Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1994, **4(1)**, 12–14

Mendeleev
Communications

On the Combustion of 1,6-Dicarba-*closo*-hexaborane

Vladislav G. Slutsky,[a*] Matthias Hofmann[b] and Paul von Ragué Schleyer[b*]
[a] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 117977 Moscow, Russian Federation. Fax: +7 095 938 2156*
[b] *Institut für Organische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, D–91054 Erlangen, Germany. Fax: +49 9131 852536. E-mail: pvrs@organik.uni-erlangen.de*

The *ab initio* structures and thermodynamic properties of 1,6-dicarba-*closo*-hexaborane (1,6-$C_2B_4H_6$) and its isomers support the possibility that at very high combustion temperatures, rearrangement into a higher energy, but more reactive, isomer with an *exo*-BH_2 group may precede the actual oxidation process.

At elevated temperatures, even the normally stable *closo*-carboranes ($C_2B_nH_{n+2}$, $3 \leqslant n \leqslant 10$)[1] exhibit extremely high reactivity. At $T > 1300$ K, 1,6-$C_2B_4H_6$ **1** is more reactive than hydrogen in the air and even water can serve as an oxidizing agent.[2] Due to these properties and the fairly high heats of combustion,[3] carboranes have considerable potential as speciality fuels.

Specific mechanisms for carborane oxidations have not been reported before. Shock tube investigations on **1** gave a surprising result: within experimental error, the reaction rate did not depend on the concentration of the oxidizing agent (oxygen or water vapour).[2b] A rather low activation energy (E_a) was determined, equation (1).

$$E_a = 30 \pm 2 \text{ kcal mol}^{-1} \qquad (1)$$

This suggests that the rate limiting step involves some transformation of **1** itself, rather than its oxidation. As bond ruptures would require more energy than 30 kcal mol^{-1}, we considered the possibility that **1** might be isomerizing to a higher energy, but more reactive, $C_2B_4H_6$ isomer. Carborane skeletal reorganizations require much less energy than bond rupture.[4] Assuming this postulated isomer to be in equilibrium with **1**, we estimated the equilibrium constant, K_p, from the shock tube data,[2b] equation (2):

$$\ln K_p = 6.8 \pm 1.3 - \Delta H/RT,\ \Delta H < E_a \qquad (2)$$

The usual oxidation mechanisms, *e.g.*, for hydrocarbons, involve radical chains. Our paper explores the basically different mechanistic possibility for **1**, that isomerization precedes the actual oxidation. We have sought suitable isomers of $C_2B_4H_6$ **1** computationally. While the interlocked *closo* structure of **1** might resist attack, isomers *e.g.*, with an *exo* BH_2 group, should exhibit the extremely high reactivity characteristic of some boranes and alkylboranes. Oxidation of an *exo* BH_2 group would afford access to further attack of the $C_2B_3H_4$ residue. While insuficient information is available to identify the actual intermediate(s) involved in the oxidation process, we now report a new $C_2B_4H_6$ isomer whose thermochemistry is at least consistent with the available experimental data, equations (1) and (2). All the alternative candidates examined before[4] are too high in energy to qualify.

In 1988, McKee[4] reported an extensive *ab initio* investigation of various $C_2B_4H_6$ isomers. While the relative energies were quite dependent on the level of theory employed, **1** was the most stable form when electron correlation (*e.g.* at MP2) was included. Besides the 1,2-$C_2B_4H_6$ *closo* carborane isomer, the next most stable alternative **2** located by McKee did indeed possess an *exo*-B-BH_2 moiety and a 1,5-C_2B_3 *closo*-carborane

Table 1 MP2(fc)/6–31G* results of some $C_2B_4H_6$ isomers.

Structure			Absolute energy/a.u.	ZPE[a]/ kcal mol^{-1}	NIMAG[b]	Lowest freq./cm^{-1}	$H_{1500}-E^c$ /kcal mol^{-1}	$S_{1500}{}^d$ /cal mol^{-1} K^{-1}
1	1,6–$C_2B_4H_6$	(D_{4h})	−178.56238	55.1	0	+424.8	116.4	135.0
2	2–(BH_2)–1,5–$C_2B_3H_4$, perp. CBC	(C_{2v})	−178.50120	53.3	0	+174.1	116.1	144.7
2a	2–(BH_2)–1,5–$C_2B_3H_4$, par. CBC	(C_{2v})	−178.48819	52.9	1	−312.6	113.1	139.8
3	Benzvalene-like	(C_{2v})	−178.49974	53.5	0	+190.2	116.0	142.6
4	1–(BH_2)–1,5–$C_2B_3H_4$, bisected	(C_s)	−178.51432	52.5	0	+ 41.5	115.6	149.2
4a	1–(BH_2)–1,5–$C_2B_3H_4$, eclipsed	(C_s)	−178.51429	52.4	1	− 44.1	112.6	140.8

[a] Zero point vibrational energy. [b] Number of imaginary frequencies. [c] H_{1500}: enthalpy at 1500 K; H_{1500}–E: heat enthalpy at 1500 K. [d] Entropy at 1500 K.

