

tor of the apparent first-order coefficient  $f$  is  $8 \times 10^{12} \text{ sec.}^{-1}$ . The value deduced from the velocity coefficient and the activation energy (Table III) corresponds to a steric factor of 0.01 for reaction F.

TABLE III

Quantity	Source	Value at 20°, l. mole <sup>-1</sup> sec. <sup>-1</sup>	Pre- exponential factor	Acti- vation energy kcal.
$a/b$	Gas phase <sup>a</sup>	$3 \times 10^{-11}$ mole l. <sup>-1</sup>		$20 \pm 3$
$c$	$c(a/b), a/b$	$5 \times 10^4$	$2 \times 10^{13}$	11.5
$d$	Assumed	$2 \times 10^8$		Low
$e$	$d/e, d$	$2 \times 10^8$		Low
$f$	$f/e, e$	$8 \times 10^4 \text{ sec.}^{-1}$	$8 \times 10^{10b}$	8

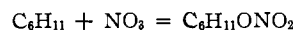
<sup>a</sup> Ref. 15a. <sup>b</sup>  $8 \times 10^9 \text{ l. mole}^{-1} \text{ sec}^{-1}$  if the "concn." of  $\text{CCl}_4$  is factored out.

From the results in Table III it is easily seen that with the high concentration of nitrogen dioxide a number of intrinsically fast reactions are not important in this system. In a typical experiment

( $[\text{C}_6\text{H}_{12}] = [\text{N}_2\text{O}_5] = [\text{N}_2\text{O}_4] = 0.2 M$ ) the concentrations of the various radicals relative to  $\text{NO}_2$  are, at 20°

$$\begin{array}{lll} [\text{NO}_2]/[\text{NO}_2] & [\text{C}_6\text{H}_{11}]/[\text{NO}_2] & [\text{CCl}_3]/[\text{NO}_2] \\ 3 \times 10^{-7} & 2 \times 10^{-10} & 6 \times 10^{-12} \end{array}$$

Thus the formation of cyclohexyl nitrate by direct radical union



is insignificant compared with the reaction E through nitrite. Similarly, the solvent is the only species able to compete successfully with nitrogen dioxide for cyclohexyl radicals ( $[\text{CCl}_4]/[\text{NO}_2] = 2 \times 10^3$  for  $[\text{N}_2\text{O}_4] = 0.2 M$ ); the union of two cyclohexyl radicals, or of cyclohexyl and trichloromethyl radicals, is negligibly slow by comparison. Any latent tendency of the system toward a chain mechanism is suppressed by the nitrogen dioxide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

## Proton Hyperfine Interactions in Paramagnetic Resonance of Semiquinones<sup>1</sup>

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Semiquinones formed by the oxidation of hydroquinones or the reduction of quinones in alkaline media have been studied by paramagnetic resonance absorption spectroscopy. The *p*-benzosemiquinone ion has been observed for the first time in solution; its existence has been established by examination of the structure of its paramagnetic resonance spectrum. It has been confirmed that certain structure observed in the paramagnetic resonance spectra of some free radicals is due to intramolecular magnetic hyperfine interaction between the unpaired electron and protons. The magnitude of the hyperfine interaction constant for the *p*-benzosemiquinone ion was found to be  $6.54 \pm 0.06 \text{ Mc./sec.}$ , and the magnitude of the constant for the durosemiquinone ion was found to be  $5.28 \pm 0.15 \text{ Mc./sec.}$  Although theoretical interpretation of the magnitude of the interaction constants has not been satisfactory, it is believed that relative values of these constants can be interpreted in terms of relative odd-electron densities at the protons. The magnitude of the hyperfine interaction in the durosemiquinone ion may represent direct confirmation of the phenomenon of hyperconjugation. Paramagnetic spectra were observed from the *p*-toluensemiquinone ion, the 9,10-phenanthrenesemiquinone ion, and the radical formed from a mixture of benzil and benzoin. Evidence was found for the existence of two or more radicals in an alkaline alcoholic solution of *p*-benzoquinone exposed to the air.

### Introduction

During the 1930's, it was demonstrated, principally by Michaelis and his co-workers,<sup>2</sup> that the bivalent oxidation of hydroquinones, or the reduction of quinones, proceeds through an intermediate compound containing an odd number of electrons, a semiquinone free radical. This conclusion was reached through the study of potentiometric oxidation-reduction titrations of these materials<sup>3</sup> and, in a few cases, by the measurement of the change in the magnetic susceptibility that took place during

the course of a reduction of a quinone.<sup>4</sup> The magnetic method is too insensitive and slow for general applications, and the potentiometric method, which is capable of higher sensitivity than the magnetic technique, can only be applied to systems that produce a reasonably stable potential in an electromotive cell. Although this work showed that the stability of a semiquinone increases with increasing *pH* when no side reactions take place, many quinone systems are unstable in alkaline solution, and the simplest semiquinone, that of *p*-benzoquinone, was not detected in solution.

Considerable knowledge of the mechanism of the autooxidation of hydroquinones has been obtained by Weissberger and his collaborators,<sup>5</sup> and it was postulated that a semiquinone intermediate is formed in these oxidations. Complete interpretation of the autooxidations and of the general behavior of photographic developing agents is made dif-

(1) Supported in part by Squier Signal Laboratory, U. S. Army Signal Corps. Presented before the Division of Physical and Inorganic Chemistry at the 126th Meeting of the American Chemical Society, New York, September, 1954.

