Reduction of Organic Azides by Chromium(II) in Aqueous Solution

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Abstract: The stoichiometry of the reduction of organic azides (RN$_3$, where R = methyl through n-hexyl, cyclohexyl, and phenyl) by chromium(II) in acidic aqueous solution was determined. Some C–N bond cleavage occurs in most of the reactions, but not in the presence of sufficient chloride ion. A reaction scheme is proposed that invokes a predominantly innersphere attack by chromium(II) at the adjacent nitrogen of the organic azide in the rate-determining step to produce a coordinated amino radical intermediate, Cr(RNH)$^{3+}$. The probable fate of this intermediate is discussed. For the experimentally determined rate law $-d[RN_3]/dt = k[RN_3][Cr^{2+}]$, the rate parameters at 20 °C are: for CH$_3$N$_3$, $k = 14.6 \pm 0.8$ M^{-1} s^{-1}, $\Delta H^* = 3.9 \pm 0.5$ kcal/mol, $\Delta S^* = -40 \pm 4$ cal/deg mol; for C$_2$H$_5$N$_3$, $k = 3.6 \pm 0.1$ M^{-1} s^{-1}, $\Delta H^* = 2.2 \pm 0.1$ kcal/mol, $\Delta S^* = -49 \pm 2$ cal/deg mol; and for n-C$_3$H$_7$N$_3$, $k = 2.6 \pm 0.1$ M^{-1} s^{-1}, $\Delta H^* = 2.5 \pm 0.6$ kcal/mol, $\Delta S^* = -48 \pm 8$ cal/deg mol. The stoichiometry of the reduction of several N-organohydroxylamines by chromium(II) was measured, and the implications of these results on the proposed reaction scheme are discussed. A convenient synthesis of Cr(RNH$_2$)$^{3+}$ complex ions is outlined.

Introduction

There is an extensive literature on the synthesis and reactions of organic azides.[1] The generation of a number of nitrenes by thermolysis or photolysis of organic azides has been the impetus for many of the studies.[1,2] Mechanistic studies of azide reactions and the use of azides as synthetic starting materials have also received considerable attention.

We have studied the reduction of several alkyl azides and phenyl azide by chromium(II) in aqueous perchloric acid solution. The investigation was prompted by our interest in the mechanistic aspects of the oxidation–reduction reactions of hydrazoic acid and azidometal ion complexes.[3] The introduction of the carbon center into the azide reactant has provided a useful label in elucidating the course of the reaction.

The stoichiometry of the chromium(II) reduction of hydrazoic acid in aqueous perchloric acid solution has been reported:[4]

$$2Cr^{2+} + HN_3 \xrightarrow{H^+} 0.95CrNH_3{}^{3+} + 0.95Cr^{3+} + 0.05Cr(NH)Cr^{4+} + N_2 \quad (1)$$

The stoichiometry is simplified in the presence of high concentrations of chloride ion:

$$2Cr^{2+} + HN_3 + Cl^- + 2H^+ \rightarrow CrNH_3{}^{3+} + CrCl^{2+} + N_2 \quad (2)$$

Reaction 2 followed by ion exchange separation provides a convenient synthesis of amminechromium(III).[5] The central feature in the mechanistic interpretation was the production of the CrNH$_2$$^{3+}$ radical as a consequence of the rate-determining step. Amino radicals and amino radical cations, R$_2$N and R$_3$N$^+$, have been postulated previously as important intermediates in the oxidation of certain amines,[6] the reduction of various hydroxylamines,[7] and some reactions of hydrazines.[8]

The reduction of organic azides by chromium(II) has provided a convenient synthesis of Cr(RNH$_2$)$^{3+}$ complexes. Amino radicals predominantly coordinated to chromium(III) appear to be crucial intermediates. The reactions are complicated, however, and we are unable to provide a detailed mechanistic interpretation, although certain features have been elucidated. A complementary study of the reduction of several hydroxylamines of the type RNH$_2$OH$^+$ by chromium(II) has yielded pertinent information.

Experimental Section

Reagents. Solutions of chromium(II), vanadium(II), and europium(II) were prepared by reduction of chromium(III), vanadium(IV), and europium(III) perchlorate solutions with amalgamated zinc in the absence of oxygen. Literature syntheses of the organic azides were used: CH$_3$N$_3$[9] (potassium methyl sulfate was used instead of dimethyl sulfate), C$_2$H$_5$N$_3$[9] (potassium ethyl sulfate was used instead of diethyl sulfate), n-RN$_3$[10] (R = C$_3$H$_7$–, C$_4$H$_9$–, C$_5$H$_{11}$–, and C$_6$H$_{13}$–), cyclohexyl azide,[10] and phenyl azide.[11] The azides were purified by distillation and stored at temperatures well below their boiling points. The ultraviolet and infrared spectra of each azide agreed well with those reported in the literature.

N-Methylhydroxylamine solutions were prepared from the hydrochloride (Aldrich). Chloride ion was removed by precipitation as silver chloride by the addition of slightly insufficient silver perchlorate. N-Ethyl- and N-propylhydroxylamine were obtained in poor yield by the reduction of the corresponding nitroalkane in ether solution with amalgamated aluminum.[12] N-Ethylhydroxylamine was isolated as the hydrochloride; N-propylhydroxylamine was separated as the free base in crystalline form and immediately dissolved in perchloric acid to prevent decomposition.[13] The preparation of N-phenylhydroxylamine has been previously described.[14] The solid was stored at −78 °C to prevent decomposition and dissolved in acid just prior to use to minimize rearrangement.[15]

Triply distilled water, once each from acid chromium trioxide and permanganate, was used.

