2153 (1971).
(37) D. Brault and M. Rougee, *Biochemistry*, **13**, 4591 (1974).
(38) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, pp 353–357.
(39) G. C. Pimintel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman, San Francisco, Calif., 1960, pp 197–199.
(40) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).
(41) J. H. Wang in "Oxygenases", O. Hayaishi, Ed., Academic Press, New York, N.Y., 1962, p 499.
(42) W. S. Caughey in "Hemes and Hemoproteins", R. E. Estabrook and T. Yonetani, Ed., Academic Press, New York, N.Y., 1966, p 285.
(43) J. P. Collman and C. A. Reed, *J. Am. Chem. Soc.*, **95**, 2048 (1973).
(44) D. Brault and M. Rougee, *Biochem. Biophys. Res. Commun.*, **57**, 654 (1974).
(45) G. C. Wagner and R. J. Kassner, *Biochim. Biophys. Acta*, **392**, 319 (1975).
(46) G. N. LaMar and F. A. Walker, *J. Am. Chem. Soc.*, **94**, 8607 (1972).
(47) F. A. Walker and D. Reis, manuscript in preparation.

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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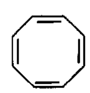
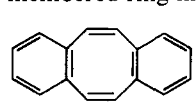
Abstract: A study of the electroreduction of *sym*-dibenzocyclooctatetraene (DBCOT), *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (DBCOD) and *sym*-dibenzo-1,3,5-cyclooctatrien-7-yne (DBCOM) in DMF–TBAP solutions was carried out to investigate the effects of differences in the structure of the central eight-membered ring on the electrochemical behavior. The reversible half-wave potentials ($E_{1/2}{}^r$), 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 $E_{1/2}{}^r$ 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 ($COT\cdot^-$); 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). The central eight-membered ring in these com-


COT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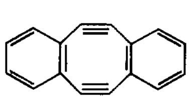
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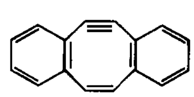
DBCOM

pounds 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 ($E_{1/2}{}^r$), rate constants for heterogeneous electron transfer (k_s), transfer coefficients (α), 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-tetrabromo-*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. (Hawthorn, 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

Table I. Reversible Half-Wave Potentials and Rate Constants

	$R + e \rightleftarrows R\cdot^-$				$R\cdot^- + e \rightleftarrows R^{2-}$			
Compd	$E_{1/2}^r(1)$, V vs. SCE	$k_s(1)$,[a] cm/s	α	$t_{1/2}$,[b] s	$E_{1/2}^r(2)$, V vs. SCE	$k_s(2)$,[a] cm/s	$t_{1/2}$,[b] s	ΔE[c]
DBCOT	−1.935 (±0.003)	0.004 (±0.001)	0.70 (±0.05)	>10^2	−2.020 (±0.003)	0.02 (±0.01)	>10^2	0.085
DBCOD	−1.610 (±0.003)	0.05 (±0.01)		0.3	−2.1[d] (±0.1)		<10^{-2}	0.5
DBCOM	−1.730 (±0.003)	0.04 (±0.01)		>10^2	−2.13 (±0.01)		>10^2	0.40

[a] Uncorrected for the diffuse d.l. effect. [b] Half-life of the product of electron transfer ($R\cdot^-$ or R^{2-}) assuming a pseudo-first-order chemical reaction. [c] $\Delta E = E_{1/2}^r(1) - E_{1/2}^r(2)$. [d] Large uncertainty in this value because of rapidly following chemical reaction of R^{2-} and kinetic complications in this wave.

electrode (SCE), used as the reference electrode, was separated from the solution by two medium-porosity fritted-glass disks and an agar salt bridge. A three-electrode configuration was employed, with iR drop compensation adjusted to be almost equal to the uncompensated solution resistance (ca. 80 Ω). No appreciable current appeared to −2.30 V vs. SCE with the Pt electrode and to −2.70 V with the dropping mercury electrode (DME) in the background solution (DMF-0.5 M TBAP). A PAR Model 170 electrochemistry system (Princeton Applied Research Corp., Princeton, N.J.) or the combination of a PAR Model 173 potentiostat and a PAR Model 175 universal programmer were used for electrochemical experiments. Current-voltage curves were recorded on a Houston Instrument Model 2000 x-y recorder or on a Tektronix Type 564 storage oscilloscope.

