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Alkali Metal Reductions of Some Trimethylamine–Haloboranes and Bis(trimethylamine)dihydroboronium Iodide

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Received January 16, 1976

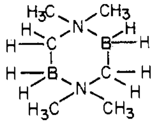
AIC60048V

Trimethylamine–bromoborane and trimethylamine–iodoborane were reduced with Na–K alloy in several solvents. The data obtained support the contention that a reactive intermediate, $[(CH_3)_3NBH_2:]^-$, was produced which reacts via two paths, in varying degrees of significance, depending on the solvent used. The synthesis of $(CH_3)_3NBD_2H$ was demonstrated. The synthesis of 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane was improved. An improved synthesis for 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratocyclohexane was also found.

A limited number of diborane(4) adducts have been reported. In 1962 the first adduct of diborane(4), $(C_6H_5)_3P\cdot BH_2BH_2\cdot P(C_6H_5)_3$, obtained from the cleavage of trimethylamine–triborane(7) was reported.[1]

The bis(trifluorophosphine) adduct of diborane(4), $F_3P\cdot BH_2BH_2\cdot PF_3$, was prepared by treating the dimethyl ether adduct of triborane(7) with PF_3.[2,3] This adduct is a useful reagent for preparing other substituted fluorophosphine adducts of diborane(4).[4]

The bis(trimethylamine) adduct of diborane(4), $(CH_3)_3N\cdot BH_2BH_2\cdot N(CH_3)_3$, was reported to be formed by allowing $(CH_3)_3N\cdot BH_2Br$ to react with Na–K alloy in $(CH_3)_3N$ as solvent at 0 °C.[5] However, additional work has shown that 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratocyclohexane is the product and not $(CH_3)_3N\cdot BH_2BH_2\cdot N(CH_3)_3$.[6,7] This interesting product has been prepared previously by two different methods and has been referred to as dimethylaminomethylborane cyclic dimer, $[(CH_3)_2NCH_2BH_2]_2$,[8,9] referred to as I by the present authors.



I

The purpose of the work reported here was to try to prepare $(CH_3)_3N\cdot BH_2BH_2\cdot N(CH_3)_3$ and elucidate the reaction sequence leading to the production of I from $(CH_3)_3N\cdot BH_2Br$.

The coupling of two boron atoms to give a normal two-electron bond by reducing boron–halogen bonds with active metals has met with remarkable success.[10] Therefore, the present authors continued along similar lines using trimethylamine–iodoborane as the starting material instead of trimethylamine–bromoborane, after the iodoborane was found to be more reactive with Na–K alloy than the bromoborane.

Experimental Part

Trimethylamine–borane was obtained from Callery Chemical Co. and was used without further purification.

Sodium–potassium alloy was a 25:75 mixture by weight, respectively, and was prepared by placing clean chunks of the metals into a flask containing benzene and stirring until a liquid formed. One gram of this alloy provided 30 mmol of electrons available for reduction purposes.

Heptane, benzene, diethyl ether, glyme (1,2-dimethoxyethane) and diglyme [bis(2-methoxyethyl) ether] were obtained dry and oxygen free by using a mixture of Na metal and benzophenone in each solvent to react with water and dissolved oxygen. When the solutions turned blue, they were distilled in 1-l. quantities using a vacuum manifold (except for diglyme which was distilled at atmospheric pressure).

Methylene chloride was purified by stirring with $MgSO_4$ and CaH_2 for several weeks and then distilled in 1-l. quantities using a vacuum manifold.

Infrared spectra were obtained using a Beckman IR-10 spectrophotometer.

Melting points were recorded on a Thomas-Hoover apparatus.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

The ^1H NMR spectra were obtained at 60 MHz, using a Varian Model A-60A spectrometer.

All inert atmosphere work was done in a Vacuum/Atmospheres drybox equipped with Dri-Train HE-93B. Charging of the individual reaction vessels was done in this drybox, unless otherwise noted.

A standard vacuum line with a three-trap system was used for all reduced pressure work.

