terest, the four carbons attached to the iron are chemical shift equivalent on the NMR time scale. We also assumed that the only observable species was $(LFe(CO)_4)^+$. With these two considerations it was possible to simplify the line-shape program to an easily manageable form. Instead of treating four exchanging nuclei, all initially spin coupled to phosphorus, we considered the following exchange:

$$[>P_1 - Fe(CO)_4]^+ \rightleftarrows [>P_1 - Fe(CO)_3]^+ + CO$$

$$CO + [>P_2 - Fe(CO)_3]^+ \rightleftarrows [>P_2 - Fe(CO)_4]^+$$

P_1 and P_2 each have an equal probability of being an α (spin up) or β (spin down) spin state to that, on the average, a given carbonyl exchanges between two equally populated chemical environments.

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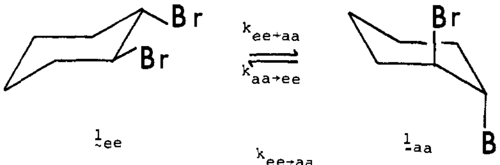
Conformational Analysis of *trans*-1,2-Dibromocyclohexane by Low-Temperature Cyclic Voltammetry

Sir:

Different conformations of a molecule should exhibit different electrochemical behavior. It has been shown that certain cyclic tetraalkylhydrazines give separate oxidation peaks for each of their two principal conformations when studied by cyclic voltammetry (CV) at temperatures sufficiently low to prevent conformational interconversion on the time scale of the experiment.[1] We now report the first example of an electrochemical reduction which shows a separate CV peak for each of two interconverting conformers.

Solutions of *trans*-1,2-dibromocyclohexane (**1**) contain two conformers, axial-axial ($\mathbf{1}_{aa}$) with the bromines anti and equatorial-equatorial ($\mathbf{1}_{ee}$) with the bromines gauche. The



$$K = \frac{k_{ee \to aa}}{k_{aa \to ee}}$$

conformational equilibrium is highly solvent dependent with $\mathbf{1}_{aa}$ being favored in nonpolar solvents and roughly equal populations of $\mathbf{1}_{aa}$ and $\mathbf{1}_{ee}$ present in polar solvents suitable for electrochemical studies.[2] An early ^{1}H NMR study[3] indicated a barrier to ring inversion (see Table I) which is high enough to "freeze out" conformational interconversion on the CV time scale at accessible low temperatures. Also, reference to studies of the electrochemical reduction of rigid cyclic 1,2-dibromides[4] suggests that $\mathbf{1}_{aa}$ should be reduced at a potential several tenths of a volt positive from the reduction of $\mathbf{1}_{ee}$.

At room temperature on Pt or glassy carbon electrodes in dimethylformamide with 0.10 M tetraethylammonium perchlorate or *n*-butyronitrile with 0.10 M tetrabutylammonium perchlorate, a single reduction peak is observed by CV. This peak is due to the totally irreversible, two-electron (confirmed by coulometry) reduction of rapidly interconverting $\mathbf{1}_{aa}$ and $\mathbf{1}_{ee}$ producing bromide ions and cyclohexene. No evidence of reversibility (anodic peak) was found even at scan rates up to 100 V/s, though anodic peaks due to bromide oxidation were always found at positive potentials. Cyclohexene is electroinactive in the potential region studied.

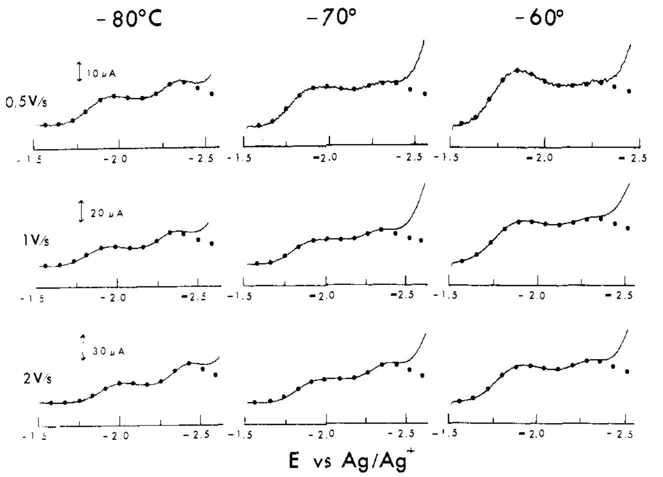


Figure 1. Voltammograms of 1.5 mM *trans*-1,2-dibromocyclohexane: curves, experimental; points, simulations; 0.10 M tetra-*n*-butylammonium perchlorate (TBAP) in *n*-butyronitrile; 0.089-cm^2 planar glassy carbon electrode. Reference electrode uses 0.010 M $AgNO_3$ and 0.10 M TBAP in *n*-butyronitrile. See Table I for simulation parameters.

