(Scheme II). Oxidation of A^{2-} involves the $A^{-}\cdot/A^{2-}$ couple for which $E° = +0.03 \pm 0.02$ V while oxidation of $A^{-}\cdot$ involves the $A/A^{-}\cdot$ couple for which $E° = -0.14 \pm 0.02$ V. Thus the rate constant for the oxidation of the radical is smaller despite the fact that the driving force for this reaction is greater than for the oxidation of A^{2-}. As above, the self-exchange rate (eq 10) is estimated from the $A^{-}\cdot/\mathrm{Fe^{III}}(\mathrm{cyt}\ c)$ reaction rate constant; a rate constant $k_{22} \leq 10^{-1}$ M^{-1} s^{-1} is thus obtained. Thus we arrive at the conclusion that the $A^{-}\cdot/A$ couple has a rather high intrinsic electron-transfer barrier. While the evidence is limited, sluggish redox properties for this couple might have been predicted on the basis of the structures IV and VI shown in Figure 1. The water-equilibrated form of dehydroascorbic acid (whose properties Ball's thermodynamic measurements should reflect) has a bicyclic monoketo structure. It seems likely that oxidation of $A^{-}\cdot$, a monocyclic species with extensive radical delocalization over three $>C{=}O$ groups, yields initially the monocyclic triketo form of dehydroascorbic acid V. Rearrangement of V to the stable form VI would then ensue. Alternatively, rearrangement of the radical to a species more strongly resembling VI could precede the electron-transfer step. These alternative mechanisms are summarized in Schemes III and IV where A(V) and A(VI) depict dehydroascorbic acid in forms V and VI, respectively, and $A^{-}\cdot'$ depicts a form of ascorbate radical that is structurally similar to VI rather than to V. Neither thermodynamic nor kinetic data bearing on the equilibrium between structures V and VI are available; nor is there any indication that $A^{-}\cdot'$ exists. Thus the mechanism of ascorbate radical oxidation cannot be clarified to any greater extent at this time. It is worth noting, however, that, on the basis of Scheme III or IV, neither the self-exchange estimate obtained above nor the overall $E°$ given in Table II is for the simple process implied by eq 10 and that far from simple kinetic behavior may be anticipated for reactions involving the $A^{-}\cdot/A$ couple.

Scheme III

$$A^{-}\cdot \rightarrow A(V) + e^{-}$$

$$A(V) \rightleftharpoons A(VI)$$

Scheme IV

$$A^{-}\cdot \rightleftharpoons A^{-}\cdot'$$

$$A^{-}\cdot' + e^{-} \rightarrow A(VI)$$

We mention one other complicating feature in passing. While in most reactions involving ascorbate as a reductant eq 11 is likely to represent the initial step, it is worth reiterating

$$HA^{-} + OX \rightarrow HA\cdot + RED \qquad (11)$$

that at pH 0–13 the stable form of the ascorbate radical is the anionic species $A^{-}\cdot$. Thus above pH ~0 eq 11 is expected to be followed by very rapid deprotonation of $HA\cdot$, eq 4. With

$$HA\cdot \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} H^{+} + A^{-}\cdot \qquad (4)$$

the assumption that k_{-5} is nearly diffusion controlled ($k_{-5} = 10^{9}$ M^{-1} s^{-1}), proton dissociation could proceed with $k_5 = 3.5 \times 10^{8}$ s^{-1}; thus the lifetime of $HA\cdot$ may in some instances be less than 10 ns. The rapid deprotonation of $HA\cdot$ introduces an additional subtlety into the behavior of ascorbate systems: while the rate of production of ascorbate radicals is related to the properties ($E°$, k_{11}) of the $HA\cdot/HA^{-}$ couple, subsequent reactions are determined by the properties of the $A^{-}\cdot/A^{2-}$ and $A/A^{-}\cdot$ couples discussed above. The rapid deprotonation of $HA\cdot$ (as well as the sluggishness of the $A^{-}\cdot/A$ couple) may be of particular importance in the photochemical systems[4] where it may provide a "switching" mechanism, effectively slowing down some of the reactions that destroy reactive intermediates. In the thermal reactions reviewed in this paper these interesting complications may also play an important, if infrequently recognized, role. We hope that further detailed studies of ascorbate reactions will lead to a fuller understanding of these questions.

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Electron Correlation Effects in B_4H_{10} Structures

Sir:

The experimental geometry of B_4H_{10} is well established[1] as a molecule of C_{2v} symmetry of *styx* topology 4012 in which each of the two BH_2 groups is joined by bridged hydrogens to a singly bonded pair of BH units. An early proposal,[2] also of topology 4012, is the bis(diborane) structure, in which two B_2H_5 units are joined by a single bond. Here, we address the question, "What level of theoretical accuracy yields the observed structure in preference to the bis(diborane) structure?"