Reaction of Trimethylamine–Bromoborane with Sodium–Potassium Alloy in Trimethylamine at 0 °C. Trimethylamine–bromoborane (5 g, 32.9 mmol) was allowed to react with excess Na–K alloy in trimethylamine for 15 h at 0 °C. The products obtained were trimethylamine–borane ($(CH_3)_3N\cdot BH_3$), dimethylaminomethylborane cyclic dimer (I), and 3.77 g of benzene- and CH_2Cl_2-insoluble material that was not investigated.

The weight of $(CH_3)_3N\cdot BH_3$ produced (0.426 g) corresponded to a 17.7% yield based on the amount of $(CH_3)_3N\cdot BH_2Br$ added. The weight of I produced (0.189 g) corresponded to an 8.2% yield based on the $(CH_3)_3N\cdot BH_2Br$ added.

Reaction of Trimethylamine–Iodoborane with Sodium–Potassium Alloy in Trimethylamine at 0 °C. A sample of $(CH_3)_3N\cdot BH_2I$ (5.48 g, 27.4 mmol) and Na–K (2.28, 68.4 mmol of available electrons) were allowed to react in $(CH_3)_3N$ at 0 °C for 3 h. The products were $(CH_3)_3N\cdot BH_3$, $(CH_3)_3N$ (obtained after warming the nonvolatile residue at 45 °C on the vacuum line), I, bis(trimethylamine)dihydroboronium iodide, noncondensable gas (1.34 mmol), and Na–K (recovered from two sources: a Hg amalgam produced H_2 equivalent to 4.4 mmol of available electrons, and 0.76 g was recovered as a liquid from the reaction residue; this weight corresponded to 22.8 mmol of available electrons).

The reduction of $(CH_3)_3N\cdot BH_2I$ proceeded to completion over a 3-h period to produce a 44.4% yield of $(CH_3)_3N\cdot BH_3$, a 10.7% yield of I, and 1.8 mmol of $[(CH_3)_3N]_2BH_2^+I^-$. No other boron-containing compounds soluble in benzene or CH_2Cl_2 were obtained. Materials

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with B–H bonds were present in the CH_2Cl_2- and the benzene-insoluble portion of the reaction mixture.

Reaction of Trimethylamine–Iodoborane with Sodium–Potassium Alloy in Benzene between 10 and 13 °C. A sample of $(CH_3)_3N{\cdot}BH_2I$ (7.02 g, 35.1 mmol) and Na–K (2.70 g, 81 mmol of available electrons) were allowed to react in benzene between 10 and 13 °C for 3 h on the vacuum line.

Trimethylamine (15.6 mmol) was obtained from the reaction mixture by pumping on the solution for 15–30 s within 5 min after each addition of solid $(CH_3)_3N{\cdot}BH_2I$ from an addition tube. The only benzene-soluble, boron-containing product was $(CH_3)_3N{\cdot}BH_3$ (27.7% yield).

The benzene-insoluble portion was found to contain at least 12.5 mmol of available electrons and 8.29 g of boron-containing material. Dimethyl sulfoxide partially dissolved this solid but vigorous gas evolution was observed. Diglyme dissolved part of the solid with no apparent reaction, but the mixture could not be filtered because of particle size. Separation was effected by decantion after allowing the mixture to settle overnight. The majority of the boron-containing material was in the insoluble portion based on comparison of Nujol mull infrared spectra in the B–H stretching region of the soluble and insoluble portions.

Reaction of the Diglyme-Insoluble Portion (from the Reduction of Trimethylamine–Iodoborane with Sodium–Potassium Alloy between 10 and 13 °C in Benzene) with Anhydrous Hydrogen Chloride. The diglyme-insoluble portion (4.17 g) was heated to 220 °C while attached to the vacuum line with a resulting loss in weight of 0.54 g (mostly diglyme). A noncondensable gas (0.17 mmol) and $(CH_3)_3N$ (0.01 g) were collected on the vacuum line. The remaining solid was brown and gave a Nujol mull infrared spectrum very similar to that of BH_4^- but with the bands shifted to lower energy: 2270 (s), 2200 (s), 2120 (s) cm^{-1}, with an additional broad band centered at 1240 cm^{-1}.

