Table XII. Conformational Equilibrium Constants Derived from the Nmr Study of the Cyclohexyl-2,2,6,6-d_4 Methyl Ethers

	Chemical shifts, cps[a]						Equilibrium constants		
	Increasing field[b]			Decreasing field[b]			Inc	Dec	
Solvent	*trans*	*cis*	Unsubstd	*trans*	*cis*	Unsubstd	field	field	Av *K*
Cyclohexane	−175.7	−198.0	−183.9	−174.5	−197.7	−183.0	1.72	1.73	1.73 ± 0.01
CCl_4	−175.9	−198.7	−184.3	−174.4	−198.0	−182.9	1.71	1.78	1.75 ± 0.04
Nitrobenzene	−175.3	−198.5	−183.4	−176.6	−199.4	−184.4	1.86	1.92	1.89 ± 0.03
p-Dioxane	−177.2	−199.5	−184.5	−176.5	−199.0	−183.8	2.05	2.08	2.07 ± 0.02
DMSO-d_6	−179.0	−201.4	−186.2	−177.7	−200.1	−185.2	2.11	1.99	2.05 ± 0.06
Acetonitrile	−179.0	−200.9	−184.6	−178.0	−200.5	−184.3	2.91	2.57	2.74 ± 0.17
Chloroform-d_1	−180.6	−202.9	−187.0	−179.9	−202.2	−186.2	2.48	2.54	2.51 ± 0.03
t-Butyl alcohol	−179.6	−200.8	−185.8	−179.3	−200.6	−185.4	2.42	2.49	2.46 ± 0.04

[a] The chemical shifts are relative to TMS (2% v/v of solvent) at 41°. [b] The values given are the average of a minumum of four sweeps.

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Electrochemical Behavior of Trifluoromethyl-Substituted Nitrobenzene

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Abstract: The electrochemical behavior of *o*- and *m*-trifluoromethylnitrobenzene in N,N-dimethylformamide was investigated employing cyclic voltammetric, polarographic, and potentiostatic techniques. These compounds undergo reduction *via* two polarographic steps. The first is a diffusion-controlled, one-electron transfer producing a stable anion radical. The second is an ece process producing a trifluoromethyl-substituted nitrosobenzene anion radical. Mass electrolysis experiments show the long-term electrolysis product to be trifluoromethyl-substituted azoxybenzene. Addition of hydroquinone as a source of protons enhances the formation of the nitroso intermediate.

Numerous electron spin resonance studies on the electrochemically generated anion π radicals of substituted nitrobenzenes in aprotic media have been reported.[2–4] The major attention has been focused on the study of anion radicals prepared by the one-electron reduction of the parent molecule. Through these studies a great amount of data has been accumulated on π-electron densities, bonding, and structure. Esr has also proved to be a useful tool in characterizing reactions of nitro-substituted aromatic radical ions in solution.[5,6] However, there are only a very few reported studies on the reduction products of aromatic nitro compounds in which the esr information is coupled with a complete electrochemical characterization of the system.[7]

In most cases the product of the first reduction step of a nitroaromatic in aprotic solvent is the paramagnetic monoanion radical of the parent molecule.[3–5] In general, an electron-transfer step occurring at a potential more negative than that necessary to produce the monoanion results in a diamagnetic dianion or electroinactive products produced by subsequent chemical reactions of the dianion. Paramagnetic species produced at reduction potentials more negative than the second polarographic half-wave potential have been reported in a few cases.[6,7] Rogers and Watson have observed the esr spectrum of a paramagnetic species generated from 2-trifluoromethylnitrobenzene in N,N-dimethylformamide (DMF) at a potential corresponding to the second polarographic reduction wave of the parent compound.[8] This system proved to be particularly interesting since *in situ* controlled-potential reduction of 2-trifluoromethylnitrobenzene in dry DMF at −2.0 V *vs.* saturated calomel electrode (sce) produced species yielding an esr spectrum characteristic of a combination of the hyperfine splittings of the anion radical and a second paramagnetic substance. Although loss, or decrease, in coupling to the ^{14}N nucleus was reported, the exact nature of the high potential reduction product was not determined.

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(1) To whom correspondence and requests for reprints should be directed.

(2) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

(3) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).

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

(5) R. D. Allendoerfer and P. H. Rieger, *J. Am. Chem. Soc.*, 88, 3711 (1966).

(6) I. Bernal and G. K. Fraenkel, *ibid.*, 86, 1671 (1964).

(7) J. Q. Chambers and R. N. Adams, *J. Electroanal. Chem.*, **9**, 400 (1965).

(8) J. W. Rogers and W. H. Watson, *J. Phys. Chem.*, **72**, 68 (1968).

