ELECTROCHEMICAL STUDIES OF THE FORMATION AND DECOMPOSITION OF 2- AND 3-HALOGENATED BENZONITRILE RADICAL ANIONS

by

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INTRODUCTION

Electrochemical and electron spin resonance studies of numerous sub-stituted aromatic nitrile radicals in N,N-dimethylformamide have been reported by Rieger, et al.[1] Although reduction of the cyano and nitro derivatives of benzonitrile was observed to give stable radical anions, the radical anions of 4-amino- and 4-fluorobenzonitrile were found to decompose rapidly. Since the esr spectrum of the radical anion of 4,4'-dicyanobiphenyl was observed upon electrolytic reduction of 4-amino- and 4-fluorobenzonitrile, these workers suggested that the radical anions of the latter two compounds decom-posed 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 radical anion were postulated for the remaining steps in the decomposition pathway.

Previous studies of the decompositions of the radical anions of halogen-ated nitrobenzenes[2,3] and nitrobenzyl halides [4,5] have shown that the rate of halide ion loss increases with decreasing strength of the carbon-halogen bond.[2-6] This order of reactivity leads one to predict that the bromo- and chlorobenzonitrile radical anions should form the corresponding cyanophenyl radicals more rapidly than 4-fluorobenzonitrile radical anion and that 4,4'-dicyanobiphenyl should be the expected product of the decomposition of the radical anions of all 4-halogenated benzonitriles. However, in the case of the one bromo- and chlorobenzonitrile which has been studied (4-chlorobenzo-nitrile), 4,4'-dicyanobiphenyl radical anion was not an observed product of the reduction.[1] This result not only requires the decomposition pathways of 4-chloro- and 4-fluorobenzonitrile radical anions to differ, but also requires

the decomposition pathway for 4-fluorobenzonitrile anion radical to be more complex than the one originally proposed by Rieger, et al.[1]

The work which is reported here is concerned with the formation and the decomposition of several halogenated benzonitrile radical anions. Because of the multitude and complexity of the reaction pathways which were encountered, this report is limited to the discussion of the 2- and 3-bromo-, chloro-, and fluorobenzonitriles. The electrochemical behavior of the 4-halogenated benzonitriles has been studied by another member of our research group and those studies will be reported elsewhere.[7]

RESULTS AND DISCUSSION

I. 2- AND 3-BROMO- AND 2- AND 3-CHLOROBENZONITRILES

Since these four bromo- and chlorobenzonitriles exhibit nearly identical cyclic voltammetric, chronoamperometric, and coulometric behavior, the experimental results which were obtained for 2-chlorobenzonitrile have been chosen arbitrarily for discussion and interpretation; data for the other bromo- and chlorobenzonitriles are summarized in Table 1. Unless stated otherwise, all electrochemical experiments were performed in dimethylformamide (DMF) with tetraethylammonium perchlorate as the supporting electrolyte.

Cyclic Voltammetry. The cyclic voltammetric behavior of 2-chlorobenzonitrile is shown in Figure 1. Two reduction waves are seen near -1.91 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 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 ($E_{switching}$ = -2.1 V) at scan rates up to 100 V/sec. By comparison of Figures 1 and 2, 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 can conclude that benzonitrile is the only stable electroactive product formed in the electroreduction of 2-

Table 1. Cyclic Voltammetric and Coulometric Data for Several Substituted Benzonitriles.[a]

Compound	First Wave		Second Wave	Exhaustive Reduction	
	E_p[b]	$E_{p/2}$[b]	E_p[b]	n_{exptl} F/mole	% Yield Benzonitrile[c]
2-chlorobenzonitrile	-1.91	-1.80	-2.32	2.20	90
3-chlorobenzonitrile	-1.99	-1.91	-2.32	2.10	89
4-chlorobenzonitrile[e]	-1.96	-1.88	-2.32	2.02	85
2-bromobenzonitrile	-1.87	-1.79	-2.32	1.99	88
3-bromobenzonitrile	-1.95	-1.85	-2.32	2.09	90
4-bromobenzonitrile[e]	-1.92	-1.83	-2.32	1.92	92
2-fluorobenzonitrile	-2.17	-2.11	-2.32	2.02	104
3-fluorobenzonitrile	-2.19		-2.86	1.05	45
4-cyanobenzonitrile	-1.57	-1.51	-2.39[d]		
4-nitrobenzonitrile	-0.83	-0.77	-1.64		
4,4'-dicyanobiphenyl	-1.63	-1.57	-2.06		
4-methylbenzonitrile	-2.36	-2.30			
benzonitrile	-2.32	-2.26			
fluorobenzene	-2.86				

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. The yields were determined by flame-ionization gas chromatography. Benzonitrile and fluorobenzene were the only products 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. Reduction is accompanied by decomposition of the electrode product.

e. D. E. Bartak, Ph. D. thesis, Kansas State Univ., Manhattan, 1972.

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Figure 1. Cyclic voltammogram of 1.40×10^{-3} M 2-chlorobenzonitrile in 0.1 M tetraethylammonium perchlorate (TEAP)-DMF at a scan rate of 80.6 mV/sec. Numbers 1 and 2 represent cycles 1 and 2, respectively.
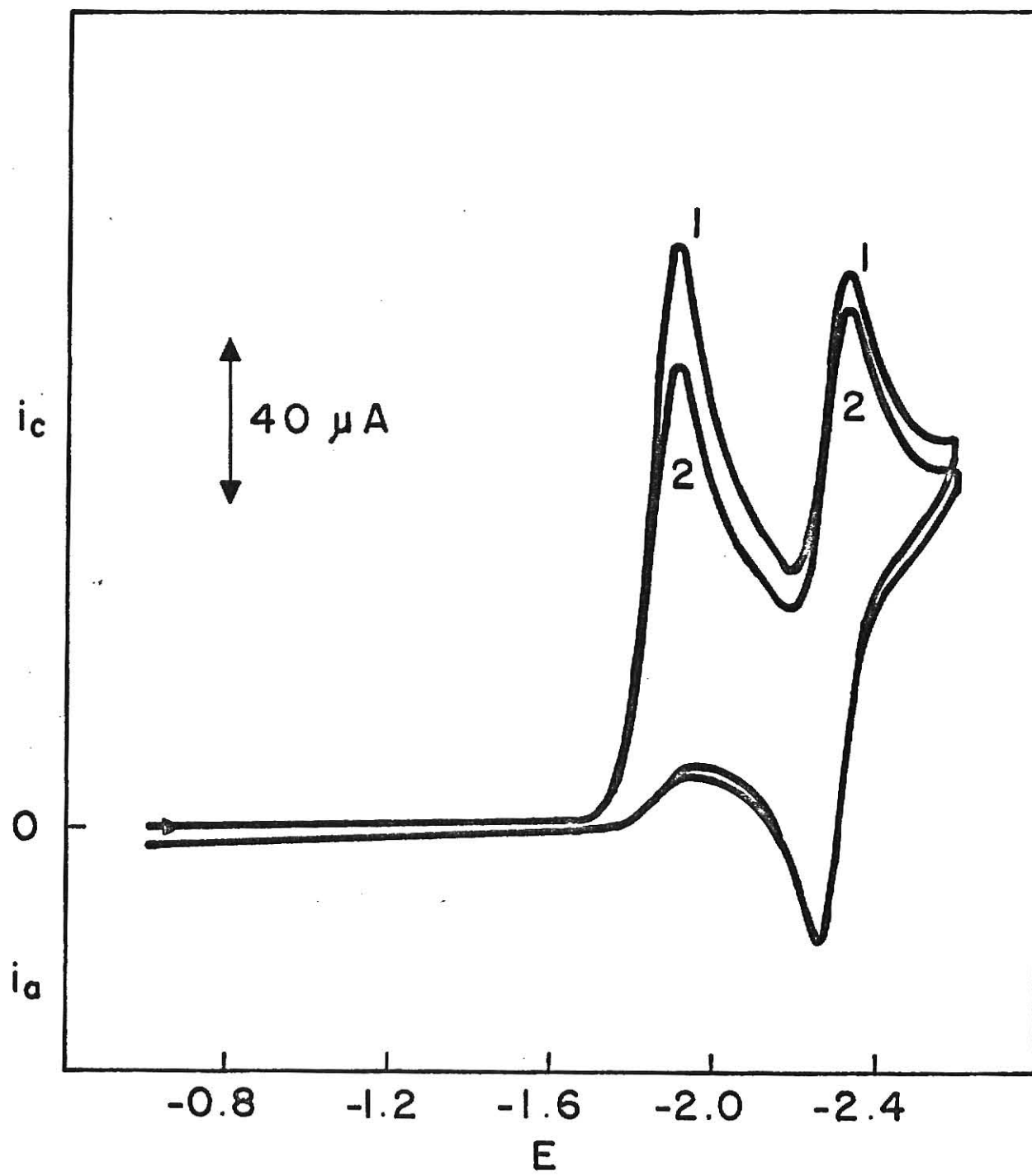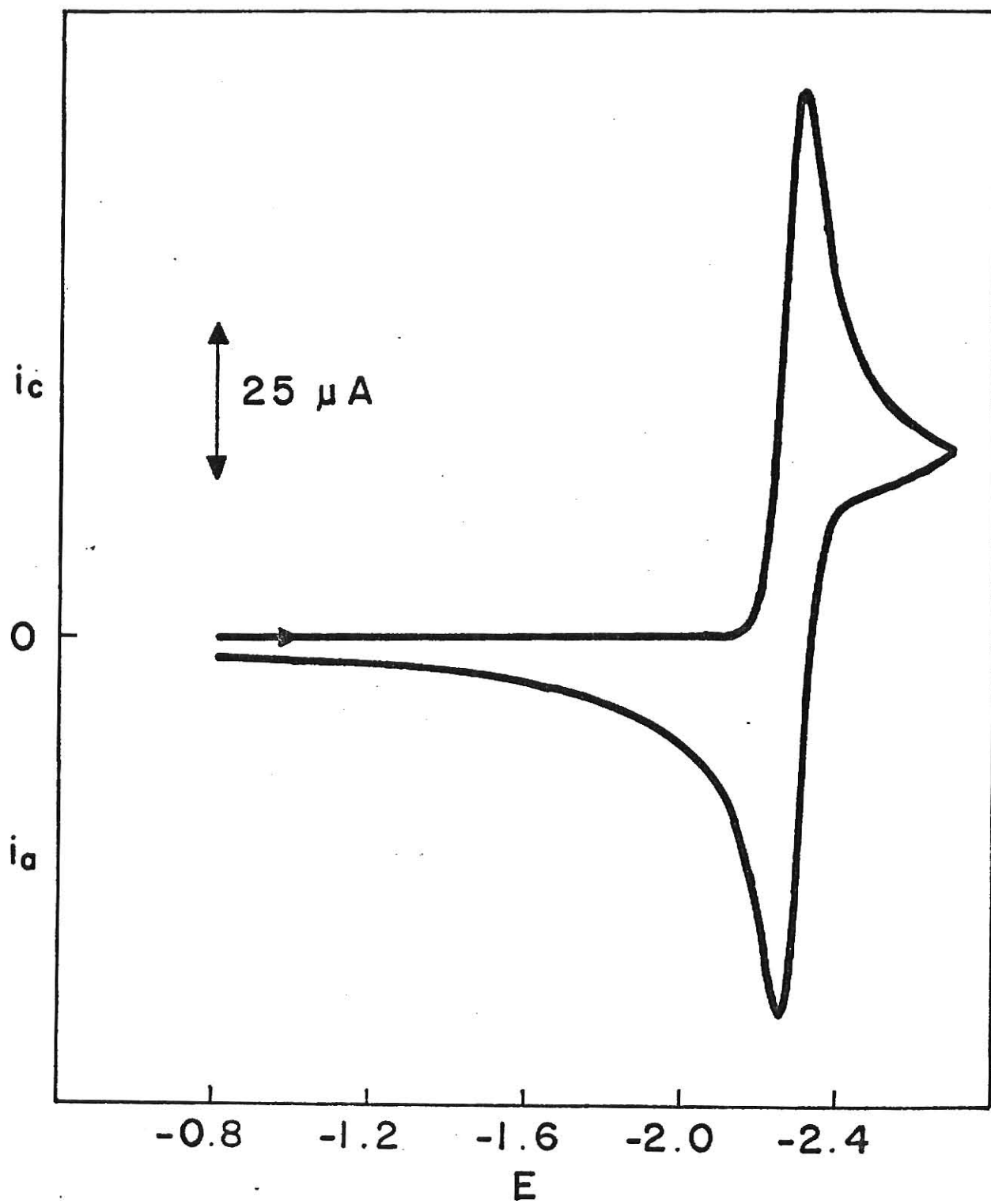
Figure 2. Cyclic voltammogram of 1.44×10^{-3} M benzonitrile in 0.1 M
TEAP-DMF at a scan rate of 80.6 mV/sec.

