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A theoretical characterization of the structure formation enthalpy, and fluzional behaviour of B_2H_6 and $AlBH_6$

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Summary. A comprehensive study of the binary association complexes B_2H_6 and $AlBH_6$ has been performed by *ab initio* molecular orbital theory. Reliable formation enthalpies can be computed only be extended basis sets and a reasonably complete account of correlation. The greater stability towards neutral dissociation of $AlBH_6$ with respect to B_2H_6 obtained at the Hartree–Fock level employing the 6-21G* basis set (≈ 10 kcal/mol) is reduced to only ≈ 2 kcal/mol when the basis set is sufficiently saturated and correlation energy properly included. The value of the activation energy for hydrogen scrambling in $AlBH_6$ is much less sensitive to the method used, although correlation still plays a significant rôle reducing the potential energy barrier from 11.4 to 7.7 kcal/mol.

Key words: Diborane — Aluminoborane — CI — Thermodynamic stability — Hydrogen scrambling

1. Introduction

Binary association complexes between borane and other electron deficient hydrides have been studied for a long time due to the use of some compounds of this class in homogeneous catalysis and metallorganic chemistry [1–3].

Binding energies of such molecules, which have weak dative bonds, have been difficult to ascertain because of the very short lifetime of BH_3 (due to its reactivity) and the lack of definite information about the reaction mechanism. In principle theoretical studies do not suffer from these problems, but the electron deficient nature of these compounds coupled with the quasi-degeneracy of atomic

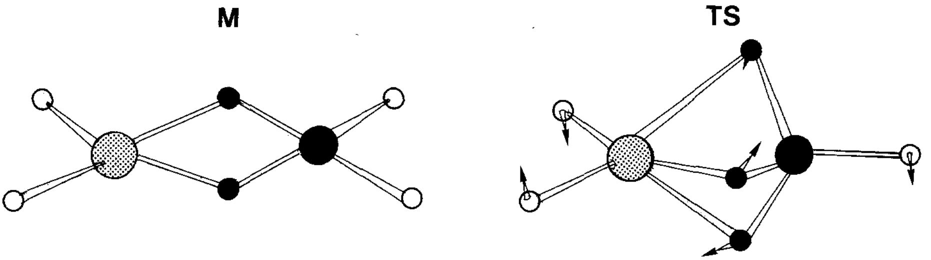

Fig. 1. The stable configuration of group three borane complexes {*M*} is shown together with the transition structure and the related transition vector for hydrogen scrambling in aluminoborane {*TS*}. Full circles represent bridged hydrogen atoms and open circles terminal hydrogens

s and *p* orbitals requires an extensive treatment of electronic correlation. Systematic studies of $LiBH_4$ [4–11], $BeBH_5$ [4, 10–13], B_2H_6 [4, 11, 14–19], $NaBH_4$ [6, 9, 10, 20–22], and $AlBH_6$ [20, 21] have thus been performed only in recent times. Further investigation of significant aspects such as the thermochemistry of the association reactions, the kinetics of hydrogen scrambling, and some geometrical parameters of third-group complexes is, however, required. The situation is particularly unclear for $AlBH_6$, whose experimental structure can be only guessed from parent compounds [23, 24], whereas the geometrical parameters of diborane are experimentally well characterized [25, 26]. Furthermore the thermochemical data are still unsatisfactory for diborane [27–29] and completely lacking for aluminoborane. Finally, the coalescence of NMR signals for the bridged (H_b) and terminal (H_t) hydrogen atoms in X_2AlBH_4 compounds at moderate temperatures [23, 24] implies quite a low activation energy for hydrogen scrambling, whereas this is not the case for diborane. The scrambling of X_2AlBH_4 can occur by fragmentation (to X_2AlBH_6 and BH_3) and successive fast recombination only if the first step is much less endothermic than the process $B_2H_6 \rightarrow BH_3$ ($\Delta Hf_0^\circ \approx 35$–$40$ kcal/mol [18, 29]). However, in view of some propensity of Al for coordination numbers higher than 4, a concerted mechanism, whose transition state is characterized by a formally pentacoordinated Al atom (Fig. 1) may be followed. Previous studies [20–22] indicate other possible mechanisms [2] need not be considered.

The purpose of this work is to use refined post Hartree–Fock methods to analyze the stability and structure of B_2H_6 and $AlBH_6$, and the kinetics of hydrogen scrambling in the latter compound.

