Electron Spin Resonance of Electrolytically Generated Nitrile Radicals[1,2]

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Electron spin resonance spectra have been obtained for a series of anion radicals of aromatic and aliphatic nitriles. The radicals were generated by electrolytic reduction in N,N-dimethylformamide solution. Polarographic investigations, both conventional and oscillographic, were also performed. In obtaining the E.S.R. spectra, techniques were employed by which the starting material could be almost completely reduced to the radical, and thus the broadening of the lines in the spectra that arises from intermolecular electron exchange was largely eliminated. In most cases, a well-resolved E.S.R. spectrum was obtained from the radical expected as the product of a simple reduction process, but in some reductions complex reactions took place. In a few reductions, unresolvable spectra, or no spectra at all, were obtained. Many of the radicals were stable for long periods of time (several hours or more), but a few decayed quite rapidly (a few minutes or less). Some of the compounds were reduced at potentials corresponding to several different polarographic waves and resulted in more than one type of radical from a single starting material. A number of reduction mechanisms were elucidated by a comparison of polarographic and E.S.R. data. The majority of the spectra were completely interpreted and assignment of the splitting constants to the appropriate nuclei (H, N^{14}, N^{15}, C^{13}) in the molecule was possible. Qualitative observations of electron exchange reactions and of solvent effects were also made.

I. Introduction

Most of the organic free radicals studies in solution by electron spin resonance (E.S.R.) have been generated by chemical oxidation or reduction. Austen, Given, Ingram and Peover,[5] however, employed electrolytic techniques and were able to detect anion radicals by E.S.R. in frozen N,N-dimethylformamide solutions of anthracene, benzophenone and anthraquinone. Their work was followed by Maki and Geske,[6-9] who obtained E.S.R. spectra of the electrolytically generated anion radicals of many nitro compounds in acetonitrile solution at room temperature under polarographic conditions. Maki[10] has since studied the E.S.R. spectrum of the terephthalaldehyde anion radical in dimethyl sulfoxide, and Piette, Ludwig and Adams[11] have observed electrolytically generated anion radicals of nitro compounds in aqueous solution. Extension of the technique to still other classes of compounds and to other solvent systems is proceeding rapidly.

In the preparation of radicals for study by E.S.R., electrolysis offers two distinct advantages over oxidation or reduction by chemical reagents: (1) A continuous and easily adjustable range of oxidation or reduction potentials is available; (2) tetraalkyl ammonium salts, which can be used as the supporting electrolytes for electrolysis, interact with anion radicals to a much smaller extent than the smaller cations formed when alkali metal or similar metallic reductants are employed.

E.S.R. investigations of electrolytically produced radicals can also be used as an aid to the interpretation of polarographic measurements since qualitative identification of radical species is frequently possible. Conversely, polarographic measurements, both conventional and oscillographic, are helpful in establishing the optimum conditions for carrying out the electrolytic reductions.

We have investigated the E.S.R. spectra of a series of electrolytically generated nitrile anion radicals. Polarographic studies have also been performed. In obtaining the E.S.R. spectra, techniques were employed

by which the starting material could be almost completely reduced to the radical so that the broadening of the lines of the spectra resulting from intermolecular electron exchange[12,13] was largely eliminated. Some of the compounds were reduced at potentials corresponding to several different polarographic waves and the reduction mechanisms elucidated from a comparison of the polarographic and E.S.R. data.

The evaluation of the π-electron spin densities in the radicals from the isotropic hyperfine interactions, and a comparison of these spin densities with valence theory calculations, are presented elsewhere.[14]

II. Experimental Techniques

1. **Electrochemical Cell and Generation of Radicals.**—Several factors influence the design of electrolytic cells to be used for E.S.R. studies. Geske and Maki[6] chose an *intra muros* technique, with the mercury pool cathode within the microwave cavity. This has the advantages of simplicity and ease of operation. In the present work, however, we have placed the cell outside this cavity, an arrangement which necessitates transfer of the solution prior to E.S.R. observation but allows rapid quantitative reduction of appreciable amounts of material because it permits the use of a large electrode area. Complete reduction is desirable because many of the radicals undergo rapid electron exchange reactions with their precursors that broaden the lines in the spectrum. Complete reduction is particularly important when more than one polarographic wave occurs and the products of the successive reductions are to be examined. The use of an external electrolytic cell with known concentrations and volumes of material, together with measurement of the number of coulombs passed during the electrolysis, permits control of the radical concentration in stoichiometric reductions. Under these controlled experimental conditions, absolute measurement of E.S.R. signal strengths, and therefore of the radical concentrations, can be used to evaluate the efficiency of the reduction. In addition, external generation provides convenient access to the cell for observation of color changes, gas evolution, etc. For unstable radicals, the generating cell must be coupled to a fast flow system. The lifetimes of radicals investigated in the present work, however, ranged from the order of minutes to several hours or more.

The electrochemical cell is pictured in Fig. 1. A mercury-pool cathode A is connected by mercury in a Nalgon tube at B to a mercury reservoir where electrical contact is made. The reservoir may be raised or lowered to adjust the volume of the cathode compartment. An inlet tube C is attached through a Teflon tube to a solution reservoir in which the reference electrode makes contact. An outlet tube D is attached through a Teflon tube to the glass sample tube mounted in the microwave cavity of the spectrometer, and a rubber tube equipped with a screw clamp is attached to the sample tube below the cavity to adjust the flow of solution from the cell to the cavity. The upper anode compartment E is held to the lower chamber by rubber bands on the hooks F. Separating the anolyte from the catholyte is a thin Teflon membrane[15] G. The bottom of the anode compartment is a coarse fritted glass disk H designed primarily to give mechanical support to the Teflon membrane against the constant hydrostatic

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(3) National Science Foundation Coöperative Predoctoral Fellow, 1959–1961.

(4) Socony Mobil Predoctoral Fellow, 1961–1962.

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

(6) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

(7) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).

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(12) R. L. Ward and S. I. Weissman, *ibid.*, **76**, 3612 (1954); **79**, 2086 (1957).

(13) P. J. Zandstra and S. I. Weissman, *J. Chem. Phys.*, **35**, 757 (1961).

(14) P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 2795 (1962).

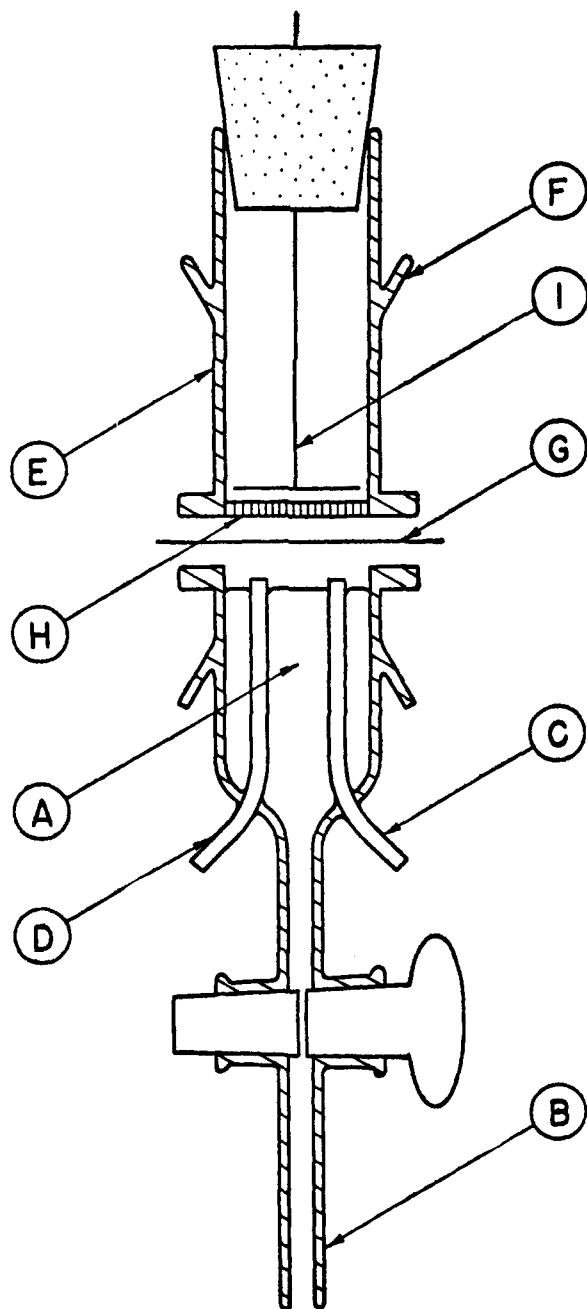(15) ¹/₃ mil thickness, obtained from Dilectrix, Inc., Farmingdale, L. I., N. Y.

Fig. 1.—Electrochemical cell: A, mercury-pool cathode; B, connection to mercury reservoir; C, inlet tube from solution reservoir; D, outlet tube to sample tube in microwave cavity; E, anode compartment; F, rubber band hooks; G, Teflon membrane; H, coarse fritted glass disk; I, platinum anode. The Ag–AgClO₄ reference electrode is placed in the solution reservoir connected to the cell through C.

pressure from the solution reservoir. Finally, the platinum-disk anode I is mounted through a cork in the top of the anode compartment.

Samples for electrolysis, usually 0.005 M in reducible material and 0.1 M in supporting electrolyte, were degassed on a vacuum line before use. Prepurified nitrogen, which had been passed through a liquid-nitrogen trap, was continuously run through the solution reservoir attached to the cell to prevent contamination by oxygen or water vapor. The concentration of 0.005 M was chosen as sufficiently low to be comparable with polarographic conditions (solutions were 0.001 M for the polarographic studies) and still high enough to ensure a good signal-to-noise ratio for the very weak lines frequently observed from the hyperfine splitting of carbon-13 nuclei in natural abundance. Other considerations which govern the choice of the concentration of reducible material are discussed in section IV.

