Table VII. INDO (CS) Calculated Difference of the Total Energy of R′COC$_6$H$_4$COR Cis and Trans Isomers.[a] Calculated Constants of the Cis ↔ Trans Equilibrium at Room Temperature

Substituent	$R = CH_3$; $R' = H$	$R = R' = CH_3$	$R = CH_3$; $R' = C_2H_5$	$R = R' = H$
$E_{\text{cis-trans}}$	−0.065	−0.109	−0.108	−0.035
$K_{\text{cis-trans}}$	1.12	1.2	1.2	1.06

[a] Energy values are in kilocalories per mole.

Table VIII. INDO (CS) Calculated C–H Bond Energies in R′CH$_2$C$_6$H$_4$COR[a]

Bond energy	C–H$_{\alpha}$[b]	C–H$_{\alpha'}$[b]	C–H$_{\beta'}$[b]	C–H$_{\gamma'}$[b]
R′ = H; R = Me	−467.10	−468.14		
R′ = Me; R = Me	−467.14	−460.66	−471.80	
R′ = Et; R = Me	−467.13	−461.36	−464.27	−472.03
R′ = Et; R = Et	−460.247	−460.667	−471.84	

[a] Energies are in kilocalories per mole. [b] Subscripts α, α', β', and γ' refer to the positions from the ring of the substituent carbon atoms.

acting as an electron acceptor (step 4) until step 1 becomes rate determining. One may expect that the consequence of this autocatalyzed mechanism would be the occurrence of an inductive phase until neutral diketone concentration becomes high enough. After step 4 the reaction would proceed as follows.

$$R'\dot{C}HC_6H_4COR + O_2 \longrightarrow R'CHOO\dot{}C_6H_4COR \quad (4')$$

$$R'\dot{C}O^-C_6H_4COR + O_2 \longrightarrow R'COC_6H_4COR + O_2\cdot^- \quad (5')$$

$$R'CHOO\dot{}C_6H_4COR + O_2\cdot^- \longrightarrow R'CHOO^-C_6H_4COR \text{ to step 3} \quad (6')$$

Mechanism of *p*-Tolunitrile, *p*-Tolualdehyde, and Para-Substituted Nitrobenzene Oxidation

Russell's mechanism will also apply to the oxidation of *p*-tolunitrile, *p*-tolualdehyde, and para-substituted nitrobenzenes. The fact that the oxidation of the methyl group occurs readily for these compounds, while it was difficult in *p*-methylacetophenone, must be understood in terms of the σ^- values of NO$_2$, CN, and CHO groups being greater than $\sigma^-_{\text{COCH}_3}$.

p-Methylnitrobenzene and *p*-ethylnitrobenzene radical anions from 10^{-3} *N* solutions may be formed either by direct reduction of the nitrobenzenes by the strong base[12] or by reaction (step 4) with the carbanion formed in step 1, the nitrobenzenes acting as catalyst. This reaction would compete with that of the carbanion with the neutral ketone formed in step 3.

In conclusion, alkylbenzenes which are substituted in the para position by strong electron-attracting groups behave as acidic hydrocarbons and lead to carbanions which can autoxidize to ketones. We are at present investigating the extension of the autoxidation reaction to other series of organic compounds. Quantitative studies of the reaction kinetics and application to ketone synthesis will be discussed in following papers.

Acknowledgments. We thank Dr. J. Devanneaux for his help with the INDO calculations. We wish also to express our gratitude to Mrs. M. Loízos for her invaluable aid.

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[12] Nitrobenzene (10^{-3} *N*) in HMPA–NaOMe leads to the formation of the nitrobenzene radical anion.

