on the analysis of the amount of **6** were performed by collection of the anisole from preparative glpc at 115° using a 5 ft × 0.25 in. 20% SE-30 column. Methylanisoles were collected by preparative glpc at 160° using a 2.2 m × $^{3}/_{8}$ in. 16% SE-30 column. Analysis for phenol was performed by pentane extraction of the acidified quench of the last reaction sample (360 min) with 1,3,5-trichlorobenzene added as an internal standard for glpc analysis with a 3.25 m × $^{1}/_{8}$ in. 10% Dow 710 column at 105°. Control experiments were carried out under the same conditions and with the same analysis as that specified above except for methyl chloride and methyl chloroformate. The yield of methyl chloride was determined relative to cyclohexane as an internal standard by integration of peak areas in a reaction carried out in a sealed nmr tube with the yield of methylanisoles subsequently determined by glpc. The amount of methyl chloride relative to methyl-d_3 chloride was determined from mass spectral analysis of a reaction of methyl-d_3 chloroformate. An nmr experiment similar to the above but with methyl-d_3 chloroformate was monitored for methyl chloroformate in the presence of cyclohexane as an internal standard and showed that no more than 1% methyl chloroformate was produced under the reaction conditions.

Acknowledgment. Various parts of this work were supported by the National Science Foundation, the National Institutes of Health, and the U. S. Atomic Energy Commission. We appreciate this support.

Electrochemical Studies of the Formation and Decomposition of the Fluorobenzonitrile Radical Anions

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Abstract: The electrochemically generated radical anions of the three isomeric fluorobenzonitriles have been shown to be unstable in *N,N*-dimethylformamide and to decompose by at least four different reaction pathways. Benzonitrile, the final reduction product of 2-fluorobenzonitrile, is suggested to arise by a pathway involving the dimerization ($k_d = 1.35 \times 10^3\ M^{-1}\ \text{sec}^{-1}$) of 2-fluorobenzonitrile radical anions and the subsequent, slow disproportionation ($k = 1.0 \times 10^{-2}\ \text{sec}^{-1}$) of a dimeric dianion intermediate. Benzonitrile and 4,4′-dicyanobiphenyl are the products observed for the reduction of 4-fluorobenzonitrile. Benzonitrile is shown to arise by a pathway involving the loss of fluoride ion ($k = 11\ \text{sec}^{-1}$) from the 4-fluorobenzonitrile radical anion and the subsequent rapid abstraction of a hydrogen atom by the 4-cyanophenyl radical. The formation of 4,4′-dicyanobiphenyl is proposed to occur by the dimerization ($k_d \sim 10^3\ M^{-1}\ \text{sec}^{-1}$) of 4-fluorobenzonitrile radical anions, followed by the rapid loss of two fluoride ions from the dimeric dianion which is formed as an intermediate. 3-Fluorobenzonitrile radical anion is the only one of the three radical anions which decomposes by loss of cyanide ion. The 3-fluorophenyl radical which results then abstracts a hydrogen atom from a component of the solvent system to form fluorobenzene, the observed reduction product.

The first extensive electrochemical and electron spin resonance studies of substituted benzonitrile radical anions were reported by Rieger, *et al.*[1] These workers found that reduction of the cyano and nitro derivatives of benzonitrile gave stable radical anions, but that the radical anions of 4-amino- and 4-fluorobenzonitrile decomposed rapidly. Since the esr spectrum of the radical anion of 4,4′-dicyanobiphenyl was observed upon reduction of these two benzonitriles, it was suggested that 4-amino- and 4-fluorobenzonitrile radical anions decomposed with loss of amide and fluoride ions, respectively, to give the 4-cyanophenyl radical. Dimerization of 4-cyanophenyl radicals and the subsequent reduction of 4,4′-dicyanobiphenyl to its radical anion were postulated to be the remaining steps in the decomposition pathway.

The loss of an anionic group has since been reported to occur in many other substituted benzonitrile[2–4] and nitroaromatic radical anions.[5–10] However, in contrast to the results reported for the 4-fluoro- and 4-aminobenzonitrile radical anions, the formation of a biphenyl has not been observed in the decompositions of the radical anions of the iodonitrobenzenes and the other halogenated benzonitriles.[4–7] Since the intermediacy of phenyl radicals has been demonstrated unequivocally in the decomposition of these radical anion systems,[4,11] it seems unlikely that the formation of 4,4′-dicyanobiphenyl could be the result of 4-cyanophenyl radical dimerization. Accordingly, we have undertaken more detailed electrochemical studies of the decomposition pathways of the three isomeric fluorobenzonitrile radical anions.

Results and Discussion

2-Fluorobenzonitrile. Cyclic Voltammetry. The only

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

(2) A. R. Buick, T. J. Kemp, G. T. Neal, and T. J. Stone, *J. Chem. Soc. A*, 666 (1969).

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(9) A. R. Metcalfe and W. A. Waters, *J. Chem. Soc. B*, 918 (1969).

(10) P. Peterson, A. K. Carpenter, and R. F. Nelson, *J. Electroanal. Chem. Interfacial Electrochem.*, 27, 1 (1970).

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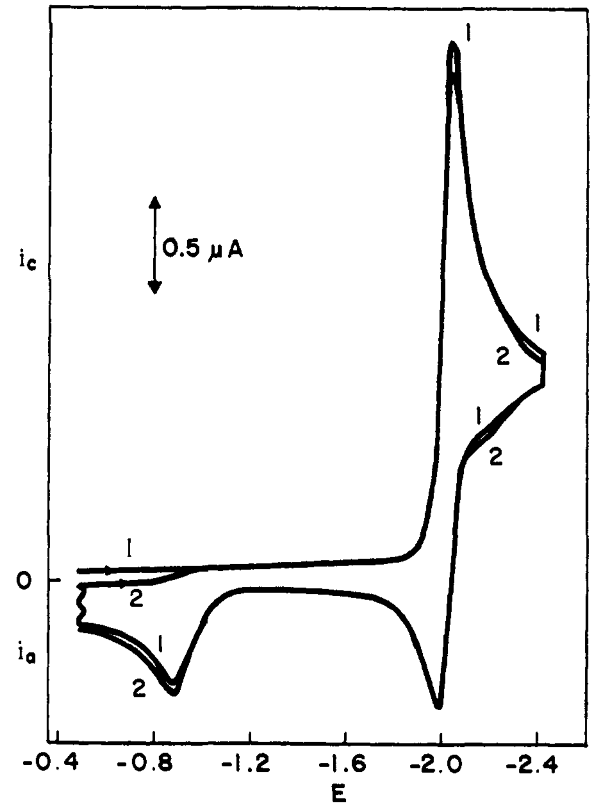

Figure 1. Cyclic voltammogram of 1.40×10^{-3} *F* 2-fluorobenzonitrile in DMF with 0.1 *F* TEAP as the supporting electrolyte. The scan rate on the 3.1×10^{-3} cm^2 platinum electrode is 1 V/sec.