chlorobenzonitrile.

Inspection of the cyclic voltammetric data for benzonitrile, 4-methyl-benzonitrile, 4-cyanobenzonitrile, 4-nitrobenzonitrile, and 4,4'-dicyanobiphenyl (Table 1) 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, electron transfer must be rapid for each of these non-halogenated benzonitriles.[8] 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 110 mV (Table 1) and E_p for 2-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 radical anion.[8,10]

Chronoamperometry. In order to estimate the number of electrons involved in the two cathodic processes, chronoamperometric $it^{1/2}/C$ values for 2-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 $sec^{1/2}$ $mole^{-1}$ cm^3 from t = 4 msec to t = 8 sec at an applied potential of -2.60 V. Since a similar measurement for 2-chlorobenzonitrile at a potential of -2.50 V gave a constant value of 120 A $sec^{1/2}$ $mole^{-1}$ 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 radical anion, the reductive dehalogenation of 2-chlorobenzonitrile (E_p = -1.89 V) must be an overall two-electron process.

Coulometry. Although the cyclic voltammetric and chronoamperometric results leave little doubt that benzonitrile is the principal product formed by the two-electron reduction of 2-chlorobenzonitrile, the interpretation was verified by controlled-potential coulometry (Table 1). Exhaustive electrolysis of 2-chlorobenzonitrile at a potential between the first and second cathodic waves (-2.08 V) gave an n-value of 2 (n_{exptl} = 2.20). 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 88% yield. No other product was detected under the experimental conditions by either cyclic voltammetry or gas chromatography.

Reaction Pathways. A mechanism consistent with these data involves the two-electron reduction of the halogenated benzonitrile to the corresponding 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 radical anion.

The formation of the cyanophenyl anion is presumed to occur by one of the two schemes described below. In the first scheme the initially formed radical anion 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 this reaction scheme has gained wide acceptance for the description of the reduction of alkyl halides,

$$RX + e \rightleftharpoons RX^{-} \xrightarrow{k} R \cdot + X^{-} \tag{1}$$
$$\xrightarrow{e} R^{-}$$

the principal reaction pathways for phenyl radicals in dipolar, aprotic solvents is hydrogen atom abstraction rather than reduction.[3,11]

Thus, a second scheme, 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 anion from an aromatic ring is well docu-

$$RX \underset{e}{\overset{e}{\rightleftharpoons}} RX^{-} \underset{e}{\overset{e}{\rightleftharpoons}} RX^{2-} \xrightarrow{fast} R^{-} + X^{-} \tag{2}$$

mented and is observed in such systems as terephthalonitrile dianion (loss of cyanide ion)[1] and the dianions of the 4-bromo- and 4-chlorobenzenes (loss of halide ion).[12] However, unlike those systems where the cathodic peaks were separated by 600 mV or more, our present results require that the $\underline{E}^{\circ}$ 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 radical anion 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 radical anion.[8]

Since a unique feature of equation 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.[13-15] In this experiment 2-chlorobenzonitrile was reduced electrolytically at a potential of -1.90 V in the cavity of an esr spectrometer with tetraethylammonium cyanide present as the

supporting electrolyte. Although no spectrum could be recorded in the absence of the applied potential, a spectrum (a_3^H = 0.42 G, 2H; a_4^H = 4.12 G, 2H; a^N = 1.75 G, 2N) nearly identical with the one reported by Rieger, et al.,[1] for the phthalonitrile radical anion (a_3^H = 0.42 G, 2H; a_4^H = 4.13 G, 2H; a^N = 1.75 G, 2N) was recorded upon electroreduction of 2-chlorobenzonitrile (equation 3 and 4). This result constitutes strong evidence for the intermediacy of cyanophenyl

$$2\text{-}NCC_6H_4Cl + e \rightleftharpoons [2\text{-}NCC_6H_4Cl]^{-} \xrightarrow{\text{fast}} [2\text{-}NCC_6H_4\cdot] + Cl^{-} \tag{3}$$

$$[2\text{-}NCC_6H_4\cdot] + CN^{-} \longrightarrow [2\text{-}NCC_6H_4CN]^{-} \tag{4}$$

radical and suggests that equation 1 is the more plausible of the two proposed pathways for the reduction of the 2- and 3-bromo- and the 2- and 3-chlorobenzonitriles.

Although the esr experiment proves some capture of cyanide ion by 2-cyanophenyl radical, the low single to noise ratio (Figure 3) of the 2-cyanobenzonitrile radical anion spectrum in the presence of tetraethylammonium cyanide suggests 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 nitrile ions to give 2-cyanonitrobenzene radical anion and o-dinitrobenzene radical anion, respectively.[14]

Although absolute rate constants for reactions such as hydrogen atom abstraction and coupling with cyanide ion have not yet been measured for 2-cyano- and 2-nitrophenyl radicals, it is improbable that the reaction rates of these radicals should differ significantly.[16,17] Hence, the cause for the difference in the observed reaction pathways of 2-cyano- and 2-nitrophenyl radicals

Figure 3. First derivative of the E.S.R. absorption vs. magnetic
        field of the 2-cyanobenzonitrile radical anion, produced by
        the decomposition of 2-chlorobenzonitrile radical anion in
        the presence of cyanide ion.

