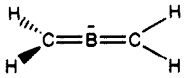
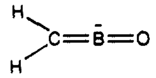
deuteriated precursor ions confirm that the major losses of H_2 and CH_4 occur as shown in eq 3–6.[10]

The results of ab initio calculations are shown in formulas 7–12



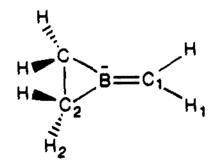
7[12]



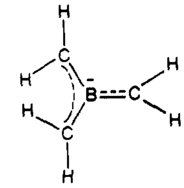
8[13]

and ref 12–17. Geometries are at HF/6-31+G*//6-31+G* level; energies at the MP2/6-31+G*//6-31+G* level.[11] The bismethyleneborane ion **7** has an "allene" structure; the alternative configuration where the hydrogens are eclipsed is not a local minimum. The oxa analogue $[CH_2BO]^-$ is isoelectronic with ketene; its structure **8** is shown. The methylene groups in these systems are planar, consistent with ground-state structures having minimal carbanion character.

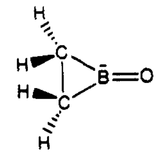
The structures of "$[B(CH_2)_3]^-$" and "$[(CH_2)_2BO]^-$" are more complex. Singlet trismethyleneborane $[B(CH_2)_3]^-$ is not a local minimum in D_{3h} or lower symmetry and relaxes to the stable cycloborapropane ion **9**.[14] The triplet trismethyleneborane anion



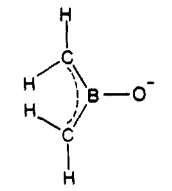
9[14]



10[15]



11[16]



12[17]

is directly analogous to the isoelectronic trimethylenemethane.[3] It has the D_{3h} structure **10** in which the methylene groups are all in one plane,[18] and lies 33.7 kcal mol^{-1} above the cyclic structure **9**. The BC bond length of **10** is calculated to be 1.544 Å, a value intermediate between a single (B–C, 1.63–1.66 Å) and a double bond (B=C, 1.43–1.46 Å).[12–17] An analogous situation pertains for the oxa ion $[(CH_2)_2BO]^-$. The singlet C_{2v} or C_2 versions of this ion are not local minima but relax to the cyclic species **11**.[16] The stable C_{2v} $[(CH_2)_2BO]^-$ structure is a triplet (**12**), 75.0 kcal mol^{-1} in energy above **11**. Calculations of the bonding in **12** indicate CB bonds (1.519 Å) with appreciable double bond character, whereas the BO bond (1.478 Å) is essentially a single bond [B–O, 1.49–1.53; B=O, 1.26–1.29[7,12–17]].

In summary, ab initio calculations confirm the stability of the bismethyleneborane anion and indicate that its structure is similar to that of allene, in accord with classical theory. The trismethyleneborane anion is unstable with respect to the isomeric methylene cycloborapropane anion and is thus analogous in behavior to the isoelectronic trimethylenemethane.

(10) The collisional activation mass spectra of the labeled compounds are as follows [m/z (loss) abundance]: $[Me(CD_3)^{11}BCH_2]^-$ 57(H•)100, 56-(H_2,D•)89, 55(HD)12, 42(Me•)1.2, 41(MeD)1.8, 39(CD_3H)4.0; $[Me_2{}^{11}BCD_2]^-$ 56(H•)100, 55(H_2,D•)64, 54(HD)14, 42(Me•)2, 41(CH_4)9, 40(MeD)1; $[(CD_3)_2{}^{11}BCH_2]^-$ 60(H•)100, 59(D•)65, 58(HD)8, 57(D_2)<1, 43(CD_3•)1, 42(CD_3H)1.2, 41(CD_4)3.8; $[Me(CD_3)^{11}BO]^-$ 59(H•)50, 58(D•)29, 57(HD)24, 43(MeD)25, and 41(CD_3H)29. Pronounced deuterium isotope effects are apparent for the various losses of H_2 and CH_4.