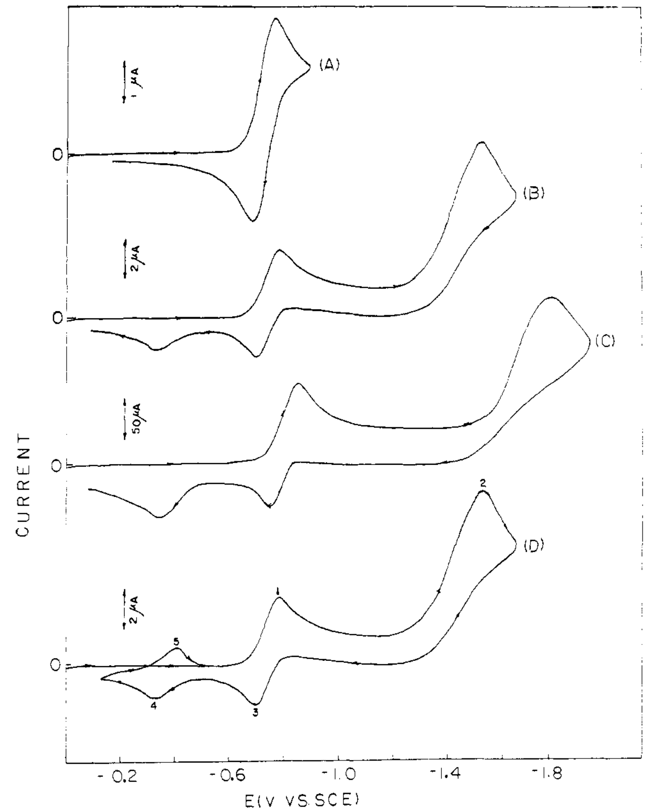
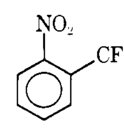


Figure 1. Cyclic voltammograms of *o*-trifluoromethylnitrobenzene in DMF containing 0.1 *M* TPAP: (A) excursion and reversal past first wave at hmde, (B) excursion and reversal past second wave at hmde, (C) ppde, (D) multisweep voltammogram at hmde.

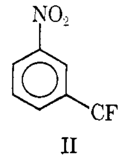
To determine the nature of the observed radical intermediate and to formulate a general mechanism for the electrochemical reduction of *o*- and *m*-trifluoromethylnitrobenzene in DMF, a variety of electrochemical techniques have been employed. The voltammetric behavior of these compounds at mercury and platinum electrodes in the absence and presence of proton donors is described. The potentiostatic reduction and the analysis of products arising from mass electrolysis are discussed. A mechanism consistent with the electrochemical results is postulated.

Results

Voltammetric Methods. *o*-Trifluoromethylnitrobenzene (I) and *m*-trifluoromethylnitrobenzene (II) both



I



II

exhibit two diffusion-controlled polarographic reduction waves; the first wave, in each case, appears to be a reversible, one-electron reduction and the second is typical of an electron-transfer step complicated by a following chemical reaction. The pertinent electrochemical data are summarized in Table I.

The cyclic voltammetric behavior of compound I at both a hanging mercury drop electrode (hmde) and a planar platinum disk electrode (ppde) in DMF is shown in Figure 1. There are no significant differences in the voltammetric behavior of the hmde and the ppde. Voltage excursion and reversal past the first reduction wave produces a wave exhibiting a large anodic current. The ratio of the cathodic peak current to anodic peak current $(i_p)_c/(i_p)_a$ is approximately 1.0 for both electrodes and is independent of sweep rate, Table II. The cathodic half peak $(E_{p/2})$, to cathodic peak $(E_p)_c$ separation of 60 mV and the cathodic peak position do not change with potential scan rate (v), Table II. This behavior is indicative of a one-electron-transfer process producing a radical species which is stable for the duration of the experiment.[9] Previous esr measurements show the species is the simple monoanion radical of I.[8]

Table I. Polarographic Data for Reduction of *o*- and *m*-Trifluoromethylnitrobenzene

Mercury head, cm	$id/h^{1/2}$, $\mu A/cm^{1/2}$	Log plot slope[b]	$id/h^{1/2}$, $\mu A/cm^{1/2}$	Log plot slope[b]
	o-Trifluoromethylnitrobenzene[a]			
	$E_{1/2} = -0.72$ V		$E_{1/2} = -1.42$ V[d]	
65	1.00	60	2.33	72
60	1.00	60	2.31	72
50	0.92	60	2.23	72
40	0.94	60	2.32	72
32	0.93	60	2.23	72
	m-Trifluoromethylnitrobenzene[c]			
	$E_{1/2} = -0.70$ V		$E_{1/2} = -1.50$ V[d]	
65	1.48	59	3.09	80
55	1.46	59	3.08	80
45	1.40	59	3.13	80
35	1.50	59	3.22	80

[a] Compound was 0.96 m*M* in 0.1 *M* solution of TPAP in DMF. [b] Slope of plot of *E vs.* log $i/(id - i)$, millivolts. [c] Compound was 1.25 m*M* in 0.1 *M* solution of TPAP in DMF. [d] Value only approximate since wave distorted by maximum.

