Electron Paramagnetic Resonance and Nuclear Spin Polarization Study of the Photooxidation of Phenol in Water

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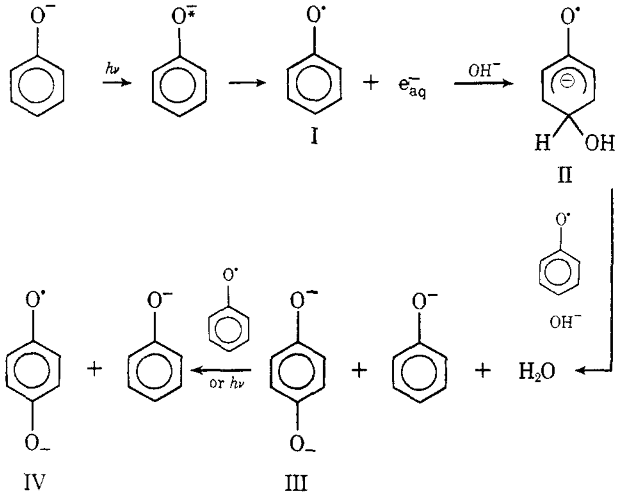
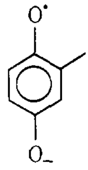
Received February 2, 1972

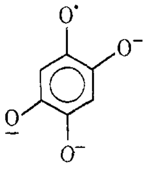
Abstract: Irradiation of a deoxygenated solution of phenol in water at pH > 8 results in the formation of benzosemiquinone intermediates which can be detected by means of electron paramagnetic resonance spectroscopy (epr). Because of the transient nature of the intermediates, a flow system was employed to increase the intensity of their epr spectra. The intermediates which were observed are *o*- and *p*-benzosemiquinone as well as oxy- and dioxybenzosemiquinone. It was found that the concentration of intermediates depends on the pH of the solution and the flow rate. Oxy- and dioxybenzosemiquinone were observed only above pH 12 and at low flow rates. Because oxygen is excluded from the system, a mechanism involving hydroxide ion attack of the phenoxyl radical is proposed. The phenoxyl radical is formed by photoelectron ejection from the phenoxide ion. Support for the proposed mechanism is obtained from nuclear spin polarization observed by means of nuclear magnetic resonance spectroscopy. During irradiation of a solution of phenol at pH 11 in 99.8% D_2O, both the ring protons of phenoxide ion and the HDO proton exhibit nuclear spin polarization. This polarization is consistent with the mechanism used to explain the epr results.

In a previous paper,[2] we reported preliminary results of a study of the photooxidation of phenol in water at pH > 7. In the absence of oxygen, benzosemiquinone intermediates were detected by means of electron paramagnetic resonance (epr) spectroscopy. Since evidence indicates that phenoxide ion undergoes photoelectron ejection,[3] we suggested that the semiquinone intermediates occur *via* oxidation of the phenoxyl radical I. Based on the fact that the relative amounts of these intermediates depend on the concentration of hydroxide ion and that oxidation of *p*-benzosemiquinone (IV) requires the presence of phenoxyl radical, we suggested the mechanism given in Scheme I. In this mechanism, phenoxide ion which has been promoted to an electronic excited state emits an electron to form a phenoxyl radical (I) and a hydrated electron. Attack by hydroxide ion leads to the formation of intermediate II. An additional phenoxyl radical removes the hydrogen atom from II and in the presence of base results in the formation of the dianion of *p*-hydroquinone (III) and phenoxide ion. *p*-Benzosemiquinone (IV) is obtained either by electron transfer from III to I or by photoelectron ejection from III. By the same process, IV is oxidized to oxybenzosemiquinone (V) which in turn is oxidized to dioxybenzosemiquinone (VI). In the present paper, we present additional epr and nuclear magnetic resonance (nmr) data which support this mechanism.

Scheme I




V


VI

Experimental Section

Materials. The organic compounds were purified either by sublimation or recrystallization. Phenol-*2,4,6-d_3* was prepared by H–D exchange in D_2O using 3 M DCl as a catalyst. The progress of the exchange was monitored by means of proton nmr. The water used as solvent was distilled. Deuterated water was obtained from Diaprep and used without further purification.

Solutions. Solutions were prepared gravimetrically. The pH was controlled by means of a borax buffer. When solutions were degassed, a vacuum line equipped with an oil diffusion pump was employed. Pressures less than 2 μ were attained. In addition for the epr experiments, oxygen was purged from the solution by bubbling in argon gas. As an added precaution, chromous ion scrubbers were used to remove any oxygen which might be in the argon. These scrubbers consisted of 15 g of $HgCl_2$, 5 g of Zn dust, 5 g of $CrCl_3$ and 200 ml of H_2O.[4]

Epr and Nmr. The epr spectra were obtained at room temperature using a Varian E-12 spectrometer to which was added a flow system driven by a peristaltic pump. With this system, flow rates could be varied between 0.1 and 36 ml/min.

