Kinetics of iodination of some amine-boranes with molecular iodine in toluene

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$R_3N.BH_3$ ($R = Me, Et, Prn$) at room temperature reacts with $I_2$ in toluene quantitatively to produce $R_3N.BHzl$ when concentrations of the reactants are kept low. But with reactant concentrations $> 50$ mmol dm$^{-3}$, $R_3N.BH_3l$ and $H_2$ are produced as observed earlier (Inorg Synth, 12 (1970) 120). A reaction scheme has been proposed to explain this difference. Production of $R_3N.BHzl$ from $R_3N.BH_3$ proceeds in two consecutive steps:

$$R_3N.BH_3 \xrightarrow{k_1} R_3N.BHzl \xrightarrow{k_2} R_3N.BH_2l.$$ 

Both steps are first order each in $[borane]$ and $[I_2]$. $k_1$ is greater than $k_2$ but both increase in the order $Et > Me > Prn$. The secondary amine-borane $(Et)_2NH.BH_3$ reacts with $I_2$ much faster than any of the three tertiary amine-boranes studied. The observed order of reactivity of amine-boranes with homopolar $I_2$ is the same as that observed by earlier workers with heteropolar $HOCl$. A bimolecular mechanism with a four-membered transition state and pentacoordinate $B$ is proposed and the sequence of reactivity appears to be primarily a result of steric influence, though electronic effects might have a modifying role.

Amine-boranes are halogenated by a diverse array of halogenating agents$^{1-5}$. The extent and site of halogenation strongly depend on the halogenating agent chosen. For example, trimethylamine borane, $Me_3N.BH_3$, reacts with $HBr$ to produce the monobromo derivative, $Me_3N.BH_2Br$, but the tribromo product $Me_3N.BHBr_3$ is produced by the action of $Br_2$ or $BBF_3$ (ref. 6). HF appears to be a very strong halogenating agent and forms $Me_3NHBF_4$ (ref. 7) as the ultimate product of its reaction with $Me_3N.BH_3$. It appears, that both the extent and rate of $B$-halogenation increase with the thermodynamic oxidizing strength of the halogenating agent increasing in the order: $HX < X_2 < HOX$ for a given halogen $X$ in different oxidation states, and in the order: $I_2 < Br_2 < Cl_2 < F_2$ for different halogens in their elemental states. It is also generally observed that rate decreases with increased extent of halogenation, e.g. the rate of chlorination by $HOCl$ decreases in the order$^{6,7}$:

$$Me_3N.BH_3 > Me_3N.BH_2Cl > Me_3N.BHCl_2.$$ 

In some cases, $N$-halogenation has been noted$^{8,9}$ instead of the usual $B$-halogenation. Thus $HOCl$ reacts with secondary amine-borane adducts to produce $N$-chlorinated amines, whereas usual $B$-chlorinated products are obtained with tertiary amine-boranes. Relative influence of steric versus electronic effects on such switchover in reaction pathways is not well understood.

Compared to $HOCl$, $I_2$ is a bulkier molecule and unlike $HOCl$, it is a non-polar addendum. A comparison between the kinetics of reactions of $HOCl$ versus $I_2$ may, therefore, provide further insight into the role of steric and electronic influences of molecular structure on the reactivity of amine-boranes.

In this backdrop, kinetics of iodination of $Me_3N.BH_3$ by molecular $I_2$ have been determined. The results are described in this paper.

**Experimental**

Sodium borohydride (S.D. Fine Chemicals) and trimethylamine hydrochloride (Fluka, Germany), were used as received. Iodine (E. Merck) crystals were further purified by sublimation. Triethylamine and tripropylamine were stored over sodium hydroxide pellets and distilled prior to use. Toluene (AR Grade) was dried by refluxing over freshly cut sodium and distilled prior to use.

Tri- and dialkylamine-boranes were prepared and purified by published methods$^{11}$. C, H, N and $B$ analyses indicated a purity better than 99%. Boron was estimated volumetrically$^{13,14}$, while a Perkin-Elmer 240C elemental analyser was used for C, H, N.

Reaction stoichiometry was determined by spectrophotometric titration of $I_2$ with alkylamine-borane. Different amounts of alkylamine-borane were mixed with a fixed amount of $I_2$ and the difference between initial and final absorbance ($\Delta A = A_0 - A_f$) at 500 nm was determined as a function of the amine-borane concentration. Final absorbance was measured after completion of reaction as indicated by a constant value of $A_f$ over a period of 2 hours or more. Values for $A_0$ were obtained from a standard calibration curve.
constructed at 500 nm for I₂ in this concentration range in toluene. Beer’s law was strictly obeyed in this range.

