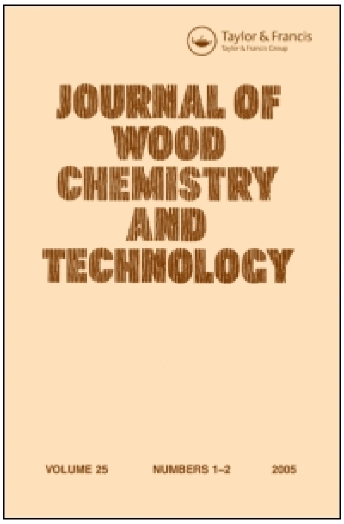


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Some Mechanistic Insights into a Model Bleaching Process of Quinones by Bisulfite and Dithionite: An ESR-CIDEP Study

R. S. Pemberton[a]; M. C. Depew[a]; C. Heitner[b]; J. K. S. Wan[a]
[a] Department of Chemistry, Queen's University, Kingston, Canada [b] Pulp and Paper Research Institute of Canada, Pointe Claire, Canada

To cite this Article Pemberton, R. S. , Depew, M. C. , Heitner, C. and Wan, J. K. S.(1995) 'Some Mechanistic Insights into a Model Bleaching Process of Quinones by Bisulfite and Dithionite: An ESR-CIDEP Study', Journal of Wood Chemistry and Technology, 15: 1, 65 — 83

To link to this Article: DOI: 10.1080/02773819508009500

URL: http://dx.doi.org/10.1080/02773819508009500

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 15(1), 65-83 (1995)

SOME MECHANISTIC INSIGHTS INTO A MODEL BLEACHING PROCESS OF QUINONES BY BISULFITE AND DITHIONITE: AN ESR-CIDEP STUDY

R. S. Pemberton[1], M. C. Depew[1], C. Heitner[2] and J. K. S. Wan[1*]
[1]Department of Chemistry, Queen's University, Kingston, Canada K7L 3N6
[2]Pulp and Paper Research Institute of Canada, Pointe Claire, Canada H9R 3J9

ABSTRACT

The free radical mechanisms of a model bleaching system involving quinones and bisulfite and dithionite in solutions were investigated by time-resolved ESR techniques. The major role of the radical anion, $SO_2^{\bullet -}$, is established with a number of different parent ions, depending upon the environment. The reduced colorless products are mainly the hydroquinone dianions which can effectively be photoionized into semiquinone radical anions (thus the color reversal) and solvated electrons. The strongly polarized semiquinone radical anion and the solvated electron confirm the mechanisms of the photoionization. Addition of calcium carbonate to the system helps to stabilize the hydroquinone dianions by the formation of the Ca^{++}/Q^{2-} ion pairs and thus reduces the effects of photoreversion.

INTRODUCTION

The mechanisms of reactions of bisulfite and dithionite in the enhancement of the brightness of mechanical pulps is not only important to pulp and paper science[1,2] but also of fundamental significance in the understanding of the chemistry of inorganic-organic interactions. Despite the enormous industrial interests, progress towards the basic understanding of the mechanisms of bleaching processes has been minimal in the past few decades. The overwhelming reason, no doubt, is the incomprehensibly complex nature of such a chemical system. Analogous to the fable of nine blind persons examining the elephant, no single physical or chemical technique, no matter how powerful, is able to give a complete true picture of the chemistry of such a complex system. In this paper, we employ the combined ESR - CIDEP techniques to probe the free radical mechanisms in a model bleaching system involving quinones and bisulfites and dithionites. We must emphasize that the overall bleaching processes include other thermal, non-radical reactions which our ESR technique would not be able to follow. Nevertheless, the "insights" obtained here by examining part of the "elephant" will one day hopefully be able to contribute to the unravelling of the complete picture.

The advantages of combined ESR-CIDEP techniques as applied to lignin chemistry and related systems have been demonstrated in our recent studies[3-6]. In this article we establish the major role of the free radical anion, $SO_2^{\bullet-}$, in the bisulfite and dithionite bleaching of quinones in solution. The precursors of this radical anion, however, can be different species, depending upon the acidity/basicity of the solution and the experimental conditions. In addition, photoenhanced bleaching may be involved with some implications for the roles of both the $SO_2^{\bullet-}$ radical anion and the $^{\bullet}OH$ radical. As the effect of photo-induced color reversion may be associated with some of the products generated by the bleaching action, we have also studied the free radical processes in the model solutions after the bleaching has taken place for a period of time. In the case with ortho-quinones, the bleached products are mainly the hydroquinone dianions. Photolysis of the dianions leads to photoionization giving the semiquinone radical anion (color reversal) and unexpectedly the observation of the solvated electrons. Both the semiquinone radical anion and the solvated electron are strongly spin polarized and thus establish the photochemical mechanisms in the reversion. As well, addition of calcium carbonate to the system substantially reduces the amount of photochemically produced semiquinone radical anions and this effect can be explained by the stabilization afforded via the formation of the hydroquinone-calcium ion pairs.