(11) Calculations were performed with GAUSSIAN 86 (Gaussian 86. Release C, Frisch, M.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Martin, R.; Stewart, J. J. P.; Bobrowicz, F.; DeFrees, D.; Seeger, R.; Whiteside, R.; Fox, D.; Fluder, E.; Pople, J. A. Carnegie Mellon University) at the RHF/6-31+G* level. Genuine minima were confirmed by harmonic frequency analyses and by standard tests of wave function stability by release of the RHF constraint. Cited energies were determined with the additional MP2 correlation level.

(12) E = −103.04507 au, D_{3h}, BC = 1.4345 Å, CH = 1.0820, BCH = 122.9295°.

(13) E = −139.02607 au, C_{2v}, BO = 1.2329 Å, BC = 1.4569, CH = 1.0295, BCH = 122.2031°.

(14) E = −142.21374 au, C_{2v}, BC_1 = 1.4475 Å, BC_2 = 1.5777, C_1H_1 = 1.0846, C_2H_2 = 1.0846, C_2C = 1.5592, C_1BC_2 = 150.3872°, BC_1H_1 = 123.2724, BC_2H_2 = 121.6633, $H_2C_2BC_1$ = 76.2326°.

(15) E = −142.15996 au, D_{3h}, BC = 1.5442 Å, CH = 1.0860, BCH = 123.5845°.

(16) E = −178.16843 au, C_{2v}, BO = 1.2641 Å, BC = 1.5950, CC = 1.5807, CH = 1.0861, OBC = 150.2976, BCH = 122.2759, HCBO = 77.2241°.

(17) E = −178.04867 au, C_{2v}, BO = 1.4784 Å, BC = 1.5188, CH_1 = 1.0840, CH_2 = 1.0832, OBC = 118.5059, BCH_1 = 124.9628, BCH_2 = 121.2106°.

(18) This should be compared with the structure $[P(CH_2)_3]^-$, an ion of D_3 symmetry. The PC bonds show appreciable double bond character, but the planar methylene groups are twisted out of the plane by some 20°.[1,2] However, $[P(CH_2)_2]^-$ is coplanar.[2]

Additions and Corrections

Gated Electron Transfer: When Are Observed Rates Controlled by Conformational Interconversion? [*J. Am. Chem. Soc.* **1987**, *109*, 6237–6243]. BRIAN M. HOFFMAN* and MARK A. RATNER*

Errors have been found in several equations in this text. The following are the corrections for these equations.

Equation 3b: $k_1 = k_+ + k_d + k_u + k_D$.
Equation 4: (A^*) should be $(A^*)/A^*_0$.
Equations 9 and 11: k_{tC} should be $k_{tC}A^*_0$.
Equation 11: k_+ should be k_{+1}.
Equation 12: k_d, k_u should be k_{d1}, k_{u1}.
Equations 13, 15, 16, and 17: (I) should be $(I)/k_{tC}A^*_0$.
Equations 15–17: Delete k_{obsd} from numerator; these results assume $k_{bC} = k_{d1} = 0$.

Adenosine 5′-[α,β-Imido]triphosphate, a Substrate for T7 RNA Polymerase and Rabbit Muscle Creatine Kinase [*J. Am. Chem. Soc.* **1988**, *110*, 4060–4061]. QI-FENG MA, PATRICIA C. BABBITT, and GEORGE L. KENYON*

We have now found that adenosine 5′-[α,β-imido]triphosphate (AMPNPP) is not a substrate for T7 RNA polymerase and that our earlier results were evidently due to contamination of the AMPNPP with low levels of ATP. Control experiments with low levels of ATP in the absence of AMPNPP gave results identical with those obtained by incubating the initially synthesized AMPNPP and other substrates with T7 RNA polymerase in the absence of added ATP. Further, AMPNPP synthesized by an alternative method does not act as a substrate for T7 RNA polymerase. The results reported for creatine kinase are unchanged.