Electrolyses were performed using a regulated power supply so designed that the maximum potential between the silver–silver

perchlorate reference electrode (see part 3 of this section) and the mercury cathode could be controlled. This maximum electrolysis potential was chosen to be more cathodic than the half-wave potential obtained from the d.c. polarogram of the material (see part 3), and usually at as cathodic a potential as practicable below the second wave. In this way, after sufficiently prolonged electrolysis, the concentration of unreduced material could be made very small and thus the line-broadening caused by electron exchange between the radical and its precursor could be minimized.

In practice, the electrolysis current was limited to 5 to 10 ma. by the resistance of the Teflon membrane. Consequently, at the beginning of an electrolysis, the reference potential was usually somewhat more anodic than the preset potential. As electrolysis proceeded, however, the concentration of unreduced material fell, and the reference potential shifted to its preset value. When the current had remained at less than 1 ma. for several minutes, the solution was generally considered to be completely reduced. In several cases, it was necessary to ensure more complete reduction. This was accomplished by techniques described in section III.

2. Choice of Solvent.—N,N-Dimethylformamide (DMF) was the solvent in most of the present experiments. Its choice was suggested by the work of Wawzonek,[16-18] Given,[19,20] and co-workers. These authors found that aromatic hydrocarbons,[16,17,19] carbonyl compounds,[18,20] and nitrogen heterocyclics[19] reduce by one-electron steps in DMF. The E.S.R. studies of radical anions in DMF solution by Austen, et al.,[5] and macro electrolysis experiments as well, have demonstrated that many electrolytically produced free radicals have remarkable stability in DMF. Thus Wawzonek[17] showed that electrolysis of a DMF solution of naphthalene proceeds through the formation of naphthalene anion radical at the cathode and its discharge at the anode, with almost quantitative recovery of unchanged naphthalene after many hours of electrolysis.

Wawzonek, et al.,[17,18] have investigated anion radical decay in DMF. Benzophenone anion radical, for example, reacted slowly with the solvent to produce benzhydrol and carbon monoxide. They proposed a mechanism in which proton abstraction from DMF is followed by decomposition to carbon monoxide and dimethylamide ion. Although no reactions attributable to these species were observed in the present work, their effect is significant in some cases.[21]

3. Polarographic Measurements.—Polarographic measurements were made with a dropping mercury electrode in a three-electrode cell using an electronic polarograph similar to one described by Kelley, et al.,[22] The dropping mercury electrode served as the indicator electrode and a silver–silver perchlorate electrode in DMF was used as the reference [Ag|AgClO₄ (0.1 M); (C₃H₇)₄NClO₄ (0.1 M)]. Potentials were measured with a vacuum tube voltmeter to an accuracy of ±0.02 v. Cell temperature and mercury height were not rigorously controlled, nor were accurate measurements of diffusion currents made. Triangular wave chronoamperometry (oscillopolarography) was performed, using the same cell arrangement, with an apparatus described by Smith and Reinmuth.[23] Frequencies ranged between 0.1 and 500 c.p.s. and peak-to-peak amplitudes of applied potential between 0.5 and 2.0 v. Polarographic solutions were approximately 0.001 M in the compound studied and 0.1 M in tetra-n-propylammonium perchlorate.

4. E.S.R. Spectrometer.—A modified version of the X-band superheterodyne spectrometer described by Hirshon and Fraenkel[24,25] was employed with a Varian model V4012-3B 12-inch magnet. All field measurements were made directly from field-calibrated strip-chart recordings. The field calibration was performed at approximately one-gauss intervals on the chart by using an appropriately stabilized proton resonance oscillator.[26] When sensitivity permitted, direct oscilloscopic presentation of the spectra was found to be convenient for the rapid observation, immediately after electrolysis, of signals from rapidly decaying radicals.

5. Materials.—Benzonitrile, phthalonitrile, terephthalonitrile, 4-tolunitrile, 4-fluoronitrile, 4-nitrobenzonitrile, 4-aminobenzonitrile, 4-chlorobenzonitrile, 4-anisonitrile and benzoylacetonitrile were obtained from Eastman Organic Chemicals, and, except for benzonitrile and p-aminobenzonitrile, were used without further purification. Benzonitrile was purified by vapor-phase

(16) S. Wawzonek, E. W. Blaha, R. Berkey and M. E. Runner, J. Electrochem. Soc., **102**, 235 (1955).

(17) S. Wawzonek and D. Wearring, J. Am. Chem. Soc., **81**, 2067 (1959).

(18) S. Wawzonek and A. Gunderson, J. Electrochem. Soc., **107**, 537 (1960).

(19) P. H. Given, J. Chem. Soc., 2684 (1958).

(20) P. H. Given, M. E. Peover and J. Schoen, ibid., 2674 (1958).

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(22) M. T. Kelley, D. J. Fisher and H. C. Jones, Anal. Chem., **31**, 1475 (1959); **32**, 1262 (1960).

(23) D. E. Smith and W. H. Reinmuth, ibid., in press.

(24) J. M. Hirshon and G. K. Fraenkel, Rev. Sci. Instr., **26**, 34 (1955).

(25) J. W. H. Schreurs and G. K. Fraenkel, J. Chem. Phys., **34**, 756 (1961).

chromatography. The amino compound was recrystallized twice from water and dried over phosphorus pentoxide before use. 4-Cyanopyridine and 3,5-dinitrobenzonitrile, obtained from Aldrich, were used without additional purification. 4-Cyanobenzoic acid, also obtained from Aldrich, was recrystallized from water. Benzoyl cyanide was obtained from K and K Laboratories, Inc., and used without further purification. Tetracyanoquinodi-methane and potassium tetracyanoethylenide were obtained from Dr. T. L. Cairns of E. I. du Pont de Nemours. Sodium 1,1,3,3-tetracyano-2-dimethylaminopropenide and sodium 1,1,3,3-tetracyano-2-ethoxypropenide were obtained from Dr. W. D. Phillips of E. I. du Pont de Nemours. Tetramethylammonium 1,1,2,3,3-pentacyanopropenide was prepared by the method of Middleton, et al.[26] Pyromellitonitrile was obtained from Drs. E. A. Lawton and H. H. Krause of Battelle Memorial Institute.

Isophthalonitrile was synthesized from m-dibromobenzene by the Rosenmund–von Braun method[27] using cuprous cyanide prepared according to Barber.[28] White crystals were obtained, melting at 158–159.5°, uncorrected (lit.[29] value 161.5–162°). Benzonitrile, C^{13}-enriched in the cyanide group, was prepared from bromobenzene and enriched $Cu_2(CN)_2$ by a procedure similar to that employed in the synthesis of isophthalonitrile. The crude product was purified by vapor-phase chromatography. Similarly, terephthalonitrile was prepared with 16% C^{13} in one cyanide group by starting with p-bromobenzonitrile.

N,N-Dimethylformamide (DMF), used as the solvent in most of the work, was Fisher reagent grade further purified by vacuum distillation from anhydrous potassium carbonate. Acetonitrile, employed as the solvent in some experiments, was also Fisher reagent grade and was purified by several vacuum distillations from phosphorus pentoxide. Tetra-n-propylammonium perchlorate, used as supporting electrolyte in the electrolyses, was prepared from Eastman-tetra-n-propylammonium hydroxide following the procedure of Geske and Maki.[6]

III. Results

Experimental results, d.c. polarographic, oscillopolarographic, and spectral, are discussed separately for each compound. Polarographic half-wave potentials are summarized in Table I. Hyperfine splitting constants are summarized in Table II.

Benzonitrile.—Electrolytic reduction of benzonitrile at −2.9 v. yielded a red-orange solution which gave a clearly resolved E.S.R. spectrum of 48 lines. Fifty-four lines would be expected from the hyperfine interaction of the unpaired electron with the nitrogen nucleus, two equivalent *ortho* protons, two equivalent *meta* protons, and the *para* proton of the anticipated one-electron reduction product. The E.S.R. signal decayed with a half-life of about 20 minutes, a period sufficiently long that no difficulty was encountered in recording complete spectra for accurate measurements of splitting constants. Interpretation of the spectrum was straightforward, and the splitting constants are presented in Table II. The assignment of the splittings to ring positions is discussed in section IV. Ths six anticipated, but unobserved, lines in the spectrum were obscured by overlap because the splitting constant for one pair of equivalent protons closely approximates twice the difference between the splitting constants of the nitrogen nucleus and the other pair of equivalent protons. The line width was about 0.15 gauss.[30]

Benzonitrile enriched with 16% C^{13} in the cyano group gave a similar spectrum except for clearly observed satellites with about 8% of the intensity of the normal lines. The C^{13} splitting constant was 6.12 gauss,[31] in good agreement with the value of 6.4 gauss found by Ward[32] for the radical generated by reduction

(26) W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

(27) C. F. Koelsch, *ibid.*, **58**, 1328 (1936).

(28) H. J. Barber, *J. Chem. Soc.*, 79 (1943).

(29) "Dictionary of Organic Compounds," I. M. Heilbron and H. M. Bunbury, ed., Oxford University Press, New York, N. Y., 1936, Vol. II, p. 446.

(30) Line widths quoted are the full width between derivative extrema.