EXPERIMENTAL

All chemicals and solvents were purchased from Aldrich Chemical Co. UV-visible spectra were recorded using a Hewlett Packard 8451A Diode Array Spectrophotometer. Unless otherwise specified, all model solutions contained a 2 or 3-fold excess of hydrosulfite or dithionite with respect to the organic quinones in molar ratios. The model quinones used in the experiments were phenanthrenequinone (PQ), 3,5-di-tert-butyl-ortho-benzoquinone (DBOQ), and 2,5-di-methyl-p-benzoquinone (DMPQ). Solutions were normally not degassed and the bleaching reactions were carried out at room temperature.

Time-resolved CIDEP and conventional ESR experiments were conducted using either a Varian E-104 spectrometer or a customized Bruker X-band spectrometer, as previously described[3]. The light source used for in-situ irradiation was either a super high pressure 200 W mercury lamp, a Lambda-Physik EMG101-MSC XeCl excimer laser at 308 nm, or a Quanta-Ray GCR-11 Nd:YAG solid state laser equipped with all four harmonic generators.

Solutions were flowed through a suprasil flat cell (0.1 mm thick) at rates between 0.1 - 5.0 mL/min in order to minimize any secondary product reactions. Time-resolved polarization evolution profiles for transient radicals were measured at a constant magnetic field and monitored by both a Hitachi 40 MHz digital oscilloscope and a Stanford Research Systems gated integrator/boxcar averager at 5 ns resolution, and both coupled to a 486 PC desk-top micro-computer for analysis. Molecular orbital calculations of thermodynamic and spectral properties of radical ions were carried out using the PM3 semi-empirical method with the Hyperchem program.

RESULTS AND DISCUSSION

In general, the interaction between organic quinones (Q) and inorganic dithionite ions can be represented as an overall two-electron reduction process:

$$Q + S_2O_4^{2-} = Q^{2-} + 2\ SO_2 \qquad [1]$$

The reduction is accompanied by the color change of the solution from yellow (Q) to colorless (Q^{2-}). A similar color bleaching also occurs when bisulfite anions, HSO_3^-, are used instead of the dithionite. In the latter case, the overall mechanisms are uncertain. We therefore began our ESR study by establishing the formations of radical ions in a number of inorganic systems alone under various conditions.

1. Formations of $SO_2^{\bullet-}$ Radical Ions in Dithionite and Bisulfite Solutions.

Aqueous solutions of sodium dithionite were found to be sensitive to air oxidation. They were relatively stable when buffered in a sodium acetate solution (pH 8). At room temperature, a buffered aqueous solution of dithionite exhibits a single band ESR spectrum (g = 2.005), as shown in Fig. 1. Photolysis enhanced slightly the steady-state ESR observation and led to a weak CIDEP spectrum of the same intermediate (Fig. 1a). The time-resolved CIDEP observation definitively showed that the radical species can be generated by photolysis, in addition to the thermal equilibrium of the dissociation. Freezing the solution to 77 K revealed a typical anisotropic ESR spectrum which can be assigned to the $SO_2^{\bullet-}$ radical anions, consistent with the previous literature assignments[7,8]. Fresh unbuffered solutions of dithionite also exhibit the same $SO_2^{\bullet-}$ radical anion spectrum only for a period of several minutes before the parent ions become oxidized. The results suggest the following effective thermal equilibrium:

$$S_2O_4^{2-} = 2\ SO_2^{\bullet-} \qquad [2]$$

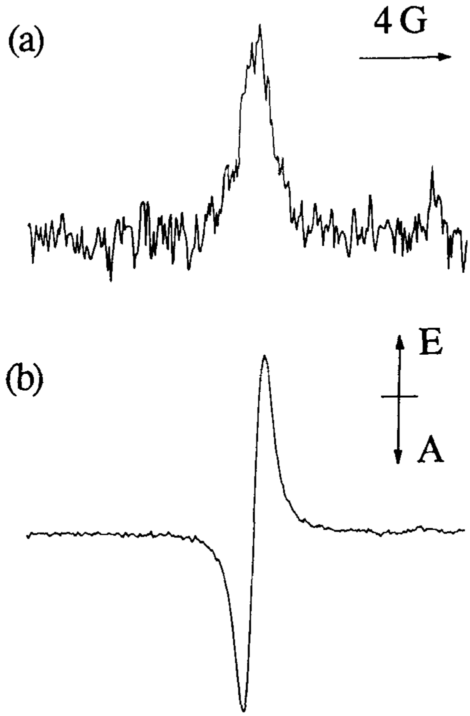


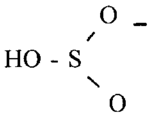
Fig. 1. Simultaneous measurements of the time-resolved CIDEP and the ESR spectra of the $SO_2^{-\bullet}$ radical anions in an aqueous solution of sodium dithionite. (a) Emissive CIDEP spectrum at 1 μs after the laser pulse. (b) First derivative 100 kHz modulated ESR spectrum.