Results

DBCOT. A dc polarogram of DBCOT showed one wave with a half-wave potential, $E_{1/2}$, of −1.95 V with no other waves up to −2.60 V in a 0.5 M TBAP-DMF solution at the DME. The limiting current and diffusion current constant corresponded to a two-electron reduction wave, i.e., the diffusion coefficient, D, determined from the diffusion current at the DME was 7.3×10^{-6} cm²/s (assuming $n = 2$) as compared to anthracene, a molecule of similar size, which has a D of 7.7×10^{-6} cm²/s in this medium. CV at slow scan rates showed one reduction wave with a single anodic wave on reversal (Figure 1). At scan rates over 2 V/s, however, the anodic wave was separated into two peaks. Ac polarography showed a very broad wave with the width at a half-wave height of about 150 mV. These observations suggest that the reduction wave consists of two closely spaced consecutive one-electron transfer reactions. The sharp peak of the cathodic wave and the broad peak of the anodic one suggests that the first electron-transfer step is slow, while the second is fast. Since the ratio of anodic to cathodic peak heights (i_{pa}/i_{pc}) is independent of the scan rate (v), the contribution of any following chemical reaction is negligible for the CV time scale. At low v a shoulder appears on the rising portion of the cathodic wave, while the anodic wave remains very round. This is a characteristic feature of an α larger than 0.5 for the first wave.[14] Digital simulations[15] for CV of this system, assuming different values for the reversible half-wave potentials ($E_{1/2}^r$), heterogeneous rate constants for electron transfer (k_s), and transfer coefficients (α) for the two-electron transfer steps, were carried out. The procedure employed for fitting the curves was as follows: the first fit was accomplished by adjusting three parameters, $k_s(1)$, $\alpha(1)$, and the separation between the waves, $\Delta E_{1/2}^r$, since the absolute location of the wave on the potential axis is not needed in fitting the curve and $k_s(2)$ can be set at a large value, based on the behavior of the COT system. After a best fit based on these 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 $E_{1/2}^r(1)$ and $E_{1/2}^r(2)$. 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

