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ELECTROCHEMICAL CHARACTERIZATION OF AZOCINYL DIANIONS[1a]

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Interest in monocyclic 10π electron systems has been intense in recent years largely because of curiosity concerning the factors that control the somewhat delicate balance between aromaticity and angle strain in such molecules. Results reported to date show that [10]annulenes are stable at ordinary temperatures when bridged by a monoatomic 1,6-substituent,[2] but not otherwise.[3] The nine-membered heterocycle N-carbethoxyazonine, the (4n+2)π homolog of pyrrole, also appears to be labile.[4] In contrast, the isoelectronic cyclononatetraenyl[5] and cyclooctatetraenyl anions[6] enjoy appreciable π-electron stability. Although Hückel theory also predicts comparable stability for the dianion of azocine and monoanion of azonine, attention to date has been directed solely to a study of the carbocyclic congeners. In this communication we wish to record experimental substantiation of the manner in which simple azocines readily undergo two-electron reduction.

Polarograms of five 2-methoxyazocines,[7] together with those of cyclooctatetraene (COT) and methoxy COT, were obtained on 1.25 mM solutions in dry dimethylformamide containing 0.10 M tetrabutylammonium iodide as the supporting electrolyte. The electrochemistry of methoxy COT, the most appropriate link between the 2-methoxyazocine and COT series, has not been previously reported. Although the general polarographic characteristics of methoxy COT resemble very closely those of the parent hydrocarbon, the expected effect of the methoxyl substituent[8] may be seen in the *ca.* 100 mV cathodic shift of both half-wave potentials (Table I).

In contrast, the azocines present a strikingly different electrochemistry. In each instance, only a single polarographic reduction wave is produced, the diffusion current of which is clearly indicative of an overall transfer of two electrons. For 2-methoxyazocine (**1**), the half-wave potential appears very close to that of the first wave of methoxy COT;

Table I. Polarographic Constants of Cyclooctatetraene, Methoxycyclooctatetraene, and Selected 2-Methoxyazocines at 25°.

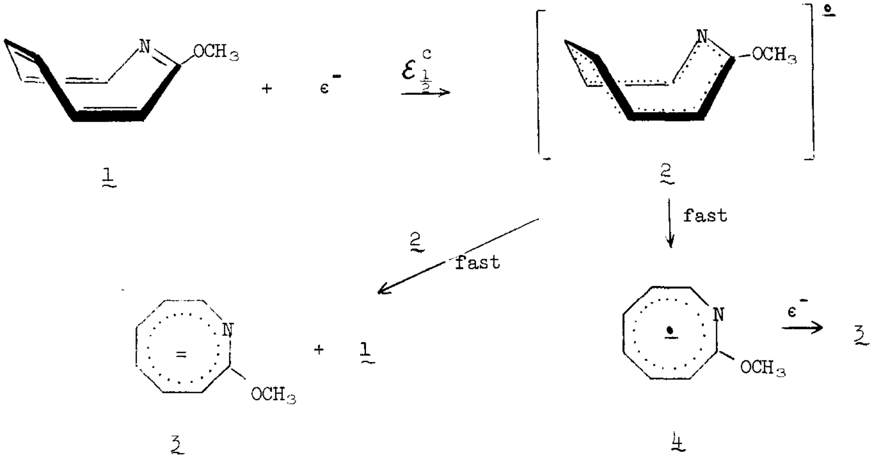
Polyene	$\mathcal{E}_{\frac{1}{2}}$[a]	Slope[b]	i_d[c]
Cyclooctatetraene	-1.74	0.073	7.70[d]
	-1.97	0.077	
Methoxycyclooctatetraene	-1.87	0.083	6.46[d]
	-2.05	0.068	
2-Methoxyazocine	-1.84	0.111	6.69
8-Methyl-2-methoxyazocine	-1.92	0.107	6.33
3,8-Dimethyl-2-methoxyazocine	-2.17	0.100	5.80
4,6,8-Trimethyl-2-methoxyazocine	-2.22	0.116	5.42
3,5,6,8-Tetramethyl-2-methoxyazocine	-2.46	0.103	5.39

[a] Half-wave potentials vs s.c.e. (accuracy ± 0.01 v); values determined at point where log $(i_d-i)/i$ was zero. [b] Reciprocal slope from plot of log $(i_d-i)/i$ vs $\mathcal{E}$; estimated accuracy ± 0.001. [c] Diffusion current in arbitrary units with estimated accuracy of ± 0.05. [d] Values represent the total diffusion current for both waves.

as regards the higher methylated derivatives, incremental cathodic shifts are seen to parallel the extent of alkyl substitution (Table I). The fact that the reciprocal slopes of plots of log $(i_d-i)/i$ vs $\mathcal{E}$ for all of the azocines are significantly greater than 0.059/2 indicates the presence of chemical or electrochemical kinetic complications to simple nernstien electron transfer.

