filtered and the solvent of the filtrate evaporated to give sodium trihydrido(3,5-dimethyl-1-pyrazolyl)borate in almost quantitative yield. The analytical sample was recrystallized from anisole.

Sodium Dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate (3). Sodium trihydrido(3,5-dimethyl-1-pyrazolyl)borate (**2**) (1.6 g, 12.1 mmol) and pyrazole (0.89 g, 13 mmol) were dissolved in dimethylacetamide, and the resulting solution was heated to 100–140 °C. After the evolution of 240 mL of hydrogen the solvent was evaporated under high vacuum. Although the resulting white residue was recrystallized several times from toluene, a white solid was obtained, which contained dimethylacetamide. This was used to prepare the metal chelates without further purification. For characterization, the free acid was prepared by dissolving a sample in water and adding several drops of acetic acid. The white precipitate that formed immediately was filtered, washed with cold water, and dried.

Transition-Metal Dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate Complexes. To a solution of sodium dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate in water was added, with stirring, a 50% exces of a 0.5 M solution of the appropriate metal ion. The mixture was filtered, and the precipitate was dissolved in methylene chloride. The solution was washed several times with water, dried with $MgSO_4$, and concentrated. After chromatography using a short column of silica gel (1-cm i.d., 10-cm length) and methylene chloride as the eluant, the solvent was evaporated and the residue recrystallized from toluene/hexane.

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Registry No. 1b, 82963-91-5; **2**, 82963-92-6; **3**, 82963-93-7; **4** (C_i form), 83023-55-6; **4** (C_2 form), 82963-97-1; **5**, 82963-96-0; **6**, 82963-95-9; hydrogen dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate, 82963-94-8; 3,5-dimethylpyrazole hydrochloride, 31705-88-1; lithium borohydride, 16949-15-8; sodium hydride, 7646-69-7; pyrazole, 288-13-1.

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Reduction of Potassium Ion in Liquid Ammonia by Hydrogen to Potassium Amalgam

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The equilibrium constant at 25 °C of the reaction $e^-(am) + NH_3(l) \rightleftarrows NH_2^-(am) + {}^1/_2H_2(g)$ was recalculated on the basis of recently measured activity coefficients of potassium amide in liquid ammonia, with a result of $(5 \pm 2) \times 10^5$. The possibility of using mercury to extract potassium from H_2/KNH_2 in liquid ammonia was examined thermodynamically and found to be feasible ($\Delta G = -9.8$ kcal for the reaction $K^+(am) + NH_2^-(am) + {}^1/_2H_2(g) + Hg(l) \rightleftarrows K/Hg + NH_3(l)$, where the mole fraction of potassium in the amalgam is 0.05). This conclusion was confirmed experimentally, when amalgams of up to 0.044 mole fraction of potassium were prepared. Zinc also served as a successful reducing agent. Potassium bis(trimethylsilyl)amide in the solvent hexamethylphosphoramide was partially reduced by hydrogen to potassium amalgam. The densities of potassium amide solutions in liquid ammonia were determined.

Introduction

The formation of trace concentrations of the ammoniated electron, $e^-(am)$, on reduction of potassium amide in liquid ammonia by hydrogen at high pressure, has been studied by Kirschke and Jolly.[1] They found for the reaction

$$e^-(am) + NH_3(l) \rightleftarrows NH_2^-(am) + {}^1/_2H_2(g) \qquad (1)$$

an equilibrium constant of 5×10^4 at 25 °C. At a hydrogen pressure of 100 atm, concentrations of the ammoniated electron of approximately 10^{-5} M were noted. Since mercury readily extracts alkali metals (e.g., $K^+(am) + e^-(am)$) from liquid ammonia,[2] there is the intriguing possibility of reducing appreciable quantities of potassium ion to potassium amalgam by hydrogen. The main purposes of this paper are to demonstrate both by calculation and by experiment that this proposition is valid. Use of zinc as a reducing agent instead of hydrogen and use of another potassium salt [$KN(SiMe_3)_2$] in a different solvent [$(Me_2N)_3PO$] were also briefly investigated.

