Discussion

Reductions of Cr(VI) have been the subjects of many mechanistic studies, and extensive evidence exists for series of one-electron transfers analogous to those shown by eq 2-4. Because of this evidence we think these steps probably do occur during net reaction 1, and in the following discussion we assume they do occur. However, our data, as those of earlier workers,[4,5] imply that additional steps occur.

Our data show that the elementary reaction(s) yielding $Cr(H_2O)_5Cl^{2+}$ and the elementary reaction(s) yielding $Cr_2(H_2O)_8(OH)_2{}^{4+}$ compete more effectively (with elementary steps yielding $Cr(H_2O)_6{}^{3+}$) at high [Cr(II)] and at high $[Cl^-]$. These observations cannot be rationalized solely by any combination of reactions 2-8.

Reactions 2-4 and various combinations of reactions 6-11

$$2Cr^{2+} + Cl^- = Cr_2Cl^{3+} \qquad Q_9 << 1 \tag{9}$$

$$Cr_2Cl^{3+} + Cr(VI) \rightarrow Cr(H_2O)_6{}^{3+} + Cr(H_2O)_5Cl^{2+} + Cr(IV) \tag{10}$$

$$Cr_2Cl^{3+} + Cr(V) \rightarrow Cr(H_2O)_5Cl^{2+} + Cr_2(H_2O)_8(OH)_2{}^{4+} \tag{11}$$

are consistent with the observations listed just above. Each of reactions 10 and 11 competes more effectively than the other reactions discussed here at high [Cr(II)] and at high $[Cl^-]$ and yields $Cr(H_2O)_5Cl^{2+}$ along with $Cr(H_2O)_8(OH)_2{}^{4+}$ or a presumed precursor of $Cr(H_2O)_8(OH)_2{}^{4+}$. Other reactions involving higher polymers of Cr(II) would also be in accord with our data. Our failure to find spectral evidence for a Cr(II) dimer indicates that (if it is indeed formed) the extent of formation is small, or the visible spectrum is similar to that of monomer.

The small amounts of $^{51}Cr(H_2O)_5Cl^{2+}$ and $^{51}Cr(H_2O)_6{}^{3+}$ produced in the labeling experiment indicate the pathways taking Cr(VI) to monomer are not major pathways under the conditions of that experiment. Yet, in the experiments at lowest $[Cr(II)]_0$ and $[Cl^-]$, greater than 75% of the product was monomer, indicating that a significant amount of Cr(VI) had to be converted to monomer. These observations are in accord with eq 10 (to produce the $Cr(H_2O)_5Cl^{2+}$) followed by eq 6a, or 7, or 8 (to produce $Cr(H_2O)_6{}^{3+}$ from Cr(VI), in greater amounts at lower Cr^{2+}) but are not in accord with eq 11. A sequence involving eq 10 as the sole process leading to $Cr(H_2O)_5Cl^{2+}$ predicts that even at very low $[Cr(II)]_0$, a labeling experiment would yield no $^{51}Cr(H_2O)_5Cl^{2+}$, but a significant amount of $^{51}Cr(H_2O)_6{}^{3+}$. We did not test this prediction by experiment, but it appears that it would have to be approximately true regardless of the mechanism, owing to the very small *total* amount of $Cr(H_2O)_5Cl^{2+}$ and the large amount of total monomer that is produced at low $[Cr(II)]_0$.

