be the result of its semiquinone radical anion.[27]

Experimental Section

Materials.—2,6-Dimethoxy-*p*-benzoquinone, mp 257–258° (lit.[28] 255°), was prepared from 2,6-dimethoxyphenol by lead tetraacetate oxidation. 2-Methoxy-*p*-benzoquinone, mp 147–148° (lit.[29] 144–145°), was prepared by a chromic acid oxidation[30] of 2-methoxyhydroquinone, which was prepared by a Dakin oxidation of vanillin.[31]

Spectra.—All esr measurements were made in a flat quartz cell in the cavity of an E-3 Varian spectrometer. The instrument operated at 9.5 GHz with a frequency modulation of 100 kHz. In those cases where it was desired to exclude air, there was attached to the cell a special glass mixing device, consisting of two chambers, one of which contained the weighed quantity of solid substrate and the other of which contained the alkaline solution of buffer. Before mixing, the apparatus was flushed with nitrogen and the solution was deaerated by bubbling nitrogen through it for 15 min. The apparatus was then stoppered. It was not feasible to use a solution of the quinone because of its limited solubility in water.

Ultraviolet and visible spectra were measured in a Cary Model 14 spectrophotometer.

Esr Spectra of Alkanolic Solutions.—A 2.5×10^{-3} M solution of quinone **3** in 0.1 *M* sodium ethoxide was prepared by diluting a 5×10^{-3} *M* solution of quinone with an equal volume of 0.2 *M* sodium ethoxide in ethanol. The latter was made by dissolving the appropriate amount of sodium metal in ethanol. This mixture gave a signal for the primary radical **5**. When 1.0 *M* sodium ethoxide was used, a signal for radical **7** was obtained. The same conditions were used to generate radicals **5** and **7** from isopropyl alcohol *n*-propyl alcohol. When the solvent was *tert*-butyl alcohol, with 0.2 *M* potassium *tert*-butoxide, a radical with only one methoxyl exchanged was observed. With 1.0 *M* potassium *tert*-butoxide, distorted spectra were obtained.

Radical signals could be observed in the presence of air, if a sufficiently high concentration of quinone were used (usually

(24) V. Sundman and K. Haro, *Finska Kemistsamfundets Medd.*, **75**, 111 (1966).
(25) W. Flaig, *Chem. Geol.*, **3**, 161 (1968).
(26) T. N. Kleinert, *Holzforsch. Holzverwert.*, **22**, 94 (1970).
(27) C. Nagata and A. Matsuyuma, "Progress in Antimicrobial and Anticancer Chemotherapy," Vol. II, University Park Press, Baltimore, 1970, pp 423–425.
(28) H. D. Becker, *J. Org. Chem.*, **30**, 982 (1965).
(29) T. Fukuzumi, *Bull. Agr. Chem. Soc. Jap.*, **24**, 278 (1960).
(30) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1956, p 745.
(31) H. D. Dakin *Amer. Chem. J.*, **42**, 477 (1909).

about 5×10^{-3} M). At lower concentrations, there was enough dissolved oxygen to scavenge any semiquinone radicals which were formed.

Thin Layer Chromatography of Lignin Extracts.—Brauns native lignin samples such as aspen and Black Spruce[32] (0.1 g) were refluxed for 2 hr (with and without oxygen) in 5 ml of 1.0 M NaOH and neutralized with dilute HCl, followed by extraction with ethyl ether. The concentrated ether extracts were chromatographed on silica gel plates using benzene–ethanol (4:1) by volume) or the organic layer from a mixture of n-butyl alcohol–acetic acid–water (4:1:5 by volume) as developing solvents. The spots were visualized with 2,4-dinitrophenylhydrazine. The first solvent mixture proved best for separation of syringaldehyde from vanillin, while the latter mixture gave better separation of 2,6-dimethoxybenzoquinone from the other two components.

Commercial (alkali) lignin samples such as Meadol and kraft were extracted by boiling water followed by chloroform extraction of the aqueous solutions, or by extracting the solid lignin samples directly with chloroform. The concentrated chloroform extracts were chromatographed using the above developing solvents.

Synthesis of the Semiquinone of 2-Hydroxy-6-methoxybenzoquinone (2).—The structure of the secondary radical **2** was previously confirmed[6] by the Fremy's salt oxidation of the monomethyl ether of phloroglucinol to 2-hydroxy-6-methoxybenzoquinone, and treatment of this compound with alkali to give the corresponding semiquinone.