(2) For a review, including an extensive bibliography, see L. Michaelis, *Ann. N. Y. Acad. Sci.*, **40**, 39 (1940). For later work, see references 2 and 3 below, and L. Michaelis, M. P. Schubert and S. Granick, *THIS JOURNAL*, **62**, 204 (1940); S. Granick, L. Michaelis and M. P. Schubert, *ibid.*, **62**, 1802 (1940); S. Granick and L. Michaelis, *ibid.*, **62**, 2241 (1940); L. Michaelis, S. Granick and M. P. Schubert, *ibid.*, **63**, 351 (1941); L. Michaelis and S. Granick, *ibid.*, **63**, 1636 (1941); **66**, 1023 (1944); and S. Granick and L. Michaelis, *ibid.*, **69**, 2983 (1947).

(3) L. Michaelis and M. P. Schubert, *Chem. Revs.*, **22**, 437 (1938). See also, L. Michaelis in A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1940. 2nd Ed., Vol. 1, Part 11, p. 1713.

(4) L. Michaelis, G. F. Boeker and R. K. Reber, *THIS JOURNAL*, **60**, 202 (1938); L. Michaelis, R. K. Reber and J. A. Kuck, *ibid.*, **60**, 214 (1938); L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck and S. Granick, *ibid.*, **60**, 1678 (1938); L. Michaelis, *ibid.*, **63**, 2446 (1941); L. Michaelis and S. Granick, *ibid.*, **65**, 1747 (1943); **70**, 624, 4275 (1948).

(5) For a survey and references to earlier work, see J. E. LuValle and A. Weissberger, *ibid.*, **69**, 1567, 1576, 1821 (1947).

ficult, however, by the existence of complicated side reactions that may involve free radical intermediates. Any method for the detection of radical intermediates would therefore be of appreciable assistance in reaching an understanding of these reactions.

The recently developed technique of paramagnetic resonance absorption is well suited for the study of free radicals in both equilibrium and non-equilibrium systems. Weissman, *et al.*,<sup>6</sup> have, in fact, employed this technique to study the free radicals formed by the oxidation of substituted *p*-phenylenediamines, the Wurster's salts. These compounds, some of which are quite stable, are closely related to the semiquinones. Intense paramagnetic absorption spectra can be observed from solutions of the Wurster's salts, and these spectra, as well as the absorptions from certain negative ions of aromatic nuclei,<sup>6a,7</sup> were found to exhibit a great deal of fine structure. The structure has been attributed to nuclear magnetic hyperfine interactions.

Magnetic hyperfine splitting of paramagnetic resonance spectra was first observed by Penrose,<sup>8</sup> who studied a magnetically-dilute single crystal of a cupric salt. Hyperfine splitting has been found in a large variety of spectra of other crystalline salts of paramagnetic metallic ions,<sup>9</sup> and also in solutions of mangaous salts.<sup>10</sup> Hyperfine splitting due to nitrogen was observed by Hutchison, *et al.*,<sup>11</sup> by Pake, *et al.*,<sup>12</sup> by Jarrett<sup>13</sup> and by Kikuchi and Cohen,<sup>14</sup> in solutions, and hyperfine splitting due to a C<sup>13</sup> isotope at the methyl position in triphenylmethyl was found by Weissman and Sowden.<sup>15</sup> Splitting caused by boron also has been observed.<sup>6a</sup>

The great complexity of the spectra of the aromatic negative ions and of the Wurster's salts has been attributed to proton hyperfine splitting.<sup>6,7</sup> A similar explanation was offered by Jarrett and Sloan to account for the complicated set of lines observed in the spectra of triphenylmethyl and dimesitylmethyl.<sup>16</sup> If this splitting is truly caused by protons, its investigation could be of considerable general utility. The splitting that would arise from a proton interaction is determined by the density of the unpaired electron at the proton, and therefore the measurement of such splittings can be a source of information about the location in the radical of the unpaired electron. Although the nature of

the splitting has not yet been confirmed, Weissman showed that part of the structure observed in the spectrum of the *N,N*-dimethyl-*p*-phenylenediaminal ion changed when deuterium was substituted for hydrogen in the *N'*-position.<sup>6b</sup> Another partial confirmation of the nature of the splitting is provided by the work of Jarrett and Sloan on dimesitylmethyl<sup>16</sup>: the spectrum showed a large splitting that presumably is due to the methyl proton. In neither of the experiments cited, however, was the entire spectrum interpretable and the nature of the interactions could not be unequivocally established.

The semiquinones might be a suitable series of compounds for testing the hypothesis of proton hyperfine splitting. They can be produced readily in alkaline solution by oxidizing the hydroquinones, by reducing the quinones, or by mixing equivalent amounts of the quinone and the hydroquinone. Since quinones or hydroquinones containing only a small number of protons closely associated with the  $\pi$ -orbitals of the benzene ring can be made, it should be possible to produce semiquinones that would give simple splitting patterns. Experiments were undertaken, therefore, to prepare semiquinones and to study their spectra. The major portion of the research described in the following paragraphs relates to the production of the semiquinone of *p*-benzoquinone and to the study of its spectrum. In addition, the phenomenological theory of the hyperfine splitting is developed, and a brief account is given of some preliminary experiments performed on other semiquinones.

#### Techniques and Materials

The spectrometer used for the paramagnetic resonance measurements, which has been described elsewhere,<sup>17</sup> operates at a wave length of 3.2 cm. Samples were contained in small thin-walled capillary tubes and were located at the center of a TE<sub>102</sub> rectangular cavity. Spectra were observed either by taking pictures of all or part of a spectrum displayed on an oscilloscope screen, or by recording the derivative of the paramagnetic absorption.

