magnesium sulfate at −20°. The solvent was evaporated *in vacuo* and the residue was immediately examined by nmr spectroscopy. The presence of naphthalene was easily confirmed, but other absorptions were too broad and overlapping for possible assignment. Vpc indicated the presence of naphthalene and a number of less volatile components. Column chromatography on Woelm basic alumina (activity I) with petroleum ether gave 0.40 g (22%) of naphthalene. Continued elution with more polar solvents gave only dark viscous oils which could not be characterized.

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Electrochemical Studies of the Reduction of 2-Methoxyazocines in Aprotic Solvents. Comparison with the Cyclooctatetraene System[1]

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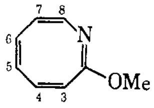
Abstract: The polarographic reduction of each of the five different 2-methoxyazocines studied was observed to be nonnernstian. In tetrahydrofuran (THF) or dimethylformamide (DMF) solutions containing 0.1 *M* tetra-*n*-butylammonium perchlorate (TBAP) background electrolyte, the reduction occurs by the addition of two electrons to the parent azocine to form directly the dianion product. Cyclic voltammetry of the azocines indicates that the dianion product is not reoxidized at the mercury drop electrode until the potential is scanned nearly 1-V anodic of the initial reduction wave. This behavior is in strong contrast to the previously reported mechanism for the reduction of cyclooctatetraene (COT), the hydrocarbon analog. COT and its derivatives undergo two nearly nernstian one-electron reductions separated by ∼0.24 V. A mechanism is proposed for the azocine reduction process. Addition of the first electron is thought to be accompanied by considerable ring flattening, producing a planar or nearly planar anion radical. This radical is more easily reduced than the parent heterocycle, resulting in the immediate introduction of a second electron to form the stable dianion. The reason for the spontaneous addition of a second electron at the same potential as the addition of the first is thought to be the favorable energy gain upon formation of a ten π-electron aromatic dianion. The significance of these results in interpreting the previously reported behavior of cyclooctatetraene and its derivatives is discussed.

Electrochemical techniques are recognized to be capable of providing invaluable diagnostic information concerning the generation and chemical reactivity of cyclic conjugated olefins containing $(4n + 2)$ π electrons.[3-9] A case in point is the direct correlation that exists between the free energy of the electron-transfer reaction and the energy of the molecular orbital accepting or donating the electron.[10] Most importantly, electron-transfer reactions that take place at inert electrode surfaces are devoid of undesirable side reactions generally associated with alkali metal reductions. Because alkali metal ions are known to form strong ion-pair complexes with radical anions and dianions, the utilization of metal cation-free reduction techniques are best suited to the study of electron transfer reactions *per se*. Recently a convenient synthesis of π-equivalent nitrogen analogs of cyclooctatetraene (COT) was developed in this laboratory.[1] Because of the ready availability of 2-methoxyazocines and their close structural, but electronically different, relationship with COT, a study of their electrochemical behavior was undertaken.[11]



1a, 2-methoxyazocine (MA)
b, 8-methyl-2-methoxyazocine (MMA)
c, 3,8-dimethyl-2-methoxyazocine (DMMA)
d, 4,6,8-trimethyl-2-methoxyazocine (TMMA)
e, 3,5,6,8-tetramethyl-2-methoxyazocine (TTMA)

In a chemical system composed of a parent compound and its dianion in equilibrium with an inert electrode, the following chemical and electrochemical reactions may be defined.

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[1] Unsaturated Heterocyclic Systems. LXXIV. For the previous paper in this series, see L. A. Paquette, T. Kakihana, J. F. Hansen, and J. C. Philips, *J. Amer. Chem. Soc.*, **93**, 152 (1971).

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[9] N. Tokel, V. Katovic, K. Farmery, L. B. Anderson, and D. H. Busch, *J. Amer. Chem. Soc.*, **92**, 400 (1970).

[10] (a) G. J. Hoijtink, *Recl. Trav. Chim. Pays-Bas*, **74**, 1525 (1955); (b) G. J. Hoijtink, E. deBoer, P. H. van der Meij, and W. P. Weijland, *ibid.*, **75**, 487 (1956).

[11] A preliminary account of a portion of this work is to be found in L. A. Paquette, J. F. Hansen, T. Kakihana, and L. B. Anderson, *Tetrahedron Lett.*, 533 (1970).

$$\mathrm{R} + \mathrm{e}^- \underset{}{\overset{E_a{}^{\circ\prime}}{\rightleftharpoons}} \mathrm{R}\cdot^-;\ \Delta G_a \qquad (1)$$

$$\mathrm{R}\cdot^- + \mathrm{e}^- \overset{E_b{}^{\circ\prime}}{\rightleftharpoons} \mathrm{R}^{2-};\ \Delta G_b \qquad (2)$$

$$\mathrm{R} + 2\mathrm{e}^- \overset{E^{\circ\prime}}{\rightleftharpoons} \mathrm{R}^{2-};\ \Delta G_T \qquad (3)$$

$$2\mathrm{R}\cdot^- \overset{K_D}{\rightleftharpoons} \mathrm{R} + \mathrm{R}^{2-};\ \Delta G_D \qquad (4)$$

