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Short communication

Thermal stability of the diazohydroborate $[1\text{-}N_2B_{10}H_9]^-$: degradation to $[B_{20}H_{18}]^{2-}$ anion

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The thermal stability of the monodiazohydroborate $NMe_4[1\text{-}N_2B_{10}H_9]$ was studied by thermogravimetric analysis. Under two different atmospheres (air and argon), the thermal decomposition starts at a temperature between 140 and 160 °C. The decomposition residue obtained was separated on a silica gel column. ^{11}B NMR, IR and electrospray mass spectroscopy analyses of the different fractions separated showed that the above decomposition produces $(NMe_4)_2[B_{20}H_{18}]$ as major product (90%), along with smaller amounts of residual $NMe_4[1\text{-}N_2B_{10}H_9]$ (5%), $(NMe_4)_2[B_{12}H_{12}]$ and boric acid.

KEYWORDS: hydroborate; decaborate; diazonium salt; TGA

Monodiazohydroborate anion $[1\text{-}N_2B_{10}H_9]^-$ is an important reagent in organic synthesis. The diazo group is the only known one to be substituted by a nucleophile L. This substitution reaction takes place at a temperature of 120 °C to produce $[1\text{-}LB_{10}H_9]^-$.[1,2] In addition, this substitution produces a variety of products of the type $[1\text{-}LB_{10}H_9]^-$ that have very important applications as active agents in boron neutron capture therapy[3] and as potential extractants of radioactive cations in nuclear fuels reprocessing.[4]

We reported the substitution of the diazo group of $[1\text{-}N_2B_{10}H_9]^-$ by a nucleophilic ligand L (amines or phosphines) at a temperature greater than 120 °C.[5] When $[1\text{-}N_2B_{10}H_9]^-$ was reacted with bulky tertiary amines or tertiary phosphines, the major product obtained was $[B_{20}H_{18}]^{2-}$.[5] This product is prepared in a high yield with aqueous ferric or ceric ion oxidation of $[B_{10}H_{10}]^{2-}$.[6] Oxidation of $[B_{10}H_{10}]^{2-}$ by copper(II) chloride led to products that were more difficult to analyze.[7] The oxidation with carbon monoxide or carbon dioxide produced $[(NO)B_{20}H_{18}]^{3-}$, whose structure has been studied.[8] The oxidizing agents $Fe(NO_3)_2$ produced $[(NO)B_{20}H_{18}]^{3-}$, $FeCl_3$ led to $[1,6,8\text{-}Cl_3B_{10}H_7]^{2-}$ and [1,6-(or 2,4-)$Cl_2B_{10}H_8]^{2-}$, and $KClO_3$ resulted in $[Cl_6B_{10}H_4]^{2-}$ respectively.[9] Oxidization by permanganate ions $MnO_4{}^-$ did not produce $[B_{20}H_{18}]^{2-}$ because decomposition resulted in boric acid.[10] This decomposition was related to the formation of the derivatives $[(OH)_xB_{10}H_{10-x}]^{2-}$, whose hydroxyl groups destabilize the B_{10} cage to form the boric acid.[11] $[B_{20}H_{18}]^{2-}$ was prepared by electrochemical oxidation of $[B_{10}H_{10}]^{2-}$.[12]

The decomposition of $[N_2B_{10}H_9]^-$ has not been studied in detail. It has been mentioned briefly that it decomposes from 120 °C accompanied by the release of nitrogen molecule.[13,14] The nature of the resulting products was not mentioned. In order to explain the formation of $[B_{20}H_{18}]^{2-}$ during the reaction of $[N_2B_{10}H_9]^-$ with bulky amines or phosphines, we studied the thermal stability of pure $NMe_4[1\text{-}N_2B_{10}H_9]$ by thermogravimetric analysis (TGA) under two different atmospheres, i.e. argon and air.

The thermal stability was studied by TGA on 50 mg samples; the temperature was raised at a 2 K min^{-1} heating rate. The decomposition reaction started at 150–160 °C under air atmosphere or argon atmosphere (Fig. 1). In order to obtain sufficient amounts of product for analysis, 0.2 g samples were also pyrolyzed under air or argon up to 200 °C at a 6 K min^{-1} heating rate. The residual solid contained $\{N(CH_3)_4\}_2[B_{20}H_{18}]$ (90%), residual $NMe_4[N_2B_{10}H_9]$ (5%) and $[B_{12}H_{12}]^{2-}$ as characterized by electrospray mass spectrometry ($m/z = 216$, calculated for $N(CH_3)_4[B_{12}H_{12}]^-$: 215.6) and

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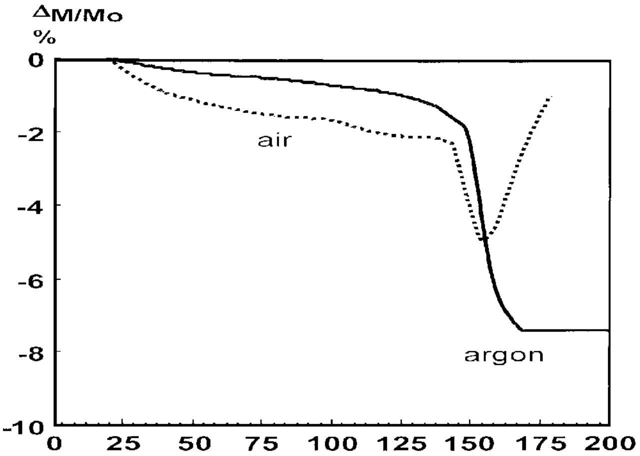


