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Electrochemical Generation of Free Radicals and Their Study by Electron Spin Resonance Spectroscopy; the Nitrobenzene Anion Radical

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The nitrobenzene anion radical, $(\cdot C_6H_5NO_2)^-$, has been prepared by constant potential electrolysis of nitrobenzene solutions at a mercury pool electrode placed directly inside the microwave cavity of an electron spin resonance spectrometer. Acetonitrile was used as a solvent with tetra-*n*-propylammonium perchlorate as supporting electrolyte. Well-resolved electron spin resonance spectra of the radical reduction product exhibit a hyperfine structure consisting of fifty-four components. Hyperfine coupling constants have been assigned for the interaction of the unpaired electron with the various ring protons and the nitrogen nucleus. The odd electron distribution in the molecule is seen to be at least qualitatively in agreement with that predicted by conventional valence bond theory. The large hyperfine interaction with the nitrogen nuclear moment is presumed to arise from a $\sigma-\pi$ exchange interaction on the nitrogen atom. Electrochemical generation in acetonitrile offers advantages over conventional alkali metal reductions in solvents such as tetrahydrofuran and 1,2-dimethoxyethane.

Vigorous development of electron spin resonance spectroscopy (e.s.r.s.) over the past fifteen years has provided the chemical world with a physicochemical tool of unique selectivity and wide versatility. Among the diverse applications of e.s.r.s. the study of dilute solutions of organic free radicals has been particularly significant. The interest in this study stems mainly from the rich hyperfine structure exhibited by spectra of these radicals; the hyperfine structure is attributed to interaction of the magnetic moment of the unpaired electron with the magnetic nuclei in the molecule. Ideally, such hyperfine structure can lead to a "mapping" of density of the unpaired electron throughout the molecule.[1]

Spin resonance studies of solid polycrystalline free radicals are generally unfruitful in mapping unpaired electron density. The hyperfine structure is usually not observed because of several factors: anisotropy in the g-factor and hyperfine coupling constants, strong intermolecular dipolar broadening and electron exchange interactions. Usually the latter effect is most pronounced in solid free radicals and a single exchange narrowed[2] line with a g-factor near 2.00 is observed.

To observe hyperfine structure most readily, measurements are made on dilute fluid solutions so that the dilution minimizes the effects of exchange and dipolar broadening and the rapid molecular tumbling averages out the anisotropic contributions to the g-factor and hyperfine coupling.[3] Measurements made on dilute radical solutions in glassy media also suffer from the effects of anisotropy and usually little hyperfine structure is resolved.

Considerable attention has been focused on the study of organic radicals prepared by one-electron reduction of the parent molecule, usually in 1,2-dimethoxyethane or tetrahydrofuran solution. The conventional preparative procedure, which involves use of alkali metals as the reducing agent, has several intrinsic difficulties. Not only is the preparation laborious but the presence of metal in the solution may complicate interpretation of the spectrum.[4]

In this context the use of an *electrode* as a selective reducing agent is particularly attractive. In fact, one-electron reductions, and hence generation of free radicals, have been observed by polarographic techniques when an aprotic solvent system has been used. Furthermore, Austin, *et al.*,[5] have used e.s.r.s. to verify the occurrence of free radicals in the polarographic reduction of anthracene, benzophenone and anthraquinone in N,N-dimethylformamide solution. Samples were taken during the course of a controlled potential electrolysis, frozen in liquid nitrogen and transferred to the spectrometer; the spin resonance was measured at liquid oxygen temperature. Since the measurements were done on a solid sample, considerable broadening of the lines occurred (because of the g-factor and hyperfine anisotropy) and no hyperfine structure was observed in the spectra.

This paper presents electron spin resonance data obtained for a dilute acetonitrile solution of the nitrobenzene anion radical, $(\cdot C_6H_5NO_2)^-$. The radical was generated electrochemically by constant potential electrolysis in a cell placed directly in the microwave resonance cavity (*intra muros*). This *intra muros* technique has been reported previously.[6]

Acetonitrile was chosen as solvent for three reasons: (1) acetonitrile is rather inert, *i.e.*, is a weaker base and a much weaker acid than water; (2) the dielectric constant is reasonably high, 36.0, so that ion clustering is decreased in comparison to solvents like tetrahydrofuran; (3) a significant body of polarographic data already has been obtained using acetonitrile as solvent.[7-12]

The nitrobenzene anion radical was chosen for this illustrative study because the radical has

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[1] H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956); R. Bersohn, *ibid.*, **24**, 1066 (1956); S. I. Weissman, *ibid.*, **25**, 390 (1956).