Stoichiometric Studies. Methyl, ethyl, and n-propyl azide were sufficiently water soluble to allow homogeneous conditions in their reactions with chromium(II). The reactants were mixed in the absence of oxygen either conventionally or in the mixing chamber of a Durrum D-110 stopped-flow instrument in a continuous flow mode; the stoichiometric results were independent of the mixing procedure. The remaining organic azides were added neatly to an appropriate chromium(II) solution with vigorous stirring, but were only partially soluble. The stoichiometric results were nevertheless reproducible for these azides. The N-organohydroxylamine–chromium(II) reactions were considerably slower and required approximately 1.5 h to proceed to completion under the experimental conditions used.

The various chromium(III) reaction products were separated by ion exchange, using Dowex 50-WX8 resin and various hydrochloric acid solutions as the eluting agent. The chromium(III) species were eluted in the following order: CrCl^{2+}, Cr^{3+}, CrNH$_3$$^{3+}$, and Cr(RNH$_2$)$^{3+}$ [complete separation of the amine complexes was not achieved], and finally Cr(NR)Cr^{4+}. The separation of the monomeric and dimeric organoaminechromium(III) products was very difficult for the larger organic azide systems. Total chromium in the fractions was determined spectrophotometrically as chromate ion.[16]

In preliminary experiments on the methyl azide–chromium(II) reaction, the amine products were distilled from a portion of the reaction solution containing excess sodium hydroxide and recovered as the solid hydrochlorides. The solid was mixed with barium oxide, heated on a vacuum line, and the released amines were admitted into a gas chromatograph of local construction. A ¼ in. × 6 ft column, packed with Porapak Q coated with polyethylenimine to retard tailing of the amines, was employed at a column temperature of 50 °C with helium as the carrier gas. Blank experiments demonstrated that ammonia was eluted in a few minutes, but methylamine much later as a tailing peak. In this manner both ammonia and methylamine were identified as reaction products.

A general method for quantitatively assaying mixtures of ammonium and an organoammonium chloride was developed. The amine products of the reaction solution or separated chromium(III) product were distilled from basic solution into 2 M HCl, taken carefully to dryness (overheating results in loss of the salt and underheating causes retention of water and HCl), and the hydrochloride salt mixture was weighed. The salt was then dissolved in water and passed onto a thoroughly rinsed column of Dowex 50-WX8 resin in the ammonium ion form, and the ammonium chloride was rinsed off with water. This effluent was acidified with HCl, taken to dryness as before, and weighed. The second weight determined the total moles of amine in the original sample, and the difference in weights allowed the calculation of the moles of ammonia and organoamine.

The accuracy of this method is indicated by the following experiment. A solution containing 0.1620 g of CH_3NH_3Cl, 0.1788 g of NH_4Cl, and 1.5 mmol of Cr^{3+} in 100 mL of 1 M HCl was treated as above. The analytical results are shown in Chart I. The determination of the total millimoles of amines is quite accurate by this method, the mixture composition somewhat less so (ca. ±5%). The procedure proved to be quite general, but suffers the experimental drawback that moderately large quantities are required. The presence of only ammonia and propylamine as amine products in the *n*-propyl azide-chromium(II) reaction was demonstrated by proton NMR analysis; only *n*-propylamine was detected, eliminating the possibility of mixtures of lower amines which would analyze similarly to a mixture of ammonia and *n*-propylamine by this method.

Chart I

	Found	Actual
Wt of amine hydrochlorides, g	0.3400	0.3407
Wt of NH_4Cl after ion exchange, g	0.3047	0.3071
NH_3, mmol	3.22	3.34
CH_3NH_2, mmol	2.50	2.40
Total mmoles of amines	5.72	5.74
CH_3NH_2, %	44	42

Methyl alcohol was identified as a product of the methyl azide-chromium(II) reaction by gas chromatography. Assay was achieved by distilling the alcohol from the acidic reaction solution and titrating by cerium(IV) oxidation procedure.[17,18] Except for the ethyl azide system, the alcohol product in the remaining organic azide-chromium(II) reactions was not characterized or assayed.

The chromium(III) product separation in the reduction of methyl and ethyl azide by a mixture of chromium(II) and vanadium(II) was facilitated by oxidation of the vanadium in the spent reaction solution to a mixture of VO^{2+} and VO_2^+ with chlorate ion.[3c]

Complex ions of the formula $Cr(RNH_2)^{3+}$ are produced in the organic azide-chromium(II) reactions. Since these have not been synthesized previously, their absorption spectra were measured. The reactions were conducted in the presence of sufficient chloride ion to eliminate the $CrNH_3^{3+}$ and $Cr(NR)Cr^{4+}$ products, and the desired complex was isolated by ion exchange.

Kinetic Studies. The rates of the reduction of methyl, ethyl, and *n*-propyl azide by chromium(II) were monitored spectrophotometrically with a Zeiss PMQ-II instrument equipped with a thermostated (±0.1 °C) sample compartment. Oxygen was removed by continuously flushing the entire sample compartment with tank CO_2 and the reaction cuvette containing the desired solution, except for the reactants with CO_2 that had passed through a chromium(II) trap. After temperature equilibration and deoxygenation, an aliquot of chromium(II) was added and the absorbance noted. The reaction was initiated by injection of the organic azide solution. Rapid mixing (<1 s) was achieved by means of a magnetic stirring device. The alkyl azide stock solutions were assayed prior to, during, and after a series of kinetic experiments to minimize concentration uncertainties due to volatilization. The reactions were monitored at or near 270 nm, where the predominant absorbance change is due to formation of $Cr(NR)Cr^{4+}$. Bubble formation due to the N_2 product was negligible over the concentration range utilized, but precluded observation in the visible region where more concentrated solutions are required.