The nmr spectra were obtained at 100 MHz using a Varian HA 100-15 spectrometer, in which the rf unit was modified to operate in a time-division mode.[5] In this mode, the gating of the transmitter and receiver is effected by means of Tektronix Model 160

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[1] (a) National Research Council Postdoctoral Fellow; (b) National Research Council Graduate Fellow.

[2] M. Tomkiewicz, A. Groen, and M. Cocivera, *J. Amer. Chem. Soc.*, **93**, 7102 (1971).

[3] (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).

[4] N. Bunce, personal communication.

[5] S. Meiboom and D. Gill, *Rev. Sci. Instrum.*, **29**, 688 (1958).

pulsing units. This mode permits the use of an all-quartz, variable-temperature probe which was fabricated in this laboratory according to a design by Meiboom.[6] Consequently, the sample can be irradiated while in the probe. Quartz sample tubes were obtained from Wilmad.

For both the epr and the nmr experiments, the light source was a Hanovia 1000-W high-pressure mercury xenon lamp in a Schoeffel housing. The nearly collimated light from the housing was condensed on the sample using one *f* 2.0 and two *f* 2.5 lenses.

Results and Discussion

Epr. The epr spectra were obtained by irradiating solutions of phenol in water at pH values between 8.2 and 14. The concentration of phenol ranged from 10^{-3} to 5×10^{-2} *M*. No filtering was employed; consequently, the solution was irradiated with the whole spectrum of the mercury arc lamp. When the irradiation was stopped the epr spectrum disappeared. Although spectra could be obtained at flow rates as low as 0.1 ml/min, no radicals could be detected when the flow was stopped. Thus, to maintain a measurable concentration of radicals, it was necessary to flow the solution through the cavity. For most of the solutions, oxygen was excluded by purging with argon which had been bubbled through a series of chromous ion scrubbers to remove traces of oxygen. Consequently, the oxidation of phenol is occurring without involving molecular oxygen since the oxygen is at too low a concentration to be significant kinetically. Additional support for this conclusion is given below.

As illustrated in Figure 1, the details of the epr spectrum are dependent on the flow rate and the pH of the solution. Spectra A, B, and C are obtained at pH 12 and the following flow rates: greater than 1.5 ml/min, between 1.5 and 0.3 ml/min, and below 0.3 ml/min, respectively. Spectra D and E are obtained at pH 9.8 and flow rates of 6 and 10 ml/min, respectively. At flow rates higher than 10 ml/min there is no improvement in the signal-to-noise ratio. Spectrum A can be analyzed in terms of a radical having four equivalent protons with a hyperfine coupling constant (2.37 G) which is identical with the value measured for *p*-benzosemiquinone (IV).[7] Spectrum B is a superposition of the spectrum of IV (lines labeled a) and the spectrum of oxybenzosemiquinone (V) (lines labeled b) which has three inequivalent protons with hyperfine coupling constants 4.82, 1.32, and 0.60 G as found previously.[8] Spectrum C is a superposition of the lines due to V (labeled b) and dioxybenzosemiquinone (VI) (two equivalent protons, hyperfine 0.79 G).[9] In addition, the central line of *p*-benzosemiquinone (IV) (labeled a) is observed. The lines of IV (again labeled a) are observed also in spectra D and E which were obtained at lower pH and faster flow rates than the other spectra. The lines labeled d in spectrum D can be assigned to a radical which has four protons in equivalent sets of 2:2. The hyperfine coupling constants for this radical (3.67 and 0.75 G) are identical with those measured for *o*-benzosemiquinone (VII).[10] Some lines due to a third radical are observed also in D. However, these lines are distinguished more easily in spectrum E which is obtained at a faster flow rate (10 ml/min) and half the sweepwidth used for spectrum D. In this spectrum, one can identify the lines due to IV (labeled a) and VII (labeled d). The remaining lines (labeled e) may be assigned to part of a spectrum for a radical containing five protons in equivalent sets 2:2:1 with coupling constants 1.77, 0.97, and 3.55 G, respectively. This analysis must be regarded as tentative since the spectrum is weak and some of the lines are not detectable; however, the analysis includes all observed lines, and no strong lines are unaccounted for. Allowing for the tentative nature of this analysis, we would like to speculate about the possible structure of this radical. Although this radical appears to have the same number of protons and equivalent sets as phenoxyl radical, the values for the hyperfine coupling constants differ significantly.[11] Consequently this structure is unlikely. Furthermore, in view of the more complicated spectrum observed when a *p*-phenoxyphenol solution is irradiated, it seems unlikely that this radical is formed from that type of dimerization prod-

