particular complex the nitrosyl ligand (which has a rather high ν_{NO}, 1771 cm^{-1}) may be a poorer π acceptor than the carbonyl ligands.

Registry No. **1**, 25360-92-3; **3**, 37402-69-0; **6**, 37402-71-4; **7**, 37438-57-6.

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Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

Preparation of Ethylamine-Borane by Electrolysis of Sodium Tetrahydridoborate in Ethylamine

L. A. Melcher, I. A. Boenig, and K. Niedenzu*

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Electrochemical studies in inorganic chemistry are primarily concerned with redox reactions of metal salts and/or polarographic investigations. However, boron compounds have received only scattered attention in this respect and experiments have been confined mainly to the preparation of perborates and of elemental boron[1] and the electrolysis of alkali metal tetrahydridoborates for the generation of diborane(6).[2] Also, it has been reported[3] that diborane(6) can be prepared by passing a mixture of boron trihalides and hydrogen into an electrolyzed melt of alkali metal halides and cursory reference[4] is made to some technical reports[5] describing the formation of amine-boranes by electrochemical methods. In the present work the preparation of ethylamine-borane, $C_2H_5NH_2 \cdot BH_3$, by electrolysis of sodium tetrahydridoborate in ethylamine is described.

Experimental Section

All reactions were carried out in a nitrogen or argon atmosphere and reagents were thoroughly dried by standard procedures before use.

Infrared spectra were obtained under standard operating conditions on a Perkin-Elmer Model 621 spectrometer on solutions of compounds in benzene, on the neat materials, and/or on KBr pellets. Proton magnetic resonance spectra were obtained on a Varian T60 instrument using internal TMS as reference. Boron-11 nuclear magnetic resonance data were obtained on a Varian HA60-IL spectrometer operated at 19.3 MHz and using external boron trifluoride etherate as reference. The Raman spectrum was recorded on the neat liquid on a Jarrell-Ash 25-300 Raman spectrometer. Mass spectra were provided by the University of Kentucky Mass Spectroscopy Center and were obtained with a Hitachi Perkin-Elmer double-focusing instrument, Model RMU-7.

Electrolysis with two-electrode circuitry was conducted on a series circuit consisting of a Kepco Model JQE 100-1M power supply, the cell, and a Decade resistance box (Muirhead & Co., D-825-N). An X-Y recorder (Hewlett-Packard Model 700/AM) was connected across the resistance box to measure the voltage drop across this known resistance (range from 0.1 to 10.0 ohms). The current, the voltage drop across the cell, and the cell resistance could be calculated. The glass cell was equipped with a thermometer and a Dry Ice condenser leading to a mercury bubbler. During electrolysis a platinum foil was used as the anode and a mercury pool as the cathode.

Table I. Vibrational Spectrum of Ethylamine-Borane, $C_2H_5NH_2 \cdot BH_3$[a]

Ir	Raman	Ir	Raman
3420 vw, b		1367 m	1363 w, b, dp?
3455 vs, b	3244 m, p	1344 vm	
3164 m	3164 w, p	1279 ms	1280 w, b
2988 m	2973 s, dp	1165 s, b	1172 m, dp
2949 m	2943 s, p	1113 ms	1116 m, p
2907 wm, sh	2931 ms, p	1059 m, sh	
2886 w	2885 m, p	1046 m	1051 wm, p
2555 vw, sh		967 w	
2370 vs, b	2383 vs, p	939 vw	942 wm, p
2320 vs, b	2362 s, p	877 w	880 m, p
2280 vs	2275 vs, p	796 w	800 vw, dp?
2134 vw			755 m, dp
1596 m	1596 w, dp		718 wm, p
1471 wm		692 vw	
1456 wm		417 vw	415 m, p
1405 w		319 vw	332 w, b, dp?
1390 m		270 vw?	

[a] Neat compound; frequencies in cm^{-1}. Key: w, weak; m, medium; s, strong; v, very; sh, shoulder, p, polarized; dp, depolarized.