In two previous calculations the observed structure is not preferred. A 4-31G* study showed that bis(diborane) is more stable than the observed structure by 16.5 kcal/mol. Neither the addition of configuration interaction nor modification of this basis set altered this conclusion.[3] A study by Kleier,[4] who used the PRDDO method,[5] yielded the gauche form of bis(diborane) as more stable than the trans form by about 1 kcal/mol, and more stable than the cis form by about 3 kcal/mol. The observed structure of C_{2v} symmetry was about 5 kcal/mol less stable than the gauche form of bis(diborane).[4]

In the present study geometries were optimized[6] with use of a double-ζ basis set (3-21G),[7] assuming symmetry C_{2v} for the observed structure, C_{2h} for *trans*-bis(diborane), C_{2v} for *cis*-bis(diborane), and C_1 for *gauche*-bis(diborane). The gauche form optimized to C_2 symmetry. These optimized geometries (Table I) yielded the energies listed in Table II at the levels 6-31G and 6-31G* (polarization added) and Møller–Plesset (MP) corrections[8] to third order[9] for the 6-31G basis (configuration interaction). In Table II we add the

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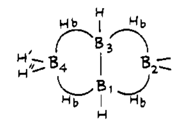
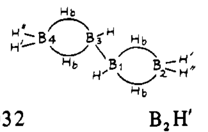
Table I. Optimized Distances (Å) for B_4H_{10} Structures

C_{2v}, Known Structure (I)



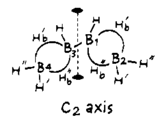
B_1B_3	1.7326 (1.718)[a]	B_2H'	1.1813
B_1B_2	1.9017 (1.854)	B_2H''	1.1841
B_2B_4	2.8510	B_1H_b	1.2477 (1.428)
B_1H	1.1770	B_2H_b	1.4296 (1.425)

C_{2h} Bis(diborane) Structure (II)



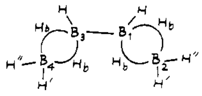
B_1B_3	1.7032	B_2H'	1.1831
B_1B_2	1.8020	B_2H''	1.1827
B_2B_3	3.0526	B_1H_b	1.3208
B_2B_4	4.7150	B_2H_b	1.2170
B_1H	1.1866		

C_2 Bis(diborane) Structure (III)



B_1B_3	1.6973	B_2H''	1.1827
B_1B_2	1.7975	B_1H_b'	1.3224
B_2B_3	3.0662	B_1H_b''	1.3245
B_2B_4	4.0371	B_2H_b'	1.3146
B_1H	1.1872	B_2H_b''	1.3114
B_2H'	1.1838	HB_1B_3H	67.3°

C_{2v} Bis(diborane) Structure (IV)



B_1B_3	1.7132	B_2H'	1.1826
B_1B_2	1.8023	B_2H''	1.1823
B_2B_3	3.1098	B_1H_b	1.3214
B_2B_4	3.7490	B_2H_b	1.3159
B_1H	1.1865		

[a] Experimental values in parentheses are from: Simmons, N. P. C.; Burg, A. B.; Beaudet, R. A. *Inorg. Chem.* **1981**, *20*, 533.

polarization and configuration interaction corrections in order to obtain the last column. In a previous study of eight molecules[10] (H_2O, NH_3, N_2, F_2, B_2H_4, $BH_3 \cdots H_2$, BH_5, and B_2H_6) we have shown that addition of these two corrections gives very nearly the same result as a full calculation in which both polarization and MP3 correlation corrections are included. The cost of doing both in B_4H_{10} is prohibitive at the present time.

Our results show that the observed structure is more stable than the *gauche*-bis(diborane) structure by only 2.7 kcal/mol (Table II, last column). It is likely that further corrections for electron correlation will increase the relative stability of the observed structure as predicted by theory. Further study is required to determine whether the bis(diborane) structures lie in local minima relative to the observed structure and whether they are involved in chemical properties of B_4H_{10}.

Correlation corrections account for about 40–45% of the dissociation energy of B_2H_6 to 2 BH_3 molecules. The Hartree–Fock limit is about 20 kcal/mol,[11,12] and the theoretical value[12] including correlation is 36.6 kcal/mol in agreement with the experimental value[13] of 35.5 kcal/mol. Correlation corrections favor more highly bridged structures of B_3H_7 and B_4H_8,[14] are required in the isomerization of hypothetical B_4H_4[15] and in distinguishing relative stabilities of classical and nonclassical isomers,[16] and may yet favor the C_1[17] vs. the C_s[18] structure of B_5H_{11}. Also correlation will be required for a theoretical understanding of the pyrolysis reaction, which yields higher hydrides from diborane.

Table II. Energies of B_4H_{10} Structures Relative to the Observed Form[a]

	6-31G	6-31G*	MP3/6-31G	6-31G* + MP3/6-31G
obsd (C_{2v})	0	41.85	204.32	246.17
	(0)	(0)	(0)	(0)
gauche-bis(diborane)	0	43.14	193.42	236.56
(C_2)	(−6.92)	(−8.21)	(3.98)	(2.69)
trans-bis(diborane)	0	43.07	192.37	235.44
(C_{2h})	(−6.26)	(−7.48)	(5.69)	(4.47)
cis-bis(diborane)	0	43.08	192.26	235.34
(C_{2v})	(−4.64)	(−5.87)	(7.42)	(6.19)

[a] A negative number in parentheses means stability with respect to the observed structure of B_4H_{10}. All energies are in kcal/mol. Values not in parentheses are energy lowerings relative to the 6-31G basis as zero for each separate geometry. The last column is obtained by addition of corrections of the second and third columns. Values in parentheses are referred to the zeros of energy for the observed geometry at each level of approximation. The total energy of the observed (C_{2v}) structure for B_4H_{10} is 104.390 070 hartrees.

Finally, we have yet to find the limitation to the additivity of polarization and configuration interaction corrections. We anticipate that difficulties will occur when heavier elements and metastable states are studied.

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Correct Assignment of Stretching Frequencies of Tetraoxometalates in Unusual Oxidation States

Sir:

Recently, an interesting paper was published on the CaO–Cr_2O_3–O_2 system[1] in which an incorrect assignment for the

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