Magnetic field measurements were made in terms of the proton nuclear magnetic resonance frequency. These frequencies were measured with a BC-221 frequency meter and, in most cases, the uncertainties in the measured splittings and line widths were due to the limited precision of this meter for the determination of small frequency increments. Spectroscopic splitting factors (*g*-values) were determined by using the proton resonance frequency to measure the difference between the resonant values of the magnetic field for the compound being investigated and for a standard. The standard was a polycrystalline sample of 1,1-diphenyl-2-picrylhydrazyl the *g*-value of which was taken to be 2.0037.<sup>18</sup> Although this *g*-value has been reported to vary slightly with the nature of the polycrystalline sample,<sup>11</sup> and may therefore not be a reliable standard, we have found that two particular samples prepared by different methods have the same *g*-value, and our measurement of the *g*-value of the peroxyamine disulfonate radical agrees with the value found by Townsend and reported by Lloyd and Pake.<sup>19</sup>

The homogeneity of the magnetic field was controlled by shims attached to the magnet pole faces and it was checked by observing the spectra of the radical obtained by adding alkali to a solution of benzil and benzoin. This radical is useful because its paramagnetic spectrum exhibits splittings of the order of 0.1 gauss between individual components.

(6) (a) S. I. Weissman, J. Townsend, D. E. Paul and G. E. Pake, *J. Chem. Phys.*, **21**, 2227 (1953); (b) S. I. Weissman, *ibid.*, **22**, 1135 (1954).

(7) D. Lipkin, D. E. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534 (1953); T. L. Chu, G. E. Pake, D. E. Paul, J. Townsend and S. I. Weissman, *J. Phys. Chem.*, **57**, 504 (1953).

(8) R. P. Penrose, *Nature*, **163**, 992 (1949).

(9) B. Bleaney and K. W. H. Stevens, *Repts. Progr. in Phys.*, **26**, 108 (1953).

(10) M. Tinkham, R. Weinstein and A. F. Kip, *Phys. Rev.*, **84**, 848 (1951); E. E. Schneider and T. S. England, *Physica*, **17**, 221 (1951).

(11) C. A. Hutchison, Jr., R. C. Pastor and A. G. Kowalsky, *J. Chem. Phys.*, **20**, 534 (1952).

(12) G. E. Pake, J. Townsend and S. I. Weissman, *Phys. Rev.*, **85**, 682 (1952); J. Townsend, S. I. Weissman and G. E. Pake, *ibid.*, **89**, 606 (1953).

(13) H. S. Jarrett, *J. Chem. Phys.*, **21**, 761 (1953).

(14) C. Kikuchi and V. W. Cohen, *Phys. Rev.*, **93**, 394 (1954).

(15) S. I. Weissman and J. C. Sowden, *THIS JOURNAL*, **75**, 503 (1953).

(16) H. S. Jarrett and G. J. Sloan, *J. Chem. Phys.*, **22**, 1783 (1954).

(17) J. M. Hirshon, R. L. White and G. K. Fraenkel, *Rev. Sci. Instr.*, **23**, 772 (1952); J. M. Hirshon and G. K. Fraenkel, *ibid.*, **26**, 34 (1955).

(18) A. N. Holden, C. Kittel, F. R. Merritt and W. A. Yager, *Phys. Rev.*, **77**, 147 (1950); C. H. Townes and J. Turkevich, *ibid.*, **77**, 148 (1950).

(19) J. P. Lloyd and G. E. Pake, *ibid.*, **94**, 579 (1954).

The magnet shims were adjusted until the best possible resolution of this spectrum was obtained.

The radicals were produced by a variety of techniques. Atmospheric oxidation was employed to form radicals in solutions of hydroquinone and *p*-toluhydroquinone. The solutions were made alkaline by adding a few drops of dilute aqueous sodium hydroxide solution and were then placed in the spectrometer. About two to three minutes were required, after the addition of the alkali, until the spectrometer was adjusted to observe a resonance, and no attempt was made to detect an absorption in less than about two minutes. Oxidation of hydroquinone by controlled amounts of oxygen was studied in an apparatus similar to that described by Michaelis and Fetcher.<sup>20</sup> Radicals were produced from duroquinone and 9,10-phenanthrenequinone by adding dilute aqueous sodium hydroxide to an alcoholic solution containing the appropriate quinone and an excess of glucose. This reduction proceeds slowly and the radical concentration passes through a maximum.<sup>4</sup> Radicals were obtained from a mixture of benzil and benzoin in ethanol by adding dilute aqueous sodium hydroxide.

A flow apparatus was used when a steady concentration of an unstable radical species had to be maintained in the spectrometer. This apparatus consists of two open glass reservoirs each of which is connected by 0.2 mm. capillary tubing to a small mixing chamber (*ca.* 0.2 ml.). The mixing chamber is attached to a thin-walled capillary that serves as the sample tube and is inserted through the microwave cavity of the spectrometer. The length of the capillaries determines the flow rate; with dilute alcoholic solutions the rate was about 1 drop out of the sample tube every 6 to 7 seconds. When used with hydroquinone, an alcoholic solution of the hydroquinone is placed in one reservoir, an alcoholic solution of 1% potassium hydroxide is placed in the other reservoir, and the mixture is allowed to flow through the apparatus. The concentration of the hydroquinone was adjusted to obtain a convenient intensity of the paramagnetic resonance absorption. A more uniform flow was obtained when an alcoholic solution rather than an aqueous solution of potassium hydroxide was employed.

