

Kinetics and mechanism of hydroboration reactions of $\text{HBBr}_2 \cdot \text{SMe}_2$ and $\text{HBCl}_2 \cdot \text{SMe}_2$ – Application of ^{11}B NMR spectroscopy

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Abstract

The kinetics and mechanism of the hydroboration reactions of 1-octene with $\text{HBBr}_2 \cdot \text{SMe}_2$ and $\text{HBCl}_2 \cdot \text{SMe}_2$, in CH_2Cl_2 as a solvent, were studied. Rates of hydroboration were monitored using ^{11}B NMR spectroscopy. The reactions exhibited simple second-order kinetics of the form $k_{\text{obs}} = k_2[\text{Nu}]$. The $\text{HBCl}_2 \cdot \text{SMe}_2$ was found to be 20 times more reactive than the $\text{HBBr}_2 \cdot \text{SMe}_2$. The overall activation parameters (ΔH^\ddagger , ΔS^\ddagger) for the reaction of $\text{HBBr}_2 \cdot \text{SMe}_2$ with 1-octene were found to be $82 \pm 1 \text{ kJ mol}^{-1}$, $-18 \pm 4 \text{ J K}^{-1} \text{ mol}^{-1}$ and with 1-hexyne were $78 \pm 4 \text{ kJ mol}^{-1}$, $-34 \pm 12 \text{ J K}^{-1} \text{ mol}^{-1}$. For the reaction of $\text{HBCl}_2 \cdot \text{SMe}_2$ with 1-octene, ΔH^\ddagger and ΔS^\ddagger were $104 \pm 5 \text{ kJ mol}^{-1}$ and $43 \pm 16 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The activation parameters (ΔH^\ddagger , ΔS^\ddagger) for the dissociation of Me_2S from $\text{HBBr}_2 \cdot \text{SMe}_2$ were found to be $104 \pm 2 \text{ kJ mol}^{-1}$, $+33 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. Based on the activation parameters, it was concluded that the detaching of Me_2S from the boron centre follows a dissociative mechanism, while the hydroboration process follows an associative pathway. It was also concluded that the dissociation of Me_2S from the boron centre is the rate determining step.

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1. Introduction

The importance of the hydroboration reaction in organic chemistry has been well established in the chemical literature [1–3]. Considerable effort has gone into delineating the mechanism of the hydroboration reaction for both dimeric and monomeric boranes [4–10], as well as establishing the relative reactivities of these compounds [11–15]. Findings indicate that structural and electronic differences of organoboranes as well as that of olefins play an influential role on hydroboration kinetics.

Information on rates of hydroboration indicates that hydroboration of terminal olefins is independent of the chain length, and proceeds faster than that of internal olefins, which is retarded due to steric effects around the double bond. The retardation of the rate is also observed when branching is introduced in the alkyl chain. Insertion of a methyl substituent at an α -position to the terminal double

bond is reported to enhance the rate of hydroboration due to electron donation while conjugating an aromatic ring has an opposite effect. In addition to this, Brown and co-workers have shown that hydroboration of *cis*-isomers proceeds faster than that of *trans*-isomers and that the drive to relieve the ring strain facilitates the faster hydroboration of cyclic alkenes [5,14].

The widely accepted mechanistic pathway for hydroboration with boron compounds attached to a Lewis base involves a prior dissociation of the Lewis base from the boron centre, followed by the addition of an olefin [4,8]. In the case of haloborane complexes, it is believed that the Lewis base re-attaches itself back to the boron complex after hydroboration [8]. However, conclusive mechanistic studies that support this generally accepted mechanism have not been conducted. To support and shed some light in terms of the observed reactivities and mechanistic behaviour, computational modelling of hydroboration reactions have been shown to be useful [16]. Yet, simple kinetic information in the literature dates back to the 1980s.