Sweep excursion and reversal past the potential of the second polarographic plateau produces a voltammogram exhibiting no anodic current at sweep rates up to 500 mV/sec, Figure 1B. The cathodic peak potential of the second wave (peak 2 in Figure 1D) shifts toward more negative potentials with increasing scan rate and the current function, $(i_p/v^{1/2})_c$, decreases about 20% for a tenfold increase in v, Table II. This behavior suggests that the process occurring at the second wave is of the ece type (a chemical reaction coupled between two reversible electron transfers) with the product of the chemical reaction being electroactive at a potential less cathodic than the starting material.[10]

The number of electrons (n) involved in the reduction process occurring at the second peak may be estimated by taking the two-thirds root of the ratio of the second peak current to the first peak current.[10] An estimate of this type yields 1.9 for the apparent value of n. Thus, the over-all process carried to potentials above the second polarographic wave requires three electrons.

A third anodic peak current at a potential less cathodic than the oxidation peak of the monoanion radical appears in cyclic voltammograms after sweep reversal past the second polarographic plateau (peak 4 in Figure 1D). This oxidation does not appear upon reversal past peak 1. Multiple-sweep voltammograms exhibit

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(9) R. S. Nicholson and I. Shain, *Anal. Chem.*, 36, 706 (1964).
(10) R. S. Nicholson and I. Shain, *ibid.*, 37, 178 (1965).

Table II. Cyclic Voltammetric Data for the Reduction of Compounds I and II in DMF at Hmde[a]

		o-Trifluoromethylnitrobenzene (I)			
	First wave			Second wave	
Scan rate, V/min	$((E_p)_c/2) - (E_p)_c$, mV	$(E_p)_c$, V[b]	$(i_p)_c/(i_p)_a$[c]	$(E_p)_c$, V[b]	$(i_p)_c/v^{1/2}$, μA sec$^{1/2}$ [d]
1.2	60	−0.76	0.94	−1.49	3.53
2.4	60	−0.77	0.94	−1.50	3.20
6.0	61	−0.77	0.97	−1.52	3.15
12.0	62	−0.77	0.97	−1.54	2.95
		m-Trifluoromethylnitrobenzene (II)			
	First wave			Second wave	
Scan rate, V/min	$((E_p)_c/2) - (E_p)_c$, mV	$(E_p)_c$, V[b]	$(i_p)_c/(i_p)_a$[c]	$(E_p)_c$, V[b]	$(i_p)_c/v^{1/2}$, μA sec$^{-1/2}$ [d]
1.2	60	−0.74	1.00	−1.55	7.93
2.4	60	−0.74	1.00	−1.58	7.67
6.0	61	−0.74	0.96	−1.60	7.23
12.0	61	−0.75	1.00	−1.62	6.39

[a] The solution was 0.1 *M* in TPAP. [b] Small $(E_p)_c$ shift probably due to uncompensated ir drop. [c] Scan reversal 100 mV past $(E_p)_c$. [d] i_p measured by extrapolating current from first peak.

a reversible oxidation–reduction couple with an $(E_p)_c$ of 0.42 V at a hmde and −0.50 V at a ppde, Figure 1D.

It is concluded that the electroactive material undergoing oxidation at peak 4 is a radical product of the ece process postulated as responsible for the second polarographic plateau. The follow-up couple appears in all cyclic voltammograms down to sweep rates of 1.2 V/min. The magnitude of the anodic and cathodic currents of this wave may be increased markedly by pausing at potentials above the second polarographic wave before sweep reversal.

The stability of the ece product may be illustrated in a cyclic sweep experiment in which the potential sweep is reversed past peak 2 on the first cycle, and past peak 1 on all subsequent cycles. Voltammogram currents of the follow-up couple decrease only slightly during the course of several cycles. This indicates that the product produced at peak 2 remains near the working electrode, available for oxidation and rereduction, for several seconds, apparently removed by diffusional processes alone, Figure 2. The voltammetric wave exhibits characteristics indictive of a reversible one-electron transfer producing a radical species stable during the course of the experiment,[10] Table III.

Table III. Cyclic Voltammetric Data for Follow-Up Wave from Reduction of I and II at a Hmde[a]

	o-Trifluoromethylnitrobenzene (I)		
Scan rate, V/min	$(E_p)_c$, V[b]	$(i_p)_c/(i_p)_a$[c]	$((E_p)_c/2) - (E_p)_c$, mV
1.2	−0.41	1.0	60
2.4	−0.41	1.1	60
6.0	−0.41	1.1	60
12.0	−0.42	1.1	60
	m-Trifluoromethylnitrobenzene (II)		
Scan rate V/min	$(E_p)_c$, V[b]	$(i_p)_c/(i_p)_a$[c]	$((E_p)_c/2) - (E_p)_c$, mV
1.2	−0.40	1.0	60
2.4	−0.40	1.0	60
6.0	−0.40	1.0	60
12.0	−0.41	1.0	60

[a] The solution was 0.1 *M* in TPAP. [b] Small shift in $(E_p)_c$ is probably due to uncompensated ir drop. [c] Ratios taken from cyclic voltammograms of intermediate in mass-electrolyzed solution of parent compound. See section on mass electrolysis.