The paramagnetic spectra of many of the solutions showed the effects of dipolar broadening: the individual components became narrower as the concentration of the radical was decreased. In some cases the solutions had to be diluted to obtain narrow lines, but controlled experiments of the effect of concentration of line width were not made.

All of the organic chemicals used except duroquinone were commercially available materials. The duroquinone, prepared from durene (Eastman Kodak Co. White Label product, m.p. 79–80°) by the method of Smith and Dobrovolny,<sup>21</sup> was recrystallized from 95% ethanol; m.p. 112–113°. The *p*-benzoquinone was purified by sublimation and the 9,10-phenanthrenequinone was recrystallized from 95% ethanol. The melting points of all compounds were checked. The inorganic chemicals used were of reagent grade.

### Theoretical Description of Hyperfine Splitting

The effect on paramagnetic resonance spectra of the magnetic hyperfine interaction between an unpaired electron and a nucleus with a magnetic moment has been discussed by Abragam and Pryce<sup>22a</sup> and by Weissman.<sup>22b</sup> Abragam and Pryce, who were concerned with the spectra of the transition elements, made use of a spin Hamiltonian that operates only on spin variables. Weissman treated the problem for polyatomic molecules and pointed out that the anisotropic part of the interaction vanishes for a molecule subjected to the impacts of a solvent of low viscosity. The spin Hamiltonian for a rapidly tumbling molecule containing one unpaired electron and a number of nuclei with magnetic moments is therefore

$$H = g\beta\mathbf{S}\cdot\mathbf{B} - \sum_i g_i \beta_N \mathbf{I}_i \cdot \mathbf{B} + \sum_i a_i \mathbf{S} \cdot \mathbf{I}_i \quad (1)$$

where  $\mathbf{B}$  is the external magnetic field and the summation is extended over all nuclei. The spectroscopic splitting factor of the electron is designated by  $g$ ,<sup>23</sup> and  $g_i$  is the  $g$ -factor of the  $i^{\text{th}}$  nucleus,  $\beta$  is the Bohr magneton, and  $\beta_N$  is the nuclear magneton. The spin angular momenta, designated by  $\mathbf{S}$  for the electron and  $\mathbf{I}_i$  for the  $i^{\text{th}}$  nucleus, are measured in units of  $\hbar/2\pi$ . The interaction constant between the unpaired electron and the  $i^{\text{th}}$  nucleus,  $a_i$ , was originally calculated by Fermi,<sup>24</sup> who employed the Dirac equation, but it can also be evaluated from essentially classical considerations by a technique due to Sessler and Foley.<sup>25</sup> The value of this constant is  $a_i = (8\pi/3)g\beta g_i \beta_N \psi^2(i)$ , where  $\psi(i)$  is the normalized wave function of the unpaired electron at the position of the  $i^{\text{th}}$  nucleus. The spectroscopic splitting factor,  $g$ , may differ slightly from the free-electron value of  $g = 2.0023$ ,<sup>26</sup> and presumably such departures from the free-electron value for molecules in solution can be accounted for by second-order spherically symmetric spin-orbit interactions.

The solution of eq. 1 for any value of magnetic field can be obtained by generalizing the Breit-Rabi formula,<sup>27</sup> but the high field approximation to this solution is valid for electron resonance experiments that are performed at microwave frequencies on polyatomic molecules. The eigenvalues of eq. 1 at high fields are given by

$$E = g\beta M B - \sum_i g_i \beta_N m_i B + \sum_i a_i m_i M \quad (2)$$

where  $M$  and  $m_i$  are the components of  $\mathbf{S}$  and  $\mathbf{I}_i$ , respectively, in the direction of the magnetic field. At high fields, the selection rules for the transitions induced by radiation, when the magnetic vector of the radiation is perpendicular to the steady magnetic field  $B$ , are either that  $\Delta M = \pm 1$  and  $\Delta m_i = 0$ , or that  $\Delta m_i = \pm 1$ ,  $\Delta m_j = 0$  for  $i \neq j$ , and  $\Delta M = 0$ . The first set of selection rules corresponds to electron resonance, and the second set to nuclear resonance. The latter probably cannot be observed in paramagnetic polyatomic molecules because the absorption lines are so broad under ordinary circumstances that insufficient signal intensity is available for detection of the resonance. The transition frequencies for the electron resonance are therefore  $\hbar\nu = g\beta B + \sum_i a_i m_i$ , and the values of the magnetic field at which the transitions take place when radiation of a fixed frequency is used are

$$B = (g\beta)^{-1}(\hbar\nu - \sum_i a_i m_i) \quad (3)$$

Total number of allowed transitions,  $\Pi_i(2I_i + 1)$ , is equal to the number of nuclear orientations, but many of these transitions coincide when degeneracy exists.

When a solution containing the paramagnetic molecules is placed in a magnetic field, each molecule remains in a state with a definite orientation of electron and nuclear spins for a time that is determined by the mechanism of the relaxation proc-

(20) L. Michaelis and E. S. Fetcher, Jr., *THIS JOURNAL*, **59**, 1246 (1937).

(21) L. I. Smith and F. J. Dobrovolny, *ibid.*, **48**, 1420 (1926).

(22) (a) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)*, **A205**, 135 (1951); (b) S. I. Weissman, *J. Chem. Phys.*, **22**, 1378 (1954).

(23) C. Kittel, *Phys. Rev.*, **76**, 743 (1949).

(24) E. Fermi, *Z. Physik*, **60**, 320 (1930).