However, if in the azocine series additional chemical reactions (*e.g.*, ion associations, protonations, or molecular rearrangements) become admixed with these equilibria, eq 1–4 would require further amplification before serving as an exact model for the two-electron reduction process. As will be seen, the derived electrochemical results are entirely consistent with reactions 1–4; additionally, chemical reduction of the azocine does not give rise to skeletal rearrangement products.[12] As a result, our interpretation of the behavior of azocines and cyclooctatetraenes is based on this uncomplicated model. The effects of solvent dielectric on these reactions appear to be negligible, since similar results were obtained in THF (D = 7.2) and DMF (D = 37.6).

As a result of these studies, detailed evidence has been obtained on the following aspects of azocinyl and cyclooctatetraenyl dianion formation. (1) The azocinyls examined herein represent the first examples of 4n π-electron molecules that are highly favorable to multielectron addition at the discharge potential. (2) The process of ring flattening involves a delicate balance between electron repulsion, bond strain, and delocalization energy. These energy requirements appear to dictate planar or nearly planar structures for the azocine radical anions and dianions, as well as the COT dianion. The COT radical anion on the other hand would seem to be significantly less planar than the above. (3) In all known cases,[5,6,13] COT and its derivatives exhibit spectroscopic and electrochemical behavior consistent with a positive value for ΔG_D (eq 4), whereas the azocines uniformly exhibit negative values for ΔG_D. Some justification for this behavior may be derived from the contrasting π-electron energy levels calculated for azocine and COT.[12] (4) The rate of the heterogeneous electron transfer to azocine to form the dianion is very slow when compared to the rates observed for each of the one-electron reductions of COT. This is adequately explained by hypothesis of an azocine radical anion as a high-energy intermediate in azocine reduction.

Experimental Section

Electrochemical Measurements. Polarographic studies in THF solvent were carried out on a specially designed vacuum-line electrochemical cell allowing all preparations and measurements to be carried out under conditions of rigorous exclusion of air and water.[14] The cell was assembled and attached to the vacuum line by ground-glass joints and evacuated for several minutes to remove volatile residues and adsorbed water from the glass surfaces. The cell was then isolated from the vacuum line and checked for leaks by noting its ability to maintain a high vacuum. THF solvent containing 0.1 M TBAP was added to the working cell compartment and to the salt bridge leading to the reference electrode. Sufficient THF containing 0.1 M $AgClO_4$ was then added to the reference electrode compartment in order to equalize the levels of solution in both compartments. The cell was then bled up to atmospheric pressure with argon gas. The reference electrode was an Ag wire |0.1 M Ag^+ couple in THF with a measured potential of +0.49 V *vs.* aqueous sce. The value calculated assuming $E^\circ{}_{Ag^+|Ag}$ = 0.80 V *vs.* nhe and neglecting liquid junction potentials is +0.50 V *vs.* sce.

Background polarograms on the solution at this point revealed a small anodic wave at +0.14 V *vs.* sce (presumably Cl^-) indicating an $\sim 2 \times 10^{-5}$ M impurity level. A second unknown impurity at $\sim 1 \times 10^{-5}$ M level produced a small reversible cathodic wave at −1.2 V *vs.* sce. Neither of these waves interfered with the electrochemical measurements of interest, and the remaining background appeared to be a near-linear rise of 0.15 μA/V between 0.0 and −3.0 V *vs.* sce due to charging phenomena. Discharge of solvent appears precipitously just beyond −3.0 V, and reaches a current of 1 μA by −3.1 V. Other studies[14] have indicated that the addition of small amounts of water ($\sim$1 mM) to such solutions does not result in appearance of any discrete waves, but has the effect of generally raising the level of the background in the region from −2.0 to −3.0 V *vs.* sce and making the final current-rise somewhat earlier and less precipitous. The level of water and other protonic impurities is estimated to be below the 10^{-6} M level in these solutions. Alkali metal ion impurities, easily identified by their electrochemical activity near −2.0 V *vs.* sce, were below the detectable limit.

Weighed amounts of the organic depolarizers were dissolved in dry THF and measured volumes of the quantitatively diluted samples were added to the prepared cell by injection with a microliter syringe through a rubber septum covering a cell entry port. This procedure does not introduce detectable amounts of impurities when the cell is under 1 atm of argon gas.

Polarograms were run on an ordinary commercially produced three-electrode instrument (Beckman Electroscan, Model "30"). Cyclic voltammograms were taken with a Chemtrix Type 300 Polarographic Unit and Type 205 Time-Base Unit inserted in a Tektronix Model 564 oscilloscope. Traces were recorded by first displaying them on the retentive phosphor of the scope, and then photographing the CRT with a Tektronix Model C-12 camera system fitted with a Polaroid roll-film back. The Chemtrix unit was set to record the voltammograms beginning at 1.1 sec after drop fall from the dropping mercury electrode (m = 1.05 × 10^{-3} g/sec at h_{corr} = 52.5 cm). Because theoretical equations have not been derived for the current behavior during cyclic voltammetry on a growing mercury drop, these results may only be considered to be semiquantitative. Results at the higher scan rates (0.1 sec/cycle) should, nevertheless, be a fairly good approximation to behavior at a hanging mercury drop.