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Traditionally, gas chromatography has been the technique used in the kinetic investigations of hydroboration reactions. The analysis of residual alkene or alcohol in the products allowed for the monitoring of the reaction progress and selectivity of the hydroboration reaction [11–15]. Several problems arise when considering both analysis of residual alkene or alcohol content by gas chromatography; not least being the tediousness of the sampling and quenching process. Furthermore, this method is particularly unsuitable for reactions whose reaction lifetime is within that of the sampling and quenching time. The quality of the data from this type of analysis suffers from the limit placed on the number and size of sample aliquots that may be removed from the reaction medium.

Modern spectroscopic set-up offers a solution to these problems in providing non-destructive, *in situ* analysis under inert atmosphere conditions. To this end, infrared (IR) spectroscopy has been employed in kinetic investigations of various organoboranes [5–10,17,18]. ^{11}B NMR spectroscopy has also been shown to be an invaluable qualitative and analytical tool for many studies [19–25]. Yet, despite all these applications, ^{11}B NMR spectroscopy has not been exploited in the direct investigation of kinetic and mechanistic aspects of the hydroboration reaction, up until a recent publication by Jaganyi and Mzinyati [26].

In order to test the generally accepted mechanism, we have undertaken a detailed kinetic and mechanistic study of $\text{HBBr}_2 \cdot \text{SMe}_2$ and $\text{HBCl}_2 \cdot \text{SMe}_2$ with 1-octene and 1-hexyne. In addition, the role of the Lewis base (Me_2S) in the mechanistic route through which these haloboranes undergo hydroboration has been investigated. We report the kinetic data that have been obtained by exploiting the applicability of ^{11}B NMR spectroscopy as a tool to study hydroboration kinetics.

2. Experimental

Standard techniques for handling of air- and moisture-sensitive materials were used [26]. $\text{HBBr}_2 \cdot \text{SMe}_2$ (1 M solution in CH_2Cl_2) and $\text{HBCl}_2 \cdot \text{SMe}_2$ (in excess Me_2S) were purchased from Sigma–Aldrich and 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) that was used as a solvent for preparation of solutions was distilled over P_2O_5 prior to use.

^{11}B NMR spectra were recorded on Varian Unity Inova 500 spectrometer at 160 MHz in 5 mm quartz tubes. $\text{BF}_3 \cdot \text{OEt}_2$ was used as an external reference. The reactions were monitored by following the intensity of the signal area of the $\text{HBBr}_2 \cdot \text{SMe}_2$ (doublet, $\delta^{11}\text{B} = -7$ ppm at 25 °C, $J_{\text{B-H}} = 162$ Hz) and $\text{HBCl}_2 \cdot \text{SMe}_2$ (doublet, $\delta^{11}\text{B} = 2$ ppm at 25 °C, $J_{\text{B-H}} = 158$ Hz) peaks as a function of time.

In order to ensure pseudo first-order conditions with respect to the boron complex and to force the reaction to completion, all the kinetic runs were performed in the presence of a large excess of nucleophile (1-octene or 1-hexyne).

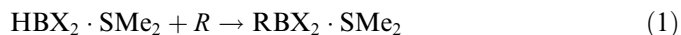
The concentration of the haloboranes was kept constant at 0.05 M by diluting known volumes from stock solutions with freshly distilled CH_2Cl_2 , the same solvent used to prepare the nucleophile solutions. The observed pseudo first-order rate constants, k_{obs} , were obtained by using Origin 5.0 statistical software to analyse the kinetic traces. The equation employed was first-order exponential decay.

