shortage of length to fill the space or:

$$x_gA(\Delta n)l = \text{volume vacant space} \tag{14}$$

x_g is the number of moles of guest per mole of dodecyl chain; $\Delta n = (12 - n)$, where n is the number of carbons in the guest chain length. Using (11) and (12) with (10), we obtain:

$$\frac{K}{2.25}\left\{\sum_i\left[\frac{(\Delta\nu_i)_{\mathrm{ng}}}{(\Delta\nu_1)_{\mathrm{ng}}} - \frac{(\Delta\nu_i)_{\mathrm{wg}}}{(\Delta\nu_1)_{\mathrm{wg}}}\right]\right\} = \Delta n x_g \tag{15}$$

Δn does not contain information about the defects in the shorter chain, which is also not an all-trans chain. A satisfactory plot (Figure 5) of the summation term on the left-hand side of eq 15 against the assumed Δn reveals that the basic model of avoidance of free volume in bilayers is a determining factor in the resultant bilayer thickness. The simple proportionality of eq 15 is not precisely followed because Δn is not really an integer as we have assumed. It is evident, however, that the shortening by one segment has the smallest relative effect as would be expected. The decrease in bilayer thickness increases with the shorter and shorter guest chains.

This result has important consequences in biological bilayers since lipids such as cholesterol have not only a stiffer backbone, a point previously discussed, but also a shorter length than most other lipids. This, along with other heterogeneities in length of lipid chains in the biological mix, can be a useful factor in accommodation to the required conformation to local protein inclusions of the bilayer thickness.

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Electron-Transfer Reactions and Associated Conformational Changes. Electrochemical Reduction of Some Vicinal Dibromides

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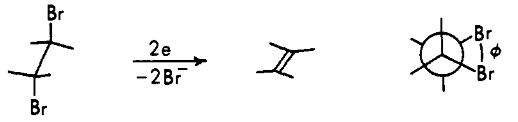
Abstract: The effect of molecular conformation on the electrochemical reduction of derivatives of *trans*-1,2-dibromocyclohexane (**1**–**4**) and substituted 1,2-dibromoethanes (**5**–**8**) has been investigated by low-temperature cyclic voltammetry. Reduction via conformations with antiperiplanar bromine atoms is preferred and conformational interconversion prior to electron transfer was observed in *trans*-1,2-dibromocyclohexane (**1**), 1,1-dimethyl-*trans*-3,4-dibromocyclohexane (**2**), *meso*- and *dl*-1,2-dibromo-1,2-diphenylethane (*meso*-**5** and *dl*-**5**), and 2,3-dibromo-2,3-dimethylbutane (**8**). Digital simulation of the low-temperature voltammetric data has provided thermodynamic and kinetic information on the conformational interconversion in **1**, **2**, **5**, and **8**. The energy barriers to conformational interconversion in *meso*- and *dl*-2,3-dibromobutane (*meso*-**6** and *dl*-**6**) are quite small, and conformational effects in the electrochemical reduction of **6** could not be detected at temperatures as low as −135 °C. 1-Methyl-*cis*-3,*trans*-4-dibromocyclohexane (**3**), 1-methyl-*trans*-3,*cis*-4-dibromocyclohexane (**4**), and *meso*- and *dl*-3,4-dibromo-2,5-dimethylhexane (*meso*-**7** and *dl*-**7**) exist almost entirely in a single conformation. Voltammetric peak potentials of **3**, **4**, *meso*-**7**, and *dl*-**7** reflect the geometry of their principal conformation.

In the past 10 years, direct experimental evidence has indicated that in certain cases there is a distinct structural arrangement of either the product or reactant which is preferred in an electrode reaction. Conformational effects may be manifested prior to electron transfer, following electron transfer, concurrently with electron transfer, or some combination of all three. If these effects are to be observed by modern electrochemical methods, the electrode reactions of different conformers (or isomers) must occur at potentials different enough to be resolved by these methods. This dissimilarity in potential can have a thermodynamic basis or be caused by differences in rate constants for the heterogeneous electron-transfer reactions or coupled chemical reactions of the conformers.

Examples of structural rearrangement prior to electron transfer have been found in cases where two different conformations react at an electrode at distinctly different potentials.[1,2] The electrochemical reaction will proceed via the more readily reduced (or oxidized) conformer. The most prevalent cause of different molecular conformations exhibiting separate electron-transfer processes is an acceleration in the rate of the electron-transfer reaction for a particular geometry.

Scheme I



Conformational changes have also been observed to occur following electron transfer. Most commonly reaction of a principal conformation (or isomer) at the electrode produces a short-lived intermediate which undergoes structural rearrangement to a preferred geometry. Many examples of electrochemically induced isomerizations have been reported for activated olefins[3] and or-

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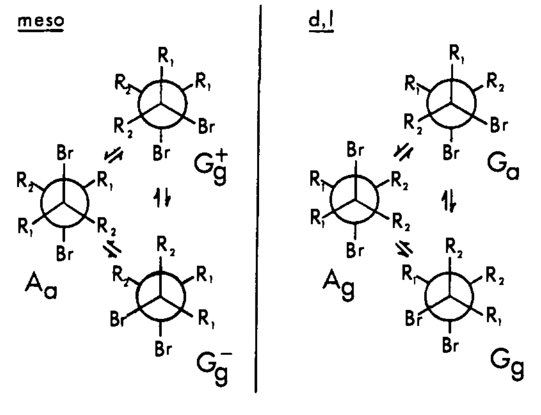
Scheme II



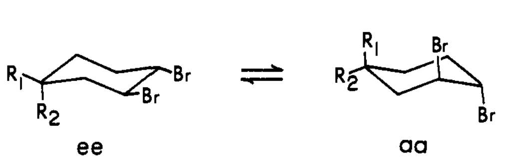
ganometallic complexes.[4] In addition, highly hindered ethylenes[5] exhibit electrochemically induced structural changes.

In certain cases it is not possible to distinguish whether conformational changes occur concurrently with or subsequent to electron transfer. A slow rate of the electron-transfer reaction is characteristic of significant structural rearrangement occurring along with electron transfer. Perhaps the most intensively investigated example of this third type of conformational effect is the reduction of cyclooctatetraene and related compounds.[6]

Previous studies have indicated that the molecular conformation of a vicinal dibromide should play an important role in its reaction at an electrode. A significant body of literature regarding the electrochemical reduction of vicinal dibromides has accumulated through the years and has been reviewed in several places.[7] It was established quite early that the electrochemical reduction of vicinal dihalides produces olefin in a two-electron process.[8] The reductive elimination has been found to be quite stereospecific; reaction via the antiperiplanar conformation is preferred.[9] The reaction is often represented as an essentially concerted process with no detectable intermediates. Attempts to trap carbanionic intermediates during electrolysis of seven representative dihalides were unsuccessful.[9a]

Orbitals in the reactant molecule are in the best position to be converted rapidly into the π bond of the product olefin when they are coplanar. The dihedral angle, ϕ (Scheme I), has been found to be the most important parameter governing the half-wave potentials of rigid cyclic vicinal dibromides.[10] When $\phi = 0°$ or 180° corresponding to the synperiplanar and antiperiplanar arrangements, the pertinent orbitals are coplanar and reduction occurs quite readily.

trans-1,2-Dibromocyclohexane (**1**) exists in two principal conformations, one having equatorial bromine atoms (**1ee**) and the other having axial bromine atoms (**1aa**). At room temperature, reduction occurs quite readily via **1aa** ($\phi \sim 180°$).[10] Recently a low-temperature study of the electrochemical reduction of **1** has been reported.[2] Between −60 and −90 °C, a second reduction process was found to grow in at more negative potentials at the expense of the first peak. This second reduction process was ascribed to the direct reduction of **1ee** ($\phi \sim 60°$). Here we report additional studies of **1** undertaken to obtain improved results at low temperatures. Derivatives of *trans*-1,2-dibromocyclohexane (**2–4**) have also been investigated in search of similar conformational effects.