It was, however, surprising that the photo-CIDEP spectrum of $SO_2^{\bullet -}$ is clearly polarized in a totally emissive manner. Such a polarization can not be accounted for by the radical pair theory, when only the identical $SO_2^{\bullet -}$ radicals are involved in the "pair". On the other hand, the large spin-orbit coupling associated with the parent dithionite ion might enhance the intersystem crossing making it possible for the triplet decomposition mechanism. The relatively weak emission spectrum indicates a minor role of the triplet polarization mechanism and it can not exclude the singlet decomposition leading to unpolarized radicals.

Aqueous solutions of sodium bisulfite have a pH of about 5 and are relatively stable to air oxidation. They do not, however, exhibit any thermal ESR spectrum at room temperature. Upon photolysis, a $SO_2^{\bullet -}$ radical anion spectrum can be detected but no polarization is observed. The results suggest that the following thermal dissociation does not occur:

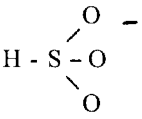
$$HSO_3^- \quad = \quad SO_2^{\bullet -} + {}^{\bullet}OH \qquad [3]$$

This is not surprising as our PM3 molecular orbital calculations show that the solvated bisulfite anion is more stable than the $SO_2^{\bullet -}$ anion by some 400 kJ/mole. On the other hand, photolysis of the bisulfite anion does lead to dissociation as in reaction [3]. Perhaps, it is instructive to consider here the structure of the "bisulfite" anion as the precursor to the photochemical formation of $SO_2^{\bullet -}$ radical anion. It has been proposed by Golding[9] that the structure of bisulfite anion is concentration dependent:



(low concentration)

vs



(high concentration)

Our molecular orbital calculations of these two forms of solvated anions in water indicate that they are both stable with the heat of formation being -944 kJ/mole for the $HO\text{-}SO_2^-$ structure and -900 kJ/mole for the $H\text{-}SO_3^-$ structure. As the sodium bisulfite concentration in the present study was in the range of less than 0.05 M, it is reasonable that the precursor in reaction [3] is the $HO\text{-}SO_2^-$ form which when photodecomposed, yields the $SO_2^{\bullet -}$ radical anion and an ${}^{\bullet}OH$ radical.

It is noteworthy that Jeevarajan and Fessenden[10] have also observed by ESR the formation of $SO_2^{\bullet -}$ radical anion in the photolysis of low concentration of bisulfite ions. While there is no possibility that the counter $^{\bullet}OH$ radicals can be observed in liquid solutions by ESR (due to their rapid anisotropic relaxation and perhaps also their high reactivity), their presence is certainly implicated in the reaction [3]. Even more significant is the implication that bleaching reactions involving bisulfite might be substantially enhanced photochemically by the reactivity of $^{\bullet}OH$ radicals. For the dithionite system, there is also a possibility that some minor thermal reactions such as [4] may lead to a small concentration of bisulfite ions:

$$2\ S_2O_4^{2-} + H_2O = 2\ HSO_3^- + S_2O_3^{2-} \qquad [4].$$

Thus, photoenhancement of bleaching action might be possible in both dithionite and bisulfite systems.

We are as well, very much interested in the other possible structure of the bisulfite anion, $HS\text{-}O_3^-$. This structure represents an inorganic "thiol" and the labile S-H bond would make it also a good radical scavenger. It is well established in literature[11] that organic thiols are good inhibitors for photoyellowing, mainly as effective radical scavengers. An interesting question arises: can the "thiol" form of the bisulfite ion prevent photoyellowing?