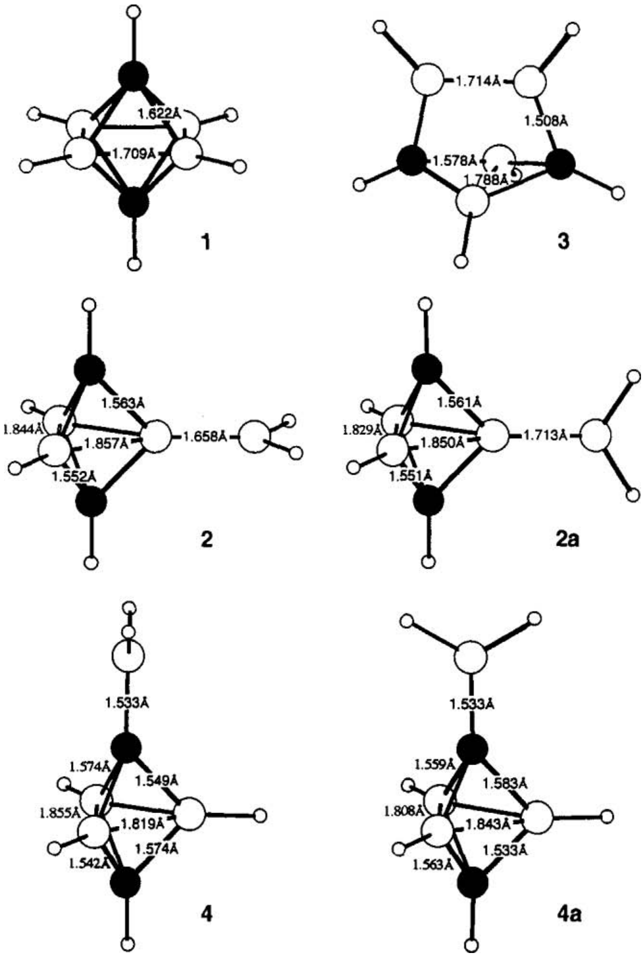

Fig. 1 The MP2(fc)/6–31G*-optimized structures of $C_2B_4H_6$ isomers **1**–**4**. All are minima, except the rotational transition structures, **2a** and **4a**. Note that the *exo*-B–BH_2BB bond lengths differ in **2** and **2a** (reflecting the appreciable rotational barrier), whereas the C–B *exo* bond lengths in **4** and **4a** are essentially the same.

skeleton. However, **2** was 40 kcal mol^{-1} less stable than **1**, and the relative energies of the other isomers were much higher!

Using the GAUSSIAN 92 program,[5] we have now extended this study to higher theoretical levels: **1**, **2** and McKee's benzvalene-like alternative (**3**, C_{2v}) were optimized, first at HF/6–31G* and then at the electron correlated MP2 (frozen core)/6–31G* level. The frequencies and thermodynamic data, computed at MP2(fc)/6–31G*, provided the zero point energies (scaled by 0.93)[6] and the thermal corrections. The computed data are summarized in Tables 1 and 2.

Our further exploration revealed a new $C_2B_4H_6$ isomer **4**, with an *exo* BH_2 group attached to carbon rather than to boron on the *closo* 1,5-C_2B_3 skeleton. At our highest level of theory, **4** is significantly more stable than either **2** or **3**. Furthermore, the *exo* BH_2 group in **4** has nearly free rotation (note the nearly identical energies of **4** and **4a**); this contributes to the entropy of **4**, which is the largest among the isomers considered (Table 2). The rigid structures of **1** and **3**, the high symmetry of **1**, and the relatively high barrier to rotation of the *exo* BH_2 group in **2** (compare the energies of **2** and **2a**) are unfavourable in this respect.

Table 2 Thermodynamic data for four minima on the $C_2B_4H_6$ potential energy surface.

