confidence) must be rate-limiting in the buffer-catalyzed reaction.

Rates of glucation of hemoglobin under an atmosphere of air were measured by following the appearance of glycated product.[7] Glucohemoglobin HbA_{1c} was eluted from a cation-exchange column and measured spectrophotometrically at 415 nm (Sigma Kit[7] no. 440). Hemoblogin concentrations of 0.03–0.04 mM were employed with glucose at 40 mM. Reaction media were 0.15 M in sodium chloride, buffered at 37 °C with mixtures of NaH_2PO_4 and Na_2HPO_4 at pH 7.3. Reactions in deuterium oxide were conducted at the "corresponding pD" of 7.8. D-Glucose-*2-d* (97 atom %) was obtained from Sigma Chemical Co. The kinetics exhibited both a buffer-independent term (reflecting reaction assisted by water, lyons (hydroxide or hydronium ions), or protein functional groups) and a first-order term in phosphate buffer.

For the buffer-independent term, the substrate isotope effect of 2.2 ± 0.1 shows the proton-abstraction step of the Amadori rearrangement at least partially to determine the rate. The proton-abstracting base could in principle be (a) water, (b) hydroxide ion, or (c) a basic functional group of the protein. The solvent isotope effect can be predicted for each case. Water as abstracting base should give k_{HOH}/k_{DOD} = 1.0–2.1, depending on transition-state structure;[9] hydroxide ion as abstracting base should give k_{HOH}/k_{DOD} = 0.5–1.0, depending on transition-state structure;[9] a protein functional group should give k_{HOH}/k_{DOD} = 1.0, since the use of "corresponding pD" will cause the fractional ionization to be the same in the two isotopic solvents.[8] The data shown in Figure 2 yield k_{HOH}/k_{DOD} = 1.1 ± 0.1. While not decisive because consistent with any base if the transition-state structure is "early," the data are most readily reconciled with a protein functional group as the proton-abstracting base.

For the buffer-dependent term, the absence of a statistically meaningful solvent isotope effect (the data of Figure 2 yield k_{HOH}/k_{DOD} = 0.7 ± 0.2) excludes proton donation from the buffer as the rate-limiting step; the absence of a substrate isotope effect (1.1 ± 0.1) means that proton abstraction is not rate-limiting. Thus a kinetic event other than proton transfer must limit the rate. The most straightforward hypothesis is that a protein structural change before or during the Amadori rearrangement is rate-limiting for the phosphate-accelerated process. It cannot be said with any general reliability whether a protein conformational change would exhibit a solvent isotope effect; this will be determined by whether changes in binding at exhangeable protonic sites occur in the course of the conformational change.[8] It is conceivable that phosphate binding induces such a conformational change, and then the ensuing proton-transfer step or steps are more rapid than in the absence of phosphate. It is known[6] that non-phosphate buffers such as MOPS or TAPSO are less effective in promoting glucation and that 2,3-diphosphoglycerate, an effector of hemoglobin action, accelerates glucation. Therefore a specific binding site, such as the 2,3-diphosphoglycerate site, may be involved.

Although nonenzymic protein glycation is commonly regarded as an adventitious feature of in vivo protein chemistry, the possible involvement of protein functional groups and specific binding sites for hemoglobin raises the possibility that some programmatic biological significance may attach to the process.

Acknowledgment. This research was supported by the National Institutes of Health (U.S.A.) by means of research Grant GM-20198. J.F.M.-S. is a recipient of a Research Career Award of the Costa Rican National Council of Scientific and Technological Research.

(7) The technique is that described by the following: Bunn, H. F.; Haney, D. N.; Kamin, S.; Gabbay, K. H.; Gallop, P. M. *J. Clin. Invest.* **1976**, *57*, 1652. Stevens, V. J.; Vlassara, H.; Abati, A.; Cerami, A. *J. Biol. Chem.* **1977**, *252*, 2998. Bunn, H. F.; Haney, D. N.; Gabbay, K. H.; Gallop, P. M. *Biochem. Biophys. Res. Commun.* **1975**, *67*, 103.

(8) Schowen, K. B.; Schowen, R. L. *Methods Enzymol.* **1982**, *87*, 551–607.

(9) For water as base, the transition state L_2O^+–H···S (L = H, D) will give $k_{HOH}/k_{DOD} = 1/(0.69)^2 = 2.1$ as solvent isotope effect, while the transition state L_2O···H–S will give 1.0. For hydroxide ion as base, the transition state LO–H···S will give 0.5 (the fractionation factor for LO^-), while LO^-···H–S will give 1.0. See: Schowen, R. L. *Prog. Phys. Org. Chem.* **1972**, *9*, 275. Alvarez, F. J.; Schowen, R. L. *Isotopes Org. Chem.* **1987**, *7*, 1.

Bismethyleneborane, $[B(CH_2)_2]^-$, and Trismethyleneborane, $[B(CH_2)_3]^-$, Anions. Do They Exist in the Gas Phase?