Electrochemical Studies of the Formation and Decomposition of Halogenated Benzonitrile Anion Radicals

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Abstract: The electrochemical reduction of a series of bromo-, chloro-, and iodobenzonitriles in *N*,*N*-dimethylformamide has been shown to be an overall two-electron process which gives benzonitrile as the principal product. Since reduction of one of these halogenated benzonitriles (4-chlorobenzonitrile) in the presence of cyanide ion gives rise to a small amount of terephthalonitrile anion radical, the intermediacy of cyanophenyl radicals is suggested. A reaction pathway consistent with these data involves the initial one-electron reduction of the halogenated benzonitrile, rapid loss of halide ion from the anion radical to give the corresponding cyanophenyl radical, and subsequent reduction of the cyanophenyl radical at the electrode surface to cyanophenyl anion. Abstraction of a proton from the solvent system by the cyanophenyl anion yields benzonitrile and completes the reaction pathway. The results obtained here are contrasted with previously reported decomposition pathways of the anion radicals of 4-fluoro- and 4-aminobenzonitrile.

Electrochemical and electron spin resonance studies of numerous substituted aromatic nitrile radicals in *N*,*N*-dimethylformamide (DMF) have been reported by Rieger, *et al.*[1] Although reduction of the cyano and nitro derivatives of benzonitrile gave very stable anion radicals, the anion radicals of 4-amino- and 4-

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[1] P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 85, 683 (1963).

Table I. Cyclic Voltammetric and Coulometric Data for Several Substituted Benzonitriles[a]

	First wave		Second wave	Exhaustive reduction	
Compound	E_p[b]	$E_{p/2}$[b]	E_p[b]	n_{exptl}, F/mol	% yield of benzonitrile[c]
4-Chlorobenzonitrile	−1.96	−1.88	−2.32	2.02	85, 95[d]
3-Chlorobenzonitrile	−1.99	−1.91	−2.32	2.10	89
2-Chlorobenzonitrile	−1.91	−1.80	−2.32	2.20	90
4-Bromobenzonitrile	−1.92	−1.83	−2.32	1.92	92, 100[d]
3-Bromobenzonitrile	−1.95	−1.85	−2.32	2.09	90
2-Bromobenzonitrile	−1.87	−1.79	−2.32	1.99	88
4-Iodobenzonitrile[e]	−1.84	−1.71	−2.32		
Terephthalonitrile[f]	−1.57	−1.51	−2.39[g]		
4-Nitrobenzonitrile[f]	−0.83	−0.77	−1.64		
4,4′-Dicyanobiphenyl[f]	−1.63	−1.57	−2.06		
Benzonitrile[f]	−2.32	−2.26			
Tolunitrile[f]	−2.36	−2.30			

[a] The solutions are 0.1 M tetraethylammonium perchlorate in DMF; the scan rate in cyclic voltammetric experiments is 80.6 mV/sec. [b] Potentials are in volts *vs.* an aqueous saturated calomel electrode. [c] Unless the data are specified otherwise, the yields were determined by flame-ionization gas chromatography. Benzonitrile was the only product found by either cyclic voltammetry or gas chromatography. The potential of the working electrode in the coulometric reductions was typically −2.10 V. Less than 1% of the starting material remained upon termination of the electrolysis. [d] Analysis by cyclic voltammetry. [e] Prepeak is observed at approximately −1.35 V. The supporting electrolyte is 0.1 M tetraethylammonium iodide. [f] The first wave corresponds to the one-electron reduction of the parent compound to its anion radical. The second wave, if present, results from the reduction of the anion radical to the corresponding dianion. [g] Reduction of the anion radical results in the loss of cyanide ion from the dianion and the subsequent formation of benzonitrile.[1]

fluorobenzonitrile were found to decompose rapidly. Since the esr spectrum of the anion radical of 4,4′-dicyanobiphenyl was observed, these workers suggested that 4-amino- and 4-fluorobenzonitrile anion radicals decomposed with loss of amide and fluoride ions, respectively, to give 4-cyanophenyl radical. Dimerization of 4-cyanophenyl radicals and the subsequent reduction of 4,4′-dicyanobiphenyl to its anion radical were postulated for the remaining steps in the decomposition pathway.