(31) For convenience in most of the text, we write splitting constants as positive quantities even though their signs are not determined from the spectra and they are frequently known to be negative on theoretical grounds. Theory shows that splittings from ring protons at positive spin-density positions are negative.

(32) R. L. Ward, *J. Chem. Phys.*, **32**, 1592 (1960).

TABLE I
POLAROGRAPHIC DATA

Compound	First wave $E_{1/2}{}^a$	n^b	Second wave $E_{1/2}{}^a$	n^b
Benzonitrile	−2.74	1	....	..
Phthalonitrile	−2.12	1	−2.76	2
Isophthalonitrile	−2.17	1	....	..
Terephthalonitrile	−1.97	1	−2.64	1[c]
			−2.74	1[c]
Pyromellitonitrile	−1.02	1	−2.07	1
4-Tolunitrile	−2.75	1	....	..
4-Aminobenzonitrile	−3.12	3/2	....	..
4-Fluorobenzonitrile	−2.69	3/2	....	..
4-Cyanopyridine	−2.03	1	−2.87	1
4-Nitrobenzonitrile	−1.25	1	−1.9[e]	2
3,5-Dinitrobenzonitrile	−0.96	1	−1.5[e,f]	1
4-Cyanobenzoic acid	−1.91	1	−2.53	1
Tetracyanoquinodi-methane	−0.19[d,g]	..	−0.75[d,g]	..
Tetracyanoethylene	−0.17[d,g]	..	−1.17[d,g]	..
Tetramethylammonium 1,1,2,3,3-pentacyano-propenide	−1.76	1	−2.30[h]	1
Sodium 1,1,3,3-tetracyano-2-dimethyl-aminopropenide	−2.75[d]	..	?	..
4-Chlorobenzonitrile	−2.4[d,e]	..	..	..
4-Anisonitrile	−2.95[d]	..	..	..
Benzoylacetonitrile	−2.09[d]	..	..	..
Benzoyl cyanide	−1.45[d,e]	..	..	..
Sodium 1,1,3,3-tetra-cyano-2-ethoxypropenide	−2.25[d,e]	..	−2.40[d,i]	..

[a] Potentials measured in volts *vs.* Ag–AgClO₄ electrode. [b] Estimated number of electrons in the reduction as obtained from qualitative observations rather than careful measurements. [c] Two waves poorly separated. [d] Because of drift in the potential of the Ag–AgClO₄ reference electrode, these potentials may be inconsistent with the other polarographic data. [e] Wave obscured by maximum. [f] Three-electron wave at −2.1 v. [g] Polarogram run in acetonitrile. [h] Third one electron wave at −2.75 v. [i] Third wave at −2.75 v. obscured by maximum.

of C^{13}-enriched benzonitrile with potassium in 1,2-dimethoxyethane.

Oscillopolarographic study showed symmetrically disposed peaks on anodic and cathodic half-cycles centered around the d.c. polarographic half-wave potential at all frequencies up to 500 c.p.s. The decrease in slope of the rising portion of these peaks at higher frequencies was of a magnitude consistent with the assignment of its cause to uncompensated ohmic potential drop in the polarographic capillary (*ca.* 100 ohm). The result indicates a rapid simple reduction uncomplicated by chemical kinetic factors and is consistent with the E.S.R. spectrum.

Phthalonitrile.—Reduction of phthalonitrile at −2.2 v. gave a yellow-orange solution with a spectrum of nine broad lines. Markedly improved resolution was obtained, however, after reduction at −2.7 v., the potential of the second polarographic wave, for about one minute after "complete" electrolysis at −2.2 v. The lines narrowed from almost one to about 0.07 gauss. The 45 clearly resolved lines led unequivocally to the splitting constants listed in Table II for the expected one-electron reduction product. Several low-intensity lines, probably due to C^{13} in natural abundance, were also observed, but no attempt was made to interpret them because of the difficulty of assignment. The radicals were very stable; no decay was observed in the spectrum over several hours. Complete electrolysis at −2.85 v. resulted in decay of the 45-line spectrum, and its replacement by a spectrum identical with that obtained on reduction of benzonitrile.
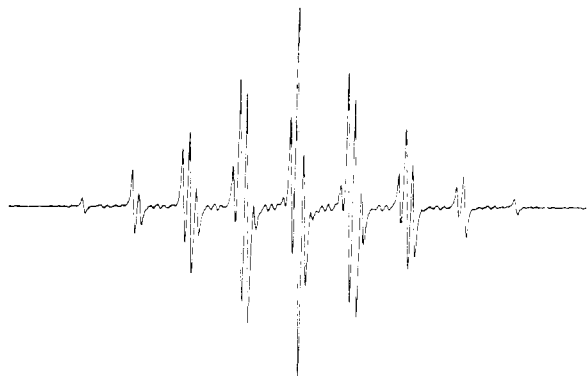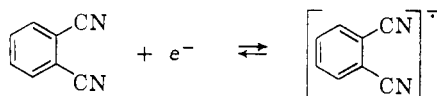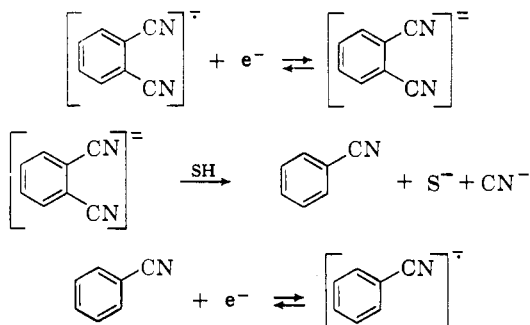
Fig. 2.—First derivative of the E.S.R. absorption vs. magnetic field of the terephthalonitrile anion radical. The magnetic field increases to the right.

These results suggest the reactions:

First polarographic wave

Second polarographic wave

where SH is the solvent and S⁻ is the anion obtained by proton abstraction. Benzonitrile is, of course, reduced at −2.85 v. since its half-wave potential is −2.74 v. The line-width effects described above may be explained on the basis of this mechanism. Electron exchange between phthalonitrile and its anion radical is presumed to be rapid, thus broadening the spectral lines (see section IV). The narrowing of the lines on momentary electrolysis at −2.85 v. shows that benzonitrile anion radical $(E_{1/2}$ −2.74 v.) scavenges the solution of remaining traces of phthalonitrile $(E_{1/2}$ −2.12 v.) and indicates that the oxidation–reduction reaction between them proceeds in homogeneous solution.

The oscillopolarogram of phthalonitrile showed symmetrical reversible peaks corresponding to the first d.c. polarographic wave at scan rates up to 500 v./sec. The second d.c. wave appeared as two components: the first, at −2.75 v., was also reversible; the second, at −2.95 to −3.2 v., shifted cathodically with frequency and showed a reduction peak with little or no indication of reoxidation up to the highest frequencies applied (1 volt peak-to-peak at 500 c.p.s.). The wave at −2.75 v. is attributable to the reduction of benzonitrile, and the more cathodic wave to the irreversible reduction of phthalonitrile. The cathodic shift in potential of the second wave with increasing frequencies was in good qualitative accord with the predictions of theory assuming either irreversible reduction or reversible reduction followed by rapid chemical reaction.[33] When the span of potential was broadened to include the range from −1.0 to −3.0 v., a wave at −1.1 v. appeared. The shape of the peaks was that characteristic of the formation of an insoluble material, and the wave is at-

(33) W. H. Reinmuth, Anal. Chem., 33, 1793 (1961).

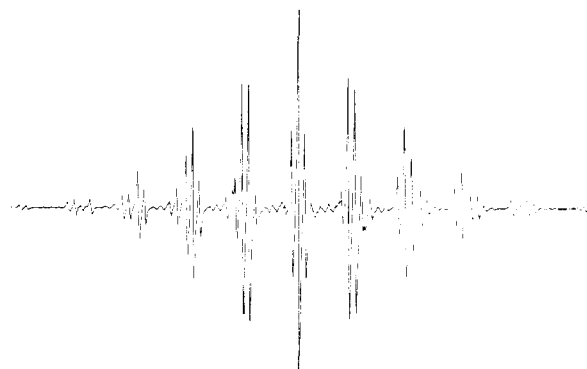Fig. 3.—First derivative of the E.S.R. absorption vs. magnetic field of the terephthalonitrile anion radical enriched with C¹³ in one nitrile position. The magnetic field increases to the right.

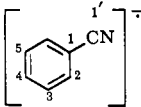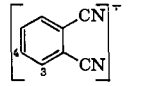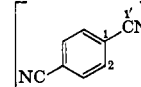tributed to oxidation of mercury to form insoluble species with one or more of the reaction products.
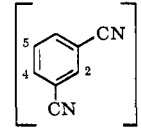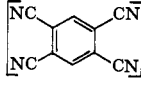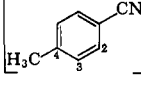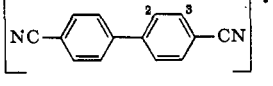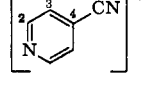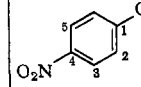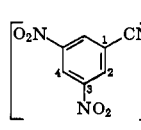
Terephthalonitrile.—Electrochemically, terephthalonitrile was similar to phthalonitrile. At −2.1 v., nine broad lines were found. Complete reduction of the compound, assured by brief electrolysis at −2.7 v., resulted in the very sharp 25-line spectrum shown in Fig. 2 from which the splitting constants given in Table II were obtained. Again, prolonged electrolysis at high potentials resulted in the production of benzonitrile anion radical. Oscillopolarographic results were consistent with a mechanism similar to that proposed for phthalonitrile.

