Table II. Summary of Kinetic Data Obtained for $LiCH_3$–$Mg(CH_3)_2$ and $LiCH_3$–$Zn(CH_3)_2$ Systems in Ether

System	Nucleus exchanging	Arrhenius activation energy	Temp dependence of log k_1[a]
$LiCH_3$–$Li_2Zn(CH_3)_4$	^7Li	10.9	$-2380(1/T) + 11.6$
$LiCH_3$–$Li_2Zn(CH_3)_4$[b]	^7Li	12.0	$-2630(1/T) + 12.7$
$LiCH_3$–$Li_2Zn(CH_3)_4$	^1H	8.5	$-1860(1/T) + 9.33$
$LiCH_3$–$Li_2Mg(CH_3)_4$	^7Li	10.3	$-2260(1/T) + 10.6$
$LiCH_3$–$Li_2Mg(CH_3)_4$	^1H	≈ 10	
$Mg(CH_3)_2$–$Li_2Mg(CH_3)_4$	^1H	15.0	$-3180(1/T) + 16.9$

[a] k_1 is derived from $1/\tau$ in each case by use of eq 6–9 as appropriate for $Li/Mg(Zn) > 2$, and eq 11 for $Li/Mg < 2$. [b] From observation of $1/\tau_T$ alone; see text.

where eq 11 gives the relationship between $1/\tau$ obtained from the computer program and the rate constant, k_1.

In the zinc system, a separate resonance representing dimethylzinc was not observed, even at −107°. Methyl-group exchange is clearly more rapid than in the magnesium system. The mechanism of exchange is probably the same. The difference in rate may be associated with the fact that solvent is coordinated more strongly to dimethylmagnesium than dimethylzinc, as evidenced by dipole moment measurements.[16]

Finally, it has been noted that methyl group exchange between dimethylmagnesium and dimethylzinc in ether is rapid even at −103°. Table II provides a summary of all the quantitative results obtained.

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Kinetics of Electrochemical Oxidative Coupling of Decahydroclovodecaborate(2−) in Acetonitrile[1]

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Abstract: A variety of electrochemical techniques have been used to establish that the oxidation of $B_{10}H_{10}^{2-}$ at a platinum electrode in acetonitrile proceeds by an initial one-electron transfer to form a free radical which undergoes a second-order chemical reaction to form $B_{20}H_{19}^{3-}$, which is oxidized to $B_{20}H_{18}^{2-}$ at a slightly greater potential than $B_{10}H_{10}^{2-}$. The second-order rate constant for the chemical coupling reaction has been determined by chronopotentiometry with current reversal. Twenty determinations gave an average value of $k = 2.8 \times 10^3$ l. mole^{-1} sec^{-1}, with a standard deviation of 0.2×10^3 l. mole^{-1} sec^{-1}.

The aqueous chemical oxidation of $B_{10}H_{10}^{2-}$ produces $B_{20}H_{18}^{2-}$, the result of a two-electron oxidation per B_{10} unit.[2–6] Under milder conditions, it is also possible to isolate good yields of $B_{20}H_{19}^{3-}$, the result of a one-electron oxidation of $B_{10}H_{10}^{2-}$.[4–6] Under appropriate conditions, $B_{20}H_{19}^{3-}$ can be converted to $B_{20}H_{18}^{2-}$ and *vice versa*, but neither has been reduced back to $B_{10}H_{10}^{2-}$.[4–6] It is logical to suggest, on the basis of this chemical evidence, that $B_{10}H_{10}^{2-}$ undergoes an initial oxidation followed by an irreversible coupling reaction to form $B_{20}H_{19}^{3-}$, which is subsequently oxidized to $B_{20}H_{18}^{2-}$. If the electrochemical oxidation of $B_{10}H_{10}^{2-}$ were to follow a similar scheme, some of the more rapid electrochemical techniques should be applicable to the study of the coupling reaction itself.

Results

Voltammetry. At a rotating platinum electrode, a split anodic wave is observed for solutions of $B_{10}H_{10}^{2-}$ in acetonitrile containing 1.0, 0.63, or 0.10 $M(C_2H_5)_4NClO_4$ as supporting electrolyte. The apparent heights of the two parts of the wave are unequal, the less anodic predominating. As the concentration of $B_{10}H_{10}^{2-}$ is decreased, holding the concentration of supporting electrolyte constant, two changes are observed. The first wave (less anodic portion of the split wave) seems to increase at the expense of the second, and the second part now occurs at a less anodic potential. The first

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part of the first wave is found at the same potential, and the total limiting current remains proportional to the concentration of $B_{10}H_{10}^{2-}$, over the range 1×10^{-2} to 3×10^{-5} *M*. In the most concentrated solutions, the waves are well enough split that plots of log $i/(i_l - i)$ *vs.* *E*, assuming i_l to be one-half the total observed limiting current, can be made for over half the first wave. The slopes are about 0.05, as are measurements of $E_{3/4} - E_{1/4}$. Similar plots from the current–voltage data near the total limiting current do not give good straight lines for either log $i^2/(i_l - i)$ or log $i/(i_l - i)$ *vs.* *E*, but both limiting slopes and estimated values of $E_{3/4} - E_{1/4}$ give values much larger (>0.06) than those of comparable reversible systems (0.03).

