in contrast to a report[18] that I does not form an adduct with the weaker Lewis acid CROTO and that the adduct with ACRYL is unstable in air. Moreover, the spectral shifts $\Delta\bar{\nu}_{CO}$ reflect a slight, but consistent increase for V relative to I and, hence, increased interaction of Lewis acid and metal complex. Such a result, although surprising in terms of the electronic properties of the ligands, seems to indicate that the fluoro complex V is more basic than its chloro analog I.

A plausible explanation for this apparent enhanced basicity seems to be difficult, as it cannot be ascribed to a single factor, and probably should await further results from measurements of accurate thermodynamic parameters in nonpolar solvents.

Conclusion

On the basis of chemical reactivity data which have been presented for isostructural and isoelectronic iridium(I) complexes with Lewis acids, we propose the following tentative order of relative basicity: $IrClCO(As(C_6H_5)_3)_2 > IrClCO(P(C_6H_5)_3)_2 > IrClCS(P(C_6H_5)_3)_2$. Such reactivity seems to increase with increasing basicity of the metal center which is a function of the neighboring ligands in agreement with previous results.[8,9] The relative basicity of $IrFCO(P(C_6H_5)_3)_2$ *vs.* the parent complex cannot be decided at the moment as noted earlier.

Registry No. *trans*-$IrCl(CO)(AsPh_3)_2$, 23954-42-9; *trans*-$IrCl(CS)(PPh_3)_2$, 30106-92-4; *trans*-$IrF(CO)(PPh_3)_2$, 32356-62-0; *trans*-$IrCl(CO)(PPh_3)_2$, 15318-31-7; *trans*-$IrCl(N_2)(PPh_3)_2$, 21414-18-6; *p*-$O_2NC_6H_4CON_3$, 2733-41-7; CH_3CN, 75-05-8; $[Ir(CO)(CH_3CN)(PPh_3)_2]BF_4$, 39196-84-4; NH_4F, 12125-01-8; SO_2, 7446-09-5; O_2, 7782-44-7; $BF_3\cdot O(C_2H_5)_2$, 109-63-7; $IrCl(CO)(AsPh_3)_2\cdot SO_2$, 39111-71-2; $IrCl(CO)(AsPh_3)_2\cdot SO_4$, 39111-72-3; $IrCl(CO)(AsPh_3)_2\cdot O_2$, 39111-73-4; $IrCl(CO)(AsPh_3)_2\cdot SbF_3$, 39196-85-5; $IrCl(CO)(AsPh_3)_2\cdot SbCl_3$, 39111-74-5; $IrCl(CO)(AsPh_3)_2\cdot$FUM, 36483-99-5; $IrCl(CO)(AsPh_3)_2\cdot$ACRYL, 39040-91-0; $IrCl(CO)(AsPh_3)_2\cdot$CROTO, 39040-92-1; $IrCl(CO)(AsPh_3)_2\cdot$ALLYLCY, 39040-93-2; $IrCl(CO)(PPh_3)_2\cdot SbF_3$, 39111-75-6; $IrCl(CO)(PPh_3)_2\cdot SbCl_3$, 39196-86-6; $IrCl(CS)(PPh_3)_2\cdot$TCNE, 39040-94-3; $IrCl(CS)(PPh_3)_2\cdot$FUM, 39040-95-4; $IrCl(CS)(PPh_3)_2\cdot xBCl_3$, 39040-85-2; $IrCl(CS)(PPh_3)_2\cdot xBBr_3$, 39040-89-6; HCl, 7647-01-0; $IrHCl_2(CS)(PPh_3)_2$, 39040-90-9; $IrF(CO)(PPh_3)_2\cdot SO_2$, 39111-81-4; $IrF(CO)(PPh_3)_2\cdot O_2$, 39111-82-5; $IrF(CO)(PPh_3)_2\cdot$TCNE, 39151-91-2; $IrF(CO)(PPh_3)_2\cdot$FUM, 39040-96-5; $IrF(CO)(PPh_3)_2\cdot$ACRYL, 39151-92-3; $IrF(CO)(PPh_3)_2\cdot$CROTO, 39151-93-4.

Acknowledgment. We are indebted to Professors D. F. Shriver and K. Nakamoto for helpful discussions.