1, $R_1 = R_2 = H$
2, $R_1 = R_2 = CH_3$
3, $R_1 = CH_3$; $R_2 = H$
4, $R_1 = H$; $R_2 = CH_3$

We have also investigated the electrochemical behavior of several acyclic vicinal dibromides. When each carbon in ethane has the same three different substituents, three isomers, *meso* and a *dl* pair, will exist. Each of these isomers has three possible staggered conformations. In the case of substituted 1,2-dibromoethanes, one conformer has anti bromine atoms while the other two conformers have bromine atoms in a gauche position. The conformers of *meso* and one member of a *dl* pair are shown in Scheme II. A and G denote anti and gauche bromine atoms, while subscripts a and g refer to anti and gauche alkyl or aryl groups. The two meso G_g conformers are mirror images and are distinguished by superscripts + and −.

In the absence of severe molecular distortions, conformers with gauche bromine atoms have dihedral angles of about 60° while conformers with anti bromine atoms have $\phi \sim 180°$. The barriers for conformational interconversion in the dibromoethanes are somewhat lower than in the cyclohexanes so it was necessary to examine their electrochemical behavior at the lower limit of low-temperature electrochemistry.

Experimental Section

trans-1,2-Dibromocyclohexane (**1**) and *meso*-1,2-dibromo-1,2-diphenylethane (*meso*-**5**) were obtained from Aldrich Chemical Co. **1** was used as received and *meso*-**5** was recrystallized from dioxane, mp 240 °C (lit.[11] mp 237–239 °C). 2,3-Dibromo-2,3-dimethylbutane (**8**) was obtained from Pfaltz and Bauer Research Chemicals and was used as received. All other dibromides, **2–4**, **6**, and **7**, were obtained from the

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bromination of the appropriate olefin. 1,1-Dimethyl-*trans*-3,4-dibromocyclohexane (**2**) was obtained from the bromination of 4,4-dimethylcyclohexene (Chemicals Procurement Laboratories) according to a known procedure[12] and was purified by using preparative-scale gas chromatography. 1-Methyl-*cis*-3,*trans*-4-dibromocyclohexane (**3**) and 1-methyl-*trans3*,*cis*-4-dibromocyclohexane (**4**) were obtained as a mixture of isomers (10% **3** and 90% **4**) from the bromination of 4-methylcyclohexene[12] (Aldrich Chemical Co). The isomer **3** was very difficult to isolate, since thermal isomerization to **4** occurs at the elevated temperatures employed in gas chromatography. The isomerization was minimized by operating at a column temperature of 100 °C and an injector/detector temperature of 150 °C. At this detector temperature, some condensation occurs in the effluent exit tube and it was necessary to clean the tube with a pipe cleaner moistened with acetone between fraction collections. At best **3** was obtained 90% pure. Repeated collections and reinjections were made until **3** was obtained 99% pure. **4** was much easier to isolate and was obtained 99% pure. *dl*-1,2-Dibromo-1,2-diphenylethane was prepared from the bromination of *cis*-stilbene according to a known procedure.[11] The white solid isolated was recrystallized from methanol/H_2O, mp 111.5–112.0 °C (lit.[11] mp 110–111 °C). 2,3-Dibromobutane, *dl*-**6**, and *meso*-**6**, were obtained from the bromination of *cis*-2-butene and *trans*-2-butene (Linde Division of Union Carbide), respectively, according to the procedure followed in the bromination of substituted cyclohexenes[12] and were purified by using preparative gas chromatography. 3,4-Dibromo-2,5-dimethylhexane, *dl*-**7**, and *meso*-**7**, were obtained from the bromination of *cis*-2,5-dimethyl-3-hexene (ICN, K+K Pharmaceuticals, Inc.) and *trans*-2,5-dimethyl-3-hexene (Pfaltz and Bauer Research Chemicals).[12] *dl*-**7** and *meso*-**7** were purified by using preparative gas chromatography.

Butyronitrile and propionitrile (Eastman Kodak) were purified according to the procedure of Van Duyne and Reilley.[13] Alumina (super 1-type W200, neutral; Woelm, ICN Nutritional Biochemicals) was activated by heating at approximately 500 °C in a tube furnace overnight. The purified butyronitrile and propionitrile were stored over activated alumina. Tetrabutylammonium perchlorate (Eastman Kodak) was recrystallized 3 times from ethyl acetate/pentane and dried overnight at 100 °C in a vacuum oven.

Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 173 potentiostat equipped with a PAR Model 176 current-to-voltage converter. The desired voltage ramp was generated by a PAR Model 175 universal programmer. Cyclic voltammograms were acquired and stored with a Nicolet Explorer IIIa digital oscilloscope. Hard copies of the digitized voltammograms were recorded on a Hewlett-Packard (HP) Model 7004B X-Y recorder. The digitized data was also stored on magnetic mini-disks by a Commodore Model 2040 dual floppy disk drive via a Commodore PET series 2001 minicomputer. The experimental data could also be transferred from the Commodore PET to a Harris/7 computer via a TNW-2000 Serial Interface for comparison with theoretical calculations.

A Varian Model 3700 equipped with thermal conductivity and flame ionization detectors, with column temperature programming capabilities, was employed in gas chromatographic studies. Chromatograms were recorded on a HP 7127A strip chart recorder. Preparative-scale preparations were achieved on a 6 ft, $^3/_8$ in. diameter stainless steel column packed with 1% neopentylglycol succinate (NPGS) on Chromosorb W, 80/100.

For analytical determinations, a 6 ft, $^1/_8$ in. diameter stainless steel column packed with the same material was used. Both columns were purchased from Varian. The thermal conductivity detector was used exclusively. Helium was employed as the carrier gas.

Two different cell designs were employed in the low-temperature voltammetric experiments. One cell is suitable for studies down to −80 °C, while the other one can be used when lower temperatures are required. Both cells are constructed of Pyrex glass and are fitted with five inlet ports (₸ 14/20) which accommodate the working electrode, a platinum coil counter electrode, a cracked glass bead reference electrode probe, a nitrogen purge tube, and a thermocouple probe. The cell which was used for temperatures down to −80 °C, has an elongated body, 5.5 in. long and 1 in. diameter. The electrodes and other probes are sufficiently long to reach down into the bottom portion of the cell. The extra length of the cell allows the solution in the cell to be completely immersed in a temperature controlling cooling bath. The cell used in the very low temperature range (below −80 °C) has a solution compartment surrounded by two jacketed compartments, an outer evacuated jacket for insulation and an inner jacket which has inlet and outlet ports through which cooled nitrogen gas can be circulated.

FTS Systems' heating element, temperature probe, heater-controller Model TCH-1, compressor cooler Model LC-100, stirrer Model ST-2, and cryostat Model ILS-8 were employed to control cell solution temperature for studies down to −80 °C. The cryostat was filled with methanol and the long-body cell was partially immersed in the coolant. The cell was supported by a cryostat cover constructed of high-density polyethylene through which entry holes for the cell and cooling probe were drilled. The temperature control achieved with this system was quite good, ±0.2 °C. However, −80 °C is the practical lower limit of the cryostat unit. For still lower temperatures the jacketed cell, cooled by circulating cold nitrogen gas, was employed. The nitrogen gas was passed through a cooling coil constructed of six turns of $^3/_4$ in. o.d. aluminum tubing which was immersed in liquid nitrogen in a 4-L Dewar flask. The temperature was lowered by increasing the flow rate of the nitrogen gas. To avoid heating the solution, the nitrogen gas for solution purging was also passed through six turns of $^1/_4$ in. o.d. aluminum tubing immersed in the same Dewar. All connections were made as short as possible with $^5/_8$ in. o.d. thick walled, black rubber tubing. The lower temperature limit of this cooling system is well below the point at which butyronitrile freezes. Unfortunately, temperature control with this system is not outstanding, and temperature gradients develop during the course of the voltammetric experiment. For the slowest scan rate employed, 0.05 V/s, temperature control was ±0.5 °C during the time required to obtain a voltammogram.