2. Method of calculation

Three different basis sets of increasing flexibility were used in the computations, namely:

1. The 6-21G* basis set [30], which is of split valence quality and augmented by polarization functions on non-hydrogen atoms (hereafter referred to as SV*).

2. A triple zeta basis set augmented by polarization functions on all atoms (hereafter referred to as TZP) consisting of the (5)/[3] basis of Krishnan et al. [31] for H, the [5, 3] contraction of the Huzinaga (10, 6) primitives proposed by Dunning [32] for boron, and the (12, 9)/[6, 4] basis of McLean and Chandler [33] for Al. The orbital exponents of the polarization functions are taken from the 6-311G** basis set [31] for H and B ($Z_p(H) = 0.75$; $Z_d(B) = 0.401$), and from the 6-31G* basis set [34] for Al ($Z_d(Al) = 0.325$).

3. An extended basis (hereafter referred to as EXT) obtained from the TZP one by adding a diffuse shell of type s to hydrogen ($Z_s = 0.036$ [35]), of type p to boron ($Z_p = 0.019$ [36]), and of type sp to Al ($Z_s = Z_p = 0.0318$ [37]). The number of polarization functions on non-hydrogen atoms was also doubled by replacing the original set of functions with exponent Z_d by two sets having exponents $\frac{1}{2}Z_d$ and $2Z_d$ [37].

As a general procedure, correlation energy was estimated by Møller–Plesset perturbation theory [38, 39] (hereafter referred to as MPn where n indicates the order of the perturbative treatment). All the electrons were correlated in the perturbative treatment, but SV* computations were repeated within the frozen core approximation [40] (hereafter referred to as fc).

The molecular structures of all the systems were fully optimized by a gradient procedure [41] at the Hartree–Fock (HF) and MP2 levels by the SV* and TZP basis sets. Analytical second derivatives were then calculated by the SV* basis set at the HF level and used to determine the nature (minimum or transition state) of the stationary points previously found.

The HF/SV* vibrational frequencies (scaled by a factor 0.90 [41]) were used to compute zero-point vibrational energies (ZPE), absolute entropies (S°), and specific heats (c°) by standard methods [42].

The rate constant ($K(T)$) for hydrogen scrambling in $AlBH_6$ was then computed using the activated complex theory [43].

All calculations were performed by the GAUSSIAN/82 system of programs [44] on VAX 11/750 and CRAY-X-MP/12 computers.

3. Results and discussion

Molecules containing two and three bridging hydrogen atoms (see Fig. 1) were investigated. In the case of diborane, as already reported by DeFrees et al. [11], the molecule with three such linkages rearranged without activation to the di-bridged molecule. The same analysis in the case of $AlBH_6$ leads to two stationary points, characterized by 0 and 1 negative eigenvalues of the Hessian matrix, respectively. Therefore once again the di-bridged structure is the only energy minimum, but interconversion between two equivalent structures of this kind occurs through a well-defined three-bridged transition state.

Information about the different characteristics of these complexes (together with those of the most significant fragments) are given in Table 1 (optimized geometrical parameters), Table 2 (energies), Table 3 (vibrational frequencies) and Table 4 (electronic characteristics).

Table 1. Geometrical parameters for B_2H_6, $AlBH_6$, [both equilibrium $\{M\}$ and transition structure for hydrogen scrambling $\{TS\}$], and their fragments obtained by different methods. Bridge and terminal hydrogen atoms are indicated by H_b and H_t, respectively

Parameter	HF/SV*	HF/TZP	MP2/TZP	EXP[a]
BH_3				
B–H (Å)	1.188	1.189	1.188	—
BH_4^-				
B–H (Å)	1.241	1.244	1.235	—
B_2H_6				
B–B (Å)	1.776	1.781	1.763	1.770
B–H_t (Å)	1.185	1.186	1.186	1.192
B–H_b (Å)	1.311	1.322	1.313	1.329
H_tBH_t (°)	122.35	122.03	122.19	121.8
H_bBH_6 (°)[b]	94.72	95.29	95.65	96.5