Table I. Chromium(III) Product Distribution of the Soluble RN_3-Cr^{2+} Reactions in Perchloric Acid Solution

		(Millimoles of product)/(Millimoles of azide consumed)		
Azide[a]	$[HClO_4]_0$, M[b]	Cr^{3+}	$CrNH_3^{3+}$ + $Cr(RNH_2)^{3+}$	$Cr(NR)Cr^{4+}$
HN_3	2.0	0.94	0.90	0.08
HN_3	0.50	0.88	0.90	0.11
CH_3N_3	2.0	1.06	0.76	0.09
CH_3N_3[c]	2.0	1.08	0.70	0.11
CH_3N_3[d]	2.0	1.10	0.70	0.10
CH_3N_3	1.2	1.00	0.70	0.15
CH_3N_3	0.50	0.86	0.66	0.24
CH_3N_3[e]	0.20	0.76	0.54	0.34
$C_2H_5N_3$	2.0	0.96	0.92	0.06
$C_2H_5N_3$	0.80	0.84	0.80	0.18
n-C_3H_7-N_3[f]	2.0	0.96	0.80	0.11

[a] Conditions: 25 °C, $[RN_3]_0 = 0.14$ M, $[Cr^{2+}]_0 = 0.22$ M unless otherwise indicated. [b] One millimole of H^+ is consumed per millimole of Cr^{2+} that is oxidized. [c] $[CH_3N_3]_0 = 0.028$ M, $[Cr^{2+}]_0 = 0.044$ M. [d] $[CH_3N_3]_0 = 0.080$ M, $[Cr^{2+}]_0 = 0.20$ M. [e] $[CH_3N_3]_0 = 0.028$ M, $[Cr^{2+}]_0 = 0.044$ M. [f] This reaction was partially heterogeneous.

The vanadium(II) reduction of ethyl azide is quite slow and experimentally difficult to measure. An estimate of the second-order rate constant for this reaction was obtained from initial rate data collected at 271 nm.

Results

Stoichiometric Results of the Reduction of Organic Azides by Chromium(II). The reactions of the moderately soluble organic azides proceeded rapidly in perchloric acid solution with the evolution of a gas and the formation of various chromium(III) products. Analysis of the reaction mixture indicated that the organic azide is reduced quantitatively to an amine and nitrogen gas as the chromium(III)/amine ratio was 2.0 ± 0.1, as was observed with hydrazoic acid.[4] The amine product contained both the corresponding organic amine and ammonia and was found both as protonated ions and coordinated to chromium(III). Three types of chromium(III) species were produced: (1) hexaaquochromium(III), (2) chromium(III) complexes containing one ammonia or organic amine ligand, and (3) a dimeric chromium(III) species containing one organic amine ligand. These results are summarized in Table I.

The stoichiometric results were independent of the mixing procedure, which was either conventional or utilized the mixing chamber of a stopped-flow apparatus. The product distribution also was insensitive to the concentrations of the reactants. The results for hydrazoic acid are in good agreement with those previously reported[4] for much lower reactant concentrations.

The distribution of the organic amine and ammonia among the reaction products is summarized in Table II. The relative amounts of RNH_3^+ and NH_4^+, and $Cr(RNH_2)^{3+}$ and $CrNH_3^{3+}$ in the red monomeric chromium(III) fraction were independent of the $[H^+]$. The percentage of the organic amine product in the reaction mixture increased with decreasing $[H^+]$. This is a direct result of increased dimer production at lower $[H^+]$; the dimeric product contained only the organic

Table II. Amine Product Distribution of the Soluble RN_3-Cr^{2+} Reactions in Perchloric Acid Solution

Azide[a]	% RNH_2, reaction mixture[b]	Millimoles of product/millimoles of azide consumed[c]					
		NH_4^+	RNH_3^+	$CrNH_3^{3+}$	$Cr(RNH_2)^{3+}$	$Cr(NR)Cr^{4+}$	ROH
CH_3N_3	70	0.12	0.03	0.15	0.61	0.09	0.27
$C_2H_5N_3$	50	0.00	0.02	0.52	0.40	0.06	0.52
n-$C_3H_7N_3$	70	0.01	0.08	0.32	0.48	0.11	

[a] Conditions: 25 °C, $[RN_3]_0 = [Cr^{2+}]_0 = 0.14$ M, and $[HClO_4]_0 = 2.0$ M. [b] Entry ≡ (mmol of $RNH_2 \times 10^2$)/(mmol of RNH_2 + mmol of NH_3) as determined for the reaction mixture. [c] The remaining chromium(III) product is Cr^{3+}.

Table III. Effect of Added Anions on the Product Distribution of the Soluble RN_3-Cr^{2+} Reactions

Azide[a]	Added anion,[b] X^-	Millimoles of product/millimoles of azide consumed			
		CrX^{2+}	Cr^{3+}	$Cr(RNH_2)^{3+}$	$Cr(NR)Cr^{4+}$
CH_3N_3[c]	0.05 M Cl^-	0.54	0.58	0.78	0.05
CH_3N_3	0.50 M Cl^-	1.00	0.00	1.00	0.00
CH_3N_3[d]	0.50 M Cl^-	0.98	0.00	1.02	0.00
CH_3N_3	1.0 M Cl^-	0.98	0.00	1.02	0.00
CH_3N_3	0.50 M Br^-	0.98	0.00	1.02	0.00
CH_3N_3	1.0 M HSO_4^-	e	0.54	0.44	0.07
$C_2H_5N_3$	0.50 M Cl^-	0.82	0.36	0.82	0.00
$C_2H_5N_3$	1.0 M Cl^-	0.88	0.18	0.94	0.00
n-$C_3H_7N_3$	0.50 M Cl^-	1.00	0.00	1.00	0.00
n-$C_3H_7N_3$	1.0 M Cl^-	0.94	0.14	0.92	0.00

