The Application of Molecular Orbital Calculations to Wood Chemistry. VI. The Reactions of Anthraquinone Under Pulping Conditions

Thomas J. Elder Associate Professor[a]; Douglas J. Gardner surnameAssistant Professor[b]; M. L. McKee Associate Professor[c]; S. D. Worley Professor[c]

[a] School of Forestry and Alabama Agricultural Experiment Station Auburn University, Alabama [b] Division of Forestry, West Virginia University, Morgantown, West Virginia [c] Department of Chemistry, Auburn University, Alabama

PLEASE SCROLL DOWN FOR ARTICLE

THE APPLICATION OF MOLECULAR ORBITAL CALCULATIONS TO
WOOD CHEMISTRY.   VI.   THE REACTIONS OF ANTHRAQUINONE
UNDER PULPING CONDITIONS.

Thomas J. Elder, Associate Professor
School of Forestry and
Alabama Agricultural Experiment Station
Auburn University, Alabama

Douglas J. Gardner, Assistant Professor
Division of Forestry
West Virginia University
Morgantown, West Virginia

M. L. McKee, Associate Professor
S. D. Worley, Professor
Department of Chemistry
Auburn University, Alabama

ABSTRACT

Molecular orbital calculations were performed on
anthraquinone, the anthrahydroquinone radical anion,
and dianion. The semi-empirical, self-consistent
fields method of modified neglect of diatomic overlap
(MNDO) was used to calculate energetic and electronic
parameters for the anthraquinone species. The role of
anthraquinone in the depolymerization of lignin is
discussed in terms of the proposed adduct and single
electron transfer (SET) mechanisms.

INTRODUCTION

Since its introduction as a pulping catalyst[1],
anthraquinone (AQ) has received a great deal of
attention from wood chemists, and the chemistry of
anthraquinone in wood pulping has been summarized[2]. It
is generally accepted that oxidation and reduction
reactions occur during anthraquinone pulping, resulting
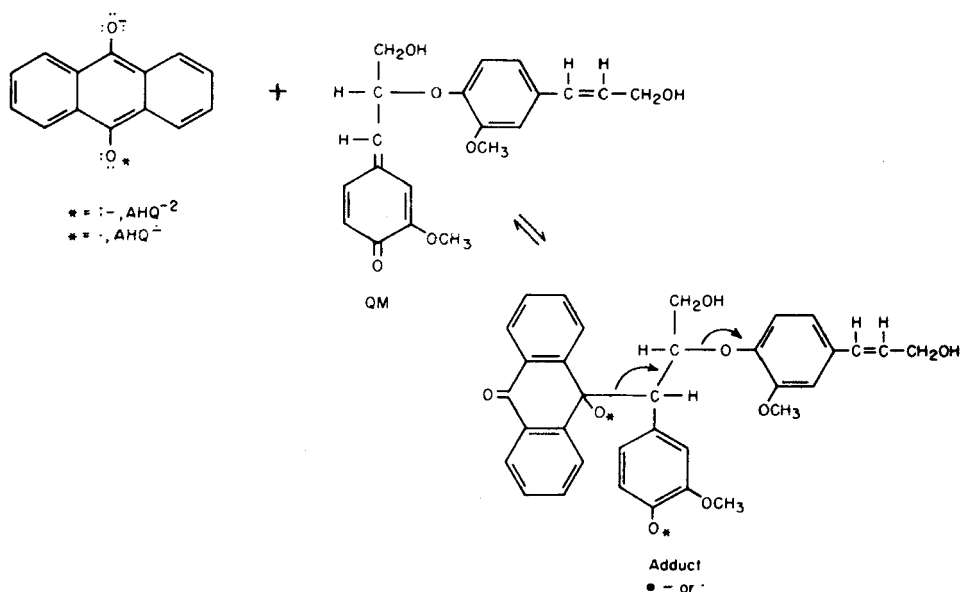
FIGURE 1.   The proposed "adduct" mechanism between anthrahydroquinone and lignin quinone methide (Adapted from Dimmel and Schuller 1986).

in the formation of anthrahydroquinone radical anion $(AHQ\cdot-)$ and dianion (AHQ^{-2}) species, which react with lignin to promote depolymerization.