At high concentrations, bisulfite ions may also "dimerize" as follows:

$$2\ HSO_3^- = S_2O_5^{2-} + H_2O \qquad [5].$$

In a separate series of experiments with aqueous solutions of $Na_2S_2O_5$, it was demonstrated that thermal decomposition did not occur at room temperature and no $SO_2^{\bullet -}$ radical anions were formed. However, upon photolysis the solution exhibited a strong ESR spectrum of the $SO_2^{\bullet -}$ radical anion. We have therefore covered a variety of reaction conditions and a range of parent anions which can yield $SO_2^{\bullet-}$ radical anions either by thermal decomposition or by photolysis. The results clearly establish the presence of $SO_2^{\bullet-}$ radical anions in the dithionite and bisulfite systems under a variety of experimental conditions. Nevertheless, in the actual bleaching processes a number of secondary complicated equilibria may occur. For example, when $SO_2^{\bullet-}$ radical anion transfers the unpaired electron to some organic substrate and becomes a neutral SO_2 molecule, it can be hydrated rapidly[12] according to the equation

$$SO_2 + H_2O = HSO_3^- + H^+ \qquad [6].$$

Since we have observed in the laboratory that bisulfite anions also bleach the color of quinones, this may explain the persistent bleaching actions of dithionite subsequent to the initial dissociation of the dithionite anions.

We shall next consider their primary chemical processes in terms of electron transfer reduction of organic substrates.

2. *ESR Evidence of the Primary Electron Transfer Reactions of $SO_2^{\bullet-}$ Radical Anions.*

Although it is reasonable to assume that the bleaching reactions of colored organic compounds such as quinones, by $SO_2^{\bullet-}$ radical anions proceed via a primary electron transfer mechanism

$$SO_2^{\bullet-} + Q = SO_2 + Q^{\bullet-} \xrightarrow{SO_2^{\bullet-}} Q^{2-} + SO_2 \qquad [7]$$

the overall bleaching reaction rates are so large in our experiments that the intermediate $Q^{\bullet-}$ radical anions escape direct ESR detection. In systems where the polarized $SO_2^{\bullet-}$ radical anions were generated by pulsed laser photolysis, weakly polarized quinone radical anions as a result of secondary polarization transfer in reaction [7] were sometime observed. However, in a time-resolved photo-CIDEP system, there are other photochemical reactions which can lead to the formation of polarized quinone radical anions (see discussion in a later section). It is also possible that the second step of reduction from $Q^{\bullet -}$ to Q^{2-} may involve other parent (non-radical) anions. We have therefore carried out a separate series of experiments to confirm the nature of the primary electron transfer reactions between $SO_2^{\bullet -}$ radical anions and some standard organic electron acceptors, such as the methyl viologen dications (MV^{2+}) and tetracyanoethylene (TCNE).

When an alcoholic solution of MV^{2+} was added dropwise to all thermal and photochemical solution systems in which $SO_2^{\bullet -}$ radical anions were present, a characteristic ESR spectrum of the well known $MV^{+\bullet}$ radical cations[13] was observed and its intensity increased as the intensity of the single band of the $SO_2^{\bullet -}$ radical anions decreased. The characteristic blue color of the $MV^{+\bullet}$ radical cations was also noted. These observations confirm the primary electron transfer process,

$$SO_2^{\bullet -} + MV^{2+} = SO_2 + MV^{+\bullet} \qquad [8].$$

Fig. 2 shows the ESR spectrum exhibiting both the radical cation and the radical anion in a photolyzed bisulfite solution when a drop of the methyl viologen solution was added.

Similar results were obtained when tetracyanoethylene was used as the electron acceptor. In all cases, the characteristic ESR spectrum of the $TCNE^{\bullet -}$ was observed.

We should emphasize that in the solution containing only bisulfite and MV^{2+} and without photolysis, neither the $SO_2^{\bullet -}$ radical anion nor the $MV^{+\bullet}$ radical cation is observed. Thus, the mechanisms of the primary interactions between the bisulfite anion and an organic substrate, such as quinone, remain uncertain. However, it is reasonable to speculate that bisulfite anions *reduce* the quinones to hydroquinones, similar to the biological oxidation of bisulfites[14]. It is therefore more interesting to examine the photo-reversion phemonenon in the model quinone