[a] Conditions: 25 °C, $[RN_3]_0 = 0.12$-0.20 M, $[Cr^{2+}]_0 = 0.20$-0.25 M, and $[H^+]_0 = 2.0$ M ($HClO_4$ for $X^- = Br^-$, $HClO_4 + H_2SO_4$ for $X^- = HSO_4^-$, and $HClO_4$ + HCl for $X^- = Cl^-$) unless otherwise indicated. [b] Br^- furnished by the sodium salt. [c] $[CH_3N_3]_0 = 0.124$ M, $[Cr^{2+}]_0 = 0.190$ M. [d] $[H^+]_0 = 0.50$ M. [e] Three bands of chromium(III) species with charge $\leq +2$ were observed. The total chromium(III) in these bands was 0.88 mmol.

amine ligand. Material balance requires another product containing the alkyl group; where tested, this was found to be ROH as shown in Table II.

In the presence of several added anions the chromium(III)/amine ratio was still 2.0 ± 0.1, but the product distribution was dramatically altered. These data are summarized in Table III. RNH_2 was the only amine product when stoichiometric excesses of Cl^-, Br^-, and HSO_4^- were present; the average percent yield of RNH_2 in the reaction mixture was 101 ± 5 for all the entries except the first. The first entry shows essentially quantitative Cl^- incorporation into the $CrCl^{2+}$ product. Excess Br^- and Cl^- completely suppress the production of the dimeric species and eliminate Cr^{3+} as a product in the methyl azide system.

The other organic azides studied were not sufficiently soluble to allow homogeneous reaction mixtures. The reactions did proceed slowly to completion with vigorous stirring, and the product distribution was reproducible. Stoichiometric data collected on these systems are summarized in Table IV. Phenyl azide was the oxidant that gave a Cr(III)/amine ratio of 2.0 in perchloric acid solution. Only for n-butyl and n-pentyl azide did this ratio become 2.0 ± 0.1 even in the presence of excess Cl^-. No C–N bond cleavage occurred for phenyl and cyclohexyl azide in perchloric acid solution; this feature obtained for the other azides only with excess Cl^- present. Apparently only when a Cr(III)/amine ratio of 2.0 was found was the "monomeric amine chromium(III)" product a true 1:1 complex. In the absence of added Cl^-, all the organic azides except phenyl azide apparently produced a dimeric chromium(III) species, but attempts to cleanly separate this product were unsuccessful.

Other Reactions of the Soluble Organic Azides. Cr(VI) (0.010 M), HNO_2, or BrO_3^- failed to react with 0.010 M CH_3N_3 in 2 M $HClO_4$ at 25 °C over a 10-min time period. Co^{3+} was only partially reduced under the same conditions. Eu(II) and Ti(III) reacted with CH_3N_3 very slowly. Amalgamated zinc, aluminum, and V(II) reduced both methyl and ethyl azide to the organic amine; no C–N bond breaking was detected. The second-order rate constant for the V^{2+}–$C_2H_5N_3$ reaction was determined to be ca. 0.04 $M^{-1}\ s^{-1}$ in 2.0 M $HClO_4$ at 20 °C. Experiments monitored at 425 nm, an absorption maximum for VOV^{4+}, indicated that only traces of this dimer are formed. This result indicates that V(II) acts as a one-equivalent reductant in this reaction.[19]

A mixture of Cr(II) and V(II), with $[V(II)]_0/[Cr(II)]_0 = 5$-8, was used to reduce methyl and ethyl azide. Also, a mixture of Cr(II) and Eu(II), with $[Eu(II)]_0/[Cr(II)]_0 = 6$-$16$, was used to reduce ethyl and propyl azide. The results of these experiments are summarized in Table V.

Absorption Spectra of $Cr(RNH_2)^{3+}$ Complexes. The reduction of organic azides by chromium(II) in the presence of excess chloride ions allows a convenient isolation of solutions of $Cr(RNH_2)^{3+}$ complexes by ion exchange separation. The absorption maxima of the pure complexes obtained in this study are summarized in Table VI.

Chromium(II)-Catalyzed Aquation of $Cr(C_6H_5NH_2)^{3+}$. Chromium(II) was found to catalyze the aquation of $Cr(C_6H_5NH_2)^{3+}$. The complex disappeared by a first-order process, but the rate parameter increased with increasing $[Cr^{2+}]_0$ according to the expression

$$-d[Cr(C_6H_5NH_2)^{3+}]/dt = (k_1 + k_2[Cr^{2+}]_0)[Cr(C_6H_5NH_2)^{3+}] \quad (3)$$

At 25 °C, 1.0 M $HClO_4$, $[Cr(C_6H_5NH_2)^{3+}]_0 = (4.96$-$5.61) \times 10^{-4}$ M and $[Cr^{2+}]_0 = 0.052$-0.161 M, values of $k_1 = 2 \times 10^{-6}\ s^{-1}$ and $k_2 = 4 \times 10^{-4}\ M^{-1}\ s^{-1}$ were determined. This catalysis is rapid enough to affect the stoichiometric results obtained for the $C_6H_5N_3$-Cr^{2+} reaction and possibly the $C_6H_5NH_2OH^+$-Cr^{2+} reaction (vide infra).