Two theories have been proposed in attempts to explain the role of the anthrahydroquinone species in the delignification of wood[2,3].   The adduct mechanism (Figure 1) involves bond formation between lignin quinone methide intermediates and anthrahydroquinone (AHQ), while the single electron transfer (SET) mechanism (Figure 2) involves the transfer of an electron between AHQ and lignin followed by fragmentation.   The reactivity and structure of anthraquinone adducts with a large number of lignin
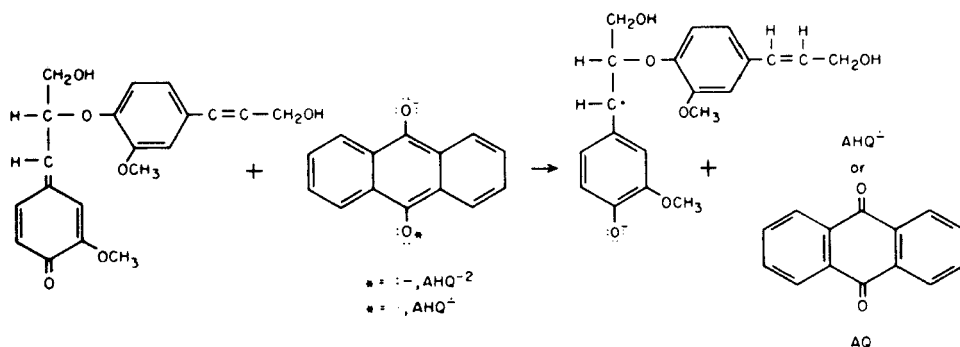
FIGURE 2. The proposed mechanism for single electron transfer between anthrahydroquinone and lignin quinone methide (Adapted from Dimmel and Schuller 1986).

model compounds has been reported by Ralph and co-workers[4]. It was found that adducts can be formed, and that for β-aryl-ether model compounds, anthranol adds much more readily than anthrahydroquinone. The current study will utilize the methods of computational chemistry to examine anthraquinone and the anthrahydroquinone radical anion and dianion in an attempt to elucidate the electronic or energetic factors that may influence the reaction.

Previous research has reported the use of theoretical methods in the study of anthraquinone and related compounds with respect to biochemical and pharmacological properties[5,6,7]. These papers have employed self-consistent Hückel molecular orbital theory[7] and ab initio methods to study electronic spectra[5].

METHODS

The computational procedure used in this study is the molecular orbital package AMPAC[8]. Within AMPAC the MNDO (modified neglect of diatomic overlap) Hamiltonian[9] was used. MNDO is a semi-empirical, self-consistent field, all electron method, which addresses overlap, and has been utilized in studies on a wide variety of compounds[9],[10]. An extensive index of MNDO calculations can be found in Clark[11]. MNDO has been used to calculate a number of molecular properties with experimental accuracy. These properties include heats of formation, dipole moments, vibrational frequencies, electron affinities, ionization potentials, along with the eigenvectors describing the electronic structure of compounds. The MNDO method iteratively optimizes the geometry of a structure to calculate an energetic minimum.

Furthermore, MNDO has been explicitly employed in calculations of electronic excited states[12]. It is reported that the calculated energies of polyenes, such as napthalene agree well with experiment. Success with compounds related to anthraquinone indicate the applicability of this method to the current research.