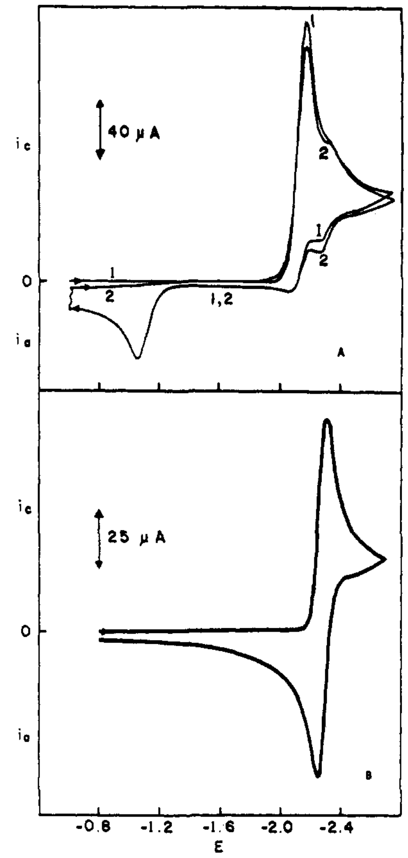

Figure 2. Cyclic voltammograms in 0.1 *F* TEAP–DMF at a scan rate of 80.6 mV/sec: (A) 2.64×10^{-3} *F* 2-fluorobenzonitrile, (B) 1.44×10^{-3} *F* benzonitrile. The numbers 1 and 2 represent cycles 1 and 2, respectively The electrode area is approximately 0.25 cm^2.

discernible electrode process at a sweep rate of 100 V/sec is the one-electron reduction of 2-fluorobenzonitrile to its radical anion. As the scan rate is decreased, however, the ratio of $i_{p,a}/i_{p,c}$ for the 2-fluorobenzonitrile redox couple becomes detectably less than unity, and a new anodic peak appears near -1.05 V (Figure 1). Since subsequent cycles show that this new anodic wave grows in magnitude while the ratio of $i_{p,a}/i_{p,c}$ of the 2-fluorobenzonitrile system decreases, the anodic peak near -1.05 V must be due to the oxidation of some product which results from the disappearance of 2-fluorobenzonitrile radical anion. The absence of a corresponding reduction wave near -1.05 V on the second and all subsequent cycles (Figure 1) indicates that the product of this anodic process is also unstable.

At the still slower scan rate of 0.1 V/sec (Figure 2), a relatively 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 be the product of a comparatively slow solution reaction. By setting the anodic and cathodic switching limits to -1.6 and -2.6 V, respectively, it is readily ascertained that it is not necessary to cause the oxidation at -1.05 V to obtain the redox couple which is electroactive at -2.32 V. The result implies that the precursor of the new couple must be either 2-fluorobenzonitrile radical anion or a product of the decomposition of 2-fluorobenzonitrile radical anion. It is readily concluded from the comparison of Figures 2a and 2b that the redox behavior of benzonitrile is consistent with this reversible process. In order to confirm this tentative identification, solutions of 2-fluorobenzonitrile were submitted to exhaustive electrolysis.

Coulometry. Exhaustive, controlled-potential electrolysis of 2-fluorobenzonitrile at a potential of -2.15 V showed the reduction to be a two-electron process (Table I). Ccyclic voltammetric examination of the solution, whether partially or exhaustively electrolyzed, indicated no accumulation of the product which is oxidizable at -1.05 V. Both cyclic voltammetric and gas chromatographic analyses indicated that benzonitrile, the final product, is formed in quantitative yield (Table I). No other product was detected by either analytical 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. In this series of experiments, the *ratio* of the anodic current to the cathodic current was held constant ($i_a/i_c = -0.225$), while the *absolute* currents were varied at each of several values of the cathodic electrolysis time ($t_c \leq \tau$). At each value of t_c, the ratio of the anodic transition time (t_a) for the reoxidation of the radical anion to the electrolysis time for the generation of the radical anion was observed to decrease with increasing current density. This result precludes as the principal reaction pathway not only a scheme including the loss of fluoride ion from the radical anion, but also a scheme involving the coupling of the radical anion with the parent species.

Table I. Coulometric Data for the Reduction of the Fluorobenzonitriles[a]

Compd	E_{applied}, V	n_{exptl}, F/mol	Principal product	% yield of principal product[b]
2-Fluorobenzonitrile	−2.10	2.02 ± 0.04	Benzonitrile	101 ± 3
3-Fluorobenzonitrile	−2.10	1.05 ± 0.03	Fluorobenzene	45 ± 2[c]
4-Fluorobenzonitrile[d]	−2.40		Benzonitrile[e]	

[a] All electrolyses were performed in DMF on solutions which were 1–5 mM in the fluorobenzonitrile. Each fluorobenzonitrile was electrolyzed a minimum of three times. The potential is in volts *vs.* an aqueous saturated calomel electrode. The supporting electrolyte was 0.1 F tetraethylammonium perchlorate. [b] The yields were determined by flame-ionization gas chromatography. With the exception of 4-fluorobenzonitrile, less than 1% of the starting material remained upon termination of the electrolysis. [c] No other product was detected by either gas chromatography or cyclic voltammetry. [d] The product of this reduction, benzonitrile, is electroactive at the applied potential. Since benzonitrile radical anion decomposes on the coulometric time scale to form an unidentified electroactive species, quantitative results could not be obtained for 4-fluorobenzonitrile. [e] A small amount (<5% yield) of material which has electrochemical properties identical with 4,4′-dicyanobiphenyl was detected by cyclic voltammetry. The reduction of 4,4′-dicyanobiphenyl occurs in two reversible one-electron steps with cathodic peak potentials of −1.65 and −2.09 V.