Table IV. Product Distribution of the Slightly Soluble RN_3-Cr^{2+} Reactions in Perchloric Acid and with Added Cl^-

	Reaction mixture		Fraction of total Cr(III) produced in each species[c]			
Azide[a]	Cr(III)/amine	% RNH_2[b]	$CrCl^{2+}$	Cr^{3+}	"$Cr(RNH_2)^{3+}$"[d]	
n-$C_4H_9N_3$	2.4	70	0.00	0.43		(1.23)
n-$C_4H_9N_3$, 0.5 M Cl^-	2.2	108	0.51	0.00	0.49	
n-$C_4H_9N_3$, 1.0 M Cl^-	2.0	104	0.48	0.07	0.45	
n-$C_5H_{11}N_3$	2.4	80	0.00	0.44		(1.13)
n-$C_5H_{11}N_3$, 0.5 M Cl^-	2.1	101	0.41	0.15	0.44	
n-$C_5H_{11}N_3$, 1.0 M Cl^-	2.1	94	0.45	0.13	0.42	(1.05)
n-$C_6H_{13}N_3$	2.4	65	0.00	0.64		(1.23)
n-$C_6H_{13}N_3$, 0.5 M Cl^-	2.3	99	0.39	0.25		
n-$C_6H_{13}N_3$, 1.0 M Cl^-	3.1	100	0.45	0.13		
$C_6H_{11}N_3$[e]	2.7	100	0.00	0.61		(1.54)
$C_6H_{11}N_3$, 0.5 M Cl^-	2.3	100	0.33	0.30		(1.38)
$C_6H_{11}N_3$, 1.0 M Cl^-	3.1	96	0.41	0.30		
$C_6H_5N_3$[f]	2.0	100	0.00	0.68	0.32	(0.98)
$C_6H_5N_3$, 0.5 M Cl^-	2.0	99	0.15	0.53	0.32	
$C_6H_5N_3$, 1.0 M Cl^-	2.1	98	0.18	0.48	0.34	

[a] Conditions: 25 °C, $[Cr^{2+}]_0$ ca. 0.40 M and excess RN_3, $[H^+]_0 = 2.0$ M. [b] Entry ≡ (mmol of $RNH_2 \times 10^2$)/(mmol of RNH_2 + mmol of NH_3). [c] Entry ≡ (Cr(III) in species)/(total Cr(III) produced). This change in data presentation is due to Cr(III)/amine ≠ 2.0 in some cases. [d] The experimental Cr(III)/amine ratio for this fraction is indicated in parentheses where determined. [e] Cyclohexyl azide. [f] Phenyl azide.

Table V. Stoichiometric Results for the Reduction of the Soluble Organic Azides by V(II), Cr(II) and Eu(II), Cr(II) Mixtures[a]

			F[b]		Reaction mixture	
Azide	$[V(II)]_0/[Cr(II)]_0$	$[Eu(II)]_0/[Cr(II)]_0$	Cr^{3+}	$Cr(RNH_2)^{3+}$	Cr(III)/amine	% RNH_2[c]
CH_3N_3[d]	5.2		0.44	0.56	0.97	101
CH_3N_3		11.9	0.08	0.92	0.65	91
$C_2H_5N_3$[d]	7.6		0.66	0.34	0.91	95
$C_2H_5N_3$	5.1		0.67	0.33		
$C_2H_5N_3$		15.8	0.25	0.75	0.95	96
$C_2H_5N_3$		6.1	0.22	0.78	1.09	104
n-$C_3H_7N_3$		8.1	0.32	0.68	1.28	93

[a] Conditions: 25 °C, $[Cr^{2+}]_0 = 0.038$-0.076 M, $[V^{2+}]_0 = 0.27$ M, $[Eu^{2+}]_0 = 0.46$-0.61 M. $[RN_3]_0 > [Cr^{2+}]_0$ unless otherwise indicated. [b] F ≡ (mmol of Cr(III) product)/(total mmol of Cr(III)). [c] Entry ≡ (mmol of $RNH_2 \times 10^2$)/(mmol of RNH_2 + mmol of NH_3). [d] $[RN_3]_0 = [Cr^{2+}]_0 = 0.0127$ M.

Table VI. Absorption Maxima of $Cr(RNH_2)^{3+}$ Complexes at 25 °C

R	λ_{max}, nm (ϵ, M^{-1}, cm^{-1})
H[a]	545 (22.1), 397 (21.8)
CH_3	546 (21.4), 397 (21.7)
C_2H_5	547 (22.6), 396 (23.1)
n-C_3H_7	547 (23.6), 398 (24.8)
n-C_4H_9	548 (23.5), 398 (24.5)
n-C_5H_{11}	555 (20.8), 404 (22.8)
C_6H_5	562 (33.2), 399 (37.8), 251 (4600)

[a] Reference 5.

Stoichiometry of the Reduction of N-Organohydroxylamines by Chromium(II). The products of the reduction of several N-organohydroxylamines by chromium(II) were analyzed, and the results are summarized in Table VII. The excess Cr^{2+} was oxidized with O_2 to produce a dimeric Cr(III) species[20a] at the conclusion of the reaction. In the presence of 1 M Cl^- under our experimental conditions, ca. 22% $CrCl^{2+}$ and 19% Cr^{3+} are also formed. Small corrections to the stoichiometric data were made for this contribution.

The results for NH_3OH^+ differ in two respects from those reported earlier.[7a] First, a small amount of $CrNH_3{}^{3+}$ was observed. Second, in the presence of 1 M Cl^-, substantial amounts of $CrCl^{2+}$ are formed. The earlier study used much smaller $[Cl^-]$ and did not report any $CrCl^{2+}$ product.

Essentially no C-N bond breaking was found in the reduction of the N-organohydroxylamines except for N-ethylhydroxylamine, where the cleavage was nearly complete. The presence of ethyl alcohol in the latter reaction solutions was qualitatively demonstrated.