Temperatures were measured with a Doric digital thermometer Model 410A with J-plug for iron–constantan thermocouples. A hanging mercury drop electrode (HMDE) and a platinum disk electrode were employed as working electrodes. Construction details of the HMDE[14] and Pt disk[15] electrode have been previously described. Of course, at temperatures below the freezing point of mercury (−39 °C) the HMDE is a solid electrode. The mass of the mercury drop was typically 5 mg. All potentials reported in this work are with respect to the Ag/Ag^+ reference electrode (AgRE). The reference electrode consisted of a silver wire immersed in 0.10 M $(n\text{-}C_4H_9)_4NClO_4$/0.010 M $AgNO_3$ in butyronitrile.[16] The reference electrode was at room temperature in all experiments and its potential has been found to be +0.355 V vs. aqueous SCE.[5a]

Solution resistance was compensated by using the positive feedback circuit of the PAR 173 potentiostat. To evaluate the completeness of compensation, a reversible electrode reaction (reduction of nitrobenzene) was studied at low temperature (−67 °C). The theoretical value of the separation of anodic and cathodic peaks (40 mV at −67 °C) was achieved with 2400 Ω of compensation for 0.10 M $(C_4H_9)_4HClO_4$ in butyronitrile. Complete compensation required the addition of a 100-pF stabilizing capacitor between auxiliary and reference electrodes. Under the condition of complete compensation, the peak separation was not affected by changes in concentration or scan rate.

With the stabilizing capacitor, incipient oscillation was encountered near the point of complete compensation at −67 °C. Hence, the point of incipient oscillation was selected as the point of optimum compensation for all other temperatures. Little error due to residual uncompensated resistance was present as judged by the fact that the data for peak shape and peak position in dibromide reductions were well accounted for by the same α value at all scan rates. When residual uncompensated resistance is present, $E_p - E_{p/2}$ will increase at higher scan rate and $dE_p/\log v$ will be inconsistent with α obtained from the peak shape for an irreversible reduction. A small but significant error may have remained at temperatures below −100 °C where slightly smaller values of α were found at the higher scan rates.

The solvent/electrolyte contribution to the measured current was subtracted from the experimental data. The background signal was acquired with a blank solution (consisting of solvent and electrolyte) and was stored on disk. The background and raw data were recalled into PET memory, and the background current was subtracted point-by-point from the raw data.

The technique of digital simulation was employed to extract thermodynamic and kinetic information from the voltammetric data. The general mechanism simulated is a chemical reaction preceding electron transfer (CE) in which both the reactant and the product of the homogeneous chemical reaction are electroactive but at two different potentials (Scheme III). Two approaches to the simulation were utilized, the direct method[17] and the heterogeneous equivalent approach.[18] The latter ap-

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Table I. Kinetic and Equilibrium Data[a]

compound	temp, °C	k_f, s^{-1}	k_b, s^{-1}	K^b	$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg.mol
trans-1,2-dibromocyclohexane (**1**)	−60	19 ± 5	32 ± 8	(0.60)	11.1		
	-65^c	13	22	(0.59)	11.0		
	−70	6 ± 1	10 ± 2	(0.59)	11.0		
	-75^c	5	9	(0.58)	10.8		
	−80	2.6 ± 0.2	4.8 ± 0.5	0.57	10.8		
					10.9 ± 0.1	7.5 ± 1	−18 ± 5
1,1-dimethyl-*trans*-3,4-dibromocyclohexane (2)	−10	170 ± 40	3000 ± 700	$(0.057)^d$	12.6		
	−20	55 ± 5	1100 ± 100	$(0.051)^d$	12.7		
	−30	17 ± 4	380 ± 80	$(0.045)^d$	12.8		
	−40	5.0 ± 0.8	130 ± 20	$(0.039)^d$	12.8		
					12.7 ± 0.1	13.5 ± 0.7	3 ± 3
dl-1,2-dibromo-1,2-diphenylethane (*d,l*-5)	−98	2.8 ± 0.3	8.7 ± 0.8	(0.32)	9.7		
	−103	1.0 ± 0.2	3.1 ± 0.4	(0.31)	9.8		
	−109	0.40 ± 0.09	1.3 ± 0.3	(0.29)	9.7		
	−120			0.27			
					9.7 ± 0.1	9.1 ± 1	−4 ± 6
meso-1,2-dibromo-1,2-diphenylethane (*meso*-5)	−110	10 ± 3	12 ± 4	(0.87)	8.6		
	−115	3 ± 1	4 ± 1	(0.86)	8.7		
	−120	0.9 ± 0.3	1.1 ± 0.3	(0.86)	8.8		
	−130			0.85			
					8.7 ± 0.1	10 ± 1	8 ± 6
2,3-dibromo-2,3-dimethylbutane (8)	−90	1.7 ± 0.3	0.6 ± 0.1	(2.9)	10.3		
	−95	1.1 ± 0.2	0.36 ± 0.08	(3.0)	10.2		
	−100	0.46 ± 0.05	0.15 ± 0.02	(3.1)	10.2		
	−120			3.5			
					10.2 ± 0.1	8.4 ± 0.6	−10 ± 3

[a] Rate and equilibrium constants defined in Scheme III. Activation parameters calculated from k_f and correspond to gauche → anti reaction. Rate constants are averages from 3–4 scan rates at each temperature. Experiment conditions given in Figures 2–6. [b] Definition of equilibrium constant for each compound: **1** and 2, $K = [aa]/[ee]$; *dl*-**5**, $K = [A_g]/([G_g] + [G_a])$; *meso*-**5**, $K = [A_a]/([G_g^+] + [G_g^-])$; 8, $K = [A]/[G]$ (cf. Scheme II). Values in parentheses calculated from value obtained at lowest temperature assuming $\Delta S^\circ = 0$. [c] Single scan rate only, 2.00 V/s. [d] Calculated (see text).

proach was employed when the equilibrium constant was less than 0.1. The equilibrium constant was determined from best fit simulations of data acquired at a temperature and scan rate such that the rate of conformational interconversion is too slow to occur on the time scale of the experiment. Rate constants for the conformational interconversion were determined from best fit simulations of data acquired at higher temperatures. Simulation programs are available on request.

Results

Low-temperature cyclic voltammetry reveals that conformational interconversion occurs prior to electron transfer in the electrochemical reduction of **1**, **2**, **5**, and **8**. In general, a single irreversible reduction process is observed at room temperature (illustrated for *trans*-1,2-dibromocyclohexane (**1**) in Figure 1A).[19] As the temperature is lowered, a second reduction process involving reduction of the ee conformation becomes evident at more negative potentials (Figure 1B).[20] As the temperature is lowered further or the scan rate is increased, the second peak grows and the first peak diminishes in height. When the conformational interconversion has become too slow to occur on the time scale of the experiment, the relative peak heights no longer change with temperature and scan rate and they represent the equilibrium populations of the two conformations. The temperature at which this phenomenon is observed depends on the activation energy required for the conformational interconversion as well as the equilibrium constant.