In contrast to the behavior reported for 4-amino- and 4-fluorobenzonitrile, the electrochemical reduction of 4-chlorobenzonitrile did not give an observable radical.[1] Since previous studies of the decompositions of anion radicals of halogenated nitrobenzenes[2–4] and nitrobenzyl halides[5–7] have shown that the rate of halide ion loss decreases in the order of I > Br > Cl > F, it is apparent that the decomposition of the 4-chlorobenzonitrile anion radical must proceed quite differently from the pathway postulated for the anion radicals of 4-amino- and 4-fluorobenzonitrile. The present study is concerned principally with the formation of the anion radicals of a series of bromo- and chlorobenzonitriles and their subsequent mode of decomposition.

Results and Discussion

Bromo- and Chlorobenzonitriles. Since all six bromo- and chlorobenzonitriles exhibit nearly identical cyclic voltammetric, chronoamperometric, and coulometric behavior, the experimental results which were obtained for 4-chlorobenzonitrile have been chosen arbitrarily for discussion and interpretation; data for the other bromo- and chlorobenzonitriles are summarized in Table I.

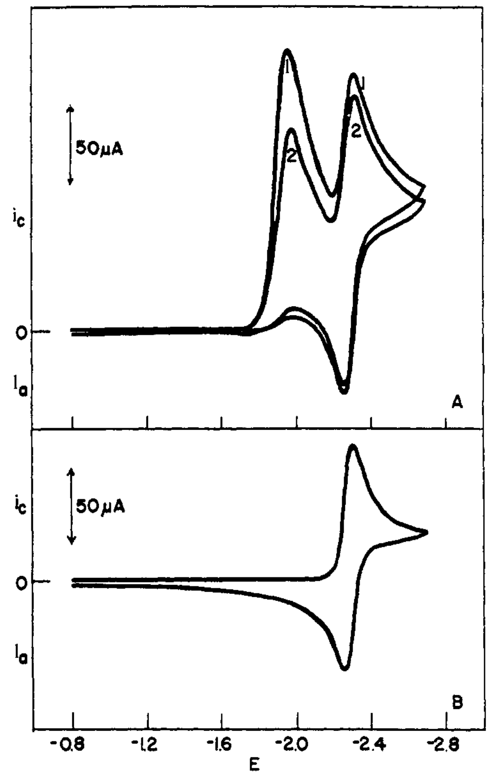

Figure 1. Cyclic voltammograms in 0.1 M tetraethylammonium perchlorate–DMF at a scan rate of 80.6 mV/sec on a platinum button electrode: (A) 2.15 × 10^{-3} M 4-chlorobenzonitrile; (B) 1.44 × 10^{-3} M benzonitrile. Numbers 1 and 2 represent cycles 1 and 2, respectively.

The cyclic voltammetric behavior of 4-chlorobenzonitrile in DMF is shown in Figure 1A. Two reduction waves are seen near −1.96 and −2.32 V on the first cathodic sweep, while a single oxidation wave corresponding to the oxidation of the product formed by the more cathodic process is evident on the reverse anodic sweep. Since subsequent cycles show that the second cathodic wave grows in magnitude relative to the first wave, the redox couple which occurs near −2.32 V must arise from decomposition of the product formed by the

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(2) T. Kitagawa, T. P. Layloff, and R. N. Adams, *Anal. Chem.*, **35**, 1086 (1963).

(3) J. G. Lawless and M. D. Hawley, *J. Electroanal. Chem. Interfacial Electrochem.*, **21**, 365 (1969).

(4) E. T. Seo and R. F. Nelson, 133rd National Electrochemical Society Meeting, Boston, Mass., May 1968, Abstract No. 207.

(5) J. G. Lawless, D. E. Bartak, and M. D. Hawley, *J. Amer. Chem. Soc.*, **91**, 7121 (1969).

(6) M. Mohammad, J. Hajdu, and E. M. Kosower, *ibid.*, **93**, 1972 (1971).

(7) D. E. Bartak and M. D. Hawley, *ibid.*, **94**, 640 (1972).

first cathodic process. Decomposition of the initial electrode product must also be relatively rapid, since no reoxidation wave is observed when the scan is reversed between the two cathodic peaks ($E_{\text{switching}} = -2.1$ V) at scan rates up to 100 V/sec. By comparison of Figures 1A and 1B, the species arising from the decomposition of the initial electrode product can be identified readily as benzonitrile. Since no additional anodic or cathodic wave is seen in the potential range of 0.0 to −2.6 V, we conclude that benzonitrile is the only stable electroactive product formed in the electroreduction of 4-chlorobenzonitrile.