(25) A. M. Sessler and H. M. Foley, *Phys. Rev.*, **92**, 1321 (1953).

(26) The free-electron  $g$ -value is discussed by: J. Schwinger, *Phys. Rev.*, **73**, 416 (1948); P. Kusch and H. M. Foley, *ibid.*, **74**, 250 (1948); H. Taub and P. Kusch, *ibid.*, **75**, 1481 (1949).

(27) G. Breit and I. I. Rabi, *ibid.*, **38**, 2082 (1931).

esses. If this time is sufficiently short, the system will be in thermal equilibrium, and although relaxation times for nuclei alone can be quite long, the presence of the unpaired electrons causes interactions that are sufficient to ensure that the nuclear spins are maintained at thermal equilibrium. The number of molecules in a given state is therefore determined by the Boltzmann distribution, but since the energy of nuclear orientation is very small, the distribution over the nuclear states may be considered, to a high degree of approximation, to be uniform. The intensity of each component line in the spectrum is thus proportional to the degeneracy of the component, and if the lines were all of the same shape and width, the peak intensities of the components would be in the ratios of the respective degeneracies. Since the magnetic moment of the electron is much larger than the moments of the nuclei, the main contributions to line broadening and relaxation mechanisms arise from interactions with the electrons, and the widths are not likely to depend appreciably on the nuclear orientations. In particular, at the high fields employed in the microwave region, the energy due to the nuclear orientations is much smaller than the energy of the electron in the magnetic field, so the widths of the components should be independent of nuclear orientations. At low fields, however, it is possible that the widths may vary from one component to another. A spectrum observed in the microwave region should thus give components with peak intensities and derivative amplitudes that are in the ratio of the respective degeneracies provided, of course, that overlapping between the components is negligible.

Under certain situations, the system may depart from thermal equilibrium. This condition, which can occur when the level of the radio-frequency power is too high and the relaxation mechanisms too weak, is known as saturation. When saturation takes place, each component of the spectrum decreases in amplitude, and increases in width, without affecting the intensity or shape of any of the components which occur at different values of the magnetic field.

We will be concerned here only with paramagnetic molecules that contain protons and no other magnetic nuclei. The  $g_i$  are then equal and the  $m_i$  can take on the values of  $+1/2$  or  $-1/2$ . If there are  $N$  protons located at equivalent positions in the molecule, the  $a_i$ 's are equal, and there are  $2^N$  transitions which give rise to  $2(N/2) + 1 = N + 1$  distinct lines. The separation between the components is  $a/g\beta$  gauss or  $a/h$  cycles per second. It can be shown that the number of transitions which contribute to a given absorption line are distributed according to the binomial coefficients  $N!/[(N-n)!n!]$ , where  $n$  designates the component, ordered from low field to high field, and  $n = 0, 1, 2, \dots, N$ . The peak intensities in a spectrum of completely resolved lines are thus in the ratio of the respective binomial coefficients.

When the protons are not all equivalent, the spectrum cannot be so simply described. If there are  $N_a$  equivalent protons with interaction constant  $a$ ,  $N_b$  with constant  $b$ ,  $N_c$  with constant  $c$ ,

etc., where  $a > b > c \dots$ , the spectrum can be computed as follows: If the  $N_a$  protons in the first group were present alone, there would be  $N_a + 1$  lines, with intensities distributed according to  $N_a!/(N_a - n_a)!n_a!$ , which would be separated from each other by  $a/g\beta$  gauss. Each of these  $N_a + 1$  lines is further split by the second group of protons into  $N_b + 1$  lines with intensities distributed according to  $N_b!/(N - n_b)!n_b!$  and with separations  $b/g\beta$  gauss. If  $a$  and  $b$  are not commensurate, these two groups of protons would give rise to  $(N_a + 1)(N_b + 1)$  lines, and each of these lines would be further split by the third group of protons, etc. If  $a > N_b b > N_b N_c c \dots$ , the spectrum would consist of groups of binomially distributed lines, but in the general case, such a simple pattern is not to be expected.

The complete paramagnetic absorption spectrum, or its derivative, can be computed when the line-shape function is known. If the normalized line-shape function is  $g(x)$ , where  $x = (B - B_0)/\Delta$ ,  $\Delta$  is a parameter descriptive of the line width, and  $B_0$  is the value of the magnetic field at the center of the line, the absorption curve (un-normalized) for  $N$  equivalent protons would be

$$G(B) = \sum_{n=0}^N [N!/(N-n)!n!]g(x_n) \quad (4)$$

where  $x_n = [(B - B_0)/\Delta] + [(N - 2n)a/2g\beta\Delta]$ . For a particular line shape, and with given intensity factors to account for the degeneracy, an absorption curve such as  $G(B)$  depends only on the ratio of the splitting constants to the line-width parameter. Curves of  $G(B)$  and its derivative have been computed, when  $N = 4$ , for Lorentz and Gaussian line-shape functions in order to estimate the extent of overlap between the components of the spectrum obtained from the oxidation of hydroquinone. These are discussed in the following section.

## Results

(a) **Hydroquinone.**—Solutions of hydroquinone in water or ethanol were treated with a few drops of alcoholic or aqueous potassium or sodium hydroxide in the presence of air. Immediately after the addition of alkali, a yellow color developed and, at the end of the two minutes which is required to position the sample and adjust the spectrometer, a strong paramagnetic absorption was observed. In some cases the radical concentration was as high as 0.005  $M$ . The intensity of the resonance decreased monotonically with time until no magnetic absorption could be detected, and the color of the solution turned to dark brown. The stability of the radical decreased at high pH.