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Reduction of Coordinated Nitrosyls. Preparation, Characterization, and Reduction of Nitrosylpentaaquochromium(2+)[1]

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Received October 6, 1972

A direct, quantitative, and convenient method for the preparation of $CrNO^{2+}$ has been achieved by a detailed study of the reduction of the nitrosyl complex by Cr^{2+}. The reaction of NO with Cr^{2+} is rapid and produces only $CrNO^{2+}$ provided that the NO is kept in excess over the Cr^{2+}. Addition of an excess of Cr^{2+} reduces the coordinated nitrosyl in a simultaneous two-electron step to NH_3OH^+ and the Cr dimer. The general form of the rate law for the nitrosyl reduction is $-d[CrNO^{2+}]/dt = [k_1 + k_2/H^+][Cr^{2+}][CrNO^{2+}]$. The values of k_1 (M^{-1} sec^{-1}) and k_2 (sec^{-1}) at 25.4° are 0.490 and 2.9×10^{-2}, respectively.

Introduction

On initiating our studies on the reactivity of coordinated nitrosyls, chromous ion was chosen to investigate the reducibility of a variety of metal nitrosyls. Chromous ion possesses a fairly high reduction potential and yet is sufficiently stable in acidic solutions. When oxidized, it yields substitution-inert complexes which aid in the identification of the mechanism of electron transfer. When bridging ligands are present, Cr^{2+} reductions are often quite rapid.[2] Thus, the possibility emerges that Cr^{2+} cannot only reduce the nitrosyl or the metal center but may also retain the nitrosyl function in the process of electron transfer. In order to pursue this area of interest, it was necessary to explore the previously reported $Cr(H_2O)_5NO^{2+}$.[3] Ardon and Herman[3] have reported that the oxidation of Cr^{2+} by NO_3^- or NO produces $CrNO^{2+}$ (<50%), Cr^{3+}, and the Cr dimer. In the course of our work, we have (1) improved the method of preparing $CrNO^{2+}$, (2) characterized the $CrNO^{2+}$ complex further, and (3) studied in detail the kinetics and stoichiometry of the reduction of $CrNO^{2+}$ by Cr^{2+}.

Experimental Section

Reagents. $LiClO_4$ was made by the method of Olson.[4] The Li^+ concentration was determined by adding an aliquot of $LiClO_4$ to a column containing Dowex 50W-X8, 200–400 mesh, in the acid form. (The resin was cleaned according to the method of Deutsch.[5]) After washing the column with water, the acid in the eluent was determined by titration with a standard NaOH solution. Chromium(II) perchlorate solutions were prepared by the reduction of the chromium(III) salt with amalgamated zinc under a stream of argon. Stock solutions of chromium(III) perchlorate were prepared by reduction of primary standard $K_2Cr_2O_7$ with acidic H_2O_2 and boiling the solu-

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(1) Presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 28, 1972; see Abstract No. INOR 31.

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tion for several hours.[6] The solution was cooled overnight, and the $KClO_4$ was removed by filtration. The perchlorate concentration in the Cr(III) solution was determined by ion exchanging an aliquot on Dowex 50W-X8 in the H^+ form and titrating the released acid with standard NaOH. The acidity of the Cr(III) solution was determined by potentiometric titration, after complexation of the Cr(III) with oxalate.[7] Chromium(III) was analyzed spectrophotometrically at 372 nm (ϵ 4815 M^{-1} cm^{-1}) after oxidation with alkaline peroxide.[8] Nitric oxide from the cylinder (Matheson) was rigorously scrubbed[9] to remove NO_2. The system was previously purged with Cr^{2+}-scrubbed argon. All gases were contained in an all-glass line. Distilled water was redistilled using an alkaline permanganate, all-glass still. Stock solutions of $CrNO^{2+}$ were prepared by the dropwise addition of 0.5 *M* Cr^{2+} (10 ml) (less than 1 ml/20 min) to a stirred solution of 200 ml of 0.1 *M* $HClO_4$. The latter solution was continuously saturated with NO by means of a gas-dispersion tube. After the Cr^{2+} addition was completed, the NO flow was switched to argon. Stock solutions of ~0.025 *M* $CrNO^{2+}$ (stored at 5°) were kept for periods of 2 months with only slight decomposition into Cr^{3+} and highly charged Cr species.[10] For all experiments, the $CrNO^{2+}$ stock solution was diluted with an equal volume of water and absorbed onto a column of Dowex 50W-X8, 200–400 mesh, in the H^+ form. The $CrNO^{2+}$ was eluted cleanly with either 0.3 or 0.5 *M* $HClO_4$ and used within 1 hr. With 0.5 *M* $HClO_4$, 0.04 *M* solutions of $CrNO^{2+}$ could be obtained by isolating the most concentrated portion of the band.