Preparation of Ethylamine-Borane (Typical Experiment). A mixture of 1.29 g of $NaBH_4$ (0.0342 mol) and 100 ml of anhydrous ethylamine was electrolyzed at ice-bath temperature at +20 V and an initial current rate of 97 mA; electrolysis was continued until the current dropped to 2.8 mA for a total consumption of 3.79×10^3 C. Excess ethylamine was evaporated by removing the Dry Ice condenser and warming the reaction vessel to room temperature. The residue was extracted with dry benzene, and after removal of solvent from the filtrate at room temperature under vacuum a partly crystalline material remained, mp 26-27°, which was identified as ethylamine-borane (yield was *ca.* 60% based on the number of Faradays of electricity which were passed through the reaction mixture).

If the ethylamine is not completely removed before work-up of the reaction mixture, partial decomposition of the ethylamine-borane may occur to yield tris(ethylamino)borane, $B(NHC_2H_5)_3$.

Identification of Products. Neither ethylamine-borane nor ethylaminoborane, $C_2H_5NHBH_2$, is characterized completely in the literature. The former has been noted[6] to have a melting point of 19° and reportedly decomposes at a temperature of 30-40° under formation of hydrogen and ethylaminoborane. The latter is listed[7] to have a melting point of 76.5° but no further characterization is given.

Ethylamine-Borane. The boron-11 nuclear magnetic resonance spectrum of ethylamine-borane in benzene solution exhibited a quartet with a chemical shift (relative to boron trifluoride-etherate) of +19.6 ppm ($J_{\mathrm{BH}} = 92$ Hz). The chemical shift value is indicative of four-coordinate boron as found in other amine-boranes, *e.g.*, $\delta(^{11}\mathrm{B})$ of dimethylamine-borane in benzene solution is +15.1 ppm.[8] The proton magnetic resonance spectrum of ethylamine-borane in carbon tetrachloride consists of three peaks with δ values of 1.20 (triplet, $\mathit{CH}_3\text{-CH}_2$), 2.80 (quartet, $\mathrm{CH}_3\text{-}\mathit{CH}_2$), and 3.83 ppm (broad singlet, NH_2), respectively, with an area ratio of 3:2:1.8 ($J_{\mathrm{HCCH}} = 7 \pm 0.5$ Hz). These data already seem to confirm the identification of ethylamine-borane which is further substantiated by the vibrational spectrum of the material as listed in Table I.

The BH valence vibrations of amine-boranes are normally[9] observed in the 2200-2300-cm^{-1} region whereas BH stretching of aminoboranes occurs at *ca.* 150 cm^{-1} higher frequencies. Also, the observed NH stretching modes near 3160 and 3250 cm^{-1} lend credence to the identification of the material as an amine-borane rather than an aminoborane.[10]

Mass spectral data do not unequivocally support the structure of the product since the observed parent peak corresponds to ethylaminoborane rather than ethylamine-borane. However, in view of

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the ready dehydrogenation of ethylamine–borane at temperatures just above room temperature, and considering the inlet temperature of the mass spectrometer of *ca.* 170°, this observation cannot be taken as an indication for the formation of the aminoborane in the electrolysis procedure.

Tris(ethylamino)borane. In the course of this work tris(ethylamino)borane, $B(NHC_2H_5)_3$,[11] was isolated as a product of the thermal decomposition of ethylamine–borane in the presence of excess ethylamine.

The boron-11 chemical shift of tris(ethylamino)borane was observed on the neat liquid at δ −23.5 ppm which value is in agreement with data reported for other tris(amino)boranes. Solutions of the material in deuteriochloroform gave ^1H chemical shift values of δ 1.08 (triplet, $C\mathit{H}_3$-CH_2) and 2.90 ppm (quartet, CH_3-$C\mathit{H}_2$), in a 3:2 ratio ($J_{HCCH} = 7 \pm 0.5$ Hz). No resonance signal could be identified for the nitrogen-bonded protons, probably due to quadrupole broadening. The infrared spectrum of the material compared with literature data.[12]

Registry No. $NaBH_4$, 16940-66-2; $C_2H_5NH_2 \cdot BH_3$, 15860-41-0; ethylamine, 75-04-7.