Taking the potential at one-fourth the total limiting current as a measure of the potential of the first anodic process, we find this to be constant for different concentrations of $B_{10}H_{10}^{2-}$ in 1.0 *M* $(C_2H_5)_4NClO_4$, at +0.49 v (sce reference). In 0.1 *M* $(C_2H_5)_4NClO_4$, this characteristic potential is +0.43 v, and in 0.1 *M* $LiClO_4$, it is +0.375 v.

Peak polarograms at a stationary platinum electrode in acetonitrile have two anodic peaks. Both the relative peak currents and the peak potential difference change as a function of scan rate. At faster scans (up to 25 v/min) the second peak is much smaller than the first, and the peak potentials are closer to each other. Cyclic scans slower than 10 v/min show only the two anodic peaks between +0.1 and +0.8 v (sce), and the ratio of the second peak current to the first increases on repeated cyclic scans (triangular wave voltammetry). When the scan rate is increased, a small cathodic peak appears at a potential about 0.1 less anodic than the first anodic peak.

Cyclic voltammetry of a 10^{-3} *M* solution of $[(CH_3)_4N]_3B_{20}H_{19} \cdot 0.5H_2O$ shows an anodic peak at about +0.7 v and a cathodic peak at −0.1 v which increases on each cycle, assumed to be due to the H^+ liberated by the oxidation of $B_{20}H_{19}^{3-}$ to $B_{20}H_{18}^{2-}$. There is no evidence that the oxidation of $B_{20}H_{19}^{3-}$ is reversible in the potential range +0.8 to −0.2 v.

At a dropping mercury electrode, a solution of $[(CH_3)_4N]_2B_{20}H_{18}$ gave a cathodic wave at −1.48 v (sce).

Controlled Potential Electrolysis. One of the products of the partial electrolysis of $B_{10}H_{10}^{2-}$ at +0.4 or +0.6 v was $B_{20}H_{19}^{3-}$, identified by the infrared spectrum of its tetramethylammonium salt. Exhaustive electrolysis (final current less than 1% of initial current) at +0.9 v yielded only $B_{20}H_{18}^{2-}$, identified by the infrared and ultraviolet spectra of its tetramethylammonium salt. From a silver coulometer in series with the cell, *n* values of 2.0 and 2.2 electrons per $B_{10}H_{10}^{2-}$ were obtained.

When a 10^{-3} *M* solution of $[(C_2H_5)_3NH]_2B_{10}H_{10}$ was electrolyzed at +0.55 or +0.8 v in an epr cavity, a weak signal was observed at $g = 2.0$, with a width of 20 gauss.

Chronopotentiometry. For a solution of $B_{10}H_{10}^{2-}$, two transition times having a ratio of 1:3 and a difference in hold-up potential of about 0.1 v were observed. At a higher current density, the second transition time was observed to be less than three times the first. Varying the current from $i = 20$ to 428 μa gave transition times $\tau = 33.7$ to 0.082 sec for a 2×10^{-3} *M* solution of $B_{10}H_{10}^{2-}$. The values of $i\tau^{1/2}$, a measure of the number of electrons involved in the electrode process, did not deviate by more than 10% from the average of 37 determinations.

The first electron-transfer step is reversible (note cyclic voltammetry), so the rate of disappearance of the oxidation product of $B_{10}H_{10}^{2-}$ can be followed by chronopotentiometry with current reversal. Working curves were computed by the method of Feldberg and Auerbach,[7] assuming chemical reaction to be second order with respect to $B_{10}H_{10}^{-}$, irreversible, and leading to a product that is not electroactive in the potential region of the chronopotentiometry. Ratios of forward and reverse transition times for different values of forward and reverse current densities and different initial concentrations of $B_{10}H_{10}^{2-}$ gave consistent values of the second-order rate constant *k* (see Table I). From 20 determinations we calculate an average value of $k = 2.8 \times 10^3$ l. mole^{-1} sec^{-1}, with a standard deviation of 0.2×10^3. All measurements were made at 25°.