Electrochemical measurements in DMF solvent were made in an H-type polarographic cell filled on both sides with the test solution containing 0.1 M tetra-*n*-butylammonium iodide (TBAI) and connected *via* aqueous salt bridge to an aqueous saturated calomel electrode. A Pt auxillary electrode was placed in the salt-bridge side and the DME and nitrogen deaeration system were inserted, through a neoprene stopper, into the other side of the H-cell. Polarograms and cyclic voltammograms were run with an Indiana Instruments, ORNL Model 1988-A Polarograph and data were recorded, where appropriate, on a Honeywell Brown Electronik recorder, a Hewlett Packard–Moseley Model 2D-2M recorder, or a Tektronix Model 564 oscilloscope fitted with two Type 2A63 plug-in amplifiers. This procedure is capable of maintaining the solution oxygen free, but cannot be expected to exclude rigorously water. Evidence was observed for the formation of protonation products of the azocine dianions produced electrochemically under these circumstances. At the slower scan rates, <1 V/sec, more than one peak was observed during the anodic portion of the triangular sweep. As the scan rate was increased, one of these peaks (usually the most cathodic one) grew in height at the expense of the others until at scan rates from 10 to 20 V/sec, only one anodic peak remained. Such slow protonations are not expected to affect materially the polarographic results, and observed agreement between results in THF and DMF bear out this conclusion. The estimated concentration of water is from 1 to 10 mM in the DMF solutions used.

Chemicals. The DMF was reagent grade and was further purified by azeotropic removal of water with benzene and distillation of the DMF two times from anhydrous Na_2CO_3. The TBAI was recrystallized twice from methanol–ether and dried under vacuum. The azocines were analytically pure materials obtained by preparative scale vpc purification techniques.[1]

THF solvent was reagent grade, and was predried over calcium

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[12] L. A. Paquette, J. F. Hansen, and T. Kakihana, *J. Amer. Chem. Soc.*, **93**, 168 (1971).

[13] C. S. Baxter, P. J. Garratt, and K. P. C. Vollhardt, *ibid.*, **91**, 7783 (1970).

[14] J. L. Mills, R. Nelson, S. Shore, and L. B. Anderson, *Anal. Chem.*, in press.

Table I. Diffusion Coefficients of Azocines

	DMF^a			THF^b		
Depolarizer	$i_d/C°$, μA/mM	I_{norm}	$D \times 10^5$, cm^2/sec	$i_d/C°$, μA/mM	I, μA mM^{-1} g$^{-2/3}$ $t^{1/2}$	$D \times 10^5$, cm^2/sec
COT (both waves)	9.62	(650)	(1.5)			
Methoxy COT (both waves)	8.07	(545)	(1.1)			
MA	8.37	(565)	(1.1$_2$)	7.55	565	1.1$_2$
MMA	7.93	(527)	(1.0)			
DMMA	7.25	(511)	(0.9)	6.43	518	1.0$_0$
TMMA	6.78	(482)	(0.8)			
TTMA	6.74	(516)	(0.9)			

[a] Normalized diffusion current constants have been corrected for the effect of drop-time dependence on the potential at which i_d is measured. These values as well as D values in parentheses are only *relative* values and should be compared only with other values in the same column. [b] The values of D measured in THF have been calculated using the modified Ilkovic' equation: J. Heyrovsky and J. Kuta, "Principles of Polarography," Academic Press, New York, N. Y., 1966, p 98.

hydride with subsequent distillation and storage over Na-K alloy, in an evacuated vessel. With occasional swirling of the flask and contents, the solvent may be kept dry and oxygen free indefinitely and the surface of the liquid alloy remains mirror clean. TBAP was analytical reagent grade (Southwestern Analytical Chemicals), and was used as delivered after vacuum drying at 100° in small (<10 g) batches. The polarographic behavior has been described above, and attempts to purify further the salt by recrystallization succeeded only in degrading the quality of the background polarogram.

Results and Discussion

Polarography. The polarographic behavior of the entire family of 2-methoxyazocines is typified by the behavior of 3,8-dimethyl derivative, **1c**. Figure 1 shows a polarogram of 0.21 mM **1c** in THF medium. The diffusion current, i_d, in Table I indicates an overall two-electron transfer process, while plots of log $(i/i_d - i)$ *vs.* E gave a reciprocal slope of 0.097 indicating that the wave is nonnerstian and that $\alpha_a n_a$ is approximately 0.6.