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Contribution from the Department of Chemistry, State
University of New York at Buffalo, Buffalo, New York 14214

Kinetics and Mechanism of Isomerization of α-Carbonato(triethylenetetramine)cobalt(III) Ion in Basic Aqueous Solution

T. P. Dasgupta and G. M. Harris*

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The tris-chelated complexes of cobalt(III) exhibit, almost without exception, unusual resistance to stereochemical rearrangement involving the cobalt(III) center. The racemization rates, for example, are exceedingly slow in aqueous solution except at elevated temperatures (usually well in excess of 50°) for such species as the tris(ethylenediamine),[1] bis(ethylenediamine)oxalato,[2] and bis(ethylenediamine)carbonato[3] complexes of cobalt(III). More recent studies[4,5] have demonstrated a similar stability for a number of β-diketone-cobalt(III) derivatives. The only apparent exception to this pattern is for the tris(oxalato) species,[6,7] the behavior of which, however, is complicated by the oxalate-cobalt(III) redox couple which, surprisingly enough, is not at all operative in the monooxalato system mentioned above.[2] With two of the bidentate species replaced by a tetradentate ligand such as triethylenediaminetetramine (trien) the same resistance to rearrangement at the cobalt(III) center is still observed[8] as expected, though loss of optical activity at other centers of asymmetry may occur rather readily even at room temperature.[9,10] The present study concerns the geometrical rearrangement of the "α" form of the tris-chelate complex ion $Co(trien)CO_3^+$ to the "β" analog, which occurs at a conveniently measurable rate in slightly basic aqueous solution at temperatures in excess of 50°. The pH dependence of the reaction, coupled with a knowledge of other kinetic and equilibrium properties of this complex ion,[11] enables some definite conclusions to be drawn concerning the mechanism of the isomerization.[12]

Experimental Section

α-Carbonato(triethylenetetramine)cobalt(III) perchlorate was prepared from *cis*-dichloro(triethylenetetramine)cobalt(III) following the method of Sargeson and Searle.[13] β-Carbonato(triethylenetetramine)cobalt(III) perchlorate was prepared as described in our earlier study.[11] The purity of the complexes was checked by analysis,[14] yielding the following data. *Anal.* Calcd for $[Co(trien)CO_3]ClO_4 \cdot H_2O$: Co, 15.40; C, 21.96; H, 5.23; N, 14.64. Found for α species: Co, 15.30; C, 21.85; H, 5.30; N, 14.50. Found for β species: Co, 15.35; C, 21.88; H, 5.30; N, 14.63.

The isomerization was studied at 55, 60, and 65° and $I = 0.5\ M$ ($NaClO_4$) on a Beckman DU spectrophotometer with a Gilford Model 220 digital readout attachment, utilizing the 503-nm peak at which the change in absorbance during the reaction is conveniently large.[15] The requisite amounts of sodium borate, perchloric acid (or sodium hydroxide, depending on the desired pH[16]), and sodium perchlorate solutions were placed in a 25-ml flask and thermostated long enough to achieve temperature equilibrium. A weighed amount of solid complex was then added and quickly dissolved, and the solution was made up to volume by addition of water at the experimental temperature. Aliquots of the borate-buffered reaction mixture were withdrawn at suitable intervals by means of an ice-jacketed pipet and the absorbances (A) were quickly determined, as were the pH's (utilizing a Beckman Expandomatic pH meter).

Results and Discussion

The pseudo-first-order rate constants for the α to β conversion were evaluated from conventional log $(A_\infty - A_t)$ *vs.* time plots, which were linear during several half-times of reaction. The final spectra indicated that the product was entirely the β form of the complex. Data were obtained at three temperatures within the acidity range $7 < \mathrm{pH} < 10$ and are recorded in Table I. Plots of these data are sigmoid in form with a clearly apparent tangential approach to minima in the observed rate constant, k_{obsd}, below pH 8. There also appears to be an approach to maxima above pH 10 but it was

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