Table I. Conformational Equilibrium and Kinetic Data for *trans*-1,2-Dibromocyclohexane in *n*-Butyronitrile

temp, °C	K	$k_{ee \to aa}$, s^{-1} [a]	$\Delta G^\ddagger$, kcal/mol [b]
−90	0.55	0.53[c]	10.8
−80	(0.55)[d]	2.3	10.8
−70	(0.55)[d]	5.2	11.1
−60	(0.55)[d]	29.0	11.0
−55	0.52[e]		
−84 to −89	1.14[f]		10-12[f]

[a] Average of values used to simulate voltammograms in Figure 1. Average deviation from the three simulations: ±15%. [b] Data for −60, −70, and −80 °C (most reliable) give $\Delta H^\ddagger$ = 9.9 kcal/mol and $\Delta S^\ddagger$ = −5.1 eu. [c] Obtained from low scan rate data (<1 V/s). [d] Assumed value. [e] In DMF-d_7.[2] [f] In acetone.[3]

As the temperature is lowered, a second, more negative peak grows in at faster scan rates. This is attributed to the reduction of $\mathbf{1}_{ee}$ which has a longer lifetime at the lower temperature. The heterogeneous rate constant for reduction of $\mathbf{1}_{ee}$ is smaller (hence the overpotential is larger) than for $\mathbf{1}_{aa}$ because the bromine atoms in $\mathbf{1}_{ee}$ are not in the anti configuration advantageous for trans elimination.

Figure 1 shows data obtained at a number of scan rates and temperatures along with digital simulations.[5] The current-potential curves are averages of five scans (background subtracted) obtained with the computer-controlled system described earlier.[6] The electrochemical cell and temperature control system have been described.[1b] Temperatures were maintained constant to within ±0.5 °C. The current increase observed at very negative potentials is associated with solvent breakdown and indicates inadequate background subtraction in this region. The return scans are eliminated for clarity.

At −90 °C the relative heights of the two peaks are independent of scan rate above 1 V/s; i.e., conformational equilibrium is "frozen out" and the peak heights reflect the equilibrium concentrations of $\mathbf{1}_{ee}$ and $\mathbf{1}_{aa}$ and so the equilibrium constant, K, can be derived directly from the simulation. K should be almost constant over the range of temperatures employed;[2] so the value of K obtained at −90 °C was used in the simulations of the higher temperature data.

At −90 °C the height of the first peak is proportional to the

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equilibrium concentration of 1_{aa}. At higher temperatures the height of the first peak grows relative to the second owing to the conversion of some 1_{ee} to 1_{aa} near the electrode during the experiment. At lower scan rates (longer experiments) even more 1_{aa} is formed and the height of the first peak increases. This reaction occurs in the solution within a thin (of the order of 1 μm) diffusion layer adjacent to the electrode surface. Thus in our model the rate and equilibrium constants are those of the solution species rather than adsorbed molecules. The dependence of relative peak height on temperature and scan rate is illustrated in Figure 1. In the digital simulations the relative peak height is governed by the interrelated parameters K and $k_{ee \to aa} + k_{aa \to ee}$. Since K was obtained from the low-temperature data, the rate constants could be calculated from the simulation parameters for the higher temperature data. The results are summarized in Table I.

The internal consistency of the data and the good agreement with earlier reports of K and $\Delta G^{\ddagger}$ lend credence to our model in which 1_{aa} is the more easily reduced conformer and conformational interconversion occurs in solution near the electrode surface. Thus, 1,2-dibromides appear to be another class of compounds in which the electrode reaction occurs preferentially via a given conformer. Other examples are currently being investigated.

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Two Conformations of the Pentadienyl Radical[1]

Sir:

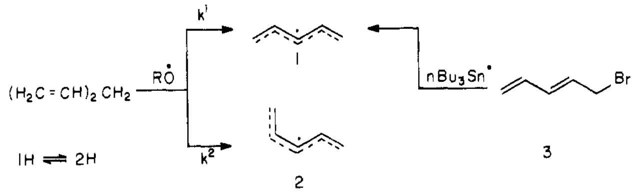
Pentadienyl is the simplest acyclic hydrocarbon radical having five conjugated π electrons. This has made pentadienyl the subject of numerous theoretical studies[2-11] but, prior to the present work, it had not been observed. We have now identified pentadienyl by EPR spectroscopy and we find that, when it is generated by hydrogen atom abstraction from 1,4-pentadiene, it can exist in two distinct conformations, a possibility overlooked in the theoretical treatments. The conformers are not in equilibrium with one another; instead the relative concentrations of the two conformers are determined by kinetic factors.