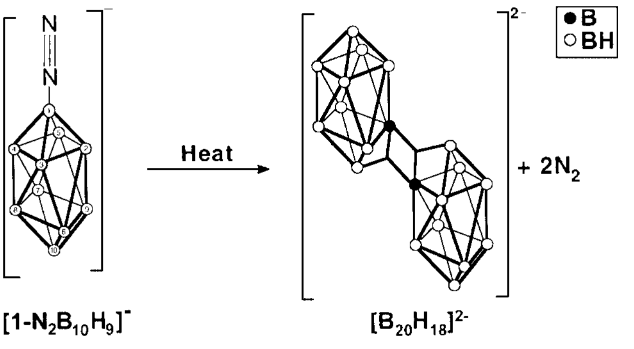
Figure 1. TGA of $NMe_4[N_2B_{10}H_9]$ under air and argon.

^{11}B NMR δ −14.83 (lit.[14–16] −15.63). Pure $[B_{20}H_{18}]^{2-}$ was isolated by chromatography on a silica gel column using 30:70 $CH_3CN:CH_2Cl_2$ as eluent; the first fraction was $NMe_4[N_2B_{10}H_9]$; the second fraction was $[B_{20}H_{18}]^{2-}$; and the third fraction was a mixture of $[B_{20}H_{18}]^{2-}$ and $[B_{12}H_{12}]^{2-}$. Consistent with the literature data, $[B_{20}H_{18}]^{2-}$ proved to be a hydrophobic anion and was detected by thin-layer chromatography on DEAE cellulose at $R_f = 0$. ^{11}B NMR data (CH_3CN, J/H_3) were in agreement with Ref. 17: δ 30.55 (d, $J_{B-H} = 148$, 2B), 15.97 (s, 2B), −6.84 (d, $J_{B-H} = 142$, 2B), −12.35 (d, $J_{B-H} = 146$, 4B), −15.86 (d, $J_{B-H} = 140$, 4B), −19.29 (d, $J_{B-H} = 135$, 4B), −25.53 (d, $J_{B-H} = 148$, 2B). Electrospray mass spectrometry: $m/z = 308.5$ for the most intense peak, calculated 308 for $N(CH_3)_4[B_{20}H_{18}]^-$.

$NMe_4[1\text{-}N_2B_{10}H_9]$ decomposes to $\{N(CH_3)_4\}_2[B_{20}H_{18}]$ according to the oxidation reaction shown in Scheme 1.

The formation of $[B_{20}H_{18}]^{2-}$ was also accompanied by its slow degradation, giving the very stable $[B_{12}H_{12}]^{2-}$ and other unidentified products. The formation of $[B_{12}H_{12}]^{2-}$ can be attributed to polyhedral rearrangements, which have been observed at temperatures as low as 150–160 °C.

The theoretical loss of mass for the previous reaction is equal to 12.78%, which corresponds to the dinitrogen formed.



Scheme 1.

According to Fig. 1, the experimental loss of mass is 5% under air and 7.5% under argon. This difference between the theoretical and experimental losses can be explained by the following considerations. (1) The decomposition reaction is not straightforward. It produces not only $[B_{20}H_{18}]^{2-}$ but also $[B_{12}H_{12}]^{2-}$ and other products due to hydrolysis. (2) The starting product $NMe_4[N_2B_{10}H_9]$ contains water chemically bound to the product. Drying this product under vacuum at ambient temperature could not remove the water. While drying the product under vacuum at 90 °C over 8 h, we observed a partial decomposition of $NMe_4[N_2B_{10}H_9]$ to $(NMe_4)_2[B_{20}H_{18}]$ and to boric acid. Under an argon atmosphere, $NMe_4[N_2B_{10}H_9]$ decomposes to $(NMe_4)_2[B_{20}H_{18}]$ at 150 °C. This latter is stable until 200 °C. Under air, the decomposition starts at 143 °C, then the $(NMe_4)_2[B_{20}H_{18}]$ formed decomposes to boric acid and other unidentified products of hydrolysis.

The reaction of $NMe_4[N_2B_{10}H_9]$ with bulky amines or phosphines proceeded with difficulty because of steric hindrance and formed a complex mixture of products consisting mainly of $(NMe_4)_2[B_{20}H_{18}]$ when increasing the temperature to 150 °C. This could be explained by the secondary reaction shown in Scheme 1.

EXPERIMENTAL

^{11}B NMR spectra were obtained at 96.29 MHz on a Brucker WF-300 spectrometer and were externally referenced to $Et_2O{\cdot}BF_3$ (positive values downfield). IR spectra were recorded on a Nicolet Magna 550 FT spectrometer using KBr pressed discs. Electrospray mass spectrometry measurements were performed in the Mass Spectrometry Laboratory, Central Analytical Service of the CNRS, Solaize (France) on a VG-Platform Micromass spectrometer. The sample was introduced to the spectrometer as an acetonitrile solution. Decomposition products were separated by liquid–solid chromatography on silica gel using a 70:30 dichloromethane:acetonitrile mixture. TGA was performed on a B70 Setaram apparatus.

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