Cyclic voltammetric data for compound II at a hmde are given in Table II. These data indicate that compound II undergoes the same electrochemical and chemical transformations as does I under similar experimental conditions. Expected $(E_p)_c$ differences are noted. The stability of the ece product is comparable to that from I.

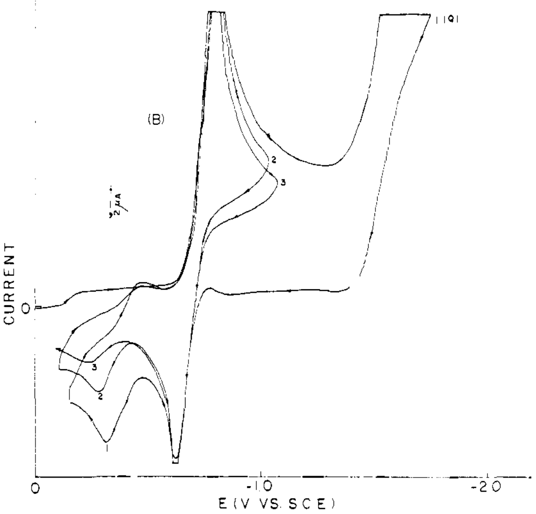

Figure 2. Multisweep voltammogram (numbers indicate cycle sequence) with excursion 1 reversed at point Q and subsequent excursions 2 and 3 at potentials less cathodic than second wave. Sweep rate is 12.5 V/min.

Potentiostatic Method. The Alberts and Shain[11] potentiostatic treatment of ece processes was applied to the second reduction stage of compounds I and II. With no change in slope for the plot of *i vs.* $t^{-1/2}$, the potentiostatic experiments in conjunction with the previous cyclic voltammetry reaffirm a very rapid chemical step in an over-all ece process. From the potentiostatic data, it was possible to obtain an accurate value of $n = 2$ for the second reduction step of each compound.

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(11) G. S. Alberts and I. Shain, *Anal. Chem.*, **35**, 1859 (1963).

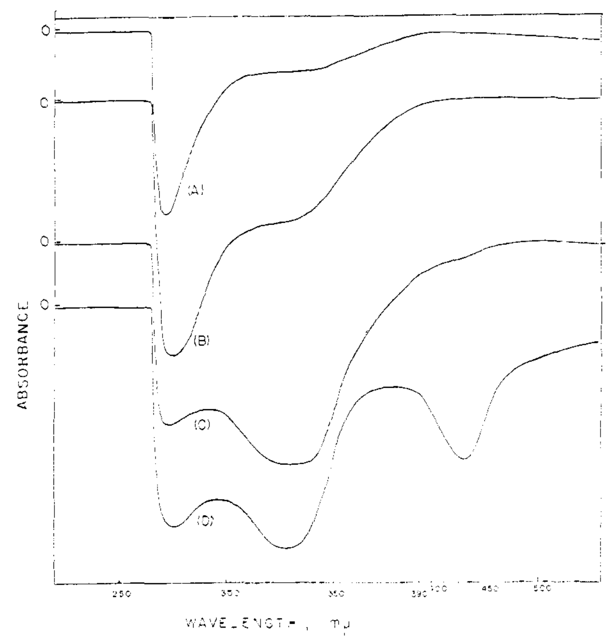
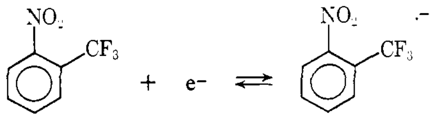


Figure 3. Ultraviolet spectra of *o*-trifluoromethylonitrobenzene during various stages of reduction at −1.8 V in DMF containing TPAP: (A) unreduced, (B) after 30 min of electrolysis, (C) after 1 hr of electrolysis, and (D) after 5 hr of electrolysis. Flat portion up to 250 mμ due to solvent cutoff.

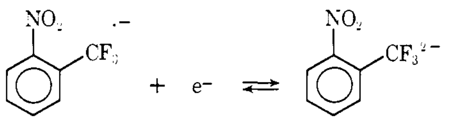
The voltammetric and potentiostatic results suggest the following mechanism.

At potentials corresponding to the first wave

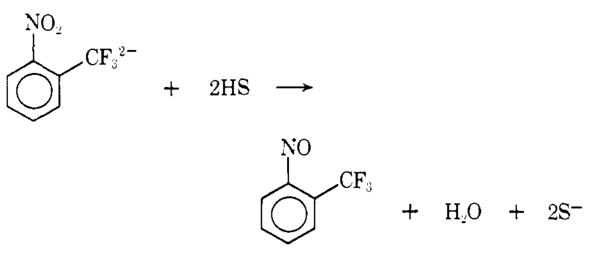


(1)

At potentials corresponding to the second wave



(2)



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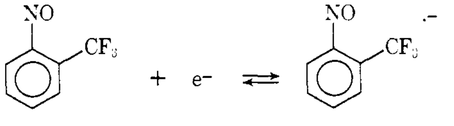