[2] J. H. Van Vleck, *Phys. Rev.*, **74**, 1168 (1948).

[3] S. I. Weissman, *J. Chem. Phys.*, **22**, 1378 (1954).

[4] (a) F. C. Adams and S. I. Weissman, THIS JOURNAL, **80**, 1518 (1958); (b) R. L. Ward and S. I. Weissman, *ibid.*, **79**, 2086 (1957); T. R. Tuttle, Jr., R. L. Ward and S. I. Weissman, *J. Chem. Phys.*, **25**, 189 (1956).

[5] D. E. G. Austen, P. H. Given, D. J. F. Ingram and M. E. Peover, *Nature*, **182**, 1784 (1958).

[6] A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **30**, 1356 (1959). See also *Anal. Chem.*, **31**, 1450 (1959).

[7] S. Wawzonek and M. E. Runner, *J. Electrochem. Soc.*, **99**, 457 (1952).

[8] S. Wawzonek, E. W. Blaha, R. Berkey and M. E. Runner, *ibid.*, **102**, 235 (1955); **103**, 456 (1956).

[9] I. M. Kolthoff and J. F. Coetzee, THIS JOURNAL, **79**, 870, 1852, 6110 (1957).

[10] A. I. Popov and D. H. Geske, *ibid.*, **79**, 2074 (1957); **80**, 1340, 5346 (1958).

[11] D. H. Geske, *J. Phys. Chem.*, **63**, 1062 (1959).

[12] D. H. Geske, THIS JOURNAL, **81**, 4145 (1959).

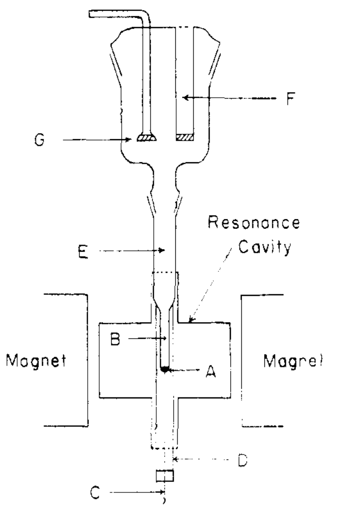

Fig. 1.—Electrochemical cell and its placement in microwave resonance cavity. See text for description.

been previously subjected to thorough investigation employing conventional preparative techniques. Weissman, *et al.*,[13] observed the spin resonance when nitrobenzene dissolved in 1,2-dimethoxyethane was reduced with metallic sodium. Assignment of hyperfine coupling constants in the previously observed ten line spectrum has been done by means of deuterium and N^{15} substitutions in the molecule.[14]

Experimental

Electrochemical Cell.—Several alternatives are available when considering placing a mercury electrode assembly into a resonance cavity for purposes of studying hyperfine structure in the radical spectrum. A conventional dropping mercury electrode could be employed; however, the dropping action of the electrode would periodically distort the concentration profile of the newly-generated radical and cause corresponding distortions in the recorded spectrum and also result in considerable electronic noise. A hanging mercury drop would overcome this difficulty but the drop is subject to accidental dislodgement during handling of the cell assembly. Our experience has been that a mercury pool electrode is the most convenient choice for the study of long-lived radicals.

The all-glass electrochemical cell and its position in the microwave cavity are shown in Fig. 1. A mercury pool, A, which has an exposed area of 2.5×10^{-2} cm.², is placed at the bottom of tube B (3 mm. o.d. Pyrex). A platinum wire, C, sealed into the bottom of B contacts the mercury pool and is held firmly in place by a collar at the bottom of tube D. Quartz tube D, which is connected to the body of tube E with Epoxy resin, protects tube B in handling and also allows the entire cell assembly to be clamped in place above and below the microwave cavity. An aqueous saturated calomel electrode which makes electrolytic contact through a soft glass–Pyrex Perley seal is placed into insert tube F which has a sintered-glass disk end. In practice the sample solution is subjected to preliminary degassing by extending a fine glass capillary through a pinhole in the top of the cell to within one mm. of the mercury pool and passing nitrogen through both the capillary and through sintered-glass disk G. The flow of nitrogen is continued through G during the electrolysis run. Resistance of the cell circuit was approximately 20×10^3 ohms with the sample solutions studied.