A sample of this solid was sent for elemental analysis. Anal. Found: C, 2.32; H, 0.97; N, 0.13; B, 3.04. This 4.17-g sample would then contain approximately 11.7 mmol of boron.

A 1.85-g sample of this brown solid was treated with gaseous HCl (9 mmol) at CS_2 slush temperature (–112 °C) according to Shore's procedure.[11] A total of 6 mmol of HCl was consumed and 3.03 mmol of H_2 (noncondensable gas) was collected along with 0.31 mmol of B_2H_6 corresponding to a 11.9% yield of B_2H_6 based on boron present in the sample by elemental analysis.

Reaction of Trimethylamine–Iodoborane-d_2 with Sodium–Potassium Alloy in Benzene. A sample of $(CH_3)_3N{\cdot}BD_2I$ (14 mmol), prepared from $(CH_3)_3N{\cdot}BD_3$,[12] and Na–K (excess) were allowed to react in benzene. The iodoborane was added slowly over a 2-h period.

During the reduction of $(CH_3)_3N{\cdot}BD_2I$ in benzene solution, the trimethylamine–borane that was produced (30% yield) obtained the third hydrogen isotope from either $(CH_3)_3N$ or benzene. The solution infrared spectrum in benzene shows substantial normal hydrogen incorporation over that found in the starting material.

Elemental analysis gave good agreement for one normal hydrogen and two deuteriums on the boron in each molecule of trimethylamine–borane produced. Anal. Calcd for $C_3H_{10}D_2N_1B_1$: C, 48.06; H, 16.48; N, 18.69; B, 14.42. Found: C, 47.91; H, 16.66; N, 18.36; B, 14.48.

Reaction of Trimethylamine–Iodoborane-d_2 with Sodium–Potassium Alloy in Benzene-d_6. Trimethylamine–iodoborane-d_2 (7.9 mmol) and Na–K (excess) were allowed to react in benzene-d_6 as solvent for 1 h.

The third hydrogen isotope appearing in the reaction product, trimethylamine–borane, came from the solvent, benzene-d_6. Since there was no additional normal hydrogen incorporation, detectable in the infrared spectrum in benzene solution, $(CH_3)_3N$ was not involved to a measurable extent in the reaction to produce trimethylamine–borane.

Reaction of Trimethylamine–Iodoborane with Sodium–Potassium Alloy in Cyclohexene at 0 °C. A two-necked flask was charged with 20 ml of cyclohexene, excess Na–K alloy, and a glass-coated stirring bar. The flask was fitted with an addition tube containing $(CH_3)_3N{\cdot}BH_2I$ (4 g, 20 mmol) and was equipped to maintain a N_2 atmosphere.

Trimethylamine–iodoborane was added in small portions over a period of 6 h. Nitrogen was passed above the surface of the solution during this time. After addition of the $(CH_3)_3N{\cdot}BH_2I$, the reaction mixture was stirred overnight and allowed to warm to room temperature. After a total reaction time of 14 h, the reaction mixture was removed from the hood and taken into the drybox where if was filtered.

A cyclohexene solution infrared spectrum was obtained of the soluble portion. The only absorptions in the B–H stretching region were identical in position and shape with the absorptions of $(CH_3)_3N{\cdot}BH_3$ obtained in CH_2Cl_2 and benzene solutions. The amount of $(CH_3)_3N{\cdot}BH_3$ was small and no attempt was made to isolate it from solution. A rough estimate, based on solution infrared spectra of $(CH_3)_3N{\cdot}BH_3$ obtained at known concentrations in CH_2Cl_2 and benzene, would be approximately 30 mg (0.41 mmol) or a 2% yield based on the amount of $(CH_3)_3N{\cdot}BH_2I$ added.

The cyclohexene-insoluble portion (3.84 g) was shown to contain the same BH_4^--like material obtained when benzene was used as the solvent.