Since a decrease in the ratio of t_a/t_c with increasing current density is consistent for a reaction pathway involving the dimerization of radical anions (eq 1 and 2), double potential chronoamperometry was selected for a more detailed study of the radical anion decomposition.[12,13] In this technique 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 value 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.

$$RX + e \rightleftharpoons RX\cdot^-, \text{ where } RX = 2\text{-}FC_6H_4CN \qquad (1)$$

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

The method given by Olmstead and Nicholson[12,14] 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. Although the cyclic voltammetric, coulometric, and long-term chronoamperometric (*vide infra*) results suggest that the product of the dimerization reaction 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 3. The close agreement of the experimental data with the model for numerous 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.[16]

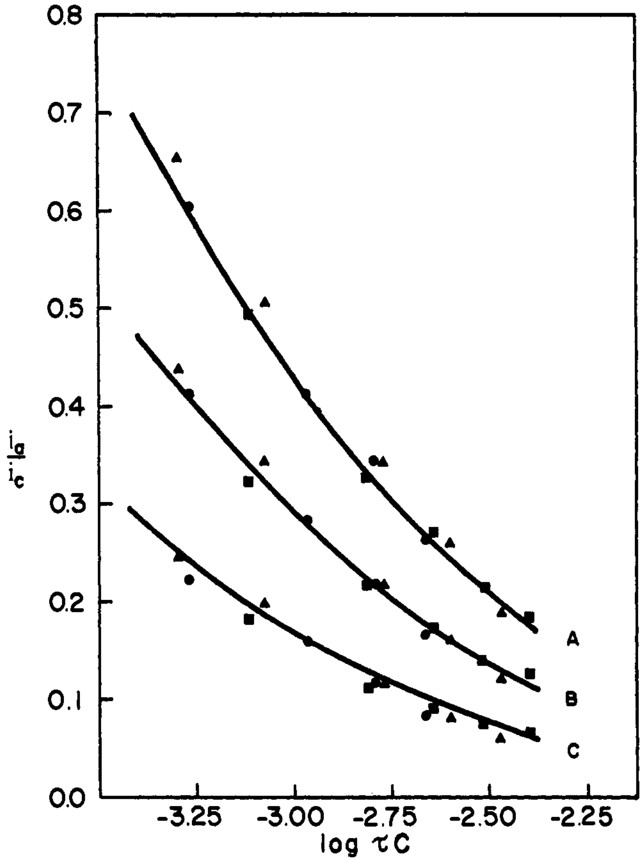

Figure 3. Double potential step chronoamperometric data for the kinetic study of the disappearance of 2-fluorobenzonitrile radical anion. Concentrations of 2-fluorobenzonitrile in 0.1 F TEAP–DMF are: (●) 1.08×10^{-3} F, (▲) 1.69×10^{-3} F, and (■) 3.82×10^{-3} F. The solid curves were obtained by the digital simulation[18] of the processes described by eq 1 and 2 with $k_d = 1.35 \times 10^3$ M^{-1} sec^{-1} for the following ratios of t_a/τ: A, 0.2; B, 0.3; and C, 0.5. The cathodic electrolysis time is denoted by τ; the anodic electrolysis time is given by t_a.

Kinetics of the Formation of Benzonitrile. The sequence of reactions proposed below (eq 3–7) can be described formally as the disproportionation of the 2-fluorobenzonitrile radical anion. However, unlike

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(12) M. L. Olmstead and R. S. Nicholson, *Anal. Chem.*, 41, 851 (1969).

(13) W. V. Childs, J. T. Maloy, C. P. Keszthelyi, and A. J. Bard, *J. Electrochem. Soc.*, 118, 874 (1971).

(14) Since we define $d[RX\cdot^-]/dt = -2k_d[RX\cdot^-]^2$, the rate constants obtained by the Olmstead–Nicholson treatment were divided by 2.0.[15]

(15) S. W. Feldberg, *J. Phys. Chem.*, 73, 1238 (1969).

(16) In addition to the dimerization of 2-fluorobenzonitrile radical anions, the reduction of 2-fluorobenzonitrile in the presence of tetraethylammonium cyanide in the cavity of an esr spectrometer gives rise to a small but detectable amount of phthalonitrile radical anion. The latter species would be an anticipated product if 2-fluorobenzonitrile radical anion were to decompose by loss of fluoride ion to give the corresponding 2-cyanophenyl radical. The coupling of phenyl radicals with cyanide[11] and nitrite ions[11,17] has been shown to be an extremely facile process. However, the fact that phthalonitrile radical anion is observed by esr but not by electrochemical methods indicates that the loss of fluoride ion from the 2-fluorobenzonitrile radical anion and the formation of the corresponding 2-cyanophenyl radical are but a minor decomposition pathway.

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

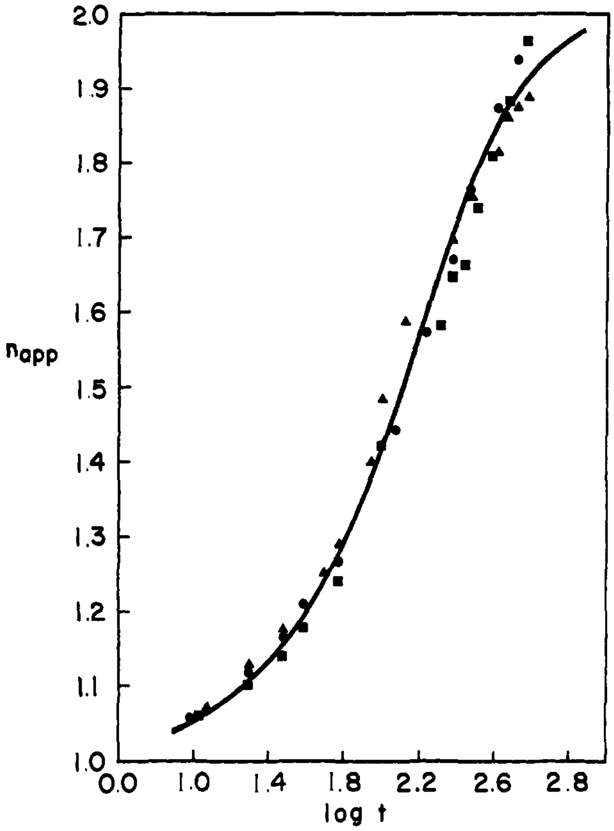

Figure 4. Single potential step chronoamperometric data for the formation of benzonitrile. The solid curve was obtained by the digital simulation of eq 3–7 with the first-order rate constant k specified as 1.0×10^{-2} sec^{-1}. Concentrations of 2-fluorobenzonitrile in 0.1 F TEAP–DMF are: (▲) 6.7×10^{-4} F; (●) 1.96×10^{-3} F; and (■) 3.77×10^{-3} F.

