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Change in mechanistic pathway of hydroboration: A detailed kinetic study of $H_2BBr{\cdot}SMe_2$ and $HBBr_2{\cdot}SMe_2$

N. Xaba, D. Jaganyi *

School of Chemistry, University of KwaZulu Natal, Private Bag X01, Scottsville, Pietermaritzburg, 3209 KwaZulu-Natal, South Africa

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Abstract

Hydroboration reactions of 1-octene and 1-hexyne with $H_2BBr{\cdot}SMe_2$ in CH_2Cl_2 were studied as a function of concentration and temperature, using ^{11}B NMR spectroscopy. The reactions exhibited saturation kinetics. The rate of dissociation of dimethyl sulfide from boron at 25 °C was found to be $(7.36 \pm 0.59$ and $7.32 \pm 0.90) \times 10^{-3}\ s^{-1}$ for 1-octene and 1-hexyne, respectively. The second order rate constants, k_2, for hydroboration worked out to be $7.00 \pm 0.81\ M\ s^{-1}$ and $7.03 \pm 0.70\ M\ s^{-1}$, while the overall composite second order rate constants, k K, were $(3.30 \pm 0.43$ and $3.10 \pm 0.37) \times 10^{-2}\ M\ s^{-1}$, respectively at 25 °C. The entropy and enthalpy values were found to be large and positive for k_1, whilst for k_2 these were large and negative, with small values for enthalpies. This is indicative of a limiting dissociative (*D*) for the dissociation of Me_2S and associative mechanism (*A*) for the hydroboration process. The overall activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, were found to be $98 \pm 2\ kJ\ mol^{-1}$ and $+56 \pm 7\ J\ K^{-1}\ mol^{-1}$ for 1-octene whilst, in the case of 1-hexyne these were found out to be $117 \pm 7\ kJ\ mol^{-1}$ and $+119 \pm 24\ J\ K^{-1}\ mol^{-1}$, respectively. When comparing the kinetic data between $H_2BBr{\cdot}SMe_2$ and $HBBr_2{\cdot}SMe_2$, the results showed that the rate of dissociation of Me_2S from $H_2BBr{\cdot}SMe_2$ is on average 34 times faster than it is in the case of $HBBr_2{\cdot}SMe_2$. Similarly, the rate of hydroboration with $H_2BBr{\cdot}SMe_2$ was found to be on average 11 times faster than it is with $HBBr_2{\cdot}SMe_2$. It is also clear that by replacing a hydrogen substituent with a bromine atom in the case of $H_2BBr{\cdot}SMe_2$ the mechanism for the overall process changes from limiting dissociative (*D*) to interchange associative (I_a).

Keywords: Kinetics; Hydroboration; Mechanism; $H_2BBr{\cdot}SMe_2$; $HBBr_2{\cdot}SMe_2$

1. Introduction

Haloborane addition complexes were discovered by Brown and Tiernery in the late 1950s [1]. Synthesis of these complexes (which are of the type $HBX_2{\cdot}LB$ and $H_2BX{\cdot}LB$, where X = Br, Cl or I and LB = Lewis base, e.g. Me_2S, THF or Et_2O) as well as their hydroboration reactions is well established [1–11]. The information in the literature provides a record on the investigations conducted on hydroboration reactions of these complexes, as well as their feature of being excellent intermediates for a wide variety of synthetic applications, among which is synthesis of dialkylboranes and their derivatives [12–14], synthesis of *nido*-$B_{11}H_{14}$ anion [15], synthesis of alkyldihaloboranes [16] and synthesis of silyl substituted organoboranes [17]. The usefulness of these haloborane addition complexes have also been utilized in synthesis of ionic liquids [18], in the chemistry of ring opening [19], as well as in polymerisation through hydroboration [20,21].

However, kinetic information based on relative reactivities and indirect mechanistic information available in the literature for $HBBr_2{\cdot}SMe_2$ dates back to the 1980s [10,12]. Nonetheless, not much with regard to the kinetics and the mechanism $H_2BBr{\cdot}SMe_2$ exists. As it has been highlighted in our previous papers [22,23], the necessity to pursue detailed mechanistic studies on

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* Corresponding author. Tel.: +27 33 260 5452; fax: +27 33 260 5009.
E-mail address: Jaganyi@ukzn.ac.za (D. Jaganyi).