The structures that will be discussed are shown in Figures 3-6. The trial geometry for each molecule is input by specifying bond lengths, bond angles, dihedral angles, and connectivity for all atoms in the molecule. The initial geometries began with standard bond lengths and angles, and were allowed to optimize, but with retention of D_{2h} symmetry. The same beginning geometry was used for each structure, but with input modifications to reflect the appropriate charge and multiplicity.
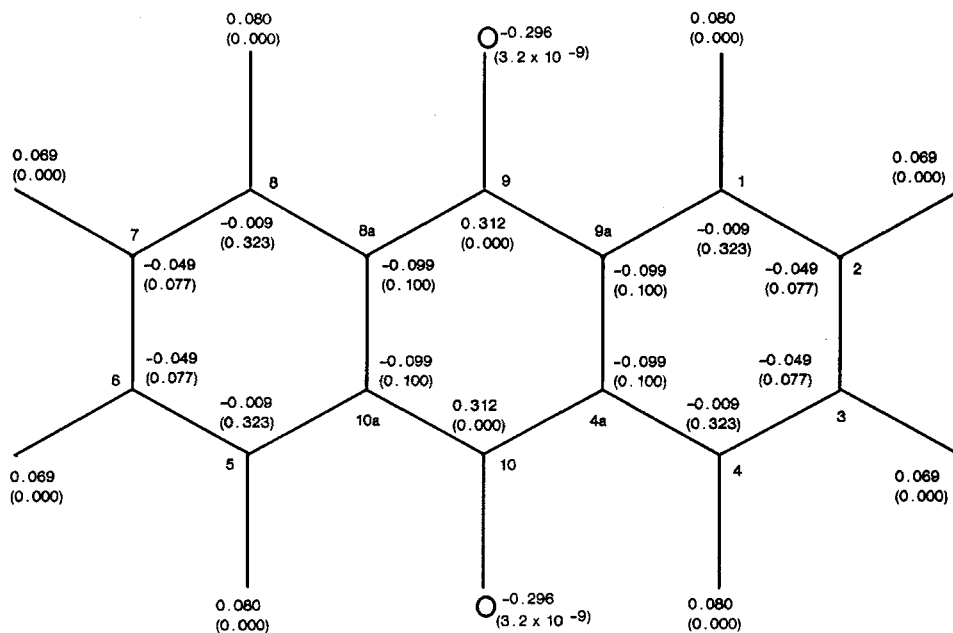
FIGURE 3. Total charge, (HOMO electron densities) for AQ, and the numbering system used throughout this paper.

Both half-electron (HE) and unrestricted Hartree-Fock (UHF) calculations were used to evaluate the anthraquinone anionic radical. The half-electron method for an open shell system is a calculation in which singly occupied orbitals contain not one electron, that would have a single spin, but rather two half electrons of opposite spin. This allows all orbitals to be doubly occupied by electrons, except for the highest, which is occupied by "half electrons". The energy corresponding to the spurious repulsion of the two half-electrons is subtracted from the electronic energy at the end of the calculation.
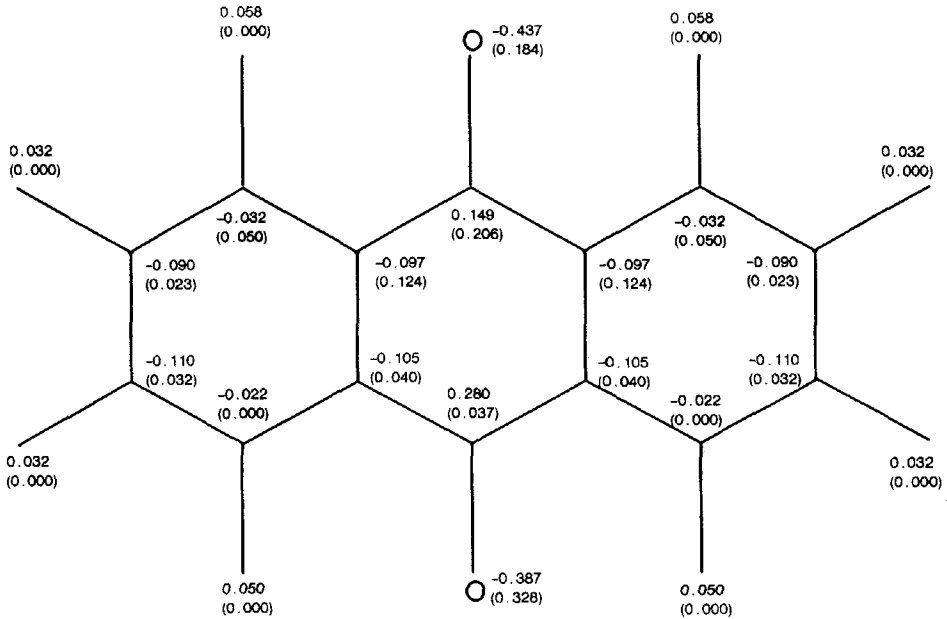
FIGURE 4. Total charge and (SOMO electron densities) for AHQ·−, UHF.