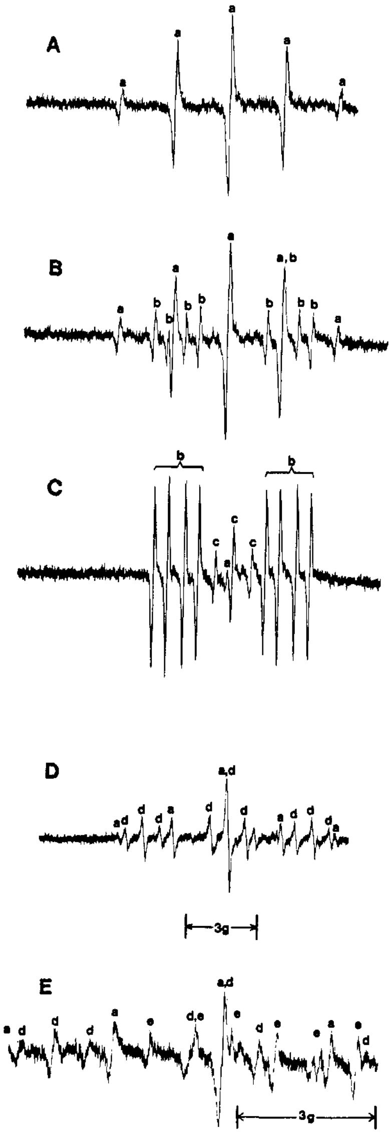

Figure 1. Epr spectra observed during the irradiation of phenol in water at about 30° and at values of pH and flow rate as follows: (A) 12 and 1.5 ml/min, (B) 12 and 0.3 ml/min, (C) 12 and 0.1 ml/min, (D) 9.8 and 6 ml/min, and (E) 9.8 and 10 ml/min.

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(6) L. C. Snyder and S. Meiboom, *J. Chem. Phys.*, **47**, 1480 (1967).

(7) M. Adams, M. Blois, Jr., and R. H. Sands, *ibid.*, **28**, 774 (1958).

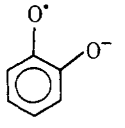
(8) T. J. Stone and W. Waters, *J. Chem. Soc.*, 1488 (1965).

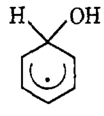
(9) M. Das and S. Fraenkel, *J. Chem. Phys.*, **42**, 1350 (1965).

(10) I. Smith and A. Carrington, *Mol. Phys.*, **12**, 439 (1967).

(11) T. J. Stone and W. Waters, *Proc. Chem. Soc., London*, 253 (1962).

uct.[12] We suggest II as a possible structure for this radical.[13] The five ring protons form the appropriate equivalent sets, and the hyperfine splitting due to the OH proton is not observed, perhaps because of rapid proton exchange with water under these conditions and/or a very small hyperfine coupling constant. A small value is not unreasonable. In a study of pyrogallol, Carrington assigned a value of 0.33 G to one OH proton.[14] Furthermore, reaction of hydroxyl radical with benzene results in a radical whose epr spectrum is consistent with the hydroxycyclohexadienyl radical VIII.[15] Hyperfine splitting due to the OH proton is not observed for this radical.


VII


VIII

In addition to the spectra illustrated in Figure 1, spectra were obtained at pH values ranging from 8.2 to about 14. Below 8.5, only the spectrum of *p*-benzosemiquinone could be identified conclusively. Some weak lines, which are also observed, could be due to *o*-benzosemiquinone (VII). In this pH region, the most intense spectrum is observed at a flow rate of 10 ml/min. Below this flow rate no additional radicals are observed. Between pH 8.5 and 9.8, *p*-benzosemiquinone (IV), *o*-benzosemiquinone (VII), and the radical assigned structure II can be detected when the flow rate is 10 ml/min. When the flow rate is reduced to 6 ml/min, lines of the last radical become weaker and barely detectable, whereas IV and VII still can be detected easily. Reducing the flow rate further leads to no additional radicals. Below pH 12, oxybenzosemiquinone and dioxybenzosemiquinone are not detected, even at low flow rates. At pH 12 or higher, the detection of these radicals is dependent on the flow rate as illustrated in Figure 1A–C.

The dependence of the epr spectrum upon hydroxide ion concentration and flow rate qualitatively support the proposed mechanism (Scheme I). When the concentration of hydroxide ion is low (pH between 8.5 and 9.8), its addition to IV or VII is sufficiently slow so that the reaction does not proceed on to the oxy- and dioxybenzosemiquinones (V and VI), even at slow flow rates. On the other hand, increasing the flow rate to about 10 ml/min permits the observation of II in addition to IV and VII. At higher hydroxide ion concentrations, the rate of addition to *p*- or *o*-benzosemiquinone is accelerated and the observation of the V and VI becomes possible at appropriate flow rates. A fast flow rate results in a residence time too short compared to the rate of formation of V and VI. Consequently only *p*-benzosemiquinone is observed. As the flow rate is reduced, oxybenzosemiquinone (V) 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 (VI).