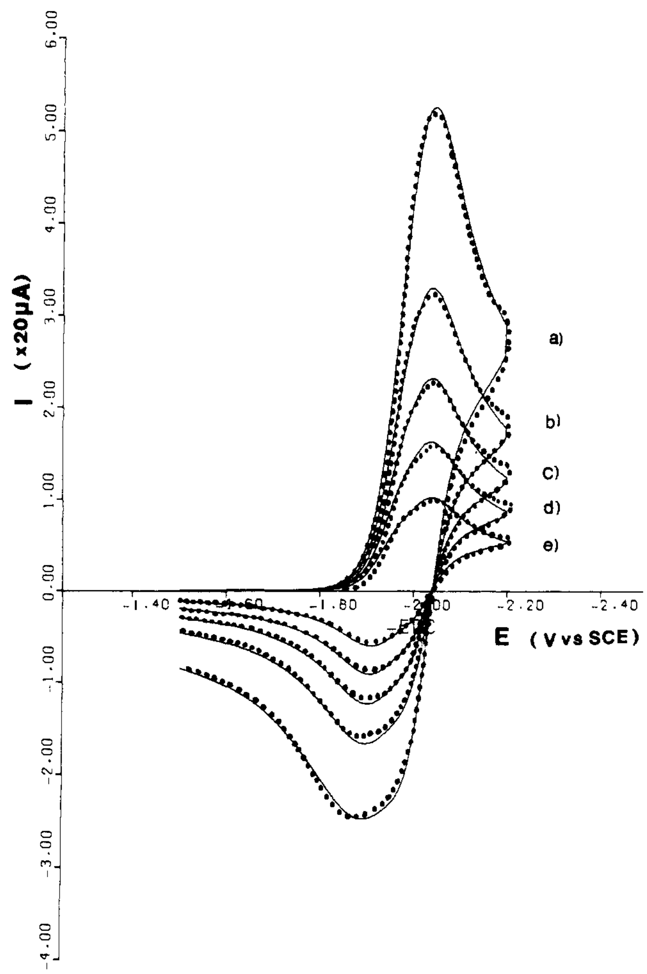

Figure 1. Digital simulation of the cyclic voltammogram for 0.66 mM DBCOT-0.5 M TBAP of DMF solution. The points are experimental results and the solid lines are the simulation with the parameters $E_{1/2}^r = -1.935$; $k_s = 0.004$; $\alpha = 0.70$ for the first reduction and $E_{1/2}^r = -2.020$; $k_s = 0.02$; $\alpha = 0.50$ for the second reduction. The area of the platinum electrode was 0.177 cm². D was assumed to be the same for the neutral molecule and anion, 7.30×10^{-6} cm²/s. The scan rates were (a) 0.5, (b) 0.2, (c) 0.1, (d) 0.05, and (e) 0.02 V/s.

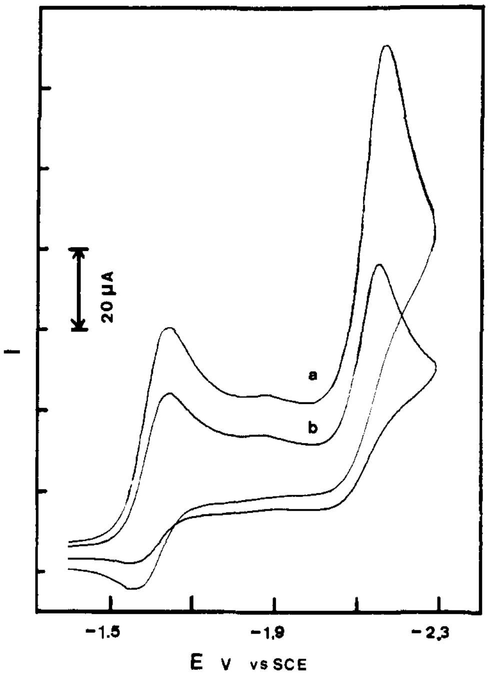

Figure 2. Cyclic voltammogram of DBCOD. The solution contained 0.54 mM DBCOD and 0.5 M TBAP in DMF. Scan rates at Pt electrode: (a) 0.5 and (b) 0.2 V/s.