To determine the overall activation parameters, ΔH^\ddagger and ΔS^\ddagger , rate constant values, k'_2 , for the reaction involving the nucleophile at concentration of 0.5 M were plotted as a function of temperature. Temperatures employed were 15 °C, 20 °C, 25 °C and 30 °C. Investigation of the effect of the concentration of Me_2S on the rate of hydroboration was conducted, at 25 °C, by varying the concentration of the Me_2S from 0.050 M to 0.085 M, whilst holding the concentration of $\text{HBBr}_2 \cdot \text{SMe}_2$ constant at 0.05 M, and that of 1-octene at 10-fold excess to the boron complex. A temperature dependence study (15 °C to 30 °C) was also conducted at variable concentration of Me_2S (0.050–0.085 M) in order to determine the activation parameters for the detaching of Me_2S .

Product characterization was achieved through Varian CP-3800 GC, employing a Teknokroma capillary column (phase TR-FFAP, 30 m × 0.53 mm × 1 μm) in the case of hydroboration of 1-octene, whilst ^1H NMR and ^{13}C NMR were employed in the case of 1-hexyne. On characterization of products, oxidation using $\text{NaOH}/\text{H}_2\text{O}_2$ mixture was performed after completion of hydroboration. In the case of 1-octene, the product obtained was 1-octanol (retention time = 14.01 min). In the case of 1-hexyne, 1-hexanal was found to be dominant product indicated by an aldehyde hydrogen ($\delta^1\text{H} = 9.7$ ppm) and an aldehyde carbon ($\delta^{13}\text{C} = 203.1$ ppm).

3. Results and discussion

The disappearance of the ^{11}B NMR doublet peak and the emergence of a singlet peak, as shown in Fig. 1, is evidence that the process monitored is that described in Eq. (1):



where $\text{X}_2 = \text{Br}_2$ or Cl_2 and $\text{R} = 1$ -octene or 1-hexyne.

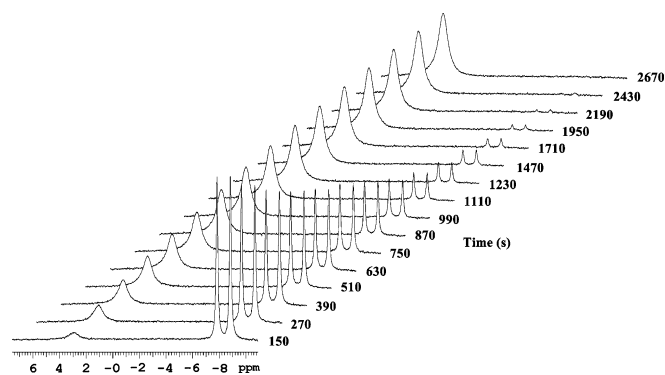


Fig. 1. ^{11}B NMR kinetic array showing disappearance of $\text{HBBr}_2 \cdot \text{SMe}_2$ and formation of $\text{RBBr}_2 \cdot \text{SMe}_2$.

The progress of the reaction of $\text{BHX}_2 \cdot \text{SMe}_2$ with excess nucleophile (1-octene or 1-hexyne) was monitored spectroscopically by following the change in intensity of the signal area as a function of time in the ^{11}B NMR spectrum, as shown in Fig. 1. The data points for the kinetic plots were fitted using a non-linear least-square procedure. A representative plot of the concentration *vs.* time, showing an excellent fit to a single exponential, is shown in Fig. 2.

The pseudo first-order rate constants, k_{obs} , were plotted against the concentration of the entering nucleophile, $[\text{Nu}]$. Linear dependence on $[\text{Nu}]$ with insignificant intercepts was observed for both 1-hexyne and 1-octene, an indication of the absence of a back reaction as well as any parallel reaction. Representative plots shown in Fig. 3 demonstrate that the reactions are first-order with respect to incoming nucleophile.

The overall process can therefore be expressed by the rate law given in Eq. (2):

$$k_{\text{obs}} = k'_2/[\text{Nu}] \quad (2)$$

This is in agreement with the practically irreversible nature of the reaction given in Eq. (1). The composite second-order rate constants, k'_2 , were obtained by least-square analysis of the plots for different temperatures, ranging from 15 °C to 30 °C. The values of k'_2 obtained as a function of temperature, were used in plotting the Eyring plots shown in Fig. 4, whose slope and intercept were used to calculate the activation parameters summarised in the upper section of Table 1.