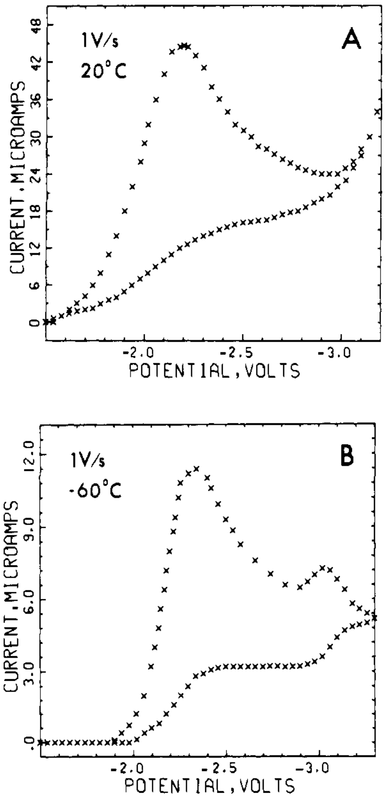

Figure 1. Cyclic voltammograms of *trans*-1,2-dibromocyclohexane (**1**) 0.10 M $(C_4H_9)_4NClO_4$, in butyronitrile, at Hg.

In Figure 2 voltammograms for **1** obtained at constant scan rate and three different temperatures are shown. The effect of temperature on the relative heights of the peaks for reduction of **1aa** at −2.3 V and **1ee** at −3.0 V is clearly evident. At constant temperature, the second peak grows at the expense of the first as the scan rate is increased. At −80 °C for scan rates greater than 20.0 V/s, the relative peak heights no longer vary with scan rate. The conformational interconversion is "frozen out" and an equilibrium constant $K = [\mathbf{1aa}]/[\mathbf{1ee}] = 0.57$ was determined from digital simulation. The value of K at the higher temperatures will be slightly different, and values were calculated from K at −80

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(18) Ruzic, I.; Feldberg, S. *J. Electroanal. Chem.* **1974**, *50*, 153–162.

(19) The background current has not been subtracted from the data in Figure 1A to illustrate the importance of accurate background correction especially at potentials near solvent breakdown past −3 V.

(20) The steeper slope of the rising portion of the −2.3-V peak in Figure 1B compared to that in Figure 1A does not signify a change in mechanism but merely reflects the effect of temperature on the $(\alpha nF/RT)$ factor in the expression for the potential dependence of the heterogeneous electron-transfer rate constant. The value of $n\alpha$ obtained from $E_{p/2} - E_p$ is the same at the two temperatures.

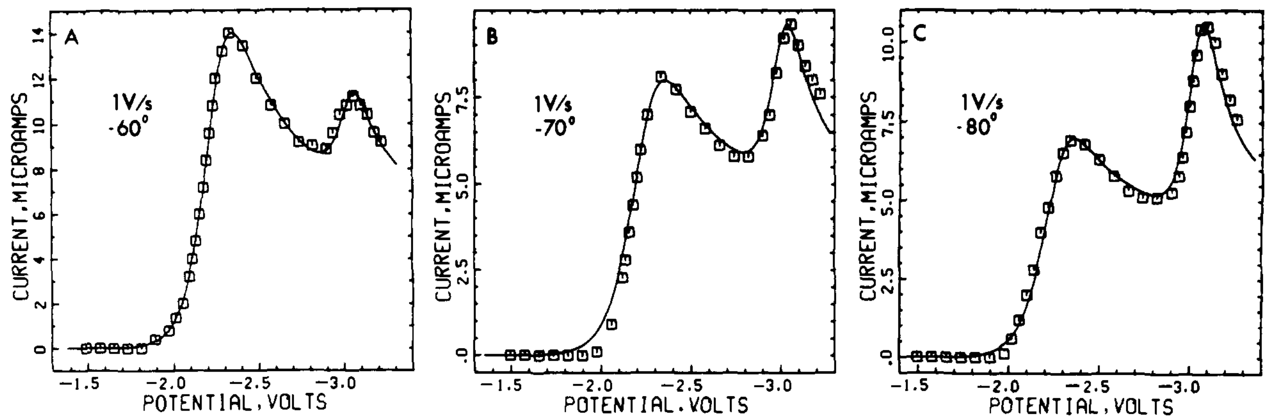

Figure 2. Voltammograms of 2.0 mM *trans*-1,2-dibromocyclohexane (**1**) 0.10 M $(C_4H_9)_4NClO_4$ in butyronitrile, at Hg, 1.00 V/s. Symbols: background corrected experimental data; smooth curve: best fit simulation. (A) −60 °C, 3.2 kΩ compensated; (B) −70 °C, 4.4 kΩ compensated; (C) −80 °C, 6.1 kΩ compensated.

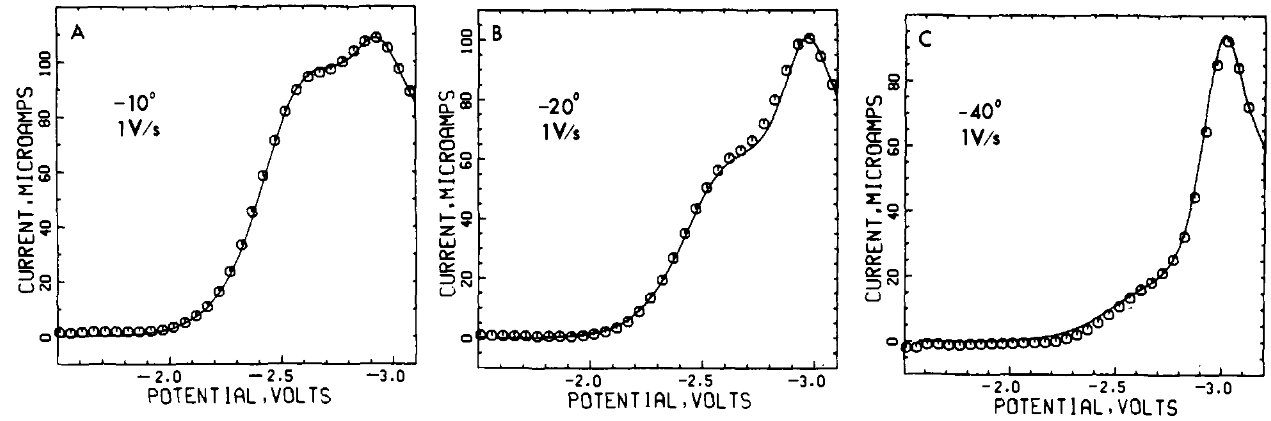

Figure 3. Voltammograms of 4.0 mM 1,1-dimethyl-*trans*-3,4-dibromocyclohexane (**2**) 0.10 M $(C_4H_9)_4NClO_4$ in butyronitrile, at Hg, 1.00 V/s. Symbols: background corrected experimental data; smooth curve; best fit simulation. (A) −10 °C, 750 Ω compensated; (B) −20 °C, 950 Ω compensated; (C) −40 °C, 1.4 kΩ compensated.

°C, assuming that the entropy change in the reaction is negligible.

Rate constants for the **1ee** ⇌ **1aa** reaction were obtained from digital simulation of voltammograms obtained at three different scan rates for each of three different temperatures. The results are summarized in Table I. All of the experimental voltammograms with comparison to digital simulations for **1** and the other compounds studied in this work are available as supplementary material.

The free energy of activation for the forward reaction (**1ee** → **1aa**) was calculated at each temperature and was found to fall over the narrow range of 10.8–11.1 kcal/mol. The five-point Arrhenius plot gave an activation energy from which the enthalpy of activation was calculated ($\Delta H^{\ddagger} = E_a - RT$) and the activation entropy was obtained from the relationship $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$. The results are also summarized in Table I.

The diaxial conformation of 1,1-dimethyl-*trans*-3,4-dibromocyclohexane (**2aa**) is reduced at somewhat more negative potentials than **1aa** (Figure 3). Its reduction appears as a shoulder on the **2ee** reduction peak which occurs at nearly the same position as **1ee**. Also the splitting of the voltammetric peak occurs at a higher temperature than for **1** due to a larger activation energy and a smaller equilibrium constant. In fact K is so small that the shoulder for **2aa** reduction is not detectable at −40 °C, 10.0 V/s, and the only conclusion that can be drawn is that $K \leqslant 0.05$.