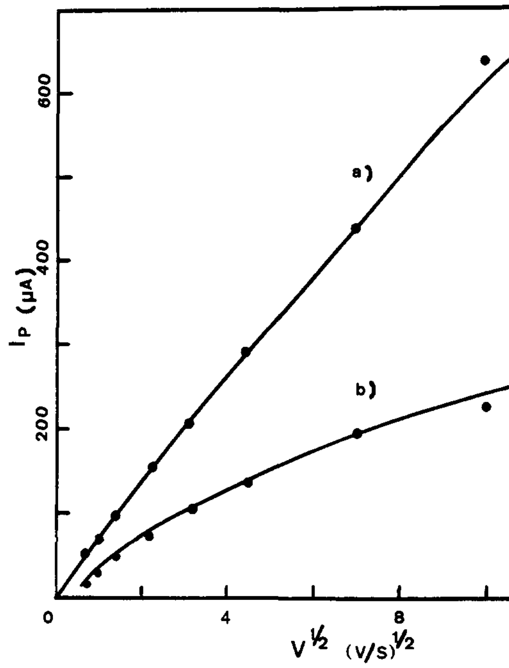

Figure 3. Dependence of peak height (i_p) on square root of the scan rate ($v^{1/2}$) for the (a) cathodic and (b) anodic (reversal) waves for DBCOD. The dots are experimental values and the solid lines are simulated with the parameters for the digital simulation $E_{1/2}{}^r = -1.610$; $k_s = 0.05$; $\alpha = 0.50$; $k_1 = 0$; $D = 7.30 \times 10^{-6}$. The anodic peak current was defined as the height from the base line after removing the contribution of the charging current. The conditions of the system are the same as that of Figure 2.

to the main parameters, $k_s(1)$, $\alpha(1)$, and $\Delta E_{1/2}{}^r$, 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 *cis*-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 Paquette[8c] 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.[8c] was a two-electron wave. In this case the $R/R\cdot^-$ wave is shifted towards negative potentials because of the conformational change on reduction and the $R\cdot^-/R^{2-}$ 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 ammonia[17] 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 (>2 V/s), suggesting the presence of a following chemical reaction of the radical anion.[18] The i_{pc} of the first wave was linear with $v^{1/2}$ (Figure 3). The k_s 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 $k_s = 0.05$ cm/s. The same value was obtained from the increase in the peak separation of the cathodic and anodic waves (ΔE_p) with v.[15] The rate constant for the following chemical reaction, k_1, was calculated from the ratio of i_{pa}/i_{pc}, assuming a first-order or pseudo-first-order reaction,[18] and with scan rates of 0.1–0.5 V/s. Comparison of the experimental results and digital simulation curves (Figure 4), taking $k_s = 0.05$ 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 $i_p/v^{1/2}$ *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

$$A + 2e \rightarrow B$$

$$B + A \xrightarrow{k_2} AB$$

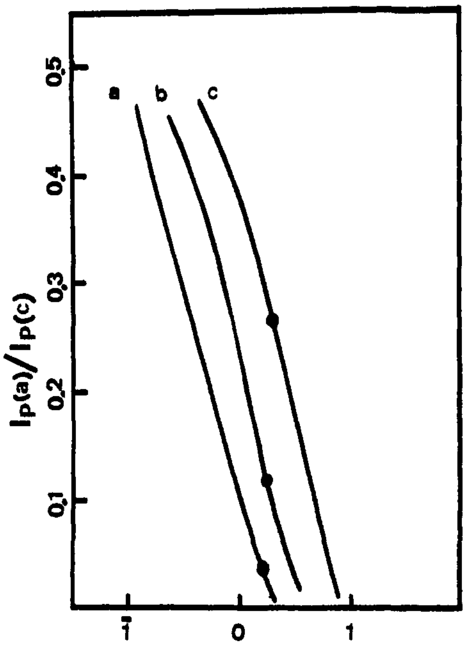

Figure 4. Determination of the rate constant of the following chemical reaction for the radical anion of DBCOD. The vertical axis is the ratio of the anodic to cathodic peak currents (i_{pa}/i_{pc}) and the horizontal axis is the logarithm of a pseudo-first-order rate constant (k_1). The solid lines 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 k_1). The experimental conditions were those of Figure 2.