$$\mathrm{RX} + \mathrm{e} \rightleftarrows \mathrm{RX}\cdot^{-};\ E_1 \tag{3}$$

$$2\mathrm{RX}\cdot^{-} \xrightarrow{k_\mathrm{d}} (\mathrm{RX})_2{}^{2-} \tag{4}$$

$$(\mathrm{RX})_2{}^{2-} \xrightarrow{k} \mathrm{RX} + \mathrm{R}^- + \mathrm{X}^- \tag{5}$$

$$\mathrm{R}^- + \mathrm{H}^+ \xrightarrow{\text{fast}} \mathrm{RH} \tag{6}$$

$$\mathrm{RH} + \mathrm{e} \rightleftarrows \mathrm{RH}\cdot^{-};\ |E_2| > |E_1| \tag{7}$$

most disproportionation mechanisms which have been considered previously,[15] the rate of formation of the product which is presumed to be a dimeric dianion considerably exceeds its rate of decomposition into the cyanophenyl anion (R^-) and 2-fluorobenzonitrile.

The disproportionation of the dimeric dianion was digitally simulated using Feldberg's procedures for the single potential step chronoamperometric technique.[18] Since $d[RX\cdot^-]/dt \gg d[(RX)_2{}^{2-}]/dt$, the reaction sequence was simplified for digital simulation by rewriting eq 3 and 4 as $2RX + 2e \rightarrow (RX)_2{}^{2-}$. The working model requires the potential of the working electrode to be sufficiently negative so as to reduce the concentration of 2-fluorobenzonitrile (RX) to zero at the electrode surface, but not so negative as to cause the concomitant reduction of benzonitrile (RH), one of the products which is expected to result from this reaction sequence (eq 6 and 7). A dimensionless working curve was constructed from the values of n_{apparent} $([it^{1/2}]/[it^{1/2}]_{k=0})$ calculated for numerous values assigned arbitrarily to log kt; as one would expect for this model, n_{apparent} approaches a lower limit of 1.0 for small values of kt and an upper limit of 2.0 for large values of kt. While the working curve is identical in shape with the working curve reported by Alberts and Shain[19] for a first-order ECE process, it differs from the latter curve by being displaced 0.3 log unit to the right along the abscissa.

The results of the unidirectional chronoamperometric experiment are shown in Figure 4. Data obtained at three different concentrations of 2-fluorobenzonitrile 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}.

Anodic Wave at -1.05 V. The cyclic voltammetric examination of 2-fluorobenzonitrile at several different scan rates suggests that the anodic wave at -1.05 V may be linked kinetically to the disappearance of 2-fluorobenzonitrile radical anion. However, since cyclic voltammetric studies of partially and exhaustively electrolyzed solutions show accumulation of benzonitrile only, the species which gives rise to the anodic wave must be transient. Inspection of the cyclic voltammogram (Figure 1) also shows that this oxidation does not yield a product which is sufficiently stable to give a corresponding reduction wave on the second cathodic scan. In addition, despite the rapid decomposition of the oxidation product, no additional redox processes are discernible on the second cycle.

Numerous attempts were made, without success, to relate the rate of disappearance of the 2-fluorobenzonitrile radical anion to the rate of formation of the transient species. Double potential step chronoamperometric experiments[20] showed that the oxidations of both the unreacted 2-fluorobenzonitrile radical anion and the transient species were kinetically controlled. Specifically, it was observed that the ratios of $n_{\mathrm{anodic}}/n_{\mathrm{cathodic}}$ at each value of t_a/τ from 0.1 to 0.5 decreased as the concentration of 2-fluorobenzonitrile was decreased; for example, for t = 10 sec and $t_a/\tau = 0.1$, values of 0.83, 0.74, and 0.56 were obtained for concentrations of 2-fluorobenzonitrile which were 3.77, 1.99, and 0.67 mM, respectively.

Although we are unable to write a reaction sequence which includes the species oxidized at -1.05 V, two reaction pathways which were considered plausible initially can be eliminated. First, the anodic wave at -1.05 V cannot be an overall two-electron oxidation of a dimeric species which results in the regeneration of 2 mol of starting material. If this scheme were correct, the ratio of $n_{\mathrm{anodic}}/n_{\mathrm{cathodic}}$ would be expected to be 1.0 for all values of t_a/t_c in the double potential step chronoamperometric experiments described above. Second, a simple one-electron oxidation of a dimeric dianion is also precluded since this scheme would lead to the prediction that the ratio of $n_{\mathrm{anodic}}/n_{\mathrm{cathodic}}$ would be increased by a decrease in the concentration of 2-fluorobenzonitrile.

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[18] S. W. Feldberg, "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1969, pp 199–296.

[19] G. S. Alberts and I. Shain, *Anal. Chem.*, **5**, 1859 (1963).

[20] For this experiment the potential was stepped cathodically (-2.20 V) to cause the diffusion controlled reduction of 2-fluorobenzonitrile and then stepped anodically sufficiently far (-0.8 V) so as to cause the concurrent oxidation of 2-fluorobenzonitrile radical anion and the transient species.

3-Fluorobenzonitrile. Cyclic Voltammetry. The cyclic voltammmetric behavior exhibited by 3-fluorobenzonitrile is markedly dependent upon scan rate. At the relatively slow scan rate of 0.1 V/sec (Figure 5), the two principal cathodic peaks located near −2.19 and −2.86 V are preceded by two small prepeaks (−1.66 and −1.82 V). Since subsequent cycles show that the reduction peak at −2.86 V grows in magnitude relative to the peak at −2.19 V, the species reduced near cathodic background must arise from the decomposition of the product formed by the first, principal cathodic process. From a comparison of the cyclic voltammograms of 3-fluorobenzonitrile and an authentic sample of fluorobenzene, it is readily determined that the latter species is the electroactive material which is reduced near cathodic background.

