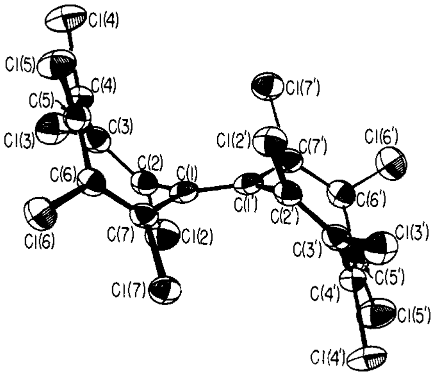


Figure 1. Configuration of the perchloroheptafulvalene molecule, $C_{14}Cl_{12}$, which possesses crystallographic site symmetry C_i-$\bar{1}$; its geometry closely conforms to C_{2h}-$2/m$ symmetry. Intra-ring bond lengths are C(1)–C(1′), 1.332 (5) Å; C(1)–C(2), 1.484 (4) Å; C(2)–C(3), 1.331 (4) Å; C(3)–C(4), 1.459 (4) Å; C(4)–C(5), 1.342 (4) Å; C(5)–C(6), 1.465 (4) Å; C(6)–C(7), 1.333 (4) Å; C(7)–C(1), 1.487 (4) Å. The six independent C–Cl bond lengths range from 1.724 (3) to 1.728 (3) Å. The nonbonding intra-ring Cl···Cl contacts range from 3.098 (1) to 3.170 (1) Å. Intra-ring angles subtended at C(n) are C(1), 112.3 (2)°; C(2), 121.7 (2)°; C(3), 122.3 (2)°; C(4), 124.1 (2)°; C(5), 125.2 (2)°; C(6), 122.3 (2)°; C(7), 121.2 (2)°. The anisotropically refined carbon and chlorine atoms are shown as 50% probability ellipsoids.

(**5**), mp 255° (lit.[15] 255°), with an infrared spectrum identical with that of an authentic sample. In view of the lability of the analogous hydrocarbon the remarkable thermal stability and resistance to oxidation of **1** provide another dramatic example of the great change in properties often conferred on a hydrocarbon by complete chlorine substitution.

[15] J. D. Brooks, P. J. Collins, and H. S. Silberman, *Aust. J. Chem.*, **19**, 2401 (1966); M. Ballester, *Bull. Soc. Chim. Fr.*, 7 (1966). We are grateful to Dr. Brooks of CSIRO, Australia, and Professor Ballester of Instituto de Quimica "Alonso Barba," Spain, for authentic decachlorophenanthrene samples.

Michihiro Ishimori, Robert West*
Boon Keng Teo, Lawrence F. Dahl
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received July 31, 1971

Electron Paramagnetic Resonance Spectra of Semiquinone Intermediates Observed during the Photooxidation of Phenol in Water

Sir:

We wish to report the observation of electron paramagnetic resonance (epr) signals of semiquinone intermediates during the photooxidation of phenol in water containing NaOH. These spectra were obtained at room temperature using a Varian E-12 spectrometer[1] to which we have added a flow system driven by a peristaltic pump. With this system, flow rates could be varied between 0.1 and 36 ml/min. Oxygen was excluded by purging the solution with argon which was bubbled through a series of chromous ion scrubbers.[2]

The epr spectrum obtained during irradiation with the full spectrum of a Hanovia mercury–xenon arc lamp is dependent upon the flow rate as can be seen in Figure 1. Figure 1A which is the spectrum of p-benzosemiquinone (proton–electron hyperfine, 2.37 G)[3] is obtained at flow rates greater than 1.5 ml/min. The spectrum in Figure 1B is obtained at flow rates between 0.3 and 1.5 ml/min and is a superposition of spectra due to p-benzosemiquinone and oxybenzosemiquinone (three inequivalent protons with hyperfine 4.82, 1.32, and 0.60 G).[4] At flow rates below 0.3 ml/min, the spectrum given in Figure 1C is obtained. This is a superposition of spectra due to oxybenzosemiquinone and dioxybenzosemiquinone (two equivalent protons with hyperfine 0.79 G).[5] A weak line due to p-benzosemiquinone can be detected, also.