It should be mentioned that it is possible to observe some of the lines due to *o*-benzosemiquinone (VII) and the radical assigned structure II at higher pH if the flow is fast enough. However, as indicated in Figure 1A, at flow rates below 3 ml/min the steady-state concentration of *p*-benzosemiquinone becomes larger than the concentration of these radicals. Presumably *p*-benzosemiquinone (IV) is less reactive than II. In comparison with VII, IV is either formed at a faster rate or reacts more slowly. In addition, the concentration of the semiquinone intermediates depends upon the concentration of phenoxide ion. This dependence does not appear to be the result of only the change in the absorbance of the solution. For example, based on 0.05 cm for the cell length and 500 for the average extinction coefficient, the amount of light absorbed decreases by a factor of 15 when the concentration of phenoxide ion is changed from 5×10^{-2} to 1×10^{-3} *M*. On the other hand, the intensity of the *p*-benzosemiquinone quintet is reduced by only a factor of 3 under these conditions. The short lifetime of the excited singlet state of phenoxide ion[16,17] precludes self-quenching as the reason for this nonlinear dependence of the spectrum of IV on light absorption. At any rate, in view of the variety of reaction paths available to I and IV, the intensity of the spectrum due to IV is not necessarily expected to have a linear dependence on the amount of light absorbed. In addition to the reaction paths suggested in Scheme I, reactions which result in the formation of diamagnetic species, such as recombination of the radicals with the hydrated electron or dimerization of phenoxyl radicals,[3a] could be important. The present results are insufficient for a kinetic analysis of this system.

In Scheme I, a phenoxyl radical is needed to remove a hydrogen atom from II to give the dianion of *p*-hydroquinone (III). Formation of III or IV *via* an excited state of the phenoxyl radical I does not seem possible because the concentration of this radical is too low to absorb a significant amount of light. The steady-state concentration of this radical probably is less than 10^{-6} *M* since its epr signal is not observed.[18] Consequently, because the molar extinction coefficients of the phenoxyl radical at 4000 and 2900 Å are only 2200 and 4000, respectively,[19] a mechanism involving excited phenoxyl radical seems unlikely.

In order to check for the involvement of hydroxyl radicals in the photooxidation of phenol, a solution of phenol was irradiated under the same conditions mentioned above except that approximately 1 *M* ethanol was present. It was found that the presence of ethanol had no significant effect on the epr intensities. Since ethanol is a scavenger of hydroxyl radicals,[20] we conclude that this radical is not involved in the photooxidation of phenol under the conditions employed in this study.

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[12] Irradiation of a solution of *p*-phenoxyphenol under the same conditions used for phenol results in an epr spectrum with many more lines than any of the spectra given in Figure 1. We have not analyzed this spectrum yet.

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

[14] A. Carrington and I. Smith, *Mol. Phys.*, **8**, 101 (1964).

[15] (a) W. Dixon and R. Norman, *J. Chem. Soc.*, 4857 (1968); (b) K. Eiben and R. Fessenden, *J. Phys. Chem.*, **75**, 1186 (1971).

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

[17] For substituted phenols, H. Joschek and L. Grossweiner [*J. Amer. Chem. Soc.*, **88**, 3261 (1966)] have suggested tentatively that the electron is released from a temporary complex involving the excited singlet state and water.

[18] This conclusion is based on the specifications for the instrument.

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

[20] G. Adams, J. Boag, and B. Michael, *ibid.*, **61**, 1417 (1965).

Since we suggest that II can be observed by epr, the concentration of this radical is about 10^{-5} *M*. Consequently we must consider the possibility that *p*-benzosemiquinone is formed *via* an excited state of II. While the optical absorption spectrum of II does not seem to be available, the molar extinction coefficient at 3300 Å for the protonated analog, *i.e.*, $C_6H_5(OH)_2\cdot$ is reported[20] to be 4400. If one assumes that II has the same value, one calculates that the fraction of light absorbed by II is very small since the cell length is about 0.05 cm. Therefore, formation of significant amounts of *p*-benzosemiquinone *via* an excited state of II seems unlikely.

Additional support for this conclusion comes from a study of the irradiation of either *p*-hydroquinone or catechol (*o*-hydroquinone) under the same conditions used for phenol. In these studies, preparation of solutions was more of a problem than in the case of the phenol. For example, a solution of *p*-hydroquinone or catechol in water at pH 11 darkens in a short time if left open to air. On the other hand, an acidic solution does not darken quickly. To prevent darkening, an acidic solution of *p*-hydroquinone or catechol first was purged of oxygen as described above and then was made basic. Although this precaution prevents darkening of the solution, it does not prevent the formation of radicals in the absence of irradiation. That is, in acidic solution of *p*-hydroquinone or catechol, no radicals could be detected without irradiation. However, when the solution was made basic, *p*-benzosemiquinone (IV) is observed in the *p*-hydroquinone solution and *o*-benzosemiquinone (VII) in the catechol solution. One might argue that our method for purging oxygen is not efficient and leaves oxygen in the solution. We have tested this possibility using *dl*-dopa which is an amino acid substituted catechol and forms an *o*-semiquinone. In this experiment, *dl*-dopa crystals and alkaline water were degassed on a vacuum line to a pressure less than 2 μ and then mixed. For this solution the epr spectrum of a substituted *o*-semiquinone is observed. Since the Henry's law constant for the oxygen–water system is 4.6×10^4 atm/mole fraction,[21] the concentration of oxygen is about 10^{-9} *M* at 2 μ. On the basis of the intensity of the epr spectrum, the concentration of *o*-semiquinone is about 10^{-5} *M*. Consequently it seems unlikely that the formation of the semiquinone involves reaction of molecular oxygen with dopa under these conditions. This work will be presented in detail in another publication concerning the photooxidation of tyrosine.