Inspection of the cyclic voltammetric data for benzonitrile, tolunitrile, terephthalonitrile, 4-nitrobenzonitrile, and 4,4′-dicyanobiphenyl (Table I) shows that the difference between $E_{p/2}$ and E_p is approximately 60 mV. Since a difference of 57 mV is predicted between $E_{p/2}$ and E_p for systems which are both electrochemically and chemically reversible,[8] electron transfer must be rapid for each of these nonhalogenated benzonitriles. Although one might also expect electron transfer to be rapid for the halogenated benzonitriles,[9] an EC mechanism in which reversible electron transfer precedes a rapid follow-up chemical reaction requires that $E_{p/2} - E_p = 48$ mV and that E_p shift cathodically 30 mV for a tenfold increase in scan rate.[8] Since we observe $E_{p/2} - E_p$ to vary from 80 to 130 mV (Table I) and E_p for 4-chlorobenzonitrile to shift cathodically by approximately 75 mV for each tenfold increase in the scan rate, we conclude that electron transfer, even though rapid, must be slow relative to the rate of loss of halide ion from the anion radical.[8,10]

In order to estimate the number of electrons involved in the two cathodic processes, chronoamperometric $it^{1/2}/C$ values for 4-chlorobenzonitrile were compared with the value for tolunitrile. The reduction of tolunitrile, which is known to be a reversible one-electron process,[1] gave a diffusion-controlled value of 42 A sec$^{1/2}$ mol^{-1} cm^3 from $t = 4$ msec to $t = 8$ sec at an applied potential of −2.60 V. Since a similar measurement for 4-chlorobenzonitrile at a potential of −2.60 V gave a constant value of 120 A sec$^{1/2}$ mol^{-1} cm^3 (4 msec $\leq t \leq$ 8 sec), it is reasonable to conclude that a total of three electrons is involved in the two cathodic processes. Thus, since the second cathodic process ($E_p = -2.32$ V) arises from the reduction of benzonitrile to its anion radical, the reductive dehalogenation of 4-chlorobenzonitrile ($E_p = -1.96$ V) must be an overall two-electron process.

Although the cyclic voltammetric and chronoamperometric results leave little doubt that benzonitrile is the principal product formed by the two-electron reduction of 4-chlorobenzonitrile, the interpretation was verified by controlled-potential coulometry (Table I). Exhaustive electrolysis of 4-chlorobenzonitrile at a potential between the first and second cathodic waves (−2.08 V) gave an n value of 2 ($n_{\text{exptl}} = 2.02$). Cyclic voltammetric examination of the electrolyzed solution immediately after electrolysis indicated a nearly quantitative yield of benzonitrile; a gas-chromatographic analysis of the same solution showed that benzonitrile was formed in 85% yield. No other product was detected under the experimental conditions by either cyclic voltammetry or gas chromatography.

4-Iodobenzonitrile. In contrast to the behavior of the bromo- and chlorobenzonitriles, the reduction of 4-iodobenzonitrile gives rise to a prepeak near −1.35 V. The prepeak is unusually broad and both its location and height are dependent upon electrode pretreatment. The appearance of a prepeak and its anomalous behavior suggest adsorption of the electrode product.[11] Although a study of the adsorption of the anion radical is not possible because of its extremely rapid rate of decomposition, chronocoulometry was used to test for the possible adsorption of the reactant. We conclude that adsorption of 4-iodobenzonitrile cannot be occurring to a significant extent, however, since the intercept of a Q *vs.* $t^{1/2}$ plot is not altered by the addition of 4-iodobenzonitrile to a solution containing the supporting electrolyte.[12,13]

Despite the apparent adsorption of the electrode product, all chemical reactions interposed between electron-transfer steps must be very rapid in the reduction of 4-iodobenzonitrile. Chronoamperometric $it^{1/2}/C$ values obtained at a potential sufficiently negative (−2.60 V) so as to cause concurrent reduction of 4-iodobenzonitrile and benzonitrile indicate a diffusion-controlled electrode reaction (1 msec $< t <$ 4 sec, 110 A sec$^{1/2}$ mol^{-1} cm^3) and are consistent with an overall-three-electron reduction process. Thus, since the reduction of benzonitrile to its anion radical is a one-electron process, the formation of benzonitrile by the reductive dehalogenation of 4-iodobenzonitrile must involve two electrons.