Equilibrium Constant of the NH_2^-/H_2 Reaction. Kirschke and Jolly measured the ammoniated electron concentration resulting from reaction 1, by both spectrophotometric and ESR techniques. Although measured activity coefficients of alkali metals in liquid ammonia were available, experimental data on potassium amide were not; consequently, activity coefficients of ammonium chloride were employed as an approximation. In the meantime, laboratory measurements of the activity coefficients of potassium amide in liquid ammonia have been made by Moreau and Lepoutre,[3] who employed mole fraction rather than molarity (moles per liter of solution) as concentration units. So that the activity coefficients of Moreau and Lepoutre can be converted to the basis of molarity, by using the equations of Harned and Owen,[4] the densities of KNH_2 solutions in liquid ammonia at 25 °C are needed. These densities were determined (see Experimental Section). These adjusted activity coefficients for KNH_2 in liquid ammonia at 25 °C proved to be much higher than the values for ammonium chloride used by Kirschke and Jolly. Similarly, Marshall's[5] activity coefficients of potassium in liquid ammonia, with Johnson and Meyer's[6] values of densities, were converted from values based on molality to those based on molarity (at −33 to −35 °C).

Equilibrium constants for reaction 1 were computed by using Kirschke and Jolly's data with the adjusted activity coefficients. The results ranged from 1×10^6 (0.067 M KNH_2) to 3×10^6 (1.0 M KNH_2). Plotting and extrapolating to zero concentration gave a constant of $(5 \pm 2) \times 10^5$, 10 times that of Kirschke and Jolly.

Standard free energies of formation at 25 °C of the species involved in reaction 1 are given by Lepoutre and Demortier,[7]

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(1) Kirschke, E. J.; Jolly, W. L. *Inorg. Chem.* **1967**, *6*, 855.

(2) Bergstrom, F. W. *J. Am. Chem. Soc.* **1925**, *47*, 2317. Russell, J. B.; Sienko, M. J. *Ibid.* **1957**, *79*, 4051. Warf, J. C.; Gutmann, V. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1583.

(3) Moreau, C.; Lepoutre, G. *Bull. Soc. Chim. Fr.* **1970**, 428.

(4) Harned, H. S.; Owen, B. B. "The Physical Chemistry of Electrolytic Solutions"; Reinhold: New York, 1950; p 9.

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(6) Johnson, W. C.; Meyer, A. W. *J. Am. Chem. Soc.* **1932**, *54*, 3621.

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Table I. Reduction of KNH_2 by H_2 to K/Hg

	run no.					
	1	2	3	4	5	6
amt of K, mg	45.8	46.7	57.6	53.1	62.7	62.7
KNH_2 concn, M	0.039	0.030	0.045	0.052	0.043	0.067
amt of Hg, g	4.6	4.6	4.6	4.6	4.6	9.2
time, h	1.0	2.0	166	240	138	194
catalyst	Fe	Fe	Fe	Pt	Pt	Fe
partial press. of H_2, atm	9.1	0.17	0.99	1.6	14.2	12.9
% K amalgamated	8.0	14.3	13.4	32.0	66.4	63.0
stirring	continuous	continuous	intermittent	intermittent	continuous	continuous

by Jolly,[8] or by Coulter et al.[9] The 35.0 kcal/mol value for $\Delta G°_f$ of $NH_2^-(am)$ was based by Coulter et al. on an activity coefficient of 0.25 for 0.0434 M $NaNH_2$. A better approximation is 0.70, on the basis of the measured values of KNH_2,[3] which yields a revised value of 33.7 kcal/mol for $\Delta G°_f[NH_2^-(am)]$. Thus for reaction 1, $\Delta G°_{298} = \Delta G°_f[NH_2^-(am)] - \Delta G°_f[e^-(am)] - \Delta G°_f[NH_3(l)] = 33.7 - 44.6 - (-2.7) = -8.2$ kcal; error limits are estimated at ±0.5 kcal. This range of values of $\Delta G°_{298}$ corresponds to an equilibrium constant for reaction 1 between 4.4×10^5 and 2.4×10^6; the value newly calculated here from adjusted data of Kirschke and Jolly, 5×10^5, is close to the lower limit.