Kinetic Studies of the Reduction of the Soluble Organic Azides by Chromium(II). The kinetic experiments were monitored at 270 nm, where the dimeric chromium(III) product, $Cr(NR)Cr^{4+}$, is the principal absorbing component. The data obeyed the empirical rate expression 4 adequately for at least 80% reaction:

$$-d[RN_3]/dt = k_0[RN_3][Cr^{2+}] \qquad (4)$$

A summary of the k_0 values determined for the soluble organic azides over a variety of conditions is presented in Table VIII. Since the yield of the dimeric product decreased with increasing $[H^+]$ and $[Cl^-]$, the viable range of the concentrations of these ions was severely limited. Attempts to monitor the reaction in the visible region (where all the chromium(III) reaction products absorb) were unsuccessful due to bubble formation at the higher reactant concentrations required.

No $[H^+]$ dependence was detected for the CH_3N_3 system, but an apparent slight inverse dependence was observed for the other two azides. Only at high ionic strengths was an effect of

Table VII. Stoichiometric Results for the Reduction of *N*-Organohydroxylamines, RNH_2OH^+, by Chromium(II)[a]

		Millimoles of product/millimoles of hydroxylamine consumed			Reaction mixture	
R	$[Cl^-]_0$, M	$CrCl^{2+}$	Cr^{3+}	$Cr(RNH_2)^{3+}$	Cr(III)/amine	% RNH_2[b]
H[c]	0	0.00	1.70	0.08		
H[c]	1.0	0.96	0.98	0.06		
CH_3	0	0.00	1.84	0.16	2.1	95
CH_3	1.0	0.66	1.34	0.00	2.1	95
C_2H_5	0.05	0.26	1.66	0.08	1.9	4
C_2H_5	1.0	0.94	1.06	0.00	2.0	8
n-C_3H_7[d]	0	0.00	1.77	0.04	2.0	94
n-C_3H_7[d]	1.0	0.60	1.28	0.00	2.0	93
C_6H_5	0	0.00	2.00	0.00	2.1	95
C_6H_5	1.0	0.70	1.30	0.00	1.9	93

[a] Conditions: 25 °C, $[Cr^{2+}]_0 = 0.16–0.25$ M, $[RNH_2OH^+]_0 = 0.064–0.072$ M, and $[H^+]_0 = 2.0$ M. [b] Entry ≡ (mmol of $RNH_2 \times 10^2$)/(mmol of RNH_2 + mmol of NH_3). [c] The remaining Cr(III) product is presumably $Cr(OH)_2Cr^{4+}$, as was reported earlier.[7a] [d] An unidentified orange band containing ca 7% of the total Cr(III) produced in the reaction eluted after the Cr^{3+} but before the $Cr(n\text{-}C_3H_7NH_2)^{3+}$ in the ion exchange separation of these reaction mixtures.

Table VIII. Kinetic Results of the Reduction of the Soluble Organic Azides by Chromium(II)[a]

Azide	$[HClO_4]$, M	T, °C	k_0, $M^{-1}\,s^{-1}$
CH_3N_3[b]	0.049	20.1	14.6 ± 0.8
	0.10	20.2	14.6 ± 1.0
	0.20	20.1	14.7 ± 0.1
	0.30	20.0	14.6 ± 0.8
	0.49	20.0	14.5 ± 0.2
$I = 0.17$ M[c]	0.10	20.2	15.7 ± 1.1
$I = 0.16$ M	0.10	20.2	14.6 ± 0.8
$I = 0.53$ M	0.10	20.3	14.5 ± 0.6
$I = 1.5$ M	0.10	20.1	13.5 ± 0.5
$I = 2.0$ M	0.10	20.4	9.5 ± 1.4
	0.10	15.2	12.2 ± 0.1
	0.10	10.4	11.2 ± 0.5
	0.10	4.8	9.4 ± 0.7
$[Cl^-]_0 = 8.9 \times 10^{-3}$ M	0.051	5.3	10.5 ± 0.2
$[Cl^-]_0 = 4.2 \times 10^{-2}$ M	0.051	5.1	15.8 ± 0.3
$C_2H_5N_3$[d]	0.048	20.2	3.6 ± 0.1
	0.20	20.3	3.3 ± 0.1
$[Cl^-]_0 = 4.8 \times 10^{-2}$ M	0.048	20.2	5.3 ± 0.3
	0.049	13.1	3.2 ± 0.1
	0.050	4.3	2.7 ± 0.1
n-$C_3H_7N_3$[e]	0.050	20.0	2.6 ± 0.1
	0.20	20.0	2.3 ± 0.1
	0.49	20.3	2.1 ± 0.1
$[Cl^-]_0 = 4.4 \times 10^{-3}$ M	0.049	20.2	3.8 ± 0.1
	0.051	13.2	2.2 ± 0.1
	0.051	5.2	2.0 ± 0.1

[a] Monitored at 270 nm, $I = 1.0$ M ($LiClO_4$) unless otherwise indicated. Uncertainties in k_0 are average deviations of three determinations. [b] $[CH_3N_3]_0 = (0.64–2.11) \times 10^{-3}$ M, $[Cr^{2+}]_0 = (1.20–3.00) \times 10^{-3}$ M. [c] Monitored at 286 nm. [d] $[C_2H_5N_3]_0 = (1.44–2.28) \times 10^{-3}$ M, $[Cr^{2+}]_0 = (1.00–1.97) \times 10^{-3}$ M. [e] $[n\text{-}C_3H_7N_3]_0 = (0.97–1.14) \times 10^{-3}$ M, $[Cr^{2+}]_0 = (0.74–1.53) \times 10^{-3}$ M.