Reaction Pathways. A mechanism consistent with these data involves the two-electron reduction of the halogenated benzonitrile to 4-cyanophenyl anion and halide ion. The cyanophenyl anion must then abstract a proton from the solvent system to form benzonitrile, which is subsequently reduced at more negative potential to its anion radical.

The formation of the 4-cyanophenyl anion is presumed to occur by one of the two equations described below. In the first scheme the initially formed anion radical decomposes with loss of halide ion to form a cyanophenyl radical. The radical must then be reduced, either chemically or electrochemically, to the corresponding cyanophenyl anion (eq 1). Although

$$\begin{tikzcd} \mathrm{RX} + e \arrow[r, shift left] & \mathrm{RX}\cdot^- \arrow[l, shift left] \arrow[r, "k"] & \mathrm{R}\cdot + \mathrm{X}^- \arrow[d, "e"] \\ & & \mathrm{R}^- \end{tikzcd} \qquad (1)$$

this reaction scheme has gained wide acceptance for the description of the reduction of alkyl halides, the principal reaction pathway for phenyl radicals in dipolar, aprotic solvents is hydrogen atom abstraction rather than reduction.[14,15] Thus, a second scheme,

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[8] R. S. Nicholson and I. Shain, *Anal. Chem.*, 36, 706 (1964).

[9] P. A. Malachesky, T. A. Miller, T. P. Layloff, and R. N. Adams, "Symposium on Exchange Reactions," International Atomic Energy Agency, Brookhaven National Laboratory, Upton, N. Y., 1965, pp 157–171.

[10] D. H. Evans, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, Abstract No. 62.

[11] R. H. Wopshall and I. Shain, *Anal. Chem.*, 39, 1514 (1967).

[12] F. C. Anson, *ibid.*, 38, 54 (1966).

[13] An intercept of 4 μC was obtained for a potential step from −0.80 to −2.60 V. The supporting electrolyte was 0.1 *M* tetraethylammonium iodide; the area of the platinum electrode was approximately 0.25 cm^2.

[14] The electrochemical reduction of phenyl radicals is apparently quite unusual. Although phenyl radicals are reported to be formed in the electrochemical reduction of halogenated nitrobenzenes,[3] diazonium salts,[16] and chlorobenzene,[17] the phenyl radicals are not reduced in these systems to their corresponding anions.

which involves stepwise reduction of the halogenated benzonitrile and subsequent loss of anion from the dianion, might also be plausible (eq 2). The loss of an

$$RX \underset{e}{\overset{e}{\rightleftharpoons}} RX^{\cdot -} \underset{e}{\overset{e}{\rightleftharpoons}} RX^{2-} \xrightarrow{\text{fast}} R^- + X^- \qquad (2)$$

anion from the aromatic nucleus is well documented and is observed in such systems as terephthalonitrile dianion (loss of cyanide ion)[1] and the dianions of the 4-bromo- and 4-chloronitrobenzenes (loss of halide ion).[20] However, unlike those systems where the cathodic peaks were separated by 600 mV or more, our present results require that the $E°$ values for the stepwise processes differ by less than approximately 300 mV. If the difference in standard reduction potentials were larger, it would be impossible for the peak reduction potential of the halogenated anion radical to be shifted in the anodic direction sufficiently by the decomposition of the dianion to permit the merger of the reduction peaks of the halogenated benzonitrile and its corresponding anion radical.[8]