	ΔMP2[a]	ΔZPE[b]	Δ(H_{1500}–E)[c]	$\Delta S_{1500}{}^d$	$\Delta G_{1500}{}^e$
1 1,6–$C_2B_4H_6$	0.0	0.0	0.0	0.0	0.0
2 2–(BH_2)–1,5–$C_2B_3H_4$	+38.4	−1.7	−0.4	+ 9.7	+23.5
3 Benzvalene-like	+39.3	−1.4	−0.5	+ 7.6	+27.4
4 1–(BH_2)–1,5–$C_2B_3H_4$	+30.2	−2.5	−0.9	+14.3	+ 7.8

[a] Relative electronic energies at //RMP2(fc)/6–31G* in kcal mol^{-1}. [b] Differences in zero point vibrational energies in kcal mol^{-1}, corrected by 0.93 (see ref. 6). [c] Differences in thermal enthalpies at 1500 K in kcal mol^{-1}. [d] Differences in entropies at 1500 K in cal mol^{-1} K^{-1}. [e] Differences in free energy at 1500 K in kcal mol^{-1} ($\Delta G_{1500} = \Delta\mathrm{MP2} + \Delta(H_{1500} - E) + (1500\ \mathrm{K})\Delta S_{1500}$).

The data of Table 2 allow the computation of the equilibrium constant between **1** and **4**. Equation (3), which holds over the 298–2000 K range,

$$\ln K_p = 6.8 \pm 0.4 - (29.0 \pm 0.5)\ \mathrm{kcal}/RT \qquad (3)$$

agrees well with the experimental estimation. The large exponential factor compensates for the moderately large isomerization endothermicity at the combustion temperatures: *e.g.*, at 1500 K, ln $K_p = -2.64$. This corresponds to a 6.7% concentration of **4** in binary equilibrium with **1**. (At 1800 K, 26.2% **4** would be present.) An instructive comparison is provided by the oxidation of the H_2 by oxygen in air over the 1500–1800 K range: the computed concentration of radicals, averaged over the period of H_2 half-conversion, does not exceed 5% of the initial H_2 content.[7]

Our computations suggest that the oxidation of stable *closo*-carboranes at high temperatures need not necessarily be initiated by the direct attack of oxygen or water. Instead, isomerization to a higher energy, but more reactive isomer may occur initially. The formation of this isomer and its oxidation define the reaction rate.

This work was supported at Erlangen by the Deutsche Forschungsgemeinschaft (including a study visit of V.G.S.), the Fonds der Chemischen Industrie and the Convex Computer Corporation. We also thank Professor H. Gr. Wagner for assistance with the arrangements.

References

1 (*a*) R. N. Grimes, *Carboranes*, Academic Press, N.Y., 1970; (*b*) E. Muetterties, *Boron Hydride Chemistry*, Academic Press, N.Y., 1975, p. 374; (*c*) *Advances in Boron and the Boranes* (*Molecular Structure and Energetics*), ed. J. F. Liebman, VCH Publishers, New York, 1988. The combustion of boron hydrides is reviewed by S. H. Bauer, pp. 410–413; (*d*) B. E. Gelfand, S. A. Tsyganov, V. G. Slutsky and E. S. Severin, in *Combustion of Boron-based Solid Propellants and Solid Fuels*, ed. K. K. Kuo and R. Pein, CRC Press, 1993, 196.

2 (*a*) E. V. Bespalov, B. E. Gelfand, O. D. Kazakov, V. N. Kalinin, A. B. Petrunin, E. S. Severin, V. G. Slutsky and S. A. Tsyganov, *Dokl. Akad. Nauk SSSR*, 1991, **317**, 661 [*Dokl. Phys. Chem. (Engl. Transl.)*, 1991, **317**, 269]; (*b*) V. G. Slutsky and S. A. Tsyganov, *Zh. Fiz. Khim.* (*Russ. J. Phys. Chem.*), 1993, in press.

3 G. L. Galchenko, N. B. Tamm, E. P. Brykina, D. V. Bekker, A. B. Petrunin and A. F. Zhigach, *Zh. Fiz. Khim.*, 1985, **59**, 2689 (*Russ. J. Phys. Chem.*, 1985, **59**, 1610).

4 M. L. McKee, *J. Am. Chem. Soc.*, 1988, **110**, 5317.

5 GAUSSIAN 92: M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomberts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, GAUSSIAN Inc., Pittsburgh PA, 1992.

6 W. J. Hehre, L. Radom, P.v.R. Schleyer and J. A. Pople, *Ab initio Molecular Orbital Theory*, Wiley, New York, 1986.

7 E. S. Oran, T. R. Young, J. P. Boris and A. Cohen, *Combust Flame*, 1982, **48**, 135.

Received: Cambridge, 23rd August 1993
Moscow, 5th October 1993; Com. 3/05095E