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ELECTROCHEMICAL AND EPR STUDIES ON 1,3,5,7-TETRAPHENYLCYCLOOCTATETRAENE

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The electrochemical[1,2,3] and alkalai metal[4,5] reduction of cyclooctatetraene (COT) have received considerable attention in recent years. In addition a study of the electrochemical behavior of the isoelectronic methyl substituted 2-methoxyazocines has been reported.[6] We wish in this communication to present our initial results on a series of phenylated cyclooctatetraenes and, in particular, on 1,3,5,7-tetraphenylcyclooctatetraene (TPCOT).

COT shows two separate one electron reduction steps electrochemically.[1,3] The 2-methoxyazocines undergo a single two electron reduction which is electrochemically irreversible, but chemically reversible.[6] In contrast to both, TPCOT undergoes electrochemical reduction[7] to the dianion in a single reversible 2 electron wave.

Simple dc polarography at a dropping mercury electrode (dme) showed only one wave with an $E_{1/2}$ value of -1.67 V. The diffusion current, i_d, varied as the square root of the corrected height of the mercury column, indicating linear diffusion conditions. The $E_{3/4} - E_{1/4}$ value is -28 mV. Further, the diffusion current constant, I_d, was calculated to be 3.11 which is nearly the same value observed for the sum of the two one electron waves (2.90) for COT.[8] When small amounts of water are added to the solution, the wave shifts anodically ($E_{1/2}$ = -1.61 V) but retains its original height. In addition, 2 new waves appear with $E_{1/2}$ = -2.00 V and $E_{1/2}$ = -2.20 V; when sufficient water is present, the sum of the diffusion currents for these new waves equals the diffusion current for the original wave. Thus the TPCOT is still reduced to the dianion at the first wave, but now protonates to the two possible isomeric trienes.[9]

Controlled potential electrolysis experiments[7] both in the EPR spectrometer cavity and in a remote vacuum cell system at a potential of -1.7 V produced only diamagnetic colored solutions, further substantiating a 2 electron reduction.

Cyclic voltammetric studies (Fig. 1) also support this conclusion, and provide proof of reversibility. Only one peak is seen on the initial cathodic scan; the anodic half cycle shows the oxidation peak, for $TPCOT^{=}$ back to TPCOT, separated from the cathodic peak by 30 mV, the value predicted for a reversible 2 electron transfer.[10]

Further, at slow sweep rates TPCOT$^{=}$ protonates to the TPCOTH^{-} carbanion which is then detected as an anodic peak at -1.05 V to form TPCOTH$^{\cdot}$; the reduction of TPCOTH$^{\cdot}$back to carbanion is detected by the cathodic peak at -1.10 V on successive (after the first) cycles.[11] The TPCOT dianion is exceptionally stable since a significant anodic peak is still present even at sweep rates as slow as 0.017 V/sec. Addition of small amounts of water eliminates the TPCOTH^{-} $\rightleftharpoons$ TPCOTH$^{\cdot}$ couple, makes irreversible the TPCOT$\rightleftharpoons$TPCOT$^{=}$ couple (no anodic wave) and the cathodic peaks attributed to the isomeric trienes appear at $E_{1/2}$ = -2.00 V and $E_{1/2}$ = -2.20 V.

Additional evidence for the unusual stability of the TPCOT dianion comes from EPR studies employing alkalai metal reduction. TPCOT, when reduced by standard methods using ethereal solvents (THF, DME, diglyme) with an alkalai metal (Li, Na, K), forms only the yellow dianion. No EPR absorption can be detected even at a temperature of -120° C. Even when TPCOT dianion (with K cations) was mixed with an equal amount of unreduced TPCOT plus a large excess of the polyether chelate dicyclohexyl-18-crown-6, no EPR signal could be detected. However, when TPCOT is reduced (Li or K) in the presence of 10% hexamethylphosphoramide,[13] a powerful cation solvating medium, an EPR signal of the planar radical anion appears.

Analysis of the hyperfine structure gives the following coupling constants: for the 4 octagon ring protons (quintet splitting in the ratio 1:4:6:4:1) a_H = 3.30 G, for the 8 ortho and 4 para phenyl protons a_H = 0.40 G, and for the 8 meta protons a_H = 0.20 G. Using a line width of 0.195 G, the spectrum is simulated perfectly with the preceeding values.

The potential required to add the first electron will be determined primarily by the lowest occupied MO energy of the planar system, flattening energy, solvation and outer sphere solvent reorganization energies. On adding phenyl substituents to COT, the potential for adding the first electron should shift anodically due to increased delocalization. However, the increases in flattening and solvent reorganization energies will tend to shift the reduction potential cathodically. The potential of the second electron addition is in all cases shifted anodically by the addition of phenyl groups.

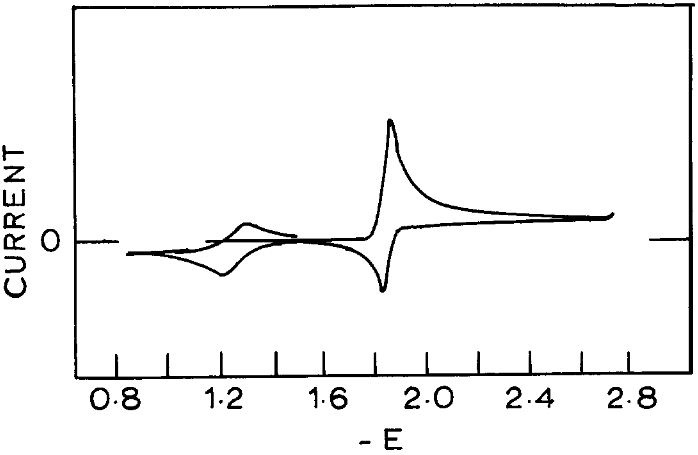
In PCOT (Table I), the potential for addition of the first electron is essentially unchanged from COT, indicating a near cancelling of those factors which affect the first wave. However, the potential of the second electron addition is so close to the first that CV is required to demonstrate it is cathodic of the first. For 1,3,5,7,-TPCOT the energy factors combine to give not only 90 mV anodic shift (relative to COT) but also a reduction potential for the second electron addition that is anodic of the first, hence the 2 electron wave. 1,2,4,7-TPCOT (Table I) appears to have the reduction potential of the second electron addition anodic of the first. However the observed reduction potential, 130 mV cathodic to COT, now reflects the severe steric interaction on flattening between the phenyls in the 1,2 positions. Molecular models substantiate this interaction. Clearly then, ring flattening occurs simultaneously with reduction, whether via a 1 or a 2 electron step.[14]

TABLE I. Polarographic Reduction Data for Cyclooctatetraene and Phenyl Substituted Cyclooctatetraenes

Compound	$E_{\frac{1}{2}}$[a](V)	I_d	n[b]
COT	-1.76 -1.89	1.57[c] 1.33[c]	1 1
PCOT	-1.76	3.50	2
1,3,5,7-TPCOT	-1.67	3.11	2
1,2,4,7-TPCOT	-1.87	3.37	2

[a] All potentials versus SCE. [b] n equals the number of electrons transferred.
[c] In DMF solvent, see Reference 7.

Fig. I Cyclic voltammogram of 1,3,5,7-tetraphenylcyclooctatetraene in CH_3CN at a scan rate of 0.167 V/sec.



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