Free Energy for the Reduction of Potassium Ion to Potassium Amalgam by Hydrogen. The reaction of interest (eq 5 below) can be written as the sum of three reactions (eq 2–4).

$$NH_2^-(am) + {}^1/_2H_2(g) \rightleftarrows e^-(am) + NH_3(l) \qquad (2)$$

$$e^-(am) + K^+(am) \rightleftarrows K(s) \qquad (3)$$

$$K(s) + Hg(l) \rightleftarrows K/Hg \qquad (4)$$

$$K^+(am) + NH_2^-(am) + {}^1/_2H_2(g) + Hg(l) \rightleftarrows K/Hg + NH_3(l) \qquad (5)$$

For reaction 2, $\Delta G°_{298}$ was evaluated above at 8.2 ± 0.5 kcal. For reaction 3, $\Delta G°_{298} = -\Delta G°_f[e^-(am)] - \Delta G°_f[K^+(am)] = -44.6 - (-47.0) = 2.4$ kcal (data from ref 7 and 8). LaMantia[10] measured potentials of the cell K‖K/Hg at 352–450 °C and found that they change but little for the potassium mole fraction 0.4 and below and that this change is a linear function of temperature. This behavior permitted estimation of potentials at 25 °C. While standard free energy changes for reaction 4 can evidently not be computed from LaMantia's data, the free energy change from standard states (pure potassium and mercury) to any specified composition can be determined. If we choose 0.05 mole fraction of potassium in the amalgam as the product, the potential observed (0.8867 V) corresponds to $\Delta G = -nFE = -20.4$ kcal.

The free energy change in reaction 5, if an amalgam of 0.05 mole fraction of potassium is produced, can now be estimated at $8.2 + 2.4 - 20.4 = -9.8$ kcal, with an uncertainty of ±0.9 kcal. It is therefore expected that hydrogen at a partial pressure of 1 atm will reduce potassium ion in liquid ammonia solutions of the amide in the presence of mercury; in fact, it is calculated that more than 99% of the potassium ion is converted to amalgam if equilibrium is attained.

Experimental Section

Reaction of Potassium Amide Solutions in the Presence of Mercury. Heavy-walled glass flasks (30–60 mL) with small necks and side arms were constructed and carefully annealed. Each side arm was sealed to a Kovar glass–metal junction. Swagelok stainless steel fittings (Crawford Fitting Co., Solon, OH 44139) and needle valves were employed. Such flasks were usually capable of withstanding pressures of 50 atm. Standard high-vacuum techniques were followed throughout. Potassium metal in narrow glass tubing was weighed and introduced into the flask, along with a short iron rod or some platinized platinum gauze. After the flask was sealed, ammonia from a reservoir containing sodium was condensed in the flask. Standing overnight at room temperature was sufficient under catalysis to form a yellow solution of KNH_2. After removal of the ammonia and evacuation, mercury was introduced through the steel valve and a measured amount of ammonia condensed in. Hydrogen from a cylinder was admitted, and the pressure was monitored while the reaction mixture at 25 °C was stirred magnetically. After several hours or days, the hydrogen and ammonia were removed and helium was admitted. The mercury, now containing potassium, was filtered centrifugally through fritted glass and treated with water and a platinum wire (to hasten the conversion of dissolved potassium to KOH). The base was titrated with standard HCl and the mercury recovered and weighed. Finally, the glass tubing segments, formerly full of potassium, were recovered from the reaction flask and weighed.

When zinc was used as a reducing agent instead of hydrogen, much the same technique was followed. The zinc, as a single piece held in a length of glass tubing inside the neck of the reaction flask, was dropped from a magnet-activated support. In this way the zinc was immersed in the KNH_2 solution but was not in physical contact with the mercury. After the KOH was titrated at the end, more HCl was added, and the mixture was allowed to stand several days to remove any zinc in the mercury. The aqueous phase was analyzed for zinc spectrophotometrically with use of dithizone.

Attack of Mercury by Potassium Amide in Liquid Ammonia. Two blank experiments were conducted in which the conditions of the $H_2/KNH_2/Hg$ reaction were maintained but in the absence of hydrogen. The mercury was kept in contact with the potassium amide solution at room temperature for prolonged periods (61 and 80 days, respectively). The mercury phase was separated and analyzed for potassium as before.