Table I. Second-Order Rate Constants from Chronopotentiometry with Current Reversal

i_f/i_r (μa/μa)	t_f/τ_r (sec/sec)	k (l. mole^{-1} sec^{-1}) $\times 10^{-3}$
	$[B_{10}H_{10}^{2-}] = 1.02 \times 10^{-3}$ *M*	
200/10.3	3.90/1.26	2.7
250/10.4	2.36/1.30	2.6
300/10.3	2.01/1.34	2.6
400/10.3	1.14/1.30	2.8
	1.10/1.34	2.7
500/10.3	0.87/1.38	2.8
	$[B_{10}H_{10}^{2-}] = 2.16 \times 10^{-3}$ *M*	
100/41.4	0.175/0.115	3.0
	0.28/0.17	3.0
	0.16/0.115	2.5
	0.28/0.165	2.6
	$[B_{10}H_{10}^{2-}] = 3.09 \times 10^{-3}$ *M*	
100.2/10.3	1.97/1.14	2.9
	2.01/1.18	2.7
125/10.3	1.50/1.18	2.6
	0.905/1.14	2.5
	1.34/1.22	2.75
150/10.3	1.14/1.22	3.2
	1.14/1.26	3.1
	0.985/1.26	2.8
200/10.3	0.69/1.24	3.3
	0.59/1.24	2.9

Discussion

Voltammetry of solutions of $B_{10}H_{10}^{2-}$ and $B_{20}H_{19}^{3-}$ clearly show that two anodic processes take place for $B_{10}H_{10}^{2-}$, and that the second of these is probably the oxidation of $B_{20}H_{19}^{3-}$. The isolation of $B_{20}H_{18}^{2-}$ as the only significant product of the exhaustive electrolysis of $B_{10}H_{10}^{2-}$ and $B_{20}H_{19}^{3-}$ from the partial electrolysis

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of $B_{10}H_{10}^{2-}$ supports this hypothesis. The 1:3 ratio of first and second transition times in chronopotentiometry shows that the same number of electrons per $B_{10}H_{10}^{2-}$ is involved in both oxidations. The formation of $B_{20}H_{19}^{3-}$ requires a loss of one electron per $B_{10}H_{10}^{2-}$; the oxidation of $B_{20}H_{19}^{3-}$ to $B_{20}H_{18}^{2-}$ is a two-electron change, or one per original $B_{10}H_{10}^{2-}$.

Several pieces of evidence show that $B_{20}H_{19}^{3-}$ is formed according to scheme I rather than II. One is the observation of a free radical in the electrolysis,

$$\begin{gathered} B_{10}H_{10}^{2-} \longrightarrow B_{10}H_{10}^{-} + e^{-} \\ 2B_{10}H_{10}^{-} \longrightarrow B_{20}H_{19}^{3-} + H^{+} \end{gathered} \tag{I}$$

$$\begin{gathered} B_{10}H_{10}^{2-} \longrightarrow B_{10}H_{10} + 2e^{-} \\ B_{10}H_{10} + B_{10}H_{10}^{2-} \longrightarrow B_{20}H_{19}^{3-} + H^{+} \end{gathered} \tag{II}$$

although this would also be found if $B_{10}H_{10}$ were formed in a triplet state. Similar radicals have been observed in the chemical oxidation of $B_{10}H_{10}^{2-}$.[2,8] Another is the constancy of $i\tau^{1/2}$ for the first transition time in chronopotentiometry. By scheme I, the first transition time will always appear to correspond to one electron per $B_{10}H_{10}^{2-}$. By scheme II, the first transition time will also appear to correspond to one electron per $B_{10}H_{10}^{2-}$ if the follow-up chemical reaction is sufficiently rapid. By increasing the current density, it should be possible to arrive at the transition time ($[B_{10}H_{10}^{2-}] = 0$ at the electrode) fast enough that not all the $B_{10}H_{10}$ can react with $B_{10}H_{10}^{2-}$ before all the $B_{10}H_{10}^{2-}$ is oxidized, so that the transition time should approach a time characteristic of two electrons per $B_{10}H_{10}^{2-}$ at very high current densities. This was not observed, but the accessible transition times would require that k be less than 10^3 l. mole^{-1} sec^{-1} to find a variation in $i\tau^{1/2}$.

No study was made of the effect of hydrogen ion activity on the rate constant, but previous reports[9,10] that the potential of the first anodic wave of $B_{10}H_{10}^{2-}$ at a carbon paste electrode in water is independent of pH causes us to favor the proton-transfer sequence shown.

The behavior of the anodic wave in the voltammetry of $B_{10}H_{10}^{2-}$ at the rotating platinum electrode can be explained in terms of an ece mechanism (two electron transfers coupled by a chemical reaction). The current–potential curve for the second process (oxidation of $B_{20}H_{19}^{3-}$) has a flatter slope (more irreversible) than that of the first process, and it is displaced to less anodic potentials in more dilute solutions. Because the potential of the first process is insensitive to concentration, the region of overlap of the two processes is concentration dependent. The different slopes of the two components of the over-all current–potential curve give rise to an apparent break in the curve that is not at one-half the total limiting current and which varies with concentration, as the region of overlap varies.