When oxygen-free alkali was added to an oxygen-free alcoholic solution of the hydroquinone, a pale yellow color developed. This solution did not show any paramagnetic absorption, and on the basis of the spectrometer sensitivity in these experiments, we conclude that the radical concentration was less than about  $10^{-6}$  molar. It is possible that the yellow color could be accounted for by very slight oxidation of the hydroquinone caused by impurities in the alcohol. When oxygen was added to the alkaline solution, the color changed to bright yellow.

low and the solution showed a paramagnetic spectrum which was qualitatively identical to the spectrum obtained in the air oxidation. The concentration of the radical, as indicated by the magnitude of the resonance absorption, increased with the amount of oxygen added until a maximum was reached; on further addition of oxygen, the concentration of radical decreased until a spectrum was no longer detectable. The color of the solution changed from pale yellow to bright yellow, to orange, and finally to dark brown, as more and more oxygen was introduced. When the solution was sealed from the atmosphere after the addition of a small amount of oxygen, the concentration of the radical decreased less rapidly than when the system was left open to the air. In a closed system to which sufficient oxygen had been added to produce an initially bright yellow color, the concentration of radical decreased a thousandfold after a period of twelve hours. The solution was almost colorless at the end of this period, but when it was exposed to the atmosphere, a yellow color developed and a strong magnetic absorption was observed.

These experiments with controlled amounts of oxygen show that the paramagnetic resonance spectrum observed arises from the oxidation products of hydroquinone. The spectrum is shown in Fig. 1, which is a plot of the magnetic absorption, in arbitrary units, as a function of the applied field. Figure 2 shows the derivative of the magnetic absorption *versus* magnetic field and is obtained by using small-amplitude magnetic field modulation and a narrow-band detector. These spectra were taken with the flow apparatus so as to maintain an approximately constant radical concentration in the spectrometer.

The position of the central peak in the absorption spectrum of oxidized hydroquinone corresponds to a spectroscopic splitting factor of  $g = 2.0057 \pm 0.0004$ . The spacing between consecutive peaks is  $2.33 \pm 0.02$  gauss and, within the experimental error, is uniform throughout the spectrum. The width between points of extreme slope for the individual components is  $0.18 \pm 0.02$  gauss; the widths were found to be the same for all the components.

Approximate measurements of the peak intensity of the individual components indicated that this spectrum could be fitted by a set of five lines with relative intensities given approximately by the ratios 1:4:6:4:1. A theoretical spectrum was then computed from eq. 4, with  $N = 4$ , in order to determine the effects of overlap between the components. A plot of the absorption curve calculated using 2.33 gauss for the separation of the components and 0.18 gauss for the width between points of extreme slope, and a similar plot of the computed derivative curve, indicated that a Lorentz-type line shape was a better approximation to the experimental curves than a Gaussian shape. These plots showed that the positions of the peaks of the absorption, or the positions of the points of maximum, minimum, or zero slope, were essentially unaffected by overlap of the components. The peak amplitudes on the computed Lorentz-type absorption curve were measured and the ratios of the amplitudes between the different components calcu-

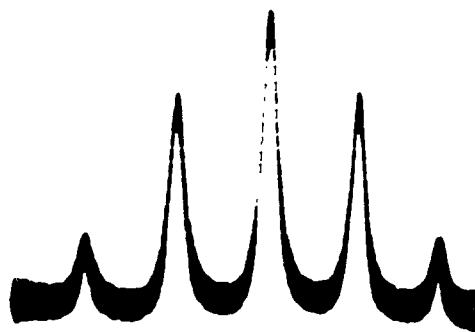


Fig. 1.—Paramagnetic absorption *vs.* magnetic field from a solution of the *p*-benzo-semiquinone ion.

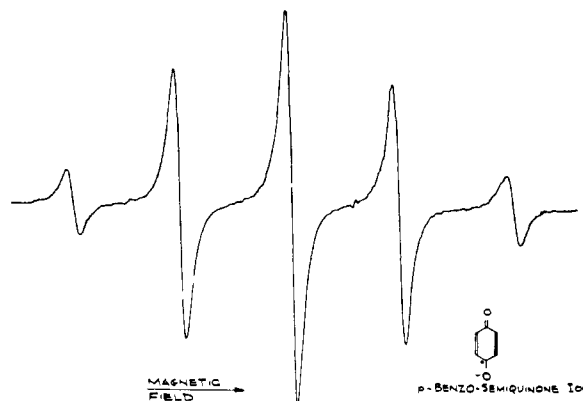
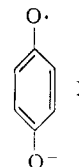


Fig. 2.—Derivative of the paramagnetic absorption *vs.* magnetic field from a solution of the *p*-benzo-semiquinone ion.

lated. These ratios are:  $(0)/(\pm 1) = 1.49$ , and  $(\pm 1)/(\pm 2) = 3.89$ . The peaks have been designated by numbers starting at the low-field side of the spectrum and progressing consecutively, in the order  $(-2)$ ,  $(-1)$ ,  $(0)$ ,  $(+1)$ ,  $(+2)$ , to the high-field side. The corresponding ratios for a non-overlapping spectrum would be 1.50 and 4.00, respectively. Similar measurements were made on the computed derivative curve and the ratios of peak-to-peak amplitudes were found to be:  $(0)/(\pm 1) = 1.50$ , and  $(\pm 1)/(\pm 2) = 4.00$ . The peak-to-peak amplitude, which is the sum of the absolute value of the maximum and minimum amplitude of the derivative of a single component, resulted in ratios that were less affected by overlap than were the ratios of the maximum or minimum amplitudes of the derivative.