Table I summarizes the average diffusion coefficients calculated for the various 2-methoxyazocines in THF. The D values obtained agree very well with the literature values for similar organic compounds. The two values taken in THF solvent also show the slightly smaller D predicted by the Stokes-Einstein relation for the slightly higher molecular volume of the dimethyl derivative. The presence of polarographic maxima as well as the presence of traces of water in the DMF solvent make the absolute values of diffusion coefficients in DMF unreliable; however, their relative values show the expected decrease with increasing substitution. The D value for COT is significantly higher than that for any of the azocines or for methoxy COT, presumably because of the lesser degree of solvation of the less polar hydrocarbon.

Upon variation of the mercury column height, h, the current at a fixed potential near the base of the wave does not change, whereas, i_d is proportional to $h^{1/2}$. This behavior is typical of irreversible electron-transfer processes. Further evidence of irreversible behavior as well as absence of coupled chemical reactions is the observation of a 10-mV cathodic shift of $E_{1/2}$, the half-wave potential, when h is doubled.

The potential $E_{1/2}$ was found to be independent of $C°$, the concentration of depolarizer, in the region from 1 to 4 × 10^{-4} M azocine. The ratio $i_d/C°$ was also independent of $C°$ over the same region of concentration. Polarographic results obtained with other azocines were comparable and are summarized in Table II.

Table II. Polarographic Results^a

Polyene	$E_{1/2}$^{b}		Slope^c		$\alpha_a n_a$ apparent	n^e overall
COT	−1.74		0.073		0.81	1
	−1.97		0.077		0.77	1
MeOCOT	−1.87		0.083		0.71	1
	−2.05		0.068		0.86	1
MA	−1.84	−1.94^d	0.111	0.075^d	0.78^d	2
MMA	−1.92		0.107		0.55	2
DMMA	−2.17	−2.28^d	0.100	0.099^d	0.60^d	2
TMMA	−2.22		0.116		0.51	2
TTMA	−2.46		0.103		0.57	2

[a] Data taken on 1.25 mM polyene in DMF solvent, 0.1 M TBAI background electrolyte, except as noted. [b] Half-wave potentials, volta *vs.* aqueous sce. [c] Reciprocal slope from plot of log $(i/(i_d - i))$ *vs.* E. [d] Data taken on 0.1–1 mM polyene in THF solvent. 0.1 M **TBAP** background electrolyte. [e] Taken as nearest integral number, $n_{unk} = I_{unk}(n_{COT}/I_{COT})$. See Table I.

A small solvent effect on $E_{1/2}$ was observed. In each case that comparative tests were made (see Table II) the values obtained in THF media were ~0.10 V more cathodic than those obtained in DMF media. The cathodic shift as well as the approximate magnitude is

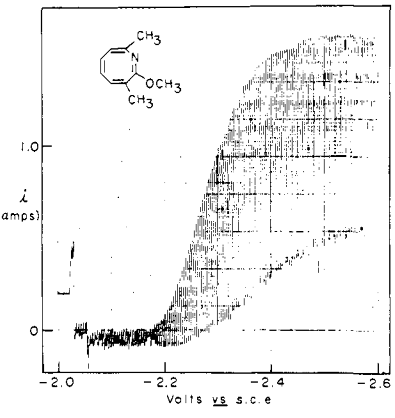


Figure 1. Polarogram of 0.244 mM DMMA in THF solution containing 0.1 M TBAP.

not unexpected, because of the higher dielectric constant of DMF, which should favor formation of the highly ionic transition state. No quantitative conclusions should be drawn from these shifts, however, since the contributions of liquid junction potentials and double layer phenomena are unknown.

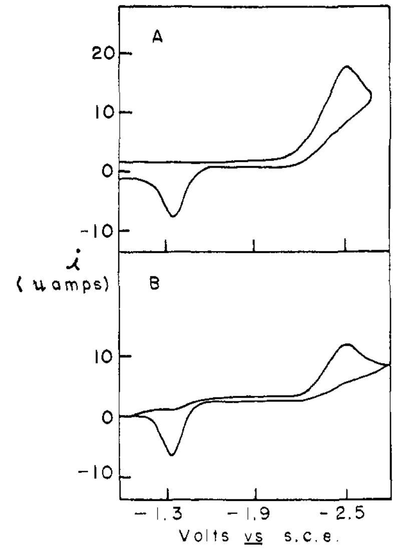
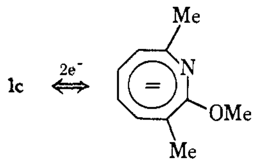


Figure 2. Cyclic voltammetry of DMMA: A, single sweep voltammogram, THF solvent, $v = 4$ V/sec; **B**, steady-state voltammogram, DMF solvent, $v = 12.8$ V/sec.

Cyclic Voltammetry. The nature of the overall electron-transfer reaction, as well as the identity of the reduction products may conveniently be studied with cyclic voltammetry. Figure 2a shows the behavior of 0.49 mM **1c** in THF at an intermediate scan rate, v, of 4.0 V/sec. No anodic current appears at the potential of the cathodic wave (*ca.* 2.5 V *vs.* sce), verifying the electrochemically irreversible nature of the polarographic reduction. The two-electron addition product is not reoxidized until ~0.8 V more anodic than the reduction of **1c**. This behavior is consistent with reduction of **1c** directly to a very stable aromatic dianion (**2**) at −2.5 V and reoxidation to the parent azocine at − 1.6 *vs.* sce.