Although the magnitudes of the prepeaks (−1.66 and −1.82 V) are relatively small at a scan rate of 0.1 V/sec, their magnitudes increase rapidly with an increase in scan rate. In addition, an increase in scan rate also causes a third prepeak to appear near −1.2 V. At a scan rate of 100 V/sec, the prepeaks appear to be the principal electrode processes and nearly obscure the cathodic peak seen near −2.10 V in Figure 5. The anomalous behavior of the prepeaks with increasing scan rate suggests the strong adsorption of the initial electrode product.[21] Unfortunately, double potential step chronocoulometry cannot be used to study the adsorption of 3-fluorobenzonitrile radical anion since the latter species is undergoing very rapid decomposition. No reoxidation wave can be observed for the 3-fluorobenzonitrile radical anion even when the direction of the potential scan is reversed between any of the cathodic peaks at a scan rate of 100 V/sec.

Chronoamperometry. Since adsorption complicates the interpretation of the cyclic voltammetric results, single potential step chronoamperometry was used to test for possible kinetic behavior. At an applied potential of −2.5 V, 3-fluorobenzonitrile gave a diffusion-controlled value for $it^{1/2}/C$ of 44 A sec$^{1/2}$ mol^{-1} cm^3 from t = 2 msec to t = 8 sec. Since this value compares favorably with the value of 42 A sec$^{1/2}$ mol^{-1} cm^3 obtained for the reduction of 4-methylbenzonitrile to its stable radical anion, we conclude that the reduction of 3-fluorobenzonitrile is a one-electron, diffusion-controlled process.

Coulometry. Exhaustive electrolysis at a potential of −2.4 V gave an experimental n value of 1.05 for the reduction of 3-fluorobenzonitrile (Table I). Cyclic voltammetric examination of the solution immediately after electrolysis indicated only the presence of fluorobenzene; gas-chromatographic analysis showed that fluorobenzene was formed in 45% yield. No other reduction products, including biphenyls, were detected by either cyclic voltammetry or gas chromatography.

Reaction Pathways. A mechanism consistent with these data involves the initial one-electron reduction of 3-fluorobenzonitrile to its radical anion. The radical anion is unstable on the cyclic voltammetric time scale and decomposes with loss of cyanide ion to give the corresponding 3-fluorophenyl radical (eq 8).[22] This radical then abstracts a hydrogen atom from a component of the solvent system to form fluorobenzene (eq 9) which may be subsequently reduced at more negative potential.

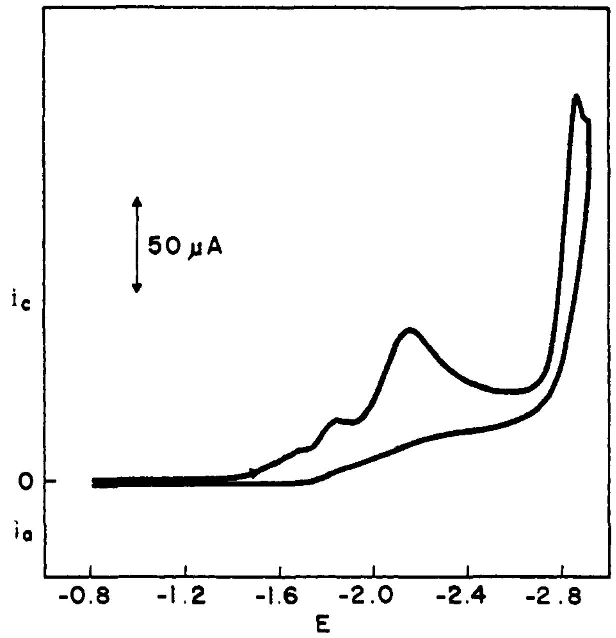

Figure 5. Cyclic voltammogram of 2.22×10^{-3} F 3-fluorobenzonitrile in 0.1 F TEAP–DMF at a scan rate of 80.6 mV/sec. The electrode area is approximately 0.25 cm^2.

$$\text{3-NCC}_6\text{H}_4\text{F} + \text{e} \rightleftharpoons [\text{3-NCC}_6\text{H}_4\text{F}]\cdot^- \xrightarrow{\text{fast}} [\text{3-FC}_6\text{H}_4\cdot] + \text{CN}^- \quad (8)$$

$$[\text{3-FC}_6\text{H}_4\cdot] + \text{HS} \longrightarrow \text{C}_6\text{H}_5\text{F} + \text{S}\cdot \quad (9)$$

Since a reoxidation wave cannot be seen for 3-fluorobenzonitrile radical anion at scan rates up to 100 V/sec, a lower limit of 1000 sec^{-1} can be set for the first-order rate constant for the loss of cyanide ion from the radical anion.[24] Although the rate constant may be several orders of magnitude larger than this lower limit, the chronoamperometric and coulometric results preclude dissociative electron transfer. If the latter had occurred, the 3-fluorophenyl radical would have been formed at the electrode surface rather than in the bulk of the solution. Since reduction of 3-fluorophenyl radical to its anion should occur more readily than hydrogen atom abstraction at the electrode surface,[4] the extremely rapid loss of cyanide ion would have given an overall two-electron process rather than the one-electron process observed here for the reduction of 3-fluorobenzonitrile.

4-Fluorobenzonitrile. Cyclic Voltammetry. The number of processes which are readily discernible upon reduction of 4-fluorobenzonitrile is dependent upon concentration. When the concentration of electroactive species is 2.5×10^{-4} F (Figure 6), a single reduction wave near −2.37 V is the only apparent cathodic process. Upon the reversal of the potential scan at −2.8 V, a small anodic wave which corresponds to the reoxidation of a product formed on the previous cathodic scan is seen near −2.32 V.

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[21] R. H. Wopshall and I. Shain, *Anal. Chem.*, **19**, 1514 (1967).