Since a unique feature of eq 1 involves the intermediacy of a cyanophenyl radical, an attempt was made to prove the presence of these radicals by a trapping experiment with cyanide ion.[21] In this experiment 4-chlorobenzonitrile was reduced electrolytically at a potential of -1.95 V in an esr cavity with tetraethylammonium cyanide present as the supporting electrolyte. Although no spectrum could be recorded in the absence of the applied potential, a spectrum (a_N = 1.825 G, a_H = 1.585G) nearly identical with the one reported by Rieger, *et al.*,[1] for the terephthalonitrile anion radical (a_N = 1.808 G, a_H = 1.592 G) was recorded readily upon electroreduction of 4-chlorobenzonitrile (eq 3 and 4). This result constitutes strong

$$4\text{-}NCC_6H_4Cl + e \rightleftharpoons [4\text{-}NCC_6H_4Cl]^{\cdot -} \xrightarrow{\text{fast}} [4\text{-}NCC_6H_4\cdot] + Cl^- \qquad (3)$$

$$[4\text{-}NCC_6H_4\cdot] + CN^- \longrightarrow [4\text{-}NCC_6H_4CN]^{\cdot -} \qquad (4)$$

evidence for the intermediacy of the cyanophenyl radical and suggests that eq 1 is the more plausible of the two proposed pathways for the reduction of halogenated benzonitriles.

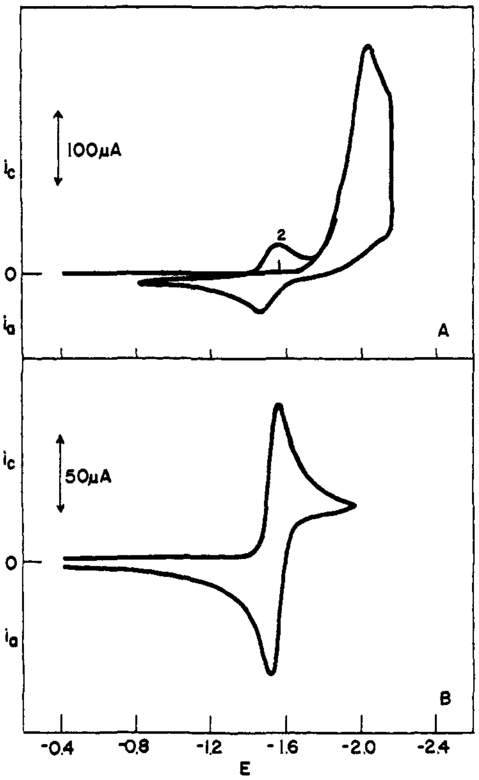

Figure 2. Cyclic voltammograms on a planar, platinum electrode in DMF. (A) 3.75 × 10^{-3} *M* 4-chlorobenzonitrile and 0.2 *M* tetraethylammonium cyanide at a scan rate of 80.6 mV/sec. The potential sweep was interrupted at -2.2 V for approximately 30 sec in order to accentuate the formation of terephthalonitrile anion radical. (B) 1.80 × 10^{-3} *M* terephthalonitrile and 0.1 *M* tetraethylammonium perchlorate at a scan rate of 80.6 mV/sec. Numbers 1 and 2 represent cycles 1 and 2, respectively.

Although the esr experiment proves some capture of cyanide ion by the 4-cyanophenyl radical, the cyclic voltammogram (Figure 2) of 4-chlorobenzonitrile in the presence of tetraethylammonium cyanide clearly shows that the principal reaction pathway for this radical is reduction rather than coupling with anion. This behavior differs markedly from the results which have been reported for nitrophenyl radicals; the latter radicals are captured quantitatively by cyanide and nitrite ions to give the 4-nitrobenzonitrile anion radical and 4-dinitrobenzene anion radical, respectively.[23]

Although absolute rate constants for reactions such as hydrogen atom abstraction and coupling with cyanide ion have not yet been measured for 4-cyano- and 4-nitrophenyl radicals, it is improbable that the reaction rates of these σ radicals should differ significantly.[25,26] Hence, the cause for the difference in the observed reaction pathways of 4-cyano- and 4-nitrophenyl radicals must certainly be due to an enhancement in the rate of 4-cyanophenyl radical reduction. We believe that an increase in the rate of 4-cyanophenyl radical reduction can result only if the decompositions of the halogenated benzonitrile anion radicals occur so rapidly that the cyanophenyl radicals are formed at the electrode surface rather than in the bulk of the solution. Experimental evidence to support this suggestion includes the coulo-