Upon irradiation of a water solution of 10^{-2} *M* *p*-hydroquinone at a pH of about 11, the spectrum of IV is made more intense; however, no other radicals are observed. Thus, the irradiation of *p*-hydroquinone under these conditions does not result in the formation of the oxy- or dioxybenzosemiquinones (V or VI) at concentrations which are measurable by epr. The same result obtains for catechol. During the irradiation of a series of catechol solutions having pH between 11 and about 13, epr spectra due to V and VI are not observed. When oxygen is passed into the *p*-hydroquinone or catechol solution, the solution darkens rapidly, and the spectrum of IV or VII disappears. No new spectrum of a previously undetected radical can be observed. On the other hand, passing oxygen into the phenol solution does not alter significantly the intensity of the epr signals observed during irradiation. Thus, if III or IV is formed by excitation of II, an analogous mechanism does not appear to apply to the formation of V or VI, since these intermediates are not observed during the irradiation of a solution containing either *p*-hydroquinone or catechol. If the formation of V occurs *via* an excited state of a radical analogous to II (*i.e.*, addition of hydroxide ion to IV or VII), irradiation of a solution containing *p*-hydroquinone or catechol should provide measurable amounts of V. Since it does not, we conclude that V and VI probably are formed by a different mechanism. Thus, a mechanism involving the excitation of II or a radical analogous to II cannot be used to explain the formation of all the intermediates. Consequently, we prefer the mechanism given in Scheme I since it can.

The results of experiments with *p*-hydroquinone and catechol also rule out the possibility that some of the other intermediates (such as the dianion of *o*- and *p*-hydroquinone and *o*- and *p*-benzosemiquinone) are being excited by the radiation or energy transfer and undergoing oxidation by a route different from Scheme I. As indicated above, only the spectra of *o*- and *p*-benzosemiquinone are observed in these experiments. The spectra for V and VI could not be detected, even at slow flow rates. Consequently, a mechanism involving direct excitation of these intermediates seems unlikely. Furthermore, these results rule out the possibility that minute quantities of oxygen in the solution are responsible for the oxidation. Thus, the presence of the phenoxyl radical I appears to be essential for the oxidation of IV, VII, and V.

Nmr. In addition to the epr study, the photooxidation of phenoxide ion was studied by means of proton nmr using the same conditions. Nmr spectra were obtained before, during, and after irradiation. During irradiation the spectrum exhibited emission lines indicating nuclear spin polarization. Experiments were performed with degassed (less than 2 μ) and air-saturated solutions. The spectrum obtained in the presence of oxygen is not significantly different from the spectrum for the degassed sample.

Figure 2 illustrates spectra for a solution of 1×10^{-1} *M* phenol in D_2O (99.8% *d*) at pH 11.5 before (A) and during (B) irradiation. The magnetic field increases from left to right. In A, the lines appearing at low field are due to the ring protons of the phenoxide ion. The line at higher field is due to the proton in HDO. As can be seen in spectrum B, both the ring protons and the HDO proton exhibit nmr emission during irradiation. This emission disappears and reverts to normal absorption after irradiation is stopped. After irradiation for about 5 min, no new resonance lines are observed when the irradiation is stopped. Although the temperature of the probe is regulated at 25° with nitrogen, the intensity of the irradiation causes local heating of the sample because of inefficient heat exchange between the sample and the cooling gas. Consequently, during irradiation the lines shift somewhat. Since the position of the HDO line is very temperature dependent, the shift is most pronounced for this line. Moreover, the temperature gradient causes some distortion of the shape of this line.

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(21) W. J. Moore, "Physical Chemistry," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1955, p 123.

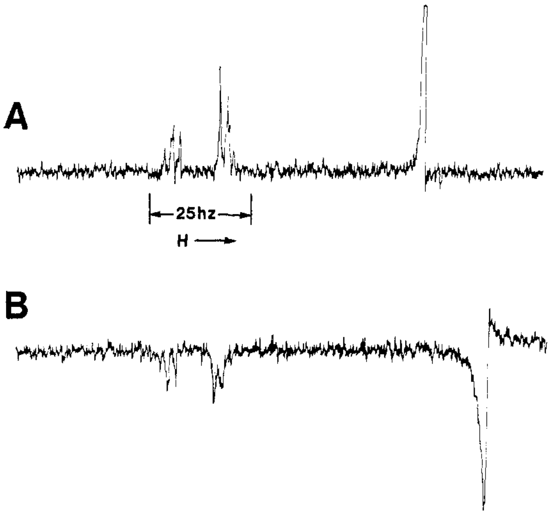


Figure 2. The 100-MHz nmr spectra of a solution of phenol in 99.8% D_2O at 25° and pH 11: (A) before irradiation and (B) during irradiation.

