A Mechanistic Study of Hydroboration of 1-Octene with 1,3,2-Dithiaborolane and 1,3,2-Dithiaborinane. Part 2. A DFT Study of Disproportionation and Hydroboration

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ABSTRACT

The hydroboration reactions of propene with 1,3,2-dithiaborolane and 1,3,2-dithiaborinane in their ground states have been studied using density functional theory (DFT) at the B3LYP/3-21+G and B3LYP/6-31+G(d) levels. Hydroboration and disproportionation transition states have been determined and activation energies for these transition states were compared. It has been shown that hydroboration reactions require slightly higher activation energies than disproportionation, and yield thermodynamically more stable products.

KEYWORDS

Hydroboration, disproportionation, DFT, transition states, potential energy surface.

1. Introduction

The hydroboration reactions of 1-octene with 1,3,2-dithia-borolane and 1,3,2-dithiaborinane have been investigated, and kinetic and thermodynamic parameters of these processes have been obtained.[1] However, the hydroborating agents disproportionated significantly during their synthesis, as was noted by Egan *et al.*[2] In the early 1960s, Rose and Shore[3] demonstrated that the oxygen analogue, 1,3,2-dioxaborolane (**9**) undergoes significant degradation (disproportionation) at 1% per minute at room temperature. A tentative disproportionation mechanism was proposed,[3] showing the association of two molecules of 1,3,2-dioxaborolane to form a 4-centre transition state (Scheme 1) which ultimately leads to the final disproportionation product 2,2-(ethylenedioxy)-bis-(1,3,2-dioxaborolane) (**11**) (Scheme 1). (The numbering of compounds in the Schemes follows on from that of reference 1.)

Computational molecular modelling was employed with the intention of comparing the activation energies required by the two boranes to disproportionate, and also to rationalise the mechanism of disproportionation, as proposed by Rose and Shore.[3]

2. Theoretical Approach

The hydroboration reaction was computed using propene,

1,3,2-dithiaborolane and 1,3,2-dithiaborinane as models. The disproportionation reaction for each hydroborating agent was modelled by pulling two molecules of the hydroborating agent under investigation close to each other in a stepwise manner. The geometries of all structures of starting hydroborating agents, propene and products in their ground states were optimized using density functional theory (DFT) with the 3-21+G basis set and verified with the larger 6-31+G(d) basis set for more accurate approximation. A potential energy surface (PES) scan following the reaction path was performed for both the hydroboration and disproportionation reactions, in order to locate the transition states (TSs) involved in these reactions. The located TSs were corroborated by vibrational frequency calculations at the same level of theory. All calculations were executed using Gaussian 03.[4]