Corey and Feiner[21] have developed a set of substituent constants to correlate conformational equilibria in substituted cyclohexanes. The increased substituent interaction energies in **2** (principally the CH_3/Br 1,3-interaction in **2aa**) were added to $\Delta G^{\circ}_{ee\to aa}$ found for **1** in the present work to obtain $\Delta G^{\circ}_{ee\to aa}$ for **2** of 1.5 kcal/mol which leads to the estimate of K = [**2aa**]/[**2ee**] = 0.05 at −20 °C. The estimated value of K permitted the evaluation of rate constants and activation parameters (Table I).

Compounds **3** and **4** contain only one methyl substituent, and consideration of the Corey and Feiner substituent constants[21] indicates that **3** will exist almost entirely as **3ee** while **4** will be **4aa**, each with the preferred equatorial methyl group. Thus **4** is reduced at a potential characteristic of a compound with diaxial bromines whereas reduction of **3** occurs at much more negative potentials. Interestingly, the conversion of **3ee** to **3aa** is so unfavorable that no peak for **3aa** could be detected even at temperatures as high as 50 °C. This observation requires $K(k_f + k_b)^{1/2} \leqslant 0.2\ s^{-1/2}$ at 50 °C. Peak potentials at 20 °C for **3** and **4** as well as all other compounds studied are presented in Table II along with the dominant conformation (if any) and the conformation through which reduction occurs at room temperature.

Turning to the acyclic compounds, 1,2-dibromo-1,2-diphenylethane (**5**) is also reduced to the olefin, but unlike the aliphatic compounds, this activated olefin (stilbene) is itself reduced at more negative potentials to the radical anion and dianion. These reactions were not extensively studied and attention was focused on the reduction of the dibromide (Figures 4 and 5). Of all the compounds studied, *dl*-**5** and *meso*-**5** were the most readily reduced (Table II), and the low barriers to rotation required that the experiments be performed at very low temperatures (Table I).

2,3-Dibromobutane (**6**) has the lowest barrier to conformational interconversion of the dibromides investigated. No splitting of the single, irreversible reduction process was observed for *dl*-**6** and *meso*-**6**, even at temperatures as low as −135 °C (our present practical lower limit), indicating that the relevant barriers must be less than about 7 kcal/mol. Peak potentials are listed in Table II.

3,4-Dibromo-2,5-dimethylhexane (**7**) also exhibits only one irreversible reduction process for both *dl*-**7** and *meso*-**7** at all

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[21] Corey, E. J.; Feiner, N. F. *J. Org. Chem.* **1980**, *45*, 765–780.

Table II. Reduction Peak Potentials and Conformational Assignments[a]

compound	E_p, V vs. AgRE	dominant conformation (if any)	conformation being reduced at 20 °C
trans-1,2-dibromocyclohexane (**1**)	−2.20, −2.64[b]		aa
1,1-dimethyl-*trans*-3,4-dibromocyclohexane (**2**)	−2.50	ee	aa
1-methyl-*cis*-3,*trans*-4-dibromocyclohexane (**3**)	−2.90	ee	ee
1-methyl-*trans*-3,*cis*-4-dibromocyclohexane (**4**)	−2.10	aa	aa
dl-1,2-dibromo-1,2-diphenylethane (*dl*-**5**)	−1.70	G_g	A_g
meso-1,2-dibromo-1,2-diphenylethane (*meso*-**5**)	−1.20		A_a
dl-2,3-dibromobutane (*dl*-**6**)	−2.26, −2.76[b]		A_g
meso-2,3-dibromobutane (*meso*-**6**)	−2.26, −2.84[b]		A_a
dl-3,4-dibromo-2,5-dimethylhexane (*dl*-**7**)	−2.76, −2.90[b]	G_a	G_a
meso-3,4-dibromo-2,5-dimethylhexane (*meso*-**7**)	−2.30, −2.62[b]	A_a	A_a
2,3-dibromo-2,3-dimethylbutane (**8**)	−1.84, −2.50[b]	A	A

[a] 20 °C, 1.00 V/s, mercury electrode. [b] Platinum electrode.

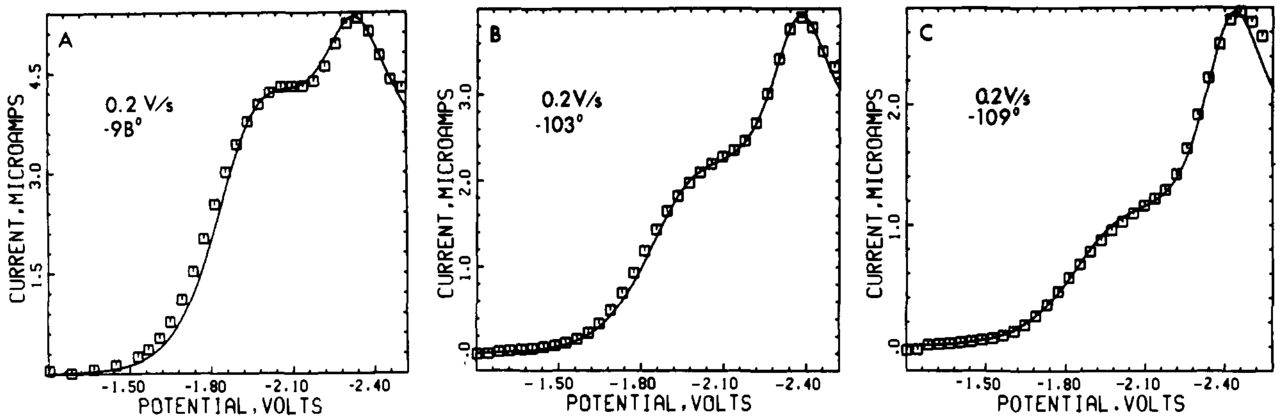


Figure 4. Voltammograms of 10.0 mM *dl*-1,2-dibromo-1,2-diphenylethane (*d,l*-**5**) 0.30 M $(C_4H_9)_4NClO_4$, in butyronitrile, at Hg, 0.20 V/s. Symbols: background corrected experimental data; smooth curve; best fit simulation. (A) −98 °C, 25 kΩ compensated; (B) −103 °C, 30 kΩ compensated; (C) −109 °C, 50 kΩ compensated.

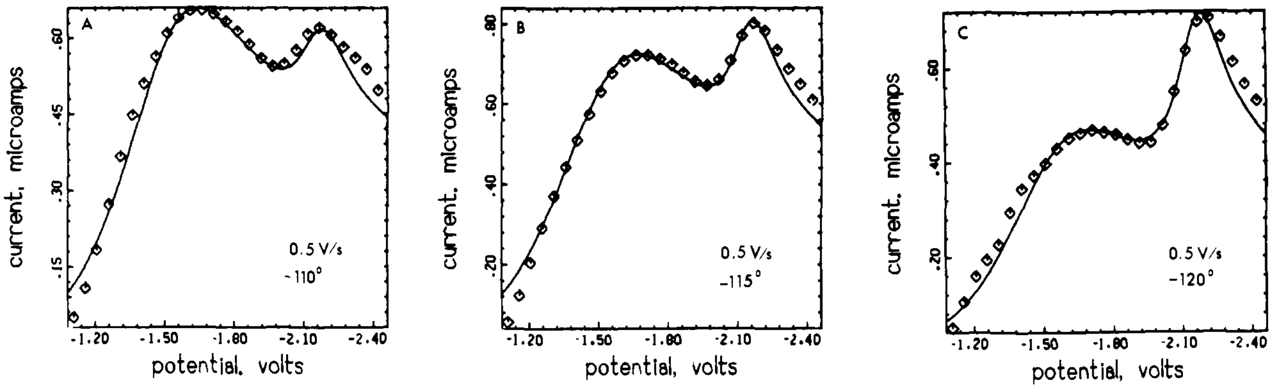


Figure 5. Voltammograms of 10.0 mM *meso*-1,2-dibromo-1,2-diphenylethane (*meso*-**5**) 0.30 M $(C_4H_9)_4NClO_4$, in butyronitrile, at Hg, 0.50 V/s. Symbols: background corrected experimental data; smooth curve: best fit simulation. (A) −110 °C, 20 kΩ compensated; (B) −115 °C, 30 kΩ compensated; (C) −120 °C, 50 kΩ compensated.

temperatures investigated, but unlike **6**, the reason is that the barriers are large and/or the equilibrium is unfavorable. The reduction of *meso*-**7** occurs at significantly more positive potentials than *dl*-**7** (Table II) presumably because the former already exists in an antiperiplanar conformation (A_a) whereas the latter is held in a conformation with gauche bromines (probably G_g). Conversion of G_g to A_g in *dl*-**7** is very difficult as evidenced by the fact that no peak for reduction of A_g could be detected at temperatures as high as 80 °C signifying that $K(k_f + k_b) < 0.2\ s^{-1/2}$.