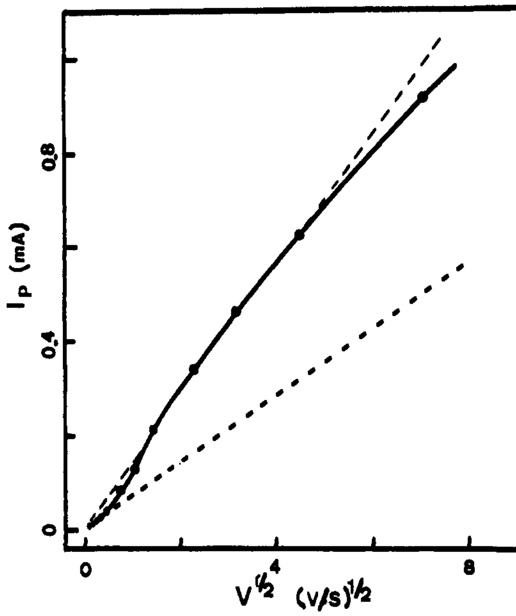

Figure 5. Dependence of the cathodic peak current (i_p) on the square root of the scan rate ($v^{1/2}$) for the second wave of DBCOD. The solid line represents the experimental result. The dotted line represents theoretical values for a Nernstian reversible reaction with $n = 1$ and 2 and $D = 7.30 \times 10^{-6}$ cm^2/s. Peak current was measured from the decaying current of the first wave as the base line.

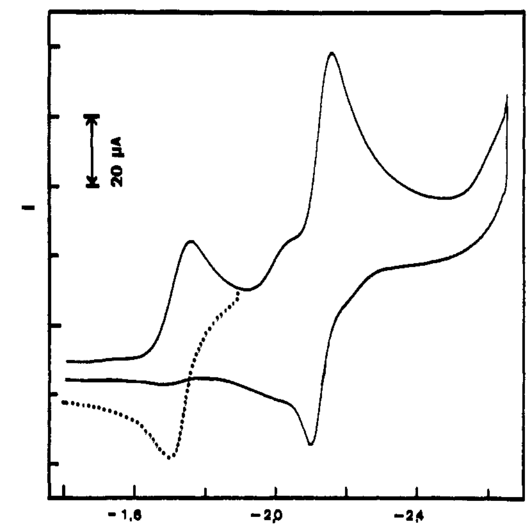

Figure 6. Cyclic voltammogram of DBCOM. The solution contained 0.4 mM DBCOM and 0.5 M TBAP in DMF. The scan rate at the hanging mercury-drop electrode was 0.2 V/s. The dotted curve represents the anodic wave when the switching potential was −1.80 V.

When v/k_2 is large, a two-electron wave is observed, while when v/k_2 is small, the overall reaction is 2A + 2e → AB and a one-electron wave results. This mechanism is related to the DIM3 scheme of Andrieux, Nadjo, and Savéant,[19] 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 $i_p/v^{1/2}$ to increase with v, but the reversal experiments indicate no adsorption of the radical anion and $i_{pc}(2)$ vs. v at high v 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 $E_{1/2}{}^r$ for the $R\cdot^-/R^{2-}$ 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 $v = 100$ 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[9] (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 (ΔE_p) with v^{15} (Figure 7) and was found to be 0.04 cm/s. The large second reduction wave at −2.16 V shows a reversal current and a similar $i_{pc}(2)$ vs. v 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 v, showed an essentially constant ratio) and therefore is probably attributable to a side product (probably *tert*-butoxy-*sym*-dibenzocyclooctatetraene)[20] which forms during the dehydrobromination reaction; it occurs at exactly the potentials where DBCOT is reduced.

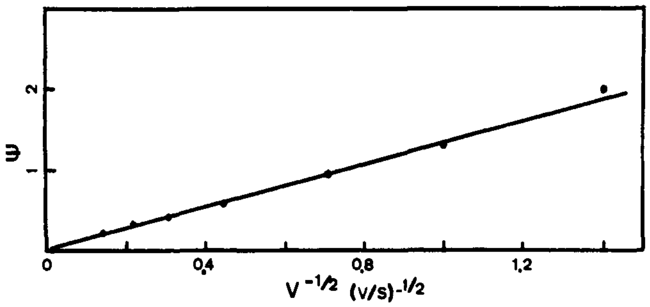

Figure 7. Determination of the heterogeneous rate constant k_s of the first reduction of DBCOM at a Pt electrode from the change of peak separation with scan rate (Nicholson's[15] method). $\psi = k_s/\sqrt{\pi a D}$, $a = nFv/RT$, and $D = 7.30 \times 10^{-6}$ cm²/s.