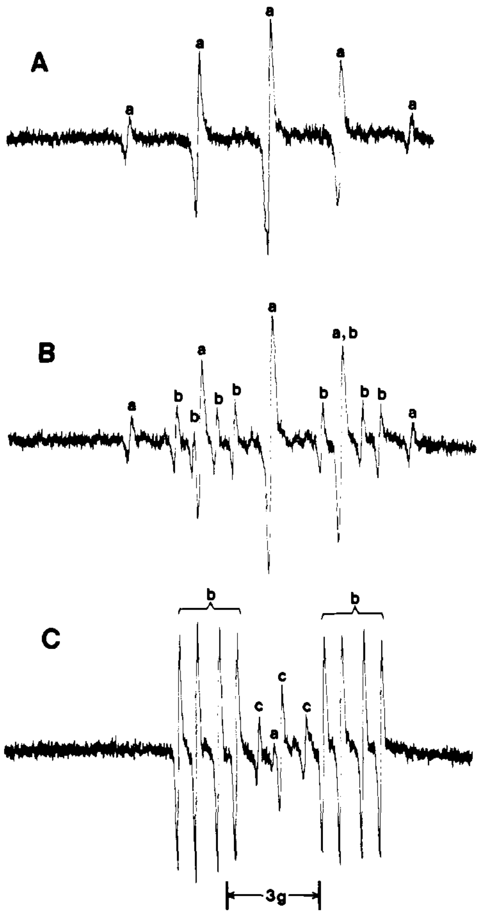


Figure 1. Epr spectra during irradiation of a solution of 0.02 M phenol in water at pH 12. Flow rate: (A) 1.5 ml/min, (B) 0.3 ml/min, and (C) 0.1 ml/min.

The appearance of these spectra depends upon the pH of the media. Between pH 11 and 12, only p-benzosemiquinone is observed, even at very low flow rates. Above pH 12, all of the intermediates are observed depending upon the flow rate employed as illustrated above. In addition we have observed a dependence upon the phenoxide ion concentration. This dependence does not appear to be the result of only the change in the absorbance of the solution. For example, changing the phenoxide concentration from 5×10^{-2} to 1×10^{-3} M decreases the amount of light absorbed by a

---

[1] The authors are indebted to Dr. M. Fujimoto for allowing the use of his spectrometer.

[2] N. Bunce, personal communication.

[3] Reported value, 2.37 G: M. Adams, M. Blois, Jr., and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958).

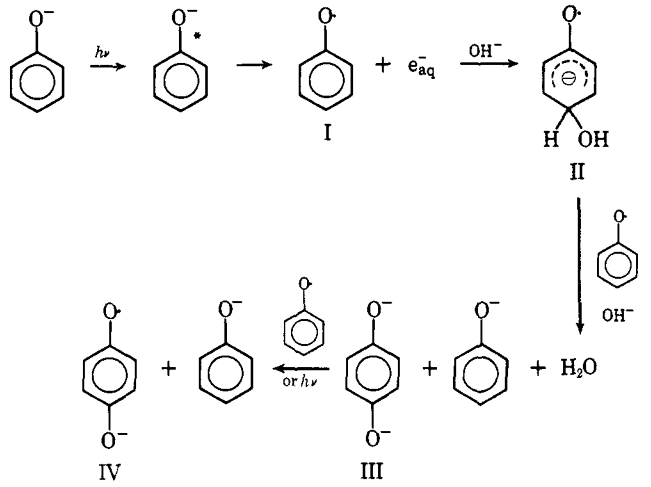
[4] Reported values, 4.8, 1.3, and 0.60 G: J. Stone and W. Waters, *J. Chem. Soc.*, 1488 (1965).

[5] Reported value, 0.79 G: M. Das and G. Fraenkel, *J. Chem. Phys.*, **42**, 1350 (1965).

factor[6] of 15, whereas the intensity of benzosemiquinone quintet is reduced by only a factor of 3.

A mechanism consistent with these observations is given in Scheme I.[7] In this mechanism, irradiation of the sample results in ejection of an electron from the phenoxide ion to produce a phenoxyl radical (I) and a solvated electron.[8] Addition of hydroxide ion to the para position of the phenoxyl radical followed by hydrogen atom abstraction by another phenoxyl radical leads to the dianion of *p*-hydroquinone (III). This dianion is oxidized by another phenoxyl radical to produce *p*-benzosemiquinone (IV). An alternative route to *p*-benzosemiquinone is irradiation induced electron ejection from III (see below). Addition of hydroxide ion to *p*-benzoquinone leads by the same process to the oxy- and dioxybenzosemiquinones. The solvated electron probably disappears according to various mechanisms[9] which do not alter the mechanism proposed in Scheme I.