Parameter	HF/SV*	HF/TZP	MP2/TZP	HF/SV*	HF/TZP	MP2/TZP
	AlH_2^+			AlH_3		
Al–H	1.547	1.538	1.536	1.587	1.577	1.568
	$AlBH_6$ $\{M\}$			$AlBH_6$ $\{TS\}$		
Al–B (Å)	2.209	2.191	2.165	2.053	2.042	2.026
BH_t (Å)	1.191	1.191	1.191	1.182	1.181	1.180
BH_b (Å)	1.294	1.295	1.276	1.243	1.245	1.237
AlH_t (Å)	1.574	1.566	1.558	1.578	1.570	1.564
AlH_b (Å)	1.748	1.741	1.736	1.934	1.921	1.914
H_tBH_t (°)	120.99	120.78	120.49	—	—	—
H_bBH_b (°)[c]	104.55	105.18	106.55	113.32	113.51	113.17
H_tAlH_t (°)	140.04	139.61	139.65	119.83	118.60	119.01

[a] From [25]

[b] This parameter is redundant, but is reported to simplify the discussion of the results (see text)

[c] H_bBH_t in the case of $AlBH_6$ $\{TS\}$; these parameters are redundant, but are reported to simplify discussion of the results (see text)

Table 2. Energies of B_2H_6, $AlBH_6$ and their fragments computed by different methods. Additive contributions are given, where appropriate, in brackets. All the abbreviations used in the table are defined in the text

Method	BH_3 E (a.u.)	AlH_3 E (a.u.)	B_2H_6 E_{ass} (kcal/mol)	$AlBH_6$	
				E_{ass} (kcal/mol)	$\Delta E^{\ddagger}$ (kcal/mol)
HF/SV*/HF/SV*	−26.372975	−243.608975	19.7	29.0	11.4
MP2(fc)/SV*//HF/SV*	−26.444086	−243.662375	38.5 (18.8)	38.7 (9.7)	9.2 (−2.2)
MP3(fc)/SV*//HF/SV*	−26.457891	−243.675726	37.6 (−0.9)	38.3 (−0.4)	9.5 (0.3)
MP2/SV*//HF/SV*	−26.447642	−243.671708	38.8 (19.1)	39.2 (10.2)	9.5 (−1.9)
MP3/SV*//HF/SV*	−26.461538	−243.685054	37.9 (−0.9)	38.9 (−0.3)	9.8 (0.3)
HF/TZP//MP2/TZP[a,b]	−26.398246	−243.637.355	21.0	26.1	10.3
MP2/TZP//MP2/TZP	−26.511345	−243.755216	41.6 (20.6)	42.8 (16.7)	7.4 (−2.9)
MP3/TZP//MP2/TZP	−26.531350	−243.773199	39.6 (−2.0)	42.0 (−0.8)	7.7 (0.3)
MP4(dq)/TZP//MP2/TZP	−26.534564	−243.776801	38.0 (−1.6)	40.8 (−1.2)	8.0 (0.3)
MP4(sdq)/TZP//MP2/TZP	−26.534856	−243.777484	38.4 (0.4)	41.2 (0.4)	8.0 (0.0)
MP4/TZP//MP2/TZP	−26.536185	−243.778698	40.5 (2.1)	42.6 (1.4)	7.7 (−0.3)
HF/EXT//MP2/TZP[c]	−26.399728	−243.640205	21.4	25.8	—
MP2/EXT//MP2/TZP	−26.516352	−243.769450	42.9 (21.5)	43.6 (17.8)	—
MP3/EXT//MP2/TZP	−26.536342	−243.788424	40.9 (−2.0)	—	—
MP4(dq)/EXT//MP2/TZP	−26.539484	−243.792151	39.2 (−1.7)	—	—
MP4(sdq)/EXT//MP2/TZP	−26.539842	−243.792985	39.7 (0.5)	—	—
MP4/EXT//MP2/TZP	−26.541416	−243.794473	42.0 (2.3)	43.4[d]	—

[a] HF/TZP//HF/TZP energies are: −26.398246 (BH_3); −243.637417 (AlH_3); −52.830093 (B_2H_6); −270.077524 ($AlBH_6$ {*M*}), and −270.061082 ($AlBH_6$ {*TS*})

[b] The MP4 energies of atoms and ionic fragments are: −0.499810 (H); −24.604321 (B); −241.953086 (Al); −27.172672 (BH_4^-) and −242.891057 (AlH_2^+)

[c] The MP4 energies of the atoms and the ionic fragments are: −0.499818 (H); −24.607311 (B); −241.972918 (Al); −27.182901 (BH_4^-) and −243.778698 (AlH_2^-)