Discussion

Estimated reversible half-wave potentials ($E_{1/2}{}^r$) for the half reactions (i.e., corrected for kinetics of the heterogeneous and following homogeneous reactions) are given in Table I. Since the diffusion coefficients of R, $R\cdot^-$, and R^{2-} are probably not very different, these values are close to the standard potentials (vs. SCE). The values are also plotted with respect to the well-known correlation of $E_{1/2}{}^r$ vs. the energy of the lowest unoccupied molecular orbital (LUMO) determined by Hückel MO calculations (m_{m+1}, in units of β) in Figure 8.[21-24] The equation given by Streitweiser and Schwager, corrected to an SCE reference electrode,[23]

$$E_{1/2}{}^r = 2.41 m_{m+1} - 0.91 \text{ (V vs. SCE)} \tag{1}$$

was employed. For purposes of comparison the $E_{1/2}{}^r$ values of COT,[2a] *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 $E_{1/2}{}^r$ 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 radical anions. If the deviation from the correlation is taken as an estimate of the energy needed to change from the tub form to a planar one, 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 energies for DBCOT and DBCOM are about 0.4 and 0.2 eV, respectively.

As concerns the second reduction step, HMO theory predicts an $E_{1/2}{}^r$ which is the same as that for the first. Inclusion of electron repulsion, however, places the $E_{1/2}{}^r(2)$ value about 0.4–0.5 V more negative than $E_{1/2}{}^r(1)$.[21,24,28,29] The fact that all three compounds show $E_{1/2}{}^r(2)$ values near one another and 0.4–0.5 V above the correlation line suggests a similarity in structure between the radical anion and the dianion. The results suggest that the tub-shaped DBCOT is reduced to a planar radical anion. Although Carrington et al.[30] first suggested on the basis of ESR measurements that $DBCOT\cdot^-$ was nonplanar, Katz et al.[11] favored a planar conformation. Our results also confirm[9,10] that DBCOD and DBCOM are planar or nearly so.

The heterogeneous electron-transfer rate constants are also consistent with the preceding structural arguments. The general experimental and theoretical[31] findings are that electron-transfer reactions which involve large configurational changes (i.e., large inner-sphere reorganizational energies) are slower than similar ones without such changes. Thus for COT, $k_s(R/R\cdot^-) = 0.002$ cm/s and $k_s(R\cdot^-/R^{2-}) = 0.15$ cm/s². The

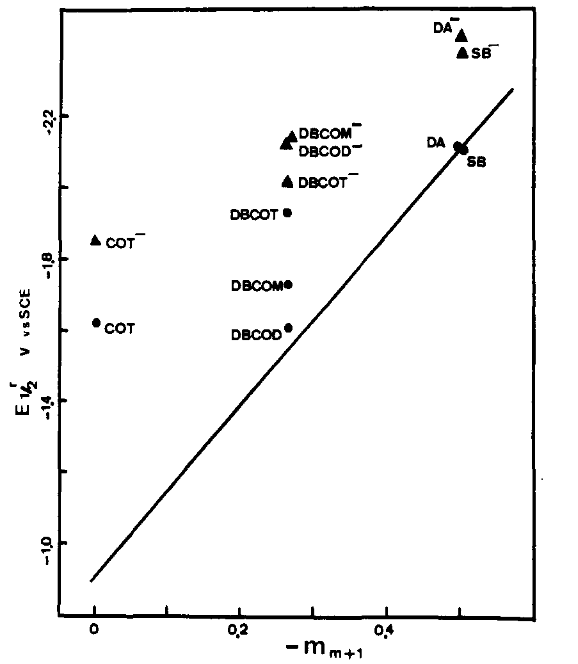

Figure 8. Comparison of the half-wave potentials with the energy of the lowest unoccupied molecular orbital (LUMO) calculated by Hückel theory. The horizontal axis is the coefficient of the LUMO in units of β. Experimental values for (●) first and (▲) second reduction waves. Line is the theoretical correlation. Abbreviations: COT, cyclooctatetraene; DA, diphenylacetylene; SB, *cis*-stilbene.