The failures to detect a large quantity of $Cr(H_2O)_5Cl^{2+}$ product when Fe(II) or Cu(I) was the reductant appear to be further evidence that Cr(VI) is not the principal source of $Cr(H_2O)_5Cl^{2+}$. This evidence and the result of the labeling experiment seem to require that $Cr(H_2O)_5Cl^{2+}$ must come primarily from the Cr(II). If Cr(II) is the source of $Cr(H_2O)_5Cl^{2+}$, then it is reasonable to expect that other oxidants could also yield $Cr(H_2O)_5Cl^{2+}$. Further, if Cr(II) *dimer* (or other polymer) is responsible for $Cr(H_2O)_5Cl^{2+}$, as we have argued, then other oxidants might also produce $Cr(H_2O)_5Cl^{2+}$ with a yield increasing with $[Cr(II)]_0$ and $[Cl^-]$. These expectations were met with molecular oxygen. In addition, oxygenation of Cr(II) has been found by other workers to be second order in Cr(II), in aqueous perchlorate media[11] and in aqueous ammonia-bromide media.[12] In both of these studies, a peroxy-bridged Cr(II) dimer was proposed. Other Cr(II) dimers that are known to exist are chromium(II) alkanoates, of which the chromium(II) acetate hydrate is the best characterized.[13]

Our attempts to gain information about the behavior of unstable Cr(IV) and Cr(V) species showed that these species do not ultimately become chlorochromium(III) species upon reduction by Cr(II) (or by Fe(II) or Cu(I)) under the conditions of our study. This result could occur because the intermediates do not form thermodynamically stable chloro complexes. If Cr(V) is an oxy anion as has been suggested,[14] then it would not be expected to form stable chloro complexes; if Cr(IV) is an aquo cation as has also been suggested,[14] then we expect it to form complexes of finite stability. The failure to convert Cr(IV) and Cr(V) to chlorochromium(III) could also arise from unfavorable rates. It is not surprising that chlorochromium(IV) complexes could form slowly relative to the lifetime of Cr(IV) or even that uncomplexed Cr(IV) could be reduced much faster than complexed Cr(IV). A more definite conclusion is that Fe(II) or Cu(I) reduction of Cr(IV) did not occur primarily by a chloride-bridged mechanism in our experiments; such reductions would have led to chlorochromium(III). It seems particularly noteworthy that even Cu(I) converted less than 10% of the Cr(VI) to $Cr(H_2O)_5Cl^{2+}$, even though Cu(I) was extensively complexed by chloride,[15] in our experiment.

The most interesting implication of this study is the unexpected one that chloride-bridged dimeric chromium(II) species exist. Our evidence indicates that this is a mechanistically significant species. We suggest that the possible existence of Cr(II) dimers should be considered in connection with other mechanistic studies, especially if complexing anions are present.

Registry No. $Cr(H_2O)_6{}^{3+}$, 14873-01-9; $Cr(H_2O)_5Cl^{2+}$, 17712-88-8; $Cr_2(H_2O)_8(OH)_2{}^{4+}$, 37380-89-5; H_2CrO_4, 7738-94-5; chromium(II) perchlorate, 13931-95-8.

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Conversion of Dihydridodiammineboron(III) Borohydride to Ammonia-Borane without Hydrogen Evolution

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It has been known for some 15 years that ammonia-borane can be formed from dihydridodiammineboron(III) borohydride.[1] In all such previous reports H_2 was observed as a product along with another product usually assumed to be $(H_2BNH_2)_n$. The equation previously written is

$$[H_2B(NH_3)_2]BH_4 \xrightarrow[\text{diethyl ether}]{NH_3} H_2 + H_3BNH_3 + (1/n)(H_2BNH_2)_n$$

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[1] S. G. Shore and R. W. Parry, *J. Amer. Chem. Soc.*, 80, 8 (1958).

Recently I have found that $[H_2B(NH_3)_2]BH_4$ will convert to H_3BNH_3 *without* H_2 evolution in a polyether solution containing B_2H_6. The data support the new equation

$$[H_2B(NH_3)_2]BH_4 \xrightarrow[B_2H_6\text{(small amount)}]{\text{polyether}} 2H_3BNH_3$$

With diglyme as solvent 91% of the original $[H_2B(NH_3)_2]BH_4$ was converted in one run to H_3BNH_3 after 40 hr at 25°. In a second run 80% of the original salt was converted after an equivalent time. When monoglyme was used as solvent, the reaction was much slower, and in two runs only 22% and 37% of H_3BNH_3 were formed after 60 hr.