Analyses. Following the procedure of Feigl[11] 1 drop of the test solution was neutralized with Na_2CO_3. Two drops of an iron(III) formaldehyde solution and a spatula tip of $(NH_4)_2(S_2O_8)$ were added. On mixing, a red or pink color developed indicating the presence of NH_2OH. Using the method of Johnson,[12] free NH_2OH was determined quantitatively by forming the *p*-nitrobenzaldoxime. In alkaline solution, the compound produces a strong yellow color with λ_m 368 nm, ϵ 1.4 × 10^4 M^{-1} cm^{-1}. Additional spot tests for NH_4^+ (Nessler's)[13] and N_2H_4 (*p*-dimethylaminobenzaldehyde)[14] were also performed on the product solutions.

Kinetics. All kinetic studies were performed by thermostating a 5-cm, serum-capped cell containing the limiting reagent. A small volume of the reagent in excess was injected into the cell. The solution was shaken vigorously and placed into the thermostated cell compartment of the Cary 14 recording spectrophotometer. The absorbance (generally at 450 nm) was then followed using a fixed chart speed. Both solutions were thermostated to within ±0.1°. The solutions were degassed with argon (scrubbed through a Cr^{2+} tower) using an all-glass system. Platinum needles were used to inject the solution through the serum caps. All reactions were followed for $>10\tau$. Kinetics for the reactions of Cr^{2+} with $CrNO^{2+}$ were studied under pseudo-first-order conditions and/or second-order conditions ($Cr^{2+}/CrNO^{2+} = 2/1$). Plots of $\ln (A - A_\infty)$ *vs.* *t* or $1/(A - A_\infty)$ *vs.* *t* (second order) were linear beyond 3τ (A = absorbance at time t; A_∞ = final absorbance). Ionic strength was maintained with $LiClO_4$ and $HClO_4$. The acidity was maintained using $HClO_4$.

Product Analysis. The products of the reaction between Cr^{2+} and NO (in excess NO or in excess Cr^{2+}) were determined by recording the uv-visible spectrum (700–200 nm). In addition, the product mixture was placed on Dowex 50W-X8. The possible components were eliminated by previously determining the flow rate (0.3 *M* $HClO_4$ for $CrNO^{2+}$, 1.0 *M* $HClO_4$ for Cr^{3+}, 3.0 *M* NaCl for Cr dimer) on this particular resin. We have observed that the green species previously described as the Cr dimer (found from the oxidation of Cr^{2+} with O_2) will only move very slightly with 3 *M* $HClO_4$, leaving a small green residue at the top of the column. However, if 3 *M* NaCl is used, all of the green band is eluted quantitatively. The spectra of the various elements were compared with those previously reported for $CrNO^{2+}$,[3] Cr^{3+},[15] $Cr_2(OH)_2{}^{4+}$,[16] $CrNH_3{}^{3+}$,[17] Cr_2NH^{4+},[18] and polynuclear Cr species.[19]

Results

Spectrum of $CrNO^{2+}$. Ardon and Herman[3] have reported the following spectrum of $CrNO^{2+}$: λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 559 (28), 449 (121), 390 sh (~90), 323 (92). We have also obtained identical spectra on our ion-exchanged species. However, on further dilution, we have observed an additional sharp band at 238 nm (ϵ 1.17 × 10^3 M^{-1} cm^{-1}). At μ = 1.3, the entire spectrum of $CrNO^{2+}$ is independent of acidity from 0.05 to 1.3 *M* $HClO_4$.

Preparation of $CrNO^{2+}$. In order to study the stability of $CrNO^{2+}$, it was necessary to prepare stock solutions with minimal impurities. Preliminary experiments indicated that the chief reason for the low yields of $CrNO^{2+}$ achieved by Ardon and Herman was based upon the low solubility of NO(g).[20] The direct preparation of $CrNO^{2+}$ as described in the Experimental Section results in no detectable amounts of the blue Cr^{3+} or the highly charged blue-green "dimer" analyzed by ion exchange. Chromium analysis and the uv-vis spectrum of the 2+ band confirmed that 100 ± 3% of the original product solution was now $CrNO^{2+}$.

In order to ascertain the rapidity of the reaction of Cr^{2+} with NO(g), a small volume of a concentrated Cr^{2+} solution (final concentration = 1 × 10^{-3} *M*) was added to a 5-cm cell containing NO-saturated $HClO_4$ (0.02 *M*). Recording the initial absorbance (within 4 sec of reaction) on a Cary 14 spectrophotometer, it was observed that the second-order reaction was already complete (100 ± 4% $CrNO^{2+}$).