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hydroboration is crucial for the commercialisation of a boron based cyclic process [23], through which high commercial value alpha olefins can be produced from internal olefins. This cycle involves three steps, namely hydroboration, isomerization and displacement or dehydroboration. Kinetic and mechanistic studies on each of these steps will provide valuable information such as specific rate constants, enthalpy, entropy and physical data in general. At present, the unavailability of this information can be attributed to the inadequacies incurred from the method of analysis, namely GC, which had all along been used in studying the kinetics of hydroboration reactions [22].

The efficiency of modern spectroscopy, especially IR as well as ^{11}B NMR in the kinetic and mechanistic monitoring of reactions involving addition complexes of boron, has in recent time allowed for some advance in this field [22–24]. However, to date, thorough kinetic studies on hydroboration reactions of $H_2BX{\cdot}LB$ as well as specific and accurate mechanistic information thereof, have not been documented.

We recently reported a detailed kinetic and mechanistic study for hydroboration of 1-octene with $HBBr_2{\cdot}SMe_2$ and $HBCl_2{\cdot}SMe_2$ [22]. The activation parameters, especially $\Delta S^{\neq}$, support the dissociation of Me_2S from the boron centre prior to hydroboration, which itself is an associative process. The present study is an extension of the previous work with regard to structure-reactivity studies of bromoborane, *viz.* varying Lewis acid character as well as the number of hydroboration sites. The outcome of this work, along with that of $HBBr_2{\cdot}SMe_2$ reported earlier [22], show that hydroboration mechanism of the mono- and di-bromoborane dimethyl sulfide complexes is different.

2. Experimental

2.1. General

Standard techniques for handling of air- and moisture-sensitive materials were used [22]. $H_2BBr{\cdot}SMe_2$ (1 M solution of CH_2Cl_2) was purchased from Sigma–Aldrich, and was used as supplied. 1-Octene (provided by Sasol Ltd.) was distilled over sodium wire and further dried with 3 Å molecular sieves. The CH_2Cl_2 (purchased from Merck) used as a solvent for preparation of solutions was distilled over P_2O_5 prior to use.

2.2. Kinetic measurements

^{11}B NMR spectra were recorded on Varian Unity Inova 500 spectrometer, using 5 mm quartz tubes, at 160 MHz and referenced externally against $BF_3{\cdot}OEt_2$. The reactions were monitored by following the intensity of the signal area of $H_2BBr{\cdot}SMe_2$ (triplet, $\delta^{11}B = -10.5$ ppm at 25 °C, $J_{B\text{-}H} = 134$ Hz) peak as a function of time. Product characterization was conducted in the same manner as reported before [22].

All kinetic runs were performed under pseudo-first-order conditions with respect to the boron complex. The concentration of $H_2BBr{\cdot}SMe_2$ was kept constant at 0.0125 M, by diluting known concentrations from the stock solution with freshly distilled CH_2Cl_2, the same solvent that was used to prepare the different nucleophile (1-octene and 1-hexyne) solutions. The nucleophile concentrations used in concentration dependence studies ranged from 10 times to 50 times that of the haloborane concentration. The observed pseudo first-order rate constants, k_{obs}, were obtained by fitting a first-order exponential decay equation, through the data points using ORIGIN 5.0 statistical software.

Activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, were determined from temperature dependence studies over the temperature range of 15 °C to 30 °C, at 5 °C interval. A wider temperature range could not be investigated because of the constrain posed by the boiling point (40 °C) of the solvent, CH_2Cl_2. Activation parameters were determined for both the dissociation of the Me_2S as well as the hydroboration step.