The terephthalonitrile spectrum showed about 40 lines of low intensity attributable to the splitting from C¹³ nuclei in natural abundance. These lines were interpreted as arising from C¹³ nuclei rather than from benzonitrile or some impurity because they occurred at exactly symmetric positions about the center of the spectrum and had relative intensities in close agreement with those expected from the 1.108% natural abundance of C¹³. In addition, the widths of the low-intensity lines were approximately the same as the widths of the major lines, and no changes in either relative intensity or line width were observed on standing for several hours. The interpretation of the C¹³ lines followed directly from examination of the intensity ratios obtained from high-gain record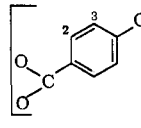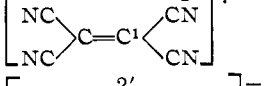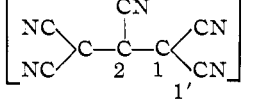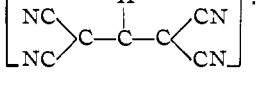ings.[34] The spectrum shown in Fig. 3 of the terephthalonitrile anion radical C¹³-enriched in one of the cyanide groups allowed unequivocal assignment of the splitting constants.

Isophthalonitrile.—Electrolytic reduction of isophthalonitrile at −2.3 v. gave an orange-yellow solution which displayed a very weak E.S.R. spectrum. Its intensity was less than 1% of the intensity of the spectrum of the terephthalonitrile radical generated and observed under identical conditions; the electrolysis current was essentially the same as in the reduction of the terephthalonitrile. The decay of the spectrum after an hour or more was negligible, and thus the small intensity could not be attributed to instability of the radical producing the spectrum. Narrow line widths were obtained even on incomplete reduction which indicates that the electron exchange reaction between the radical and the unreduced material was slower than for the other related nitriles. The spectrum was unequivocally interpretable as arising from the splitting from two equivalent nuclei of spin one (presumably N¹⁴), two equivalent nuclei of spin one half, and a single nucleus of spin one half. The isophthalonitrile radical anion contains four protons, but if a splitting existed from a fourth proton, it would have been less than the line

(34) H. L. Strauss and G. K. Fraenkel, J. Chem. Phys., 35, 1738 (1961).

TABLE II
HYPERFINE SPLITTING CONSTANTS

Starting material	Radical	Splitting constants, gauss[a]		
Benzonitrile	(ring, positions 1,1',2,3,4,5; CN at 1)	$[a_2^H] = 3.63$ $a^N = 2.15$ $a_{1'}^C = 6.12$ $[a_3^H] = 0.30$ $a_4^H = 8.42$		
Phthalonitrile	(ring with two CN, positions 3,4)	$[a_3^H] = 0.42$ $a^N = 1.75$ $[a_4^H] = 4.13$		
Terephthalonitrile	(ring, NC and CN at 1,1'; positions 2)	$a_2^H = 1.59_2$ $a^N = 1.80_8$ $a_2^C = 1.98$ $a_1^C = 8.81$ $a_{1'}^C = 7.83$		
Isophthalonitrile[b]	(ring, CN at 1 and 3 positions; 2,4,5)	$[a_2^H] = 1.44^e$ $a^N = 1.02$ $a_4^H = 8.29$ $[a_5^H] \le 0.08^e$		
Pyromellitonitrile	(ring, four CN: NC,NC,CN,CN)	$a^H = 1.11$ $a^N = 1.15$		
4-Tolunitrile	(H_3C ring CN; positions 2,3,4)	$[a_2^H] = 3.86$ $a^N = 2.08$ $[a_3^H] = 0.53$ $a_4^H = 9.29$		
4-Aminobenzonitrile 4-Fluorobenzonitrile	(NC—biphenyl—CN; positions 2,3)	$[a_2^H] = 1.80_7$ $a^N = 1.04_7$ $[a_3^H] = 0.28_6$		
4-Cyanopyridine	(pyridine ring N; CN at 4; positions 2,3)	$[a_2^H] = 1.40^e$ $[a_4^N] = 2.33$ $[a_1^N] = 5.67$ $[a_3^H] = 2.62^e$		
4-Nitrobenzonitrile	(O_2N ring CN at 1; positions 2,3,4,5)	$[a_2^H] = 0.73$ $[a_1^N] = 0.76$ $[a_4^N] = 6.24$ $[a_3^H] = 3.02$		
3,5-Dinitrobenzonitrile	(O_2N ring CN at 1; NO_2 at 3; positions 2,4)	$a_2^H = 5.00$ $[a_1^N] < 0.3$ $a_3^N = 3.00$ $a_4^H = 2.84$		
4-Cyanobenzoic acid	(anhydride/carboxyl ring CN; positions 2,3)	$[a_2^H]^c = 2.76$ $a^N = 1.96$ $[a_3^H]^c = 0.35$		
Tetracyanoethylene Tetracyanoethane Tetracyanocyclopropane	(NC)₂C=C¹(CN)₂	$a^N = 1.574$ $a_{1'}^C = 9.451$ $a_1^C = 2.92^d$		
Tetramethylammonium 1,1,2,3,3-pentacyano- propenide	(NC)₂C—C(CN)—C(CN)₂ with 2' CN, 1'	$a_1^N = 0.760$ $a_{1'}^C = 0.93$ $a_2^N = 2.635$ $a_{2'}^C$ (or a_2^C) $= 12.01$ $a_?^C = 1.79^e$		
Tetramethylammonium 1,1,2,3,3-pentacyano- propenide Sodium 1,1,3,3-tetra- cyano-2-dimethyl- aminopropenide	(NC)₂C—C(H)—C(CN)₂	$a^H = 12.87$ $a^N = 0.76$		

[a] Assignments of splitting constants to positions, when not uniquely determined by the experimental data, are placed in brackets. The choice of assignments in these cases is discussed in sect. IV. [b] It is possible that the radical observed is not that of the isophthalonitrile anion; see sect. III and IV. [c] The assignments of these splittings to ring positions is uncertain; see sect. IV. [d] In absolute ethanol solution (see sect. III). [e] This 1.79 gauss splitting may be either a_1^C, a_2^C or $a_{2'}^C$.

width, and an upper limit of 0.08 gauss is placed on the value of its splitting constant. The spectrum is not considered to be inconsistent with that expected from the isophthalonitrile anion radical, and although it may possibly arise from some other species, no reason-

able suggestions for another radical are apparent. The low efficiency of the radical production on electrolysis indicates only that side reactions are taking place and does not imply that the observed radical is different from the isophthalonitrile anion.
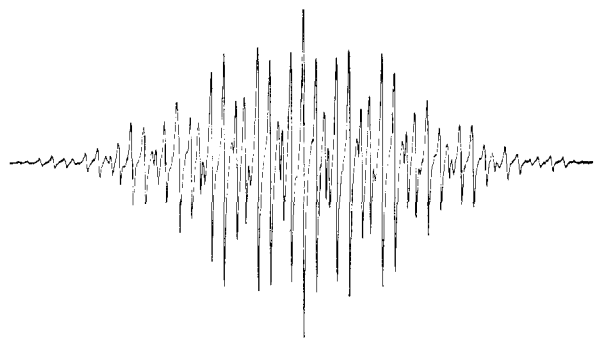
Fig. 4.—First derivative of the E.S.R. absorption *vs.* magnetic field of the 4,4'-dicyanobiphenyl anion radical generated from reduction of 4-aminobenzonitrile. The magnetic field increases to the right.

Pyromellitonitrile.—Reduction of pyromellitonitrile at -2.0 v. resulted in a pale yellow solution. The E.S.R. spectrum obtained from the reduction of a 0.0003 M solution consisted of nine triplets immediately assignable to interaction with four equivalent nitrogen nuclei and two equivalent protons with the splitting constants given in Table II. Additional lines of low intensity are also observed which probably arise from natural abundance of C^{13} and N^{15} nuclei.

4-Tolunitrile.—Reduction of 4-tolunitrile resulted in an orange solution with a strong spectrum. The short lifetime of the radical, two to three minutes, necessitated recording the spectrum in segments, using a freshly reduced solution for each segment. Measurement of the line separations was easily accomplished in this way with the results shown in Table II.

4-Aminobenzonitrile.—Electrolysis of 4-aminobenzonitrile at -3.3 v. gave a yellow-red solution which displayed the strong 63-line spectrum shown in Fig. 4. Analysis of the spectrum shows quite clearly that the radical contains two equivalent nuclei of spin one, presumably nitrogen, and eight nuclei of spin one half in two groups of four, presumably protons. The spectrum therefore suggests the anion radical of 4,4'-dicyanobiphenyl. A single wave of height suggesting a one and one-half electron reduction was found in the d.c. polarogram. Oscillographic polarography showed a cathodic peak at -3.2 v., corresponding to the d.c. wave, which was only partially resolved from the discharge of the supporting electrolyte. The anodic peak of the same wave was smaller than the cathodic peak and increased in height with increasing frequency. The behavior is suggestive of a reversible charge transfer followed by irreversible chemical decomposition of the initial product. The order of magnitude of the rates of the chemical step would be 10^5–10^6 liter mole^{-1} sec.$^{-1}$ if it were second order, or 1–10 sec.$^{-1}$ if it were first order. No attempt was made to ascertain the order of the reaction. Two small reversible waves (symmetric cathodic and anodic peaks) appeared at -2.1 and -2.5 v. when the -3.2 v. peak was included in the scan. These apparently correspond to side products of the major reaction path. In addition, a wave of shape characteristic of formation of an insoluble species appeared at -1.1 v. which presumably corresponds to a mercury salt of one of the reduction products. A suggested major reaction path is shown.