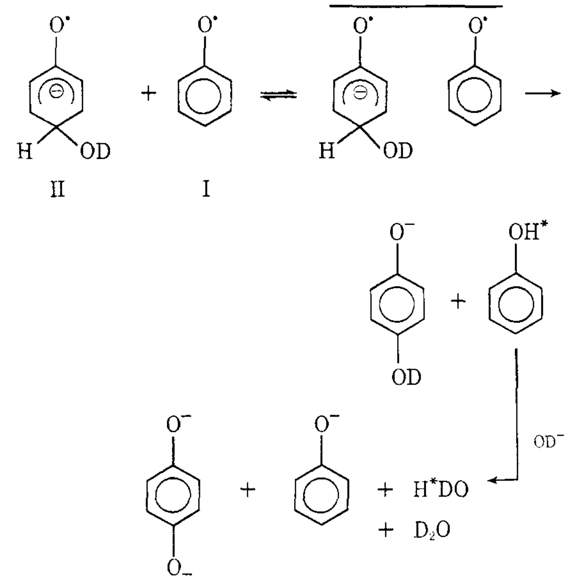
If the concentration of phenoxide ion is decreased tenfold to 10^{-2} *M*, the resonance lines due to the ring protons can no longer be observed either before or during irradiation. However, an emission line for HDO still is observed during irradiation. On the other hand, when the concentration of HDO is increased by a factor of 125 (*i.e.*, D_2O, 75% *d*), a normal absorption line is observed for the HDO proton, indicating the absence of measurable spin polarization for this proton. The ring proton resonances were not observed in this experiment. A similar experiment using H_2O as the solvent leads to the same observation: no measurable nuclear spin polarization for the water proton.

Nuclear spin polarization resulting from radical reactions has been studied in a number of laboratories.[22] A model which is consistent with the experimental results involves radical pair formation. In this pair, the unpaired electrons interact weakly, and this system is described by a time-dependent wave function which is a mixture of the singlet and triplet electron spin states. Since the nuclei of the radicals interact with the unpaired electrons, the singlet–triplet mixing depends on the nuclear spin state. As a result, because the rate of product formation is dependent on the singlet character of the wave function, nuclear spin polarization is observed in the coupling and disproportionation products. This interpretation is applied to the phenoxide ion–HDO system.

First let us consider the nuclear spin polarization observed for the HDO proton. Before deciding on a mechanism, it is necessary to know whether the polarizing effect is felt by a random fraction of water molecules or the effect is specific to protons on certain HDO molecules. If the effect is nonspecific, nmr emission should still be observed for the HDO line when the concentration of HDO is increased. On increasing the mole fraction of HDO to 0.50, the normal absorption line is observed for HDO during irradiation. The same result is obtained when H_2O is used as the solvent. Therefore, we conclude that the nuclear spin polarizing effect is selective and involves protons on a specific fraction of the HDO molecules.

The mechanism given in Scheme I can account for this selectivity. A step which involves radical pair formation is the reaction of phenoxyl radical I with II. Scheme II illustrates the manner in which polarized HDO protons can be generated in this step. In this scheme, II is formed by reaction of OD^- with I. The radical pair is denoted by the line above the structures. Disproportionation in the radical pair leads to phenol and the monoanion of *p*-hydroquinone. The asterisk indicates that the OH proton of phenol is spin polarized. At high pH, OD^- reacts rapidly with phenol to give H*DO and phenoxide ion. Since this reaction is more rapid than the nuclear spin relaxation rate, the HDO proton is polarized. When the pH is low enough to permit un-ionized phenol, the same result can be accomplished by rapid proton–deuteron exchange.[23]

Scheme II



It should be noted that this mechanism requires that the ring protons of the phenoxide ion and the dianion of *p*-hydroquinone be polarized also. The nmr emission lines observed for the phenoxide ion indicate that its ring protons are polarized. On the other hand, the nmr line for the ring protons of the dianion of *p*-hydroquinone (III) is not observed. However, since the epr results indicate that this compound is oxidized easily to *p*-benzosemiquinone under these conditions, rapid nuclear spin relaxation caused by the electron-nuclear coupling in this radical could explain this absence.

The theoretical application of the radical pair model to nuclear spin polarization[22] permits a fairly quantitative fit of some experimental spectra. However, in the present case, a number of parameters are unknown and therefore would be adjustable. Consequently, a quantitative fit of the emission spectrum given in Figure 2 has not been attempted since the result would not be conclusive. Nevertheless, the nmr emission is qualitatively consistent with the radical pair model and the mechanism given in Scheme I. Based on a

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(22) (a) R. Kaptein and L. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969); (b) G. Closs and A. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2183 (1970); (c) H. Fischer, *Z. Naturforsch. A*, **25**, 1957 (1970); (d) M. Tomkiewicz, A. Groen, and M. Cocivera, *Chem. Phys. Lett.*, **10**, 39 (1971); (e) M. Tomkiewicz, A. Groen, and M. Cocivera, *J. Chem. Phys.*, **56**, 5850 (1972).

