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THE REACTION OF BORON TRIHALIDES WITH SILANES

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Boron trichloride is reduced by Si_2H_6 [1,2] and Si_3H_8 [2] but not by SiH_4 [1] or $ClSiH_3$.[1] Similarly, BBr_3 is reduced by both SiH_4 [3] and Si_2H_6 [3] while BF_3 is not reduced by either SiH_4 [2] or Si_2H_6.[1]

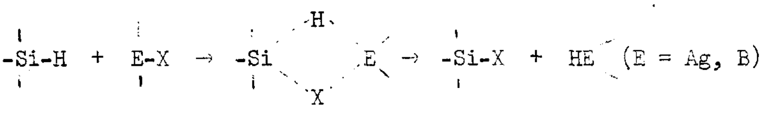
Our results, obtained under the same conditions as the above reactions, show that BCl_3 is reduced by CH_3SiH_3 while BBr_3 is reduced by $ClSiH_3$. We have also found that BF_3 is not reduced by CH_3SiH_3, 1,2-$(CH_3)_2Si_2H_4$ or Si_3H_8.

It is obvious from the above data that the relative rate of BX_3 (X = Cl,Br) reduction is: $CH_3SiH_3 > SiH_4$ or $ClSiH_3$ and $Si_2H_6 > SiH_4$. These orders are similar to those found for the reduction of AgCl where the relative rates were:[4]

$$Si_2H_6 > CH_3SiH_3 > SiH_4 > ClSiH_3.$$

For both BX_3 and AgCl the rates increase with an increase in hydride character of the silane along with the increase due to catenation. The relative rate of BX_3 reduction increases with the increase of Lewis acidity[2] ($BBr_3 > BCl_3 > BF_3$).

The activated complexes suggested for the AgCl [4] and BCl_3 [1] reductions are identical. In this activated complex,



$$-\overset{|}{\underset{|}{Si}}-H + \overset{|}{\underset{|}{E}}-X \rightarrow -\overset{|}{\underset{|}{Si}}\overset{H}{\underset{X}{\diamond}}E \rightarrow -\overset{|}{\underset{|}{Si}}-X + HE \quad (E = Ag, B)$$

the E···H interaction is stabilized by an increase in the hydridic character of H and an increase in the acidity of BX_3. The Si····X interaction should be destabilized by a decrease in acidity at Si ($CH_3SiH_3 < SiH_4 < ClSiH_3$) and possibly destabilized by a decrease in base character of the halogen (F < Cl < Br). For the monosilanes, the increase in hydridic character ($CH_3SiH_3 > SiH_4 > ClSiH_3$, based on a decrease in the weighted average of the Si-H stretching frequencies)[5] appears to be the dominant factor over the change in acidity at Si. The increased rate with Si_2H_6 compared to SiH_4 can be explained by an increase in the Lewis acidity of Si in Si_2H_6 (based on a more stable complex with $N(CH_3)_3$ for Si_2H_6 compared to SiH_4).[6]

Reaction of CH_3SiH_3 with BCl_3

In a typical experiment, 2.3 mmoles of CH_3SiH_3 and 1.1 mmoles of BCl_3 were condensed into a 32 ml Pyrex reaction vessel fitted with a Teflon valve. The reaction vessel was allowed to warm up to 0°C and held at this temperature for 17 hours. The product mixture was then removed from the reaction vessel and analyzed in a standard high vacuum system. The products were B_2H_6 (0.6 mmoles), CH_3SiH_2Cl (1.3 mmol), CH_3SiHCl_2 (0.9 mmol) and small quantities of SiH_4 and a hydrocarbon.

Reaction of $ClSiH_3$ with BBr_3

In the same reaction vessel, $ClSiH_3$ (0.5 mmoles) and BBr_3 (0.2 mmoles) were allowed to react at 0° for 8 hours. The BBr_3 was quantitatively reduced to yield 0.1 mmoles of B_2H_6. Chlorobromsilane (0.4 mmol) was isolated and a white solid product was observed.

Other Reactions

In the same reaction vessel, no reactions were observed after 17 hours at 0° between CH_3SiH_3 (1.5 mmol) and BF_3 (1.3 mmol) or after 8 hours at 0° between BF_3 (0.9 mmol) and 1,2-$(CH_3)_2Si_2H_4$ (1.6 mmol) or between BF_3 (0.4 mmol) and Si_3H_8 (1.1 mmol).

References

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