Reduction of Potassium Bis(trimethylsilyl)amide in Hexamethylphosphoramide by Hydrogen. With use of the same procedure as in the $H_2/KNH_2/Hg$ reaction, potassium amide (1.36 mmol) was prepared. The crystals were heated at 100 °C in high vacuum to remove all traces of NH_3. Toluene and the stoichiometric amount of hexamethyldisilazane were introduced, and the mixture was refluxed until the evolution of NH_3 ceased.[11] The liquid was evaporated under vacuum, leaving white crystals of $KN(SiMe_3)_2$, which were heated at 100 °C under vacuum. The solid was dissolved in 10 mL of hexamethylphosphoramide (HMPA, dried over CaH_2), and 4.6 g of mercury was introduced. Hydrogen was admitted and the pressure regulated at 14 atm for 144 h with intermittent stirring. The hydrogen was removed, the HMPA was washed out with toluene, and the mercury was filtered centrifugally through fritted glass and analyzed for potassium.

Density of Potassium Amide Solutions in Liquid Ammonia. A large (40-mL) pycnometer with a graduated neck was made from heavy-walled glass and was equipped with a Teflon valve. Potassium in glass tubing was weighed and sealed in the pycnometer along with a short iron bar. The whole assembly was accurately weighed. Ammonia was condensed in and KNH_2 produced as above. All ammonia and hydrogen were removed, and the pycnometer was filled with liquid ammonia. The iron bar served to stir the solution magnetically. After weighing, the temperature was adjusted to 25.0 °C and the volume was recorded. Finally, weighing the recovered glass tubing segments

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(10) LaMantia, C. R. Ph.D. Dissertation, Columbia University, New York, 1966; *Diss. Abstr. B.*

(11) Krüger, C. R.; Niederprüm, *Inorg. Synth.* **1966**, *8*, 15.

that formerly held the potassium gave enough data to calculate the density.

The densities of four solutions at 25 °C were (concentration of KNH_2 in units of moles per liter of solution, or M, and densities in g/mL) as follows: 0.0751, 0.606; 0.510, 0.614; 0.610, 0.617; 0.728, 0.619. The relation is nearly linear over this range, and the two variables follow the equation $d = 0.604 + 0.020$ M.

Results and Discussion

Table I summarizes the results of the $H_2/KNH_2/Hg$ reaction. The extent of the reaction depends strongly on the amount of stirring, on the length of reaction time, and on the K/Hg ratio. In run 5, in which a glass-enclosed stirring bar was used, two-thirds of the K^+ was reduced. The mole fraction of potassium in the amalgam was 0.044, and the product was a thick paste. It was necessary to dilute this amalgam with more mercury to make filtration possible. The K/Hg phase diagram[12] reveals the amalgams with potassium mole fractions higher than approximately 0.04 are solid at 25 °C. Small differences in stirring and catalysis can affect the extent of reduction strongly, producing irreproducible potassium concentrations in the amalgams. True equilibrium, especially when a viscous amalgam is the product, is reached exceedingly slowly.

When zinc was used as the reducing agent, the KNH_2 concentration was 0.12 M and the reaction time was 75 h. It was found that 17.3% of the K^+ had been reduced to amalgam, presumably $Zn(NH_2)_4^{2-}$ being formed simultaneously. The amalgam contained 4.8 mg of potassium and 0.14 mg of zinc (spectrophotometric analysis), so there was evidently some exchange of the two metals within the mercury phase.

Bergstrom[13] observed earlier that mercury is attacked by potassium amide in liquid ammonia "at an extremely slow rate". The blank experiments confirmed this statement. The 80-day exposure involved 0.093 M KNH_2 and 10.0 g of mercury. The mercury phase was found to contain 4.34 mg of potassium (4.6% of the total). Thus, while the weak reducing agent mercury can reduce K^+ under the experimental conditions, the extent of the reaction is far below that in which hydrogen is present.

Since it is well-known that hexamethylphosphoramide dissolves the alkali metals, this solvent provides an alternative medium for the reaction of interest. Potassium bis(trimethylsilyl)amide was found to dissolve readily in HMPA. With use of concentrations, hydrogen pressures, and reaction times comparable to those in the $H_2/KNH_2/Hg$ experiments, it was found that 11–12% of the total potassium ion was reduced to amalgam. Since hexamethyldisilazane is a stronger acid than ammonia, the driving force for its formation (and K/Hg simultaneously) is less than for the corresponding reaction in ammonia, but no quantitative data were found.

