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An ^{11}B NMR spectroscopy investigation of the mechanism of the reduction of nitriles by $BH_3 \cdot SMe_2$

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Abstract

A kinetic and mechanistic investigation of the reduction of acrylonitrile, propionitrile and benzonitrile by $BH_3 \cdot SMe_2$ in CH_2Cl_2 has been conducted using ^{11}B NMR spectroscopy. No reduction of propionitrile and benzonitrile was observed at 25 °C, while the reduction of acrylonitrile was monitored to the vinyliminoborane. The reaction exhibited simple second-order kinetics of the form $k_{obs} = k_2'$[acrylonitrile], with the dissociation of the dimethyl sulfide from borane playing a key role in controlling the reduction process. The activation parameters ($\Delta S^{\neq}$ and $\Delta H^{\neq}$) for the reaction of $BH_3 \cdot SMe_2$ with acrylonitrile were found to be -71 ± 10 J K^{-1} mol^{-1} and 58 ± 3 kJ mol^{-1}, respectively. The B3LYP/6-31G* results for charge distribution and transfer during the reaction show a reversal of charge in the borane–nitrile adduct for the atoms that make up the borane and the nitrogen and carbon atoms in the nitrile. The activation barriers for the reduction of acrylonitrile were found to be 6–8 kJ mol^{-1} lower than those of hydrogen cyanide, propionitrile and benzonitrile, with its product iminoborane being 30–130 kJ mol^{-1} more stable than those of the other nitriles.

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1. Introduction

The reduction of nitriles by borohydrides has long been known [1], with the reaction of diborane (B_2H_6) with acrylonitrile at room temperature shown to afford at least three products [2]. Studies on the room temperature reduction of *m*-nitrobenzonitrile [3] and benzonitrile [4,5] with diborane in ethereal solvents have shown the reaction to be rapid, reaching completion within 2 h. Investigation of the rates and stoichiometry of the reduction of capronitrile and benzonitrile with diborane in tetrahydrofuran (THF) has shown that both compounds are readily reduced even at 0 °C [6]. The route by which nitrile reduction occurs has been elucidated during the reduction, by diborane, of methyl and ethyl cyanide, as well as that of acrylonitrile, where it has been shown that methyl and ethyl cyanide react reversibly with diborane at low temperature to form borane–nitrile adducts ($RC{\equiv}N \cdot BH_3$) [7].

The stability of the ethyl cyanide adduct ($EtC{\equiv}N \cdot BH_3$) towards decomposition was found to be lower than that of the methyl cyanide adduct ($MeC{\equiv}N \cdot BH_3$). acrylonitrile and benzonitrile have also been shown to form adducts with BH_3 that are less stable to decomposition through reduction than alkyl cyanides [7]. The decomposition of the alkyl cyanide–borane adducts ($R{-}C{\equiv}N \cdot BH_3$) has been reported to eventually produce *NN′N″*-tri-*n*-alkylborazines at room temperature via two successive hydrogen shifts from the boron atom to the nitrile carbon atom (Scheme 1) [7,8]. The decomposition of the acrylonitrile–borane adduct ($CH_2{=}CH{-}C{\equiv}N \cdot BH_3$) was found to take place vigorously above 0 °C, such that borazine derivatives were not isolated [7].

Jennings and Wade have shown that the borazines constitute only part of the total product mixture for the reduction of nitriles, with the reduction of ethyl cyanide

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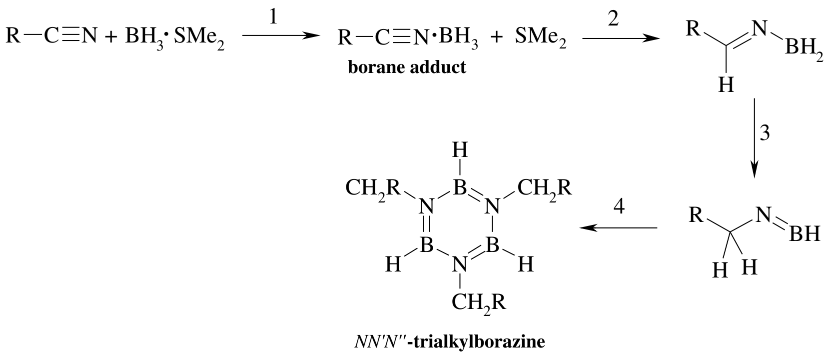

Scheme 1.

affording 35–40% *NN′N″*-triethylborazine [9]. In addition, a further 25–37% of the product distribution has been attributed to bicyclic compounds [10].