Reaction of Trimethylamine–Iodoborane with Sodium–Potassium Alloy in 1,2-Dimethoxyethane. A two-necked flask was charged with 50 ml of glyme, a glass-coated stirring bar, and 1.35 g (40 mmol available electrons) of Na–K alloy. One neck was fitted with an addition tube containing 7.30 g (36.6 mmol) of $(CH_3)_3N{\cdot}BH_2I$. The flask was evacuated and removed to the vacuum line.

The reaction flask was thermostated at 0 °C and stirring was begun. The glyme solution turned blue almost immediately. Trimethylamine–iodoborane was added in small portions over a 2.5-h period at intervals that allowed the color to return to the solution. The overgas was removed on several occasions to prevent the accumulation of $(CH_3)_3N$.

The mixture was allowed to warm to room temperature and was then filtered. The filtrate was concentrated by vacuum evaporation and a solution infrared spectrum was taken. The B–H stretching region showed only those peaks expected for $(CH_3)_3N{\cdot}BH_3$. A total of 1.1 g of $(CH_3)_3N{\cdot}BH_3$ [55% yield based on the weight of $(CH_3)_3N{\cdot}BH_2I$ that was reduced] was collected by blowing most of the glyme away with N_2 and then fractionating the remaining mixture, about 5 ml, through a 0 °C trap to isolate the $(CH_3)_3N{\cdot}BH_3$.

Reaction of Trimethylamine–Iodoborane with Sodium–Potassium Alloy in Diglyme. A sample of $(CH_3)_3N{\cdot}BH_2I$ (8.05 g, 40 mmol) and Na–K (3.25 g, 97.5 mmol available electrons) were allowed to react in diglyme of the vacuum line for 2 h. This reaction was carried out in a manner identical with the reduction of $(CH_3)_3N{\cdot}BH_2I$ with Na–K alloy in glyme.

A total of 1.10 g of Na–K was recovered as a liquid and, if the reduction was nonselective, implied that 64.5 mmol of electrons was consumed in the reaction. There was no insoluble material produced during the reaction. After filtration of the reaction mixture and addition of heptane, a total of 6.46 g of white solid was obtained. The filtrate composed of the diglyme–heptane-soluble material was concentrated by vacuum evaporation and a diglyme solution infrared spectrum was obtained. The only absorptions in the B–H stretching region were those characteristic of $(CH_3)_3N{\cdot}BH_3$. A good estimate of the amount of $(CH_3)_3N{\cdot}BH_3$ produced during the reaction of $(CH_3)_3N{\cdot}BH_2I$ with Na–K was obtained by passing gaseous HCl through the solution to produce $(CH_3)_3N{\cdot}BH_2Cl$. The H_2 produced was collected and measured on the vacuum line. The amount of H_2 collected corresponded to a weight of 1.6 g of $(CH_3)_3N{\cdot}BH_3$. Thus, a 55% yield of $(CH_3)_3N{\cdot}BH_3$ was obtained from the reduction of $(CH_3)_3N{\cdot}BH_2I$ with Na–K alloy in diglyme [based on the original weight of $(CH_3)_3N{\cdot}BH_2I$ added].

Reaction of Bis(trimethylamine)dihydroboronium Iodide with Sodium–Potassium Alloy in Trimethylamine as Solvent. A sample of bis(trimethylamine)dihydroboronium iodide (8.5 g, 33.2 mmol) and excess Na–K were allowed to react in $(CH_3)_3N$ for 96 h at 0 °C. Except for starting material, the only boron-containing compound isolated was I. The weight of I isolated corresponded to a 3% yield based on the amount of $[(CH_3)_3N]_2BH_2^+I^-$ added.