(23) Z. Luz and S. Meiboom, *J. Amer. Chem. Soc.*, **86**, 4766 (1964).

quantitative theory, Kaptein[24] and Trifunac[25] have developed a qualitative formula (eq 1) which is

$$u \cdot a_j \cdot \Delta g \cdot C = \begin{cases} + \\ - \end{cases} \qquad (1)$$

useful for predicting the direction of the polarization. In this expression, the parameters are assigned only positive or negative signs; the magnitudes are omitted. The sign for each parameter is chosen as follows: a_j, sign of the hyperfine coupling constant; Δg, sign of the difference between the g factors of the radicals; C, positive for cage product, negative for escape; and u, depends on the nature of the precursor of the radical pair, *i.e.*, positive for pairs formed either from triplet precursor or two noninteracting radicals, negative for singlet. If the product of the signs is positive, absorption is predicted; if negative, emission.

According to Scheme I, u is positive since the radical pair is formed from two noninteracting radicals, *i.e.*, no correlation between the unpaired electrons before radical pair formation. C is positive since the disproportionation products are formed in the "cage." The sign of Δg is positive for phenoxyl radical and negative for II. These signs were deduced using the following considerations. If assignment of the epr spectra is correct, II has a g factor of 2.0040. Unfortunately, while the spectrum for the phenoxyl radical has been observed,[11] its g factor was not reported. Consequently, we must infer a value from studies of similar radicals. Values have been reported for the phenoxyl radical derived from 2,6-di-*tert*-butyl-4-methylphenol,[26] 2,6-di-*tert*-butyl-4-phenylphenol,[26] 3-(*p*-hydroxyphenyl)-propionic acid,[27] and tyramine.[27] Since these values are between 2.0044 and 2.0045, we assume that the phenoxyl radical has a similar value. As a result of this argument, the phenoxyl radical is assigned a larger g value than that of II. To obtain the signs of the hyperfine coupling constants for the ring protons of the phenoxide ion, we refer to hyperfine constants derived theoretically by Pople.[28] If one considers the ring protons as a group, the net hyperfine coupling constant is negative. Thus, Scheme I and eq 1 predict emission for the ring protons of the phenoxide ion, in agreement with experiment.

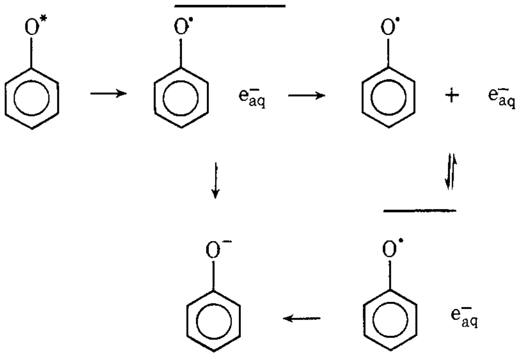
Since theoretical hyperfine coupling constants do not seem to have been derived for II, we deduce the sign of the hyperfine of the proton geminal to the OH by analogy to a similar radical, cyclohexadienyl radical.[28] A positive sign is derived for the CH_2 protons of this radical. On this basis, we assign a positive hyperfine to the proton geminal to the OH in radical II. As a result, Scheme I and eq I predict emission for the HDO proton, in agreement with experimental results.

As a further check of the mechanism given in Scheme I, the irradiation of partially deuterated phenoxide ion (phenoxide-*2,4,6-d*$_3$) in D_2O was studied under the same conditions used above. Before irradiation the nmr spectrum consists of two lines: the HDO line and a slightly broadened line downfield due to the two equivalent protons in the 3 and 5 positions of the partially deuterated phenoxide ion. During irradiation, the normal absorption line rather than an emission line is observed for HDO. Except for the usual temperature effects (distortion of the line shape and change in the chemical shift), this absorption line appears to be no different from the line observed in the absence of irradiation. On the other hand, the intensity of the single line due to the two ring protons is reduced to the extent that this line cannot be observed during irradiation. Upon stopping the irradiation after about 4 or 5 min, the spectrum of the sample becomes the same as the spectrum observed before irradiation.

The nmr spectrum obtained during the irradiation of 2,4,6-trideuterophenol supports Scheme I. According to this mechanism, no polarization should be observed for the HDO proton when the deuterated phenol is used since D_2O rather than HDO is formed. In agreement with this conclusion, an absorption rather than an emission line is observed for the HDO proton under these conditions. Likewise no nuclear spin polarization can be detected when a degassed solution of *p*-hydroquinone is irradiated under the same conditions, in agreement with the epr results. Thus, Scheme I is consistent with both the epr and the nmr results.