[d] Estimated taking third- and fourth-order MP contributions from TZP calculations

Table 3. Harmonic vibrational frequencies (cm^{-1}) and zero-point vibrational energies (kcal/mol) evaluated at the HF/SV* level

Molecule	Point group	Harmonic frequencies	ZPE
BH_3	D_{3h}	1225(a_2''), 1307(e'), 2703(a_1'), 2823(e')	15.5
AlH_3	D_{3h}	759(a_2''), 848(e'), 2026(e'), 2030(a_1')	11.0
B_2H_6	D_{2h}	425(b_{2u}), 835(a_g), 908(a_u), 910(b_{2g}), 991(b_{1g}), 1078(b_{1u}), 1144(b_{2u}), 1216(b_{3g}), 1286(b_{3u}), 1300(a_g), 1892(b_{3u}), 1978(b_{2g}), 2070(b_{1u}), 2326(a_g), 2749(b_{3u}), 2765(a_g), 2846(b_{1g}), 2859(b_{2u}).	38.0
$AlBH_6$ {*M*}	C_{2v}	240(b_2), 469(a_2), 565(a_1), 598(b_2), 601(b_1), 803(a_1), 884(b_1), 1146(b_2), 1239(a_2), 1252(a_1), 1554(b_1), 1721(a_1), 2002(b_1), 2062(a_1), 2080(b_2), 2114(a_1), 2714(a_1), 2859(b_2).	32.0
$AlBH_t$ {*TS*}	C_s	373i(a''), 305(a''), 355(a'), 630(a'), 645(a''), 669(a'), 893(a'), 1238(a''), 1259(a'), 1364(a'), 1439(a''), 1441(a'), 2046(a''), 2052(a'), 2367(a'), 2374(a''), 2413(a'), 2829(a').	31.2

Table 4. Net atomic charges of B_2H_6, $AlBH_6$ and their fragments computed at the HF level by different basis sets. Bridge and terminal hydrogen atoms are indicated by H_b and H_t, respectively

Basis set	Charges	AlH_3/BH_3	AlH_2/BH_4-	B_2H_6	$AlBH_6$ {*M*}	$AlBH_6$ {*TS*}
SV*	Al	0.4842	0.9238	—	0.6173	0.7249
	H(Al)	−0.1614	0.0381	—	−0.1284	−0.1435
	B	0.0696	−0.3264	−0.1285	−0.2315	−0.4325
	H_b	−0.0232	−0.1684	0.0471	−0.1012	−0.0509
	H_t	−0.0232	−0.1684	0.0407	0.0367	0.0517
	(BH_3)	0.0000	−0.8316	0.0000	−0.2593	−0.4826
TZP	Al	0.9165	1.0554	—	0.9135	0.9933
	H(Al)	−0.3055	−0.0277	—	−0.2500	−0.2776
	B	0.1431	−0.0520	0.0124	−0.0861	−0.2401
	H_b	−0.0477	−0.2370	−0.1452	−0.1452	−0.0630
	H_t	−0.0477	−0.2370	−0.0226	−0.0185	−0.0090
	(BH_3)	0.0000	−0.7630	0.0000	−0.2683	−0.3751
EXT	Al	0.7011	0.9800	—	0.6567	—
	H(Al)	−0.2337	0.0100	—	−0.1888	—
	B	0.0504	−0.2716	−0.0180	−0.1569	—
	H_b	−0.0168	−0.2428	−0.0348	−0.0462	—
	H_t	−0.0168	−0.2428	−0.0084	−0.0149	—
	(BH_3)	0.0000	−0.7572	0.0000	−0.2329	—

3.1. The fragments

A preliminary test of different computational models was performed on neutral (BH_3 and AlH_3) and ionic (AlH_2^+ and BH_4^-) fragments.

AlH and BH bond lengths of AlH_2^+ and BH_3 are essentially unchanged at HF and MP2 levels, whereas those of AlH_3 and BH_4^- are shortened by about 0.01 Å when correlation energy is included. Furthermore the SV* and TZP basis sets lead to comparable results for boron compounds, but to differences of about 0.01 Å for AlH bond lengths.

The optimized bond lengths change by less than 0.002 Å in going from MP2 to MP4 levels (the MP4/TZP values are 1.188, 1.236, 1.570, and 1.540 for BH_3, BH_4^-, AlH_3, and AlH_2^+, respectively) or from TZP to EXT basis sets (the MP2/EXT values are 1.188 and 1.234 Å for BH_3 and BH_4^-, respectively). Furthermore dissociation energies computed at the same computational level, but employing different geometries, are virtually identical.