Reaction of Bis(trimethylamine)dihydroboronium Iodide with Potassium Metal in Glyme. A sample of bis(trimethylamine)dihydroboronium iodide (217 mmol), K (227 mmol), and 75 ml of glyme were added to a 500-ml three-necked flask in the drybox. The flask was removed to the hood and equipped with a mechanical stirrer (avoid Teflon blades) and a reflux condenser. The third neck was stoppered. A gas-collecting and -separating system was set up. The mixture of $(CH_3)_3N$ and CH_4 was bubbled through a solution containing 300 mmol of HCl(aq). The CH_4, scrubbed of $(CH_3)_3N$, was collected over mineral oil in a graduated cylinder.

The glyme solution was heated to gentle reflux (approximately 85 °C). Methane evolution stopped after 55 min. The amount of CH_4

Table I. Yields of $(CH_3)_3N{\cdot}BH_3$ from Reactions of $(CH_3)_3N{\cdot}BH_2I$ with Na-K Alloy in Various Solvents

Solvent	Reacn conditions	% yield
Trimethylamine	0 °C, 3 h	44.4
Benzene	10–13 °C, 3 h	27.7
Cyclohexene	0–25 °C, 14 h	2 (ca.)
Glyme	0 °C, 2.5 h	55
Diglyme	0 °C, 3 h	55

collected corresponded to 110 ± 4 mmol.

The solution was refluxed for another 3 h while a slow stream of N_2 was passed above the solution to remove $(CH_3)_3N$. The solution was then taken into the drybox and filtered. A bluish white solid weighing 36.5 g, assumed to be KI (218 ± 0.5 mmol), was obtained. The glyme was removed by atmospheric pressure distillation.

The distillation residue was treated with deionized water and a viscous liquid floated to the top. This liquid was placed in a separatory funnel and washed with three 20-ml portions of deionized water. The turbid liquid weighed 10.22 g and corresponded to a 74% yield of II (80 mmol). After drying over $MgSO_4$ and filtering, 8.70 g (62% yield) of II was obtained.

The amount of unreacted H_3O^+ from the HCl solution was found to be 107 mmol. Thus, 193 mmol of $(CH_3)_3N$ had passed into the HCl solution.

Reaction of Bis(trimethylamine)dihydroboronium Iodide with Sodium Amide. A 300-ml three-necked flask was charged with $[(CH_3)_3N]_2BH_2^+I^-$ (10.21 g, 39.5 mmol), $NaNH_2$ (1.56 g, 40 mmol), and glyme (75 ml) and fitted with a mechanical stirrer. The reaction flask was removed to the hood, fitted with a reflux condenser equipped for gas collection, and then surrounded by an oil bath. The reaction mixture was brought to gentle reflux. A vigorous rate of stirring was maintained.

After a total reaction time of 5 h, the gas evolved (48.4 mmol) was collected in a calibrated bulb. The gas was indentified by a gas-phase infrared spectrum to be a mixture of NH_3 and $(CH_3)_3N$.

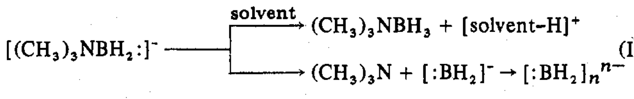
Nitrogen was passed above the surface of the glyme solution to aid in the removal of $(CH_3)_3N$. This was done for approximately 1 h. Then, the reaction mixture was taken into the drybox and filtered.

The glyme-insoluble portion weighed 2.81 g and was shown to be $[(CH_3)_3N]_2BH_2^+I^-$ (2.37 g) plus 0.42 g of unidentified material.

The glyme-soluble portion was evaporated to dryness and washed with CH_2Cl_2. A finely divided white solid was present in large quantities and could not be separated from the CH_2Cl_2-soluble material by filtration. This mixture was added to 100 ml of deionized water. The CH_2Cl_2-soluble portion was found to contain I (0.55 g, 25% yield based on the cation that reacted) in excellent purity.