Cr^{2+} + $CrNO^{2+}$. Product Analysis. Fresh solutions of $CrNO^{2+}$ (in 0.3 or 0.5 *M* $HClO_4$) were treated with varying amounts of Cr^{2+}, and the reaction was allowed to proceed to completion. The results are provided in Table I. In general, some unreacted $CrNO^{2+}$ (<1%) was observed. In addition, a small amount of a pale blue species moved with 1 *M* $HClO_4$, and the spectrum of this rinse was identical with that previously reported for $Cr(H_2O)_6{}^{3+}$ (λ_M 408 nm, ϵ 13.3 M^{-1} cm^{-1}).[15] The spectrum of the 3 *M* rinse was similar to that obtained on eluting the Cr dimer with 3 *M* NaCl.

The ratio of Cr^{2+} to $CrNO^{2+}$ suggests a 2e reduction of the $CrNO^{2+}$. If one assumes that the electron distribution of $CrNO^{2+}$ solution is Cr^{III}, NO^-, it becomes apparent that the nitrogen-containing ligand has been reduced to NH_3OH^+. Spot tests for N_2H_4 and NH_4^+ were negative. In the case of NH_4^+, the test was negative for 1.5:1 but *weakly* positive for 2:1. It may be that a slight excess of Cr^{2+} or the slowness of the action of Cr^{2+} upon $CrNO^{2+}$ (second-order conditions) resulted in some Cr^{2+} reducing NH_3OH^+ to NH_4^+. It has[21] been reported that Cr^{2+} will reduce free NH_3OH^+ to NH_4^+. The stoichiometry of the reaction is $Cr^{2+}/NH_3OH^+ = 2/1$, and the product is >95% Cr^{3+}. However, as we shall demonstrate in the next section, the reaction is approximately 35 times slower than the reaction between Cr^{2+} and $CrNO^{2+}$. A positive spot test for NH_3OH^+ was not obtained at 10^{-3} *M* levels of $CrNO^{2+}$. However, at 10^{-2} *M* levels of chromium, a definite positive result was obtained. Elution of the pro-

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Table I. Product Analysis[a]

	Cr^{2+}:$CrNO^{2+}$ [b]					
	1:1	2:1	2:1	2:1	2:1[d]	3:1
$[H^+]$, *M*	1.3	1.3	0.054	0.5	1.3	1.3
μ,[c] *M*	1.3	1.3	1.3	0.5	1.3	1.3
Amt in 0.3 *M* $HClO_4$ rinse, %	23.9[e]	2.6[f]	1.3	1	6.8	1[g]
Amt in 1.0 *M* $HClO_4$ rinse, %	14.4	6.3	2.8	4	18.5	12
Amt in 3.0 *M* NaCl rinse, %	61.5	91	96	95	77.5	84
Total, %	100	100	100	100	103	99

[a] $T = 25°$. [b] $[CrNO^{2+}] = 8.4 \times 10^{-4}$ to 3×10^{-3} *M*; analyzed after >4 hr of reaction. [c] Ionic strength maintained with $LiClO_4$ and $HClO_4$. [d] In 0.1 *M* HCl. [e] This quantity is 48% of $[CrNO^{2+}]_0$. [f] Allowed to proceed only to 97% completion. [g] 2% in rinse.

duct mixture from Dowex 50W-X8 with 0.3 *M* $HClO_4$ gave a positive test for NH_3OH^+, while the 3 *M* rinse was negative. Quantitative spectrophotometric analysis of NH_3OH^+ as the *p*-nitrobenzaldoxime confirmed that 1 mol (±5%) of NH_3OH^+ was present per mol of $CrNO^{2+}$ which reacted. The analysis when performed on the ion-exchanged portion of the product solution indicated 1 mol (±10%) of NH_3OH^+ (per mol of $CrNO^{2+}$ reacted) was present in the water and 0.3 *M* $HClO_4$ rinses, and less than 5% of free NH_3OH^+ was observed in the 3 *M* NaCl rinse.[22]

The spectrum of the product solution obtained on treating $CrNO^{2+}$ (3×10^{-3} *M*) with 2 equiv of Cr^{2+} (6×10^{-3} *M*) displayed λ_m at 580 and 420 nm with ϵ 19 and 25 M^{-1} cm^{-1}, respectively. If corrections are made for 1-3% unreacted $CrNO^{2+}$ and 5% Cr^{3+}, the spectrum conforms very closely to that obtained for the Cr dimer, λ_m 582 and 418 nm with ϵ 18.9 and 22.5 M^{-1} cm^{-1}, respectively.[16,19]