As shown in Fig. 1, the cell assembly is positioned along the axis of a cylindrical cavity with the surface of the mercury pool slightly below vertical center of the cavity. If polarographic data are not available for the system under study, a pool polarogram[15] may conveniently be taken to determine the appropriate applied potential. A simple potentiometer circuit with microammeter was used to carry out the electrolyses.

Polarographic Measurements.—Polarographic data were obtained at 25.0° using a Sargent Model XXI recording polarograph with appropriate span voltage and current sensitivity calibrations. The dropping mercury electrode had a drop time of 4.0 sec. and a flow rate of 1.4 mg. sec.$^{-1}$ at -1.3 v. *vs.* aqueous saturated calomel electrode (s.c.e.), a potential on the plateau of the first reduction wave of nitrobenzene. Half-wave potential data were corrected for *iR* drop in the cell. An aqueous saturated calomel reference electrode was used throughout.

E.s.r. Spectrometer.—The spectrometer is a conventional *x*-band apparatus employing a cylindrical reflection cavity operating in the TE_{011} mode. Frequency drift of the klystron oscillator (Varian X-13) is minimized by immersing it in a large container of mineral oil and in addition by locking its frequency to that of the sample cavity by means of a modified Pound feedback circuit operating at a frequency of 100 kc. p.s.

The microwave circuit contains a reflection cavity wavemeter that has been calibrated against a crystal harmonic *x*-band generator. This instrument is used for the measurement of the sample cavity resonant frequency for each experiment.

The 6-inch electromagnet and power supply are the Varian V4007 and V2200A and give a magnetic field homogeneity of better than 0.1 gauss over the volume of the sample and about 0.2 gauss over the probe volume of the proton magnetic resonance spectrometer used for magnetic field calibration. The width of the magnet gap is 2.75 inches, which is sufficient to allow the microwave cavity and proton resonance probe to be simultaneously inserted along the axis of the magnet gap and thereby to enable the precise determination of absolute magnetic field at the sample position.

The magnetic field is swept by means of a steadily varying d.c. potential that is applied to the magnet power supply and is simultaneously modulated over a small amplitude at 280 c.p.s. by means of modulating coils wound around the magnet pole pieces. The signal during a resonance absorption is detected at a crystal, amplified by a narrow band audio amplifier, phase detected and finally applied to a graphic recorder to produce a tracing of the first derivative of the absorption.

The magnetic field is monitored by means of repetitions of the following operations: the proton resonance spectrometer is tuned to an approximate frequency that is accurately measured by comparison with a BC-221 frequency meter. When the center of the proton resonance appears at the output a marker is applied to the electron spin resonance tracing. The proton resonance spectrometer is retuned to a higher frequency (the magnetic field is swept toward higher values), etc. The result is a series of absolute magnetic field calibration markers on the electron spin resonance spectra. The crystal of the BC-221 frequency meter was calibrated by comparison with radio station WWV at 10 megacycles.

Reagents.—Technical grade acetonitrile was purified by the method of Wawzonek and Runner.[7] After two distillations from phosphorus pentoxide the solvent had a boiling point of 81.5° at 760 mm.

Tetra-*n*-propylammonium perchlorate for use as a supporting electrolyte was prepared by neutralizing an aqueous solution of tetra-*n*-propylammonium hydroxide, obtained as a 10% aqueous solution from Eastman Kodak Co., with an equivalent quantity of perchloric acid. The solubility of tetra-*n*-propylammonium perchlorate in water at 25° is sufficiently small so that almost quantitative precipitation occurs. The salt was washed with a liberal quantity of water, filtered and recrystallized from aqueous acetonitrile (80 vol.% water) and finally dried *in vacuo* over phosphorus pentoxide.

Nitrobenzene (Eastman White Label) was used without further purification. A sample of *m*-mono*deuterio*nitrobenzene was prepared according to the method of Dauben, *et al.*[16]

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(13) T. E. Chu, G. E. Pake, D. E. Paul, J. Townsend and S. I. Weissman, *J. Phys. Chem.*, **57**, 504 (1953).

(14) R. L. Ward and M. P. Klein, *J. Chem. Phys.*, **28**, 518 (1958); **29**, 678 (1958), R. L. Ward, *ibid.*, **30**, 852 (1959)

(15) See P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p. 115 ff.

(16) W. G. Dauben, G. C. Pimentel, C. W. Vaughan, Jr., This Journal, **77**, 2889 (1955).