[22] Although the loss of cyanide ion has been reported to occur in the decomposition of several aromatic nitrile dianions[1] and one dianion radical,[23] this is apparently the first report of the loss of cyanide ion from an aromatic anion radical.

[23] J. P. Ferris and F. R. Antonucci, *J. Amer. Chem. Soc.*, **94**, 8091 (1972).

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

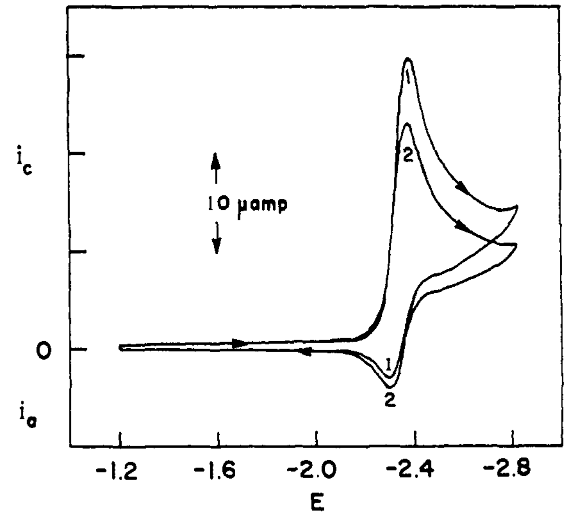

Figure 6. Cyclic voltammogram of 2.5×10^{-4} *F* 4-fluorobenzonitrile in 0.1 *F* TEAP–DMF at a scan rate of 0.1 V/sec. The electrode area is approximately 0.25 cm^2.

Since the ratio of $i_{p,a}/i_{p,c}$ in Figure 6 is less than unity, decomposition of the initial product of the cathode reaction is indicated. An examination of the ratio of $i_{p,a}/i_{p,c}$ as a function of scan rate reveals that a chemically reversible value of 1.0 is not attained until the scan rate exceeds 30 V/sec. In addition, we also find that the value of $i_p/v^{1/2}CA$ for the reduction of 4-fluorobenzonitrile decreases smoothly from an upper limit of 1.7×10^3 A V$^{-1/2}$ sec$^{1/2}$ mol^{-1} cm at a scan rate of 0.1 V/sec to a lower limit of approximately 8×10^2 A V$^{-1/2}$ sec$^{1/2}$ mol^{-1} cm at a scan rate of 100 V/sec.

Coulometry. Analysis by gas chromatography on a partially electrolyzed solution of 4-fluorobenzonitrile showed that benzonitrile was formed in substantial yield. However, quantitative determinations of *n* values and benzonitrile yields were not possible since benzonitrile is reduced slightly more easily than the starting material. Although benzonitrile radical anion is stable on the cyclic voltammetric time scale, this radical anion decomposes slowly during the long exhaustive coulometric reduction of 4-fluorobenzonitrile to generate an unknown electroactive species.

Reaction Pathway. The coulometric and qualitative kinetic results are consistent with a process in which the initial reduction product undergoes chemical reaction. The product of the chemical reaction must then be reduced in a one-electron step at very nearly the same potential as 4-fluorobenzonitrile since no additional redox systems can be seen on the second cathodic cycle. In view of our previous studies[4] of the decompositions of halogenated benzonitrile radical anions and the fact that benzonitrile is reduced to its radical anion in this potential range, it is reasonable to postulate that the first step in the decomposition of the 4-fluorobenzonitrile radical anion is the loss of fluoride ion (eq 11). The resulting 4-cyanophenyl radical then rapidly abstracts a hyrogen atom from a component of the solvent system to yield benzonitrile (eq 12). The subsequent one-electron reduction of benzonitrile to its radical anion constitutes the second electron-transfer reaction in this ECE-type process and completes the reaction pathway (eq 13).

$$\text{4-FC}_6\text{H}_4\text{CN} + \text{e} \rightleftarrows \text{4-FC}_6\text{H}_4\text{CN}\cdot^- \qquad (10)$$

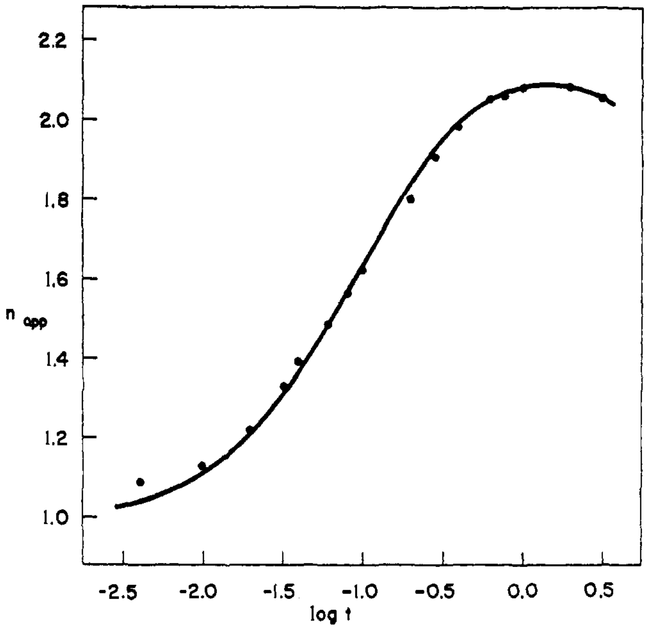

Figure 7. Single potential step chronoamperometric data for the decomposition of 4-fluorobenzonitrile radical anion. The solid line is calculated for a first-order rate constant of 11.2 sec^{-1}. The concentration of 4-fluorobenzonitrile was 2.5×10^{-4} *F*.

$$\text{4-FC}_6\text{H}_4\text{CN}\cdot^- \xrightarrow{k} [\text{4-NCC}_6\text{H}_4\cdot) + \text{F}^- \qquad (11)$$

$$[\text{4-NCC}_6\text{H}_4\cdot] \xrightarrow[\text{SH}]{\text{fast}} \text{C}_6\text{H}_5\text{CN} \qquad (12)$$

$$\text{C}_6\text{H}_5\text{CN} + \text{e} \rightleftarrows \text{C}_6\text{H}_5\text{CN}\cdot^- \qquad (13)$$