An alternative mechanism for the nuclear spin polarization is given by Scheme III. We have rejected this mechanism because it is not consistent with the experimental results. In this scheme, the radical pair (indicated by the line) involves a phenoxyl radical and a hydrated electron. This pair can be formed *via* an excited state of phenoxide ion indicated by the asterisk or by diffusion together of noninteracting radicals in the bulk. This mechanism cannot account for the polarization observed for the HDO proton since it indicates that a random fraction of water molecules can be affected (*i.e.*, there is no selectivity). As indicated earlier, the effect appears to be selective to protons on only a specific fraction of the HDO molecules.

Scheme III



To consider if this scheme is consistent with the emission observed for the ring protons of the phenoxide ion, it is necessary to know the g factor for the solvated electron. The value is reported[29] to be 2.0002. Thus, in using eq 1, Δg for the phenoxyl radical is positive. With this sign and the signs derived previously, we can use eq 1 to predict the direction of the polarization for

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either a radical pair formed *via* the excited state of phenoxide ion or one formed by diffusion together of two noninteracting radicals. Let us consider the former. Since photoelectron ejection appears to occur *via* the singlet rather than the triplet state,[17] eq 1 predicts absorption which is in contradiction with the emission observed experimentally. Therefore, a radical pair formed *via* the excited state of phenoxide ion cannot account for the experimental results. On the other hand, a radical pair formed by diffusion together of a phenoxyl radical and a hydrated electron can account for the results since eq 1 predicts emission for this pair. We have ruled out this possibility by comparing the intensity of the emission lines obtained for an air-saturated solution with the intensity of the emission lines obtained for a degassed sample at about $2\ \mu$ pressure. The concentration of oxygen in an air-saturated solution is about 10^{-4} M. Since the rate constant for reaction of oxygen with hydrated electron is[30] $1.88 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$, the rate of reaction of the hydrated electron with oxygen should be competitive with the rate of reaction with the phenoxyl radical in the air-saturated solution. In the degassed sample, the concentration of oxygen is decreased by five orders of magnitude. Consequently, if the spin polarization occurs *via* Scheme III, the intensity of the emission lines observed in the air-saturated solution should differ from the intensity for the degassed solution. It was found that there is no significant difference. Thus, we conclude that Scheme III is not consistent with the experimental results. In addition, a dimerization of phenoxyl radicals cannot account for the polarization since Δg is zero for the radical pair in this case. When Δg is zero, no net polarization occurs.[22]

Finally, in Scheme I, the formation of the hydrated electron is suggested, but a mechanism for its disappearance has not been discussed. The epr and nmr results give us no information concerning the reaction of this species. Probably it disappears according to various mechanisms which do not alter the mechanism proposed in Scheme I. For example, the hydrated electron could combine with any of the observed radicals or react with water to form hydroxide ion and hydrogen.[31]

Acknowledgment. The authors are grateful to A. A. Lamola for helpful suggestions and to M. Fujimoto of the Physics Department for allowing the use of the Varian E12. This work has been supported in part by NRC Grant No. A5874, PRF Grant No. PR4904, and DRB Grant No. 953096.

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Hindered Rotation in Halogen and Pseudohalogen Carbon-Substituted Amides

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Abstract: The barrier to rotation about the amido C–N bond has been measured for five C-substituted *N,N*-dimethylamides. Dimethylcarbamyl chloride has been extensively studied previously, and a critical survey of the systematic errors in all determinations has been achieved by a composite plot of the derived parameters $\Delta H^{\neq}$ *vs.* $\Delta S^{\neq}$. It is clear that, for the ten available results for this molecule, the linear relationship of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is an artifact of the experiment and that all results considered extrapolate at $\Delta S^{\neq} = 0$ to the same value of $\Delta G^{\neq}$. The complete line-shape-fit studies of the modified proton magnetic resonance spectra reported here take account of chemical shift dependence with temperature, the Lorentzian form of a line-shape standard whose inhomogeneously broadened resonance does not exceed 0.4 Hz, a defined error analysis over all data points of less than 2%, and a measurement of a uniform temperature to a maximum error of ±0.5°. The activation parameters are reported for the azide, cyanide, thiocyanate, and the bromide, and these are considered in terms of simple valence-bond structures. The chemical shift between methyl peaks in *N,N*-dimethylcarbamyl azide is only 1.8 Hz, and it has not been possible to assign the peaks at this stage. The azide group behaves somewhat like the fluorine substituent studied previously.

The application of nmr to the study of hindered internal rotation about partial double bonds has become very widespread, as outlined in recent comprehensive reviews.[1,2] In general, however, these parameters for any given compound show a large variance, and a semiquantitative correlation of the data available for a related series of compounds has not been possible. Although a number of substituted *N,N*-dimethylamides have been investigated using nmr, the only example of a rotational barrier that has been studied under the same experimental conditions in independent laboratories and for which all of the activation parameters are consistent within calculated error limits is that of *N,N*-dimethylformamide (DMF).[3,4] Thus the data presented in this paper for another well-

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