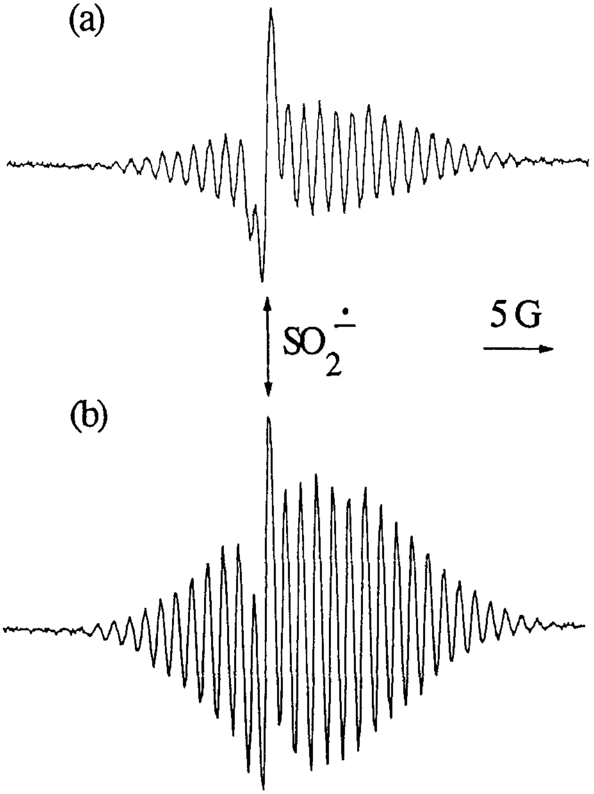


Fig. 2. First derivative 100 kHz modulated ESR spectra observed when an alcoholic solution of MV^{2+} was added dropwise to an aqueous solution of sodium dithionite at room temperature. (a) 3 drops, (b) 15 drops.

systems after bleaching by both dithionites and by bisulfites, as the product hydroquinone would be involved in both cases.

3. CIDEP Observations in the Bleached Model Quinone Systems.

In our earlier studies of the free radical processes in quinones and semiquinones[15] we have shown that the major *self-reaction* of the intermediate semiquinone radicals or the semiquinone radical anions is the disproportionation leading to the hydroquinones (or the dianions) and parent quinones:

$$2\,QH^{\bullet} \quad (\text{or } Q^{\bullet -}) \quad = \quad QH_2 \;\; (\text{or } Q^{2-}) \;+\; Q \qquad [9].$$

In the photo-reversion of the bleached quinone solutions, there are two main photochemical pathways by which the semiquinone radical anions can be regenerated:

$$Q^{2-} \;+ h\upsilon \;=\; Q^{\bullet -} \;+\; e^{-}_{\text{solv.}} \qquad [10]$$

$$R_1R_2C{=}O \;+\; h\upsilon \;=\; {}^{1}(R_1R_2CO) \;=\; {}^{3}(R_1R_2CO)$$
$${}^{3}(R_1R_2CO) \;+ Q^{2-} \;=\; R_1R_2CO^{\bullet -} \;+\; Q^{\bullet -} \qquad [11].$$

The first pathway [10] is the photoionization of the hydroquinone dianion, while the second pathway involves the well known photoreduction of some organic carbonyl functional groups which are invariably present in the lignin system. To simulate this condition, we have carried out a separate series of experiments by replacing quinones with the model lignin carbonyl compound, α-guaiacoxyl-acetoveratrone (GAV), in the bleaching system. Both of these pathways are demonstrated in our time-resolved CIDEP experiments, with some rather surprising and interesting results.

In all the model bleaching systems containing quinones and dithionites/bisulfites, a mixed solvent (usually 50:50 water and alcohol) was used to dissolve the quinones. The CIDEP observations are independent of the bleaching reagent, the dithionite or the bisulfite. In the laboratory experiments both reagents bleached the color of the parent quinone solutions. The solutions were then allowed to stand for up to 16 hours to ensure that they were as complete in the bleaching actions as possible, before the laser-CIDEP measurements. Fig. 3 shows the CIDEP spectrum of the bleached solution containing initially the

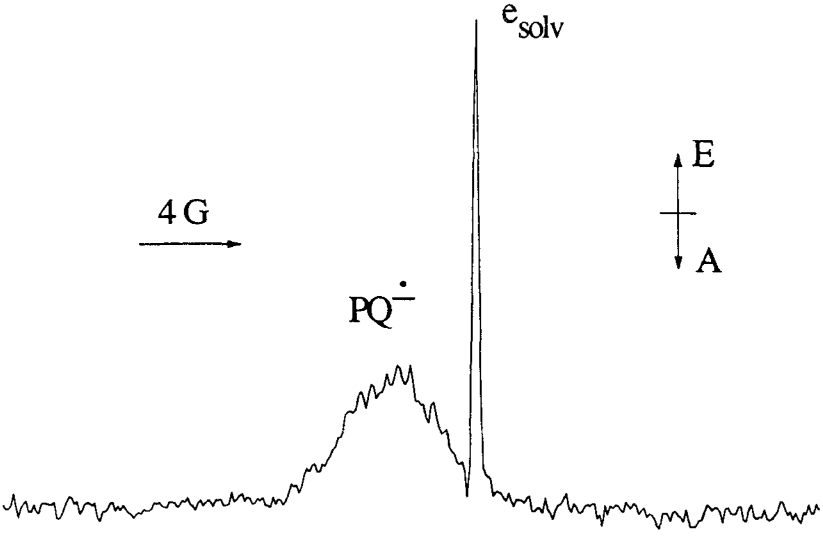


Fig. 3. The time-resolved CIDEP spectrum observed in the **bleached** solution of PQ, at 1 μs after the laser pulse.

quinone PQ. Fig. 4 is the CIDEP spectrum of the bleached solution containing initially the ortho-quinone DBOQ, and Fig. 5 gives the results for the bleached solution of a para-quinone DMPQ.