5 Gauss
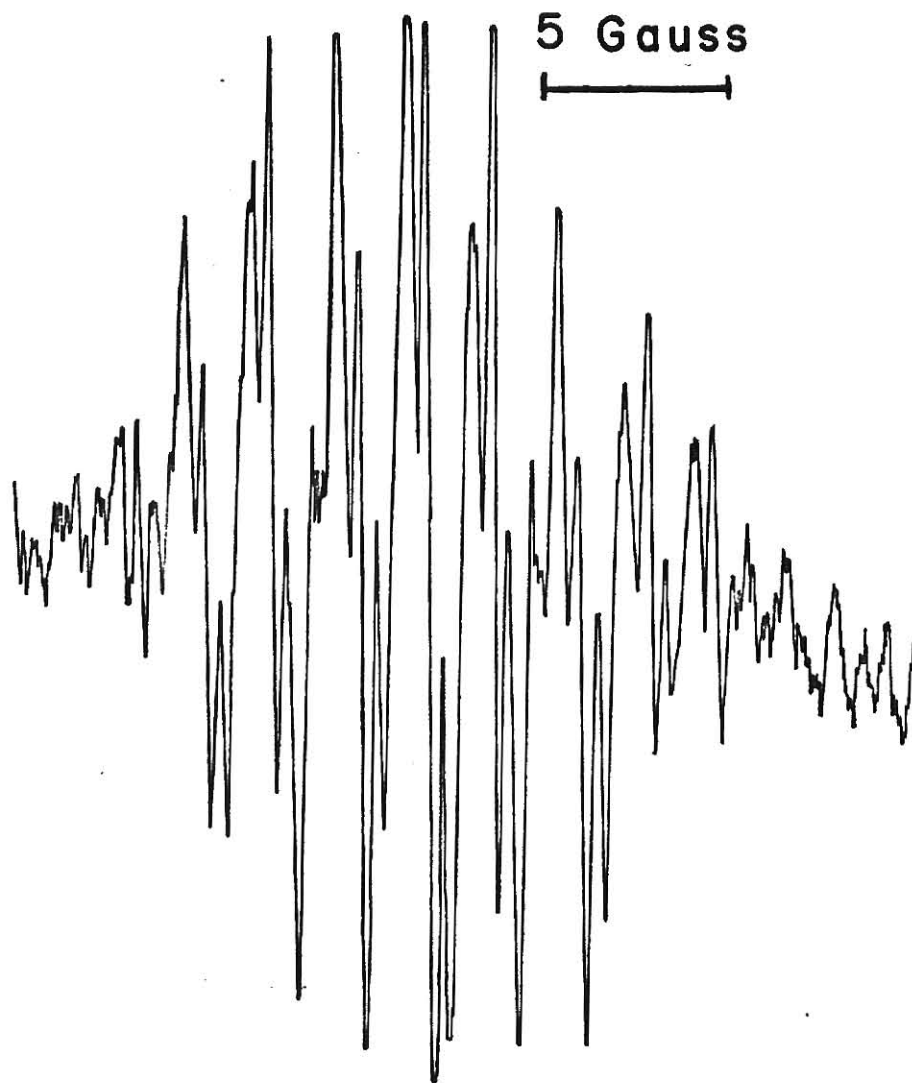
must certainly be due to an enhancement in the rate of 2-cyanophenyl radical reduction. We believe that an increase in the rate of 2-cyanophenyl radical reduction can result only if the decompositions of the halogenated benzonitrile radical anions occur so rapidly that the cyanophenyl radicals are formed at the electrode surface rather than in the bulk of the solution. Experimental evidence to support this suggestion includes the coulometric and chronoamperometric $\underline{n}$-values of 2, the failure of 2-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.

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 benzonitriles, and the appropriate σ-substituent constants. With $\rho = 0.31$ V, the half-wave potential for 2-chlorobenzonitrile is calculated to be -2.22 V. Since $\underline{E}_p = 1.91$ V and $\dfrac{nFv}{RT} = 3.15 \text{sec}^{-1}$, a lower limit of 10^{10} sec^{-1} is estimated for the rate constant for the loss of chloride ion from the 2-chlorobenzonitrile radical anion. Therefore, in order for almost complete reduction of cyanophenyl radical to occur, the rate constants for the decompositions of the bromo- and chlorobenzonitrile radical anions must be at least 10^9 sec^{-1} (assuming that $(\underline{D}t)^{1/2}$ must be smaller than 10^{-7} cm.). 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 chronoampero-

metric $\underline{i}t^{1/2}/\underline{C}$ values for the reduction of these halogenated benzonitriles should be diffusion controlled at $\underline{t}$=1 msec and that no reoxidation wave should be observed for any of these halogenated benzonitrile radical anions at a scan rate of 100 V/sec.

II. 2-FLUOROBENZONITRILE

Cyclic Voltammetry. The cyclic voltammetric behavior of 2-fluorobenzo-nitrile in DMF is illustrated in Figures 4-6. At a sweep rate of 100 V/sec (Figure 4), the only discernible electrode process on the first and all sub-sequent cycles is the reversible one-electron reduction of 2-fluorobenzonitrile to its radical anion ($\underline{E}_{p,c}$ = -2.18 V and $\underline{E}_{p,a}$ = -2.02 V). As the scan rate is decreased, however, the ratio of $\underline{i}_{p,a}/\underline{i}_{p,c}$ for the 2-fluorobenzonitrile couple becomes less than unity, and a new anodic peak appears near -1.05 V (Figure 5). Since subsequent cycles show that this new anodic wave grows in magnitude while the anodic peak height for the oxidation of 2-fluorobenzonitrile radical anion decreases, the anodic peak near -1.05 V must be the result of the disappearance of 2-fluorobenzonitrile radical anion. The absence of a cathodic wave near -1.05 V on the second and all subsequent cycles (Figure 5) indicates that the product of this anodic process is unstable. However, the decomposition of this electrode product does not appear to give rise to additional electroactive species. As long as the scan rate exceeds 1.0 V/sec, no electrode process other than the systems which have already been described can be discerned.

At a still slower scan rate, such as 80.6 mV/sec (Figure 6), a small, reversible couple appears near -2.32 V. Since this redox couple was not seen at the more rapid scan rates and since the peak heights for this couple increase with increasing number of cycles, the species reduced reversibly at -2.32 V must

Figure 4. Cyclic voltammogram of 1.40×10^{-3} M 2-fluorobenzonitrile in 0.1 M TEAP-DMF at a scan rate of 100 V/sec.
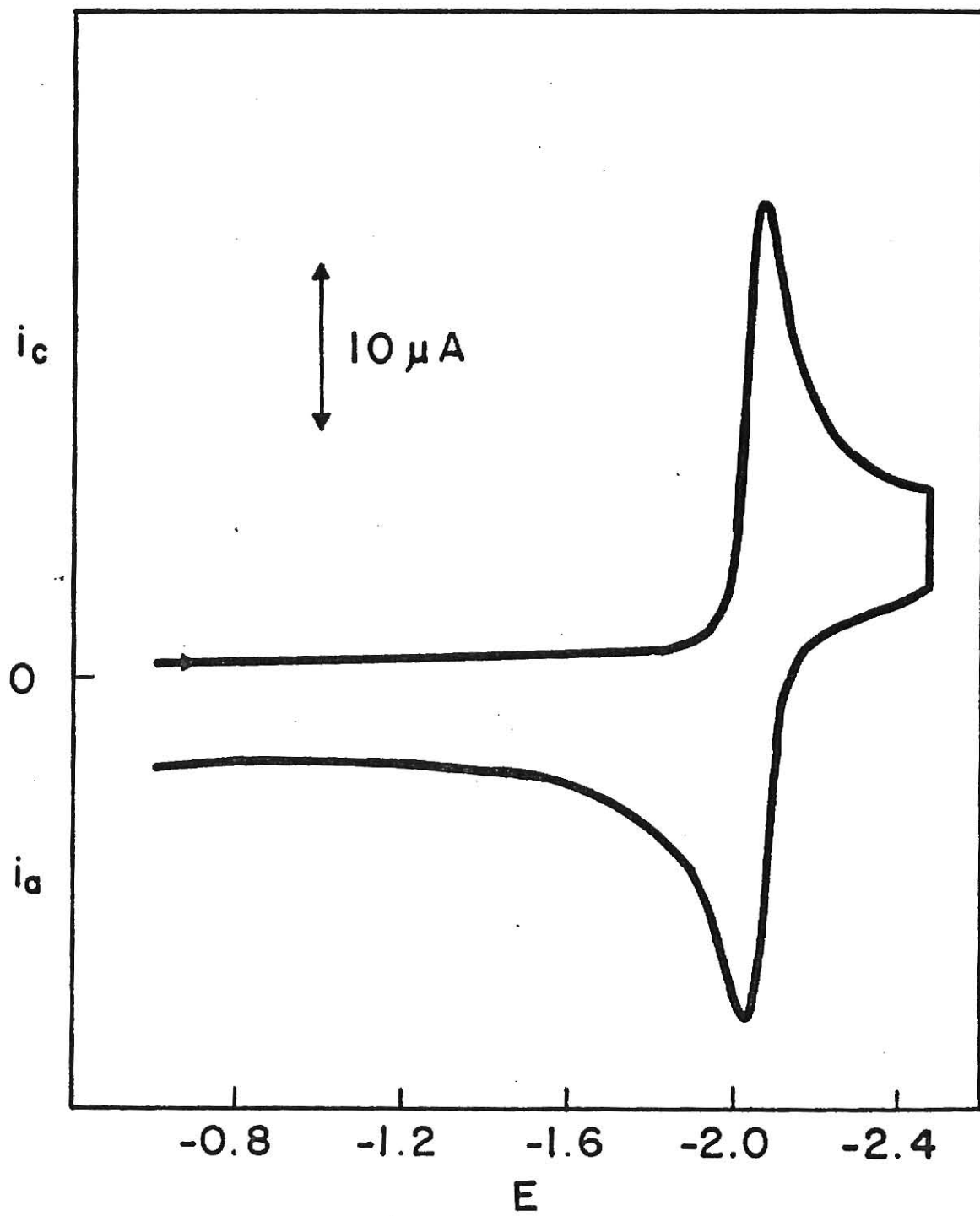
Figure 5.   Cyclic voltammogram of 1.40×10^{-3} M 2-fluorobenzonitrile in 0.1 M TEAP-DMF at a scan rate of 1.0 V/sec. Numbers 1 and 2 represent cycles 1 and 2, respectively.