this variable found on the rate parameter for CH_3N_3. All the reactions exhibited $[Cl^-]$ catalysis; this effect on k_0 for CH_3N_3 at 5 °C can be summarized by

$$k_0 = 9.4\ M^{-1}\,s^{-1} + 1.4 \times 10^2\ M^{-2}\,s^{-1}\,[Cl^-] \qquad (5)$$

The infinite absorbance of the reaction solutions, A_∞, and the apparent molar absorptivity of the products, $\bar{\epsilon} = A_\infty/(l \times [Cr(III)]_\infty)$ are proportional to the yield of $Cr(NR)Cr^{4+}$ since the absorptivity of this species dominates that of the other reaction products at 270 nm. The stoichiometric studies showed that the yield of the dimeric product decreased with increasing $[H^+]$; this result was confirmed indirectly by the kinetic studies. For example, at 20 °C the values of $\bar{\epsilon}$ for the CH_3N_3 system were 343, 259, 178, 138, and 107 $M^{-1}\,cm^{-1}$ at $[H^+] = 0.05$, 0.10, 0.20, 0.30, and 0.50 M, respectively. It was also observed that the values of $\bar{\epsilon}$ were sensitive to temperature. For example, for the CH_3N_3 system at 0.10 M $[H^+]$, values of $\bar{\epsilon}$ were 259, 211, 167, and 127 $M^{-1}\,cm^{-1}$ at 20, 15, 10, and 5 °C, respectively. The molar absorptivity of the dimeric product was demonstrated to vary only slightly with temperature. Therefore, the yield of the dimeric product decreases with decreasing temperature. A plot of ln $\bar{\epsilon}$ as a function of $1/T$ (K) was linear for all these organic azides at constant $[H^+]$.

Discussion

A plausible reaction scheme that is consistent with most of the data presented is very similar to that proposed by Linck[4b] for the reaction of HN_3 with Cr^{2+}.

$$RN_3 + Cr^{2+} \xrightarrow{k_0} Cr\overset{R}{N}N_2{}^{2+} \qquad (6)$$

$$Cr\overset{R}{N}N_2{}^{2+} \xrightarrow{H^+} Cr\overset{R}{N}H^{3+} + N_2 \qquad (7)$$

$$Cr\overset{R}{N}H^{3+} + Cr^{2+} \longrightarrow Cr(NR)Cr^{4+} + H^+ \qquad (8)$$

$$Cr\overset{R}{N}H^{3+} + Cr^{2+} \xrightarrow{H^+} Cr(RNH_2)^{3+} + Cr^{3+} \qquad (9)$$

$$Cr\overset{R}{N}N_2{}^{2+} + Cl^- \longrightarrow CrNR(Cl)^+ + N_2 \qquad (10)$$

$$CrNR(Cl)^+ + Cr^{2+} \xrightarrow{H^+} Cr(RNH_2)^{3+} + CrCl^{2+} \qquad (11)$$

The absence of any $Cr(NH)Cr^{4+}$ product and the substantial yields of $Cr(RNH_2)^{3+}$ require considerable inner-sphere attack by the Cr^{2+} at the N bonded to the organic group. That this attack occurs primarily in the rate-determining step is supported by the results that $Cr(NR)Cr^{4+}$ is the only dimeric product, but can be eliminated by the presence of sufficient Cl^-. Further, substantial amounts of $Cr(RNH_2)^{3+}$ are produced at high $[Cl^-]$ while no $CrNH_3{}^{3+}$ is observed. Other data pertinent to this point will be considered later. Reactions 7-11 are speculative but are consistent with the following stoichiometric data: (1) The dimeric product is formed in increased yields as the $[H^+]$ is decreased, (2) the yield of the dimeric product is independent of the $[Cr^{2+}]$, and (3) considerable Cr^{3+} is produced in perchloric acid solution, but in the presence of sufficient Cl^- considerable $CrCl^{2+}$ is formed instead along with no dimeric product.

A closer inspection of the data reveals that the reaction scheme is oversimplified. First, some C–N bond cleavage occurs for all the azides tested (except $C_6H_5N_3$ and $C_6H_{11}N_3$) in perchloric acid, but not in the presence of sufficient Cl^-. This suggests that an intermediate, presumably $Cr(RNH)^{3+}$, is attacked by Cr^{2+} in a path parallel to that shown in eq 9, that cleaves the N–R bond to produce $CrNH_3^{3+}$, ROH, and Cr^{3+}. At high $[Cl^-]$, this parallel path is eliminated by reaction 10. Second, some uncoordinated amine products are found for all the organic azides studied. In addition, some Cr^{3+} is formed in most of the systems even at high $[Cl^-]$. A path parallel to that shown in eq 6 to produce Cr^{3+} and RNH_2^+ is consistent with these observations.

The nature of the intermediates $Cr(RNH)^{3+}$ and RNH_2^+ appears to be that of an amino radical. Other possibilities are coordinated nitrene or imido complexes, and free nitrenes or imides.[21] Convincing evidence has been presented for the formation of coordinated nitrenes in the acid-catalyzed decomposition of $(NH_3)_5RuN_3^{2+}$ and $(NH_3)_5IrN_3^{2+}$.[22,23] However, in the present systems reduction of the organic azide is required to form the stable Cr–N bond, thus ruling out the formation of a coordinated nitrene. A Cr^{2+} catalyzed decomposition of the organic azides to produce a free nitrene seems unlikely in view of the strong reducing ability of the reductant. The initial formation of a coordinated imido complex, $CrNR^{2+}$, is in principle indistinguishable from our formulation of a coordinated amino complex, but would require the chromium to be in the strongly oxidizing and labile[24] 4+ oxidation state. Finally, the initial formation of a free imide, RN^{2-}, would require a two-equivalent step to produce Cr(IV). Available data[20] indicate that Cr(IV) should be reduced by Cr^{2+} to produce $Cr(OH)_2Cr^{4+}$; this product is not found.