Differences in the liquid junction potential between the sce and the solutions containing 1.0 M $(C_2H_5)_4NClO_4$, 0.1 M $(C_2H_5)_4NClO_4$, and 0.1 M $LiClO_4$ contribute to the differences in apparent $E_{1/2}$ values. The difference between the potentials in 0.1 M $(C_2H_5)_4NClO_4$ and 0.1 M $LiClO_4$ can be explained largely on this basis, but the difference between the 1.0 and 0.1 M $(C_2H_5)_4NClO_4$ is in the opposite direction to the change in liquid junction potential.[11]

Cyclic voltammetry shows that the first electrode process is reversible and that the second electrode process is irreversible. In the light of what is known about the different B_{10}–B_{10} linkages in $B_{20}H_{19}^{3-}$, $B_{20}H_{18}^{4-}$, and $B_{20}H_{18}^{2-}$,[12] it is not surprising that the oxidation of $B_{20}H_{19}^{3-}$ and the reduction of $B_{20}H_{18}^{2-}$ take place at such widely separated potentials.

Experimental Section

Reagents. Acetonitrile (Fisher Certified reagent) was fractionally distilled from P_2O_5 and from CaH_2. The fraction collected had less than a 0.2° boiling point range.

Tetraethylammonium perchlorate was prepared from tetraethylammonium bromide and sodium perchlorate. The crude product was crystallized from water usually six times and dried by heating *in vacuo*.

Published procedures were used to prepare $[(C_2H_5)_3NH]_2B_{10}H_{10}$,[6] $[(CH_3)_4N]_2B_{10}H_{10}$,[9] $[(CH_3)_4N]_3B_{20}H_{19} \cdot 0.5H_2O$,[5] and $[(CH_3)_4N]_2B_{20}H_{18}$.[5] The products were checked by infrared spectroscopy.

Electrochemistry. All experiments were done with a three-electrode system, using an aqueous saturated calomel electrode (sce) as the reference electrode. Potentials are reported relative to the sce. The rotating platinum electrode was a platinum wire sealed in glass. The stationary electrode was a Beckman Model 39273 platinum inlay electrode with a surface area of about 0.22 cm^2. The apparatus used for the chronopotentiometry was similar to that described by Macero and Anderson.[13] Transition times for the check of $i\tau^{1/2}$ for various current densities were determined visually or photographically from an oscilloscope display. For the determination of rate constants, current–time curves were recorded using a Moseley Model 7101A strip chart recorder. Transition times were measured by the break-potential method of Kuwana, which has been shown to be reliable.[14]

Controlled-Potential Electrolysis Products. A solution 0.01 M with respect to $[(CH_3)_4N]_2B_{10}H_{10}$ and 0.1 M with respect to $LiClO_4$ in CH_3CN was electrolyzed at a rotating platinum gauze electrode for 16 hr at +0.60 v in a two-compartment electrolysis cell. A silver coulometer indicated that *ca.* 0.8 electron per $B_{10}H_{10}^{2-}$ had been passed. The volume of the solution in the cathode compartment was reduced under vacuum, and a white solid was isolated which had an infrared absorption at 1850 cm^{-1} characteristic of a bridged B–H–B structure.

In a similar experiment, $[(C_2H_5)_3NH]_2B_{10}H_{10}$ was electrolyzed at +0.40 v for about 15 hr when *ca.* 0.66 equiv of current had passed. The volume of the solution was reduced under vacuum. Addition of a concentrated solution of $(CH_3)_4NCl$ caused the formation of a precipitate which had infrared absorption at 1850 cm^{-1} characteristic of $B_{20}H_{19}^{3-}$, and some at lower frequencies (<1000 cm^{-1}) characteristic of $B_{20}H_{18}^{2-}$. Subsequent recrystallizations afforded a solid whose infrared spectrum in Nujol was identical with that of the chemically prepared $[(CH_3)_4N]_3B_{20}H_{19} \cdot 0.5H_2O$, at 2450, 1840 (broad), 1150 (broad, weak), 990, and 940 cm^{-1} with water absorption at 3500 and 1600 cm^{-1}.

When the electrolysis was carried out at 0.90 v for 11 hr, a very pale yellow solid was isolated whose infrared spectrum matched that of chemically prepared $[(CH_3)_4N]_2B_{20}H_{18}$, in the region 4000–700 cm^{-1}.

The electrolysis cell used in the epr cavity was that of Piette, Ludwig, and Adams.[15]

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