The experimental values of the ratios of peak-to-peak amplitudes are:  $(0)/(\pm 1) = 1.47 \pm 0.06$ , and  $(\pm 1)/(\pm 2) = 3.61 \pm 0.27$ . Similar ratios of peak intensity measured from the absorption curves give values of 1.4 and 3.9, respectively.

If the radical observed in the paramagnetic resonance spectrum were the negative ion of the semiquinone of *p*-benzoquinone, represented by formula I and its resonance structures, there would be four

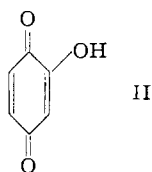


equivalent protons to produce hyperfine splitting. Four such protons in a non-overlapping spectrum would produce a splitting into five lines with peak intensity ratios of 1:4:6:4:1. The experimental measurements from the derivative curves agree with the predicted  $(0)/(\pm 1)$  ratio within 2% and with the predicted  $(\pm 1)/(\pm 2)$  ratio within 10%. The latter deviation is somewhat larger than the experimental error and may be caused by non-linearity in the spectrometer.

From the close agreement between the experimental spectrum and the spectrum predicted for the *p*-benzosemiquinone ion, we conclude that: (1) the radical species is indeed the *p*-benzosemiquinone ion and (2) the structure in the spectrum is due to proton hyperfine interaction. On the basis of this interpretation, we obtain for the value of the hyperfine interaction constant  $(a/g\beta) = 2.33 \pm 0.02$  gauss or  $(a/h) = 6.54 \pm 0.06$  Mc./sec.

(b) *p*-Benzoquinone and Quinhydrone.—When aqueous sodium hydroxide was added to an alcoholic solution of *p*-benzoquinone, in the presence of air, a dark green-yellow solution was formed. This solution exhibited a strong paramagnetic absorption which contained, in addition to the five lines found in the spectrum of the *p*-benzosemiquinone ion, a considerable number of additional lines. The intensity of these new lines appeared to change with time at a different rate from the change with time of the five-line spectrum. Qualitatively similar results were also found when quinhydrone was subjected to the same type of experiments.

It is known that *p*-quinone is oxidized in alkaline media to hydroxyquinone (II),<sup>28</sup> and part of the paramagnetic spectrum observed in these ex-



periments may be caused by the intermediate formed in the course of this oxidation. The simultaneous production of what appears to be the *p*-benzosemiquinone ion may have been brought about by a reduction of the quinone by alcohol,<sup>29</sup> but until additional controlled experiments are performed, it is not considered possible to draw any conclusions from these spectra.

(c) Duroquinone.—When an alcoholic solution of duroquinone (tetramethyl-*p*-benzoquinone) was allowed to stand for a few hours after the addition of glucose and alkali, a yellow solution was formed which exhibited paramagnetic absorption. The paramagnetic intensity increased with time and, after reaching a maximum, the magnetic absorption slowly disappeared. The absorption spectrum consists of thirteen equally spaced lines with a spectroscopic splitting factor of  $g = 2.0055 \pm 0.0004$ . The spacing between the lines is  $1.88 \pm 0.05$  gauss.

A spectrum of thirteen equally spaced lines is pre-

(28) T. H. James, J. M. Snell and A. Weissberger, *THIS JOURNAL*, **60**, 2084 (1938).

(29) L. Michaelis and M. P. Schubert, *J. Biol. Chem.*, **119**, 133 (1937).

dicted if the twelve methyl group protons are equivalent, and the predicted intensity ratios would be 1:12:66:220:495:792:924:792:495:220:66:12:1. No intensity measurements have been made on this spectrum, but the extreme outside peaks were only observed with considerable difficulty. Qualitative observations indicate that the experimental intensity ratios are probably of the correct order of magnitude. If the splitting is attributed to proton hyperfine interaction, the hyperfine splitting constant would be  $(a/h) = 5.28 \pm 0.15$  Mc./sec.

(d) Other Quinone-type Systems.—A spectrum was found from the radical formed when an alcoholic solution of *p*-toluhydroquinone was subjected to experiments similar to those performed on hydroquinone. At least twenty overlapping lines were observed in the spectrum.

Radicals have also been observed in a solution of 9,10-phenanthrenequinone when an alkaline alcoholic solution is reduced with glucose. The intensity of the magnetic absorption varied with time in a manner similar to the time variation of the spectrum of the radical formed on the reduction of duroquinone. The spectroscopic splitting factor is  $g = 2.0055 \pm 0.0004$  and the spectrum consists of five main lines which exhibit further structure.

A related type of radical has been found in the solution made by adding alkali to a mixture of solutions of benzil and benzoin. The concentration of the radical, which is unstable in the presence of oxygen, increases with increasing pH. The spectroscopic splitting factor is  $g = 2.0059 \pm 0.0004$  and at least seventeen lines are found in the spectrum.

### Discussion

The structure of the paramagnetic resonance spectrum observed in the alkaline solutions containing oxidized hydroquinone is considered to be convincing evidence that: (1) the splitting is due to protons, and (2) the radical observed is the semiquinone ion. Completely unequivocal proof of the nature of the splitting would be provided by preparing the deuterated compound, but the spectra of the radicals produced from the other hydroquinones and quinones are also at least qualitatively in agreement with the hypothesis of proton splitting: the spectrum obtained from the reduction of duroquinone has shown the predicted number of components, with intensity ratios of the correct order of magnitude, and the other compounds investigated exhibit spectra in which the complexity and the magnitude of the splittings are consistent with this hypothesis.