To rationalize our findings a modified mechanism of that proposed by Brown [7,8], Eqs. (3)–(5), was used:

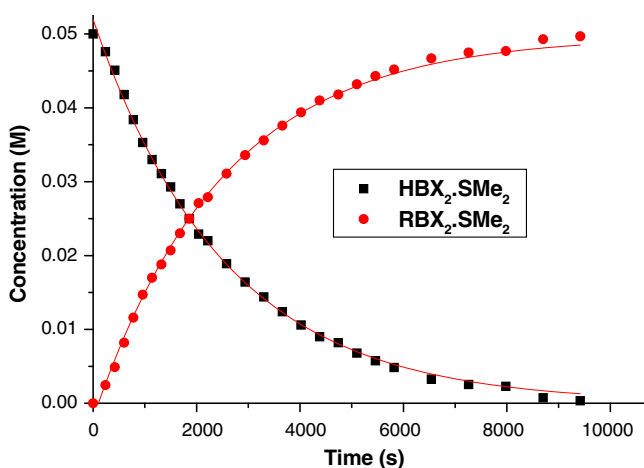
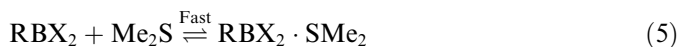
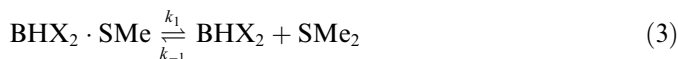


Fig. 2. Exponential decay curve for hydroboration of 0.5 M 1-octene with 0.05 M $\text{HBBr}_2 \cdot \text{SMe}_2$.

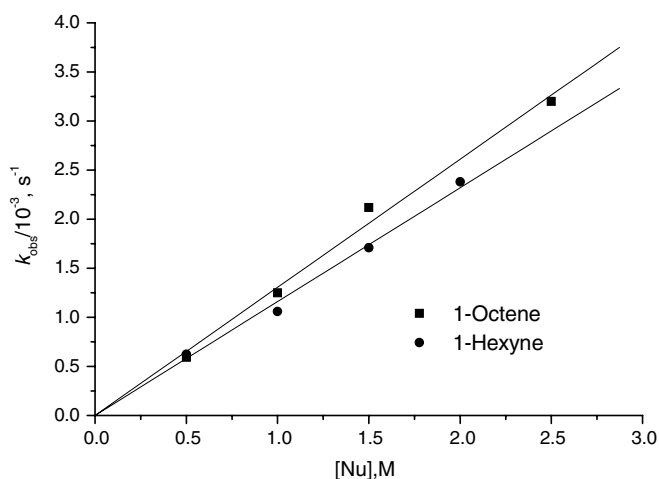


Fig. 3. Dependence of k_{obs} on $[\text{Nu}]$ in the hydroboration reactions of $\text{HBBr}_2 \cdot \text{SMe}_2$ in CH_2Cl_2 at 20 °C.

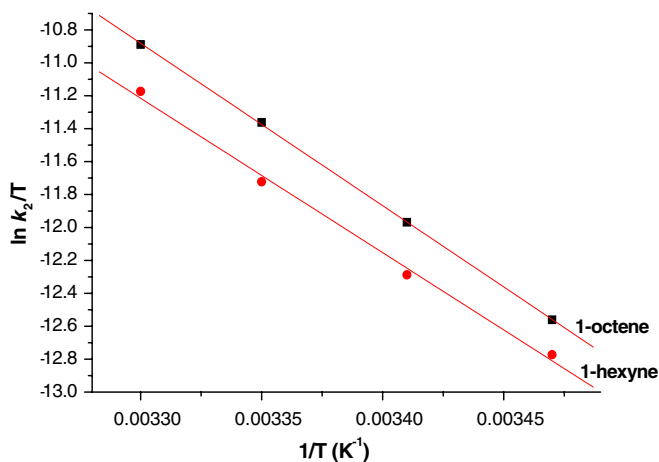


Fig. 4. Eyring plots for hydroboration of 1-octene and 1-hexyne with $\text{HBBr}_2 \cdot \text{SMe}_2$ under pseudo first-order conditions.