The reduction of 2,3-dibromo-2,3-dimethylbutane (**8**) displayed separate peaks for A and G conformations at low temperatures, and a quantitative kinetic analysis was achieved (Figure 6 and Table I).

At very low temperatures, −100 to −120 °C, a rather curious phenomenon is observed at mercury electrodes. The first reduction process (corresponding to conformations with antiperiplanar bromine atoms) begins to split into two peaks. The dependence of the two peak heights on scan rate is analogous to that observed for a CE mechanism. This phenomenon appears to be quite general, as it was observed in the simple dibromides **1**, *meso*-**6**, *dl*-**6**, *meso*-**7**, and **8**. Since **1** and **8** can only exist in two possible conformations, the three peaks observed at mercury below −100 °C cannot all be ascribed to separate electrochemical processes for different conformations. It is rather interesting to note that the potential of the new peak which emerges is very close to the first reduction peak at platinum. A possible explanation is that the reduction of anti conformations at mercury normally involves specific interaction with the surface which facilitates the reduction and this facilitated process cannot occur at very low temperatures. It is important to note that this phenomenon does not interfere with data acquired at higher temperatures. The information obtained on the thermodynamics and kinetics of the conformational interconversion in **1** acquired at mercury agrees well with that previously determined at glassy carbon[2] as well as that ob-

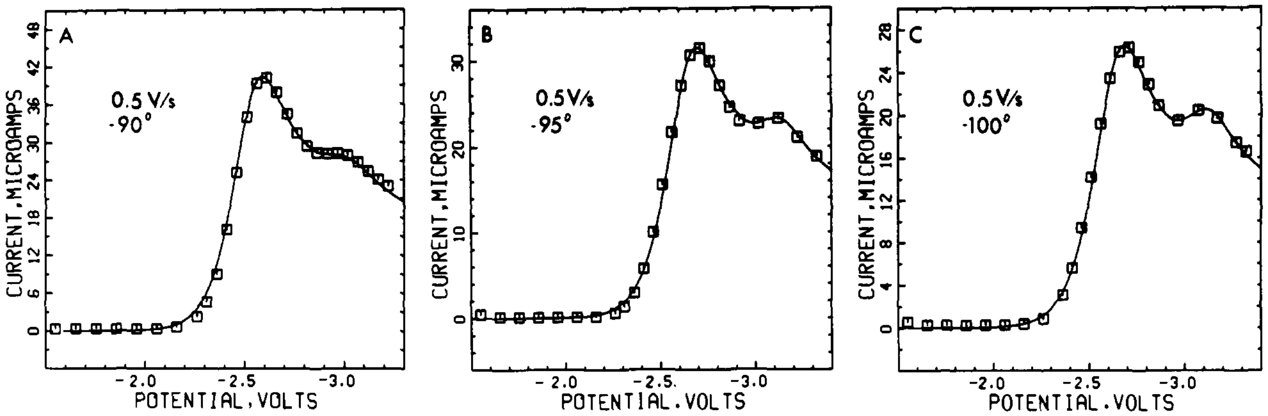
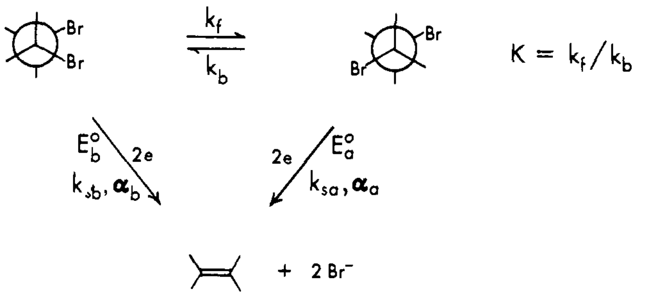


Figure 6. Voltammograms of 10.0 mM 2,3-dibromo-2,3-dimethylbutane (**8**) 0.30 M $(C_4H_9)_4NClO_4$, in butyronitrile, at Pt, 0.50 V/s. Symbols: background corrected experimental data; smooth curve: best fit simulation. (A) -90 °C, 7.2 kΩ compensated; (B) -95 °C, 9.5 kΩ compensated; (C) -100 °C, 15 kΩ compensated.

Scheme III



tained by other methods. The anomalous splitting of this peak due to reduction of anti conformers was never observed with platinum electrodes. Consequently, platinum was used for all studies of **6**–**8** below -90 °C.

Discussion

The electrochemical reduction of the vicinal dibromides has been interpreted in terms of Scheme III. The conformational interconversion between a conformer with gauche bromine atoms (diequatorial in **1**–**4**) and the conformer with anti bromine atoms (diaxial in **1**–**4**) is a first-order reaction with associated rate constants k_f and k_b and equilibrium constant K = [anti]/[gauche]. The anti conformer is reduced in a totally irreversible two-electron process with standard potential E_a°, standard heterogeneous electron-transfer rate constant k_{sa}, and electron-transfer coefficient, α_a. The gauche conformer is reduced at more negative potentials and the reaction is characterized by parameters E_b°, k_{sb}, and α_b. The olefin is formed in each reaction.

Is Scheme III an adequate model? While considering this question it is important to remember that the conformational interconversion is postulated to occur in solution near the electrode and not on the surface of the electrode itself. In fact, no adsorption of either conformer is postulated and no evidence for adsorption was found.[22]

The adequacy of the model is supported by the excellent agreement found between experiment and simulation (Figures 2–6). As required, the values of the rate constants were not functions of the scan rate (Table I). Furthermore, invariant values of K, α_a, α_b, k_{sa}, and k_{sb} were adequate to fit data at all scan rates at a given temperature.[24] When the temperature was varied, those parameters expected to be insensitive to temperature (K, α_a, α_b) remained almost constant whereas the rate constants changed in the normal manner.

Because the conformational interconversion occurs in solution near the electrode, a conclusion that the model is adequate requires that (a) the values of K and the rate constants must agree with the results of nonelectrochemical studies and (b) the results must be independent of the electrode material.

The conformational equilibrium of *trans*-1,2-dibromocyclohexane (**1**) has been previously studied with a variety of techniques.[25] The equilibrium constant is strongly dependent on solvent polarity with the more polar ee conformer being favored in highly polar solvents.[26] Values of K for several polar solvents (dielectric constant) are as follows: acetone (21) 0.85,[25a] 0.91,[25b] 1.14,[25e] acetonitrile (39) 0.66,[25a] dimethylformamide (50) 0.52.[25b] Hence, K = 0.57 found in this work for butyronitrile (20) is quite reasonable. Only one estimate of the barrier for **1** is available, 11.85 kcal/mol at -45 °C by ^{1}H NMR spectroscopy,[25e] which is in good agreement with the extrapolated value of 11.5 kcal/mol for $\Delta G^{\ddagger}_{ee\to aa}$ at -45 °C from the present work.[27]

Concerning the second requirement, the values of K and the rate constants found in the present research with a mercury electrode are identical within experimental error with those determined earlier[2] with a glassy carbon electrode. Thus, we conclude that Scheme III is an adequate description of the electrochemical reduction.