3. Results and discussion

The disappearance of the ^{11}B NMR triplet peak at $\delta^{11}B = -10.5$ ppm and the emergence of a singlet peak at $\delta^{11}B = 18.5$ ppm, as shown in Fig. 1, is evidence that the process monitored is that described in Eq. (1). The triplet represents the $H_2BBr{\cdot}SMe_2$, whilst the singlet represents $R'_2BBr{\cdot}SMe_2$. The product of hydroboration was also confirmed by quenching the reaction using H_2O_2 to form the alcohol, which was characterised through GC, as before [22]

Pseudo-first-order rate constants, k_{obs}, were obtained from ^{11}B NMR arrayed experiments followed by subsequent integration of the peaks. First-order exponential decay curves were fitted over the data points to generate the k_{obs}. A representative plot of concentration against time is shown in Fig. 2.

The k_{obs} were then plotted against the concentration of the entering nucleophile, [Nu]. Saturation kinetics were observed, as shown in Fig. 3, implying that a limiting value of k_{obs} is reached at high [Nu]. The plots exhibited no y-intercept, an indication of absence of dehydroboration.

To account for, and explain, the observed results, a mechanism represented in Eq. (2) was suggested. This involves prior dissociation of the complex into H_2BX and Me_2S, followed by the reaction of the free H_2BX with the entering unsaturated organic compound to form R_2BX. This is followed by hydrogen rearrangement and then complexation with the Me_2S that was released in the dissociation step. From the NMR spectra Fig. 1, it is clear that it is not possible to distinguish the two hydroboration steps. It could be that the two take place simultaneously, or the second step is much faster than the first one such that the life time of the intermediate species, $HBRX{\cdot}SMe_2$, is too short lived to be detected by NMR. The second assumption

$$H_2BBr{\cdot}SMe_2 + 2R \longrightarrow R'_2BBr{\cdot}SMe_2 \qquad (1)$$

R = 1-octene = Nu

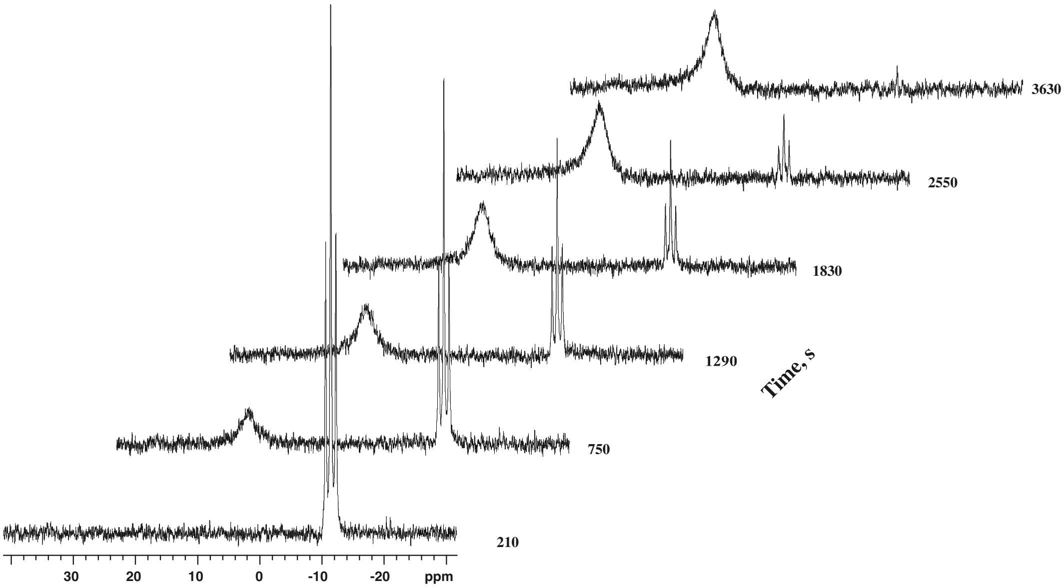

Fig. 1. ^{11}B NMR kinetic array showing disappearance of $H_2BBr{\cdot}SMe_2$ and formation of $R'_2BBr{\cdot}SMe_2$.