3. Results and Discussion

The optimized structures of the located hydroboration transition states, **TS1** (Scheme 2) and **TS2** (Scheme 3) for 1,3,2-dithiaborolane (**4**) and 1,3,2-dithiaborinane (**6**) respectively, were verified by vibrational frequency calculations, which showed the presence of only one negative eigenvalue, associated with the movement of the expected atoms in the TS. The characteristic movements involved concurrent breaking of the B-H bond of the borane and the simultaneous formation of the B-C and H-C bonds to the alkene.
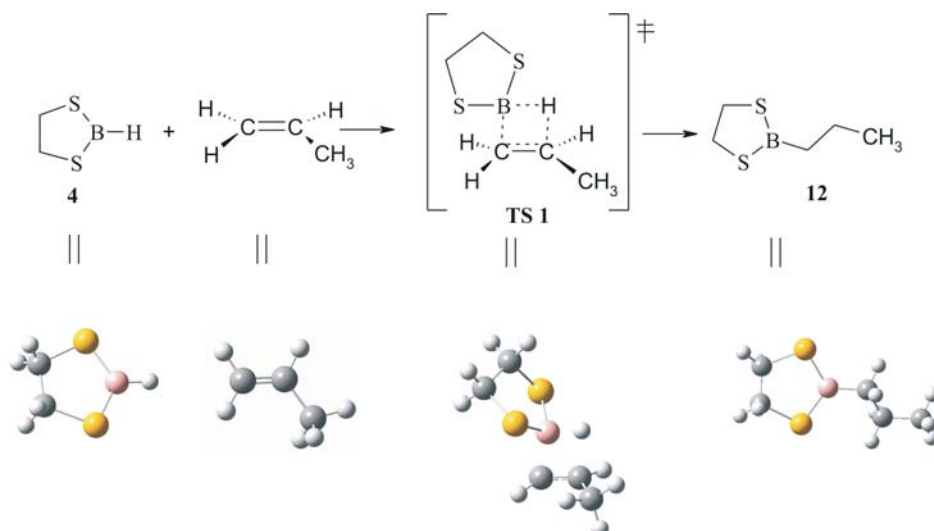
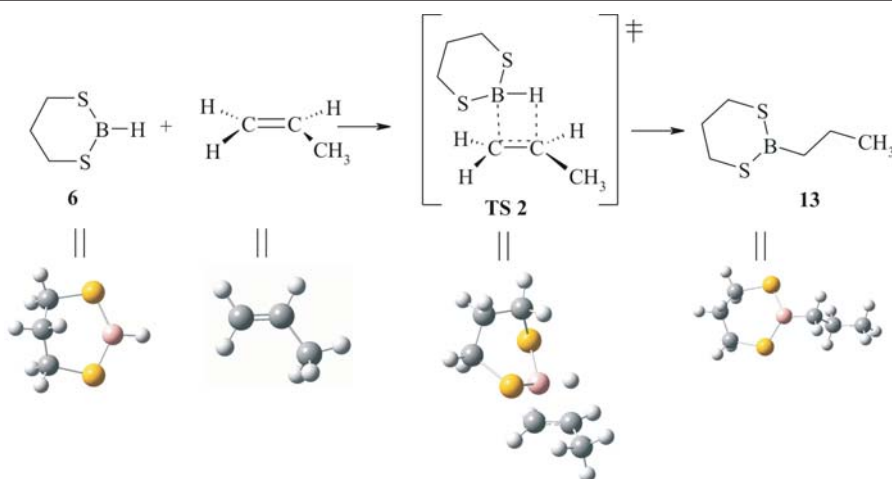The located disproportionation transition states for 1,3,2-
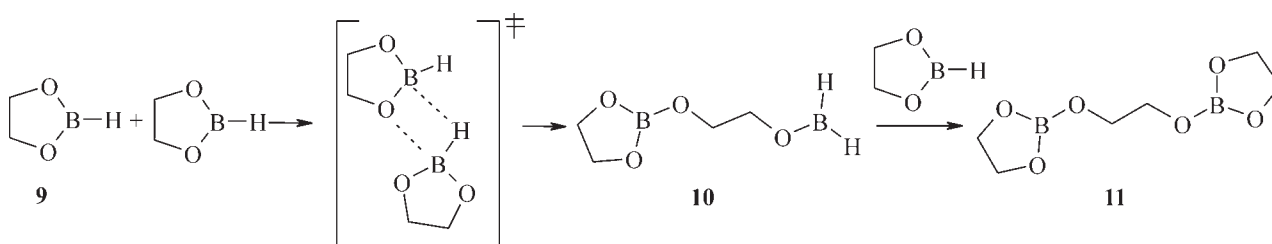
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Scheme 1

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Scheme 2

Scheme 3

dithiaborolane (**TS3**) (Scheme 4) and 1,3,2-dithiaborinane (**TS4**) (Scheme 5) are in agreement with the mechanism proposed by Rose and Shore.[3] The first stage of the proposed disproportionation mechanism involves two borane species interacting in the gas phase to form a four-centre transition state (Scheme 4). In this mechanism, the B-H bond of borane **B** breaks and the hydrogen atom is donated to the boron atom of borane **A**, forming a new B-H bond. This proceeds with concomitant breaking of the S-B bond of borane **A** and formation of a new B-S bond to borane **B** (Scheme 4). Vibrational frequency calculations on **TS3** and **TS4** confirmed the presence of only one negative eigenvalue corresponding to the proposed mechanism.