In the present work, this structure was further confirmed by preparation of 5-iodovanillin by the method of Pepper[33] and conversion to 5-hydroxyvanillin[34] followed by a Dakin oxidation to 2-hydroxy-6-methoxybenzohydroquinone. On treatment with alkali and air, this gives the esr spectrum of **2**.

Kinetic Studies. A. All esr rate studies were carried out under nitrogen in the apparatus described above. After the substrate and buffer were mixed, the spectrum was scanned at definite time intervals and the intensity of the central line of the spectrum was taken as a measure of radical concentration.

B.—Optical rate studies were made by dissolving definite quantities of the quinone in commercial (phosphate and borate) buffer solutions, which had been deaerated with nitrogen for 0.5 hr before mixing. Scanning of the quinone–base mixture was started as soon as the quinone had completely dissolved.

Ether Exchange.—In a typical experiment, quinone **3** (200 mg) was dissolved in 100 ml of ethanol containing 0.01 mol of NaOH. After 3 min of stirring, the red reaction mixture was poured into 200 ml of ice water, acidified, and extracted with chloroform. The pale yellow solid isolated from the chloroform solution was identified as 2,6-diethoxy-p-benzoquinone: mp 125–126° (lit.[9] 126–127°); nmr ($CDCl_3$) δ 1.40 (t, 6), 3.90 (q, 4), 5.75 (d, 2). When the latter was dissolved in CD_3OD in an nmr tube, and a small quantity of solid NaOH was added, instant exchange of ethoxyl groups with CD_3O^- was observed.

Registry No.—1, 33070-34-7; 2, 33070-35-8; 3, 530-55-2; 5 (R = Et), 33070-36-9; 5 (R = i-Pr), 33070-37-0; 7 (R = Et), 33070-38-1; 7 (R = i-Pr), 33070-39-2; 8, 15233-65-5; 9, 33122-24-6; 2-methoxy-p-benzoquinone, 33070-40-5; 2,6-dimethoxyhydroquinone dianion, 33070-41-6.

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Substituent Chemical Shift Correlations. Proton Magnetic Resonance Chemical Shifts for N,N,N-Trimethylphenylammonium Iodides[1a]

GARY R. WILEY[1b] AND SIDNEY I. MILLER*

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

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N-Methyl pmr chemical shifts of 21 meta- or para-substituted N,N,N-trimethylphenylammonium (TMA) iodides were determined in deuterium oxide and acetonitrile. Infinite dilution shifts were obtained from expressions of the type (M = mol/l.) δ (D_2O), Hz = δ^0_o + (28.61 ± 6.19)M and δ (CH_3CN), Hz = δ^0_o + (166.5 ± 5.7)M − (2240 ± 2.16)M^2. The corresponding Hammett correlations were δ^0 (D_2O), Hz = 5.857σ + 217.86 (r = 0.85, N = 17) and δ^0 (CH_3CN), Hz = 5.123σ + 211.0 (r = 0.89, N = 12); one Swain–Lupton surface for our meta-substituted TMA's was given by δ^0 (CH_3CN), ppm = 0.03855 F + 0.1074 R − 3.548 (r = 0.999, N = 7, % R = 64). The proportionality of pmr substituent chemical shifts, or δ–δ relations, between pairs of families was tested. In general, the Hammett and δ–δ linear relations were often poor ($r < 0.9$), while the Swain–Lupton equation was usually good ($r > 0.95$), as judged by the correlation coefficient (r). It can be shown, however, that pmr correlations which depend solely on reactivity constants (σ, F, R) are theoretically deficient and we would discourage their use. The introduction of additional terms, *e.g.*, to correct for substituent magnetic anisotropy, appears to be essential, but the merits of such a hybrid approach are doubtful.

In investigations of the relation between the transmission of electronic effects and substituent chemical shifts (SCS = δ) our group has taken diametrically opposed positions. Initially, we assumed that the usual structure–reactivity correlations of the Hammett (eq 1) or Taft type applied to proton magnetic resonance (pmr) data.[2] Recently, we tested eq 1 on *ca.* 100 systems of the type XC_6H_4–T–H and found that SCS are often poorly represented; that is, correlation coefficients for eq 1 are low ($r < 0.9$).[3] It was also significant that the variations in ρ with the nature of the transmitting group, $-C_6H_4T-$, made little chemical sense.

$$\delta = \rho\sigma + \text{constant} \quad (1)$$

Originally, the compounds (TMA) seemed interesting, because a novel group, namely positive nitrogen, was involved in relaying substituent effects to the methyl protons.[2] Later, the anilinium family became crucial to a new approach to substituent effects, embodied in the Swain–Lupton relation;[4] F and R measure

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