(15) Since Russell[18] did not observe the esr signals of the anion radicals which would result from the coupling of nitrophenyl and cyanophenyl radicals with 2-nitropropyl anion, he suggested that reduction of cyano- and nitrophenyl radicals by 2-nitropropyl anion occurred instead. However, since the anticipated coupled products should be very unstable and should lose nitrite ion to give the corresponding cumyl radicals,[19] reactions other than reduction of phenyl radical (specifically, dimerization of cumyl radicals) could explain the absence of the anticipated esr signals.

(16) F. F. Gadallah and R. M. Elofson, *J. Org. Chem.*, 34, 3335 (1969).

(17) Since the reductive dechlorination of chlorobenzene is an overall one-electron process which yields benzene and chloride ion, the reaction pathway of the intermediate phenyl radical must be hydrogen atom abstraction from the solvent system: D. E. Bartak, unpublished results.

(18) G. A. Russell, *Chem. Soc., Spec. Publ.*, No. 24, 271 (1970).

(19) N. Kornblum, T. M. Davies, G. W. Earl, G. S. Greene, N. L. Holy, R. C. Kerber, J. W. Manthey, M. T. Musser, and D. H. Snow, *J. Amer. Chem. Soc.*, **89**, 5714 (1967).

(20) J. G. Lawless and M. D. Hawley, *J. Electroanal. Chem. Interfacial Electrochem.*, **23**, 1 (1969).

(21) The coupling of radicals with anions to form stable anion radicals has been demonstrated previously.[22–24]

(22) G. A. Russell and W. C. Danen, *J. Amer. Chem. Soc.*, **88**, 5663 (1966).

(23) D. E. Bartak, W. C. Danen, and M. D. Hawley, *J. Org. Chem.*, **35**, 1206 (1970).

(24) A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc. B*, 403 (1969).

(25) P. A. Kasai, P. A. Clark, and E. B. Whipple, *J. Amer. Chem. Soc.*, **92**, 2640 (1970).

(26) K. F. Purcell and M. D. Hawley, unpublished calculations.

metric and chronoamperometric n values of 2, the failure of 4-cyanophenyl radical to capture a large amount of cyanide ion, and the fact that the shapes of the reduction peaks for the halogenated benzonitriles are controlled by the rate of electron transfer rather than by the rate of the follow-up chemical reaction.

In order for almost complete reduction of cyanophenyl radical to occur, the rate constant for the decompositions of the bromo-, chloro-, and iodobenzonitrile anion radicals must be at least 10^{10} $\sec^{-1}$.[27,28] Although this lower limit is greatly in excess of any value which we can measure experimentally by either single potential step chronoamperometry or cyclic voltammetry, the value does correctly predict that the chronoamperometric $it^{1/2}/C$ values for the reduction of these halogenated benzonitriles should be diffusion controlled at $t = 1$ msec and that no reoxidation wave should be observed for any of the halogenated benzonitrile anion radicals at a scan rate of 100 V/sec.

The results and interpretation given here for the electrochemical behavior of the bromo- and chlorobenzonitriles are also in distinct contrast to the reaction pathway reported by Rieger, *et al.*,[1] for the electrochemical reduction of 4-fluoro- and 4-aminobenzonitrile. In their electrochemical and electron spin resonance studies, they report that the initially formed anion radicals of the parent species undergo relatively slow loss of anion to form the 4-cyanophenyl radical as an intermediate. Since the esr spectrum of the 4,4′-dicyanobiphenyl anion radical is observed upon electrolysis, they suggest that 4-cyanophenyl radicals undergo dimerization and that the resulting dimer is subsequently reduced at the applied potential to its anion radical. However, since the two small waves observed by Rieger, *et al.*, in their cyclic voltammograms are almost certainly due to the stepwise reduction of 4,4′-dicyanobiphenyl (Table I), we conclude that the apparent dimerization of cyanophenyl radicals is but a minor reaction pathway and that the principal decomposition pathway remains to be identified. Studies are currently in progress which are designed to elucidate these reaction pathways.