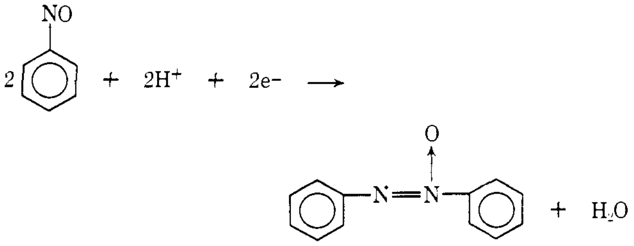
(4)

HS denotes any proton source such as solvent or water impurity. Reactions 3 and 4 are suggested by the results of Kemula and Sioda.[12] They found the nitrosobenzene anion radical to be a short-lived intermediate in the reduction of nitrobenzene in DMF solvent. Oscillopolarographic techniques with sweep rates up to 750 V/min were employed in the study. Nitrosobenzene undergoes a one-electron reduction at potentials less cathodic than nitrobenzene but does not form a long-lived radical anion[12] comparable to that suggested by the voltammetric results for trifluoromethyl-substituted nitrobenzene.

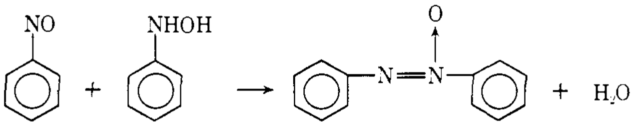
Mass Electrolysis. Electrolysis experiments at a stirred mercury pool working electrode controlled at a potential corresponding to the second polarographic wave were undertaken to investigate slower chemical reactions in the system and to study further the stability of the proposed trifluoromethylnitrosobenzene radical intermediate. Cyclic voltammograms and uv spectra of the electrolyzed solution were recorded at time intervals during the electrolysis. Aliquots of the electrolyzed solution were removed and uv spectra recorded at a later time. Cyclic voltammograms of the solution were recorded employing a three-electrode configuration *in situ*.

o-Trifluoromethylnitrobenzene (I) in DMF solvent exhibits an absorption at 270 mμ, Figure 3. Mass electrolysis of a 1 m*M* DMF–TPAP solution of I for 1 hr at potentials above the second polarographic $E_{1/2}$ produces small amounts of a substance exhibiting a broad absorption band with λ_{max} 330 mμ. The band increases in intensity with continued electrolysis and does not disappear upon prolonged contact with the atmosphere, Figure 3.

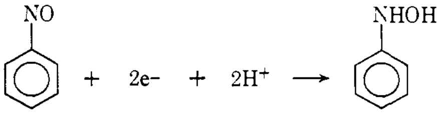
Azoxybenzene in DMF exhibits a broad uv band with λ_{max} 327 mμ. This compound is known to be produced through a coupling of two nitrosobenzene fragments[13]



or nitrosobenzene with phenylhydroxylamine



Nitrosobenzene is electrochemically reduced to phenylhydroxylamine *via* a two-electron step[13]



Based on this information it is postulated that the long-term electrolysis product of I in DMF is primarily 2,2′-di(trifluoromethyl)azoxybenzene.

A visible absorption appears at 423 mμ after prolonged electrolysis (5 hr) of I in DMF, Figure 3. Absorption in this region is characteristic of the weak visible band of azobenzene. The exhaustively electrolyzed solution appears to contain both the trifluoromethyl-substituted azoxybenzene and azobenzene compounds.

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(12) W. Kemula and R. Sioda, *Bull. Acad. Pol. Sci.*, **10**, 507 (1962).

(13) G. A. Russell and E. J. Geels, *J. Am. Chem. Soc.*, **87**, 122 (1965).

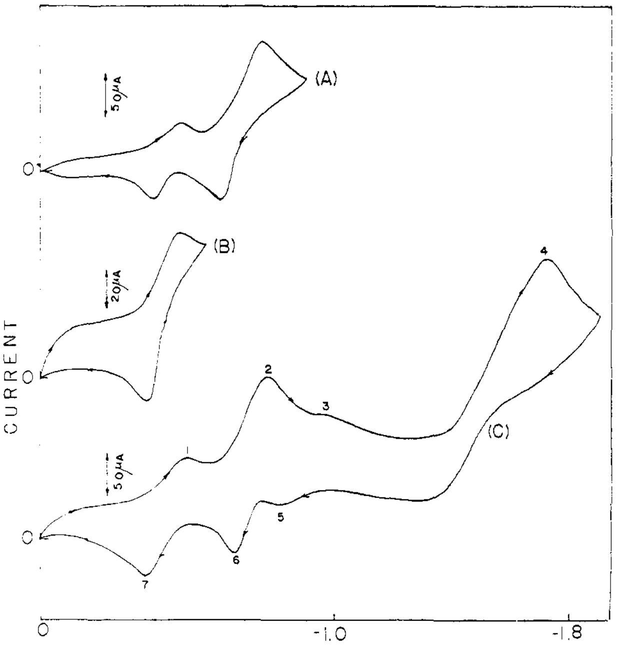


Figure 4. Cyclic voltammograms at ppde of *m*-trifluoromethylnitrobenzene in DMF during various stages of reduction at mercury pool cathode: (A) voltammogram of electrolysis solution after 30 min of electrolysis at −1.85 V (voltammogram recorded immediately after electrolyzing potential terminated), (B) voltammogram showing first wave after electrolyzing potential terminated 10 min, (C) voltammogram of electrolysis solution after 1 hr of electrolysis time. Broadening of waves results from uncompensated ir drop.