Therefore, on the basis of ion exchange, NH_3OH^+ analyses, and spectrophotometric methods of analysis, we can report that the stoichiometry of the reaction, assuming that the Cr dimer can be expressed as $(CrOH)_2{}^{4+}$, is $4Cr(H_2O)_6{}^{2+} + 2Cr(H_2O)_5NO^{2+} + 2H^+ \rightarrow 3[Cr(OH)(H_2O)_4]_2{}^{4+} + 2NH_3OH^+ + 4H_2O$.

Varying the ionic strength did not affect the product distribution. In addition, reducing the acidity from 1.3 to 0.05 *M* $HClO_4$ did not alter the product distribution. Addition of a slight excess of HCl (0.10 *M*) produced some $CrCl^{2+}$ (λ_m 428 nm, ϵ 20.8; λ_m 609 nm, ϵ 16.4 M^{-1} cm^{-1}),[23] but 77% of the polymeric Cr species was still obtained. Increasing the HCl concentration to 1.3 *M* at the same ionic strength yields increasing amounts of $CrCl^{2+}$ (24%) and Cr^{3+} (36%) and decreasing amounts of Cr dimer (40%). On varying the concentration of free Cl^-, we have observed a similar product dependence for oxidation of Cr^{2+} solutions with O_2. In 1.3 *M* HBr, the action of Cr^{2+} upon $CrNO^{2+}$ produced 15% CrBr, 21% Cr^{3+}, and 63% Cr dimer.

Kinetics. Table II lists the rates obtained under pseudo-first-order conditions for the treatment of $CrNO^{2+}$ with excess Cr^{2+}. All rates are reported at $\mu = 1.3$. Slower rates of reaction were observed at lower ionic strengths. A kinetic run at 480 nm (a minimum in product spectrum) exhibited similar kinetic behavior ($[H^+] = 1.32$ *M*, $k = 0.45$ M^{-1} sec^{-1}, $T = 25.4°$). The values of the rate constants in Table II (under similar conditions) are within 5-9% of the mean. (The larger deviation is consistently associated with the runs at lower acidity.) The scatter may be due in part to several factors such as (1) following reactions having half-lives as short as 10 sec on the Cary 14, (2) variations in maintaining ionic strength with Li^+ *vs.* Cr^{2+} (in the Cr^{2+} dependence runs), and (3) diminishing of the accuracy of total acid concentrations at less than 0.1 *M* $HClO_4$ due to increasing amounts of the acidity originating with the Cr^{2+} solution.

In order to confirm the order of the reactants in the rate law, several reactions were performed at levels of $Cr^{2+}/CrNO^{2+} = 2/1$. The reactions followed second-order behavior displaying rates similar to those obtained under the pseudo-first-order conditions. In addition, these second-order runs (where the acidity could be more accurately controlled) demonstrated a similar acid dependence. In 1.3 *M* HCl, the second-order plots indicated an acceleration in the rate to 3 M^{-1} sec^{-1} at 25.4°.

A plot of k_{obsd} *vs.* Cr^{2+} indicated that the order of the reaction in Cr^{2+} (at constant acidity) is indeed first order with the intercept intersecting the origin. On varying the acidity, small, but real, deviations in the observed rate constant were observed. The observed rate constant displays an inverse acid effect (see Figure 1) (over a factor of 25 in acidity). Therefore, the rate law for the action of Cr^{2+} upon $CrNO^{2+}$ can be written

$$-d[CrNO^{2+}]/dt = (k_1 + k_2/[H^+])[Cr^{2+}][CrNO^{2+}]$$

The sum $(k_1 + k_2/[H^+])$ is the value of k listed in Table II. The acid-independent term can be obtained from the intercept in Figure 1, and the inverse acid term can be derived from the slope in Figure 1. Plots of k *vs.* $1/[H^+]$ displayed similar linearity at 34.3 and 25.4°. Table III lists the values of k_1 and k_2 obtained from these plots.

The slight increase for the values of k_2 obtained over the tested temperature range may be fortuitous. The error in the slopes certainly would include the range demonstrated in our values of k_2. The values of $\Delta H_1{}^{\ddagger} = 9.6 \pm 0.12$ kcal/mol (errors are within one standard deviation) and $\Delta S_1{}^{\ddagger} = -27.1 \pm 0.6$ eu were obtained by a least-squares fit of the data. Values of $\Delta H_2{}^{\ddagger} = 0.7 \pm 0.7$ kcal/mol and $\Delta S_2{}^{\ddagger} = -63.3 \pm 1.2$ eu should be evaluated with some degree of caution due to the error in the slope of k *vs.* $1/[H^+]$.