Rudimentary calculations of the magnitude of the hyperfine interaction constant are not in agreement, however, with the observed values. The odd electron in the benzosemiquinone ion must be part of the  $\pi$ -electron system, but since the plane of the ring is a node of the  $\pi$ -electron wave functions, the density of the odd electron is zero at the equilibrium positions of the protons. Weissman has suggested that the requisite interaction could be accounted for by including the effects of zero-point vibrations of the protons,<sup>30</sup> and a computation based on this model has been made. Slater-type<sup>30</sup>

(30) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

2p carbon orbitals were employed to calculate the interaction between a vibrating proton and one  $\pi$ -orbital, and a rough molecular orbital calculation was used to obtain the density of the odd electron at each carbon and oxygen atom. The calculated interaction constant was about an order of magnitude too small. This lack of agreement is not considered to be a fundamental inconsistency, however, because distortions that might occur in the shape of the 2p orbitals could account for the discrepancy without seriously affecting the over-all shape and properties of the wave function.<sup>31</sup> It is not believed that this disagreement between theory and experiment is inconsistent with the interpretation of relative interaction constants for similarly situated protons in different molecules as relative electron densities at the protons.

A similar calculation for duroquinone, assuming non-vibrating methyl groups, gives a result that is two to three orders of magnitude too small. Hyperconjugation, which was neglected in this calculation, causes delocalization of the methyl group electrons into the  $\pi$ -orbitals of the ring. If this phenomenon were taken into account, the magnitude of the calculated interaction constant should be increased and although calculations of this type have not yet been performed, we believe that these

(31) Jarrett and Sloan (see ref. 16) have recently proposed a different mechanism. An indirect coupling between the electron and proton moments through the chemical bond has been suggested, similar to the coupling between nuclear moments observed in nuclear magnetic resonance spectra, but no quantitative estimates of the effect have been made.

measurements may represent the first direct evidence for hyperconjugation.

The complete interpretation of the proton hyperfine splitting in spectra from radicals containing more than one ring has not been accomplished as yet, and it may not be possible to analyze these complex spectra until extensive knowledge of the magnitudes of the splittings in simple compounds is obtained. As the number of rings is increased, the density of the odd electron at the protons is reduced to such an extent that it is not possible to obtain complete resolution of the component lines and, as the number of protons is increased, the range of intensities become so large that it is difficult to detect the weakest components.

The observation of paramagnetic resonance spectra is clearly a sensitive method for detecting and identifying free radical intermediates. The studies performed on the *p*-benzosemiquinone ion, for example, have shown that this ion is more stable than might have been supposed.<sup>32</sup> By the use of this technique, the equilibrium measurements on semiquinones carried out by Michaelis and his collaborators can be extended to relatively unstable systems. Kinetic studies of auto-oxidations can be elucidated by using the paramagnetic intensity to follow the course of the reaction, and rapid reactions can probably be studied by the use of a stirred-flow reactor. We also believe that the method will be useful in determining the nature of the side reactions that occur in many quinone systems.

(32) L. Michaelis and S. H. Wollman, *Science*, **109**, 313 (1949).

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## Studies on Ion-exchange Resins. XIII. Selectivity Coefficients of Quaternary Base Anion-exchange Resins Toward Univalent Anions

BY HARRY P. GREGOR, JACK BELLE<sup>1</sup> AND R. A. MARCUS

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Selectivity coefficients of a quaternary base ammonium anion-exchange resin toward a number of univalent anions have been measured. In some systems the selectivity coefficients varied little with composition, while in others a marked dependence was observed. Examples of the former included systems made up of various pairs of ions from Group A—halide, acetate, iodate and nitrate, or of pairs of ions from Group B—thiocyanate, perchlorate, di- and trichloroacetate, trifluoroacetate, toluenesulfonate and naphthalenesulfonate. Examples of systems where the selectivity coefficient changed markedly were made up of an anion from Group A with one from Group B. These data were interpreted in terms of two postulated types of specific interactions (ion-pair formation) of these ions with those of the resin matrix. The ion-pairs of Group A were assumed to be randomly distributed in the resin phase, while those of Group B were assumed to occur in the form of "patches," *i.e.*, form clusters. The effect of temperature on the distribution coefficient was small; the concentration of the solution (when dilute) had a negligible effect upon the selectivity.

The previous paper in this series showed that the exchange capacity of a quaternary ammonium base-anion exchange resin was the same for a number of univalent anions and that the swelled volume of the resin phase in different exchange states appeared to be a function of interactions between the movable exchange anions and the fixed groups.<sup>2</sup> This paper describes the selective uptake of one anionic species

over another for various combinations of ions with resins of different degrees of cross-linking, and the effect upon this selectivity by variations in the ionic strength of the equilibrating solution and the temperature of the system. These results are interpreted in terms of two different mechanisms of ion-pair formation.<sup>3</sup>

### Experimental

A series of benzylethanoldimethylammonium anion exchange resins (Dowex 2, Dow Chemical Co., Midland, Michigan) was used in this study. These resins were identical with ones used in the previous paper<sup>1</sup> and are desig-

(1) Taken in part from the Dissertation submitted by Jack Belle in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, Polytechnic Institute of Brooklyn, October, 1952.

(2) H. P. Gregor, J. Belle and R. A. Marcus, *THIS JOURNAL*, **76**, 1984 (1954).

(3) H. P. Gregor, *ibid.*, **73**, 3537 (1951).