Both cyclooctatetraenes unmistakably undergo reduction by way of two one-electron steps. While the first electron transfer is believed to result in flattening of the polyene ring and formation of a planar radical anion, the second step has been definitely shown to lead to a planar, delocalized aromatic dianion.[9] On the other hand, the observation that azocines give rise uniquely to single two-electron reduction waves suggests that these heterocyclic radical anions are not stable under these conditions. Disproportionation to the related dianion and parent azocine may take place immediately upon generation; alternatively, the radical anions could be much more easily reduced than the starting azocine. In this connection, charge repulsion is understandably such that it will prohibit the second electron transfer from being more facile than the first unless some concomitant process results in a favorable energy gain. In fact, two successive one-electron reduction waves are characteristically separated by about 0.4 v;[9] this value can be considered a reliable measure of the energy necessary to overcome charge repulsion. Consequently, an amount of stabilization equivalent to at least 0.4 v must be available to the azocine radical anions in order to account for the immediate introduction of the second electron in the manner observed.

If an irreversible chemical step (in the present context this would be a conformational modification of a tub-shaped to a planar entity) occurs after addition of the first electron, the reciprocal slope should be 0.06 or larger. Because the azocines exhibit slopes of approximately 0.10 (Table I), we propose that flattening of the ring occurs immediately subsequent to the first electron transfer. The balance of the energy necessary to allow rapid introduction of the second electron logically derives from the favorable aromatic properties of the delocalized 10π electron heteromonocyclic dianions. However, since the rate of disappearance of the azocinyl radical anion is extremely fast, electrochemical methods cannot unequivocally distinguish between the two electron transfer mechanisms.



Further supporting evidence for these conclusions has been derived from cyclic voltammetric studies. In Figure 1 is illustrated the cyclic voltammogram of 3,8-dimethyl-2-methoxyazocine taken at relatively rapid scan rates. As seen in the figure, no evidence was found for a reduction product oxidizable in the vicinity of -2.4 v. Rather, a well-formed two-electron wave which we attribute to the reoxidation of the aromatic azocinyl dianion is seen at approximately -1.4 v. This behavior is typical throughout the series. Clearly, the cathodic and anodic waves are of comparable shape and magnitude, thereby attesting to the overall chemical reversibility of the reduction and reoxidation steps. The very large difference ($\sim$ 1 volt) separating the $\mathcal{E}_{\frac{1}{2}}$ values of the reduction and reoxidation waves can only be reconciled with the fact that the azocines and their dianions possess different molecular conformations, since the overall reversibility precludes the generation of molecular arrangements in which σ bonds have been made or broken. These observations are therefore fully in agreement with the concept that azocinyl dianions are effectively planar and impressively stable to reoxidation.

The above data, together with other spectral and chemical information,[10] make clear that the presence of the nitrogen atom in the 10π-electron system does not affect the capability of the dianion to be highly resonance stabilized and flat. We are currently concentrating our efforts toward studying the effect produced by nitrogen in a number of related anions.[11]

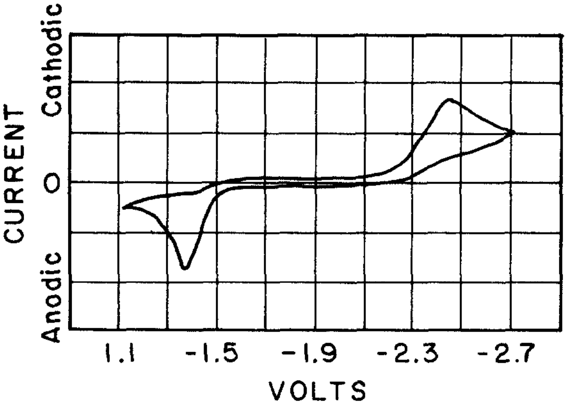


Figure 1. Cyclic voltammogram of 3,8-dimethyl-2-methoxyazocine in DMF. The scan rate was 6.4 v/sec.

REFERENCES AND FOOTNOTES

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