The mechanism involves dissociation of the complex into HBX_2 and Me_2S , followed by hydroboration of the nucleophile with the free HBX_2 , to give uncomplexed RBX_2 , which then combines with the Me_2S . This leads to a rate law given in the following equation:

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{R}] + k_{-1} k_{-2} [\text{Me}_2\text{S}]}{k_{-1} [\text{Me}_2\text{S}] + k_2 [\text{R}]} \quad (6)$$

At low temperatures, dehydroboration is not expected and hence, $k_{-2} = 0$. Eq. (6) then reduces to

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{R}]}{k_{-1} [\text{Me}_2\text{S}] + k_2 [\text{R}]} \quad (7)$$

Since we have excess Me_2S in the system, $k_{-1} [\text{Me}_2\text{S}] > k_2 [\text{R}]$, therefore

$$k_{\text{obs}} = \frac{k_1 k_2}{k_{-1} [\text{Me}_2\text{S}]} \cdot [\text{R}]$$

This can be expressed as

$$k_{\text{obs}} = k'_2 \cdot [\text{R}] \quad (8)$$

Table 1

Kinetic data for hydroboration of 1-octene and 1-hexyne with $\text{HBBr}_2 \cdot \text{SMe}_2$ and $\text{HBCl}_2 \cdot \text{SMe}_2$ in CH_2Cl_2

T ($^\circ\text{C}$)	$\text{HBBr}_2 \cdot \text{SMe}_2$		$\text{HBCl}_2 \cdot \text{SMe}_2$
	1-Octene	1-Hexyne	1-Octene
	$k'_2/10^3$ ($\text{M}^{-1} \text{s}^{-1}$)		
15	1.01 ± 0.02	0.82 ± 0.02	0.16 ± 0.003
20	1.86 ± 0.07	1.35 ± 0.08	0.32 ± 0.004
25	3.47 ± 0.04	2.42 ± 0.10	0.83 ± 0.006
30	5.66 ± 0.84	4.26 ± 0.18	1.36 ± 0.04
ΔH^\ddagger (kJ mol^{-1})	82 ± 1	78 ± 4	104 ± 5
ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)	-18 ± 4	-34 ± 12	43 ± 16
$k_1^{25^\circ\text{C}}$ (s^{-1})	1.95×10^{-4}	Data for the dissociation of Me_2S from $\text{HBBr}_2 \cdot \text{SMe}_2$	
ΔH^\ddagger (kJ mol^{-1})	104 ± 2		
ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)	$+33 \pm 8$		

which is equivalent to Eq. (2) where

$$k'_2 = \frac{k_1 k_2}{k_{-1} [\text{Me}_2\text{S}]}$$

It follows that the experimental data reported in Fig. 3 is well described by the mechanism outlined in Eqs. (3)–(5).

To further test the proposed mechanism, Eq. (7) was re-written in a linear form as in Eq. (9):

$$\frac{1}{k_{\text{obs}}} = \frac{k_{-1}}{k_1 k_2 [\text{R}]} \cdot [\text{Me}_2\text{S}] + \frac{1}{k_1} \quad (9)$$

This means that if $[\text{R}]$ is held constant while $[\text{Me}_2\text{S}]$ is varied, a plot of $1/k_{\text{obs}}$ against $[\text{Me}_2\text{S}]$ should be linear with $1/k_1$ as the y -intercept and $k_{-1}/k_1 k_2 [\text{R}]$ as the slope. This was found to be true as shown in Fig. 5.