Scheme I



Qualitatively, this mechanism is consistent with the dependence upon hydroxide ion concentration and upon flow rate. When the concentration of hydroxide ion is low, addition to *p*-benzosemiquinone is sufficiently slow so that the reaction does not proceed on to the oxy- and the dioxysemiquinones, even at slow flow rates. As a result, only the spectrum of *p*-benzosemiquinone is observed at all flow rates employed. At higher hydroxide ion concentrations, the rate of addition to *p*-benzosemiquinone is accelerated, and the spectrum becomes dependent upon the flow rate. A fast flow rate results in a residence time too short compared to the rate of formation of the oxy- and dioxybenzosemiquinones. Consequently, only *p*-benzosemiquinone is observed. As the flow rate is reduced, oxybenzosemiquinone is observed when its rate of formation becomes competitive with the flow rate. At even longer residence times, there is sufficient time to build up measurable amounts of dioxybenzosemiquinone.

An alternative mechanism involving the absorption of light by the phenoxyl radical (I) does not seem possible because the concentration of this radical is too low. Since the epr signal of this radical is not observed, the concentration of this radical must be less than 10^{-6} *M*. Consequently, because the molar extinction coefficients of the phenoxyl radical at 4000 and 2900 Å are only 2200 and 4000, respectively,[10] a mechanism involving excited phenoxyl radical seems unlikely.

To test the possibility that the dianion of *p*-hydroquinone (III) or *p*-benzosemiquinone (IV) is absorbing light and being oxidized by a route different from Scheme I, we obtained the epr spectrum during irradiation of a solution of *p*-hydroquinone under the same conditions used for the phenol. Under these conditions, only the spectrum for *p*-benzosemiquinone is observed. The spectra for the oxy- and dioxybenzosemiquinone could not be detected, even at very slow flow rates. This result rules out a mechanism involving direct excitation of III and IV. Furthermore, it rules out the possibility that minute quantities of oxygen in the solution are responsible for the oxidation. Thus, the presence of the phenoxyl radical appears to be essential for the oxidation of *p*-benzosemiquinone and oxybenzosemiquinone.

As indicated earlier, the epr intensity is not linearly dependent upon the amount of light absorbed. Self-quenching by phenoxide ion probably is not the main reason for this lack of linearity because the Stern–Volmer constant would be about 100 M^{-1} for this process. Since the lifetime of the excited singlet state of the phenoxide ion appears to be fairly short,[11,12] this value seems too large. Competing reactions involving phenoxyl radicals (such as dimerization[8a]) could account for this lack of linearity.

In Scheme I, several steps involve reaction of intermediates with the phenoxyl radical. The possible involvement of other radicals as substitutes for the phenoxyl radical in these steps cannot be precluded at this time. However, by addition of ethanol to the solution we have been able to rule out the reaction of hydroxyl radical with the phenoxyl radical to form III. It was found that the presence of ethanol had no significant effect on the epr intensities. Since ethanol is a scavenger of hydroxyl radicals,[13] we conclude that this radical is not involved in the reaction. More detailed pH and light intensity studies are underway to obtain quantitative kinetic data.

Acknowledgment. This work is supported in part by PRF Grant No. PR4904 and NRC Grant No. A5874.

Micha Tomkiewicz,[14a] Arie Groen,[14b] Michael Cocivera*
Chemistry Department, University of Guelph
Guelph, Ontario, Canada

Received July 24, 1971

---

[6] This value is obtained using a value of 0.05 cm for the cell length and an average value of 500 for the extinction coefficient of the phenoxide ion.

[7] Intermediate II has been proposed to account for some of the products observed in the photooxidation of phenol by Joschek and Miller. Because of the long periods of irradiation employed in the study, we feel that the results are not directly applicable to our work. See H. Joschek and S. Miller, *J. Amer. Chem. Soc.*, **88**, 3273 (1966).

[8] (a) G. Dobson and L. Grossweiner, *Trans. Faraday Soc.*, **61**, 708 (1965); (b) J. Jortner, M. Ottolenghi, and G. Stein, *J. Amer. Chem. Soc.*, **85**, 2712 (1963); (c) E. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2016 (1963).

[9] (a) E. Hart, *Annu. Rev. Nucl. Sci.*, **15**, 125 (1965); (b) H. Joschek and L. Grossweiner, *Advan. Chem. Ser.*, No. **50**, 279 (1965).

[10] E. Land and M. Ebert, *Trans. Faraday Soc.*, **63**, 1181 (1967).

[11] R. Williams and J. Bridges, *J. Clin. Pathol.*, **17**, 371 (1964).

[12] Electron ejection from substituted phenols appears to occur *via* the excited singlet state rather than the triplet state: H. Joschek and L. Grossweiner, *J. Amer. Chem. Soc.*, **88**, 3261 (1966).

[13] G. Adams, J. Boag, and B. Michael, *Trans. Faraday Soc.*, **61**, 1417 (1965).

[14] (a) NRC Postdoctoral Fellow; (b) NRC Graduate Fellow.