The comparison of the activation energy of disproportionation with that of hydroboration at the B3LYP/3-21+G level of theory showed that for 1,3,2-dithiaborolane (**4**) a lower energy barrier (43.5 kJ mol^{-1}) is required for disproportionation to take place, when compared with that of hydroboration (72.0 kJ mol^{-1}). A refined energy profile at the higher B3LYP/6-31+G(d) level confirmed that **4** undergoes disproportionation at *ca.* 24 kJ mol^{-1} lower than hydroboration (Table 1 and Fig. 1). The lower energy barrier for disproportionation of 1,3,2-dithiaborolane permits for an easier formation of **4C**, as has been shown experimentally.

**Table 1** Relative energies of hydroboration and disproportionation.[a]

	Relative energies/kJ/ mol^{-1}							
	Disproportionation		Hydroboration		Disproportionation		Hydroboration	
Mechanism								
Basis set	3-21+G	6-31+G(d)	3-21+G	6-31+G(d)	3-21+G	6-31+G(d)	3-21+G	6-31+G(d)
Reactants	0	0	0	0	0	0	0	0
TS	43.5	85.4	72.0	109.7	60.7	80.0	77.0	111.4
Products	3.9	24.7	154.0	118.9	21.4	28.5	1428	115.1
$\Delta E^{\neq}$	43.5	85.4	72.0	109.7	60.7	80.0	77.0	111.4