Mass electrolysis of *m*-trifluoromethylnitrobenzene produced analogous results.

Cyclic voltammograms of the mass electrolysis solution containing II, recorded at a ppde after several minutes of electrolysis, are shown in Figure 4. The redox couple, characteristic of the nitroso intermediate, is present upon termination of the electrolyzing potential and remains present for several minutes. The $(i_p)_c/(i_p)_a$ value for the wave is approximately 1.0 for both I and II at all sweep rates. The $(E_p)_c$ value does not shift with increased sweep rate. These data are consistent with that given in Table III for I and II for the same process.

A voltammetic wave appears at −1.0 V after 1 hr of electrolysis time, Figure 4C. This wave probably represents the one-electron reduction and oxidation of the long-term azoxy or azo product.

Effect of Proton Donors. The set of reactions postulated to explain the electrochemical behavior at potentials above the second polarographic plateau involve the addition of protons and the elimination of water. To substantiate this mechanism and to gain further insight into the over-all reduction mechanism, the effect of varying amounts of proton donor on the electrochemical behavior of the compounds was studied. Hydroquinone (HQ) was used as the source of protons.[14] The cyclic voltammetric behavior of I at a ppde in the presence of varying amounts of HQ is shown in Figure 5. The first wave (wave 1, Figure 1D) is not affected significantly by the addition of HQ.[15] Wave 2 is shifted 0.58 V in an anodic direction by the addition of an excess of HQ, Figure 5. The $(i_p)_c$ of wave 2 does not change significantly with respect to $(i_p)_c$ of wave 1, suggesting no change in *n* value. The anodic current of the follow-up wave (wave 4, Figure 1D) increases with addition of HQ. The $(E_p)_a$ of this wave shifts in an anodic direction with increasing amounts of HQ, while the $(E_p)_c$ remains relatively unaffected.[15]

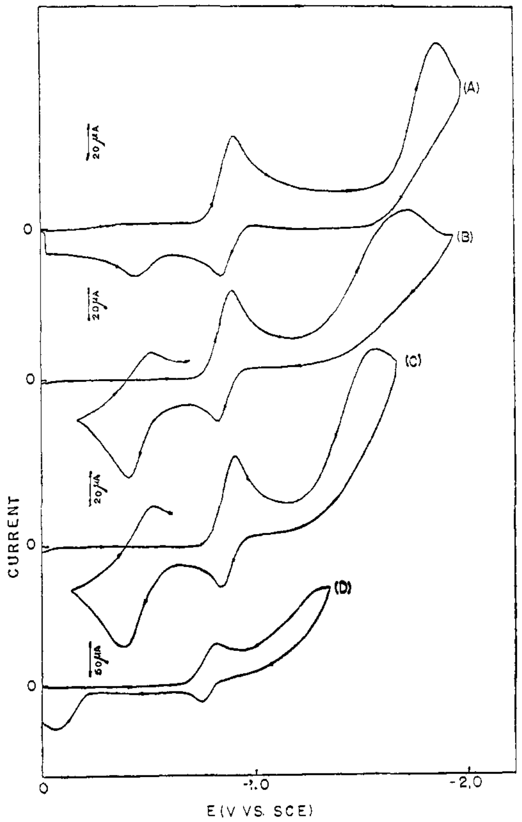
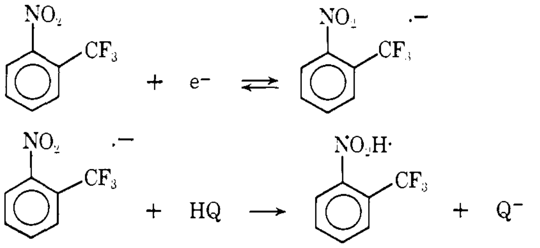


Figure 5. Cyclic voltammograms of *o*-trifluoromethylnitrobenzene 1 m*M* in DMF-TPAP solutions containing varying amounts of hydroquinone (HQ): (A) no HQ, (B) 5 m*M* HQ, (C) 10 m*M* HQ, (D) 0.2 *M* HQ. Background current due to HQ has been subtracted from each of the above voltammograms.

These observations all appear consistent with the postulated reduction mechanism. The anodic shift in the second reduction wave may be explained in terms of a protonated anion radical formed by reactions of the type shown. The neutral radical is more reducible than the unprotonated monoanion radical; consequently addition of a second electron will appear at less cathodic potentials.



The anodic shift in the $(E_p)_a$ of the follow-up couple may be explained in a similar basis. The anion radical of the nitrosobenzene, produced by the ece process, is protonated in the presence of a proton donor, producing

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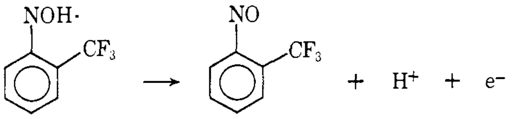
[14] J. L. Sadler and Allen J. Bard, *J. Am. Chem. Soc.*, **90**, 1979 (1968).