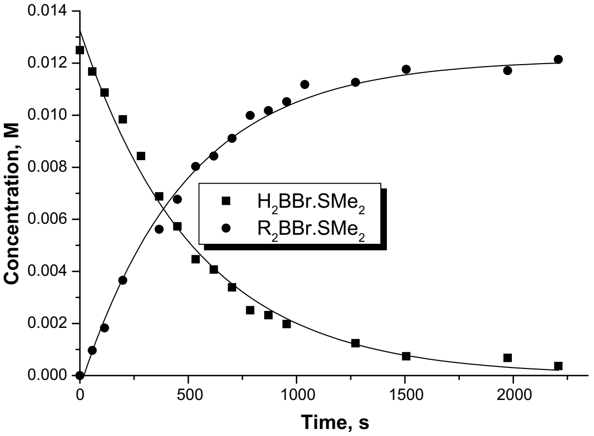

Fig. 2. Exponential decay curve for hydroboration of 1-octene with $H_2BBr{\cdot}SMe_2$ in CH_2Cl_2 at 20 °C.

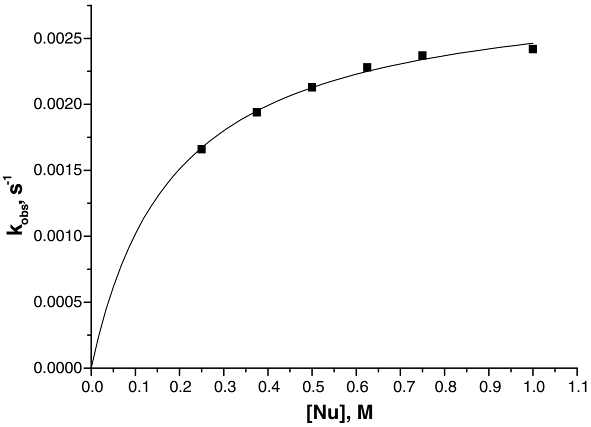

Fig. 3. Dependence of k_{obs} on [Nu] in the hydroboration reaction of 1-octene with $H_2BBr{\cdot}SMe_2$ in CH_2Cl_2 at 20 °C.

is questionable because of increase in steric hindrance after the first hydroboration. In this study we have assumed that the first assumption is more likely.

Therefore, the mechanism proposed is similar to the one in our previous publication [22], but with small modification.

$$\left.\begin{aligned} &H_2BX{\cdot}SMe_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2BX + Me_2S \\ &H_2BX + 2R \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_2BX \\ &R_2BX + Me_2S \overset{\text{Fast}}{\rightleftharpoons} R_2BX{\cdot}SMe_2 \end{aligned}\right\} \qquad (2)$$

Using the proposed mechanism the rate law can be expressed as in Eq. (3).

$$k_{obs} = \frac{k_1k_2[R] + k_{-1}k_{-2}[Me_2S]}{k_{-1}[Me_2S] + k_2[R]} \qquad (3)$$

Since dehydroboration is not expected under the conditions employed, $k_{-2} = 0$, reducing Eq. (3) to

$$k_{obs} = \frac{k_1k_2[R]}{k_{-1}[Me_2S] + k_2[R]} \qquad (4)$$

The data points in Fig. 3 were fitted to Eq. (4) using ORIGIN 5.0. This made it possible to determine the values of k_1 and k_2, which are tabulated in Table 1. Also calculated were the values of $k_1k_2/k_{-1}[Me_2S]$, which are denoted as kK in the table. This composite value represents the overall second-order rate constant, of the hydroboration reaction

Table 1
Kinetic data for hydroboration of 1-octene and 1-hexyne with $H_2BBr{\cdot}SMe_2$ in CH_2Cl_2

T (°C)	1-Octene			1-Hexyne		
	k_1 (10^{-3} s^{-1})	k_2 (M^{-1} s^{-1})	kK (10^{-2} s^{-1} M^{-1})	k_1 (10^{-3} s^{-1})	k_2 (M^{-1} s^{-1})	kK (10^{-2} s^{-1} M^{-1})
15	1.24 ± 0.32	4.12 ± 0.75	0.800 ± 0.08	2.22 ± 0.35	4.90 ± 0.67	0.654 ± 0.10
20	2.92 ± 0.64	5.62 ± 0.41	1.56 ± 0.09	3.73 ± 1.0	5.61 ± 1.3	1.26 ± 0.20
25	7.36 ± 0.59	7.00 ± 0.81	3.30 ± 0.43	7.32 ± 0.90	7.03 ± 0.70	3.10 ± 0.37
30	14.03 ± 2.3	7.68 ± 0.85	5.92 ± 0.85	14.66 ± 2.2	8.66 ± 1.1	7.56 ± 1.13
k_2/k_{-1} [Me_2S]	11			8		
$\Delta H^{\neq}$ (kJ mol^{-1})	117 ± 3	34 ± 4	98 ± 2	90 ± 5	26 ± 2	117 ± 7
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$+106 \pm 9$	-114 ± 13	$+56 \pm 7$	$+51 \pm 20$	-148 ± 8	$+119 \pm 24$