behavior of DBCOT is similar to COT, with a slower electron transfer for tub-shaped parent to planar radical anion than for reduction to the planar dianion. For the planar DBCOM and DBCOD the $k_s(R\cdot^-/R^{2-})$ values are an order of magnitude larger. A measure of the energy of the conformational change during electron transfer can be obtained by application of Marcus' theory.[31] The free energy of activation ($\Delta G^{\ddagger}$) can be expressed by the equation

$$\Delta G^{\ddagger} = m^2(\lambda_o + \lambda_i) + w^r \tag{2}$$

where λ_o is the solvation reorganization energy, λ_i is the inner sphere reorganization energy, w^r is the work term, which represents the work needed to bring the reactant to the reaction site at the electrode, and m is a parameter (usually close to one-half) which is determined by the total free-energy change in the electron transfer. If we assume the difference in rate between DBCOT and DBCOD can be ascribed to the contribution from λ_i, then we can roughly estimate its magnitude. The rate constant is related to the free energy of activation by

$$k_s = Z \exp(-\Delta G^{\ddagger}/kT) \tag{3}$$

where Z is the collision number at the electrode (about 10^4). From the measured k_s values and eq 3, we obtain 0.065 eV as the difference of the free energy of activation between DBCOT and DBCOD. If we assume that w^r is equal for these substances and $m = 1/2$, then we obtain a λ_i of about 0.26 eV. This quite rough estimate is not too far from that based on the half-wave potential measurements. The k_s values for the reduction of DBCOD and DBCOM appear anomalously small when compared, for example, with those for perylene and anthracene (5 cm/s, uncorrected for double layer effects), which are of similar size and reduce in the same region of potentials.[32,33] This perhaps can be ascribed to some residual conformational changes upon reduction, such as changes in lengths of the strained sp triple bonds or perhaps to some specific interactions with the electrode surface.