Discussion

Reaction Sequence of Trimethylamine–Iodoborane with Sodium–Potassium Alloy. If an initial two-electron transfer occurs or if a $(CH_3)_3NBH_2{\cdot}$ radical undergoes a second one-electron reduction, the same product will result $[(CH_3)_3NBH_2{:}]^-$. This anion is the conjugate base of $(CH_3)_3N{\cdot}BH_3$ and is isoelectronic with the nitrogen ylide formed by deprotonation of tetramethylammonium bromide with phenyllithium, $(CH_3)_3NCH_2$.[13] The proposed anion $[(CH_3)_3NBH_2{:}]^-$ would be a strong Bronsted base capable of abstracting protons from very weak acids to produce $(CH_3)_3N{\cdot}BH_3$ and would also account for the observed two-electron reduction. The $[BH_2{:}]^-$ moiety would probably be a weak Lewis acid; therefore, $[(CH_3)_3NBH_2{:}]^-$ could lose $(CH_3)_3N$ readily to produce $[BH_2{:}]^-$ which could react with more $[BH_2{:}]^-$ to produce the BH_4^--like species in an alternate mode of reaction. The proton abstraction reaction (see eq I)



$$[(CH_3)_3NBH_2{:}]^- \longrightarrow \begin{cases} \xrightarrow{\text{solvent}} (CH_3)_3NBH_3 + [\text{solvent-H}]^+ \\ \longrightarrow (CH_3)_3N + [{:}BH_2]^- \rightarrow [{:}BH_2]_n^{\,n-} \end{cases} \qquad (I)$$

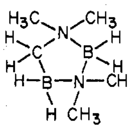
is apparently favored by the more polar solvents (Table I).

It has been shown that trimethylammonium methylide showed different stability depending on the solvent used.[14] The ylide was found to decompose to produce trimethylamine and polymethylene in varying percentages.

An alternate proposal for the production of $(CH_3)_3N{\cdot}BH_3$ would involve one primary reaction path, namely, the dissociation of $[(CH_3)_3NBH_2{:}]^-$ into $(CH_3)_3N$ and $[{:}BH_2]^-$ followed by proton abstraction by $[{:}BH_2]^-$ from solvent to produce BH_3 which would then combine with the free $(CH_3)_3N$ in a Lewis acid–base reaction to produce $(CH_3)_3N{\cdot}BH_3$.

Source of I in the Reactions of $(CH_3)_2N{\cdot}BH_2Br$ and $(CH_3)_3N{\cdot}BH_2I$ with Na–K Alloy. The reduction of $[(CH_3)_3N]_2BH_2^+I^-$ was investigated to determine if $[(CH_3)_3N]_2BH_2^+I^-$ was the source of I found in reductions of $(CH_3)_3N{\cdot}BH_2Br$ and $(CH_3)_3N{\cdot}BH_2I$.

To produce the precursor to I by reduction of $[(CH_3)_3N]_2BH_2^+I^-$ would require a one-electron reduction and subsequent cleavage of a carbon–hydrogen bond to produce $(CH_3)_3N{\cdot}BH_2CH_2N(CH_3)_2$ and $^1/_2$ H_2 or a two-electron reduction to produce $(CH_3)_3N{\cdot}BH_2CH_2N(CH_3)_2$ and H^-. Experimental data confirm a two-electron reduction of $[(CH_3)_3N]_2BH_2^+I^-$ but with subsequent carbon–nitrogen bond cleavage. The only boron-containing product detected from the reduction of $[(CH_3)_3N]_2BH_2^+I^-$ with Na–K alloy or K was II.[15]



II

The most logical sequence of reactions that will produce II is given by eq 1–3. Two points were found to be important

$$[(CH_3)_3N]_2BH_2^+I^- + 2K \rightarrow KI + K^+CH_3^- + (CH_3)_2NBH_2 + (CH_3)_3N \qquad (1)$$

$$[(CH_3)_3N]_2BH_2^+I^- + K^+CH_3^- \rightarrow KI + CH_4 + (CH_3)_3N{\cdot}BH_2CH_2N(CH_3)_2 \qquad (2)$$

$$(CH_3)_2NBH_2 + (CH_3)_3N{\cdot}BH_2CH_2N(CH_3)_2 \rightarrow (CH_3)_3N + II \qquad (3)$$

in improving the yield of II. First, the amount of K should not exceed a 1:1 molar ratio with $[(CH_3)_3N]_2BH_2^+I^-$; if it does, the yield will decrease because of the overproduction of $H_2BN(CH_3)_2$. Second, the closing of the cyclopentane-like ring is a transamination reaction and is slowed if excess $(CH_3)_3N$ is allowed to accumulate in the system. This can be prevented by passing N_2 through the system while heating to gentle reflux.