The unrestricted Hartree-Fock calculations determine two sets of molecular orbitals, one for each type of spin[11]. The half-electron method uses derivatives calculated by finite differences in which two self-consistent field calculations are needed for each gradient, and is, therefore, quite slow for the determination of optimized geometries. For this reason, the half-electron results are based on the optimized geometry from the unrestricted Hartree-Fock method, and the performance of a single self-consistent field calculation. In spite of these advantages, there are limitations to the use of the unrestricted Hartree-Fock method. Problems may occur since, with this
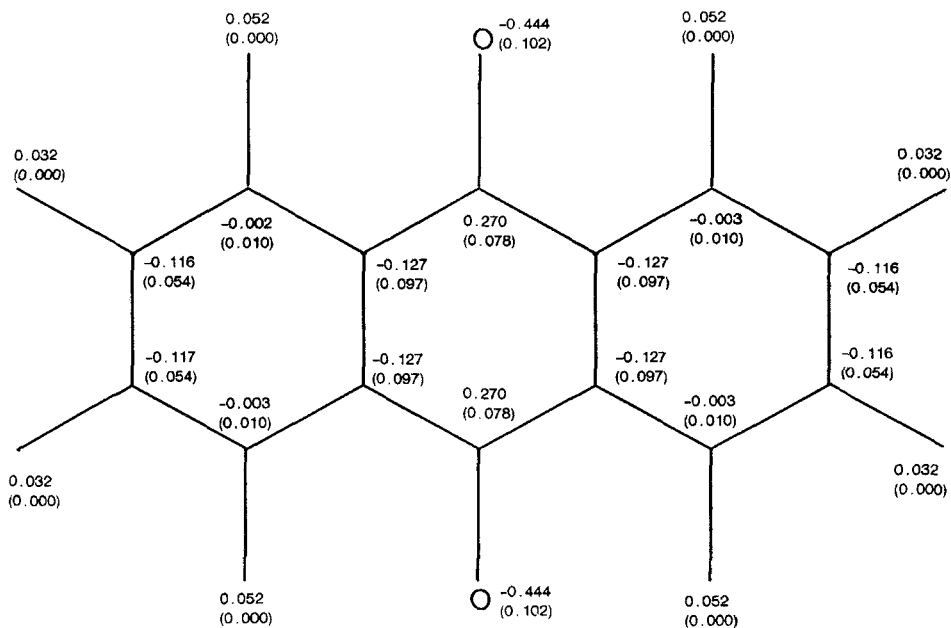
FIGURE 5. Total charge and (SOMO electron densities) for
AHQ·-, HE.

procedure the calculated wave function is not limited
to a single electronic state and can include higher
spin states. This error may lead to energies that are
too low and incorrect spin densities. The parameter of
spin contamination, or $<S^2>$, which is indicative of the
severity of this problem, has an expectation value of
0.75 for doublets, but in reality is always higher.
The lowered energy values predicted mean that direct
comparisons with closed-shell species are not
appropriate. Conversely, the results from half-
electron calculations can be compared directly with
those for closed-shell molecules[11].
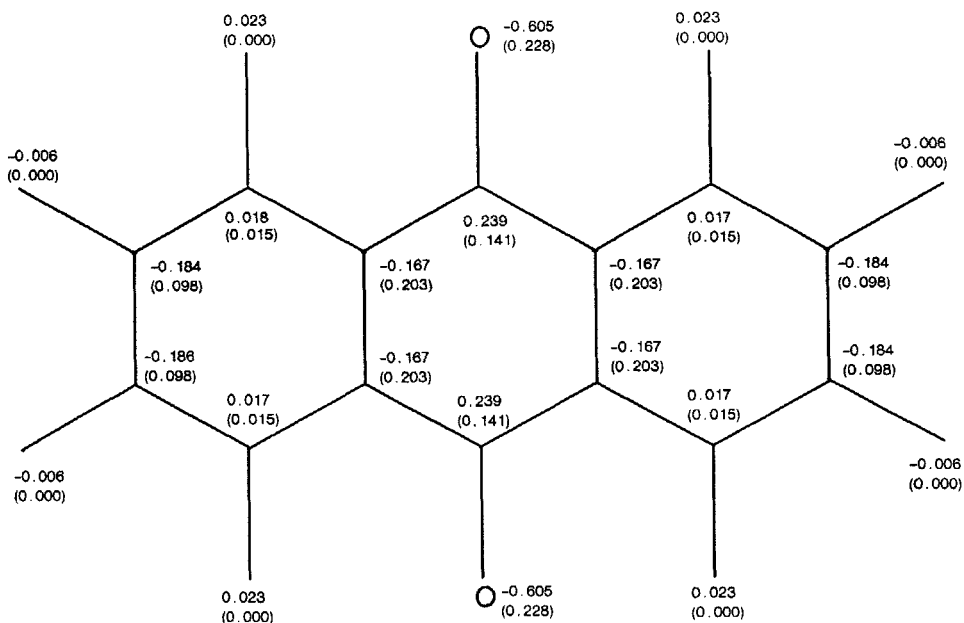
FIGURE 6. Total charge and (HOMO electron densities) for AHQ^{-2}.