It appears that NH_3 in diethyl ether catalyzes decomposition with H_2 generation while diborane in polyether yields H_3BNH_3 as the sole product of decomposition.

Contrary to earlier literature reports[1,2] I found that solid H_3BNH_3 of high purity did not undergo conversion to $[H_2B(NH_3)_2]BH_4$ even when the H_3BNH_3 was held at 50° for 13 days.

Experimental Section

General Information. Ether solvents were vacuum distilled from $LiAlH_4$ suspensions into the reaction flask. $H_2B(NH_3)_2BH_4$ was prepared in liquid ammonia[3] and extracted with diethyl ether before use to remove any H_3BNH_3 impurities. H_3BNH_3 was prepared from B_2H_6 and NH_3 in diethyl ether.[4]

$H_2B(NH_3)_2BH_4$ in Diglyme with B_2H_6. Diglyme (20 ml) was condensed onto 2.45 mmol of $H_2B(NH_3)_2BH_4$ (0.12 *M*) and 0.26 mmol of B_2H_6 was added. The evacuated system was stirred at −23° until $H_2B(NH_3)_2BH_4$ had dissolved completely. Afterward, the clear solution was warmed to room temperature and stirred with a magnetic bar for 40 hr. A 0.090-mmol amount of H_2 was formed after this period and only a trace of precipitate was formed. Diglyme was pumped off quantitatively and fractionated. A 0.21-mmol amount of B_2H_6 was recovered. From the solid nonvolatile residue 4.45 mmol of H_3BNH_3 (1.82 $H_3BNH_3/H_2B(NH_3)_2BH_4$) was extracted with diethyl ether. After pumping off the ether solvent H_3BNH_3 was washed with *n*-hexane to remove any grease impurities and characterized by its X-ray powder pattern and infrared spectrum. The ether-insoluble residue consisted of 0.22 mmol of unreacted $H_2B(NH_3)_2BH_4$ as was shown by its X-ray powder pattern. No evidence was found for the formation of any other reaction products.

In another experiment 1.36 mmol of $H_2B(NH_3)_2BH_4$ was dissolved in 15 ml of diglyme (0.091 *M*) and 0.15 mmol of B_2H_6 added. After 40 hr of reaction time at room temperature 0.045 mmol of H_2 was formed. A 0.13-mmol amount of B_2H_6 was recovered and 2.16 mmol of H_3BNH_3 (1.59 $H_3BNH_3/H_2B(NH_3)_2BH_4$) could be isolated.

$H_2B(NH_3)_2BH_4$ in Monoglyme with B_2H_6. The reaction was carried out as described above with diglyme as solvent. $H_2B(NH_3)_2BH_4$ (0.99 mmol) was dissolved in 15 ml of monoglyme (0.067 *M*) and 0.14 mmol of B_2H_6 was added. After 60 hr of reaction time at 25° 0.01 mmol of H_2 was formed. A 0.12-mmol amount of B_2H_6 was recovered and 0.44 mmol of H_3BNH_3 was isolated (0.44 $H_3BNH_3/H_2B(NH_3)_2BH_4$). The diethyl ether insoluble residue consisted again of unreacted $H_2B(NH_3)_2BH_4$.

In a second experiment a more concentrated solution was used (1.15 mmol of $H_2B(NH_3)_2BH_4$ in 5 ml of monoglyme, 0.23 *M*) and 0.15 mmol of B_2H_6 was added. After an equivalent reaction time, 0.094 mmol of H_2 and 0.13 mmol of B_2H_6 were isolated. A 0.84-mmol amount of H_3BNH_3 was formed (0.73 $H_3BNH_3/H_2B(NH_3)_2BH_4$).

Attempted Conversion of H_3BNH_3 into $H_2B(NH_3)_2BH_4$. A sample of 1.27 mmol of pure H_3BNH_3 was stored at room temperature over 4 months in an evacuated glas ampoule. No trace of H_2 was formed over this period and H_3BNH_3 was completely soluble in diethyl ether.