kK = k_1k_2/k_{-1} [Me_2S].

investigated. Increase in k_{obs} values with increase in [Nu], as seen in Fig. 3, is due to the fact that $k_2 \gg k_{-1}$.

The dissociation rate constant, k_1, was also determined by investigating a k_{obs} dependence on the concentration of Me_2S. In this study, the [Me_2S] was varied whilst [1-octene] was held constant. The data obtained was analysed using Eq. (5), which is a rearrangement of Eq. (4)

$$\frac{1}{k_{obs}} = \frac{k_{-1}}{k_1k_2[\mathrm{R}]} \cdot [\mathrm{Me_2S}] + \frac{1}{k_1} \qquad (5)$$

A plot of $1/k_{obs}$ against [Me_2S] was found be linear as shown in Fig. 4, with $1/k_1$ as the y-intercept. To be noted is that, this k_1 represent the dissociation of Me_2S from the boron atom.

The value of k_1 was calculated to be $(4.52 \pm 0.08) \times 10^{-3}$ s^{-1}, which is in close agreement with the average value obtained from the concentration dependence study at 25 °C for 1-octene.

Since it was possible to kinetically separate the values of k_1, k_2 and kK, activation parameters were determined, by plotting Erying plots, for the individual and the overall second-order rate constants. A typical Erying plot for the overall reaction, i.e. using kK values, showing a good linear relationship is shown in Fig. 5, while the activation data obtained is summarized in Table 1.

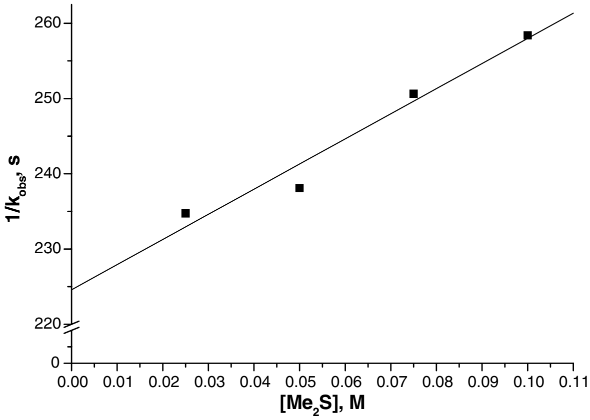

Fig. 4. Inverse relationship between [Me_2S] and k_{obs} for hydroboration of 1-octene with $H_2BBr{\cdot}SMe_2$ in CH_2Cl_2 at 25 °C.

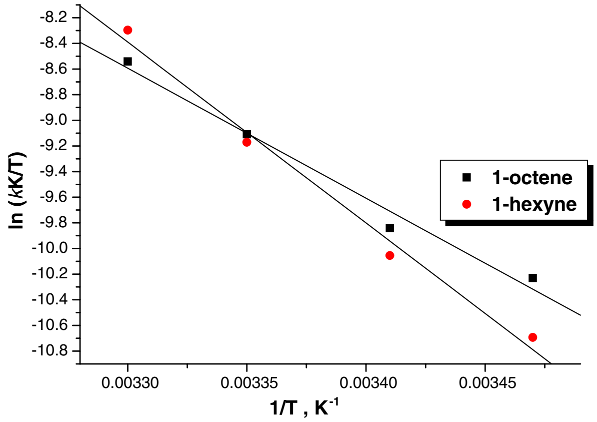

Fig. 5. Erying plots of the kK term for hydroboration of 1-octene and 1-hexyne with $H_2BBr{\cdot}SMe_2$ under pseudo first-order conditions.