Chronoamperometry. Single potential step chronoamperometry was selected for the kinetic study of the decomposition of 4-fluorobenzonitrile radical anion and the subsequent formation of benzonitrile. In this experiment the potential of the working electrode was made sufficiently negative so as to cause the concurrent reduction of all 4-fluorobenzonitrile and benzonitrile present at the electrode surface. The data were analyzed for an ECE-type process in which the effect of the homogeneous chemical reaction between benzonitrile anion and 4-fluorobenzonitrile radial anion was considered (eq 14).[25] The value chosen for the equilibrium con-

$$\text{C}_6\text{H}_5\text{CN}\cdot^- + \text{4-FC}_6\text{H}_4\text{CN} \overset{K}{\rightleftarrows} \text{C}_6\text{H}_5\text{CN} + \text{4-FC}_6\text{H}_4\text{CN}\cdot^- \qquad (14)$$

stant for the solution redox reaction, 0.1, is consistent with the observation that the reduction of benzonitrile occurs 50–60 mV more easily than the reduction of 4-fluorobenzonitrile. Obviously, in order for this treatment to be valid, the rate of electron transfer in solution must be rapid compared to the rate of the loss of fluoride ion from 4-fluorobenzonitrile radical anion. This assumption is probably justified since the first-order rate constant for the loss of fluoride ion is only 11 sec^{-1} while the rate constants for electron exchange between benzonitriles and their radical anions exceed 10^8 M^{-1} sec^{-1}.[26,27] From the satisfactory fit of the experi-

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[25] M. D. Hawley and S. W. Feldberg, *J. Phys. Chem.*, 70, 3459 (1966).

[26] B. A. Kowest, L. Marcoux, and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 5538 (1972).

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

mental data (Figure 7) with the theoretical curve for a first-order rate constant of 11.2 sec^{-1}, we conclude that the formation and decomposition of 4-fluorobenzonitrile radical anion are described adequately by eq 10–13 when the concentration of the 4-fluorobenzonitrile is less than 0.5 mM.

Effect of Concentration. An increase in the concentration of 4-fluorobenzonitrile from the previous level of 2.5×10^{-4} to 2.5×10^{-3} F causes additional redox processes to appear. At a scan rate of 30 V/sec (Figure 8), a single reduction peak (−2.36 V) is seen on the first cathodic scan, while three oxidation peaks are observed on the reverse anodic sweep. The anodic peak appearing at the most negative potential (−2.30 V) corresponds to oxidation of the electrode product formed on the previous cathodic scan, while the two anodic peaks seen at less negative potentials (−1.65 and −2.09 V) must arise from the decomposition of 4-fluorobenzonitrile radical anion. The second cycle shows that the two new processes are chemically and electrochemically reversible and that these additional peaks increase in magnitude with the repeated reduction of 4-fluorobenzonitrile.

Since two reversible one-electron processes with cathodic peak potentials of −1.65 and −2.09 V were also obtained in the cyclic voltammetric examination of 4,4′-dicyanobiphenyl, it appears that another pathway in the decomposition of 4-fluorobenzonitrile radical anion must involve the formation of this dimer. Confirmation of this interpretation was obtained by the electrochemical reduction of 4-fluorobenzonitrile in the cavity of an esr spectrometer. The spectrum recorded was identical with the esr spectrum of 4,4′-dicyanobiphenyl radical anion and the spectrum reported by Rieger, *et al.*, to arise from the reduction of either 4-fluoro- or 4-aminobenzonitrile.[28]

It has been suggested previously that the formation of 4,4′-dicyanobiphenyl arises by the dimerization of 4-cyanophenyl radicals.[1] However, if 4,4′-dicyanobiphenyl were formed by the rate-determining loss of fluoride ion and the subsequent dimerization of cyanophenyl radicals, the ratio of the peak anodic current for the reoxidation of 4-fluorobenzonitrile radical anion to the peak cathodic current for the reduction of 4-fluorobenzonitrile would be independent of the concentration of 4-fluorobenzonitrile. Thus, the fact that $i_{p,a}/i_{p,c}$ decreases with increasing concentration at constant scan rate and switching potential not only precludes the formation of the biphenyl by the dimerization of 4-cyanophenyl radicals but also suggests that dimerization of 4-fluorobenzonitrile radical anions may be a second mode of decomposition.

Attempts to measure the rate constant for the dimerization of 4-fluorobenzonitrile radical anions were made by single potential step chronoamperometry. Since the product of the chemical reaction, 4,4′-dicyanobiphenyl, is also electroactive at the potential at which 4-fluorobenzonitrile is reduced, Feldberg's treatment of a second-order ECE process was used for the kinetic study (eq 15–18).[29] In order to minimize the decomposition of 4-fluorobenzonitrile radical anion by the first-order reaction pathway, the chronoamperometric studies were limited to electrolysis times of 10 msec and less. Despite the fact that very large concentrations (5–10 mM) of 4-fluorobenzonitrile were also used, values of n_{apparent} generally did not exceed 1.3; *i.e.*, useful kinetic results could be obtained over only one decade of time. Thus, in view of the restrictions on concentration range and time, the rate constant which has been obtained from these studies, 3×10^3 M^{-1} sec^{-1}, should be regarded as an order of magnitude result only. Interestingly, however, this estimate of the rate constant for the dimerization of 4-fluorobenzonitrile radical anions does not differ appreciably from the result obtained above (1.35×10^3 M^{-1} sec^{-1}) for the dimerization of 2-fluorobenzonitrile radical anions. This similarity suggests that the dimerization pathways for the 2- and 4-fluorobenzonitrile radical anions are also similar.