The remarkable, strongly emissive sharp signal upfield of the polarized semiquinone radical anion in all three cases is due to the solvated electron. Its g-factor is dependent upon the composition of the mixed water/alcohol solvent but is always less than that of the hydroquinone radical anion. This is consistent with the elegant ESR study on solvated electrons in water and alcohols by Shiraishi, Ishigure and Morokuma[16]. The observations of the transient solvated electrons clearly establish the photoionization pathway in reaction [10]. While it is not surprising that photochemical reactions involving quinones and hydroquinones involve spin polarized triplet states due to their efficient anisotropic intersystem crossing and thus leading to a pair of totally, emissively polarized radicals[15],

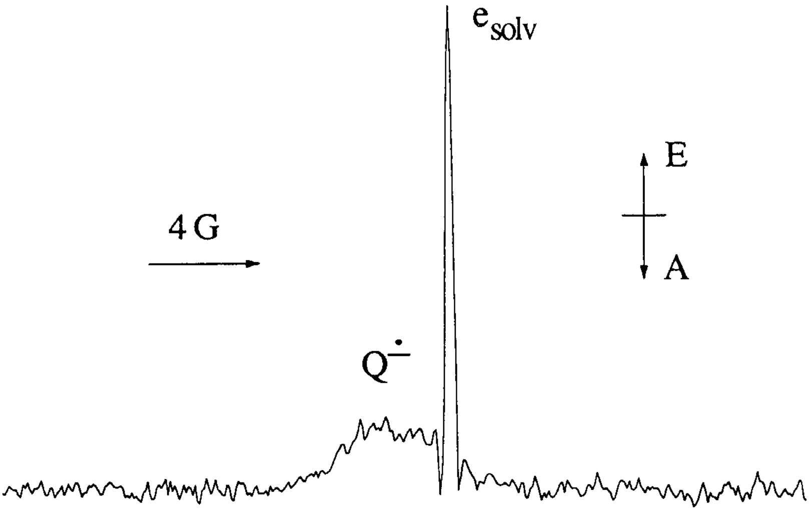


Fig. 4. The time-resolved CIDEP spectrum observed in the **bleached** solution of DBOQ, at 1μs after the laser pulse.

photoionization of phenoxide anions[10] is shown to proceed rapidly via the excited singlet state, giving an absorptively polarized electron. However, photoionization of thiophenoxide produced an emissive signal and the authors[10] suggested that the emissive polarization be best explained by a triplet mechanism. Since the present results show both the hydroquinone radical anion and the solvated electron are emissively polarized, we suggest that the best explanation here would also be that the photoionization in reaction [10] proceeds via a spin polarized triplet state of the hydroquinone dianion. There remains a possibility that some random encounters may lead to emission.

The photochemistry of the model lignin compound GAV has been well established[11] and it is generally accepted that its contribution to the photo-yellowing processes involve the oxidation of the secondary methoxyphenoxy radicals to ortho-quinones. In our experiments, an alcoholic solution of GAV was first photolyzed to a deep yellow color. Sodium dithionite solution was then

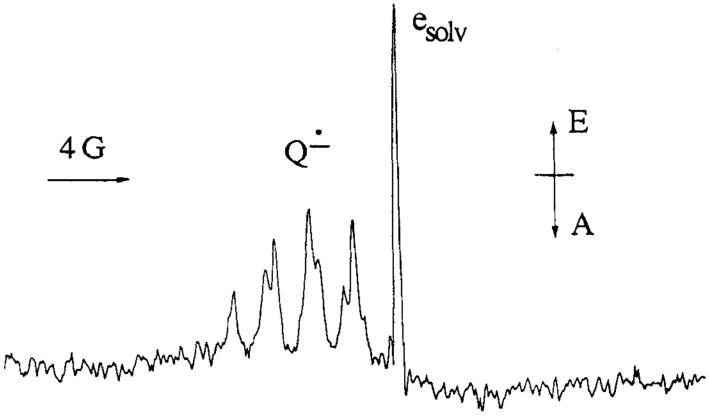


Fig. 5. The time-resolved CIDEP spectrum observed in the **bleached** solution of DMPQ at 1μs after the laser pulse.

