Electrochemical Reduction of
sym-Dibenzocyclooctatetraene,
sym-Dibenzo-1,5-cyclooctadiene-3,7-diyne, and
sym-Dibenzo-1,3,5-cyclooctatrien-7-yne

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Abstract: A study of the electroreduction of sym-dibenzocyclooctatetraene (DBCOT), sym-dibenzo-1,5-cyclooctadiene-3,7-diyne (DBCOD) and sym-dibenzo-1,3,5-cyclooctatrien-7-yne (DBCOM) in DMF-TBAP solutions was carried out to investigate the effects of differences in the structure of the central eight-membered ring on the electrochemical behavior. The reversible half-wave potentials \( E_{1/2} \), heterogeneous electron-transfer rate constants \( k_s \), transfer coefficients, and pseudo-first-order rate constants of the following chemical reactions were determined by cyclic voltammetric-digital simulation techniques. The results are consistent with reduction of tub-shaped DBCOT to a planar radical anion and dianion and of planar or almost planar DBCOM and DBCOD to planar radical anions. Estimates of the energy of the conformational change were obtained by comparison of \( E_{1/2} \) to calculated energies of the lowest unoccupied molecular orbital and from the \( k_s \) values.

The electrochemical behavior of cyclooctatetraene (COT) and related compounds and the electron spin resonance (ESR) of the associated radical anions have been the subjects of numerous investigations.\(^{2-8}\) The general picture which emerges is that reduction of the tub-shaped COT produces a planar or nearly planar radical anion (COT\(^-\)); the large change in molecular geometry leads to a high activation energy and hence slow electron-transfer rates. The second reduction step to the dianion involves only small changes in geometry and hence more rapid electron transfer. A more detailed explanation of the experimental results requires taking account of solvation changes, ion pairing effects, and following protonation reactions.

Recently, Wong, Garratt, and Sondheimer\(^9\) reported the synthesis of sym-dibenzo-1,5-cyclooctadiene-3,7-diyne (DBCOD) and sym-dibenzo-1,3,5-cyclooctatrien-7-yne (DBCOM) in DMF. The central eight-membered ring in these compounds was reported to be planar, based on the NMR and electronic spectra, and this was confirmed for DBCOD by x-ray crystallography.\(^{10}\) On the contrary, sym-dibenzocyclooctatetraene (DBCOT) is tub shaped, by analogy to COT, while its dianion was reported to be planar, based on the NMR spectra.\(^{11}\) We thought it of interest to compare the electrochemical behavior of DBCOT, which shows a large structural change on reduction, with that of DBCOD and DBCOM, which presumably do not. We describe here studies of the electroreduction of these compounds in DMF solutions by cyclic voltammetry (CV) and other electrochemical techniques and report the reversible half-wave potentials \( E_{1/2} \), rate constants for heterogeneous electron transfer \( k_s \), transfer coefficients \( \alpha \), and estimates of the half-lives of the radical anions and dianions \( t_{1/2} \).

Experimental Section

Chemicals. DBCOT was obtained by photoisomerization of dibenzobarrelene.\(^{12}\) DBCOD was prepared in London by dehydrobromination of 3,4,7,8-tetrafluoro-sym-dibenzo-1,5-cyclooctadiene,\(^9\) sent to Austin, and used after removing polymerized products by passing a pentane solution through a short alumina column. DBCOM was prepared by dehydrobromination of 7,8-dibromo-sym-dibenzo-1,3,5-cyclooctatriene.\(^9\) The product was purified by column chromatography and showed the reported uv spectrum. N,N-Dimethylformamide (DMF) and tetrabutylammonium perchlorate (TBAP) were purified as previously described.\(^{13}\)

Electrochemical Measurements. Solutions were prepared under a helium atmosphere in a Vacuum/Atmosphere Corp. (Hawthorne, Calif.) glove box. All experiments were carried out under a nitrogen atmosphere with positive pressure. The nitrogen gas (prepurified grade) was further purified by passing it over hot copper wire and a Drierite column. Dissolved oxygen in the solution was removed by bubbling nitrogen gas through the solution. A spherical platinum electrode sealed in glass was used as the working electrode in the measurement of electrochemical kinetic parameters. The electrode was polished smooth with 0.5-μm alumina polishing powder before each use. The electrode area, as determined from electrochemical measurements with phthalonitrile, whose diffusion coefficient has been determined at a mercury electrode,\(^{13}\) was 0.177 cm\(^2\). A mercury pool was used as the counter electrode. An aqueous saturated calomel
accomplished by adjusting three parameters, employed for fitting the curves was as follows: the first fit was the separation between the waves, location of the wave on the potential axis and parameters was obtained, $k_s(2)$ was varied to obtain a further refinement; because of the large $k_s(2)$ value, the fit was insensitive to variations in $\alpha(2)$. Finally the potential was adjusted to place the curve correctly on the potential axis, thus yielding $E_{1/2}'(1)$ and $E_{1/2}'(2)$. The best fit yields the results shown in Figure 1 and Table I. The sensitivity of the fit to the various parameters, shown in parentheses in Table I, was estimated by varying these parameters around their best fit values until deviation from the experimental curve could be distinguished. The sensitivity of the fit was improved by examining CV curves over a wide range of scan rate (0.02–0.5 V/s).