[15] Small shift in $(E_p)_c$ probably due to change in solution media.

the corresponding neutral nitroso radical.[16] The subsequent oxidation of this material on the anodic sweep will appear at more anodic potentials than oxidation of the unprotonated anion radical.

The enhanced $(i_p)_a$ of the follow-up couple is consistent with the postulate of proton transfer following addition of a second electron to the starting material. Addition of HQ should increase the rate of formation of the nitroso intermediate and consequently increase the intensity of the oxidation wave corresponding to the reaction



Discussion

Electrochemical results have been presented that suggest *o*- and *m*-trifluoromethylnitrobenzene in DMF are slowly reduced, at potentials above the second polarographic $E_{1/2}$, to a mixture of the corresponding azoxy and azo compounds through a long-lived nitroso intermediate. The anion radical of the nitroso compound is produced as a product of an ece process occurring at the second polarographic plateau.

Addition of a proton source such as hydroquinone enhances the formation of the postulated intermediate. The observation is consistent with the postulate of proton transfer to the dianion radical and subsequent elimination of water to produce nitrosobenzene. The anion radical of the parent molecule is protonated in the presence of HQ but does not undergo further reactions.

The source of protons in DMF solvent poses an interesting question. The dianion radical of the parent molecule possibly could exhibit sufficient base strength to abstract protons from the solvent. A more likely source of protons is trace amounts of water remaining in the solvent ($\sim$0.01%) after purification.

Nitrosobenzene has been observed as an intermediate in the electrochemical reduction of nitrobenzene in DMF.[12] Its stability is not comparable to that observed for the trifluoromethyl-substituted intermediate. Kemula and Sioda[12] found that the nitrosobenzene anion radical undergoes protonation and further reaction to form azoxybenzene. Ayscough, Sargent, and Wilson[16] observed that the nitrosobenzene anion radical ($PhNO^-$) existed only in strongly alkaline solution and in the immediate vicinity of the cathode during the electrolytic reduction of nitrosobenzene. In neutral or acid solution $PhNO^-$ is rapidly replaced by $PhNHO\cdot$. The trifluoromethylnitrosobenzene intermediates (*ortho* or *meta*) do not undergo this reaction rapidly in neutral DMF solvent. These substances have been detected and shown to be stable in a well-stirred mass-electrolyzed solution of the parent compound.

The experimental evidence presented here suggests that compounds I and II are electrochemically reduced *via* a common path. The stability of the nitroso intermediate found in the reduction of other nitrobenzenes may be attributed to charge delocalization by the negative inductive effect of the trifluoromethyl substituent. Inductive effects should be transmitted to the reaction center almost as efficiently from the *meta* position as the *ortho*. Consequently, in the absence of significant steric effects in I, the observed similarity is expected.

It has been shown that the trifluoromethyl group experiences hindrance to free rotation in the monoanion of compound I.[8] Steric interaction between the nitro and the trifluoromethyl groups does not appear to be the reason for this interaction. The esr ^{14}N coupling constant is not increased in the radical of the *ortho* isomer over that of the *meta* and the polarographic $E_{1/2}$ of the first wave is very similar for both compounds.[17]

The suggestion concerning stabilization of the nitrosobenzene anion radical through excess charge delocalization by an electron-withdrawing ring substituent suggests further study. Paez, Seo, and Silverman[18] have studied the reduction mechanisms of mono- and dinitrobenzene compounds in DMF solvent. They have reported that *m*-dinitrobenzene is reduced through an ece process at potentials above its third polarographic wave. A nitroso intermediate is postulated but no experimental evidence for its existence is presented.

Two possibilities do exist concerning the identity of the paramagnetic reduction product of I formed at potentials above the second polarographic $E_{1/2}$. The species is the long-lived *o*-trifluoromethylnitrosobenzene anion radical or a monoanion radical of the final reduction product (substituted azo or azoxybenzene). The rapid rate at which the esr signal from this species intensifies upon initiation of *in situ* electrolysis is consistent with the rate of formation of the long-lived nitroso intermediate.[8]

The failure to observe an esr spectrum of a paramagnetic species generated above the second polarographic $E_{1/2}$ of compound II is not understood. The observed esr signal of the monanion of II was reported to change upon long-term electrolysis at a potential of -2.0 V in the presence of a sce reference electrode.[8] This change was explained as being the result of a ^{14}N coupling constant shift due to water from the sce. The possibility that this spectral change is due to reduction of the nitro group to nitroso does exist.

Experimental Section

Apparatus. The voltammetric experiments were carried out using a multipurpose instrument with a three-electrode cell configuration produced by Beckman Instruments, Inc. The instrument consists of a high-speed, high-impedance potentiometric recorder, and an electrolysis module that incorporates a high-gain operational amplifier with circuits for either voltage or current control.