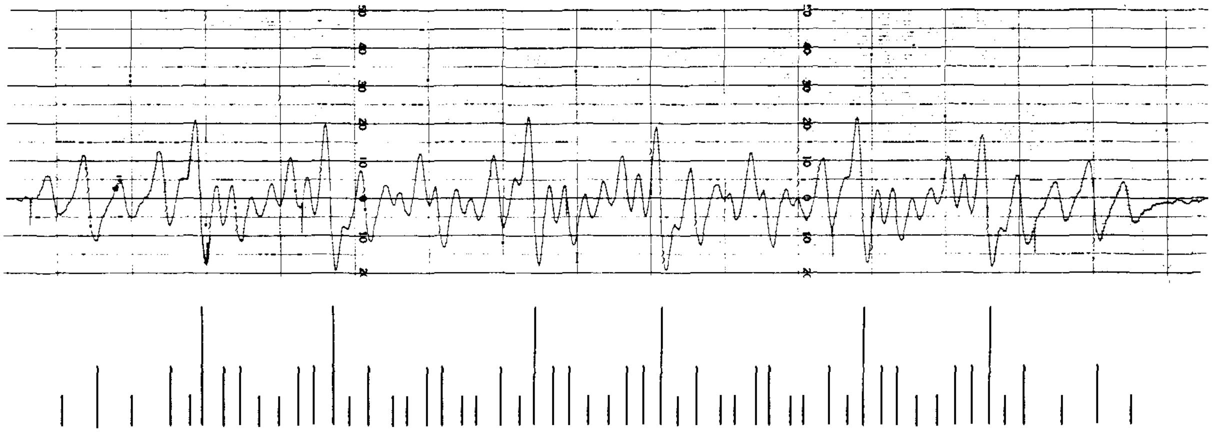

Fig. 2.—Derivative of the electron spin resonance absorption spectrum of nitrobenzene anion radical in acetonitrile plotted *vs.* magnetic field strength. Lower portion is the calculated absorption spectrum. The heights of the component lines are proportional to the calculated relative intensities.

with modifications that increased the isotopic purity of the product to > 80%. Nitrogen (Linde prepurified) was passed over hot copper gauze into a drying column and through an acetonitrile presaturator.

Results

The first of two polarographic waves in the reduction of nitrobenzene in acetonitrile[17] has been interpreted as representing a one-electron reaction. If this is the case and if the reaction product is reasonably stable, electrochemical generation offers a convenient preparative method for the nitrobenzene anion radical, $(\cdot C_6H_5NO_2)^-$

Since the available literature report[17] was brief, we undertook a preliminary study of the polarography of nitrobenzene in acetonitrile. A polarogram of 2.18 m*M* nitrobenzene in acetonitrile with 0.1 *M* tetra-*n*-propylammonium perchlorate as supporting electrolyte[18] showed two reduction waves, the first with a half-wave potential of −1.15 v. *vs.* s.c.e. and a diffusion current of 14.1 μamp. Since the second wave was distorted by a current maximum the half-wave potential, −1.9 v. *vs.* s.c.e., is only approximate. The diffusion current for the second wave was 29.6 μamp. It is evident that the waves are sufficiently separated so that with proper choice of potential only the anion radical would be produced at the electrode surface.

The diffusion current current constant, $\frac{i_d}{m^{2/3}t^{1/6}C}$, where i_d is expressed in μamp., *m* in mg./sec., *t* in seconds, and *C* in millimoles per liter, for the first reduction reaction is 4.07. This current constant can be compared with that for reduction of silver ion in acetonitrile,[10] 3.10, a known one-electron reaction. Furthermore, Wawzonek, *et al.*,[8] have postulated a one-electron process for reduction of various quinones in acetonitrile where the current constant ranged from 3.53 to 3.07. The first nitrobenzene reduction wave also fits the criteria of Tomes[19] for a reversible one-electron reaction, *i.e.*

$$E_{3/4} - E_{1/4} = -56 \text{ mv.}$$

On the basis of the foregoing evidence it is appropriate to assume that nitrobenzene in acetonitrile solution undergoes an initial one-electron reduction.

$$C_6H_5NO_2 + e \longrightarrow (\cdot C_6H_5NO_2)^-$$

With polarographic data at hand it is possible to select an appropriate potential for generation of the radical in the electrochemical cell within the resonance cavity. In the case of nitrobenzene a potential of −1.3 v. *vs.* s.c.e. was used. In contrast to the current–time behavior of a dropping mercury electrode where the current increases as the drop grows, the current observed with the essentially plane electrode (A in Fig. 1) decayed with time. The geometry of the cell is such that the current should closely follow the linear diffusion current law[20]

$$i_d = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}}$$

where *n* is the number of faradays per mole, *F* the number of coulombs per faraday, *A* the area of the electrode, *D* the diffusion coefficient and *t* is the time since initiation of the electrolysis.