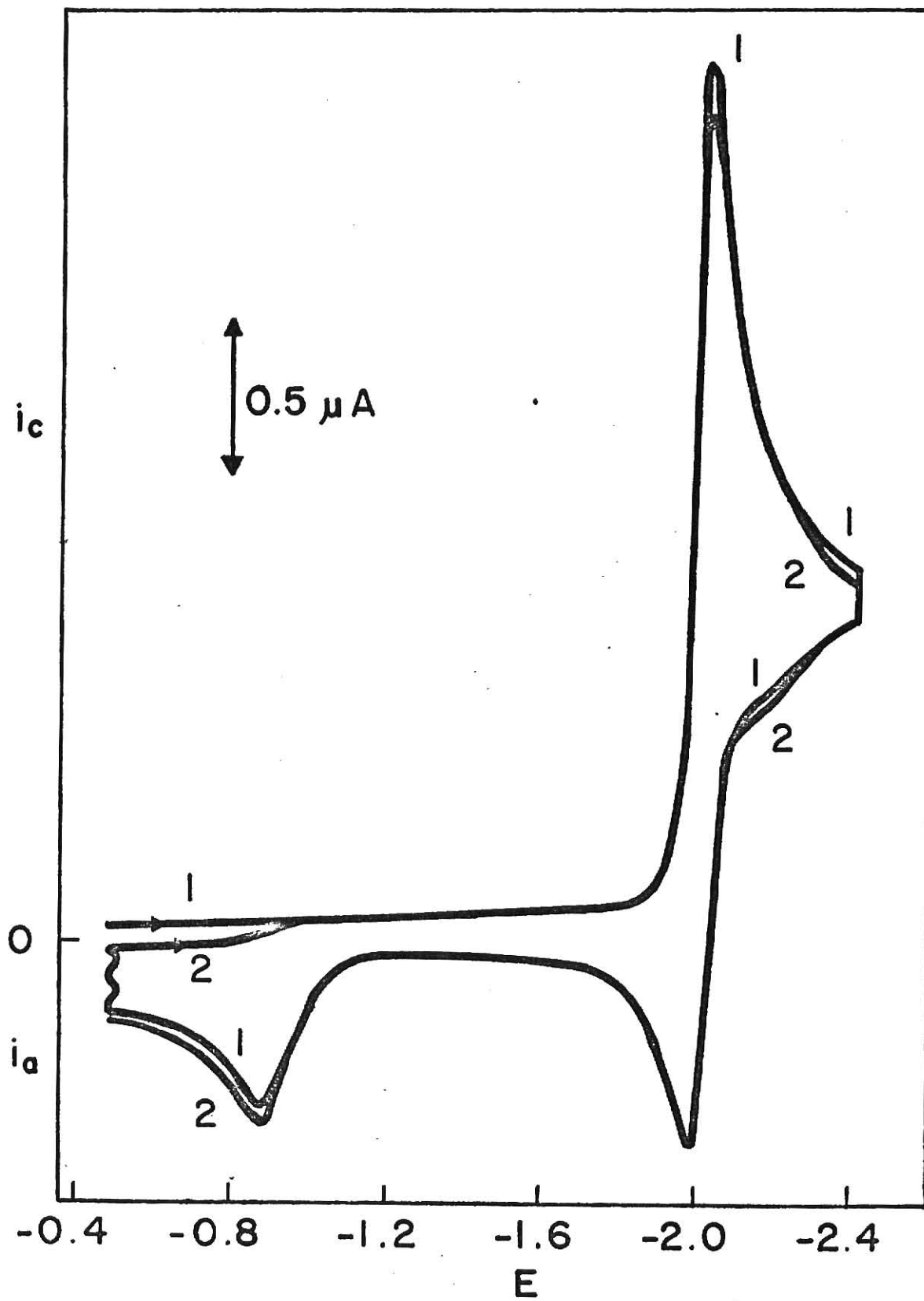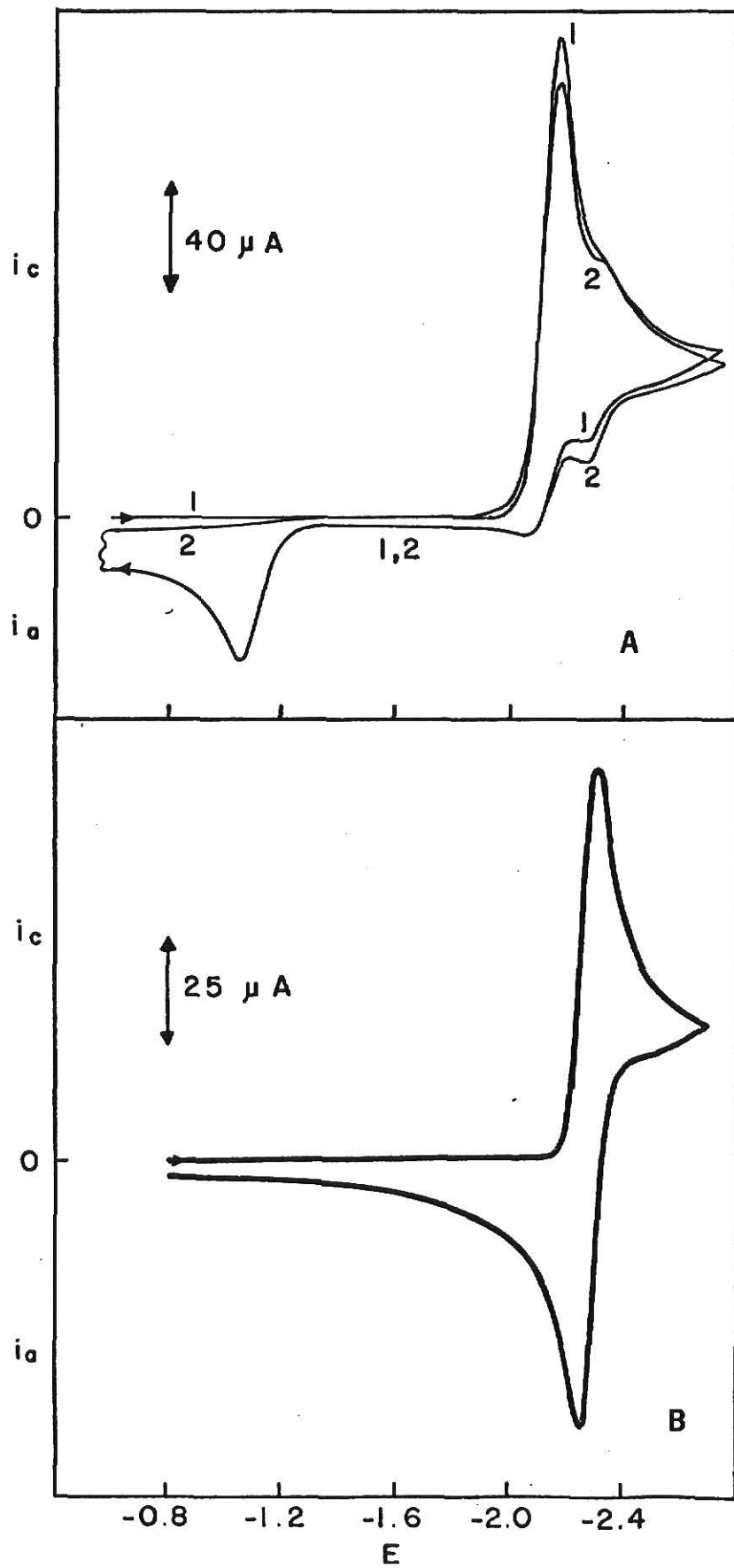Figure 6. Cyclic voltammograms in 0.1 M TEAP-DMF at a scan rate of 80.6 mV/sec: (a) 2.64×10^{-3} M 2-fluorobenzonitrile, (b) 1.44 $\times 10^{-3}$ M benzonitrile. Numbers 1 and 2 represent cycles 1 and 2, respectively.
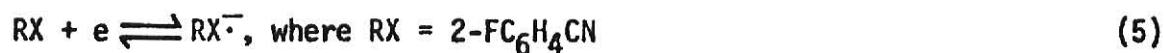
be the product of a relatively slow reaction. By setting the anodic and cathodic switching limits to -1.6 V and -2.6 V, respectively, it is readily ascertained that it is not necessary to include the oxidation process at -1.05 V in order to obtain the redox couple which is electroactive at -2.32 V. This result implies that the precursor of this new couple must be either 2-fluorobenzonitrile radical anion or the product of the reaction of 2-fluoro-benzonitrile radical anion. By comparison of Figures 6a and 6b, we find that the redox behavior of benzonitrile is consistent with this reversible process. In order to confirm this tentative identification, solutions of 2-fluorobenzo-nitrile were submitted to exhaustive electrolysis.