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(5)

Dianion **2** is stable to chemical side reactions in the dry THF solvent as indicated by the appearance of only one reduction wave and one reoxidation wave over a range of v from 1.0 to 20 V/sec. The ratio of forward to reverse peak current, $i_{p,f}/i_{p,r}$, was constant at 0.98 ± 0.05 over the same range of v. Further confirmation of the overall reversibility of the reduction–reoxidation cycle is obtained from the steady-state cyclic voltammogram (Figure 2b) that results after a large number of successive cathodic–anodic scans. There are peaks only for the single reducible and single oxidizable species.

The values of cathodic and anodic half-peak potentials were found to be essentially independent of concentration (*e.g.*, at $v = 4$ V/sec these are -2.44 ± 0.02 and -1.64 ± 0.01 V *vs.* sce, respectively). The value of $i_{p,f}/C°$ was also constant over the same fourfold change in $C°$. It is therefore possible to rule out a slow chemical step subsequent to electron transfer.

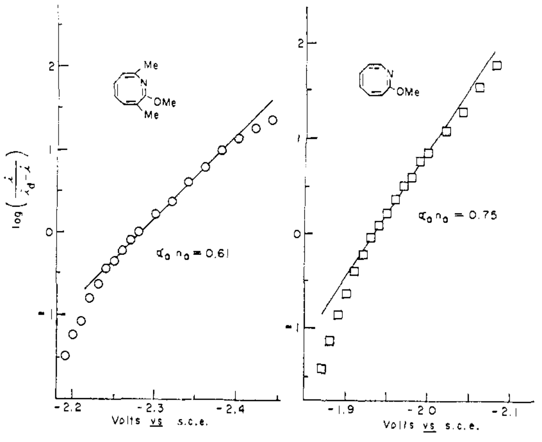
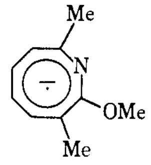


Figure 3. Log plots for two azocines in THF solutions.

In particular, it is possible to rule out a slow disproportionation of the hypothetical anion radical **3** subsequent to transfer of the first electron to the parent **1c**. Such a second-order reaction would be expected to result in a shift of $E_{p/2}$ and polarographic $E_{1/2}$ with concentration of electroactive material, and no such change is observed. We therefore conclude that the reduction is a direct two-electron transfer to parent **1c** to form dianion **2** at potentials more than 200-mV cathodic of $E°'$. Anion radical **3**, if it exists at all, lasts only a very short time, and is immediately reduced to **2** by addition of a second electron.



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Electron-Transfer Kinetics. Some insight into the kinetics of the electron-transfer process and the rate-determining step of the overall reduction may be obtained from a more detailed analysis of the shape of the polarographic and cyclic voltammetric curves. Quantitative treatment of the current which results when the electrode process involves two consecutive one-electron transfer processes has been discussed.[15] In this type of system, the current at large overvoltages (potentials greater than 200 mV distant from the equilibrium potential) is determined virtually completely by the rate of the first electron transfer (written for the reduction process)

$$i = 2i_a^\circ \exp\left[\frac{-\alpha_a n_a F(E - E_e)}{RT}\right] \qquad (6)$$

where i is the measured current, $i°_a$ is the apparent exchange current for the first electron addition to the parent azocine, α_a and n_a are the transfer coefficient and number of electrons, respectively, for the first electron addition, E is the potential of the DME, and E_e is the equilibrium potential for an equimolar mixture of azocine and azocine dianion. E_e is virtually equal to $E°'$, the formal redox potential for the overall two-electron transfer process.[15] The remaining variables have their usual significance. This expression is

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(15) P. Delahay "Double Layer and Electrode Processes," Wiley, New York, N. Y., 1966, pp 178 ff.

Table III. Kinetic Analysis of Polarographic and Cyclic Voltammetric Behavior

Azocine	$\alpha_a n_a$	k_e, cm/sec
	Polarography	
MA	0.78 ± 0.03	4×10^{-5}
DMMA	0.60 ± 0.03	$1.5 \pm 0.2 \times 10^{-6}$

Polyene	V/sec	$E^{\circ\prime}$ (V *vs.* sce)		$\alpha_a n_a$	$(1 - \alpha_b)n_b$	k_e, cm/sec
		DMF	THF			
			Cyclic Voltammetry			
COT		−1.84				4×10^{-3} (1st wave) 4×10^{-2} (2nd wave)
MeOCOT		−2.06				
MA	1–20	−1.62	−1.83 ± 0.03	0.80	0.74	8×10^{-6}
DMMA	1–20	−1.88	−2.01 ± 0.02	0.50	0.65	0.9×10^{-6}
TMMA		−2.20				
TTMA		−2.08				

identical with the corresponding equation describing the current for an irreversible one-electron transfer process except that it distinguishes $\alpha_a n_a$ as characterizing only the first electron transfer, and the current is multiplied by a factor of two to take account of the fact that addition of a second electron follows the rate-determining step immediately at $(E - E^{\circ\prime}) > 200$ mV.