Figure 2 is representative of a series of e.s.r. spectra which were obtained for an acetonitrile solution of 1.09 m*M* nitrobenzene (containing 0.1 *M* tetra-*n*-propylammonium perchlorate as supporting electrolyte) which was electrolyzed at −1.3 v. *vs.* s.c.e.

Spectra with good signal to noise ratios could not be obtained before about 10 minutes after the commencement of electrolysis. After this time, the signal to noise ratio improved with time until very good spectra could be obtained after about one-half hour.

This behavior is reasonable since the concentration profile through the solution along the axis of

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[17] M. E. Runner and G. Balog, Abstracts of 108th Meeting, The Electrochemical Society, Pittsburgh, Pa., Oct. 9–13, 1955, as reported in *J. Electrochem. Soc.*, **102**, 226C (1955). Since the completion of the present work it has come to the authors' attention that a more extensive report is found in the Ph.D. thesis of George Balog, Illinois Institute of Technology, Chicago, Ill.

[18] The purpose of the supporting electrolyte as used in both polarographic work and electrogeneration of the radical for e.s.r. study is to increase the conductivity of the solution.

[19] J. Tomes, *Collection Czechoslov. Chem. Communs.*, **9**, 12, 81, 150 (1937).

[20] See discussion by I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952, p. 21 ff.

the cavity changes as follows (assuming semi-infinite linear diffusion)[21]

$$C_{\mathrm{R}} = C_{\circ}^{0}\left[1 - erf\left(\frac{x}{2D^{1/2}t^{1/2}}\right)\right] \qquad (1)$$

where $erf(\lambda) = \frac{2}{\pi^{1/2}}\int_0^{\lambda} e^{z^2}\,dz$, x is the linear distance from the surface of the electrode, D is the diffusion coefficient of the radical (which is assumed equal to that of the unreduced species), C_{R} is the radical concentration and $C_{\circ}^{0}$ is the initial concentration of the oxidized form. Values of $C_{\mathrm{R}}/C_{\circ}^{0}$ calculated from eq. 1 are given in Table I for various values of time and distance from the electrode surface assuming a diffusion coefficient of 3.6×10^{-5} cm.^{2} sec.$^{-1}$

TABLE I

CALCULATED VALUES OF $C_{\mathrm{R}}/C_{\circ}^{0}$

	x, cm.		
t, sec.	0.1	0.2	0.3
400	0.56	0.24	0.08
900	.70	.44	.24
2500	.82	.65	.49

While we do not have an exact expression for the sensitivity of the spectrometer *versus* the distance of the sample from the surface of the electrode, we can state qualitatively that because of the geometry of the microwave magnetic field and its effect on the filling factor, the region immediately above the drop is not very sensitive and that the sensitivity increases with linear distance from the drop and decreases again as the upper wall of the cavity is approached. The time interval necessary for obtaining the best spectra is that required for a reasonable concentration of free radicals to be established in the sensitive region of the microwave cavity by the linear diffusion process.

The individual line width of well-resolved components of the spectrum in Fig. 2 is 0.32 gauss measured between points of maximum slope. Total width of the spectrum measured between centers of the two extreme components is 33.60 ± 0.08 gauss. The g-factor calculated from the magnetic field half-way between the two central components is 2.0032 ± 0.0001.

Discussion

Polarographic studies of the reduction of nitrobenzene in *aqueous* solution[22,23] have demonstrated the occurrence of two waves representing four- and two-electron reactions, respectively, at pH <5, while only the first wave occurs in more basic media. The gross difference in polarographic behavior between the aqueous and the acetonitrile systems can be largely attributed to the aprotic character of acetonitrile. Four-electron reduction to phenylhydroxylamine

$$C_6H_5NO_2 + 4e + 4H^+ \longrightarrow C_6H_5NH(OH) + H_2O$$

requires four protons; because of the relative unavailability of protons in acetonitrile, the initial one-electron reduction product does not immediately undergo protonation and further reduction, as apparently is the case in water. When a proton donor like phenol is added to acetonitrile, the second reduction wave of nitrobenzene is shifted to such positive potentials that stepwise reduction no longer is evident. Similar observations have been made for the reduction of several aromatic olefins, hydrocarbons, quinones and hydroquinones.[8]

The observation of electron spin resonance in the solution reduced at the potential of the first polarographic plateau provides further confirmation of the free radical nature of the reduction product in acetonitrile solution. The hyperfine structure exhibited by the anion in dilute solution can be examined with the intention of assigning hyperfine coupling constants which describe the magnetic interaction of the unpaired electron with the magnetic nuclei.