The two conformations are reduced at much different potentials, a fact which can be caused by differences in the standard potentials, differences in the values of k_s and α, or both. Since in all cases studied the free energies of the conformers differ by less than 1.5 kcal/mol, the standard potential for the *overall* reductions of the two conformers cannot differ by more than 0.06 V, much less in most cases. Thus, the large difference in reduction potential is attributed to differences in k_s and α. For totally irreversible processes such as the reduction of **1aa** and **1ee**, the peak potentials can be used to calculate the relative rate constants for the electrochemical reduction via eq 1.[28] In eq 1, k_a and k_b are the

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[22] Here it is meant that no adsorption of the reactant molecules occurs from the nonaqueous solvent employed in this work. Strong interaction with the electrode surface by intermediates formed in the course of the electrode reaction is likely, especially with mercury electrodes.[23] Further evidence for intimate involvement of the electrode surface in the detailed steps in the electrode reaction is found in the fact that the peak potentials are uniformly more negative on platinum than on mercury (Table II).

[23] Carroll, W. F.; Peters, D. G. *J. Electrochem. Soc.* **1980**, *127*, 2594–2599.

[24] The kinetic feature of the voltammograms (variation in the relative heights of the two peaks) is essentially a function of only one parameter, the rate constant for conformational interconversion. The equilibrium constant is established from the relative peak heights under "frozen out" conditions. The other parameters are dictated by other features of the voltammograms: α from peak shape and E° and k_s from peak position.

[25] (a) Klaeboe, P.; Lothe, J. J.; Lunde, K. *Acta Chem. Scand.* **1957**, *11*, 1677–1691. (b) Abraham, R. J.; Rosetti, Z. L. *J. Chem. Soc., Perkin Trans 2* **1973**, 582–587. (c) Subbotin, O. A.; Sergeev, N. M.; Zefirov, N. S.; Gurvich, L. G. *J. Org. Chem. USSR* (*Engl. Transl.*) **1975**, *11*, 2265–2269. (d) Altona, C.; Buys, H. R.; Hageman, H. J.; Havinga, E. *Tetrahedron* **1967**, *23*, 2265–2279. (e) Reeves, L. W.; Stromme, K. O. *Trans. Faraday Soc.* **1961**, *57*, 390–398.

[26] Abraham, R. J.; Breitschneider, E. In "Internal Rotation in Molecules"; Orville-Thomas, W. J., Ed.; Wiley: New York, 1974; pp 481–579.

[27] The value of the barrier from ref 25e is only approximate. It is based on a simplified expression for the rate constant at the coalescence temperature of the CHBr unresolved multiplets.

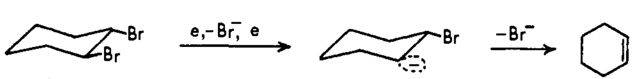
$$k_a/k_b = (\alpha_a D_a/\alpha_b D_b)^{1/2} \exp[(-\alpha_b nF/RT)(E_{pb} - E_{pa})] \tag{1}$$

forward hetereogeneous electron-transfer rate constants (at E_{pa}), D_a and D_b are the diffusion coefficients, and E_{pa} and E_{pb} are the peak potentials for reduction of **1aa** and **1ee**, respectively. At −60 °C, $E_{pb} - E_{pa} = -0.70$ V, $\alpha_a = 0.10$, $\alpha_b = 0.16$, $D_a = D_b$ (assumed), so $k_a/k_b = 1.6 \times 10^5$ (at E_{pa}) which is indicative of the substantial rate enhancement for a dihedral angle of 180° as compared to 60°.

As mentioned earlier, the large difference in rate constants can be attributed to differences in $E°$, k_s, and/or α for the two conformations as may be seen from the Butler–Volmer equation for the rate constant (eq 2). It has been shown that the values of

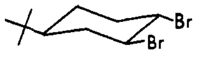
$$k = k_s \exp((-\alpha nF/RT)(E - E°)) \tag{2}$$

$E°$ for the *overall* reduction process are almost equal. Whereas it is at least possible to think of the reduction of **1aa** as a single, two-electron reduction step leading directly to cyclohexene and two bromide ions, such a representation of the reduction of **1ee** is highly improbable. For example, **1ee** could give a carbanion (via electron transfer, very rapid loss of bromide, and transfer of a second electron) in an overall two-electron, irreversible process. The carbanion would expel bromide to give the final olefin product. If this were the case, not all of the total free energy change would be experienced in the actual electrode reaction so the effective $E°$ for **1ee** would be more negative than that of **1aa**. The fact that α_b was always larger than α_a (except for **8**) is consistent with a difference in the mechanism of reduction of anti and gauche conformers.



1ee

It is also important to remember that it was not practical to identify the actual reduction product formed from gauche conformers via low-temperature electrochemical reaction. The assumption that the eventual product is olefin is supported by the excellent yield of olefin formed[9a] from the more rigid dibromide, **9**. Trapping of carbanionic intermediates has been attempted without success.[9a]



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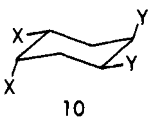

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We turn now to the conformational data obtained for the other dibromides. The results confirm the general applicability of Scheme I, in which separate electrochemical reduction processes are detected for gauche and anti conformations.

The unfavorable 1,3-diaxial methyl–bromine interactions in the aa form of 1,1-dimethyl-*trans*-3,4-dibromocyclohexane (**2**) cause **2ee** to be the preferred conformation with $K = [\mathbf{2aa}]/[\mathbf{2ee}] \leq 0.05$ (found), 0.05 (calculated). Many substituted cyclohexanes have interconversion barriers which are about the same as that of cyclohexane itself, 10.3 kcal/mol (note results for **1** in Table I) because a half-chair transition state can be achieved with insignificant movement of the substituents.[29] However, the 1,1,3,4-substitution in **2** removes this ability and the higher barrier observed for **2** ($\Delta G^{\ddagger} = 12.8$ kcal/mol (−40 °C)) is similar to those found for **10** (various X and Y).[30]

One of the unusual features of the electrochemical study of conformational equilibrium and kinetics is the ability to obtain large signals for minor conformations. In **2**, the equilibrium concentration of **2aa** is no more than 5% of the total yet the current due to reduction of **2aa** can be much larger than that for **2ee** (Figure 3) and at room temperature no peak for the principal component, **2ee**, can be detected. This useful feature exists because the electrode reaction perturbs the equilibrium. Study of minor conformations is very difficult by most other methods.

The peak potential for reduction of **2** is more negative than any of the other reductions which proceed via anti conformations (Table II). The 1,3-diaxial CH_3–Br interaction in **2aa** may prevent the attainment of the optimum angle of 180° between bromines, causing a shift to more negative potentials.

1-Methyl-*cis*-3,*trans*-4-dibromocyclohexane (**3**) exists principally as **3ee** and interconversion to **3aa** prior to electron transfer was not observed even at 50 °C. The reason for this behavior is probably a very unfavorable equilibrium constant. The substituent interaction energies of Corey and Feiner[21] may be used to estimate $\Delta G°_{ee\rightarrow aa} = 3.2$ kcal/mol, $K_{298} = 4 \times 10^{-3}$. For the same reason that **3** strongly prefers the ee conformation, 1-methyl-*trans*-3,*cis*-4-dibromocyclohexane (**4**) exists predominantly as **4aa**, the more easily reduced conformation. When the more reactive conformation is dominant, no information about the minor conformation can be obtained by electrochemistry because all of the compound is reduced via the preferred route.