The early rising portions of the polarographic waves for both DMMA and MA are closer than 200 mV to the formal potential $E^{\circ\prime}$ calculated from cyclic voltammetry (Table III). This early portion of the wave should therefore show evidence of more than one electron being involved in the rate-determining step. Plots of log $(i/i_d - i)$ *vs.* E for both systems are shown in Figure 3. In each case the reciprocal slopes in the less cathodic portions of these plots are greater than $RT/1F$, but, near the midpoint, the plots decrease in slope and the remaining points are linear with a reciprocal slope less than $RT/1F$. We conclude from these data that the azocines reduce in two coalesced one-electron steps. In the less cathodic region the rate of electron transfer is controlled in part by both steps, while in the more cathodic region the first electron transfer is rate determining. We may also eliminate on the basis of this analysis the possibility of a very rapid disproportionation of the radical anion—such a reaction would make the first electron transfer rate determining over the entire wave.

Classical polarographic theory of irreversible electron-transfer processes[16] may be applied to the linear portion of the plot of log $(i/(i_d - i))$ *vs.* E in Figure 3. At potentials where $(E - E^{\circ\prime}) > 200$ mV, these yield a reciprocal slope of $(RT/\alpha_a n_a F)$ and an intercept proportional to k_e, the standard rate constant for the electron-transfer process. The formal potential, $E^{\circ\prime}$, necessary for calculation of k_e may be obtained from the cyclic voltammetric data, assuming that $\alpha_a n_a \simeq (1 - \alpha_b)n_b$ (*vide infra*). Table III summarizes the data for the azocines and cyclooctatetraenes studied.

Analysis of the cyclic voltammetric data for MA and DMMA according to the methods of Nicholson and Shain[17] indicates that the transfer coefficients for the anodic and cathodic processes are equal within experimental error. The formal potential for the overall two-electron transfer may thus be estimated as the simple mean of $E_{p/2,f}$ and $E_{p/2,r}$, the forward and reverse half-peak potentials from the cyclic voltammetric curves. The data in Table III show that the mean is constant over a wide range of v. In addition, application of the equations for irreversible cyclic voltammetry,[17,18] although they are not strictly valid for data taken on a growing mercury drop, does give values of k_e comparable to but less certain than the polarographic values in Table III.

The dramatic difference between the rates of the electron-transfer reactions for the azocines and COT must be viewed in the context of the very different mechanisms proposed for the two reactions (Figure 4).

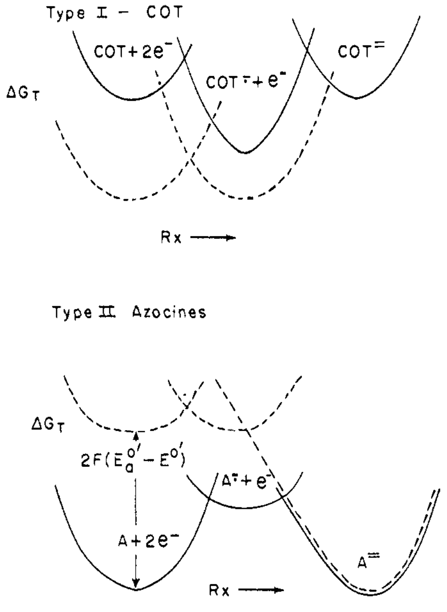

Figure 4. Hypothetical reaction profiles for systems showing one- and two-step polarographic behavior.

In the case of reduction of the azocines, a considerable amount of work must be expended to bring the product (A^{2-}) and reactant (A) to the transition state. For the parent 2-methoxyazocine, this apparently involves compression of the puckered ring to a near-planar configuration while adding the first electron. The second electron transfer then follows rapidly at potentials sufficiently cathodic for observable current flow.

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(16) See Table I, footnote *b*, p 212.

(17) R. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(18) R. S. Nicholson, *ibid.*, **37**, 1351 (1965).

During the backward reaction the work exerted on the dianion at the base of the reoxidation wave is primarily that necessary to remove an electron from the highly delocalized π system. Removal of a second electron from the resulting 9π-electron system follows rapidly, accompanied by ring puckering. The transition states in these two extreme cathodic and anodic cases are obviously not necessarily the same. The values of $\alpha_a n_a$ and $(1 - \alpha_b)n_b$ are both between 0.5 and 1.0 indicating that different transition states are approached from the cathodic and anodic sides, and a high-energy intermediate (presumably the radical anion) is interposed between them. At the potential $E°'$, the two transition states would be expected to be of nearly the same energy (Figure 4), and it is at this intermediate potential that the concentration of the intermediate would be the greatest. We estimate the order of magnitude of $(E°'_a - E°'_b)$ as the difference between the half-peak potentials at a scan rate of 1 V/sec, or roughly -0.4 to -0.6 V. From eq 1–4

$$\Delta G_D = (\Delta G_b - \Delta G_a) = -F(E°'_b - E°'_a) \simeq -0.5 \times 10^5$$

$$[A\cdot^-] = \sqrt{[A][A^{2-}]K_D} \simeq 3.5 \times 10^{-5}[A] \simeq 10^{-8}\ M$$