The k_1 value represents the dissociation rate constant of Me_2S from the boron complex. The Eyring plot for this process, from whose slope and intercept, the activation parameters $\Delta H^\ddagger = 104 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S^\ddagger = +33 \pm 8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ were calculated, is shown in Fig. 6.

3.1. Reactivity

From analysis of the kinetic data in Table 1, it is evident that, on average, the hydroboration of 1-octene with

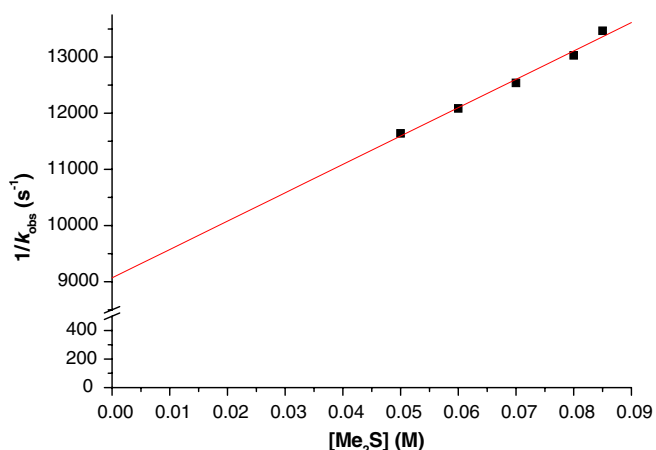


Fig. 5. Inverse relationship between $[\text{Me}_2\text{S}]$ and k_{obs} for hydroboration of 1-octene with $\text{HBBr}_2 \cdot \text{SMe}_2$ in CH_2Cl_2 at 25°C .

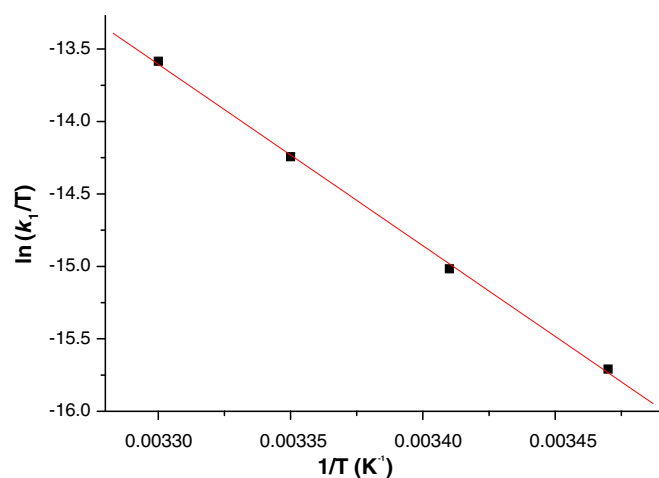


Fig. 6. Eyring plot for the hydroboration of 1-octene with $\text{HBBr}_2 \cdot \text{SMe}_2$ when the concentration of Me_2S was varied.

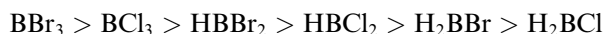
$\text{HBBr}_2 \cdot \text{SMe}_2$ is approximately 1.3 times faster than that of 1-hexyne. This is contrary to Brown's findings [8] who, based on relative reactivities and not on absolute rate constants, reported that hydroboration of 1-hexyne is approximately 3 times faster than that of 1-octene. From our results, small difference in reactivity between the two olefins is not due to energy factor since their ΔH^\ddagger values are very similar. The possible reason could be the difference in their structure.

To compare the reactivity between the $\text{HBBr}_2 \cdot \text{SMe}_2$ and the $\text{HBCl}_2 \cdot \text{SMe}_2$ an understanding of the role of the Me_2S is needed. This is because Fig. 5 clearly shows that as the amount of excess Me_2S is increased the rate of hydroboration decreases, indicative of the fact that the reactivity of these complexes is dependent on the dissociation of the Me_2S from the boron atom. Consequently, when comparing the reactivity of these two haloboranes, it is important to ensure that the amount of excess Me_2S is the same in both the systems.