Dimerization is reasonable in this case since an uncharged radical is formed by the ionization of the 4-aminobenzonitrile anion radical. This may be compared with the dinitrile case. There, anion elimination occurs on the second electron addition leaving a carbanion intermediate, while the elimination on the addition of a single electron produces a neutral free
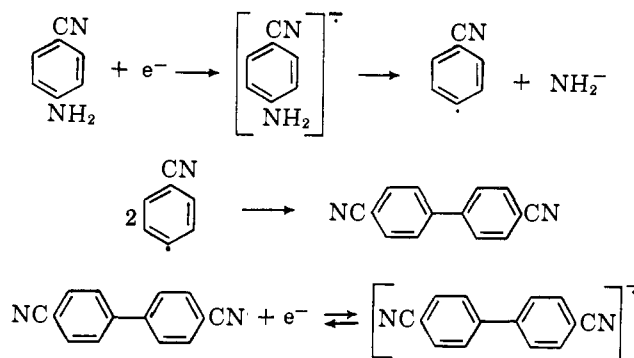
radical, causing the paths of these reductions to diverge.

4-Fluorobenzonitrile.—This compound on reduction gave a spectrum identical with that obtained from 4-aminobenzonitrile, lending further weight to the assignment as the 4,4'-dicyanobiphenyl anion radical. Oscillopolarography showed only a partially reversible wave at -2.8 v. and a wave characteristic of the formation of an insoluble species at -1.1 v.

4-Cyanopyridine.—Electrolysis of 4-cyanopyridine at -2.2 v. resulted in a yellow-orange solution with a strong resonance. Analysis of the spectrum led to the constants shown in Table II.

4-Nitrobenzonitrile.—Electrolysis of this compound resulted in a deep purple solution with a strong E.S.R. signal. This anion radical has also been studied, but with acetonitrile as solvent, by Maki and Geske.[8] The two results are in general agreement with the exception of the magnitude of the nitro nitrogen splitting: the present result is 6.24 gauss, while the earlier result was 7.15 gauss. This discrepancy presumably arises from a solvent effect (see section IV).

3,5-Dinitrobenzonitrile.—Electrolysis of 3,5-dinitrobenzonitrile resulted in an intensely colored red solution with a spectrum consisting of 18 broad lines. Good agreement with the intensity ratios is obtained if the spectrum is assumed to result from two equivalent nitrogen nuclei, two equivalent protons and a third proton. No splitting attributable to the nitrile nitrogen was found.

4-Cyanobenzoic Acid.—Electrolysis of 4-cyanobenzoic acid at -2.2 v. produced a yellow-green solution, but no resonance was detected until the more cathodic potential of -2.6 v. was reached (the second polarographic wave). The resulting yellow-orange solution gave a well-resolved 27-line spectrum which is interpreted as arising from the 4-cyanobenzoate dianion radical. The splitting constants are given in Table II.

The second d.c. polarographic wave showed reversible cathodic and anodic segments on oscillopolarographic examination. The first wave, however, showed no anodic component, and, in addition, the cathodic segment in contrast to usual behavior showed a flat plateau rather than a peak. The height of the plateau was constant at frequencies from 1 to 500 c.p.s. at an amplitude of 1 volt peak-to-peak. The behavior was strongly suggestive of charge-transfer preceded by a slow chemical reaction. This would presumably correspond to the dissociation of the acid prior to the reduction of hydrogen ion. On the assumption of a $pK_A = 7$ for the acid in this solvent, the limiting current yields a rate constant for the acid association of 10^8 liter mole^{-1} sec.$^{-1}$. This value is of an appropriate order of magnitude but, because of lack of buffering in the system, it is of doubtful quantitative significance.

Tetracyanoquinodimethane.—Tetracyanoquinodimethane is partially reduced to its anion radical by dissolution in DMF. The resulting spectrum consists of a single broad line. Electrolysis of the solution gave a

stronger, but still unresolved, single line. Electrolysis of an acetonitrile solution also gave a single broad line. In the latter case, however, the solution of the compound was observed to react with the mercury-pool cathode yielding a gray precipitate and a dark green solution. No difference could be observed in the two spectra since only the single broad line was obtained. This compound has been reduced with lithium metal in tetrahydrofuran by Phillips[35] and a good spectrum with sharp lines obtained. His splitting constants are: $a^N = 1.10$, $a^H = 1.57$ gauss. No explanation of the poor results obtained electrochemically is currently available.

Tetracyanoethylene Derivatives.—The anion radical of tetracyanoethylene is obtained by dissolving this material in DMF, and by the reduction of 1,1,2,2-tetracyanocyclopropane or 1,1,2,2-tetracyanoethane.[36] These results have been reported elsewhere.[36] The spectrum of tetracyanoethylene was originally studied by Phillips, et al.[37] In our earlier work,[36] a small-intensity splitting of 2.203 gauss was erroneously assigned to the C^{13} nuclei of the two equivalent ethylene carbon atoms. As was pointed out to us by Markau, however, this splitting actually arises from the natural abundance of N^{15} isotopes in the four nitrile positions.[38] Further study of the spectrum of the tetracyanoethylene radical prepared by dissolving the potassium salt in absolute ethanol gave a spectrum with lines of width 0.025 gauss from which it was possible to discern an additional small intensity splitting that probably is caused by the natural abundance of C^{13} nuclei in the ethylenic positions. This splitting is close to an exact multiple of the splitting constant giving rise to the major lines in the spectrum, and is probably 2.92 gauss in the absolute ethanol solution. In DMF, the splitting might be slightly different (see section IV).

Tetramethylammonium 1,1,2,3,3-Pentacyanopropenide.—Electrolysis at -2.0 v. of the bright yellow solution of this cyanocarbon salt produced a red solution which gave the strong 25-line spectrum shown in Fig. 5. The pentacyanopropene dianion radical would give rise to a 27-line spectrum if the hyperfine interactions with the N^{14} nuclei of the four cyano groups at the 1- and 3-positions were assumed to be equivalent. Two of the lines near the center of the experimental spectrum are, however, clearly overlapped, and the observed intensity ratios are in good agreement with those predicted for this radical. The splitting constants are listed in Table II.

On changing the potential of the electrolysis cathodically to -2.25 v., the potential of the second wave, the color of the solution turned from bright red to reddish-orange. The E.S.R. spectrum also changed: the line width decreased from 0.12 to 0.03 gauss, and the amplitude of the derivative signal decreased slightly. The narrower line width undoubtedly arose from a decrease in the rate of electron exchange between the radical and its precursor. With the improved resolution, about 50 additional lines were observed at symmetrical positions with respect to the main spectrum. A careful study of the intensities and splittings of these small lines, similar to that employed for the terephthalonitrile radical, showed that they were attributable to splittings from C^{13} nuclei in natural abundance with
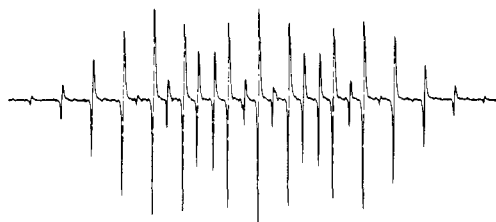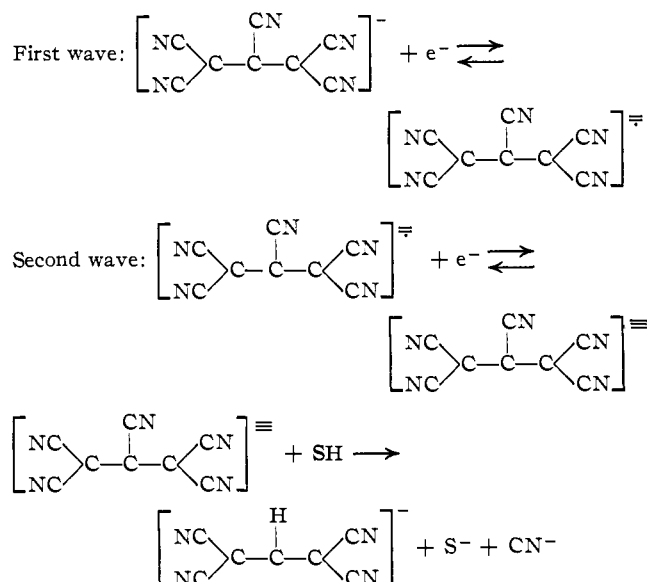
(35) W. D. Phillips, private communication.

(36) P. H. Rieger, I. Bernal and G. K. Fraenkel, *J. Am. Chem. Soc.*, **83**, 3918 (1961).

(37) W. D. Phillips, J. C. Rowell and S. I. Weissman, *J. Chem. Phys.*, **33**, 626 (1960).

(38) K. Markau, Institut für Elektrowerkstoffe, Freiburg (private communication). Both the splitting constant of 2.203 gauss and the relative intensities of a number of the lines are in very good agreement with the satellites predicted for an N^{15} splitting.

Fig. 5.—First derivative of the E.S.R. absorption *vs.* magnetic field of the 1,1,2,3,3-pentacyanopropene dianion radical. The magnetic field increases to the right.

the splitting constants shown in Table II. The intensity of the satellites with the 0.93-gauss splitting indicated that they could be assigned unambiguously to the four equivalent nitrile carbon nuclei. Similarly, the intensity of the satellites with the 12.01-gauss splitting showed that they resulted from interaction with one carbon nucleus, but they could arise either from the carbon atom at position 2 or from the nitrile carbon atom at this position. The lines from the 1.79-gauss splitting are all overlapped with the much stronger major lines of the spectrum so that their intensity could not be measured. This splitting could thus arise from the two equivalent carbon atoms at positions 1 and 3 or from the single carbon atom at position 2. A fourth C^{13} splitting was not found. Satellites from N^{15} nuclei in natural abundance are observed as shoulders on the 0.93-gauss C^{13} lines.