The vibrational frequencies were obtained only at the HF/SV* level, and show the typical overestimation by about 10% with respect to experimental values. Since, however, these values will be only used in the evaluation of zero point and temperature effects on formation enthalpies and activation energies, the standard procedure of scaling the values can be considered sufficient. This is confirmed for instance by the identical zero point energies of B_2H_6 obtained using scaled theoretical or experimental frequencies.

The dissociation energies (ΔE) of the neutral species were then evaluated from the isogyric processes

$$\mathrm{MeH_3} + \mathrm{H} \rightarrow \mathrm{Me} + 2\mathrm{H_2} \qquad \mathrm{Me} = \mathrm{B} \quad \text{or} \quad \mathrm{Al}$$

and the experimental dissociation energy of H_2 (109.48 kcal/mol) [40]. The theoretical atomization energy of BH_3 at 0 K ($AE = \Delta E + \Delta(\mathrm{ZPE})$) obtained at the MP4/TZP (265.6 kcal/mol) and MP4/EXT (265.2 kcal/mol) levels compares very well with the experimental estimate of 265.3 ± 1.7 kcal/mol recently given by Ruscíc et al. [29] and with the values of 265.1 and 265.0 kcal/mol obtained by MP4/6-311++G(2*d*, *p*) [22] and MP4/6-311++G(3*df*, 3*pd*) [18] computations.

The theoretical values of $AE(AlH_3)$ obtained at the MP4/TZP (201.6 kcal/mol) and MP4/EXT (199.0 kcal/mol) levels are significantly different from the MP4/6-31G(*d*, *p*) one (194.0 kcal/mol) and point out, once again, the similar performances of different extended basis sets and the limits of the 6-31G* basis set especially for third-row atoms [46]. Using the recent $Hf_0^{\circ}(B)$ of [27] (133.8 kcal/mol) and the JANAF(CODATA) [28] values for Al and H (78.2 and 51.63 kcal/mol, respectively), our best estimates of the formation enthalpies of BH_3 and AlH_3 at 0 K are 23.5 and 34.1 kcal/mol.

In conclusion MP4/EXT//MP2/TZP computations should provide accurate results both for geometric and energetic data of the compounds studied in the next sections. Scaled HF/SV* harmonic frequencies, although not completely satisfactory, should be sufficient to evaluate thermodynamic and kinetic parameters.

3.2. Diborane

From a methodological point of view the results of Table 1 show that both enlargement of the basis set and inclusion of correlation essentially affects only BB and BH_b (subscript denotes bridging H) bond lengths, which are, as is usual for bond lengths, shorter at the MP2 than at the HF level.

A comparison between the experimental and theoretical structures of diborane (see Table 1) is difficult since the experimental geometry was derived from a thermally averaged molecular structure. It can only be said that our results are in basic agreement with experiment and other recent computations [16–19].

The HF energy of B_2H_6 obtained by the EXT basis set is within 10^{-3} atomic units from the value determined by the larger 6-311++G(3*df*, 3*pd*) basis set [18]. The HF contribution to the dimerization energy (E_{ass}) computed by these two basis sets differs, however, by 0.5 kcal/mol. Although part of this discrepancy may be due to the different geometries employed, the same difference of 0.5 kcal/mol obtained by the Pople 6-311G(*d*, *p*) and the Huzinaga TZP basis sets in [17] suggests an inherent difference in the *sp* contribution derived from these two "families" of basis sets rather than a further effect of second polarization functions.

Inclusion of correlation at the simple MP2 level leads to values of E_{ass} which differ drastically from the HF calculations and are in good agreement with the results of more highly correlated treatments. In particular, the sum of third and fourth order contributions ranges between 0.8 and 1.1 kcal/mol for all basis sets larger than 6-31G(*d*, *p*) [17, 18]. It is also noteworthy that, due to the opposite sign of third- and fourth-order contributions, the sum of the two terms is much less sensitive to the quality of the basis set than the two separate contributions. Furthermore the data of Table 2 show that the effect of triple excitations at fourth order is to increase the dimerization energy by about 2–2.5 kcal/mol depending on the basis set. Thus, although the full fourth-order is stabilizing, single and double excitations alone would have the opposite effect and even MP4(sdq) computations are not better than MP2 ones, when compared with full fourth-order results. Therefore the best procedure for cases in which triple excitations are too expensive to be computed (see next section) is to perform MP2/EXT computations and to add third- and fourth-order corrections of TZP quality.