An interesting aspect of this reaction is that I is not produced in detectable quantities. Apparently the large amounts of dimethylaminoborane, produced in the first step of the reaction, trap the trimethylamine–(dimethylaminomethyl)borane molecules as they are generated; thus significant concentrations of the precursor to I are not allowed to accumulate.

Recent work sets forth a solvent-independent reaction sequence (see eq 4–6) that can account for the production of

$$(CH_3)_3N{\cdot}BH_2Br + 2K \rightarrow [(CH_3)_3NBH_2{:}]^-K^+ + KBr \qquad (4)$$

$$[(CH_3)_3NBH_2{:}]^-K^+ + (CH_3)_3N{\cdot}BH_2Br \rightarrow (CH_3)_3N{\cdot}BH_3 + [{:}CH_2N(CH_3)_2BH_2Br]^-K^+ \qquad (5)$$

$$2[{:}CH_2N(CH_3)_2BH_2Br]^-K^+ \rightarrow 2KBr + I \qquad (6)$$

I from $(CH_3)_3N{\cdot}BH_2Br$ with Na–K alloy in $(CH_3)_3N$.[7]

However, it was found that I was not produced during the reduction of $(CH_3)_3N{\cdot}BH_2I$ or $(CH_3)_3N{\cdot}BH_2Br$ in benzene when $(CH_3)_3N$ was removed by frequent evacuation of the reaction system; in addition, I is not produced when $(CH_3)_3N{\cdot}BH_2I$ is reduced in cyclohexene, glyme, or diglyme.

Also, deuteration experiments show that the $(CH_3)_3N{\cdot}BH_3$ produced in the reaction probably abstracts a proton from solvent and not from coordinated $(CH_3)_3N$.

Thus, an alternate proposal for the production of I from the reduction of $(CH_3)_3N{\cdot}BH_2X$ ($X^- = I^-, Br^-$) with Na–K alloy seems to be in order. The presence of free $(CH_3)_3N$ in the system is a requirement for the production of I. The sequence of reactions 7–10 leading to the production of I satisfies this

$$(CH_3)_3N{\cdot}BH_2X + 2M \rightarrow [(CH_3)_3NBH_2{:}]^- + X^- + 2M^+ \rightarrow (CH_3)_3N + BH_2^- \quad (7)$$

$$[(CH_3)_3NBH_2{:}]^- + (CH_3)_3N \rightarrow (CH_3)_3N{\cdot}BH_3 + [(CH_3)_2NCH_2{:}]^- \quad (8)$$

$$[(CH_3)_2NCH_2{:}]^- + (CH_3)_3N{\cdot}BH_2X \rightarrow (CH_3)_2NCH_2BH_2{\cdot}N(CH_3)_3 + X^- \quad (9)$$

$$2(CH_3)_2NCH_2BH_2{\cdot}N(CH_3)_3 \rightarrow 2N(CH_3)_3 + I \quad (10)$$

requirement. This side reaction would be most evident when the concentration of $(CH_3)_3N$ was as high as possible. Thus, the highest yields of I should have been produced when $(CH_3)_3N$ was used as the solvent. This was exactly the trend observed.

Improved Synthesis for 1,1,4,4-Tetramethyl-1,4-diazonia-2,5-diboratocyclohexane. The present authors sought to improve the synthesis of I by using the iodide salt of bis(trimethylamine)dihydroboronium ion which is more easily obtained than the anhydrous chloride salt.[8,9]

It is evident from the reaction sequence in which II is produced that $[:CH_3]^-$ abstracts a proton from $[(CH_3)_3N]_2BH_2^+I^-$ readily. Thus, the ideal reaction setup to produce I would be to use a Bronsted base with reasonable stability whose counterion is a cation that does not form complexes with reaction intermediates as can occur when butyllithium[9] is used. The reaction of $NaNH_2$ with $[(CH_3)_3N]_2BH_2^+I^-$ in 1,2-dimethoxyethane in a 1:1 molar ratio gave a 25% yield of cyclic dimer.