In the COT reduction, on the other hand, there are two quasi-nernstian one-electron processes, the first somewhat slower than the second. This has been explained[6] by assuming that major portions of the work terms associated with bringing the parent and radical anion to the first transition state are due to widely different organization of the solvent around the two species. Our diffusion-coefficient estimates (Table I) certainly point to large differences between the solvation of the nonpolar hydrocarbon, COT, and the more polar azocines, and equally large differences might be expected between charged and uncharged hydrocarbon. In other respects (conformation and electron delocalization), the two species must not be greatly different at the potential of the first wave, since k_e is relatively large. In the region of potential between the two waves, the COT anion radical is stable and is the predominant species in equilibrium with the electrode. Associated with the second electron transfer are again work terms due to reorganization of solvent, but in this case the difference will be between a radical anion and dianion. In DMF, the difference between the solvation of these two ions is not expected to be large.[6] Apparently the conformational change is again not precipitous between the radical anion and dianion, and the overall electron transfer is rapid. The conclusion that conformational change is not rate determining between parent and radical anion on the one hand, and the radical anion and dianion on the other seems to point to an intermediate conformation for the COT radical anion—neither completely puckered nor completely planar. The analysis of the thermodynamics of the COT reduction supports this hypothesis.

Thermodynamic Considerations. The two-electron reduction reactions of the azocines and cyclooctatetraenes may be conveniently represented in terms of the total free energy change, ΔG, of the system (polyene + 2 electrons) as the reaction proceeds along a continuous coordinate leading from the parent polyene to the dianion product. Figure 4 presents two such hypothetical diagrams which are consistent with the two distinctly different types of electrochemical behavior observed in this work for the azocine and COT systems. It has been assumed in constructing these diagrams that ΔG may be calculated according to eq 7 where

$$\Delta G = \Delta G°_T - nF(E - E°') \tag{7}$$

$E°'$ is the potential of zero net current, and $\Delta G°_T$ is the standard free energy change at potential $E°'$. The major difference between the two types of free-energy profile is the stability of the anion radical relative to disproportionation to the parent and dianion. Behavior corresponding to type I (Figure 4a) is well known;[6,10] however, there have been no previously reported organic reactions corresponding to a profile of type II (Figure 4b), in cases where *no σ bonds have been made or broken.*

The Appendix contains a summary of the relationships between the various kinetic and thermodynamic parameters that describe the behavior of systems (such as those in Figure 4) involving successive one-electron steps.

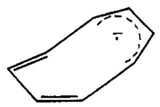
It is of interest to consider the possible implications of the fact that $E°'_a$ is more negative than $E°'_b$ by approximately 0.5 V in the azocine systems, while for COT and MeOCOT, $E°'_a$ is more positive than $E°'_b$ by some 0.25 V. Thus, at the polarographic half-wave potential, the azocine radical anion is easier to reduce than the parent heterocycle. This behavior is unprecedented in organic electrochemistry. The addition of an electron to the radical anion is a process sufficiently exothermic not only to overbalance charge repulsion (~0.4 V ≈ 9.1 kcal/mol), but also to release the free-energy equivalent of $(E°'_a - E°'_b)$ which amounts to another 0.5 V (≈11.5 kcal/mol). Since the source of this exothermicity is presumably the formation of a delocalized 10π-electron aromatic system from a relatively unstable 9π-electron radical anion, it follows that the anion radical must be virtually planar. If it were assumed that the azocine radical anion were nonplanar, then a correspondingly larger amount of energy (a total even greater than 20 kcal/mol) would have to be retrieved from the electron-delocalization process.

In the reduction of COT and its congeners, on the other hand, is evidenced a quite different division of the energy necessary to compress the ring to a planar form. The assumption that the COT radical anion is planar has led[5,6] to an estimate of 0.8 V for $(E°'_a - E°'_b)$ for the hypothetical reduction

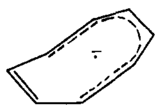
$$\mathrm{COT_{planar}} + e^- \xrightarrow{E°'_a} \mathrm{COT_{planar}}\cdot^- + e^- \xrightarrow{E°'_b} \mathrm{COT_{planar}}^{2-} \tag{8}$$

This is an unprecedentedly large separation between successive one-electron transfers to a planar conjugated hydrocarbon. The logical conclusion is that the second electron addition to COT involves expenditure of a considerable proportion of the energy necessary to compress the eight-membered ring to the presumably planar dianion. If this is true, then the COT anion radical is not planar as previously suggested.