The conformations of substituted 1,2-dibromoethanes **5**–**7** are summarized in Scheme II. **8** can be considered in Scheme II with $R_1 = R_2 = CH_3$ and the two gauche conformers being identical. When considering the electrochemical behavior of *d,l* isomers, conformations G_a and G_g in Scheme II are considered identical because the two could not be resolved by voltammetry.

Previous electrochemical studies of 1,2-dibromo-1,2-diphenylethane (**5**) have found that in the case of *meso*-**5**, stereospecific reduction to *trans*-stilbene was observed.[31,32] The electrolysis of *dl*-**5** was found in one case to produce only *trans*-stilbene[31] and in another case to give varying amounts of *cis*-/*trans*-stilbenes depending on the size of the cation of the supporting electrolyte.[32] It was found that in the presence of 0.3 M tetrabutylammonium ion, *cis*-stilbene was the major product.

Prior experimental studies on the conformations of **5** are of a qualitative nature[33] and have indicated that the conformation with anti bromines is favored in *meso*-**5** while conformations with anti and gauche bromine atoms are populated in *dl*-**5**. Molecular force field calculations have been performed for **5**.[34] These results predict that G_a is not significantly populated in *dl*-**5** and the equilibrium mixture of conformers consists of 80% G_g and 20% A_g at 300 K.[34a] *meso*-**5** was predicted to consist of 92% A_a at 300 K.[34a] The inclusion of solvation (dielectric continuum, ϵ 3.5) favors the G conformers,[34b] but calculations were not performed for solvents with as high a dielectric constant as those employed in electrochemical experiments.

The equilibrium constants determined by low-temperature cyclic voltammetry for *meso*-**5** ($K = [A_a]/([G_g^+] + [G_g^-]) = 0.85$) and *dl*-**5** ($K = [A_g]/([G_g] + [G_a]) = 0.27$) are quite consistent with these previous qualitative experimental studies and theoretical calculations. The rate constants for conformational interconversion determined by low-temperature cyclic voltammetry constitute the first evidence reported on the barrier to rotation in **5**. The free energy of activation for $G_g^+, G_g^- \rightarrow A_a$ in *meso*-**5** was found to be 8.6 kcal/mol (−110 °C). The transition state for this 120° rotation has a bromine atom eclipsing a phenyl group as well as hydrogen/phenyl and hydrogen/bromine eclipsed pairs. The free energy of activation for $G_g \rightarrow A_g$ in *dl*-**5** was found to be 9.7 kcal/mol (−109 °C). The transition state for this 120° rotation has two phenyl groups eclipsing each other as well as two hydrogen/bromine eclipsed pairs.[35]

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(35) For *d,l* isomers there are two routes to A_g from gauche conformers, $G_a \rightarrow A_g$ and $G_g \rightarrow A_g$. The barrier has been assigned to the latter process because G_a is supposed to be a minor conformer.[34] However, the possibility that the conversion occurs via $G_g \rightleftharpoons G_a \rightarrow A_g$ cannot be excluded.

The benzylic bromines in **5** are reduced at much less negative potentials than any of the other compounds.[7a] In addition the room temperature peak potential (Table II) of *meso*-**5** is about 0.5 V less negative than that of *dl*-**5**. Since the phenyl rings will tend to be coplanar in *trans*-stilbene, the product of the reduction of A_a, and because the delocalization of the developing olefinic bond may lower the transition-state energy, the reduction of A_a from *meso*-**5** may be favored compared to A_g from *dl*-5 whose gauche phenyl groups cannot be coplanar in either the transition state or the final product, *cis*-stilbene.[36]

A considerable amount of experimental evidence has been published on the relative conformer populations in 2,3-dibromobutane (**6**).[37] However, very little is known about the exact barriers to internal rotation in **6**. A ^{13}C NMR study has been recently reported[37h] in which the free energy of activation for $G_a \rightleftharpoons G_g$ in *dl*-**6** was determined to be 8.35 kcal/mol. The $G_g \rightleftharpoons A_g$ barrier as well as the barriers in *meso*-**6** were too small to be determined.

No evidence of a second reduction process growing in at more negative potentials could be found for *meso*-**6** or *dl*-**6** at the lowest temperatures investigated (−125 and −135 °C, respectively). In order for complete interconversion to be observed prior to electron transfer in *dl*-**6** at −135 °C and 1 V/s, $\Delta G^{\ddagger}_{G_a \rightleftharpoons G_g} \leq 6.8$ kcal/mol (assuming $k_f = k_b$). In order for our results to be consistent with the ^{13}C NMR study, the concentration of one of the two gauche conformers, G_a or G_g, present under the voltammetric experimental conditions must be too small to detect.

The isomers of 3,4-dibromo-2,5-dimethylhexane (*meso*- and *dl*-**7**) are reduced at quite different potentials. At room temperature, the reduction of *dl*-**7** occurs approximately 0.46 V negative of the potential at which *meso*-**7** is reduced. A single reduction process for each isomer persisted at all temperatures investigated. A previous study has indicated that *meso*-**7** exists solely as the A_a conformer and that *dl*-**7** exists primarily as G_a with perhaps G_g populated to a small degree.[38] The cyclic voltammetric data are completely consistent with these results. *meso*-**7** is reduced via the A_a conformer with no detectable reduction of a gauche conformer at temperatures as low as −125 °C. The more negative reduction potential of *dl*-**7** can be attributed to the reduction of conformers with gauche bromine atoms. The equilibrium constant must indeed be quite small (or the barrier quite high) since interconversion to A_g could not be detected at temperatures as high as 80 °C. The conversion of G_g to A_g requires an *i*-Pr/*i*-Pr passage while G_a to A_g involves two *i*-Pr/Br eclipsed pairs.

2,3-Dibromo-2,3-dimethylbutane (**8**) exists in two conformations, one with anti bromines (A) and one with gauche (G). Dipole moment data[39] have been quantitatively analyzed[39b] and the equilibrium populations were determined to be 93% A and 7% G (CCl_4) which corresponds to $K = [A]/[G] = 13$. A value of $K = 3.5$ (n-C_3H_7CN) was found in the present work. Since the high dielectric constant of butyronitrile will result in a higher population of gauche conformers than in CCl_4, the two values may be acceptably consistent.

The value of $\Delta G^{\ddagger}_{G \to A} = 10.2$ kcal/mol (−100 °C) falls nicely within the trend of barriers for various bromo- and methyl-substituted ethanes,[40] unlike an earlier value of 6–7.5 kcal/mol obtained by infrared and acoustic studies[41] which seems unreasonably low.

Our studies of conformational equilibria and kinetics by low-temperature cyclic voltammetry have provided interesting new information concerning the vicinal dibromides, some of which would be difficult to attain by the more commonly employed tools of conformational analysis. We must hasten to admit, however, that the electrochemical approach is not very general, requiring as it does that the species be electroactive and that the conformers react at significantly different potentials. Even the conceptually simple extension to vicinal dichlorides would be difficult because they are much more difficult to reduce than dibromides.[7a] Nevertheless, the present results serve to illustrate and confirm the important role of molecular conformation in redox reactions.

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Registry No. 1, 7429-37-0; **2**, 20245-21-0; **3**, 35190-00-2; **4**, 20237-14-3; *dl*-**5**, 13027-48-0; *meso*-**5**, 13440-24-9; *dl*-l, 598-71-0; *meso*-**6**, 5780-13-2; *dl*-**7**, 40084-92-2; *meso*-**7**, 84623-34-7; **8**, 594-81-0.

Supplementary Material Available: Voltammograms and digital simulations for compounds **1**, **2**, *dl*-**5**, *meso*-**5**, and **8** along with tabulated simulation parameters (22 pages). Ordering information is given on any current masthead page.

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