The excess Me_2S that was in the $\text{HBBr}_2 \cdot \text{SMe}_2$ from the suppliers was worked out to be 21%, which is 1/6 times the concentration of the $\text{HBBr}_2 \cdot \text{SMe}_2$. This was obtained through the integration of the ^1H NMR spectrum of the

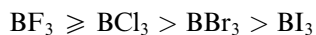
pure sample of the $\text{HBBr}_2 \cdot \text{SMe}_2$, which showed two distinct signals, *i.e.* one from the free Me_2S ($\delta^1\text{H} = 2.1$ ppm) and another from the coordinated Me_2S ($\delta^1\text{H} = 5.0$ ppm). The $\text{HBCl}_2 \cdot \text{SMe}_2$ was also subjected to the same treatment, and was found to contain an excess of 83% Me_2S , which was five times the concentration of the $\text{HBCl}_2 \cdot \text{SMe}_2$ complex.

In this investigation, the study that involved variable concentrations of excess Me_2S was used to deduce the observed pseudo first-order rate constant, k_{obs} , for the $\text{HBBr}_2 \cdot \text{SMe}_2$ reaction system whose excess Me_2S corresponded to that present in $\text{HBCl}_2 \cdot \text{SMe}_2$ reaction system. The composite rate constant, at 25 °C, for hydroboration with the $\text{HBBr}_2 \cdot \text{SMe}_2$ was calculated to be $2.05 \times 10^{-5} \text{ s}^{-1}$ while, that of $\text{HBCl}_2 \cdot \text{SMe}_2$ was found to be $4.01 \times 10^{-4} \text{ s}^{-1}$. The concentration of 1-octene in both cases was 10 times that of the boron complex. This implies that $\text{HBCl}_2 \cdot \text{SMe}_2$ is 20 times more reactive than $\text{HBBr}_2 \cdot \text{SMe}_2$. This finding is contrary to that reported in the literature, but is in support of the fact that $\text{HBBr}_2 \cdot \text{SMe}_2$ is a more stable complex than the $\text{HBCl}_2 \cdot \text{SMe}_2$ [27]. This follows the fact that BBr_3 is a stronger Lewis acid than BCl_3 and hence the bromoboranes are more acidic and more stable than the chloroboranes, in the order [27]:



The strength of coordination between the boron centre and the Lewis base is influenced by the interaction between the boron atom and the halogen substituents attached to it. This is because the halide attached to the boron atom affects the electron density of that boron atom, which in turn changes the strength of the other boron-substituent bonds, in this case B-SMe_2 .

Covalent bond formation is of major importance in boron chemistry. The formation of dative $\text{p}_\pi\text{-p}_\pi$ bond using p_π -orbitals of the halogens and the vacant p_π -orbital of boron is particular of significance in haloboranes. This boron-halogen π -bond strength increases with decreasing size of the halogen. It has been shown that the π -bonding energies of the trihalides are in the order [28]:



A bigger π -bonding energy is indicative of a higher electron density around the boron atom due to strong π -donation from the halogen. The boron atom of $\text{HBBr}_2 \cdot \text{SMe}_2$ can be expected to have lower electron density compared to that of $\text{HBCl}_2 \cdot \text{SMe}_2$. This means that the B-SMe_2 bond will be weaker in the $\text{HBCl}_2 \cdot \text{SMe}_2$ complex compared to the $\text{HBBr}_2 \cdot \text{SMe}_2$ complex. Since the reactivity depends on the dissociation of the Me_2S , the weaker the B-SMe_2 bond the faster the hydroboration, hence $\text{HBCl}_2 \cdot \text{SMe}_2$ is 20 times more reactive than $\text{HBBr}_2 \cdot \text{SMe}_2$.