Rate was measured by monitoring the decay in absorbance of I₂ at 500 nm, the visible absorbance peak of I₂ in toluene. No other species than I₂ absorbs at this wavelength under the experimental conditions. Reactions were carried out in toluene in the presence of a large excess of amine-borane over I₂ at 25°C in situ in the thermostated cell-housing of a Philips Analytical SP8-400 spectrophotometer. Pseudo-first order rate constants for the two-step, first order consecutive process were evaluated using a standard graphical technique using the relation

$$A_t = P_1 e^{-k_1 t} + P_2 e^{-k_2 t} \quad \ldots (1)$$

where $A_t$ is the absorbance at time $t$, $k_1$ and $k_2$ are the pseudo-first order rate constants characterizing the consecutive reaction, while $P_1$ and $P_2$ are two constants.

Results and discussion

Iodination of Me₃N.BH₃ by I₂ is an important synthetic reaction used to prepare Me₃N.BH₂I (ref. 10). In a typical synthesis, 0.2 mol of Me₃N.BH₃ is mixed with 0.1 mol of I₂ in cold benzene under N₂. After the vigorous gas (H₂) evolution subsides, the mixture is refluxed and then standard work-up procedures follow. Me₃N.BH₂I is thus obtained in near quantitative yield. The reported stoichiometric equation for the process is:

$$2\text{Me}_3\text{N.BH}_3 + \text{I}_2 \rightarrow 2\text{Me}_3\text{N.BH}_2\text{I} + \text{H}_2 \quad \ldots (2)$$

Surprisingly for us, we could not detect any H₂ evolving under our kinetic conditions and found a 1:2 stoichiometry (see Fig. 1) which indicates Eq. (3) and not (2).

$$\text{R}_3\text{N.BH}_3 + 2\text{I}_2 \rightarrow \text{R}_3\text{N.BH}_2\text{I} + 2\text{HI} \quad \ldots (3)$$

(R = Me, Et, Pr")

The kinetics were studied in toluene while the synthesis was carried out in benzene. Formation of mostly (CH₃)₃N.BH₃ (80%) in a synthetic reaction in refluxing toluene medium has been reported. Moreover, the very low concentrations of the reagents, viz. in the range of 10⁻⁴ mol dm⁻³ for I₂ and 10⁻³-10⁻² mol dm⁻³ for the borane, may also have influence. We propose here a unified reaction scheme [Scheme 1] which may explain the stoichiometric observations both under the preparative and the kinetic conditions:

$$\text{R}_3\text{N.BH}_3 + \text{I}_2 \rightarrow \text{R}_3\text{N.BH}_2\text{I} + \text{HI} \quad \ldots (4)$$

$$\text{R}_3\text{N.BH}_2\text{I} + \text{I}_2 \rightarrow \text{R}_3\text{N.BH}_3 + \text{HI} \quad \ldots (5)$$

$$\text{R}_3\text{N.BH}_3 + \text{HI} \rightarrow \text{R}_3\text{N.BH}_2\text{I} + \text{H}_2 \quad \ldots (6)$$

$$\text{R}_3\text{N.BH}_2\text{I} + \text{HI} \rightarrow \text{R}_3\text{N.BH}_2\text{I} + \text{H}_2 \quad \ldots (7)$$

$$\text{R}_3\text{N.BH}_3 + \text{R}_3\text{N.BH}_2\text{I} \rightarrow 2\text{R}_3\text{N.BH}_2\text{I} \quad \ldots (8)$$

Scheme 1

Hydrogen halides and B-halogenated amine-boranes are well known halogenating agents for amine-boranes. So reactions proposed in Eqs (6)-(8) are logical. Moreover, hydrogen halides halogenate amine-boranes at much slower rates than the corresponding halogens. It is quite likely, therefore, that $k_3$ and $k_4$ are much smaller than $k_1$ and $k_2$. Hence steps (6) and (7) are of little kinetic significance unless concentrations of reactants viz. R₃N.BH₂I and HI are high. Expressed in other words, (6) and (7) may be kinetically important, and evolution of H₂ may be detectable if the initial concentrations of an amine-borane and I₂ are high producing a sufficiently high concentration of HI. Therefore, H₂ evolution may not be detectable and Eq. (2) is not obeyed under our kinetic conditions with only 10⁻⁴ mol dm⁻³ of I₂.