Photolysis of a mixture of 1,4-pentadiene and di-*tert*-butyl peroxide, either neat or in a variety of hydrocarbon solvents, at ambient temperatures in the cavity of a Varian E-104 EPR spectrometer gave a spectrum which we assign to pentadienyl in the *E*,*E* conformation, **1**. Apart from a minor variation in one of the hyperfine splittings (hfs, see Table I) the spectrum was unchanged from 100 °C to ca. −60 °C. However, when the solution was photolyzed at −60 °C or below, a new spectrum appeared and became predominant at temperatures below ca. −120 °C. This new spectrum, which we assign to pentadienyl in the *E*,*Z* conformation, **2**, had the same overall width and the same g factor as **1** but showed hfs by 7 nonequivalent hydrogen atoms. Since **2** predominates at low temperatures,[12] we must conclude that, *if* **1** and **2** are in equilibrium, not only is **2** more stable than **1**, which would be surprising, but also the barrier to interconversion of **1** and **2** must be rather small.

Table I. EPR Parameters for **1** and **2** Recorded at a Microwave Power Level of 0.4 mW

1 at −40 °C, $a^{\mathrm{H}a-c}$	**2** at −160 °C, $a^{\mathrm{H}a-c}$
11.58	3.08,[e] 9.69
3.32 (**2H**)[d]	3.62,[f] 10.12
9.62 (**2H**)	8.48, 14.38
10.40 (**2H**)	9.18

[a] $g = 2.00264 \pm 0.00002$. [b] a^{H} in Gauss. [c] $\partial a^{\mathrm{H}}/\partial T \leqslant \pm 0.3$ mG/K unless otherwise noted. [d] Assigned to H_2 and H_4. $\partial a^{\mathrm{H}}/\partial T = 1.3$ mG/K (from 33 to −170 °C). [e] Assigned to H_2 or H_4. $\partial a^{\mathrm{H}}/\partial T = 1.5$ mG/K (from −91 to −170 °C). [f] Assigned to H_2 or H_4. $\partial a^{\mathrm{H}}/\partial T = 2.7$ mG/K (from −91 to −170 °C).



The simplest way to check whether **1** and **2** are in equilibrium is to generate pentadienyl from a precursor whose geometry would constrain it to yield *only* **1** or **2** initially. This was accomplished by abstraction of bromine from *trans*-bromopenta-2,4-diene,[13] **3**. The pentadienyl radicals which were produced in this way existed *solely* in conformation **1** at temperatures from 180 to −130 °C. This proves that, when **1** and **2** were generated from 1,4-pentadiene at low temperatures, they were not in equilibrium. Their relative concentrations must therefore have been determined either by their relative rates of destruction or(and) by their relative rates of formation. The former possibility can be virtually ruled out since **1** and **2** are destroyed by diffusion-controlled radical–radical reactions, which will occur at the same rate.[14] It must, therefore, be concluded that **2** is formed more readily than **1** at low temperatures. Let us designate all those conformations of 1,4-pentadiene[15] which yield **1** as **1H** and those that yield **2** as **2H**. The more facile formation of **2** at low temperatures could come about because the [**2H**]/[**1H**] ratio increases as the temperature is lowered and/or because the rate constant for H-atom abstraction from **2H**, k^2, decreases less rapidly with temperature than the rate constant for abstraction from **1H**, k^1. Unfortunately, it is not possible to determine which factor is the more important because, at each temperature, the relative amounts of **2** and **1** depend on the ratio of the products of the conformer concentration and the rate constant for their reaction with *tert*-butoxy, i.e., $[2]/[1] = k^2[2\mathrm{H}]/k^1[1\mathrm{H}]$.[16]

Models suggest that the transition state for H-atom abstraction from **2H** is sterically less crowded than that for abstraction from **1H**. For this reason, an alkoxy radical which is less bulky than *tert*-butoxy might be expected to yield relatively more **1** and less **2** than does *tert*-butoxy at the same temperature. This was indeed found to be the case using ethoxy radicals generated by photolysis of diethyl peroxide. In the temperature

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