It is likely, however, that the COT anion radical shows some degree of delocalization of charge[5c] as, for example, in the purely hypothetical structures **4** and **5**. Some delocalization of π electrons must exist



4



5

even in the reduction products of noncyclic polyunsaturated systems such as butadienes, since they may be electrochemically reduced[8,19] only if the double bonds present are conjugated. One such open chain conjugated system, divinylacetylene (6) is reported[19] to reduce in 75% dioxane in two one-electron steps at −2.07 and −2.55 V *vs.* sce. While these polaro-

$$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2$$

6

graphic results, obtained in protic solvents, are certain to be affected by protonation reactions subsequent to electron transfer, the general outlines of reducibility and the potential of initial electrochemical reduction do not appear to be grossly affected by these secondary processes.[5,10,20] We therefore conclude that the first electron addition to COT more closely resembles the reduction of an open-chain conjugated olefin, than the reduction of a polycyclic aromatic hydrocarbon. It is not until the addition of the second electron that the ring becomes essentially planar and a fully aromatic 10π-electron system is formed.

A considerable body of data[7,8] indicates that the substitution of a single nitrogen for a single carbon moiety in either an aromatic or a nonaromatic molecule containing alternant double bonds will result in an anodic shift of from 0.6 to 0.8 V in the $E_{1/2}$ of the first polarographic wave. It might thus be anticipated that introduction of the first electron into 2-methoxyazocine would take place some 0.7 V anodic of the first wave of methoxy-COT at −1.87 V *vs.* sce. However, this is not the case. The discharge potential of the two molecules is virtually identical (*vide* Table II). Such behavior is entirely consistent with our hypothesis that ring flattening accompanies addition of the first electron to the azocines but does not accompany the introduction of one electron into methoxy-COT.

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Appendix

The theoretical basis for analysis of successive electron-transfer processes has been summarized by Delahay.[15] The observed current, *i*, is controlled by the rate of passage of the molecule being reduced over the two successive energy barriers in Figure 4b

$$i/2 = FA\{k_{f,a}C_A\theta^{\alpha_a} - k_{b,a}C_{A\cdot^-}\theta^{\alpha_a-1}\} \qquad \text{(A-1)}$$

and

$$i/2 = FA\{k_{f,b}C_{A\cdot^-}\theta^{\alpha_b} - k_{b,b}C_{A^{2-}}\theta^{\alpha_b-1}\} \qquad \text{(A-2)}$$

where A is the electrode area, $k_{f,a}$ and $k_{b,a}$ are the standard heterogeneous rate constants (at $E = E°'$) for the forward and reverse steps, respectively, of the first electron transfer, $k_{f,b}$ and $k_{b,b}$ are the standard rate constants (at $E = E°'$) for the forward and reverse steps, respectively, of the second electron transfer, C_A, $C_{A\cdot^-}$, and $C_{A^{2-}}$ are the concentrations of the parent, anion radical, and dianion, respectively, α_a and α_b are the transfer coefficients for the first and second electron transfers, and $\theta = \exp[(-F/RT)(E - E°')]$.

The standard potentials $E°'_a$ and $E°'_b$ associated with the single electron transfers in eq 1 and 2 above are related to the heterogeneous rate constants by

$$E°'_a = RT/F \ln (k_{f,a}/k_{b,a}) \qquad \text{(A-3)}$$

and

$$E°'_b = RT/F \ln (k_{f,b}/k_{b,b}) \qquad \text{(A-4)}$$

In the case where $E°'_a < E°'_b$, and α_a is near 0.5, the second term on the right-hand side of eq A-1 will be much smaller than the first term where $E - E° >$ 200 mV. Equation A-1 then reduces to

$$i_{irrev} = k_{f,a}C_AFA \exp\left[\frac{-\alpha_a n_a F}{RT}(E - E°')\right] \qquad \text{(A-5)}$$

Similarly, for the oxidation of the dianion A^{2-} at potentials $|E - E°'| > 200$ mV, the relationship $k_{f,b}C_A\theta^{\alpha_b} \ll k_{b,b}C_A = \theta^{\alpha_b-1}$ holds, and the anodic current is described as

$$i_{irrev} = k_{b,b}C_{A^{2-}}FA \times \exp\left[\frac{(1 - \alpha_b)n_b F}{RT}(E - E°')\right] \qquad \text{(A-6)}$$

Equations A-5 and A-6 may be used to obtain information on the forward rate of the first electron transfer and the backward rate of the second electron transfer, respectively. Procedures have been suggested[21,22] for nonlinear best fit to equations such as A-1 and A-2, but the addition of three additional adjustable parameters ($C_{A\cdot^-}$, $k_{b,a}$, and $k_{f,b}$) in this case will make such a fit very uncertain.

Quantitative evaluation of $k_{f,b}$ and $k_{b,a}$ might better await a procedure for independently establishing $C_{A\cdot^-}$, perhaps from electron paramagnetic resonance spectra of equimolar mixtures of parent and dianion. This would reduce the number of adjustable parameters to two, and justify a more complex analysis of this electrochemical data.

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