The good fit at all scan rates and the sensitivity of the fit to various parameters, shown in parentheses in Table I, was estimated by varying these parameters around their best fit values. The sensitivity of the fit to the various parameters, shown in parentheses in Table I, was estimated by varying these parameters around their best fit values until deviation from the experimental curve could be distinguished. The sensitivity of the fit was improved by examining CV curves over a wide range of scan rate (0.02–0.5 V/s). The good fit at all scan rates and the sensitivity of the fit to various parameters, shown in parentheses in Table I, was estimated by varying these parameters around their best fit values until deviation from the experimental curve could be distinguished.
to the main parameters, $k_0$, $\alpha(1)$, and $\Delta E_{1/2}$, lends some confidence to this procedure.

Exhaustive electrolysis at potentials beyond the cathodic peak showed $n_{app}$ values greater than two. The solution initially turned red-brown upon reduction, with the color fading and disappearing during the 1-h duration of the electrolysis. After reduction two polarographic waves of equal height (each about one-half the height of the wave for the original solution) with $E_{1/2}$'s of $-2.19$ and $-2.59$ V vs. SCE appeared. This observation suggests that the DBCOT dianion, although stable on the CV time scale, undergoes a slow protonation reaction to form dibenzocyclooctatriene during coulometric reduction (as has been observed for COT, which forms 1,3,5- and 1,3,6-cyclooctatriene on reduction).2a,b The observed reduction $E_{1/2}$'s for the dibenzocyclooctatriene are near those for stilbene ($-2.07$ and $-2.36$ V vs. SCE).16 with the more negative potentials observed for the triene being perhaps caused by the greater nonplanarity of this molecule.

We might note that in a study of the reduction of DBCOT in a TBAP-tetrahydrofuran (THF) solution Anderson and Paquette5c observed a single reduction wave, which they assigned to the one-electron reduction to radical anion, with further reduction to the dianion not observable in the available potential range. However, the results found here, as well as similar studies on COT,7 suggest that the wave observed by Anderson et al.5c was a two-electron wave. In this case the R'/R2- wave is shifted towards negative potentials because of the conformational change on reduction and the R'/R2- wave is shifted in a positive direction because of strong ion pairing of the dianion in the THF. A recent study of the reduction of COT in liquid ammonia17 leads to similar conclusions.

**DBCOD.** A dc polarogram of DBCOD showed two well-defined waves at $-1.53$ and $-2.04$ V. Controlled-potential coulometry showed an $n_{app}$ value (faradays/mol) of one for each wave. A typical cyclic voltammogram is shown in Figure 2. The first wave shows no anodic reversal wave at low scan rates (<0.1 V/s), but one appears at high scan rates (>20 V/s), suggesting the presence of a following chemical reaction of the radical anion.15 The $i_{pa}$ of the first wave was linear with $v^{1/2}$ (Figure 3). The $k_1$ value for the first electron transfer was obtained by fitting digital simulation curves to the experimental ones for scan rates where the following chemical reaction of the radical anion was unimportant, assuming the same $D$ value for DBCOD as for DBCOT and $\alpha = 0.5$. The dependence of $i_{pc}$ and $i_{pa}$ (measured from the zero-current baseline after correction for charging current) on $v^{1/2}$ is shown in Figure 3. The solid lines are the calculated ones, assuming $k_1 = 0.05$ cm/s. The same value was obtained from the increase in the peak separation of the cathodic and anodic waves ($\Delta E_{1/2}$) with $v$.15 The rate constant for the following chemical reaction, $k_2$, was calculated from the ratio of $i_{pa}/i_{pc}$, assuming a first-order or pseudo-first-order reaction,16 and with scan rates of 0.1–0.5 V/s. Comparison of the experimental results and digital simulation curves (Figure 4), taking $k_1 = 0.05$ cm/s, yields an average value of $k_1$ of 1.9 s$^{-1}$.