added to the yellow solution and the color was bleached, similar to the model quinone solutions. CIDEP measurements were then carried out on these bleached solutions and a typical spectrum is shown in Fig. 6. In addition to the photodecomposition of the remaining GAV in the solution, yielding the emissive three-line spectrum of the phenacyl radical[16] and the unresolved methoxyphenoxy (and possibly together with some unresolved lines due to the quinone radical anions), the emissive signal of the solvated electrons is clearly visible. The results are consistent with the explanation that photo-yellowing of GAV leads to the formation of some ortho-quinones which were then bleached by the dithionites to yield the non-yellow Q^{2-} dianions. Subsequent photolysis of the bleached solution will involve the two pathways [10], and [11] to give the solvated electrons and the further decomposition product-radicals from the ketyl radical anions.

As the solvated electrons are clearly implicated in the bleaching-photoreversion system, further thoughts will be given to the subsequent roles played by them. How do they react with the lignin molecules and do they play a part in the overall photoenhancement in the bleaching processes?

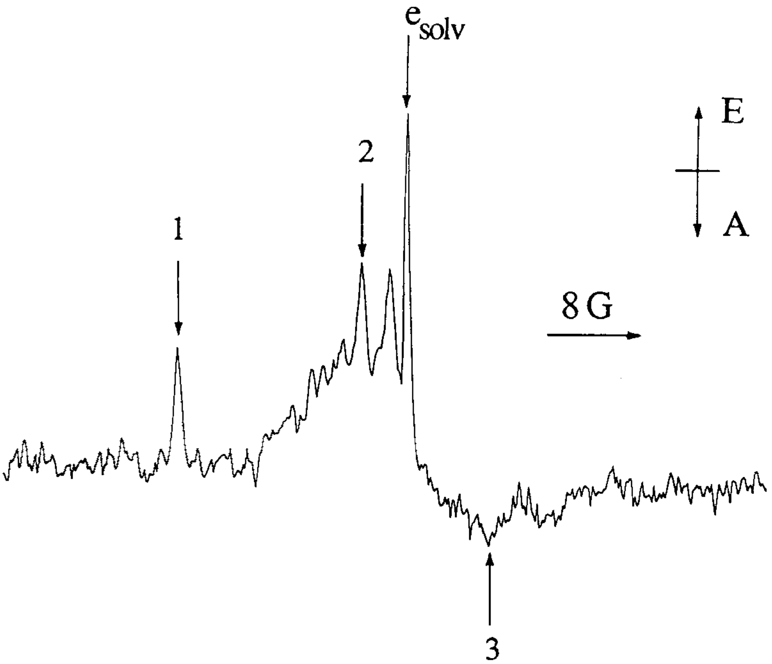


Fig. 6. The time-resolved CIDEP spectrum observed in the **bleached** solution of GAV at 1μs after the laser pulse. The resolved, numbered three-line spectrum is due to the "phenacy" radical and the unresolved broad band is composed of both the semiquinone radical anion and the methoxyphenoxy radical. The sharp emissive line is due to the solvated electron.

4. The Effects of the Addition of Calcium Carbonate.

In the paper making processes, large amounts of calcium carbonate are often used as fillers and/or acidity neutralizers. We have therefore examined the effects of calcium carbonate in our overall model bleaching systems.

When aqueous $CaCO_3$ was added to a phenanthrenequinone, PQ, and dithionite solution, it was noted that the bleaching was more visibly complete within a short period of time. In another series of photobleaching experiments, an alcoholic solution of PQ was first photolyzed to give a strong ESR spectrum of the $PQ^{\bullet-}$ radical anions. Upon addition of $CaCO_3$ to this paramagnetic solution, yellow colloids resulting from the complexation of Ca^{2+} and 2 $PQ^{\bullet-}$ were formed and all solution ESR signals were quenched. On several occasions the yellow colloidal substance was isolated and was found to be paramagnetic. Subsequent addition of dithionite to the solution consumed completely the yellow colloids and the yellow color was bleached. CIDEP measurements of the bleached solution containing Ca^{2+} ions again produced an emissively polarized spectrum of both the solvated electrons and the $PQ^{\bullet-}$ radical anion, but with a much attenuated intensity. These results can be accounted for by the following reactions:

$$2\ PQ^{\bullet-} + Ca^{2+} = Ca(PQ)_2 \downarrow \qquad [12]$$

$$Ca(PQ)_2 + 2\ SO_2^{\bullet-} = Ca^{2+} + 2\ PQ^{2-} + 2\ SO_2 \qquad [13]$$

$$Ca^{2+} + PQ^{2-} = Ca^{2+}/\ PQ^{2-} \qquad [14]$$

$$PQ^{2-} + h\upsilon = PQ^{\bullet-} + e^{-}_{solv.} \qquad [10].$$

The counter carbonate dianions do not play a part in this mechanism but their role is mainly to maintain the acidity/basicity of the system. The complexation of the Ca^{2+} with the quinone dianion in equation [14] explains the effects of stabilization of the dianion and thus reduces the photoionization in equation [10].