[a]All energies are reported relative to the sum of the energies of reactants. Cartesian coordinates of all optimized structures are available as Supplementary Material.
[b]$\Delta E^{\neq} = E_{\text{transition state}} - E_{\text{reactants}}$
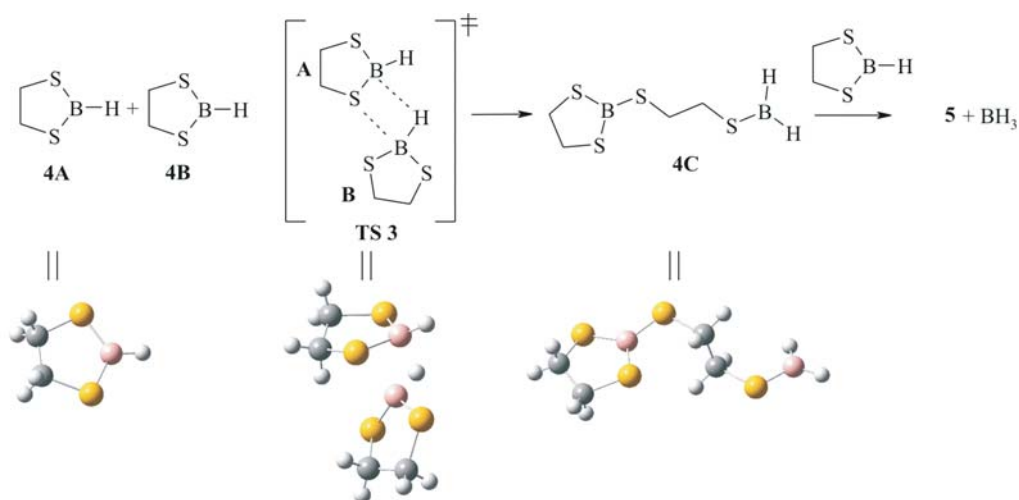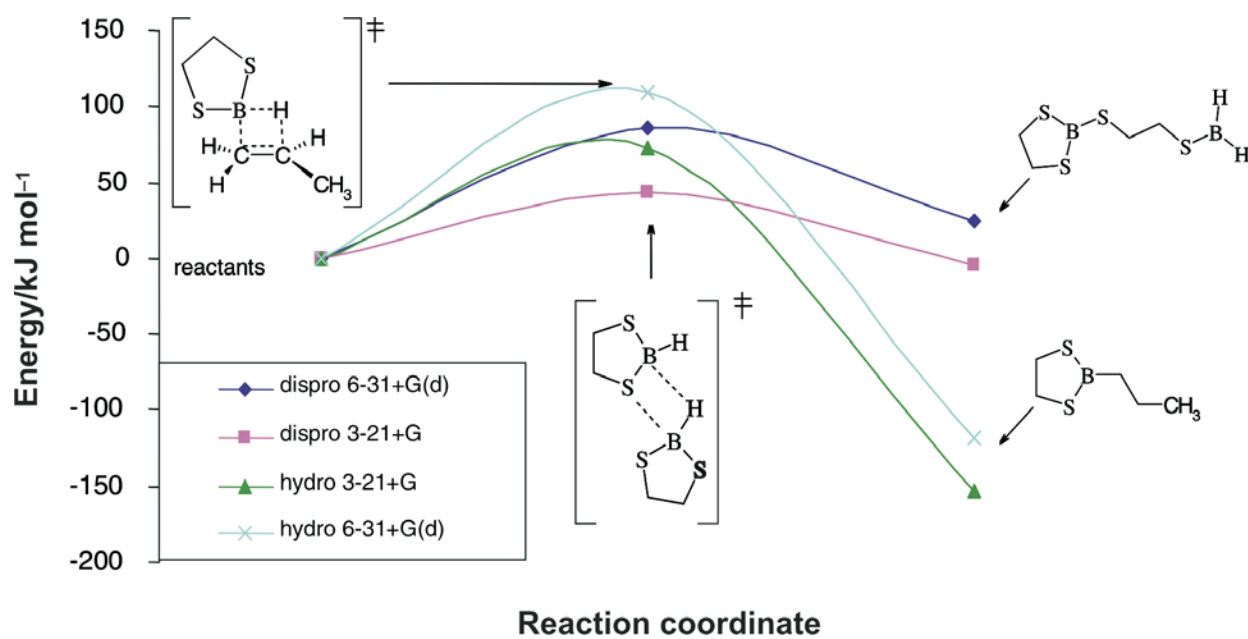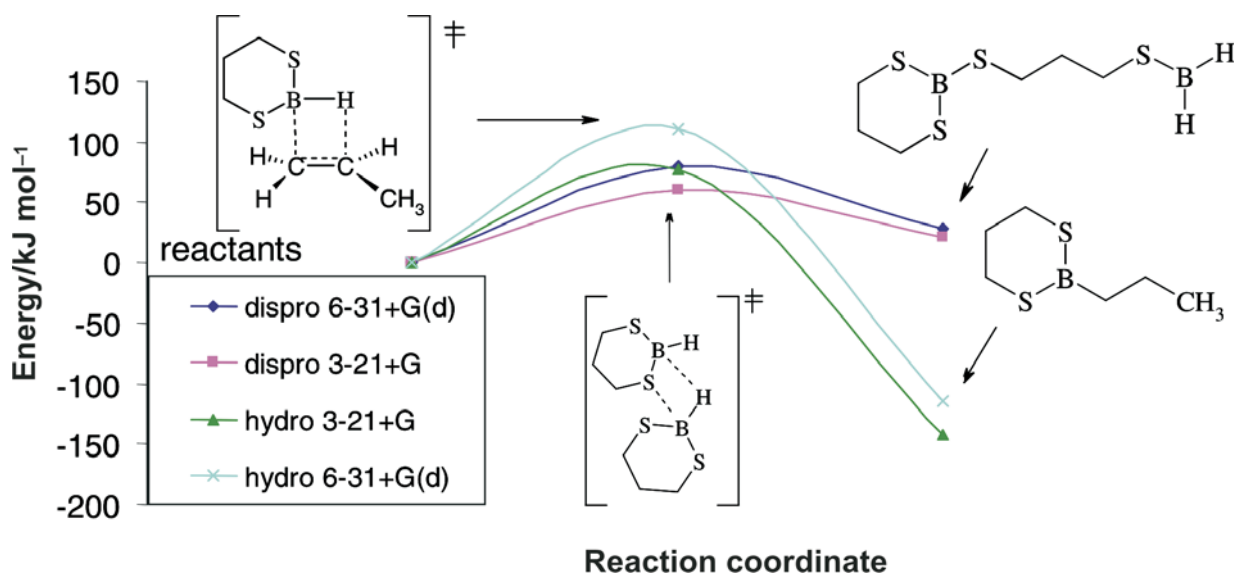
Scheme 4
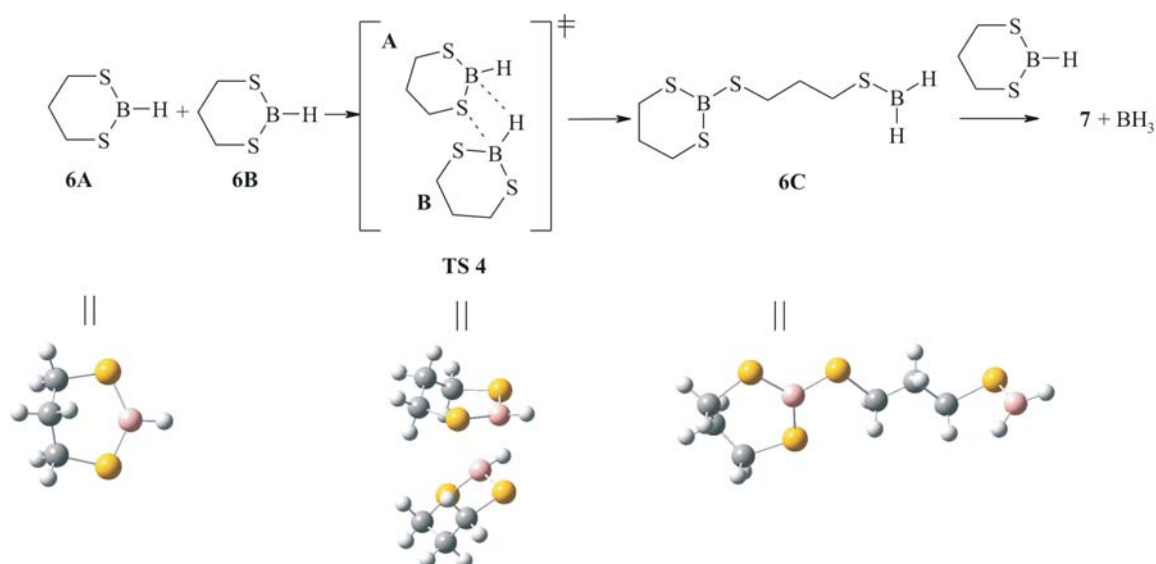
Scheme 5