This reaction is an improvement over present procedures in several ways. The boronium salt used is easier to obtain than the Cl^- salt, no particular precautions as to stoichiometry are indicated, and vacuum-line techniques and equipment are not necessary. The yields of I are essentially the same for both reactions.

Registry No. I, 14102-49-9; II, 53521-47-4; $(CH_3)_3N{\cdot}BH_2Br$, 5275-42-3; $(CH_3)_3N{\cdot}BH_2I$, 25741-81-5; $[(CH_3)_3N]_2BH_2^+I^-$, 19581-80-7; $(CH_3)_3N{\cdot}BD_2I$, 58540-75-3; $NaNH_2$, 7782-92-5.

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Formation of Nickel Acetate Complexes

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Received August 11, 1975 AIC50597L

In aqueous solutions of nickel acetate two relaxation effects are observed with $\tau_I = (0.2–0.5) \times 10^{-3}$ s depending on concentration and $\tau_{II} = 2.7 \times 10^{-8}$ s independent of concentration at 10 °C. The effects are explained by the formation of the complexes $NiAc^+$ and $NiAc_2$. Kinetic and thermodynamic parameters of these reactions are evaluated and discussed.

Introduction

Kinetic methods—especially chemical relaxation methods—have been used frequently to investigate the formation of metal complexes[1] and elucidate the mechanism of the reactions. Furthermore, if several complexes are formed in a chemical reaction, they probably form at different rates; thus a kinetic is superior to a thermodynamic (=static) method in predicting the existence of these species. In this contribution, chemical relaxation measurements on aqueous solutions containing nickel and acetate ions are reported.

Experimental Section

The kinetic measurements have been performed using several chemical relaxation techniques: a pressure-jump method with conductometric recording,[2] an ultrasonic resonator method, and a modified ultrasonic-pulse method.[3] Solutions were prepared using doubly distilled water and $NiAc_2$ and $Ni(NO_3)_2$ of analytical reagent quality ($Ac^- = CH_3COO^-$).

Results

Using the pressure-jump relaxation technique, aqueous solutions of $NiAc_2$ have been investigated for the concentration range from 5×10^{-3} to 1 M and for the temperature range from 1 to 35 °C. All measurements showed a single relaxation effect in the time range of this method (50×10^{-6} s < τ < 100 s). Table I summarizes the observed relaxation times and relaxation amplitudes at T = 10 °C and d ln τ^{-1}/ dT^{-1}, the temperature dependence of the relaxation time (10 °C has been chosen as the reference temperature, since the accuracy of the measurements has its maximum at this value). The relaxation amplitude X is defined as the relative change in electrical conductivity κ caused by the relaxation effect for a pressure jump of δP = 130 atm. Relaxation times are independent of the pH as has been shown for a 0.2 M $NiAc_2$ solution in the range of 4.8 < pH < 6.9. The probable errors

Table I. Relaxation Time τ_I, Its Temperature Dependence, and Relaxation Amplitude $X = (\delta\kappa/\kappa)_{\text{relax}}$ as a function of the Analytical Concentration $c°$ of $NiAc_2$ at 10 °C and a Pressure Jump of δP = 130 Atm

$c°$, M	0.01	0.02	0.05	0.1	0.2	0.5	0.7	1.0
$10^6\tau_I$, s	495	456	385	343	315	269	248	235
$-10^{-3}\partial \ln \tau_I^{-1}/\partial T^{-1}$, K	6.5	6.8	6.7	7.6	7.1	7.0	6.6	6.7
10^3X	2.3	3.6	5.6	5.6	7.6	8.0	9.8	8.8