The platinum working electrode (ppde) consisted of a platinum disk sealed in a soft glass tube. The area of the electrode was 80 mm^2. The hmde was a mercury drop suspended on a mercury-coated platinum wire sealed in soft glass. The auxiliary electrode was a coiled platinum wire. The reference electrode in all experiments was an aqueous sce connected to the test solution by means of an agar plug and sintered-glass disk.

Mass electrolysis techniques employed are described elsewhere.[19]

Chemicals. Compounds I and II were obtained from K & K Laboratories, Inc. They were found to be chromatographically pure and were used without further purification. Hydroquinone

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[16] P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc., B*, 903 (1966).

[17] D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Am. Chem. Soc.*, 86, 987 (1964).

[18] O. Paez, E. T. Seo, and H. P. Silverman, Technical Report ECOM-02464-1, U. S. Army Electronic Command.

[19] A. Weissberger, "Technique of Organic Chemistry," Vol. 1, Interscience Publishers, New York, N. Y., 1960.

(HQ) was obtained from J. T. Baker Chemical Co. and was recrystallized from a 50% water–ethyl ether solution before use.

Spectroquality N,N-dimethylformamide containing approximately 0.03% water was obtained from Eastman Organic Chemicals. The solvent was distilled from anhydrous $CuSO_4$ before use.

Tetra-*n*-propylammonium perchlorate was employed as supporting electrolyte throughout. The salt was prepared and purified as previously described.[8]

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Unusual Influence of Nitrogen on Rates of Anion Formation. Hydrogen–Deuterium Exchange of Pyridine and the Diazines[1,2]

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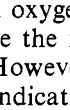
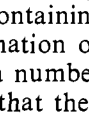
Abstract: Rates of hydrogen–deuterium exchange of pyridine (I), pyrimidine (II), pyridazine (III), and pyrazine (IV) in $CH_3OD–CH_3ONa$ at 164.6° were obtained by an nmr method. Relative rates for I at positions 2,6:3,5:4 are 1.0:9.3:12, for II at 2:4,6:5 are 1.0:3.2:48, and for III at 3,6:4,5 are 1.0:14. Log partial rate factors for nitrogen are *ortho*, 1.31; *meta*, 2.43; *para*, 2.46. Activation at a center *ortho* to nitrogen is less than at a *meta* or *para* position. Exhange is believed to take place by simple deprotonation reactions. The unusual acidity pattern may be the result of two reinforcing factors. They are (1) pair–pair electron repulsion between the carbanion and nitrogen and (2) decreased s character in the *ortho* CH bond associated with an increased *endo* ring angle.

The electron-attracting inductive effects of fluoro and oxygen-containing substituents are expected to facilitate the formation of carbanions at adjacent centers. However, a number of examples now have been found indicating that these first-row atoms either may retard anion formation or may increase the rate of anion formation to a smaller degree than would be predicted.[4,5] These deviations from expectation are larger for fluorine. The effects of fluorine and of oxygen on carbanion formation are said to be determined by the state of hybridization of the carbanion. When the anion is pyramidal net stabilization results; when the anion is part of a planar system there may be destabilization.[4,5]

Nitrogen, another first-row atom, also is expected to facilitate the formation of carbanions by means of an inductive effect. Contrary to a prediction based upon inductive activation alone, we have found that nitrogen does not facilitate the formation of carbanions at adjacent positions to the degree that it facilitates anion formation at more removed centers.

Rates of hydrogen–deuterium exchange of pyridine (I), pyrimidine (II), pyridazine (III), and pyrazine (IV) in $CH_3OD–CH_3ONa$ were determined. In the case of these substrates, H–D exchange takes place more rapidly at those positions which are more removed from the activating nitrogen atom(s).


I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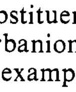
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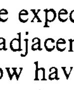
IV

Results

Deuterodeprotonation of I–IV in $CH_3OD–CH_3ONa$ was followed using nmr.[6] Determination of rate constants is complicated by the reverse reaction, D–H exchange, since the solvent pool of deuterium is not "infinitely" large relative to the hydrogen pool of substrate. Exchange reactions of I–III are further complicated because there are several positions in each substrate which introduce hydrogen into the medium at different rates. Some of the isotope lost from a less reactive position comes back into a more reactive site of substrate. The effective equilibrium hydrogen content of a position in I–III may vary with time and may be a function of the reactivity of the other positions. For the positions of IV, position 5 of II, and 4,5 of III it was possible to obtain a constant equilibrium value. But for all positions of I and 2 and 4,6 of II it was practical to obtain a single, composite equilibrium value.

In order to evaluate the effect of back-D–H exchange on the magnitude of the rate constants obtained using the standard first-order rate expression for reversible isotope exchange,[7,8] the data were treated in another way. By pretreating the data using a graphical integration, it is possible to correct for back-D–H exchange and to obtain a linear first-order rate plot which does not employ the equilibrium hydrogen concentration of

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[1] Taken in part from the Ph.D. dissertation of C. L. Smith, University of Florida, 1968.

[2] Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968, Abstract P-128.

[3] National Science Foundation Predoctoral Fellow, 1967–1968.

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