Continued electrolysis at -2.25 to -2.3 v. produced a pale yellow solution which did not display a resonance. When the potential was changed cathodically to -2.75 v., the third wave, the solution again darkened and a strong spectrum of 18 lines was observed. This radical decayed quite rapidly with a half-life of about a minute (the pentacyanopropene dianion radical was apparently stable indefinitely). The spectrum was arranged in two distinct and identical groups of equal intensity consisting of nine lines each, with the intensity ratios of each being those expected for four equivalent nitrogen nuclei. The resulting radical, containing four equivalent nitrogen atoms and one proton, was probably the 1,1,3,3-tetracyanopropene dianion This species could have been formed by the ionization of a cyanide from the pentacyanopropene trianion followed by the abstraction of a proton from the solvent to form 1,1,3,3-tetracyanopropene anion and then the reduction, at the potentials of the third wave, to the dianion radical according to the following scheme of reactions

First wave:
$$\left[\begin{matrix} NC \\ NC \end{matrix} C-\underset{\underset{CN}{|}}{C}-C \begin{matrix} CN \\ CN \end{matrix} \right]^{-} + e^{-} \rightleftarrows$$

$$\left[\begin{matrix} NC \\ NC \end{matrix} C-\underset{\underset{CN}{|}}{C}-C \begin{matrix} CN \\ CN \end{matrix} \right]^{=}$$

Second wave:
$$\left[\begin{matrix} NC \\ NC \end{matrix} C-\underset{\underset{CN}{|}}{C}-C \begin{matrix} CN \\ CN \end{matrix} \right]^{=} + e^{-} \rightleftarrows$$

$$\left[\begin{matrix} NC \\ NC \end{matrix} C-\underset{\underset{CN}{|}}{C}-C \begin{matrix} CN \\ CN \end{matrix} \right]^{\equiv}$$

$$\left[\begin{matrix} NC \\ NC \end{matrix} C-\underset{\underset{CN}{|}}{C}-C \begin{matrix} CN \\ CN \end{matrix} \right]^{\equiv} + SH \longrightarrow$$

$$\left[\begin{matrix} NC \\ NC \end{matrix} C-\underset{\underset{H}{|}}{C}-C \begin{matrix} CN \\ CN \end{matrix} \right]^{-} + S^{-} + CN^{-}$$

Third wave:

$$\left[\begin{array}{c} NC \\ NC \end{array} C-\overset{\overset{\displaystyle H}{|}}{C}-C \begin{array}{c} CN \\ CN \end{array} \right]^{-} + e^{-} \rightleftharpoons$$

$$\left[\begin{array}{c} NC \\ NC \end{array} C-\overset{\overset{\displaystyle H}{|}}{C}-C \begin{array}{c} CN \\ CN \end{array} \right]^{=}$$

where SH is the solvent and S⁻ is the solvent anion. The sequence suggested above is of course not unique, although the pale yellow color observed corresponds to that reported by Urushibara for the tetracyanopropene anion.[39] The splitting constants assigned to the assumed tetracyanopropene dianion radical are given in Table II.

This spectrum showed a number of additional lines having about 5% of the intensity of the major lines. These included two groups of five lines each (intensity ratio *ca.* 1:2:3:2:1) located between the two nine-line groups of the major spectrum. Several lines of comparable intensity were seen between components in the low-field nine-line group. Further lines might have been present on the high-field side, but the rate of decay of both radicals prevented sufficiently slow scanning of the field to detect the expected lines. The ten well-resolved lines suggest two equivalent nitrogen nuclei with splittings of about 0.5 gauss. The two five-line groups are separated by about 3.5 gauss, but this splitting could not be assigned. These lines might be due to a radical formed from some alternate decay product of the pentacyanopropene trianion such as tricyanoethylene or 1,1-dicyanoethylene.

Sodium 1,1,3,3-Tetracyano-2-dimethylaminopropenide.—Reduction of this material at −2.75 v. produced an amber solution which displayed a strong, but rapidly decaying, resonance. Since the half-life of the radical was only about 10 sec., the spectrum could only be observed by direct oscilloscopic presentation. A very large number of lines was found in the spectrum, but because of the rapid decay they could not be analyzed. As this species decayed, another spectrum was observed to grow in intensity. Except for the absence of the low-intensity lines, this spectrum was identical with that observed from electrolysis of 1,1,2,3,3-pentacyanopropenide at the third wave, and is probably the dianion radical of 1,1,3,3-tetracyanopropene. The chemical reactions taking place in this reduction, and the identity of the radical giving rise to the transient spectrum, have not been ascertained.

Other Compounds.—Electrolysis of benzoylacetonitrile resulted in a very weak spectrum which we were unable to interpret. Benzoyl cyanide, when reduced, gave a single resonance line which we could not resolve. 4-Chlorobenzonitrile gave a yellow solution on reduction, but no resonance was detected. We have no explanation for the absence of an anion radical in this case. 4-Anisonitrile also did not yield a stable anion on reduction. 4-Cyanophenol, on reduction at potentials above the first polarographic wave, did not give an anion radical. Bubbling from the cathode surface was observed, suggesting evolution of hydrogen and formation of the 4-cyanophenolate ion. At the second polarographic wave a cloudy gray solution was produced, but no resonance was detected. Reduction of sodium 1,1,3,3-tetracyano-2-ethoxypropenide gave a yellow solution at potentials below the third wave, and a cloudy gray solution at higher potentials, but no resonance could be detected.

IV. Discussion

1. Spin Density Distribution and Assignment of Splitting Constants.—One of the most significant prop-

(39) Y. Urushibara, *Bull. Chem. Soc. Japan*, **2**, 278 (1927).

erties derivable from the E.S.R. spectrum of an organic free radical is the distribution of π-electron spin densities in the molecule. Although a detailed discussion of the spin densities in the compounds studied here is presented elsewhere,[14] an important part of the required experimental data is the proper assignment of the observed hyperfine splittings to the appropriate nuclei in the radical. Certain of the splitting constants in Table II, those which are bracketed, could not be assigned to particular positions from the experimental data alone, and it is the purpose of the present discussion to indicate the reasoning employed in making assignments. Essentially the arguments depend on the consistency of the assignments in a series of related compounds and the correlation with spin-density distributions obtained from valence-bond and molecular-orbital theory calculations.

Karplus and collaborators[40] recently have performed valence-bond calculations of the π-electron spin-density distribution in the anion radicals of substituted benzenes, C_6H_5X, with strongly electron-withdrawing substituents X. On the assumption that the only important valence-bond structures are those in which the charge is localized on the substituent, conventional resonance structures can be written with the unpaired electron on X and at the *o*- and *p*-positions of the ring. These structures are very much like those employed for the triphenylmethyl radical[41,42] and lead to positive spin densities of comparable magnitude at the *o*- and *p*-positions but negative spin densities of smaller magnitude at the *m*-positions. Structures in which the charge is not localized on the substituent would lead to other spin density distributions. Although the model in which there is complete charge localization is an upper limit rather than a true representation of a real radical anion, it is in fairly good agreement[40] with the E.S.R. spectrum of the nitrobenzene anion radical produced electrolytically in acetonitrile by Geske and Maki.[6] The magnitude of the splitting at the *p*-positions was found to be $|a_4^H| = 3.97$ gauss, and by using deuterium substitution, the magnitudes of the *ortho* and *meta* splittings were found to be $|a_2^H| = 3.39$ and $|a_3^H| = 1.09$ gauss, respectively. The signs of the splitting constants could not be determined, but a number of considerations, some of which are outlined below, are in accord with the signs predicted by the valence-bond calculations.[6-8,40]

Since the nitrile group is also an electron-withdrawing substituent, the benzonitrile and nitrobenzene anion radicals would be expected to have roughly comparable spin-density distributions, and the *m*-position of the benzonitrile radical should have a smaller splitting than the *o*- or *p*-positions. The splitting from the single proton at the *p*-position, assignable unequivocally, is $|a_4^H| = 8.92$ gauss, and the two sets of equivalent pairs of protons have splittings of 3.63 and 0.30 gauss. We therefore tentatively take the *ortho* splitting to be $|a_2^H| = 3.63$ gauss and the *meta* splitting to be $|a_3^H| = 0.30$ gauss. The signs predicted for the spin densities (positive at the *o*- and *p*-positions and negative at the *m*-positions) determine the signs of the splitting constants: $a_2^H = -3.63$, $a_3^H = +0.30$ and $a_4^H = -8.92$ gauss. The magnitudes and signs of the spin densities are also in accord with molecular orbital calculations[14] and, as we shall see, are consistent with the other aromatic nitriles.

Karplus and collaborators[40] have extended the treatment of the above model with charge localized on the substituent to disubstituted benzene anion radicals.

(40) J. C. Schug, T. H. Brown and M. Karplus, *J. Chem. Phys.*, **37**, 330 (1962).

(41) F. C. Adam and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 5342 (1958).

(42) P. Brovetto and S. Ferroni, *Nuovo Cimento*, **5**, 142 (1957).