Complexes of borane with ethers (e.g., $BH_3 \cdot THF$ and $BH_3 \cdot OEt_2$) effectively convert nitriles to their corresponding amines after hydrolysis [3,4,11]. The reduction is, however, more sluggish with the dimethyl sulfide complex [12,13]. While the greater stability of the borane–dimethyl sulfide complex ($BH_3 \cdot SMe_2$) towards dissociation was cited as a reason for the retardation in reactivity, its stability towards decomposition and better handling characteristics are the reason for the choice of this complex in hydroboration and reduction reactions [13]. An improved procedure for enhancing the reactivity of the borane–dimethyl sulfide complex towards nitriles has been published and its general applicability toward nitrile reduction established [5,14]. Tetrabutylammonium borohydrides have also been used for the reduction of nitriles [15], while various strategies for the enhancement of the reactivity and selectivity of sodium borohydrides toward the reduction of nitrile compounds have also been developed [16].

The conventionally adopted method for investigating the reactivity of nitriles toward reduction by borane–Lewis base adducts has been the determination of residual hydridic hydrogen at the end of the reaction period [17]. This technique, while adequate for comparison of the relative reactivity of various boranes toward nitriles, cannot be used to determine precise kinetic and activation parameters. The applicability of infrared spectroscopy to the investigation of the hydroboration reaction has been demonstrated for some time in the literature [18–25]. Yet, ^{11}B NMR spectroscopy has not received much attention in the field of hydroboration kinetics, with the technique usually relegated to a qualitative role [26,27]. The non-destructive nature of the technique coupled with its real-time analysis, shows the potential of its use for the determination of kinetic data for various reactions. The aim of this investigation was, thus, to determine kinetic and activation parameters for the reduction of acrylonitrile using ^{11}B NMR spectroscopy.

2. Experimental

2.1. General

Borane dimethyl sulfide (1 M in dichloromethane, Sigma–Aldrich) was used without further purification. Acrylonitrile, propionitrile and benzonitrile (all Sigma–Aldrich) were dried by percolating over activated 3 Å molecular sieve before use. Nitrile and borane dimethyl sulfide solutions were diluted to the relevant concentrations with dichloromethane (Merck) distilled over calcium hydride.

Standard techniques for handling of air- and moisture-sensitive materials were used for handling syringes, needles, canulae, glassware, quartz NMR tubes and reagents [28,29].

2.2. Kinetic measurements

^{11}B NMR spectra were recorded at 160 MHz and referenced externally against $BF_3 \cdot OEt_2$ (0 ppm) on a Varian Unity Inova 500 spectrometer in 5 mm quartz tubes with proton decoupling (Waltz-16). A proton-coupled spectrum of the reaction was also recorded in order to identify reaction intermediates and products. A 1-min delay was allowed for mixing and temperature equilibration in the spectrometer, after which arrayed spectra were recorded at set time intervals. The temperature of the spectrometer was controlled at an accuracy of ±0.5 °C. The kinetic data were obtained by monitoring the signal area of the borane dimethyl sulfide peak with time. The following peaks were identified over time in the ^{11}B NMR spectrum: $BH_3 \cdot SMe_2$ [quartet, $\delta^{11}B = -20.3$ ppm, $J_{B-H} = 110$ Hz], $CH_2{=}CH{-}C{\equiv}N \cdot BH_3$ [quartet, $\delta^{11}B = -25.7$ ppm, $J_{B-H} = 104$ Hz] and vinylimino borane [triplet, $\delta^{11}B = -16.3$ ppm, $J_{B-H} = 111$ Hz], $EtC{\equiv}N \cdot BH_3$ [quartet, $\delta^{11}B = -26.2$ ppm, $J_{B-H} = 102$ Hz] and $C_6H_5C{\equiv}N \cdot BH_3$ [quartet, $\delta^{11}B = -25.8$ ppm, $J_{B-H} = 102$ Hz]. Also identified in the spectrum were impurities in the $BH_3 \cdot SMe_2$ solution [singlet, $\delta^{11}B = -10.9$ ppm; singlet, $\delta^{11}B = -13.5$ ppm; singlet, $\delta^{11}B = -17.3$ ppm; singlet, $\delta^{11}B = -15.4$ ppm; singlet, singlet, $\delta^{11}B = -23.2$ ppm; $\delta^{11}B = -29.2$ ppm].

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