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Received May 3, 1988

Recent reports[1,2] of families of anions related to $[P(CH_2)_2]^-$, $[CH_2PO]^-$, $[P(CH_2)_3]^-$, and $[(CH_2)_2PO]^-$ have led us to consider whether the cognate boron species are stable. Such boron ions are of considerable theoretical interest since conventional valence bond theory would predict that $[B(CH_2)_2]^-$ and $[B(CH_2)_3]^-$ should have allene and trimethylenemethane[3] type structures, respectively, with the latter ion being a diradical. These predictions need to be tested since (i) boron structures sometimes do not conform to classical valence bond schemes,[4] (ii) the ionic species may have some carbanion character (nonplanar CH_2 groups), and (iii) if the CH_2 groups are planar, some out of plane twisting may occur, cf. $[P(CH_2)_3]^-$.[1,2]

Ions with atomic compositions consistent with structures $[B(CH_2)_2]^-$, $[CH_2BO]^-$, $[B(CH_2)_3]^-$, and $[(CH_2)_2BO]^-$ were formed in a VG ZAB 2HF mass spectrometer as follows. The reaction between HO^- and trimethylborane in the chemical ionization source yielded the precursor ions shown in eq 1 and 2.[5,6] These

$$HO^- + Me_3B \rightarrow Me_2\bar{B}{=}CH_2 + H_2O \quad (1)$$

$$HO^- + Me_3B \rightarrow Me_2\bar{B}{=}O + CH_4 \quad (2)$$

$$Me_2\bar{B}{=}CH_2 \rightarrow [B(CH_2)_3]^- + H_2 \quad (3)$$

$$Me_2\bar{B}{=}CH_2 \rightarrow [B(CH_2)_2]^- + CH_4 \quad (4)$$

$$Me_2\bar{B}{=}O \rightarrow [(CH_2)_2BO]^- + H_2 \quad (5)$$

$$Me_2\bar{B}{=}O \rightarrow [CH_2BO]^- + CH_4 \quad (6)$$

reactions are of a standard type.[2,7] Collisional activation[8] of the precursor ions yield a number of product ions including the required species shown in eq 3–6.[9] The spectra of the corresponding

(1) Rajca, A.; Rice, J. E.; Streitwieser, A.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 4189.

(2) O'Hair, R. A.; Sheldon, J. C.; Bowie, J. H. *J. Chem. Soc., Dalton Trans.* **1988**, in press.

(3) (a) Trimethylenemethane is a triplet diradical with D_{3h} symmetry: Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. See, also: Hood, D. M.; Pitzer, R. M.; Schaefer, H. F. *J. Am. Chem. Soc.* **1978**, *100*, 2227. (b) Trimethylenemethane can be obtained as a matrix-trapped species: Haider, K.; Platz, M. S.; Despres, A.; Lejeune, V.; Migirdicyan, E.; Bally, T.; Haselbach, E. *J. Am. Chem. Soc.* **1988**, *110*, 2318. (c) Trimethylenemethane is less stable than singlet methylenecyclopropane by 14–16 kcal mol^{-1} (Feller, D.; Davidson, E. R.; Bordan, W. T. *Isr. J. Chem.* **1983**, *23*, 105), and it converts thermally to the cyclic species over a barrier of 7 kcal mol^{-1} (Dolbier, W. R.; Burkholder, C. R. *Tetrahedron* **1985**, *41*, 297. Dowd, P.; Chow, M. *Tetrahedron* **1982**, *38*, 799).

(4) Lipscomb, W. N. *Boron Hydrides*; W. A. Benjamin Inc.: New York, 1963. Wade, K. Structural and Bonding Patterns in Cluster Chemistry. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(5) (a) For experimental details concerning the operation of the VG ZAB 2HF instrument, see: Stringer, M. B.; Bowie, J. H.; Holmes, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 3888. (b) Me_3B, Me_2BCD_3, and $MeB(CD_3)_2$ were prepared by a standard procedure: Brown, H. C. *J. Am. Chem. Soc.* **1945**, *67*, 374.

(6) Ab initio calculations on the product ions of eq 1 and 2 show (i) $Me_2\bar{B}{=}CH_2$, C_{2v}, MeB = 1.6326, (B=CH_2) = 1.4648 and (ii) $Me_2\bar{B}{=}O$, C_{2v}, MeB = 1.6546, (B=O) = 1.2792 Å.

(7) (a) Hayes, R. N.; Sheldon, J. C.; Bowie, J. H. *Organometallics* **1986**, *5*, 162. (b) DePuy, C. H.; Damrauer, R.; Bowie, J. H.; Sheldon, J. C. *Acc. Chem. Res.* **1987**, *20*, 127.

(8) Helium gas in second collision cell; for details see ref 5a.

(9) (a) The mechanisms of these reactions are likely to be similar to those of cognate reactions of organophosphorus[2] and organosilicon ions[7b] (also, see: Sheldon, J. C.; Bowie, J. H.; Eichinger, P. C. H. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1263). (b) The collisional activation spectra of $(Me_2BCH_2)^-$ and $(Me_2BO)^-$ are as follows [*m/z* (loss) abundance]: $(Me_2{}^{11}BCH_2)^-$ 54(H·)100, 53(H_2)16, 40(Me·)2, 39(CH_4)9. $(Me_2{}^{11}BO)^-$ 56(H·)48, 55(H_2)20, 41(CH_4)100, 15(CH_3BO)1.

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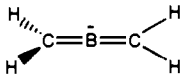
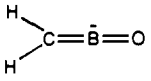
deuteriated precursor ions confirm that the major losses of H_2 and CH_4 occur as shown in eq 3–6.[10]

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



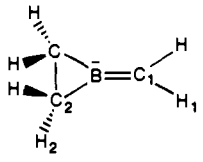
7[12]



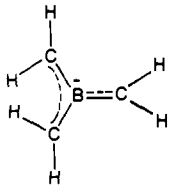
8[13]

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.

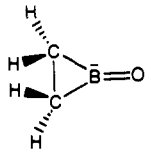
The structures of "$[B(CH_2)_3]^-$" and "$[(CH_2)_2BO]^-$" are more complex. Singlet trismethyleneborane $[B(CH_2)_3]^-$ is not a local minimum in D_{3h} or lower symmetry and relaxes to the stable cycloborapropane ion **9**.[14] The triplet trismethyleneborane anion



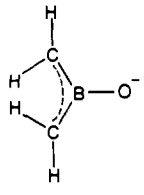
9[14]



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: $k_l = k_+ + k_d + k_u + k_D$.
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.