Discussion

Spectrum of $CrNO^{2+}$. The $CrNO^{2+}$ complex has been characterized further with respect to a new, intense band in the uv region. The appearance of an intense band in the uv region is not unexpected, since several Cr(III) complexes exhibit similar bands (*i.e.*, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): $Cr(H_2O)_5CH_3{}^{2+}$, 258 (2.16×10^3);[24] $Cr(H_2O)_5SH^{2+}$, 259 (7×10^3);[25] $Cr(H_2O)_5Br^{2+}$, 222 (8.24×10^3),[26] in addition to their d-d bands in the visible region. The significance of this new band for $CrNO^{2+}$ lies with its intensity. It is now possible to analyze for very small amounts of $CrNO^{2+}$ in a

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Table II. Kinetic Studies[a]

$10^2[Cr^{2+}]$, *M*	$10^3[CrNO^{2+}]$, *M*	$[H^+]$, *M*	$10^3 k_{obsd}$, sec^{-1}	No. of expts	*k*, M^{-1} sec^{-1}
3.20	1.30	1.14	5.13 ± 0.29[e]	5	0.160[b]
3.20	1.30	0.560	5.94	3	0.184[b]
8.00	1.30	0.562	15.9	3	0.194[b]
3.20	1.30	0.189	8.72	3	0.272[b]
3.20	1.30	0.123	12.5 ± 1.1	4	0.390[b]
3.20	1.30	0.075	16.4	3	0.514[b]
3.20	1.25	0.058	19.6	2	0.614[b]
12.8	2.48	0.551	74.1	1	0.579[c]
12.8	1.61	0.563	78.1	2	0.610[c]
8.00	1.61	0.563	49.7	2	0.622[c]
8.00	2.48	0.547	49.4	1	0.617[c]
3.20	1.24	0.557	18.7	1	0.584[c]
3.20	1.61	0.563	17.9	2	0.558[c]
1.60	2.48	0.561	8.86	1	0.554[c]
1.60	1.61	0.561	9.34	1	0.584[c]
1.65	0.930	1.26	8.36	1	0.506[c]
1.65	1.16	1.26	8.13	1	0.506[c]
1.65	1.16	1.26	7.83	1	0.472[c]
1.60	0.737	1.24	8.21	1	0.513[c]
3.20	1.18	1.14	16.7	1	0.522[c]
1.65	1.16	0.718	81.0	1	0.491[c]
1.60	0.737	0.491	86.3	1	0.576[c]
1.60	0.930	0.469	88.0	1	0.532[c]
3.17	1.18	0.451	17.4	1	0.549[c]
1.60	0.930	0.228	9.41	1	0.570[c]
1.65	1.16	0.228	10.0	1	0.606[c]
1.65	0.930	0.159	11.3	1	0.682[c]
1.60	0.737	0.117	12.2	1	0.763[c]
1.65	0.930	0.107	12.5	1	0.759[c]
1.65	1.61	0.107	12.0	1	0.728[c]
1.65	0.930-1.16	0.076	14.5	2	0.880[c]
1.60	0.925	1.24	13.7 ± 1.1	4	0.856[d]
4.80	0.925	0.562	45.5	3	0.948[d]
1.60	0.925	0.561	14.9	2	0.932[d]
1.60	0.925	0.118	17.3	3	1.08[d]
1.60	0.915	0.114	18.6	2	1.16[d]
1.60	0.915	0.077	21.6	2	1.35[d]
1.60	0.925	0.054	24.6	3	1.54[d]

[a] $\mu = 1.3$, maintained with $LiClO_4/HClO_4$; λ 450 nm. [b] 5.4°. [c] 25.4°. [d] 35.3°. [e] Deviation only reported for four or more results.

Table III. Values of k_1 and k_2 as a Function of Temperature[a]

T, °K	k_1, M^{-1} sec^{-1}	$10^2 k_2$, sec^{-1}
278.6	0.137 ± 0.003	2.8 ± 0.1[a]
298.6	0.490 ± 0.008	2.9 ± 0.1
308.4	0.842 ± 0.019	3.6 ± 0.2

[a] Errors are one standard deviation; the slope and intercept were obtained from a linear, least-squares fit of the data.

product mixture (assuming nothing else interferes with the absorbance).