For symmetric disubstitution, they suggest that the splitting at any position is the mean of the splittings in the monosubstituted radical at the appropriate relative positions. The proton splitting in terephthalonitrile predicted in this superposition approximation would thus be one-half the sum of the *ortho* and *meta* splittings of benzonitrile. Taking the *ortho* splitting to be negative and the *meta* splitting to be positive, the calculated result is −1.67 gauss as compared to the experimental value of ±1.59 gauss. Predictions of this type for the three dinitrobenzenes, for which Maki and Geske[7] made assignments by deuteration, agree with the experimental results within 12% or better except at the positions *ortho* to a nitro group in *o*-dinitrobenzene (the 3- and 6-positions). At these positions, the magnitude of the predicted splitting is 1.15 gauss compared to an experimental value of 0.42 gauss. The approximations of the theory are probably least applicable to the *ortho* disubstituted compounds.[40] The agreement with a similar analysis for the dicyanobenzenes is not quite as good as for the dinitrobenzenes, presumably because the nitrile group is not as strongly electron withdrawing as the nitro group. With the exception of the isophthalonitrile anion, however, the predicted splittings are all in the same relative order as the experimental splittings if the assignments are made as in Table II. If the *m*-position in the benzonitrile anion were not taken to be a position of negative spin density, the agreement would be poorer in all cases, and if the *ortho* and *meta* assignments in benzonitrile were reversed, poorer agreement would be found for position 4 in isophthalonitrile. The positions in phthalonitrile follow from the assignments made for benzonitrile. Except for isophthalonitrile, the assignments in Table II for the dicyanobenzenes are also in accord with the molecular orbital calculations of spin density.[14] The assignment of the splittings at the 2- and 5-positions in isophthalonitrile is uncertain. Both the valence bond[40] and molecular orbital[14] theories predict that the fourth proton should be observable, but the two theories disagree as to which position has the spin density of larger magnitude. As indicated in section III, the observed spectrum may possibly not arise from the simple anion of isophthalonitrile.

The splitting constants in the 4-toluinitrile radical differ only slightly from those of benzonitrile, and therefore the methyl group acts as only a small perturbation. The assignments are made by comparison with benzonitrile, and are also in accord with the molecular orbital theory calculations.[14]

The 4,4'-dicyanobiphenyl radical anion can be compared, as a first approximation, with the biphenyl anion radical. Some of the molecular orbital calculations[43-45] on the biphenyl radical are in fairly good agreement with the measured splittings,[46] but the assignments of the splitting constants to positions are based on the calculated spin densities rather than on experimental determinations from isotopic substitution. Assuming these assignments to be correct, the measured splittings in the biphenyl radical are $|a_2{}^H| = 2.73$, $|a_3{}^H| = 0.43$ and $|a_4{}^H| = 5.46$ gauss where the numbering system of Table II for dicyanobiphenyl is used. The ratio of the magnitudes of the splittings at position 2 to position 3 in the biphenyl anion is 6.35, and the corresponding ratio in 4,4'-dicyanobiphenyl is[47] 6.32. Another analogous compound is the 4,4'-bipyridyl radical anion in which

(43) E. de Boer and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 4549 (1958).

(44) G. J. Hoijtink, *Mol. Phys.*, **1**, 157 (1958).

(45) A. D. McLachlan, *ibid.*, **3**, 233 (1960).

(46) A. Carrington and J. dos Santos-Veiga, *ibid.*, **5**, 21 (1962).

(47) The agreement of these ratios may well be fortuitous because the approximate configuration interaction calculations indicate that the spin density in position 3 is negative in biphenyl[44,45] but positive in 4,4'-dicyanobiphenyl.[14]

Ward[48] performed isotopic substitutions to determine the assignments. The proton splittings found were $|a_2{}^H| = 2.32$ and $|a_3{}^H| = 0.45$ gauss, and the ratio is 5.15. The assignments in Table II for the 4,4'-dicyanobiphenyl radical are also in good agreement with molecular orbital calculations.[14]

The assignments of ring proton splittings in 4-cyanopyridine depend critically on the MO parameters used for the heterocyclic nitrogen atom[14] and are quite uncertain. The assignment of the nitrile-nitrogen splitting to the value of 2.33 gauss is necessitated because no other aromatic nitrile-nitrogen splitting is larger than 2.08 gauss, and it therefore seems quite unlikely for the 5.67-gauss splitting to be attributable to a nitrile. In addition, heterocyclic nitrogen splittings in several comparable radicals are of the order of 5–7 gauss.[48,49] This assignment of nitrogen splittings is also in accord with the molecular orbital calculations.[14]

The assignment in 4-nitrobenzonitrile is the same as that made by Maki and Geske.[8] Their assignment was based on the results of a series of *p*-substituted nitrobenzene anion radicals, and is also in agreement with the reasoning outlined above, including an application of the valence bond ideas to unsymmetric disubstituted benzenes.[40] The splitting at position 3 is larger than at position 2, according to this reasoning, because a nitro group is more electronegative than a nitrile group and position 3 is *ortho* to the nitro group. The analysis also indicates that the spin density at position 2 should be negative.

The assignment in the 4-cyanobenzoate radical is based on the assumption that the carboxylate group, COO, is more electronegative than the nitrile group, and therefore the splitting constants should be comparable with 4-nitrobenzonitrile. The argument is not as strong for the 4-cyanobenzonate as 4-nitrobenzonitrile, however, because there are no measurements on a series of *p*-substituted benzoate radicals.

The two nitrile groups at the 1(or 3)-positions in the 1,1,2,3,3-pentacyanopropene or the 1,1,3,3-tetracyanopropene radicals are not at equivalent positions with respect to the molecular symmetry properties if the molecules have planar conjugated structures. Differences of 10–15% have been observed for proton splittings at the 1(or 3)-position in the allyl radical[50] and in a long conjugated structure with similar geometry in the environment of the protons studied by Phillips.[35] The nitrogen splittings we have observed in these propene radicals, however, cannot be unequivalent by more than a few per cent of the splitting constant.

Maki and Geske,[7] in their study of a series of *p*-substituted nitrobenzene anion radicals, found that the sum of the *ortho* and *meta* proton splittings was a constant, $a_o{}^H + a_m{}^H = -2.3$ gauss, if $a_o{}^H$ and $a_m{}^H$ are taken to be negative and positive, respectively, except in *p*-dinitrobenzene where the single proton splitting is taken to be negative. In both benzonitrile and 4-toluinitrile, this sum is −3.33 gauss, and in terephthalonitrile it is −3.18 gauss. But the other compounds do not give the same value for this sum. In 4-nitrobenzonitrile, the value is −2.29 gauss, just as in the nitro compounds; in 4-cyanobenzoate it is −2.41 gauss; and in 4-cyanopyridine, it is either −4.02 or −1.22, depending on the choice of signs for the two splittings. In the valence-bond superposition[40] approximation for *p*-disubstituted benzene anion radicals, XC_6H_4X', the approximate constancy of $a_o{}^H + a_m{}^H$ is only expected if either of two possible conditions holds. One is that the spin density distribution in each monosubstituted radi-

(48) R. L. Ward, *J. Am. Chem. Soc.*, **83**, 3623 (1961).

(49) Results obtained in these laboratories by B. Barton.

(50) R. W. Fessenden, private communication.

cal, C_6H_5X and C_6H_5X', be approximately the same. Approximate constancy of the sum is also expected if one substituent, say X, is much more electronegative than the other, say X', since then X' acts only as a small perturbation on the spin-density distribution determined by X. In terephthalonitrile, X and X' are the same, so that the first condition is satisfied, while in 4-tolunitrile, the methyl group acts as a small perturbation on the spin-density distribution determined by the nitrile group. In the other p-substituted nitriles, however, the nitrile is less electronegative than the other substituent, so the sum $a_o{}^H + a_m{}^H$ is not the same as for benzonitrile. The constancy of the sum found by Maki and Geske for the nitrobenzenes thus results primarily from the fact that the nitro group is more electronegative than any of the p-substituents they examined, and these substituents introduce only small perturbations of the spin density.[40]

2. Line Widths and Electron Exchange.—The line widths of the E.S.R. spectra of electrolytically generated radicals were found to depend on a number of experimental variables, but the most important of these factors was the degree of completeness of the reduction. For example, incompletely reduced phthalonitrile gave a spectrum with line widths between 0.5 and 1.0 gauss, while the spectrum from more completely reduced material had line widths of about 0.07 gauss. This effect can be interpreted in terms of a rapid electron exchange reaction between the radical anion $R^{\bar{}}$ and its precursor R. Electron exchange limits the lifetime of the unpaired electron in a particular magnetic quantum state and is thus one of the factors which contributes to the line width. Weissman and co-workers[12,13] have studied the electron exchange between the naphthalene anion radical and naphthalene in some detail, and found that the exchange could be described by second-order kinetics with a rate that was proportional to the concentration of naphthalene. The contribution from electron exchange to the width (in gauss)[30] is given approximately[12,13] by the expression

$$\delta = 6.51 \times 10^{-6} k[R] \qquad (4.1)$$

where k is the specific rate constant in liter mole^{-1} sec.$^{-1}$ and [R] is the concentration of unreduced material in moles/liter. The second-order rate constants for the naphthalene–naphthalenide exchange depended on the solvent and the cation, but were in the range 10^7–10^9 liter mole^{-1} sec.$^{-1}$. An order-of-magnitude estimate for the phthalonitrile system gives a rate constant of about 10^8 liter mole^{-1} sec.$^{-1}$, a value comparable to that found by Weissman.