The spin Hamiltonian[24] for a free radical in a fluid solution may be written

$$\mathcal{H}_S = g_0\beta H\cdot S + \sum_i A_i I_i\cdot S$$

where g_0 is the g-factor of the radical, β is the Bohr magneton, H is the magnetic field vector, A_i is the hyperfine coupling constant for the ith class of nuclei[25] and S and I_i are the vector operators of electron spin angular momentum and total nuclear angular momentum of the ith class of nuclei, respectively. The solution of the spin Hamiltonian to first order for high applied magnetic fields gives the result that at fixed microwave frequency the spectrum should consist of hyperfine components whose positions are given by

$$H - H_0 = -\sum_i A_i m_i$$

H_0 is the magnetic field for resonance in the absence of hyperfine structure. m_i is the z-component of the total angular momentum of the ith class of nuclei. All possible z-components are involved in the summation. Hence, since m_i can have only integrally spaced values between I_i and $-I_i$ where I_i is the total angular momentum of the ith class, it follows that the hyperfine spectrum is symmetrically deployed in magnetic field about H_0 and that the nitrobenzene anion should contain $\prod_{i=1}^{4}(2I_i + 1) = 54$ hyperfine components. If linear combinations of the A_i with small integral coefficients are equal in magnitude to other such linear combinations, accidental degeneracies of hyperfine components may occur and the maximum possible number of components will not be resolved in the spectra. Since we observe just 54 components we are fairly certain that no such simple relationships exist between the coupling constants and that there is no observable hyperfine interaction of the electron with extraneous nuclei.

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[21] Ref. **15**, p. 47 ff.

[22] J. Pearson, *Trans. Faraday Soc.*, **44**, 683 (1948).

[23] J. E. Page, J. W. Smith and J. G. Waller, *J. Phys. Coll. Chem.*, 545 (1949).

[24] A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.* (*London*), **A205**, 135 (1951).

[25] "Class of nuclei" is used here to indicate all symmetrically equivalent nuclei, *i.e.* those whose positions are interchanged by the symmetry operations which leave the molecule unaltered. The *meta* protons of the nitrobenzene anion thus form a class of two nuclei as do the *ortho* protons. See, for example, H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944.

The values for the hyperfine coupling constants were obtained from three spectra, including the one reproduced in Fig. 2. After the hyperfine components had been identified the coupling constants were evaluated by measuring the differences in magnetic field between the most prominent and best resolved spectral components.[26] Values of the coupling constants in gauss are:

$$|A_N| = 10.32 \pm 0.03$$
$$|A_o| = 3.39 \pm 0.02$$
$$|A_m| = 1.09 \pm 0.01$$
$$|A_p| = 3.97 \pm 0.02$$

where A_N is the coupling constant of the nitrogen atom and A_o, A_m, A_p are the coupling constants of the *ortho*, *meta*, and *para* protons, respectively. Below the experimental e.s.r. spectrum in Fig. 2 is the spectrum calculated using the hyperfine coupling constants obtained from this treatment. Calculated intensities are indicated by the relative heights of the lines. Good agreement is found with respect to both line position and intensity.

Spectra of *m*-mono*deuterio*nitrobenzene anion obtained under similar experimental conditions verified that the small coupling constant was due to an interaction with the *meta* proton.

The values of the coupling constants for nitrobenzene anion in acetonitrile are largely in agreement with those determined previously by Ward and Klein[14] for the anion prepared by potassium metal reduction in 1,2-dimethoxyethane. Lack of resolution in their spectra made it impossible to distinguish between the *ortho* and *para* proton coupling constants and to obtain a value for the *meta* proton coupling constant. There is no reason to expect the coupling constants for the nitrobenzene ion to be quite the same in such different environments. The upper limit of 0.65 gauss for $|A_m|$ obtained by Ward and Klein[14] may be indicative of solvent effects upon the hyperfine structure which is observed in this radical.