The second reduction wave for DBCOD is completely irreversible, with no anodic reversal wave appearing for scan rates of up to 100 V/s. The dependence of the peak current of the second wave, $i_{pc}(2)$, measured from the decaying current of the first wave as a baseline, on $v^{1/2}$ is shown in Figure 5, where the dotted lines represent theoretical curves for one- and two-electron Nernstian reactions (calculated with $D = 7.3 \times 10^{-6}$ cm$^2$/s, the value for DBCOT). Note that at low scan rates the $i_{pc}(2)$ value follows the $n = 1$ curve, while at high scan rates it follows quite closely the $n = 2$ one. This behavior is opposite to the more frequently observed ECE mechanism behavior where $i_{pc}/v^{1/2}$ decreases from the $n = 2$ to the $n = 1$ level with increasing $v$. A general reaction scheme which accounts for this behavior involves an overall two-electron step followed by coupling with the starting substance, e.g., if A represents the radical anion and B and AB are not electroactive in this potential region

$$\begin{align*}
A + 2c &\rightarrow B \\
B + A &\rightarrow AB
\end{align*}$$
Figure 4. Determination of the rate constant of the following chemical reaction for the radical anion of DBCOD. The vertical axis is the ratio of the anodic to cathodic peak currents (I_E/I_C) and the horizontal axis is the logarithm of a pseudo-first-order rate constant (k1). The solid lines represent the calculated ratio and the dots represent the experimental ones for scan rates of (a) 0.1, (b) 0.2, and (c) 0.5 V/s. The parameters employed for the digital simulation were the same as those of Figure 3 (except for k1). The experimental conditions were those of Figure 2.

When \( u/k2 \) is large, a two-electron wave is observed, while when \( u/k2 \) is small, the overall reaction is \( 2A + 2e^- \rightarrow AB \) and a one-electron wave results. This mechanism is related to the DIM3 scheme of Andrieux, Nadjo, and Savéant, but the initial overall two-electron transfer step is more complex and probably in itself involves a sequence of steps (e.g., electron transfers and protonation or dimerization), since no reversibility is observed for this wave at high scan rates. Note that adsorption effects also tend to cause \( I_E/u^{1/2} \) to increase with \( u \), but the reversal experiments indicate no adsorption of the radical anion and \( I_E(2) \) vs. \( u \) at high \( u \) does not produce a straight line extrapolating to the origin. The complexity of the reaction scheme prevents the determination of the heterogeneous electron-transfer rate of the second reduction step or accurate determination of \( E_{1/2} \) for the \( R^-/R^{2-} \) reaction. They suggest that the dianion of DBCOD is very short-lived, however, with a half-life less than \( 10^{-2} \) s as estimated from the lack of reversal current at \( u = 100 \) V/s. The intermediate B would have a half-life of the order of \( 10^{-1} \) s.

Although controlled-potential coulometry showed an \( n_{app} \) value of one for reduction at both waves, no reduction or oxidation waves were observed in the range of 0 to \(-2.7 \) V vs. SCE following exhaustive electrolysis at either wave. The following reactions of the anion and dianion are thus not simply protonations, since these would lead to DBCOT and ultimately to the dibenzocyclooctatriene. Coupling reactions yielding nonelectroactive products is a possibility and bears further investigation.

**DBCOM.** Since this compound is very unstable in air (changing color from light to dark yellow in several minutes), the solutions were prepared and measurements made immediately after the synthesis from the dibromide. Cyclic voltammograms were not exactly reproducible for different syntheses, but a typical one is shown in Figure 6. The first wave, which showed a reversal current and an \( E_{pc} = -1.76 \) V, was assigned to formation of the radical anion. The heterogeneous electron-transfer rate constant was determined from the variation of the peak separation (\( \Delta E_p \)) with \( u^{1/2} \) (Figure 7) and was found to be 0.06 cm/s. The large second reduction wave at \(-2.16 \) V shows a reversal current and a similar \( I_E(2) \) vs. \( u \) dependence as the second wave for DBCOD. If it is assumed that the reversal wave represents oxidation of the dianion, an estimate of the standard potential for this half reaction can be given (Table I). The amplitude of the wave at \(-2.05 \) V varied for different DBCOM samples with respect to the other peak heights (which, at a given \( u \), showed an essentially constant ratio) and therefore is probably attributable to a side product (probably tert-butoxy-sym-dibenzocyclooctatetraene) which forms during the dehydrobromination reaction; it occurs at exactly the potentials where DBCOT is reduced.
that the conformational change energies for DBCOT and activation of ring inversion 0.7 eV, is in good agreement with estimates for the energy of double and triple bonds were equal; the near equality of those for DBCOT and DBCOM can thus be attributed to large electron repulsion, however, places the well-known correlation of the diffusion coefficients of COT,2a cis-stilbene (SB),16 and diphenylacetylene (DA)25 was employed. For purposes of comparison the \( E_{1/2} \) values of COT,20 cis-stilbene (SB),16 and diphenylacetylene (DA)25 are also plotted. The HMO calculations for COT, DBCOT, DBCOM, and DBCOD were carried out assuming that the molecules were planar and the resonance integrals of the double and triple bonds were equal; the near equality of \( E_{1/2} \) for DA and SB and their good correlation with eq 1 suggests that this latter assumption is reasonable. Note that only the point for DBCOD is near the correlation. The deviations of those for DBCOT and DBCOM can thus be attributed to large conformational changes that occur on reduction of these species to the radicals in agreement with the energy of activation of ring inversion (0.5–0.65 eV).26,27 This suggests that the conformational change energies for DBCOT and DBCOM are about 0.4 and 0.2 eV, respectively.