Although the electron-exchange line broadening may be of intrinsic interest in some studies, it frequently has the undesirable effect of causing poor resolution in the E.S.R. spectra. If the only important exchange reaction is between the radical $R^{\bar{}}$ and its precursor R, and if the specific rate constant is 10^8 liter mole^{-1} sec.$^{-1}$, a concentration of [R] = 5×10^{-5} M is required to reduce the value of δ to about 0.03 gauss. Under equilibrium conditions with a radical concentration of 0.005 M, the Nernst equation indicates that a potential about 0.2 v. more cathodic than the standard reduction potential would produce the desired low concentration [R] = 5×10^{-5} M. In practice, with a stable radical, the electrolysis can usually be carried out for a long enough period of time to approximate the equilibrium conditions rather closely, and thus sufficiently complete reduction can be obtained.

Many of the radicals generated electrolytically had different chemical structures from those of the starting materials, and in several of these cases the E.S.R. spectra had exceptionally sharp lines. Thus the spectrum of the tetracyanoethylene anion radical generated from either tetracyanoethane or tetracyanocyclopropane was sharper than the spectrum obtained directly from tetracyanoethylene.[36] Similarly, complete reduction was not required to obtain narrow lines in the spectrum of the 4,4'-dicyanobiphenyl radical generated from 4-fluoro- or 4-aminobenzonitrile. In these examples, the starting material is reduced at a more cathodic potential than the reduction potential of the radical eventually produced, i.e., the radical is not a strong enough reducing agent to reduce the starting material. The concentration of the oxidized form of the radical will thus be low even if the starting material is not completely reduced. Furthermore, the activation energy for the electron exchange reaction between the radical and the starting material is at least as large as the enthalpy difference between the two species, and a rapid reaction is not expected. On the other hand, if the radical is a strong enough reducing agent to reduce appreciable amounts of the starting material, incomplete reduction will not produce narrow lines because of two factors: neither the concentration of the oxidized form of the radical nor the rate of electron exchange between the radical and the starting material is necessarily low. Thus the spectrum of the benzonitrile anion radical generated at the second polarographic wave from either phthalonitrile or terephthalonitrile had line widths comparable to those in the spectrum generated directly from benzonitrile.

Electron exchange can also take place between a radical anion $R^{\bar{}}$ and the dianion $R^{=}$, or between an anion R^- and a dianion radical $R^{\bar{=}}$. The $R^{\bar{}}$, $R^{=}$ exchange has been observed in the spectrum of the cyclooctatetraene radical anion,[51] and the R^-, $R^{\bar{=}}$ type is exhibited by the 4-cyanobenzoate and the 1,1,2,3,3-pentacyanopropene dianion radicals. At the first polarographic wave, 4-cyanobenzoic acid is converted to the 4-cyanobenzoate ion, and at the second wave the benzoate ion is reduced to the dianion radical. At the second wave of the benzoate ion, incomplete reduction to the radical gave a spectrum with lines only 0.08 gauss wide. Similarly, incomplete reduction of 1,1,2,3,3-pentacyanopropenide results in a relatively sharp line spectrum. In these cases, in which electron exchange must take place between two charged species, Coulomb repulsion will undoubtedly cause a slower exchange rate than for a reaction between one charged and one uncharged species.

Most of the electrolyses conducted in the present investigation were performed on solutions 0.005 M in reducible material so that, if the reduction to a stable radical was complete, the radical concentration would have been 0.005 M. In some spectra, improved resolution is obtained with more dilute solutions because of the reduction of line-broadening effects. Dipolar interactions and quantum mechanical exchange[52,53] contribute to radical–radical line broadening. Both effects are inversely proportional to the concentration, but the dipolar broadening is proportional to the viscosity of the solvent and the quantum mechanical exchange broadening decreases with increasing viscosity. Qualitative observations indicate that the quantum mechanical exchange is less troublesome for charged than for neutral radicals, presumably because there is a smaller probability for ions to approach each other closely, and it is possible that the effects are also smaller for dianion radicals than for monoanion radicals.

3. Solvent Effects.—The N^{14} splitting constant given in Table II for the nitro group in the 4-nitro-

(51) H. L. Strauss, T. J. Katz and G. K. Fraenkel, to be published; H. L. Strauss, Thesis, Columbia University, New York, N. Y., 1960.

(52) D. Kivelson, J. Chem. Phys., **33**, 1094 (1960).

(53) G. E. Pake and T. R. Tuttle, Jr., Phys. Rev. Letters, **3**, 423 (1959).

benzonitrile radical in DMF solution is 6.24 gauss, whereas Maki and Geske[8] reported a splitting constant of 7.15 gauss for the spectrum obtained in acetonitrile solution. The differences between the splittings at the other positions in the radical were quite small. Similar effects have been obtained in nitrobenzene: Geske and Maki[6] find $a^N = 10.32$ gauss in acetonitrile, Ward finds $a^N = 10.33$ gauss in dimethoxyethane (in the presence of alkali metal ions)[54] and we have found[55] $a^N = 9.70$ gauss in DMF. The other splittings in nitrobenzene were not found to be particularly solvent dependent. Piette, et al.,[11] reported that nitrogen splittings of the nitro group of the anion radicals of aromatic nitro compounds are three to four gauss larger in water than in acetonitrile, and recently Adams[56] has shown that a^N for nitrobenzene depends on the water content of acetonitrile, rising rapidly from 10.3 gauss on the addition of a small amount of water, and leveling off to a value of about 13.5 gauss at higher water concentrations.

The effects indicate that the greatest redistribution of π-electron spin density on changing from one solvent to another is in the nitro group of a nitrobenzene derivative. The theory of C^{13} spliting[57] can be applied in a formal way to the N^{14} splitting in a nitro group and shows that the splitting is a linear function of the spin densities on the nitrogen and oxygen atoms and also of the spin density on the carbon atom of the ring to which the nitro group is bonded. As a result, small changes in the spin density on the oxygen atoms resulting from solvent interactions can have marked effects on the nitrogen splitting without appreciably affecting the overall spin-density distribution of the molecule or the splitting constants at other positions.

V. Conclusions

Electrolytic reduction of most of the nitriles studied in the present experiments has been shown to take place with a one-electron addition and the formation of an anion radical which is sufficiently stable to give an E.S.R. spectrum. Well-resolved spectra were obtained which could be fully interpreted, and the assignment of the splitting constants to particular nuclei in the radical was frequently possible. The results can therefore be used in studying the spin-density distribution in the radicals.[14]

Several compounds were also found to undergo complex reduction processes, and by combining the techniques of E.S.R. with conventional and oscillographic polarography, a number of reduction mechanisms were elucidated. Complete reduction at controlled potentials made it possible to examine the processes which take place at the second and third polarographic waves of some materials. For example, the reduction of 4-cyanobenzoic acid resulted first in the normal anion and then, at more cathodic potentials, in the dianion radical. The reduction of either 4-amino- or 4-fluorobenzonitrile resulted in the formation of 4,4'-dicyanobiphenyl, a product which arose from the ejection of the amide or fluoride ion followed by dimerization. The dimer is reduced more easily than either starting material, and thus the anion radical of the dimer was automatically formed. Similarly, the addition of a second electron to phthalonitrile or terephthalonitrile resulted in ionization to a cyanide ion and a carbanion, and the carbanion abstracted a proton from the solvent to give benzonitrile. At the potential of these reductions, benzonitrile was automatically reduced to its anion radical. The same mechanism accounts for the formation of the 1,1,3,3-tetracyanopropene dianion radical at the third polarographic wave in the reduction of 1,1,2,3,3-pentacyanopropenide. This radical is also a product of a complex sequence of reactions which occur in the reduction of 1,1,3,3-tetracyano-2-dimethylaminopropenide.

The use of electrolytic techniques for the generation of free radicals has been shown to be a highly versatile method. Accurate control of the reduction potential has been found to be important in determining the radical species generated, and thus controlled-potential electrolysis often offers distinct advantages over the use of alkali metal reductants. A wide variety of solvents can be chosen, including solvents of high dielectric constant which reduce the effects of ion pairing, and bulky supporting electrolytes can be employed which are less likely to form tight complexes with the anion radicals than alkali ions. N,N-Dimethylformamide has been shown to be a good, relatively inert, solvent for the generation of many anion radicals. Only a few of the compounds studied did not form fairly stable radicals in DMF, and some of these might well form more stable radicals in one of the many other solvents suitable for use with the technique.

Complete electrolysis has been found to be an important factor in obtaining spectra with narrow lines as well as in studying reduction processes. The principal source of line broadening was usually intermolecular electron exchange between the radical and its unreduced precursor, and thus complete reduction served to increase the lifetime of a particular spin state of the radical and sharpen the lines of the spectrum. Qualitative observations indicated that the rate of exchange between dianion radicals and monoanions was less than the rate of exchange between anion radicals and neutral molecules. It was found that if the radical had a different chemical structure from the starting material because of some complex reduction mechanism, and if the radical was not a strong enough reducing agent to reduce the starting material, sharp lines were obtained in the spectrum even if the reduction was not complete. These results are in accord with qualitative estimates of the significant rate processes.

From an electrochemical point of view, E.S.R. is an extremely useful adjunct in the elucidation of mechanisms. In contrast to macroreduction techniques, with separation and analysis of products, it can be applied under conditions that are essentially similar to those used in polarographic work. When free radical intermediates and products are involved, possible effects of concentration changes often make a comparison of the results in macro- and micro-scale reductions inconclusive. These relatively unstable products make chemical characterization a challenging task, and the qualitative identification which is often possible from the E.S.R spectra can aid in eliminating ambiguities in the reaction mechanisms.

(54) R. L. Ward, J. Am. Chem. Soc., 83, 1296 (1961).
(55) P. H. Rieger, Thesis, Columbia University, New York, N. Y. (1961).
(56) R. N. Adams, private communication.
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