In addition, it is a well documented phenomenon that the use of UHF calculations may result in broken spatial and orbital symmetry for symmetric molecules[13]. The mathematical formalism accounting for this behavior is further reported by Bénard and Paldus[14].

All calculations were performed on a MicroVax II minicomputer in the School of Forestry at Auburn University.

RESULTS AND DISCUSSION

The heats of formation for anthraquinone, the radical anion, and the dianion are shown in Table 1.

TABLE 1

Heats of Formation and Total Energy for each Structure.

Structure	ΔH_f(Kcal/mole)
Anthraquinone	-10.508
Anthrahydroquinone radical anion (half electron)	-48.516
Anthrahydroquinone radical anion (unrestricted Hartree-Fock)	-55.957
Anthrahydroquinone dianion	10.871

It can be seen that as expected, the UHF results for
the radical anion are lower than those determined by
the half-electron method. Total charge values, the
electron density in the highest occupied molecular
orbital (HOMO) for AQ and AHQ^{-2}, and the electron
density in the singly occupied molecular orbital (SOMO)
for AHQ·- are shown in Figures 3-6. Under pulping
conditions, AHQ·- and AHQ^{-2} should behave as bases or
nucleophiles, and the reactions under consideration
will be interpreted in terms of Pearson's hard-soft
acid-base (HSAB) theory. In HSAB theory, interactions
between hard acids and hard bases are primarily
controlled by coulombic attraction, as indicated by
total charge values. In contrast, soft-soft
interactions are controlled by the nature of the
frontier molecular orbitals[15]. The important frontier
molecular orbital for nucleophiles or bases is the
HOMO, while electrophiles or acids are influenced by
the lowest unoccupied molecular orbital. The frontier
molecular orbital of radicals is designated as the
singly occupied molecular orbital (SOMO). Furthermore,

hard acids bond preferentially to hard bases, while
soft acids prefer to bond with soft bases[16].

The adduct mechanism (Figure 1) is proposed to
occur through the formation of a bond between carbon 9
or 10 of either the dianion or anionic radical and the
alpha carbon of lignin quinone methide[17]. It has been
suggested that adduct formation should occur through an
ionic pathway rather than a free-radical pathway[18].
Qualitatively, this mechanism is similar to the
reaction of the SH⁻ion in kraft pulping liquor.

Although most radicals are uncharged, and thus
represent soft species, which will combine
preferentially with soft reactants, the negative charge
present on the anthrahydroquinone radical may
complicate this situation. The results of the
unrestricted-Hartree-Fock calculations on the radical
anion (Figure 4) indicate that the C-9 position has a
partial positive charge of 0.149 and a SOMO density of
0.206, while the C-10 has a positive charge of 0.280
and a much lower SOMO electron density of 0.037. All
other carbons in the radical anion have partial
negative charges, such that the C-9 and C-10 sites
represent the positions of greatest positive charge
concentration within the molecule, and the C-9 position
has the largest SOMO density. Based on total charge
values therefore, although the molecule taken as a
whole is a nucleophile, the C-9 and C-10 positions are
the hardest electrophilic sites within the radical, and
the C-9 is the softest site, as calculated by the
unrestricted Hartree-Fock method. It has been
suggested in situations such as these, where both
orbital and charge terms are large, that the charge
control is the more important parameter[19].
Furthermore, the spin contamination determined for this
calculation was 1.77, this along with the inherent

behavior of the UHF technique may explain the broken
symmetry exhibited by the electronic structure.

Similarly, the results of the half-electron
calculations (Figure 5) show that the C-9 and C-10
positions have the highest partial positive charges, at
0.270, and that all other carbons are negatively
charged. Furthermore, the C-8a, C-9a, C-10a, and C-4a
carbons, which are negatively charged, have greater
SOMO electron densities than either C-9 or C-10.