Registry No. KNH_2, 17242-52-3; Hg, 7439-97-6; H_2, 1333-74-0; Zn, 7440-66-6; $KN(SiMe_3)_2$, 40949-94-8; NH_3, 7664-41-7; mercury base, potassium alloy, 39365-58-7.

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[12] Hansen, M. "Constitution of Binary Alloys", 2nd ed.; McGraw-Hill: New York, 1958; p 818.

[13] Bergstrom, F. W. *J. Phys. Chem.* **1926**, *30*, 19.

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Kinetics of Chromium(II) Reduction of Sulfamato, *p*-Toluenesulfonamido, and Sulfamido Complexes of Pentaamminecobalt(III)

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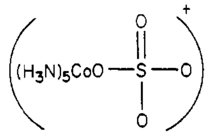
The kinetics of the chromium(II) reduction of the pentaamminecobalt(III) complexes of sulfamate, sulfamide, and *p*-toluenesulfonamide have been studied in 1 M $LiClO_4/HClO_4$. The reduction rate constant (25 °C), activation enthalpy, and entropy for $(H_3N)_5CoNH_2SO_3^{2+}$ are 3.3 ± 0.1 $M^{-1}\ s^{-1}$, 8.5 ± 0.5 kcal mol^{-1}, and −27 ± 2 cal mol^{-1} deg^{-1}, respectively. The reaction produces $(H_2O)_5CrOSO_2NH_2^{2+}$. The O- and N-bonded isomers are reduced at indistinguishable rates. Reduction of the sulfamido complex is competitive with hydrolysis. The kinetic parameters for reduction of $(H_3N)_5CoNH_2SO_2NH_2^{3+}$, in the order given above, are 0.197 ± 0.014 $M^{-1}\ s^{-1}$, 9.3 ± 1.2 kcal mol^{-1}, and −30 ± 4 cal mol^{-1} deg^{-1}, and for $(H_3N)_5CoNHSO_2NH_2^{2+}$, $(5.56 \pm 0.26) \times 10^{-2}\ M^{-1}\ s^{-1}$, 11.5 ± 0.9 kcal mol^{-1}, and −26 ± 3 cal mol^{-1} deg^{-1}. The chromium(III) product is too unstable to be fully characterized, but a kinetic–spectrophotometric analysis indicates that ligand transfer does occur. Similar kinetic results were found for the *p*-toluenesulfonamido complex, but the chromium(III) product could not be detected. The kinetic trends for the pentaamminecobalt(III) complexes with SO_4^{2-}, $NH_2SO_3^-$, and $SO_2(NH_2)_2$ are discussed, and a bridged-outer-sphere mechanism is suggested to be most consistent with the formation of ligand-transfer product, greater reactivity of the protonated complex, similar reactivity of O- and N-bonded sulfamato isomers, and lack of electron transfer through an $-NH_2-$ group.

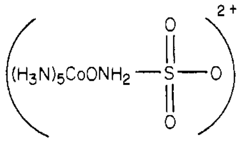
Introduction

The pentaamminecobalt(III) complexes of sulfate (A), sulfamate (B), and sulfamide (C) offer a series in which the structure of the sixth ligand is changed little while the complex charge and coordinating atom are varied. The consequences of these changes on the chromium(II) reduction of these complexes have been studied in this work.



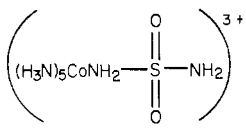
$$\left[(H_3N)_5CoO-\overset{O}{\underset{O}{S}}-O\right]^{+}$$

A



$$\left[(H_3N)_5CoONH_2-\overset{O}{\underset{O}{S}}-O\right]^{2+}$$

B



$$\left[(H_3N)_5CoNH_2-\overset{O}{\underset{O}{S}}-NH_2\right]^{3+}$$

C

The chromium(II) reduction of the sulfato complex was studied previously with reasonable agreement at least on the rate constant at 25 °C.[1,2] It seems to be assumed[3] that the reaction proceeds with sulfate ion transfer to chromium(III), apparently without actual identification of the product. Fraser[2]

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