Thereafter, a comparison was made between the results obtained from the investigation involving $H_2BBr{\cdot}SMe_2$ and that of $HBBr_2{\cdot}SMe_2$ [22]. A summary of kinetic data is given in Table 2, where k_a represents the composite rate constant shown as kK for $H_2BBr{\cdot}SMe_2$ and k_2' for $HBBr_2{\cdot}SMe_2$, as it appears in the literature [22].

3.1. Reactivity and activation parameters of 1-octene and 1-hexyne on hydroboration with $H_2BBr{\cdot}SMe_2$

In analysing the kinetic data, compiled in Table 1, it is noted that the rate constants, k_1, k_2 and composite kK, which, respectively represent the dissociation process, hydroboration and the overall reaction, are independent of the olefin type. This suggests that the limiting process controlling the hydroboration reaction is not the attack of the unsaturated organic compounds, but the dissociation of the Me_2S from the boron atom as suggested in the mechanism.

The data also shows that the k_2 values are 10^3-fold larger when compared to k_1 values, an indication that hydroboration reaction is more facile compared to the dissociation process. This difference can be accounted for in terms of enthalpy of activation ($\Delta H^{\neq}$), where that of the dissociation step, described by k_1, is approximately 3.5 times larger than that of the hydroboration step, represented by k_2. The efficiency of the olefin undergoing hydroboration com-

Table 2
Kinetic data for hydroboration of 1-octene and 1-hexyne with $H_2BBr{\cdot}SMe_2$ and $HBBr_2{\cdot}SMe_2$ in CH_2Cl_2

T (°C)	$H_2BBr{\cdot}SMe_2$		$HBBr_2{\cdot}SMe_2$ [22]		$H_2BBr{\cdot}SMe_2$	$HBBr_2{\cdot}SMe_2$ [22]
	1-Octene	1-Hexyne	1-Octene	1-Hexyne	1-Octene	
	k_a (10^{-3} s^{-1} M^{-1})				k_1 (10^{-3} s^{-1})	
15	10.4 ± 0.08	6.54 ± 0.10	1.01 ± 0.02	0.82 ± 0.02	1.24	0.043
20	15.6 ± 0.09	12.6 ± 0.20	1.86 ± 0.07	1.35 ± 0.08	2.92	0.088
25	33.0 ± 0.43	31.0 ± 0.37	3.47 ± 0.04	2.42 ± 0.10	7.36	0.20
30	59.2 ± 0.85	75.6 ± 1.13	5.66 ± 0.84	4.26 ± 0.18	14.03	0.38
$\Delta H^{\neq}$ (kJ mol^{-1})	98 ± 2	117 ± 7	82 ± 1	78 ± 4	117 ± 3	104 ± 2
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$+56 \pm 7$	$+119 \pm 24$	-18 ± 4	-34 ± 12	$+106 \pm 9$	$+33 \pm 8$

$k_a = k$K in the case of $H_2BBr{\cdot}SMe_2$.
$k_a = k'_2$ in the case of $HBBr_2{\cdot}SMe_2$.

pared to the Me_2S re-attaching itself to the three coordinate HRBX intermediate is represented by the ratio of $k_2/k_{-1}[Me_2S]$. This value is 11 and 8 for 1-octene and 1-hexyne, respectively.

In discussing the activation parameters, it is appropriate that the different stages of the reaction be looked at independently. The large and positive $\Delta S^{\neq}$ values for k_1 (i.e. $+106 \pm 9$ and $+51 \pm 20$ J K^{-1} mol^{-1} for 1-octene and 1-hexyne, respectively), which are associated with large values of $\Delta H^{\neq}$ (117 ± 3 and 90 ± 5 kJ mol^{-1} for 1-octene and 1-hexyne, respectively) are in line with the concept of a limiting dissociative pathway, as suggested in the mechanism. The difference in $\Delta S^{\neq}$ values is due to large error limit associated with $\Delta S^{\neq}$ values because of the intrinsic extrapolation involved in its determination. One would have expected these values to be approximately similar in magnitude. Looking closely at the individual k_1 values in Table 1, it can be seen that the values at 25 °C and 30 °C are comparable. The small difference is in 15 °C and 20 °C, which when plotted in the Erying plot results in the big difference.