Preparation of $CrNO^{2+}$. We have presented a quantitative and convenient method for the synthesis of $CrNO^{2+}$. In addition, it has been demonstrated that $CrNO^{2+}$ is formed rapidly upon addition of Cr^{2+} to saturated solutions of NO. The $CrNO^{2+}$ is further reduced by excess Cr^{2+} in a slower reaction which is dependent upon the concentration of Cr^{2+} and the acidity. These results explain the reasons for the side product observed upon the addition of an excess of Cr^{2+} to NO(g).[3] The acid-independent term dominates the kinetics at >1 *M* $HClO_4$, and there is no apparent dependency of the final product distribution upon the total acidity (1.3–0.05 *M* $HClO_4$).

Mechanism of Cr^{2+} + $CrNO^{2+}$. It has been argued that the appearance of the Cr dimer as the oxidized form of Cr^{2+} is suggestive of a simultaneous two-electron transfer. For example, one-electron oxidants such as Br_2,[2] Cl_2,[2] Fe^{3+},[2] or H_2O_2[16] produce $Cr^{III}X$ or Cr^{3+}. However, two-electron oxidants such as Tl^{3+}[16] and O_2[16] produce the dimeric species $(CrOH)_2^{4+}$. Ardon and Plane[16] have suggested that

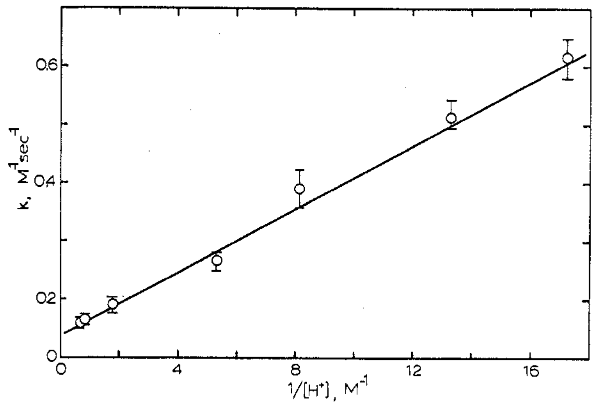

Figure 1. Plot of the specific, second-order rate constant *vs.* the reciprocal of the total acid concentration. $\mu = 1.3$, $T = 5.4°$. Similar plots were obtained at 25.4 and 35.3°.

two-electron oxidants produce Cr(IV) which then reacts further with Cr^{2+} to produce the dimer.

In the presence of Cl^-, some $CrCl^{2+}$ is formed; but the dominant product is still the Cr dimer. This is unlike the reaction of Cr^{2+} with free N_3^-, which does not produce any dimer ($CrNHCr^{4+}$) in the presence of Cl^-. The dependence of the rates and the product distribution upon halide ion suggest that these ions alter the rate of our reaction. One possibility that is often used to explain the Cl^- (or better still, Br^-) dependence in the rate law is the involvement of radicals. The radicals generated in the reaction scheme are often capable of oxidizing Br^- much more effectively than

Cl^- (perhaps due to the ease of oxidation of Br^- as opposed to Cl^-). The $Br\cdot$ or $Cl\cdot$ thus produced can react rapidly with Cr^{2+} to yield $CrBr^{2+}$ and $CrCl^{2+}$, respectively. However, despite the scavenging ability of $Br\cdot$ by Cr^{2+},[2] the yield of $CrBr^{2+}$ is not increased over that for $CrCl^{2+}$ in Cl^- media. Another possibility for the product dependence upon Cl^- and Br^- is that these anions may offer a more favorable path for reduction of the nitrosyl with production of CrX^{2+} and decreasing amounts of Cr dimer.

In the absence of Cl^- or Br^-, how can virtually all the Cr be converted to dimer? In high acid, the results dictate a mechanistic sequence which results in the attack of one molecule of Cr^{2+} upon a molecule of $CrNO^{2+}$ in the rate-determining step, followed by a faster, further attack of another molecule of Cr^{2+} (concerted or stepwise) upon the activated complex (or its product) leading ultimately to the production of 1.5 molecules of the Cr dimer and a molecule of NH_3OH^+

$$Cr^{2+} + CrNO^{2+} \xrightarrow{\text{slow}} [Cr^{2+}, CrNO^{2+}]^{\ddagger}$$

$$Cr^{2+} + [Cr^{2+}, CrNO^{2+}]^{\ddagger} \xrightarrow{\text{fast}} 1.5(\text{Cr dimer}) + NH_3OH^+$$