The electronic structure of the anthrahydroquinone
dianion (Figure 6) is somewhat similar to those
exhibited by the radicals. The positions C-9 and C-10
again have the largest partial positive charges, and
the C-8a, C-9a, C-10a, and C-4a sites have larger HOMO
electron densities. As a consequence, the C-9 and C-10
locations should, once more, be relatively hard sites.

In a previous paper, Elder et al.[20] showed that
the alpha carbon of the quinone methide derived from
erythro-guaiacylglycerol-β-coniferyl ether model
compound has a slight negative charge, but that the
LUMO (lowest unoccupied molecular orbital) density at
this position was large. These data combine to suggest
that the alpha position of the quinone methide is a
relatively soft reaction center that should combine
preferentially with a soft nucleophile.

Based on these results, and those of the current
paper, the mechanism responsible for adduct formation
may need to be reassessed. Although the
anthrahydroquinones are anions, the local charge
conditions at the C-9 and C-10 positions are found to
be positive, such that for coulombic attraction to
occur, the reactive site within the quinone methide
must, as indicated by theoretical calculations, be
negatively charged. This constitutes a reversal of the
currently postulated reaction in that the quinone

methide becomes the nucleophile and the anthrahydroquinone is the electrophile, regardless of overall charge.

Since it has been found, however, that the alpha carbon of the quinone methide has only a small negative charge, but a large LUMO density, frontier molecular orbital arguments could logically be invoked to describe the reactivity of this position. In this interpretation, the electron density in the HOMO and SOMO of the dianion and radical anion, respectively, are indicative of favorable reaction sites. The results reported show that for both the dianion and half-electron radical anion, the C-9 and C-10 positions are not the positions of greatest electron density in the appropriate molecular orbitals. The C-9 position of the radical anion, as determined by the unrestricted Hartree-Fock calculations, does have the largest SOMO electron density, but the large $<S^2>$ reported may negate this interpretation.

The single electron transfer mechanism between anthraquinone species and a lignin quinone methide, proposed by Dimmel[2] (1985) (Figure 2), occurs through the acceptance of electrons from reduced anthraquinone species, by β-aryl ether quinone methides, which rapidly fragment to phenolic products. The single electron transfer mechanism has been studied by the use of cyclic voltammetry[21] in which the lignin model quinone methides and anthraquinone are allowed to react in an organic solvent (acetonitrile) at a reduction potential of -0.9v (vs. Ag/AgCl).

The basic premise concerning mechanisms of electron transfer reactions can be rationalized by the fact that the molecules and molecule-ions on either side of the equation are "stable", i.e., strongly

internally bonded species, while the interaction between them is known from ordinary chemical evidence to be weak. Empirical studies of molecules using molecular beam methods to vary the energy of the reactants, and to monitor the energies of the products, have shown, within certain limits of reactant energy, very little kinetic energy is transferred[22].
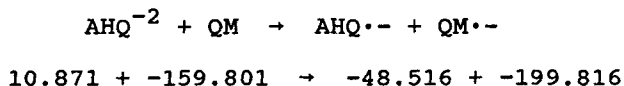
In the current paper, the single electron transfer mechanism has been examined by calculation of the heats of reaction. The results, based on the half-electron calculations for the anthrahydroquinones, are shown in equations 1 and 2. The heats of formation for the quinone methide intermediates (QM) were re-calculated from Elder et al.[20]. From Equation 1 it appears that the reaction between the anthrahydroquinone radical anion and the lignin quinone methide yields products which are only slightly more stable than the reactants. In contrast, Equation 2 show that the reaction of the anthrahydroquinone dianion with the lignin quinone methide is considerably more exothermic.

Equation 1 (HE calculations):

$$AHQ \cdot - \; + \; QM \; \rightarrow \; AQ \; + \; QM \cdot -$$

$$-48.516 \; + \; -159.801 \; \rightarrow \; -10.508 \; + \; -199.816$$
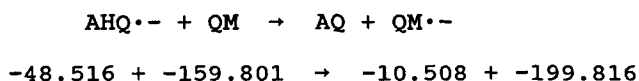
$$\Delta H_f \; = \; -2.007 \; \text{kcal/mole}$$

Equation 2 (HE calculations):

$$AHQ^{-2} \; + \; QM \; \rightarrow \; AHQ \cdot - \; + \; QM \cdot -$$

$$10.871 \; + \; -159.801 \; \rightarrow \; -48.516 \; + \; -199.816$$

$$\Delta H_f = -99.402 \; \text{kcal/mole}$$

These results do not provide information on the free energy of reaction, due to the lack of entropy

data. Based simply on the energy difference between
products and reactants the dianionic reaction appears
to be thermodynamically exothermic and may be favored.
This may be complicated, however by the findings
presented in Table 1 in which the dianion is much more
energetic than the radical species. At this point, it
is not known if the reaction is under thermodynamic or
kinetic control, and the free energy barriers that must
be overcome to reach these structures have not been
calculated.