The activation parameters obtained from using k_2 values were large, but negative for $\Delta S^{\neq}$ accompanied with moderate values of $\Delta H^{\neq}$. The $\Delta S^{\neq}$ values were -114 ± 13 J K^{-1} mol^{-1} and -148 ± 8 J K^{-1} mol^{-1}, whilst $\Delta H^{\neq}$ values were 34 ± 4 kJ mol^{-1} and 26 ± 2 kJ mol^{-1} for 1-octene and 1-hexyne, respectively. This is typical for a process that is associatively activated, which is again in agreement with the proposed mechanism.

It is important that caution is exercised when interpreting $\Delta S^{\neq}$ and $\Delta H^{\neq}$ values originating from the composite rate constants, kK. This is because these represent composite second-order rate constants, the activation parameters arising from them are, therefore, a sum of the two processes taking place, i.e. dissociation of the Me_2S from the boron atom and the hydroboration reaction. The net $\Delta S^{\neq}$ values were found to be $+56 \pm 7$ and $+119 \pm 24$ J K^{-1} mol^{-1}, whilst $\Delta H^{\neq}$ values were worked out to be 98 ± 2 and 117 ± 7 kJ mol^{-1}, for 1-octene and 1-hexyne, respectively. On the basis of the large and positive $\Delta S^{\neq}$ values, we conclude that the overall mechanism is limiting dissociative (D) in nature. This is also supported by the saturation curve shown in Fig. 3 and, the concentration dependence study involving Me_2S, where a linear plot of k_{obs} against Me_2S concentration having a negative slope was obtained. An indication that the site to which the Me_2S attaches becomes vacant, making competition for the site to be directly proportional to the concentration of Me_2S.

3.2. A Comparison between $H_2BBr{\cdot}SMe_2$ and $HBBr_2{\cdot}SMe_2$

The composite rate constant, kK, values as well as the results relating to the dissociation of Me_2S obtained in this study were compared with those obtained from the investigation conducted on hydroboration of 1-octene and 1-hexyne with $HBBr_2{\cdot}SMe_2$ [22]. These are tabulated in Table 2.

As we have established before [22], in order to be able to compare the reactivity of any given haloborane addition complexes, with regard to hydroboration, the amount of the Lewis base present in the systems being compared must be at the same level. This is because of the influence of the Lewis base on the reactivity.

Accordingly, the amount of excess Me_2S present in $H_2BBr{\cdot}SMe_2$ and $HBBr_2{\cdot}SMe_2$ solutions was determined, through integration of ^1H NMR spectra of pure samples. These showed two signals, where in the case of $H_2BBr{\cdot}SMe_2$ the one for the coordinated Me_2S appeared at $\delta^1H = 2.37$ ppm, whilst the free Me_2S appeared at $\delta^1H = 2.12$ ppm. In the case of $HBBr_2{\cdot}SMe_2$ the coordinated Me_2S appeared at $\delta^1H = 2.39$ ppm, whilst the free Me_2S appeared at $\delta^1H = 2.30$ ppm. The excess Me_2S, i.e. free Me_2S, in both the $H_2BBr{\cdot}SMe_2$ and $HBBr_2{\cdot}SMe_2$ solutions worked out to be 4% of the concentration of the bromoborane dimethyl sulphide complexes. Consequently, a direct comparison of the results obtained from this study and those of $HBBr_2{\cdot}SMe_2$ study could be made.

In general, the difference in reactivity can be attributed to the difference in the structures of the two complexes based on the number of bromine atoms. These have been shown to influence the acidity and reactivity of the boron atoms, by means of inductive effect as well as π-back donation from the halogen to the boron atom and also steric hindrance [7,22,25–27].