Ion pairing is certainly grossly smaller in acetonitrile than in solvents of much lower dielectric constant such as tetrahydrofuran and 1,2-dimethoxyethane. Quantitative evidence is found in the work of Fuoss, *et al.*,[27] who studied the conductivity of tetrabutylammonium tetraphenylborate in various acetonitrile–carbon tetrachloride mixtures. Values for the per cent. carbon tetrachloride in the mixture, the dielectric constant of the mixture and ion-pair association constant are, respectively: 0.00, 35.99, 14.3; 90.26, 7.20, 4.09×10^4; 94.97, 4.80, 2.96×10^6. Ionic solutes in tetrahydrofuran, which has a dielectric constant of 7.39[28] and 1,2-dimethoxyethane[29] would thus be highly associated. It is necessary to observe that ion-pair formation is not a simple phenomenon as at least two types of ion-pairs have been distinguished.[30] The differentiation is based upon whether or not a solvent sheath exists between the associated ions. In order for ion-pairing to result in an observable effect upon the free radical hyperfine structure, there must occur an actual sharing of the odd electron by the ions. This electron sharing has been clearly demonstrated to occur in solutions of sodium benzophenonide, $NaOC(C_6H_5)_2$, in 1,2-dimethoxyethane.[4a] Ward[31] has observed about seventy hyperfine structure components in the spectrum of dilute sodium nitrobenzenide, $NaO_2NC_6H_5$, in the same solvent. Only fifty-four components can be expected from a simple nitrobenzene negative ion so that a hyperfine interaction with the sodium nucleus is strongly suggested. It is reasonable to suggest that an intervening solvation sheath between ions greatly reduces the probability of electron transfer. Consequently, conductivity measurements, although indicative of ion-pair formation, are not necessarily indicative of an actual electron sharing between ions leading to an observable extra hyperfine structure due to the associated ion. We feel that the probability of such "close" association is decreased in solvents of high polarity due to the increased stability of the solvation sphere.

Under the conditions of our experiment no hyperfine attributable to tetra-*n*-propylammonium ion is observed. Either there is an association involving an extremely small transfer of odd electron density to the tetra-*n*-propylammonium ion or any association is of an extremely transitory nature such that the lifetime of the complex is much less than the reciprocal of the expected hyperfine interaction (expressed in cycles per second).

Not only does electrochemical generation offer an advantage in eliminating alkali metals from the solution but with proper choice of electrode potential only the monovalent reduction product is obtained. In contrast, alkali metal reductions may proceed beyond the univalent anion to a divalent anion,[32] *e.g.*, anthracene reacts with sodium to form the di-sodium adduct in tetrahydrofuran. Since paramagnetic products have been observed in this case,[33] the suggestion has been made that the rate of formation of the divalent anion is slow.[32]

McConnell and Chestnut[34] have demonstrated that in aromatic hydrocarbons a proportionality exists between the proton hyperfine coupling constant and the unpaired electron spin density in the π-orbital of the contiguous carbon atom. The ground state valence bond wave function of the nitrobenzene negative ion can be considered to be described by a linear combination of bond eigenfunctions of the types

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(26) B. Venkataraman, B. C. Segal and G. K. Fraenkel, *J. Chem. Phys.*, **30**, 1006 (1959).

(27) F. Accasina, S. Petrucci and R. M. Fuoss, THIS JOURNAL, **81**, 1301 (1959).

(28) F. E. Critchfield, J. A. Gibson and J. L. Hall, *ibid.*, **75**, 6044 (1953).

(29) Although the dielectric constant of 1,2-dimethoxyethane has not been reported in the literature, it is safe to assume that the value is close to that of tetrahydrofuran.

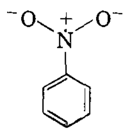
(30) E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).

(31) R. L. Ward, University of California Radiation Laboratory Report No. 5330 (1958).

(32) G. J. Holjtink, E. DeBoer, P. H. Van Der Meij and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956).

(33) D. Lipkin, D. E. Paul, J. Townsend and S. J. Weissman, *Science*, **117**, 534 (1953).