Coulometry. Exhaustive, controlled-potential electrolysis of 2-fluoro-benzonitrile at a potential of -2.15 V gave an $\underline{n}$-value of approximately 2.0 (Table 1). Cyclic voltammetric examination of either the partially or the fully electrolyzed solutions indicates that the species ($\underline{E}_{p,a}$ = -1.05 V) arising from the initial decomposition of 2-fluorobenzonitrile radical anion is unstable and decomposes rapidly on the coulometric time-scale to give benzo-nitrile. Both cyclic voltammetric and gas chromatographic analyses indicate that benzonitrile, the final product, is formed in quantitative yield (Table 1). No other product was detected by either technique.

Kinetics of the Disappearance of 2-Fluorobenzonitrile Radical Anion. Diagnostic studies of the kinetics of the decomposition of 2-fluorobenzonitrile radical anion were performed by current reversal chronopotentiometry. Decomposition schemes involving the loss of fluoride ion from the radical anion and the coupling of the radical anion with the parent species were eliminated as important reaction pathways, since the ratio of the anodic transition time

($\underline{t}_a$) for the oxidation of the radical anion to the cathodic electrolysis time (τ) was observed to decrease with an increase in the current density.

Since a decrease in the ratio of $\underline{t}_a/\tau$ with increasing current density is consistent with a second-order reaction pathway such as the dimerization of radical anions (equations 5 and 6), further study of the radical anion
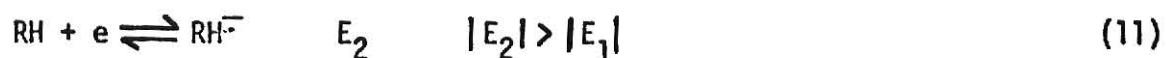
$$RX + e \rightleftharpoons RX^{\overline{\cdot}}, \text{ where } RX = 2\text{-}FC_6H_4CN \tag{5}$$

$$2RX^{\overline{\cdot}} \xrightarrow{k_d} (RX)_2^{2-} \tag{6}$$

decomposition was undertaken with double potential step chronoamperometry. In this technique[18,19] the potential is first stepped to a value sufficiently negative to cause the diffusion-controlled reduction of 2-fluorobenzonitrile to its radical anion. After a predetermined cathodic electrolysis time (τ), the potential is then stepped to a potential sufficiently positive to cause the oxidation of 2-fluorobenzonitrile radical anion, but not so positive as to cause the concurrent oxidation of the species giving rise to the anodic peak at -1.05 V.

The method given by Olmstead and Nicholson for the determination of the rate constant for the dimerization of the 2-fluorobenzonitrile radical anions requires that the reduction of 2-fluorobenzonitrile be a diffusion-controlled process.[18,20] Although the cyclic voltammetric, coulometric and long-term chronoamperometric (vide infra) results suggest that the product of the dimerization reaction, $(RX)_2^{2-}$, undergoes further chemical reaction to generate 2-fluorobenzonitrile and benzonitrile, this latter reaction is relatively slow and does not cause the chronoamperometric measurements to deviate from a diffusion-controlled value for $\tau \leq 2$ sec.

The results of the double potential step chronoamperometric experiments are shown in Figure 7. The close agreement of the experimental data with the model for varying cathodic electrolysis times, for three different ratios of t_a/τ, and for three different concentrations of 2-fluorobenzonitrile strongly suggests that the principal reaction pathway involves dimerization of the radical anion.

<u>Kinetics</u> <u>of</u> <u>the</u> <u>Formation</u> <u>of</u> <u>Benzonitrile</u>. The sequence of reactions proposed below (equations 7-11) can be described formally as the disproportion-

$$RX + e \rightleftharpoons RX^{\overline{\cdot}} \qquad\qquad E_1 \qquad\qquad\qquad (7)$$

$$2RX^{\overline{\cdot}} \xrightarrow{k_d} (RX)_2^{2-} \qquad\qquad\qquad (8)$$

$$(RX)_2^{2-} \xrightarrow{k} RX + R^- + X^- \qquad\qquad\qquad (9)$$

$$R^- + H^+ \xrightarrow{\text{fast}} RH \qquad\qquad\qquad (10)$$

$$RH + e \rightleftharpoons RH^{\overline{\cdot}} \qquad E_2 \qquad |E_2| > |E_1| \qquad (11)$$

ation of the 2-fluorobenzonitrile radical anion. However, unlike most dispro-portionation mechanisms which have been considered previously, the rate of formation of the dimeric dianion considerably exceeds its rate of decomposition into the cyanophenyl anion (R⁻) and 2-fluorobenzonitrile.[20]

The disproportionation of the dimeric dianion was digitally simulated using Feldberg's procedures for the single potential step chronoamperometric technique.[21] Since $k_d \gg k$, the reaction sequence was simplified for digital simulation by rewriting equations 7 and 8 as $2RX + 2e \longrightarrow (RX)_2^{2-}$. The working model requires the potential of the working electrode to be sufficiently neg-

Figure 7. Double potential step chronoamperometric data for the kinetic study of the disappearance of 2-fluorobenzonitrile radical anion. Concentrations of 2-fluorobenzonitrile in 0.1 M TEAP-DMF are: (●) 1.08×10^{-3} M, (▲) 1.69×10^{-3} M, and (■) 3.82×10^{-3} M. The solid curves were obtained by the digital simulation of the processes described by equations 5 and 6, $k = 1.35 \times 10^{-3} M^{-1} sec^{-1}$, for the following ratios (t_a/τ) of electrolysis times: A, 0.2; B, 0.3; and C, 0.5. The cathodic electrolysis time is τ; the anodic electrolysis time is t_a.
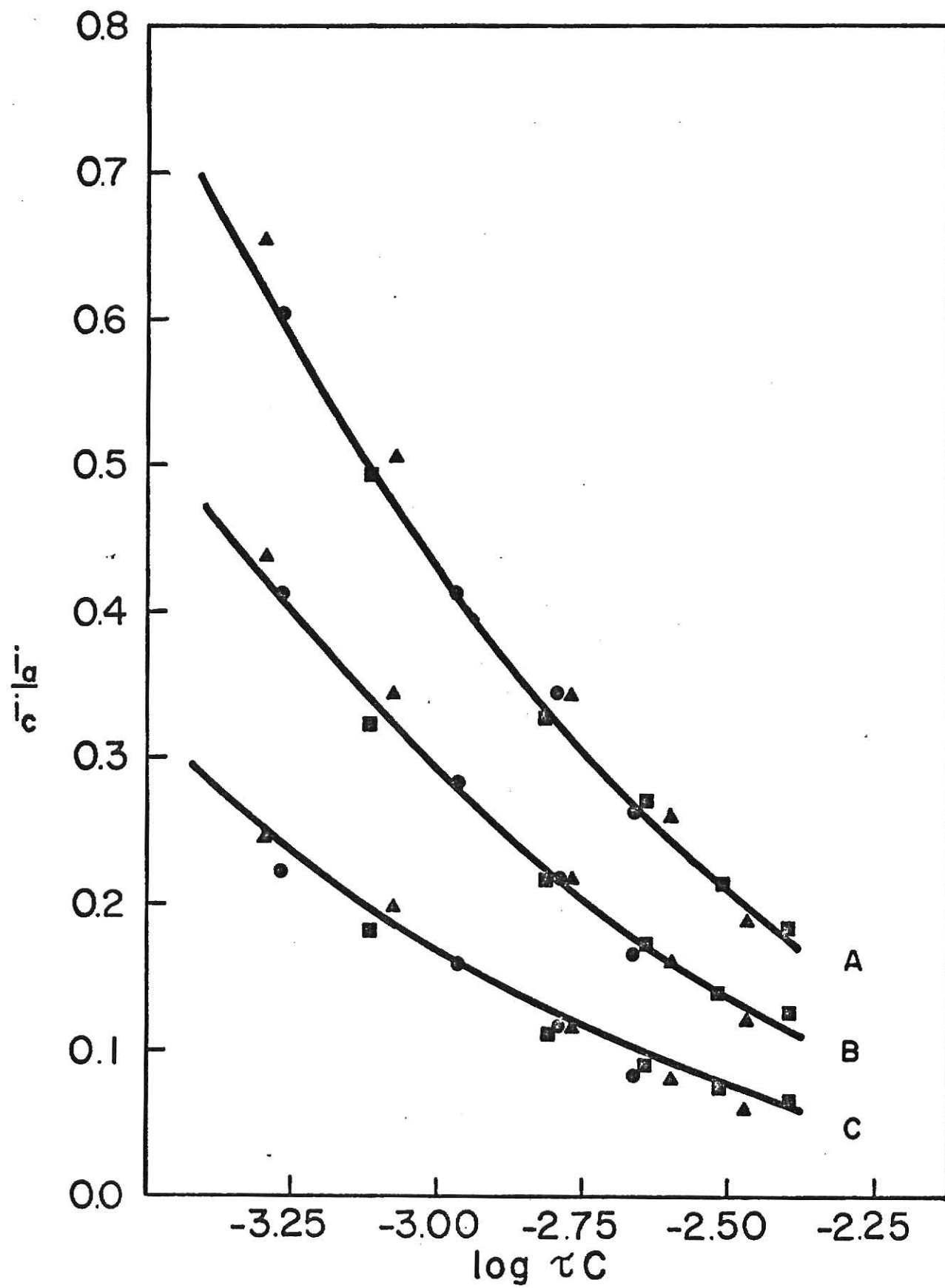
ative to cause complete reduction of 2-fluorobenzonitrile (RX), but not so negative as to cause concomitant reduction of benzonitrile (RH), one of the products which is expected to result from this reaction sequence (equations 10 and 11). A dimensionless working curve was constructed from the values of $\underline{n}_{app}$ ($\underline{it}^{1/2}/\underline{it}^{1/2}_{k=0}$) calculated for numerous values assigned arbitrarily to log $\underline{kt}$; as one would predict from this model $\underline{n}_{app}$ approaches a lower limit of 1.0 for small values of $\underline{kt}$ and an upper limit of 2.0 for large values of $\underline{kt}$. While the working curve is identical in shape to the working curve reported by Alberts and Shain[22] for a first-order ECE process, it differs from the latter curve by being displaced 0.3 log units along the abscissa.