Finally, inclusion of single and double excitations to all perturbation orders (CCSD + T(CCSD) computations of [17]) leads to differences of no more than 0.3 kcal/mol with respect to MP4 computations, irrespective of the basis set. This result indicates that perturbative corrections of order higher than fourth can be safely neglected.

The MP4/EXT value for the dimerization enthalpy at 0 K (35 kcal/mol) is in the range of the best theoretical values reported till now [18, 19] and of the most recent experimental estimate of (34.3–39.1) ± 2 kcal/mol [29]. Using our best estimate of the formation enthalpy of borane at 0 K (23.5 kcal/mol), we obtain a value of 12 kcal/mol for $\Delta Hf^{\circ}_{0}(B_2H_6)$, which is in good agreement with the well-established experimental value of 12.5 ± 0.5 kcal/mol [27].

3.3. *Aluminoborane*

From a methodological point of view, the optimized values of the valence angles remain essentially constant in all the computations performed, whereas all the bond lengths except BH_t (subscript denotes terminal H) are reduced in going from HF to MP2 levels. As a matter of fact the AlB bond length obtained at the MP2/TZP level for the equilibrium structure (2.165 Å) is not far from the experimental value (2.128 Å) found for $AlBH_4(CH_3)_2$ [24]. At the Hartree–Fock level SV* and TZP values are in remarkable agreement for geometrical parameters involving only B and H atoms, but some larger discrepancies are found for parameters involving Al. This can be traced back to similar trends found for BH_3 and AlH_3 (see Table 1) and points out the limitations of the SV* basis set for third-row atoms. The BH_b bond length is shorter in $AlBH_6$ than in B_2H_6 in accord with chemical intuition, while the opposite is true for the BH_t bond length; as a consequence the asymmetry between different BH distances is reduced (from 0.127 Å to 0.085 Å) in the mixed complex. The asymmetry of these two bond lengths is related to the ionicity of the complex and, in fact, it decreases to 0.042 Å for $NaBH_4$ using a comparable treatment [22].

At the Hartree–Fock level $AlBH_6$ is, as might be expected, more stable toward neutral dissociation than B_2H_6, the difference between the two species decreasing when the basis set is enlarged (see Table 2). The two complexes become nearly equivalent in this respect upon inclusion of correlation energy, the MP2 contribution once again being the dominant effect. Our best estimate (MP2/EXT + MP4/TZP − MP2/TZP) of the association energy (E_{ass}) of $BH_3 + AlH_3$ is 43.4 kcal/mol, whereas the corresponding value for the association of ionic species ($AlH_2^+ + BH_4^-$) is 176.3 kcal/mol. Using the formation enthalpies at 0 K obtained for BH_3 and AlH_3 in Sect. 3.1, we then get $\Delta Hf_0^0(AlBH_6) = 14.2$ kcal/mol.

The essentially covalent character of the bonding in $AlBH_6$ is confirmed by the charges reported in Table 4. As a matter of fact the total charge of the BH_3 moiety is only about -0.25 and the charge on the Al atom is not significantly modified in going from AlH_3 to $AlBH_6$.

Let us now consider the transition structure for hydrogen scrambling $\{TS\}$. The geometrical data of Table 1 suggest a stronger Al–B interaction in the transition structure than in the equilibrium structure $\{M\}$ (the corresponding MP2/TZP distances being 2.026 and 2.165 Å, respectively), which is, however, accompanied by a weaker Al–H_b (the MP2/TZP bond lengths increase from 1.736 in $\{M\}$ to 1.914 Å in $\{TS\}$) and a stronger B–H_b (the bond lengths decrease from 1.276 in $\{M\}$ to 1.237 Å in $\{TS\}$) interaction. Since the AlH_t and BH_t bond lengths remain essentially unchanged, the geometry modifications suggest that the transition structure can be viewed as resulting from the interaction between the AlH_2^+ cation and the tetrahydroborate anion. The greater ionic character of the transition structure with respect to the energy minimum is confirmed by the significant increase in the electron population of B, which essentially occurs through electron transfer from the AlH_3 to the BH_3 moieties (see Table 4).