Another sample of 1.91 mmol of H_3BNH_3 was heated for 13 days at 50°. Higher temperatures could not be used because H_2 formation became considerable. A 0.16-mmol amount of H_2 (0.084 H_2/H_3BNH_3) was formed. The solid residue was extracted with diethyl ether and 1.74 mmol of H_3BNH_3 recovered (91% of originally used material). The decomposition of 9% H_3BNH_3 corresponds well with the formation of 8.4% H_2 indicating decomposition of H_3BNH_3 into polymeric borazane. The X-ray patterns of the sample stored at room temperature and of the sample heated at 50° contained no reflections of $H_2B(NH_3)_2BH_4$.

Registry No. $H_2B(NH_3)_2BH_4$, 17125-97-2; H_3BNH_3, 17596-45-1; B_2H_6, 19287-45-7; hydrogen, 1333-74-0.

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Synthetic Procedure for Some Acidotetraaminechromium(III) Complexes

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In 1970, Vaughn, DeJovine, and Seiler published a paper in this journal describing the synthesis of *trans*-$[Cr(en)_2FCl]ClO_4$.[1] This molecule was of great interest to us so we have repeated the above-referenced synthesis. In the course of our investigation we have modified the conditions of the original technique somewhat and have found our modification to be of great utility for the synthesis of a variety of Cr(III) complexes. We have not established the limits of the applicability of the synthesis but have satisfied ourselves that the method is powerful and should be described. In this report we describe in detail the syntheses of *trans*-$[Cr(en)_2FCl]ClO_4$, *trans*-$[Cr(en)_2FBr]ClO_4$, *trans*-$[Cr(NH_3)_4F_2]ClO_4$, and *trans*-$[Cr(NH_3)_4FCl]ClO_4$ and indicate how the method of synthesis can be applied in other cases.

Experimental Section

Synthesis of *trans*-$[Cr(en)_2FCl]ClO_4$. A 10-g sample of *trans*-$[Cr(en)_2FH_2O](ClO_4)_2\cdot H_2O$, prepared as described by Vaughn, Stvan, and Magnuson,[2] was slurried with 5 g of NH_4Cl in 150 ml of methanol and stirred in the dark at 40° for 18–24 hr. The crude product was removed by filtration and recrystallized from warm water by addition of $NaClO_4$ followed by cooling. Spectral data are given in Table I. *Anal.* Calcd for *trans*-$[Cr(en)_2FCl]ClO_4$: Cr, 15.95. Found: Cr, 15.96.

Synthesis of *trans*-$[Cr(en)_2FBr]ClO_4$. A 3.5-g sample of *trans*-$[Cr(en)_2FH_2O](ClO_4)_2\cdot H_2O$ was treated with 3.5 g of NH_4Br in 25 ml of methanol. The mixture was stirred vigorously at 40° for 24 hr after which it was filtered and the precipitate dried. The crude complex was dissolved in 15° water in order to decrease the amount of complex that aquates during the recrystallization.[3] After addition of $NaClO_4$ to the filtered solution it was cooled to 0°; this yielded a precipitate that was washed with ethanol and dried *in vacuo*. The yield was 1.4 g, 45%. Spectral data are given in Table I. *Anal.* Calcd for *trans*-$[Cr(en)_2FBr]ClO_4$: Cr, 14.03; F, 5.13. Found: Cr, 14.11; F, 5.13.

Synthesis of *trans*-$[Cr(NH_3)_4F_2]ClO_4$. The starting material for this synthesis was *trans*-$[Cr(NH_3)_4ClH_2O]Cl_2$, prepared as described.[4] A sample of 6 g of this complex was treated with 6 g of finely ground NH_4F in 120 ml of methanol and the slurry was stirred at 40° in the dark for 17 hr. The solid was removed by filtration and washed with ethanol; it was then dissolved in warm, dilute HCl. The solution was filtered into solid $NaClO_4$ and cooled. The solid that resulted from this procedure was still a mixture of compounds, but a final recrystal-

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