One question relating to the fate of Lewis base after hydroboration, which needs proof, is whether the Lewis base re-attaches itself back to the boron atom. Since Et_3N can instantaneously replace Me_2S attached to boron atom leading to a change in chemical shift of boron, this

behaviour was used to answer the above question. After completion of hydroboration Et_3N was added into the reaction mixture in NMR tube. On analysis of the sample a distinct change in the chemical shift from $\delta^{11}\text{B} = 3.67$ ppm to $\delta^{11}\text{B} = 9.72$ ppm was observed. This was indicative of a change from $\text{RBBr}_2 \cdot \text{SMe}_2$ to $\text{RBBr}_2 \cdot \text{NEt}_3$, leading to a conclusion that the Lewis base does re-attach itself to the boron atom after hydroboration.

3.2. Activation parameters

The entropy values listed at the top of Table 1 need to be interpreted with caution. They represent a sum of the different processes (*i.e.* detaching of Me_2S from boron and hydroboration of the nucleophile) in the mechanism as represented by k'_2 . Evidence for the dissociation of Me_2S from boron prior to the hydroboration comes from the study involving excess Me_2S at different temperatures. In support is the ΔS^\ddagger value being positive ($+33 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$) for the dissociation of the Me_2S from $\text{HBBr}_2 \cdot \text{SMe}_2$. In addition, this is supported by the retardation effect of Me_2S on hydroboration. Having shown that the entropy value for the dissociation of Me_2S is positive, the overall negative entropy value ($-18 \pm 4 \text{ J K}^{-1} \text{ mol}^{-1}$) for $\text{HBBr}_2 \cdot \text{SMe}_2$ can indirectly be interpreted to indicate that the entropy value from k_2 (the hydroboration step) is large and negative, an indication that this process is associative in nature. Using the same argument it can be concluded that the small positive overall entropy ($+43 \pm 16 \text{ J K}^{-1} \text{ mol}^{-1}$) for the $\text{HBCl}_2 \cdot \text{SMe}_2$ indicate that the entropy value for the dissociation of the Me_2S is bigger in magnitude than that due to hydroboration. It is worth mentioning that the large error limits associated with the entropy values is due to the intrinsic extrapolation involved in their determination [29,30]. Also, in the case of non-dissociation of Me_2S the composite nature of the rate constant used to generate the values.

4. Conclusions

In conclusion, activation parameters deduced from this study reveal that hydroboration reactions of $\text{HBBr}_2 \cdot \text{SMe}_2$ and $\text{HBCl}_2 \cdot \text{SMe}_2$ go through dissociation of the Me_2S from the boron centre, which is then followed by hydroboration of the nucleophile through an associative route. In this mechanistic route, dissociation of Me_2S is the rate-determining step. The hydroboration kinetics of such boron compounds, *i.e.* those attached to a Lewis base, is controlled by the concentration of Lewis base present in the system. As such when comparing the reactivities of these complexes, it is of importance that the amount of the Lewis base present in the system is taken into account.

This work has confirmed that the reactivity of haloborane addition complexes is dependent on the type of halogen attached to the boron atom. It has also shown through the composite rate constants, at 25 °C, for hydroboration with the $\text{HBBr}_2 \cdot \text{SMe}_2$ ($2.05 \times 10^{-5} \text{ s}^{-1}$) and that of

$\text{HBCl}_2 \cdot \text{SMe}_2$ ($4.01 \times 10^{-4} \text{ s}^{-1}$), that hydroboration with $\text{HBCl}_2 \cdot \text{SMe}_2$ proceed at a rate which is 20 faster than that of $\text{HBBr}_2 \cdot \text{SMe}_2$.

Finally, we have shown that ^{11}B NMR spectroscopy can be used as a tool in the investigation of the kinetic and mechanistic studies of hydroboration reactions.

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