The difficulty in constructing a mechanism for this reaction lies with the fact that the Cr dimer [not trimer[19] (λ_m 426, 580 nm and ϵ 31.4, 19.7 M^{-1} cm^{-1}, respectively)] is produced, and only 4-5% Cr^{3+} is produced. In addition, the stoichiometry dictates two molecules of Cr^{2+} per molecule of $CrNO^{2+}$. If Cr^{2+} had reduced the ligand in a simultaneous 2e-reduction step, one would have expected $^1/_3$ Cr^{3+} and Cr^{IV}; and the Cr^{IV} would then react with Cr^{2+} to produce $^2/_3$ Cr dimer. This is clearly not the case in our reaction. Thus, we can only suggest that Cr^{2+} attacks the $CrNO^{2+}$ producing some species which then reacts further with Cr^{2+} to produce Cr dimer. The abbreviated mechanism above is only meant to account for the kinetics. We cannot arrive at a complete mechanism which accounts for all the observed results. The implication at this point is that there may be an alternative route to the production of Cr dimer (other than the often quoted reaction $Cr^{2+} + Cr^{IV} \rightarrow$ Cr dimer). The complication here may be with the fact that we are reducing a coordinated ligand, nitrosyl, which is capable of undergoing *successive* reduction.[27] Reductions of coordinated nitrosyls have received little attention[28] in the past, and this work suggests that we may need to proceed with caution before drawing parallels to other ligand systems.

It is important to note that neither $CrNH_3{}^{3+}$ nor free $NH_4{}^+$ (in significant yields) was produced in this reaction. The reaction of Cr^{2+} with free NH_3OH^+ proceeds with a rate of 1.4×10^{-2} M^{-1} sec^{-1} at 25°, $\mu = 1.3$. Therefore, the further reduction of NH_3OH^+ by Cr^{2+} in our reaction does not compete successfully with the Cr^{2+} reduction of $CrNO^{2+}$.

Registry No. $Cr(H_2O)_6{}^{2+}$, 20574-26-9; NO, 10102-43-9; $Cr(H_2O)_5NO^{2+}$, 14951-34-9.

Acknowledgment. Partial support for M. Buchbinder through the NSF-SSTP program is acknowledged. We wish to thank Miss Kan Ying Fung for her valuable technical assistance.

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(27) Presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.

(28) Presented at the American Chemical Society Symposium on the Activation of Small Molecules by Transition Metals, Buffalo, N. Y., June 1972.

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Reduction of Vanadium Tetrachloride by Trimethylamine and Dimethylaminodichloroborane[1a]

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Received November 15, 1972

Investigation of the reduction of VCl_4 by methylamino moieties has been carried out. Trimethylamine results in the formation of dimethylmethyleneammonium chloride $(CH_3)_2N{=}CH_2{}^+Cl^-$, whereas dimethylaminodichloroborane, $(CH_3)_2NBCl_2$, affords the stabilized neutral imine $CH_3N{=}CH_2{\cdot}BCl_3$ and dimethylamine-boron trichloride, $(CH_3)_2NH{\cdot}BCl_3$. Reaction mechanisms are suggested for both reductions.

Reduction of $TiCl_4$, $TiBr_4$, and VCl_4 by $B_2[N(CH_3)_2]_4$ has been investigated in considerable detail. Titanium tetrachloride results in the formation of a binuclear Ti(III) species and the oxidation product $ClB[N(CH_3)_2]_2$ whereas $TiBr_4$ affords $\{B_2Br_2[N(CH_3)_2]_2{\cdot}TiBr_3\}_2$.[2,3] From the reaction stoichiometry associated with the reduction of $TiBr_4$ it was apparent that the B-B bond was not the reducing agent. Also, it is recognized that $N(CH_3)_3$ will reduce $TiCl_4$ and VCl_4; however, the oxidation product has not been identified.[4] During the investigation of the reduction of VCl_4 by $B_2[N(CH_3)_2]_4$ it became apparent that both B-B bonds and amino groups were serving as reducing agents.[5] In order to understand this very complicated chemical system it became necessary to investigate the manner in which methylamino moieties function as reducing agents for vanadium(IV) halides because the oxidation products of $B_2[N(CH_3)_2]_4$, $ClB[N(CH_3)_2]_2$, and $Cl_2B[N(CH_3)_2]_2$ are potential amine-type reducing agents. In order further to simplify the investigation, the reduction by $N(CH_3)_3$ was first explored.

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