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References and Notes

(1) (a) University of Texas at Austin; (b) University College.
(2) (a) R. D. Allendoerfer and P. H. Rieger, *J. Am. Chem. Soc.*, **87**, 2336 (1965); (b) R. D. Allendoerfer, *ibid.*, **97**, 218 (1975); (c) B. J. Huebert and D. E. Smith, *J. Electroanal. Chem.*, **31**, 333 (1971).
(3) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784, 3785 (1960).
(4) S. Z. Goldberg, K. N. Raymond, C. A. Harmon, and D. H. Templeton, *J. Am. Chem. Soc.*, **96**, 1348 (1974).
(5) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 2360 (1963).
(6) F. J. Smentowski and G. R. Stevenson, *J. Am. Chem. Soc.*, **91**, 7401 (1969); *J. Phys. Chem.*, **73**, 340 (1969).
(7) A. J. Fry, C. S. Hutchins, and L. L. Chung, *J. Am. Chem. Soc.*, **97**, 591 (1975).
(8) (a) D. R. Thielen and L. B. Anderson, *J. Am. Chem. Soc.*, **94**, 2521 (1972); (b) L. B. Anderson, J. F. Hanson, T. Kakihana, and L. A. Paquette, *ibid.*, **93**, 161 (1971); (c) L. B. Anderson and L. A. Paquette, *ibid.*, **94**, 4915 (1972).
(9) H. N. C. Wong, P. J. Garratt, and F. Sondheimer, *J. Am. Chem. Soc.*, **96**, 5604 (1974).
(10) R. Destro, T. Pilati, and M. Simonetta, *J. Am. Chem. Soc.*, **97**, 658 (1975).
(11) T. J. Katz, M. Yoshida, and L. C. Siew, *J. Am. Chem. Soc.*, **87**, 4516 (1965).
(12) P. W. Rabideau, J. B. Hamilton, and L. Friedman, *J. Am. Chem. Soc.*, **90**, 4465 (1968).
(13) H. Kojima and A. J. Bard, *J. Electroanal. Chem.*, **63**, 117 (1975).
(14) R. S. Nicholson, *Anal. Chem.*, **37**, 1351 (1965).
(15) (a) S. W. Feldberg in "Electroanalytical Chemistry", Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1969, Chapter 4; J. S. Mattson, H. B. Mark, Jr., and H. C. MacDonald, Jr., Eds., "Computers in Chemistry and Instrumentation", Vol. 2, Marcel Dekker, New York, N.Y., 1972, Chapter 7.
(16) S. Wawzonek and D. Wearring, *J. Am. Chem. Soc.*, **81**, 2067 (1959).
(17) (a) W. Smith and A. J. Bard, *J. Electroanal. Chem.*, in press; (b) W. Smith, Dissertation, University of Texas at Austin, 1974.
(18) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964); **37**, 178 (1965).
(19) C. P. Andrieux, L. Nadjo, and J. M. Savéant, *J. Electroanal. Chem.*, **42**, 223 (1973).
(20) H. N. C. Wong and F. Sondheimer, unpublished experiments.
(21) M. Peover, in "Electroanalytical Chemistry", Vol. 2, A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1967, Chapter 1.
(22) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961.
(23) A. Streitwieser, Jr., and I. Schwager, *J. Phys. Chem.*, **66**, 2317 (1962). The potential was converted from *V* vs. Hg pool to *V* vs. SCE using the comparative data for anthracene, −1.41 V vs. Hg pool and −1.92 vs. SCE.[2]
(24) A. J. Bard, K. S. V. Santhanam, J. T. Maloy, and J. Phelps, *Discuss. Faraday Soc.*, 167 (1968).
(25) R. E. Sioda, D. O. Cowan, and W. S. Koski, *J. Am. Chem. Soc.*, **89**, 230 (1967).
(26) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962); F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *ibid.*, **86**, 3576 (1964).
(27) D. E. Gwynn, G. M. Whitesides, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 2862 (1965).
(28) N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1953).
(29) M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Am. Chem. Soc.*, **91**, 7521 (1969).
(30) A. Carrington, H. C. Longuet-Higgins, and P. F. Todd, *Mol. Phys.*, **8**, 45 (1964).
(31) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).
(32) H. Kojima and A. J. Bard, *J. Am. Chem. Soc.*, **97**, 6317 (1975).
(33) 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 triple-bond-containing species DBCOD and DBCOM react with mercury.[16,25]

Interaction of Low-Energy Electrons with Conjugated Cyclic Perchlorocarbons[1a]

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Abstract: The interactions of low-energy (<10 eV) electrons with 1,2,3,4,5-pentachlorocyclopentadiene and the conjugated cyclic C_5, C_6, C_7, and C_8 perchlorocarbons have been studied. The gas-phase nonbenzenoid aromatic cyclopentadienide anion ($C_5Cl_5^-$) has been generated from hexachlorocyclopentadiene and 1,2,3,4,5-pentachlorocyclopentadiene in a mass spectrometer with electron energies of <4 eV. $C_8Cl_6^-$ and $C_6Cl_6^-$ 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 ($C_5Cl_5^-$) from C_5Cl_6. The solution chemistry of the pentachlorocyclopentadienide anion has been studied extensively by several investigators.[2,3] The anion has six π electrons, is considered to be aromatic, and, therefore, should possess some degree of stability. Wulfsberg and West have prepared several salts of the pentachlorocyclopentadienide anion, all of which are thermally unstable at room temperature.[2] They also found the anion to be unstable in solution at temperatures above −30 °C. To our knowledge, there are no previously reported gas phase studies on the cyclopentadienide anion.

We have found that the gas phase pentachlorocyclopentadienide anion ($C_5Cl_5^-$) 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