Figure 1 Energy profile for hydroboration (hydro) and disproportionation (dispro) reaction mechanisms of 1,3,2-dithiaborolane (**4**).

Figure 2 Energy profile for hydroboration (hydro) and disproportionation (dispro) reaction mechanisms of 1,3,2-dithiaborinane (**6**).

Similar behaviour was exhibited with 1,3,2-dithiaborinane leading to the formation of **6C**. The required disproportionation energy barrier is *ca.* 17 kJ mol^{-1} lower than that of the hydroboration process at the B3LYP/3-21+G level and was found to be *ca.* 33 kJ mol^{-1} lower at the B3LYP/6-31+G(d) level (Table 1 and Fig. 2), which is closely comparable with that of 1,3,2-dithiaborolane.

4. Conclusions

Our calculations have shown that hydroboration reactions require slightly higher activation energies than disproportionation. However, hydroboration yielded thermodynamically more stable products. It has also been shown that the energy required for both hydroborating agents to undergo disproportionation reactions is *ca.* 83 kJ mol^{-1}. This means that at room temperature these hydroborating agents have enough kinetic and thermal energy to undergo disproportionation. These findings support the fact that at lower reaction temperatures, the disproportionation reactions are sluggish, therefore allowing for enhanced yields of the target hydroborating agent.

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