The results of the unidirectional chronoamperometric experiment are shown in Figure 8. Data obtained at three different concentrations of 2-fluoro-benzonitrile in DMF are consistent with the theoretical curve projected for this model if the rate constant for the decomposition of the dimeric dianion is taken as 1.0×10^{-2} sec^{-1}.

The Anodic Wave at -1.05 V. The cyclic voltammetric results suggest that the anodic wave at -1.05 V arises from the disappearance of the 2-fluoro-benzonitrile radical anion. Since double potential step chronoamperometric experiments have clearly demonstrated that this reaction is second-order in the radical anion, the simplest model which can be written for this anodic process would have a dimeric dianion being oxidized to the corresponding di-meric radical anion in a one-electron step. As evidenced by the absence of a corresponding reduction peak on the second cathodic sweep in the cyclic volt-ammogram of Figure 5, the product of this electrode reaction must decompose readily. Since no new redox processes are observed to arise from this oxidation,

Figure 8. Single potential step chronoamperometric data for the study of the decomposition of the dimeric dianion, $(RX)_2^{2-}$. The solid curve was obtained by the digital simulation of equations 7-11 with the decomposition rate constant specified as 1.0×10^{-2} sec^{-1}. Concentrations of 2-fluorobenzonitrile in 0.1M TEAP-DMF: (▲) 6.7×10^{-4} M; (●) 1.96×10^{-3} M; and (■) 3.77×10^{-3} M.
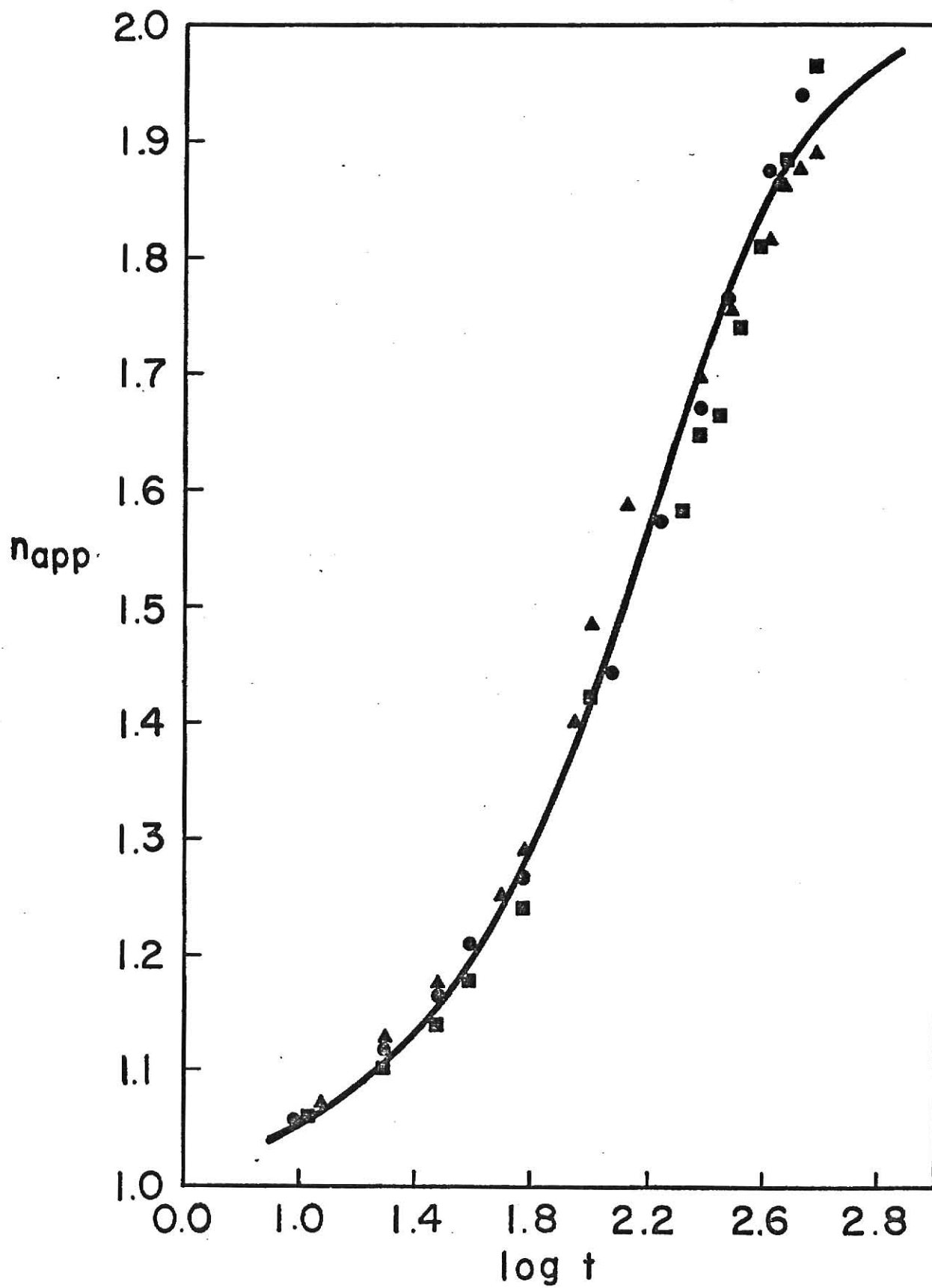
it is not unreasonable to suggest that the product of this electrode reaction dissociates to give 2-fluorobenzonitrile and 2-fluorobenzonitrile radical anion. Since the latter species is also electroactive at this potential, this should cause the oxidation of the proposed dimeric dianion to be an overall two-electron process.

This hypothetical electrode process is amenable to study by the double potential step chronoamperometric technique. For this experiment the potential is first stepped cathodically to cause the diffusion-controlled reduction of 2-fluorobenzonitrile. After a short electrolysis time (τ did not exceed two seconds), the potential is stepped sufficiently far in the anodic direction (-0.8 V) to cause the concurrent oxidation of 2-fluorobenzonitrile radical anion and the species giving rise to the anodic peak near -1.05 V.

The results of several double potential step chronoamperometric experiments show that the oxidation process at -1.05 V is considerably more complex than the simple model discussed in the preceding paragraphs. Instead of observing a diffusion-controlled, two-electron oxidation process on the reverse, anodic step, we find the anodic current to be kinetically controlled; that is, the ratio of i_a/i_c approaches the anticipated value when t_a/τ is small ($t_a/\tau \leq$ 0.05) and decreases to approximately one-half the expected value when t_a/τ is large ($t_a/\tau \geq$ 1.0). In addition, we observe a dependence on the concentration of 2-fluorobenzonitrile: the kinetic behavior occurs at a smaller value of t_a/τ as the concentration of the parent electroactive species is decreased.