As concerns the second reduction step, HMO theory predicts an \( E_{1/2} \) which is the same as that for the first. Inclusion of electron repulsion, however, places the \( E_{1/2} \) values above the correlation line, the observed value for COT, 0.7 eV, is in good agreement with estimates for the energy of activation of ring inversion (0.5–0.65 eV).26,27 This suggests that the conformational change energy for DBCOT and DBCOM is near the correlation. The deviations of those for DBCOT and DBCOM can thus be attributed to large conformational changes that occur on reduction of these species to the radicals in agreement with the energy of activation of ring inversion (0.5–0.65 eV).26,27 This suggests that the conformational change energies for DBCOT and DBCOM are about 0.4 and 0.2 eV, respectively.

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References and Notes

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(34) Because a platinum electrode was employed in these measurements, accurate data for the potential of zero charge and the double-layer capacity to allow correction for double-layer effects was unavailable. A mercury electrode could not be employed, since the single-bond-containing species DBCOD and DBCOM react with mercury.

Interaction of Low-Energy Electrons with Conjugated Cyclic Perchlorocarbons

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Abstract: The interactions of low-energy (<10 eV) electrons with 1,2,3,4,5-pentachlorocyclopentadiene and the conjugated cyclic C₅C₆C₇C₈C₉ have been studied. The gas-phase nonbenzenoid aromatic cyclopentadienide anion (C₅Cl₅⁻) has been generated from hexachlorocyclopentadiene and 1,2,3,4,5-pentachlorocyclopentadiene in a mass spectrometer with electron energies of <4 eV. C₅Cl₅⁻ and C₆Cl₆⁻ were the two major carbon-containing anionic species produced from the interaction of low-energy electrons with octachlorocyclooctatetraene and hexachlorobenzene, respectively. Only traces of anions containing carbons were observed from octachlorocycloheptatriene. Ionization efficiency curves for most of the more abundant anions, indicating the resonance capture maxima and showing the overall relationship between the electron energy and the corresponding anion intensities, have been obtained.

When low-energy electrons come in contact with organic molecules in a mass spectrometer, several events may occur. If the electron energies are below the appearance potential of the respective molecule, none of these events may be observed in the conventional positive ion mode of a mass spectrometer. Because of this, very little is known about these low-energy (i.e., <10 eV) electron interactions with organic molecules. In contrast, there are numerous studies in the literature on the ionization, fragmentation, and rearrangements that occur in organic molecules under electron impact at higher energies.

In a continuing effort to better understand these low-energy interactions, we have utilized negative ion mass spectrometry in a study of five compounds: hexachlorocyclopentadiene (I), 1,2,3,4,5-pentachlorocyclopentadiene (II), hexachlorobenzene (III), octachlorocycloheptatriene (IV), and octachlorocyclooctatetraene (V).

Generation of the Pentachlorocyclopentadienide Anion (C₅Cl₅⁻) from C₅Cl₅

The solution chemistry of the pentachlorocyclopentadienide anion has been studied extensively by several investigators. The anion has six π electrons, and therefore, it is considered to be aromatic. In general, the pentachlorocyclopentadienide anion, all of which are thermally unstable at room temperature. They also found the anion to be unstable in solution at temperatures above -30 °C. To our knowledge, there is no previously reported gas phase studies on the cyclopentadienide anion.

We have found that the gas phase pentachlorocyclopentadienide anion (C₅Cl₅⁻) can be generated from hexachlorocyclopentadiene with low-energy electrons in a mass spectrometer. And, except for Cl⁻, it is the major anion produced from hexachlorocyclopentadiene (see Table I). Two distinct