It is concluded that reaction ceases after the reaction (5) leading to the overall stoichiometry (3), if reactant concentrations are as low as used in the kinetic experiments. However, it proceeds up to reaction (8), leading to the overall stoichiometry (2) if reactant concentrations are as high as used in the preparation of Me₃N.BH₂I. Scheme 1 presume.s that R₃N.BH₂I does not consume further I₂ to form R₃N.BH₃I. This seems probable because R₃N.BH₂I is less reactive than R₃N.BH₂I towards halogenation as indicated by the observation that Me₃N.BH₂I quickly exchanges iodide with halides.
Table 1—First-order rate constants for reaction of 12 with R₃N.BH₃ (k₁) and R₃N.BH₂I (k₂) in toluene, temp. 25°C, [12] = 3 × 10⁻² mol dm⁻³.

<table>
<thead>
<tr>
<th>R₃N.BH₃ (mol dm⁻³)</th>
<th>k₁ (10⁻² s⁻¹)</th>
<th>k₂ (10⁻² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = Me</td>
<td>Me</td>
<td>Et</td>
</tr>
<tr>
<td>3.0</td>
<td>4.55</td>
<td>6.66</td>
</tr>
<tr>
<td>4.0</td>
<td>4.11</td>
<td>6.00</td>
</tr>
<tr>
<td>5.0</td>
<td>3.68</td>
<td>5.60</td>
</tr>
<tr>
<td>6.0</td>
<td>3.37</td>
<td>4.41</td>
</tr>
<tr>
<td>7.0</td>
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<td>3.92</td>
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<tr>
<td>9.0</td>
<td>1.84</td>
<td>2.88</td>
</tr>
<tr>
<td>10.0</td>
<td>1.58</td>
<td>1.19</td>
</tr>
</tbody>
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and pseudohalides but under similar conditions, Me₃N.BH₂I is unreactive. Lower activity of Me₃N.BH₂I than Me₃N.BH₃ is further indicated by the fact that Me₃N.BH₃ reacts with 12 in a 2:3 molar ratio in refluxing toluene to produce mostly Me₃N.BH₂I (30%), the triiodide Me₃N.BI₃ is only a minor product. At room temperature yield of the triiodo derivative is likely to be even less, may be insignificant.

The reactions produced a biphasic kinetic profile, with first order rate constants k₁ and k₂. Representative k₁ and k₂ values at different [R₃N.BH₃] (R = Me, Et, Pr³) are displayed in Table 1. Plots of both k₁ and k₂ against [R₃N.BH₃] are linear (r = 0.99) with insignificant intercepts. The second order rate constants k₁ and k₂ at 25°C were evaluated from the slope of these lines.

<table>
<thead>
<tr>
<th>R = Me</th>
<th>R = Et</th>
<th>R = Pr³</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁ (mol⁻¹ dm³ s⁻¹):</td>
<td>4.54</td>
<td>6.66</td>
</tr>
<tr>
<td>k₂ (mol⁻¹ dm³ s⁻¹):</td>
<td>0.84</td>
<td>1.64</td>
</tr>
</tbody>
</table>

We studied variation of rate with a change in the amine part of the amine-borane from tertiary to secondary, viz. Et₂N.BH₃. The reaction is much too fast for rate measurement by conventional spectrophotometry.

The kinetic observations for the tertiary amine-boranes are consistent with a binuclear four-membered activated state for reactions (4) and (5). An analogous mechanism is plausible for reactions (6)-(8). A tentative picturisation for the activated state for reaction (4) is I in which subsequent hydride transfer leads to products. Such an activated state without rupture of the B–N bond was proposed by Nöth and Beyer for the halogenation of Me₃N.BH₃ with boron halides. Similar activated state containing a five coordinate boron, has been fairly well established in the solvolysis reactions of amine-haloboranes and amine-cyanoboranes and in the reactions of amine-boranes with halogenating agents e.g. BX₃, ICl, HOCI and HX.

Both k₁ and k₂ increase in the order: tri(n-propyl)amine-borane ≪ trimethylamine-borane ≪ triethylamine-borane ≪ diethylamine-borane. Similar activated state containing a five coordinate intermediate should be disfavoured with a bulkier amine, the hydridic nature of B–H bond should increase with a bulkier amine because they are stronger electron donors. Oxidation of the B–H bond should thus be favoured.

An interesting comparison may arise at this point between halogenation of secondary amine-boranes by 12 and that by HOCI. Both the oxidants react very much faster with a secondary amine-borane than with a tertiary amine-borane. Kelly et al explained the situation for HOCI by postulating a change in the polarity of B–H bonds with change in the amine and a consequent change in the site of attack by O and Cl from HOCI. Such an explanation is obviously inapplicable for 12, which unlike HOCI is a symmetrical addendum. Electronic effect alone cannot be, therefore, the cause for the observed pattern of reactivity. It appears that steric effect is more important at least for 12, which is much bulkier than HOCI.
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References
6. Ref. 4, 118.
10. Ref. 4, 120.