The additional studies which would be required to elucidate this behavior will be difficult because several kinetically controlled processes precede and accompany the oxidation process. Since an understanding of this anodic process is not essential to the determination of the decomposition pathways of the fluoro-

benzonitrile radical anions, the additional studies were not undertaken as a part of this work.

III. 3-FLUOROBENZONITRILE

Cyclic Voltammetry. The cyclic voltammetric behavior of 3-fluorobenzonitrile is shown in Figure 9. Two large reduction waves are seen near -2.19 and -2.86 V on the first cathodic sweep, while no oxidation waves are observed on the reverse anodic sweep. The decomposition of the initially formed electrode product must be relatively rapid, since no oxidation wave is seen on the anodic sweep at scan rates up to 100 V/sec ($E_{switching}$ = -2.60 V). The compound reduced near cathodic background ($E_{p,c}$ = -2.86 V) is apparently a decomposition product formed by reduction of 3-fluorobenzonitrile at the potential of the first cathodic wave. As can be seen by comparing Figures 9 and 10, the second cathodic wave of Figure 9 coincides with the reduction wave of fluorobenzene. Again, the absence of a reverse oxidation wave indicates a relatively rapid decomposition of the fluorobenzene reduction product.

Chronoamperometry. The chronoamperometric $it^{1/2}/C$ value for 3-fluorobenzonitrile was compared with the value determined previously for tolunitrile. At an applied potential of -2.5 V, 3-fluorobenzonitrile gave a diffusion controlled value of 44 A $sec^{1/2}$ $mole^{-1}$ cm^3 from t = 4 msec to t = 8 sec. Therefore, since $it^{1/2}/C$ for the reduction of tolunitrile to its radical anion is 42 A $sec^{1/2}$ $mole^{-1}$ cm^3, we conclude that one electron is involved in the initial reduction of 3-fluorobenzonitrile. Since the reduction at -2.5 V is a one-electron process and since the two small cathodic waves in the range of -1.60 to -1.90 V increase in magnitude with increasing scan rate, we believe that

Figure 9. Cyclic voltammogram of 2.22 x 10^{-3} M 3-fluorobenzonitrile in 0.1 M TEAP-DMF at a scan rate of 80.6 mV/sec.
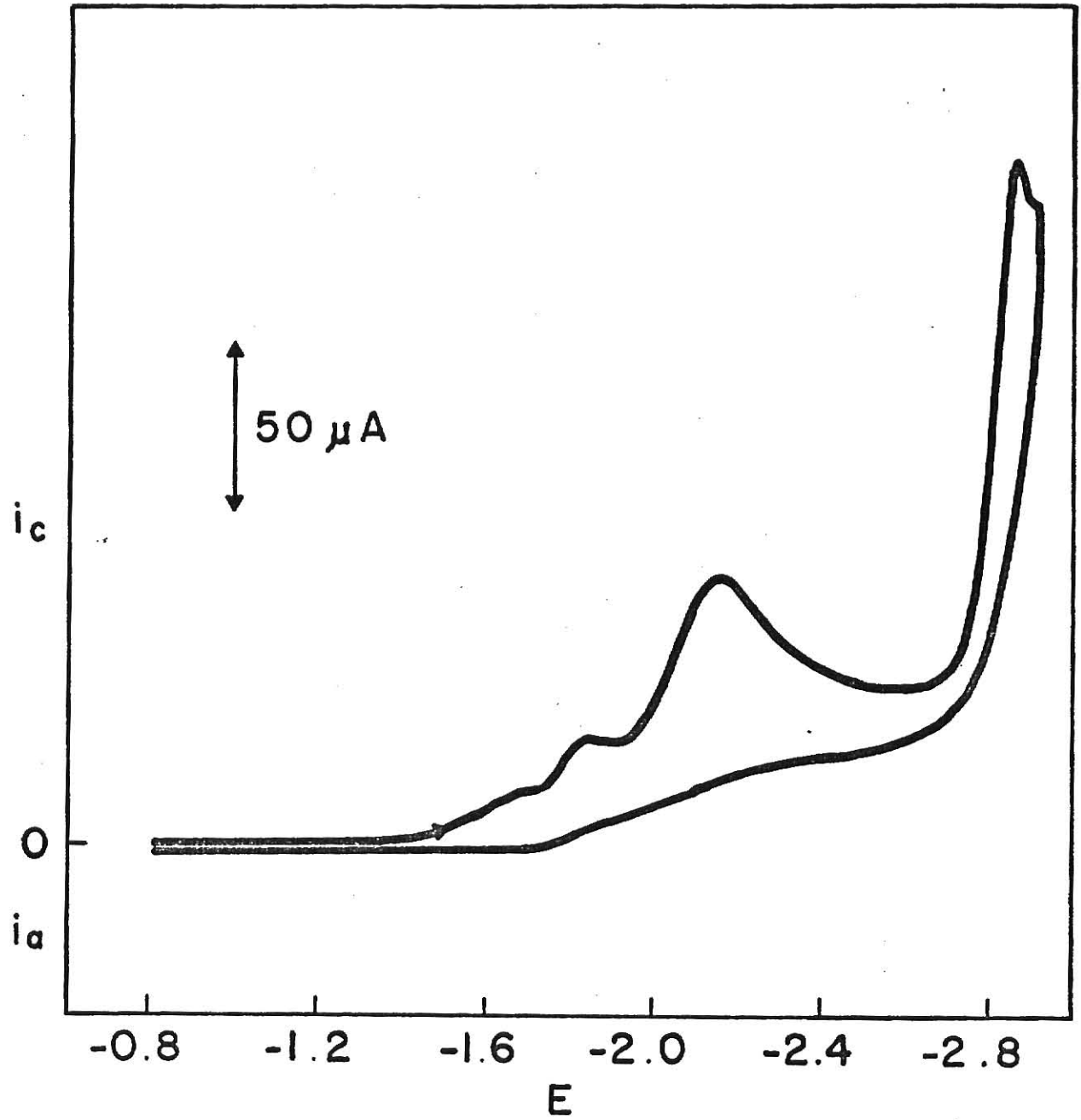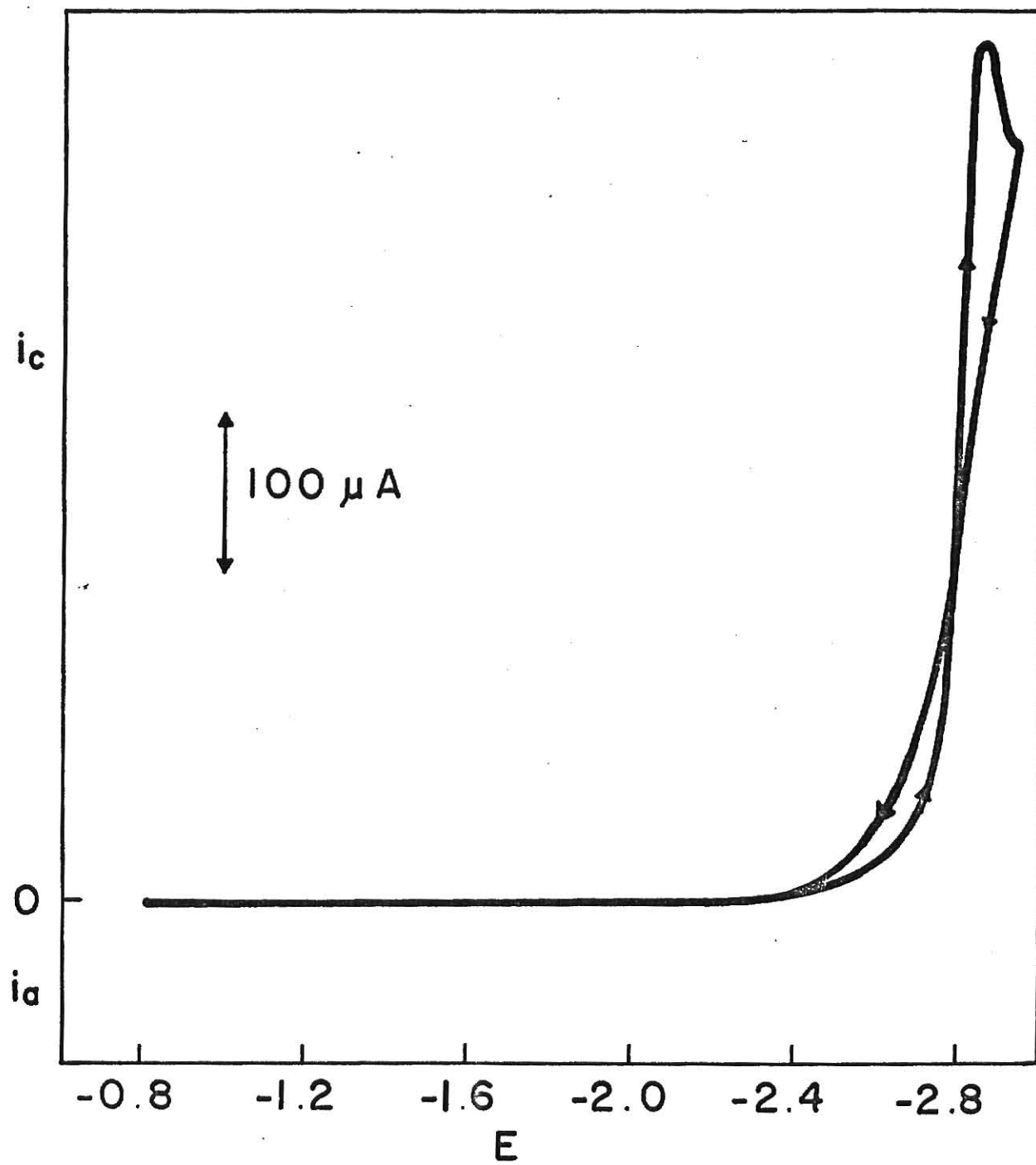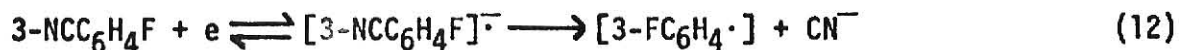
Figure 10. Cyclic voltammogram of 2.89×10^{-3} M fluorobenzene in 0.1 M TEAP-DMF at a scan rate of 0.1 V/sec.