In comparing the kinetic data between $H_2BBr{\cdot}SMe_2$ and $HBBr_2{\cdot}SMe_2$ the focus is on the rate of dissociation of

Me_2S from the boron complex and the observed second-order rate constants for the overall reaction, which is a composite of k_1, k_{-1} and k_2, as given in the relevant equations. This is because the individual rate constants could not be kinetically separated for $HBBr_2{\cdot}SMe_2$ though, this was possible for the $H_2BBr{\cdot}SMe_2$. Therefore, looking at the dissociation rate constants, k_1, and the equivalent second-order rate constant, $k_2' = k\mathrm{K} = k_a$, values in Table 2, it noted that Me_2S dissociates from $H_2BBr{\cdot}SMe_2$ at a rate 34 times faster than it does from $HBBr_2{\cdot}SMe_2$, and that hydroboration with $H_2BBr{\cdot}SMe_2$ is 11 times faster than it is with $HBBr_2{\cdot}SMe_2$.

A simple explanation for the difference in dissociation rate is based on the magnitude of the inductive effect the boron atom experiences due to the presence of bromine atoms in the two environments. In the case of $HBBr_2{\cdot}SMe_2$, the B-SMe_2 interaction can be considered to be much stronger because the withdrawing of electrons by two electronegative bromine atoms compared to the one bromine atom in $H_2BBr{\cdot}SMe_2$, results in a more positively charged boron atom, leading to a strongly coordinated Me_2S. Also, to be notated is the fact that π-back donation from the halides to the boron atom decreases due to the increase in the steric bulkiness around boron [28]. This is true in the case of $HBBr_2{\cdot}SMe_2$. The net result is a reduction of electron density around the boron of $HBBr_2{\cdot}SMe_2$ compared to that of $H_2BBr{\cdot}SMe_2$, making the B–SMe_2 coordination much stronger in the $HBBr_2{\cdot}SMe_2$ than in the $H_2BBr{\cdot}SMe_2$. Due to these two reasons, the Me_2S coordinated to the dibromoborane dissociates at a slower rate than that which is coordinated to the monobromoborane. This is supported by the entropy of activation showing that $H_2BBr{\cdot}SMe_2$ undergoes limiting dissociation (D) mechanism, whilst $HBBr_2{\cdot}SMe_2$ is interchange (I_d) activated.

The rate of dissociation of Me_2S has a direct influence on the second-order rate constant, since this is the limiting process in the hydroboration reaction. In addition to this, steric hindrance at the transition state also plays a role. The $HBBr_2{\cdot}SMe_2$ due to I_d mechanism will go through a five-coordinated intermediate in comparison to a three-coordinate intermediate, in the case of $H_2BBr{\cdot}SMe_2$, which is D activated. The olefin can therefore approach the boron atom from either side of the monobromoborane, which is sp^2 hybridized after the dissociation of Me_2S, compared to the trigonal pyramidal, which sp^3 hybridized in the case of dibromoborane.

4. Conclusions

In summary, the results reported in this paper show that hydroboration of 1-octene and 1-hexyne with $H_2BBr{\cdot}SMe_2$ involve the dissociation of Me_2S as the limiting step. The two hydroboration steps expected for this complex could not be separated under the current experimental conditions, because the first hydroboration was too fast. Hydroboration is associatively activated, but the overall process, which is made up of dissociation of Me_2S followed by the hydroboration, is dissociatively activated.

In comparing $H_2BBr{\cdot}SMe_2$ to $HBBr_2{\cdot}SMe_2$ the rate of dissociation of Me_2S from the boron atom is found to be 34 times faster in the case of $H_2BBr{\cdot}SMe_2$ than it is for $HBBr_2{\cdot}SMe_2$. Respectively, hydroboration is 11 times faster with the former compared to the latter. These differences have been attributed to the inductive effects as well as steric hindrance caused by the bromine substituents attached to the boron atom. The replacement of a hydrogen substituent from $H_2BBr{\cdot}SMe_2$ by a bromide to form $HBBr_2{\cdot}SMe_2$ results in a changeover of the mechanism from limiting dissociative (D) to dissociative interchange (I_d), with regard to the dissociation of the Me_2S from the boron atom, and from the limiting dissociative (D) to an associative interchange (I_a), with regard to the overall process.

It can, therefore, be concluded that structural difference between the $H_2BBr{\cdot}SMe_2$ and the $HBBr_2{\cdot}SMe_2$ complexes cause by the difference in the number of bromine atoms influences their kinetic and mechanistic behaviour.

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