The understanding of the role of calcium carbonate in the bleaching and paper making processes should provide further thoughts to improvements of the overall paper chemistry.

CONCLUSION

We have established the intermediacy of the $SO_2^{\bullet-}$ radical anions in the complex processes involved during bleaching of several model quinone solutions by the industrially widely used agents dithionite and bisulfite. The strongly reducing action of this radical anion is demonstrated with definitive electron transfer reactions to the acceptors methyl viologen dication and tetracyanoethylene; its mechanism of action with the quinones is shown by ESR and CIDEP experiments to be similar. Several mechanistic insights have been gained, including the novel involvement of the solvated electron - an intermediate detectable rarely and only by a few very specialized techniques including CIDEP. In addition, the empirical observation of the beneficial effects of Ca^{2+} on the bleaching actions of such agents has been explained.

While such research in model solution systems is a necessary step, and has also furthered understanding of some basic inorganic chemical processes, it examines only a small portion of the "elephantine" problem of understanding bleaching and photoreversion processes in mechanical pulps and papers. Much further work, and widespread collaboration is necessary to achieve this goal.

ACKNOWLEDGMENTS

This research is supported by the program of the Networks of Centres of Excellence, administered by the Natural Sciences and Engineering Research Council of Canada. Enlightening discussions and preliminary assistance by Drs. B.J. Zhao, P. Felder and M. Ioffe, are gratefully acknowledged.

REFERENCES

1. L.R. Beath, W.G. Mihelich, S.B. Beaulieu and D.J. Wild, Proc. International Mechanical Pulping Conference, Stockholm, 21, 1 (1973).
2. W.H. Rapson, M. Wayman, and C.B. Anderson, Pulp Paper Mag. Can., 66, T253 (1965).
3. I.A. Shkrob, P. Felder and J.K.S. Wan, J. Am. Chem. Soc., 115, 5227 (1993).

4. I.A. Shkrob, M.C. Depew and J.K.S. Wan, Chem. Phys. Lett., 202, 133 (1993).

5. J.K.S. Wan, M.Y. Tse and C. Heitner, J. Wood Chem. Technol., 13, 327 (1993).

6. I.A. Shkrob, M.C. Depew and J.K.S. Wan, Res. Chem. Intermed., 17, 271 (1992).

7. P.W. Atkins, A. Horsefield and M.C.R. Symons, J. Chem. Soc., 5220 (1964); H.C. Clark, A. Horesfield and M.C.R. Symons, J. Chem. Soc., 7 (1961).

8. K.P. Dinse and K. Mobius, Z. Naturforsch. A, 23, 695 (1968); A. Reuveni, Z. Luz and B.L. Silver, J. Chem. Phys., 53, 4619 (1970); R. Rinker, T.P. Gordon, D.M. Mason and W.H. Corcoran, J. Phys. Chem., 63, 302 (1959).

9. R.M. Golding, J. Chem. Soc., 3711 (1960).

10. A.S. Jeevarajan and R.W. Fessenden, J. Phys. Chem., 96, 1520 (1992).

11. For example, see Chapters 7 and 8 in C. Heitner and J.C. Scaiano, Eds., "Photochemistry of Lignocellulosic Materials", ACS Symposium Series 531, 1993, and references therein.

12. D.H. Petering, in "Biochemical Effects of Environmental Pollutions", S.D. Lee, Ed., Ann Arbor Science Publishers, 1977, p. 293.

13. W.R. Dunham, J.A. Fee, L.J. Harding and H.J. Grande, J. Magnetic Reson., 40, 351 (1980).

14. C. Mottley, R.P. Mason, C.F. Chignell, K. Sivarajah and T.E. Eling, J. Biol. Chem., 257, 5050, (1982).

15. M.C. Depew and J.K.S. Wan, in "The Chemistry of Quinonoid Compounds", S. Patai and Z. Rapport, Eds., Wiley & Sons, New York, 1988, Vol. 2, Chapter 16, p. 963.

16. H. Shiraishi, K. Ishigure and K. Morokuma, J. Chem. Phys., 88, 4637 (1988).

17. The reference to a "phenacyl" radical is not quite accurate. The α-methylene proton hyperfine coupling constant is in the range of 15-17 gauss, indicating a significant delocalization of the unpaired spin density onto the "carbonyl" oxygen.