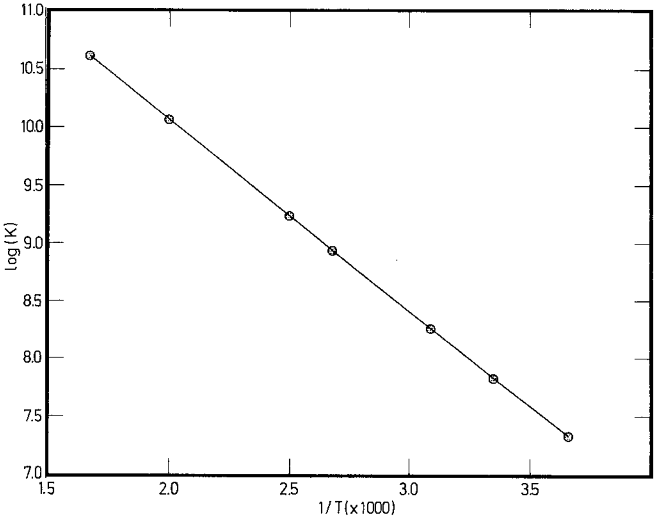

Fig. 2. Arrhenius plot for the hydrogen scrambling in aluminoborane

The energy barier ($\Delta E^{\ddagger}$) for hydrogen scrambling computed at the HF/SV* level (11.4 kcal/mol) is more than double that of the corresponding barrier in ionic complexes (e.g. $LiBH_4$ or $NaBH_4$). This difference, which could be ascribed to the well-known preference of third-row atoms for tetrahedral coordination, is only compatible with a local or deformational nonrigidity of aluminoborane. However, extension of the basis set and inclusion of correlation energy significantly reduces this difference (the MP4/TZP potential energy barriers are 7.7, 5.8, and 4.3 kcal/mol [22] for $AlBH_6$, $LiBH_6$, and $NaBH_6$, respectively) and suggests that migrational nonrigidity (i.e., nearly free migration of AlH_2^+ around an essentially undistorted tetrahydroborate ion) could also play some rôle in the reactivity of aluminoborane.

From a computational point of view, it is significant that, as has already been suggested [21], MP2 computations recover most of the correlation effects on the potential energy barrier. In addition the correlation contribution obtained at the TZP level is well reproduced by SV* and, especially, pseudopotential [21] computations. The HF contribution to the barrier is, however, very sensitive to the quality of the basis set and reliable results can only be obtained by basis sets of at least TZP quality [22].

Using the above data and the HF/SV* vibrational frequencies, the Arrhenius parameters for hydrogen scrambling have been computed as a function of temperature according to Eq. (1). Vibrational contributions to the activation barrier are very small and, in fact, the activation energy (E_a) is essentially equal to the potential energy barrier and only slightly dependent on the temperature ($E_a = 7.5$ and 7.7 kcal/mol at 273 and 600 K, respectively). The value of the pre-exponential factor A is also essentially temperature independent ($\log(A) = 13.3$ and 13.4 at 273 and 600 K, respectively) and is typical for isomerization reactions. The above effects lead to a linear Arrhenius plot for the scrambling of hydrogens in $AlBH_6$, as shown in Fig. 2.

4. Concluding remarks

The following points are worth mentioning:

1. Both extension of the basis set and inclusion of electron correlation lead to an increase of the association energies and, in the case of $AlBH_6$, to a decrease of the potential energy barrier governing hydrogen scrambling.

2. MP2 computations performed with triple zeta basis sets, including a single set of polarization functions on all the atoms, are sufficient to study the mechanism of hydrogen scrambling. By way of contrast, the computation of reliable association energies requires even more extended basis sets and inclusion of correlation energy up to the fourth order of perturbative expansion. Good results can, however, be obtained by adding third- and fourth-order contributions obtained from TZP basis sets to MP2 computations performed with larger basis sets.

3. The stability of B_2H_6 and $AlBH_6$ toward neutral dissociation is very similar ($E_{ass} = 42$–43 kcal/mol).

4. The activation energy for hydrogen scrambling in $AlBH_6$ is of the same order as in ionic compounds, so that migrational nonrigidity might also play a significant rôle in this case.

5. Vibrational contributions are quite important in the study of binary associations, but can be safely neglected in the analysis of hydrogen scrambling.

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