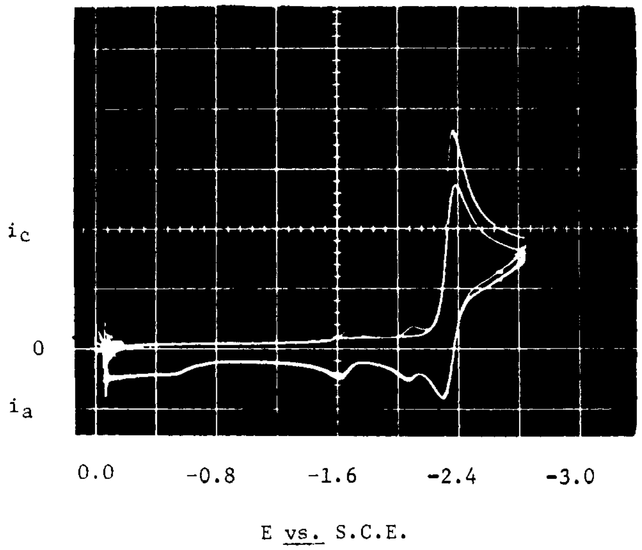

Figure 8. Cyclic voltammogram of 2.5×10^{-3} F 4-fluorobenzonitrile in 0.1 F TEAP–DMF at a scan rate of 30 V/sec. The electrode area is approximately 3.1×10^{-3} cm^2; the current scale is 10 μA/division.

$$RX + e \rightleftarrows RX\cdot^- \qquad (15)$$

$$2RX\cdot^- \xrightarrow{k_d} (RX)_2{}^{2-} \xrightarrow{\text{fast}} RR + 2X^- \qquad (16)$$

$$RR + e \rightleftarrows RR\cdot^- \underset{-e}{\overset{e}{\rightleftarrows}} RR^{2-} \qquad (17)$$

$$RR + 2RX\cdot^- \xrightarrow{K\,=\,\infty} RR^{2-} + 2RX \qquad (18)$$

The dimerization of radicals and radical anions and the subsequent loss of anion have been reported to occur in the electrochemical reductions of several pyrilium[30] and pyridinium salts[31] and for the potassium metal reduction of pyridine in 1,2-dimethoxyethane.[32] In view of the relatively high unpaired spin densities in the 4 positions of fluorobenzonitrile radical anions,[2] we propose dimeric dianions I and II as intermediates in the decompositions of 2- and 4-fluorobenzonitrile radical anions, respectively. In the case of II aromatization can be achieved rapidly by the loss of fluoride

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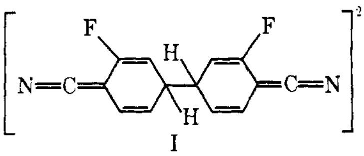
[28] The two small reversible waves at the potentials cited for 4,4′-dicyanobiphenyls (*vs.* SCE) were also observed by Rieger, *et al.*, in their studies of the reduction of 4-aminobenzonitrile.[1]

[29] R. F. Nelson and S. W. Feldberg, *J. Phys. Chem.*, 73, 2623 (1969).

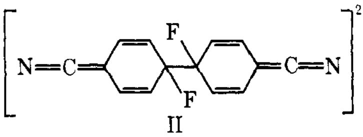
[30] A. T. Balaban, C. Brater, and C. N. Rentea, *Tetrahedron*, **20**, 265 (1964).

[31] E. M. Kosower and J. L. Cotter, *J. Amer. Chem. Soc.*, **86**, 5524 (1964).

[32] R. L. Ward, *ibid.*, **83**, 3623 (1961).



I



II

ion. In the case of I, however, aromatization can be achieved only if the loss of hydride ion were to occur. Thus, since biphenyl formation is not observed in the reduction of 2-fluorobenzonitrile, we suggest instead that structure I undergoes a relatively slow intramolecular electron transfer which results in the formation of equal amounts of fluoride ion, 2-fluorobenzonitrile, and 4-cyanophenyl anion. The latter species would then rapidly abstract a proton from a component of the solvent system to give benzonitrile, completing the reaction pathway.

Experimental Section

Instrumentation. The cyclic voltammetric, chronoamperometric, and current reversal chronopotentiometric experiments were performed on a transitorized, three-electrode potentiostat–galvanostat.[33] A digitally controlled, multipurpose function generator, circuits for digital timing and counting, and a circuit[34,35] for electronic compensation of ohmic potential loss were incorporated into the instrument. A second potentiostat was used for the coulometry studies.[8]

Readout in relatively slow cyclic voltammetric experiments (scan rate 0.1 V/sec or less) 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 scan cyclic voltammetric experiments 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 current–time and Coulomb–time curves for the long-term ($t > 5$ sec) chronoamperometric and coulometric studies.

The gas chromatograph was a Hewlett-Packard Model 700 equipped with flame-ionization detectors and SE-30 columns. The flame-ionization currents were measured with a Philbrick Model SP2A operational amplifier wired in a standard current-follower configuration. The oven temperature and nitrogen gas flow rates were 105° and 60 ml/min, respectively, for the analysis of benzonitrile and 90° and 40 ml/min, respectively, for the determination of fluorobenzene.

Chemicals. The three fluorobenzonitriles were commercially available materials. The purity of each was checked by cyclic voltammetry and by either gas–liquid chromatography or its 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;[36] tetraethylammonium cyanide was prepared by the method of Andreades and Zahnow.[37] Both supporting electrolytes were stored in a vacuum desiccator prior to their use. *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 4A Molecular Sieves.[38] The solvent was immediately transferred to the vacuum line for future use.

Cell and Electrodes. All electrochemical experiments were performed on an all-glass vacuum line.[39] 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 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 and auxiliary electrodes in all experiments by means of a glass frit and a bridge of 0.1 *F* TEAP. Several different planar platinum electrodes were used as the working electrode for the cyclic voltammetric and chronoamperometric experiments: (1) the dimerization studies ($1\ \text{msec} \leq t \leq 20\ \text{msec}$) of 4-fluorobenzonitrile radical anion were performed on an electrode with an area of 3.1×10^{-3} cm^2; (2) single- and double-potential-step chronoamperometric and most cyclic voltammetric studies ($4\ \text{msec} \leq t \leq 4\ \text{sec}$) were done on a planar platinum button electrode (Beckman No. 39273) with an area of 0.25 cm^2; and (3) long-term chronoamperometric experiments ($t > 4$ sec) were performed on an electrode which was similar to the preceding electrode but modified by the addition of a 7-mm glass mantle to minimize the effect of edge diffusion. Control experiments on this latter electrode with nitrobenzene as the electroactive species showed that chronoamperometric $it^{1/2}$ values were diffusion controlled for $t \leq 400$ sec. The working electrode for controlled-potential coulometric determinations was a large cylindrical platinum gauze. The auxiliary electrode for all experiments was a coiled platinum wire. Unless otherwise stated, the supporting electrolyte was 0.1 *F* TEAP (tetraethylammonium perchlorate).

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