An alternative interpretation can be based on the
results reported for other electron transfer reactions,
in which small energy differences have been detected.
This may indicate that the single electron transfer
mechanism will occur preferentially through the radical
anion, since the results of the calculations show only
a small difference in energy between products and
reactants.

In summary, the electronic structures calculated
for the anthrahydroquinone species and a previously
reported quinone methide[20] do not provide unequivocal
support for either mechanism. While supporters of the
adduct mechanism may be encouraged by the charge data
presented, the magnitude of the negative charge on the
quinone methide makes such an interpretation tenuous.
The adduct reaction may be further complicated by the
frontier molecular orbital results, indicating that
several other positions are more attractive than the
C-9 and C-10 sites. Based on energetic considerations
for the single electron transfer mechanism, the dianion
may be the active species, but if indeed such
mechanisms are characterized by small energy
differences, the radical anion may provide a more
favorable route for the reaction.

ACKNOWLEDGMENTS

LITERATURE CITED

1. H. H. Holton, Pulp and Paper Canada, 78, T218-T223 (1977).

2. D. R. Dimmel, J. Wood Chem. Technol., 5, 1 (1985).

3. D. R. Dimmel and Lois F. Schuller, J. Wood Chem. Technol., 6, 565 (1986).

4. John Ralph, Richard M. Ede, Nicholas P. Robinson, and Lyndsay Main, J. Wood Chem. Technol., 7, 133 (1987).

5. J. D. Petke, P. Butler, and G. M. Maggiora, Int. J. Quantum Chem., 27, 71 (1985).

6. H. L. K. Schmand, H. Kratzin, and P. Boldt, Liebigs Ann. Chem., 1976, 1560, (1976).

7. T. Kakitani and H. Kakitani, Theor. Chim. Acta (Berl.), 46,259, (1977).

8. Quantum Chemistry Program Exchange, AMPAC: Austin Method 1   Package-QCPE 506, (1987).

9. M. J. S. Dewar and W. Thiel, J. Am. Ch. Soc., 99, 4899 (1977).

10. M. J. S. Dewar and W. Thiel, J. Am Chem. Soc., 99, 4907-4917 (1977).

11. T. Clark, A Handbook of Computational Chemistry, p.98-99, John Wiley & Sons, Inc., New York, N.Y., 1985.

12. M. J. S. Dewar, Marye Anne Fox, Kay A. Campbell, Chia-Chung Chen, James E. Friedheim, Mary K. Holloway, Shi Choon Kim, Phillip B. Liescheski, Ali M. Pakiari, Tze-Pei Tien, Eve Zoebisch, J. Comput. Chem., 5, 480-485 (1984).

13.   M. Ozaki, Prog. Theor. Phys., 62(5), 83-96 (1979).

14.   M. Bénard, J. Paldus, J. Chem. Phys., 72(12), 6546-6559 (1980).

15.   I. Fleming, Frontier orbitals and organic chemical reactions, p. 34-37, Wiley-Interscience, New York, N.Y., 1976.

16.   J. March, Advanced Organic Chemistry, 2nd ed., p. 236-238, McGraw-Hill, New York, N.Y., 1977.

17.   L. L. Landucci, TAPPI, 63, 95, (1980).

18.   L. L. Landucci and J. Ralph, J. Org. Chem., 47, 3486, (1982).

19.   R. F. Hudson, Angew. Chem. (Int. Ed.), 12, 36, (1973).

20.   T. J. Elder, M. L. McKee, and S. D. Worley, Holzforschung, 42(4), 233-240 (1988).

21.   D. R. Dimmel, L. F. Perry, P. D. Palasz, and H. L. Chum, J. Wood Chem. Tech., 5, 15, (1985).

22.   R. D. Cannon, Electron Transfer Reactions, Butterworths, London, 1980.