Experimental Section

Instrumentation. The cyclic voltammetric and chronoamperometric studies were performed on a previously described potentiostat.[29] Compensation of ohmic potential loss was provided by the procedures described by Smith and coworkers.[30] Large-scale, controlled-potential reductions were performed on a second potentiostat which used a Harrison Model 6824A amplifier in the control circuit. Readout in the cyclic voltammetric and chronoamperometric experiments was to either a Moseley Model 7030A X-Y recorder or a Tektronix Model 564 oscilloscope. The latter was equipped with Type 2A63 and 2B67 plug-ins and a Model C-12 camera. The signal source for experiments of short duration (less than 1 sec) was a Hewlett-Packard Model 3300–3302 function generator.

Electron spin resonance spectra were obtained on a Varian V-4502 spectrometer. The anion radicals were produced *in situ* by the electrochemical reduction of 4-chlorobenzonitrile in the presence of the reacting anion.

The gas chromatograph was a Hewlett-Packard Model 700 equipped with flame ionization detection. SE-30 columns at 110° were employed for benzonitrile analysis at a nitrogen flow rate of 60 ml/min.

Chemicals. All electroactive chemicals were obtained from commercial sources. Each compound was further purified by either sublimation or recrystallization. Melting point determinations and gas chromatographic analysis were used to check purity. Tetraethylammonium perchlorate was prepared according to the method of Kolthoff and Coetzee.[31] Tetraethylammonium cyanide was prepared by the method of Andreades and Zahnow.[32] Dimethylformamide was dried over barium oxide, distilled at reduced pressure on a Vigreux column, and collected over activated Linde Type 4A molecular sieves.[33] The solvent was transferred immediately to a vacuum line for future use.

Electrodes and Cell. All electrochemical experiments were performed on an all-glass vacuum line.[34] The solvent (DMF) was distilled into the cell on the vacuum line; traces of oxygen, if present, were removed by several freeze–pump–thaw cycles. After the cell and its contents were brought to room temperature, helium was introduced until normal atmospheric pressure was attained. The helium was purified by successive passage of the gas through columns of BTS catalyst and anhydrous magnesium perchlorate and a trap cooled to liquid nitrogen temperature.

An aqueous saturated calomel electrode was used throughout as the reference electrode. The reference electrode compartment was isolated from the working electrode and auxiliary electrodes in all studies by means of a glass frit. The working electrode in cyclic voltammetric and chronoamperometric experiments was a modified Beckman platinum button electrode (No. 39273); a large cylindrical platinum gauze served as the working electrode in coulometric determinations. The auxiliary electrode was a platinum wire. Stirring of the cell contents was accomplished by means of a magnetic stirrer.

Acknowledgments. This work was supported by the National Science Foundation (GP-21316) and by NASA and NSF fellowships to D. E. B.

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(27) In order for reduction to be the principal reaction pathway of the cyanophenyl radical, we assume that $(Dt)^{1/2}$ must be approximately 10^{-8} cm or smaller.

(28) Since a follow-up chemical reaction shifts the reduction peak in the anodic direction, the difference between the observed peak potential and the half-wave potential should be related to the rate of the chemical reaction.[8] Although the half-wave potentials for these halogenated benzonitriles cannot be determined experimentally, these values can be calculated from the reaction constant ρ, the half-wave potential of benzonitrile, and the appropriate σ-substituent constants. With $\rho = 0.31$ V, the half-wave potential for 4-chlorobenzonitrile is calculated to be -2.22 V. Since $E_p = 1.96$ V and $nFv/RT = 3.15$ $\sec^{-1}$, a lower limit of 10^{10} $\sec^{-1}$ is estimated for the rate constant for the loss of chloride ion from 4-chlorobenzonitrile anion radical.

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