(34) H. M. McConnell and D. R. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).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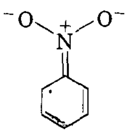
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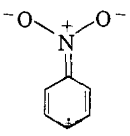
III

The hyperfine interaction with the nitrogen nucleus is presumed to arise by means of $\sigma-\pi$ configurational interaction mainly from the contribution of bond eigenfunction I to the ground state wave function. Brovetto and Ferroni[35] and McConnell[36] have shown that not only does the contribution of bond eigenfunctions II and III lead to a positive spin density on the *ortho* and *para* carbon atoms but the cross terms of these bond eigenfunctions results in a *negative* spin density on the meta carbon atoms, the magnitude of which is usually 1/3 to 1/2 that in *ortho* or *para* position.[37] The hyperfine structure does not allow the assignment of the sign of the spin density on the carbon atoms, but we feel that the ratio of the hyperfine coupling constants of the *ortho* and *para* to the *meta* protons is qualitatively in agreement with a valence bond description of the nitrobenzene anion in terms of structures I, II and III. By way of contrast, molecular orbital calculations with reasonable values for coulomb and resonance integrals for the nitro group lead to much too little unpaired electron density in the *meta* π-orbitals.

Several other approaches to electrochemical generation of radicals are available. A continuous flow system from the electrochemical cell into the microwave cavity could be employed, or a sample could be transferred from the cell into a sample tube for measurement. By comparison, the *intra muros* cell technique offers significant advantages in simplicity and convenience. The present cavity design limits the study to reasonably stable anion radicals; eventual development of techniques for observing transient radicals at a mercury electrode will provide a significant tool in the study of electrode processes.

Preliminary work has been done in this Laboratory employing a platinum electrode for generation of radicals by electroöxidation at controlled potential.

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[35] P. Brovetto and S. Ferroni, *Nuovo Cimento*, **5**, 142 (1957).

[36] H. M. McConnell, *J. Chem. Phys.*, **29**, 244 (1958); **30**, 328 (1959).

[37] The authors are indebted to both referees for pointing this out.

[CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

The Radiation Chemistry of the Symmetrical Dichloroethylenes[1]

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Purified, degassed liquid samples of *cis*- and *trans*-1,2-dichloroethylenes have been irradiated with helium ions, electrons and gamma-rays. A comparison of the radiolysis products has been made with the products formed in the polymerization of these compounds with benzoyl peroxide. Using a combination of gas chromatography and mass spectrometry, several of the high boiling products (to ~350°) have been characterized as to compound types. The yields of volatile products did not change greatly with changes in linear energy transfer but the yields of polymer products were found to increase markedly with decreasing density of ionization. A mechanism has been proposed to explain the formation of the observed products.

Introduction

As part of a program of investigating the radiation chemistry of organic compounds containing various functional groups, a number of alcohols[3] and ethers[4] have been investigated; the work has now been extended to the study of a simple olefin. The symmetrical dichloroethylenes were chosen for this purpose, as they are perhaps the simplest compounds containing the functional groupings RCH=CHR for which the phenomenon of long-chain polymerization does not dominate and obscure the other reactions taking place. A study of the more complex compound, isopropenyl acetate, has been reported elsewhere.[5] Further, the investigation of the *cis* and *trans* isomers of 1,2-dichloroethylene permits the comparison of the radiation effects on two compounds differing in their physical properties primarily in that the *cis* isomer has a large dipole moment (1.8 Debye), while the *trans* isomer has no net moment.[6] Because a difference in dielectric constant of the substrate might be expected to have an effect on rates of ionic reactions, this feature is perhaps pertinent to the issue of the importance of ionic processes in the radiation chemistry of condensed phases.[7]

Experimental

Purification of Compounds.—Eastman White Label chemicals were purified by distillation through an 85-plate adiabatic column packed with Podbielniak Helipak No. 3013

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[1] Much of the work presented here is from the dissertation submitted by Jean H. Futrell in partial fulfillment of the requirements for the Ph.D. degree in September, 1958.

[2] Author to whom requests for reprints are to be addressed.

[3] W. R. McDonnel and A. S. Newton, THIS JOURNAL, **76**, 4651 (1954).

[4] A. S. Newton, *J. Phys. Chem.*, **61**, 1485 (1957).

[5] A. S. Newton and P. O. Strom, *ibid.*, **62**, 24 (1958).

[6] G. E. K. Branch and M. Calvin, "Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, p. 138.

[7] M. Burton in "Hearings on Physical Research Program as it Relates to the Field of Atomic Energy," Subcommittee on Research and Development of the Joint Committee on Atomic Energy, Eighty fifth Congress, Second Session (United States Government Printing Office, Washington 25, D. C., 1958), p. 110.