these two reduction waves probably arise from absorption of the product on the working electrode.

Coulometry. In support of the preceding interpretation controlled-potential coulometric reduction of 3-fluorobenzonitrile (Table 1) and subsequent analysis of product were conducted. Exhaustive electrolysis at a potential of -2.4 V gave an $\underline{n}$-value of 1 ($\underline{n}_{exptl}$ = 1.05). Cyclic voltammetric examination of the electrolyzed solution immediately after electrolysis showed only the presence of fluorobenzene. Analysis of the electrolyzed solution by gas-liquid chromatography indicated that fluorobenzene was formed in 45% yield. No other product was detected by either gas chromatography of cyclic voltammetry.

Reaction Pathways. A mechanism consistent with these data involves the one-electron reduction of 3-fluorobenzonitrile to its radical anion. The radical anion is very unstable and rapidly decomposes with loss of cyanide ion to give the corresponding 3-fluorophenyl radical (eq 12). The 3-fluorophenyl radical then abstracts a hydrogen atom from the solvent system to form fluoro-benzene (eq 13). Upon scanning further cathodically the radical anion of

$$3\text{-NCC}_6\text{H}_4\text{F} + e \rightleftharpoons [3\text{-NCC}_6\text{H}_4\text{F}]^{\cdot-} \longrightarrow [3\text{-FC}_6\text{H}_4\cdot] + \text{CN}^- \tag{12}$$

$$[3\text{-FC}_6\text{H}_4\cdot] + \text{HS} \longrightarrow \text{FC}_6\text{H}_5 + \text{S}\cdot \tag{13}$$

fluorobenzene is formed. The absence of an anodic wave for the reoxidation of the fluorobenzene radical anion indicates that this radical anion is also un-stable and probably decomposes to give phenyl radical and fluoride ion.

EXPERIMENTAL

I. INSTRUMENTATION

The cyclic voltammetric, chronoamperometric, and current reversal chrono-potentiometric experiments were performed on a transistorized, three-electrode potentiostat-galvanostat.[23] The instrument also incorporates a digitally controlled, multipurpose function generator; digital timing and counting circuits; and a circuit[24,25] for electronic compensation of ohmic potential loss. A second potentiostat was used for the exhaustive electrolysis work.[4] An analog circuit for the integration of the electrolysis current was included in this instrument.

Readout in relatively slow ($v \leq 0.1$ V/sec) cyclic voltammetric experiments was to Moseley Model 7030 and 7035B X-Y recorders. Readout for chronoamperometric studies of less than 5 sec duration and for the more rapid ($v > 0.1$ V/sec) cyclic voltammetric work was to a Tektronix Model 564 oscilloscope. The latter was equipped with Type 2A63 and 2B67 plug-ins and a Model C-12 Polaroid camera. Strip-chart recorders (Moseley Model 680) were used to record the current-time and coulomb-time curves for the long-term ($t \geq 5$ sec) chronoamperometric and coulometric studies.

Electron spin resonance spectra were obtained on a Varian V-4502 spectrometer. The radical anions were produced _in situ_ by the electrochemical reduction of the respective halogenated benzonitrile in the presence of the reacting anion.

The gas chromatograph was a Hewlett-Packard Model 700 equipped with flame-ionization detection and SE-30 columns. The flame-ionization currents were measured with a Philbrick Model SP2A operational amplifier in a standard current-

follower circuit and recorded on a Honeywell Model 19 strip-chart recorder. The oven temperatures and flow rates were 105° and 60 ml/min, respectively, for benzonitrile and 90° and 40 ml/min, respectively, for fluorobenzene.

II. CHEMICALS

The benzonitriles were commercially available samples. The purity of each was checked by cyclic voltammetry and either by gas-liquid chromatography or by melting point; impure samples were fractionally distilled or sublimed repeatedly until at least 99% purity was obtained.

Tetraethylammonium perchlorate was prepared according to the method of Kolthoff and Coetzee;[26] tetraethylammonium bromide was Eastman White Label. All supporting electrolytes were stored in a vacuum desiccator prior to their use. Tetraethylammonium cyanide was prepared by the method of Andreades and Zahnow.[27] N,N-dimethylformamide (DMF) of 99% purity was dried over barium oxide, distilled at reduced pressure on a Vigreux column, and collected over activated Linde type 4A molecular sieves.[28] The solvent was immediately transferred to a vacuum line for future use.

III. CELL AND ELECTRODES

All electrochemical experiments were performed on an all-glass vacuum line.[29] 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 had reached room temperature, helium was introduced through a purification train to attain atmospheric pressure. The train consisted of an activated BTS catalyst column, an anhydrous magnesium perchlorate column, and a liquid nitrogen cooled trap.

A platinum button electrode (Beckman number 39273) with a geometric area of 0.25 cm^2 was used as the working electrode for cyclic voltammetric and chronoamperometric experiments. However, for experiments of long duration (t>15 seconds) a planar platinum button electrode, sealed in soft glass with a 7 mm mantle was employed. A large cylindrical platinum gauze served as the working electrode in controlled-potential coulometric determinations. The auxiliary electrode was a coiled platinum wire. A saturated calomel electrode (SCE) served as the reference electrode. The SCE was isolated from the cell solution by a glass frit and a bridge of 0.1 M TEAP in DMF in order to minimize the contamination of the working electrode compartment by water.

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VITA

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Kent and the former Marlene Trede were married in Macedonia, Iowa in May, 1966. They have one child, Michelle Renee.

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ELECTROCHEMICAL STUDIES OF THE FORMATION AND DECOMPOSITION
OF 2- AND 3-HALOGENATED BENZONITRILE RADICAL ANIONS

by

KENT JACOB HOUSER

B. S., Northwest Missouri State University, 1970

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AN ABSTRACT OF A MASTER'S THESIS

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ABSTRACT

The electrochemical reduction of the 2- and 3-bromo- and 2- and 3-chloro-benzonitrile in N,N-dimethylformamide (DMF) has been shown to be an overall two-electron process which gives benzonitrile in nearly quantitative yield. Since reduction of one of these halogenated benzonitriles (2-chlorobenzonitrile) in the presence of cyanide ion gives rise to a small amount of phthalonitrile radical anion, the intermediacy of cyanophenyl radicals is suggested. A reaction pathway consistent with these data involves the initial one-electron reduction of a chloro- or bromobenzonitrile, rapid loss of halide ion from the radical anion 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.

Although the electrochemical reduction of 2-fluorobenzonitrile is also a two-electron process which gives benzonitrile in quantitative yield, the reaction pathway differs distinctly from the pathway described above for the bromo- and chlorobenzonitriles. Cyclic voltammetric and single and double potential step chronoamperometric experiments show that the initial electrode reaction is the one-electron reduction of 2-fluorobenzonitrile to its corresponding radical anion. The radical anion dimerizes rapidly (1.35×10^3 M^{-1} sec^{-1}) to give an unstable intermediate which disproportionates slowly (1.0×10^{-2} sec^{-1}) to form equal amounts of 2-cyanophenyl anion, fluoride ion, and starting material. Benzonitrile, the final product of the reaction sequence, is formed subsequently by the rapid abstraction of a proton by 2-cyanophenyl anion from a component of the solvent system.

The reduction of 3-fluorobenzonitrile is also a one-electron process which gives an unstable radical anion. However, in contrast to the other halogenated benzonitriles, 3-fluorobenzonitrile radical anion decomposes rapidly with loss of cyanide ion to give 3-fluorophenyl radical. The decomposition pathway is completed when this radical abstracts a hydrogen atom from a component of the solvent system to give the observed product, fluorobenzene.