Free or protonated amino radicals have been postulated as intermediates in the reduction of hydroxylamines by Cr^{2+}, Ti^{3+}, and $e^-_{(aq)}$.[7,25] We have suggested the formation of the same intermediates in a minor, parallel path to that shown in eq 6. In order to gain insight into the fate of these species in the presence of chromium(II), the stoichiometry of the chromium(II) reduction of several *N*-organohydroxylamines was studied.[26] With the proviso that the initial step is as shown below:

$$RNH_2OH^+ + Cr^{2+} \xrightarrow{H^+} RNH_2^+ + Cr^{3+} + H_2O \quad (12)$$

the following conclusions can be drawn from the data in Table VII. First, the attack of Cr^{2+} at the nitrogen of RNH_2^+ to produce $Cr(RNH_2)^{3+}$ is only a minor pathway and is eliminated in the presence of sufficient Cl^-.[27] This result lends support to our proposal that the formation of the Cr–N bond occurs primarily in the initial step of the RN_3-Cr^{2+} reactions. Second, substantial trapping of the amino radicals by Cl^- occurs as evidenced by significant yields of $CrCl^{2+}$ and the absence of $Cr(RNH_2)^{3+}$ at high $[Cl^-]$. The previous suggestion[4b] that protonated amino radicals are weaker oxidants than when coordinated to chromium(III) is consistent with no $CrCl^{2+}$ formation in the NH_3OH^+-Cr^{2+} reaction at low $[Cl^-]$,[7a] but the present results indicate that RNH_2^+ and NH_3^+ can be effectively trapped by higher $[Cl^-]$. Third, except for $C_2H_5NH_2OH^+$, little or no C–N bond rupture occurs.[28] This result is consistent with our suggestion that this bond cleavage in the RN_3-Cr^{2+} systems occurs as a result of one path in the $Cr(RNH)^{3+}$-Cr^{2+} reaction. Finally, the free amine product in the RN_3-Cr^{2+} reactions for R = C_2H_5, C_3H_7, and C_6H_5 is primarily RNH_3^+. The origin of this product was suggested to be a minor pathway in the initial attack of Cr^{2+} to produce RNH_2^+. The *N*-organohydroxylamine data are consistent with this radical oxidizing Cr^{2+} to form RNH_3^+. Our reaction scheme is inconsistent in this regard, however, with the presence of substantial NH_4^+ in the free amine product in the CH_3N_3-Cr^{2+} reaction.

Table IX. Activation Parameters for the Chromium(II) Reduction of Azides

Azide	ΔH^*, kcal/mol	ΔS^*, cal/deg mol	Ref
HN_3	7.1 ± 0.8	−29 ± 3	4b
HN_3	4.6 ± 0.6	−36 ± 2	32
CH_3N_3	3.9 ± 0.5	−40 ± 4	This work
$C_2H_5N_3$	2.2 ± 0.1	−49 ± 2	This work
n-$C_3H_7N_3$	2.5 ± 0.6	−48 ± 8	This work

Another series of experiments designed to test the proposed reaction scheme utilized a mixture of reducing agents, V^{2+} plus Cr^{2+} and Eu^{2+} plus Cr^{2+}, for the organic azides. The goal was to find conditions where Cr^{2+} competed favorably in the first step, but the other reducing agent competed favorably in the subsequent reduction of the intermediate produced. If this goal were realized, our reaction scheme would predict no C–N bond cleavage, substantial $Cr(RNH_2)^{3+}$ and some Cr^{3+} as the only Cr(III) products, and a Cr(III)/amine ratio of 1.0. The data in Table V are not convincing confirmation of the proposed reaction scheme. Little or no C–N bond cleavage was observed for either mixed reduction system. With V^{2+}, the Cr(III)/amine ratio was near 1.0, but the yields of $Cr(RNH_2)^{3+}$ were lower than predicted. The experimental problems are at least twofold. First, the kinetic data allow an estimate of the *initial* ratio: (rate of $C_2H_5N_3$-Cr^{2+})/(rate of $C_2H_5N_3$-V^{2+}) to be ca. 15, but this ratio decreases rapidly as the reaction proceeds under our experimental conditions. Second, $k(C_2H_5N_3$-$Cr^{2+})/k(V^{3+}$-$Cr^{2+})$ is ca. 6, indicating that appreciable Cr^{3+} will be formed via the V^{3+}-Cr^{2+} reaction.[29,30] The ratios $k(RN_3$-$Cr^{2+})/k(RN_3$-$Eu^{2+})$ and $k(RN_3$-$Cr^{2+})/k(Eu^{3+}$-$Cr^{2+})$ are much more favorable,[31] and the experimental results for this mixture of reductants (Eu^{2+} + Cr^{2+}) are more closely in accord with the predicted values.

The kinetic data for the RN_3-Cr^{2+} reactions provide only limited mechanistic information. The empirical rate laws are consistent with reaction 6, but, of course, do not identify the intermediates. Relevant activation parameters are tabulated in Table IX. All the reactions are characterized by low activation enthalpies and large, negative activation entropies. This feature is not inconsistent with the predominantly innersphere attack of Cr^{2+} at the nitrogen adjacent to the organic group in the azide in the rate-determining step.

The observed chloride ion catalysis of the RN_3-Cr^{2+} reactions requires comment.[33] As Linck has stated, "To argue that $CrCl^{2+}$ arises from a nonbridging ligand effect of Cl^- on the reductant assigns too great a rate-enhancing ability of $CrCl^+$ over Cr^{2+} . . . ". Indeed, our reaction scheme incorporates a completely different mode of $CrCl^{2+}$ formation. Nevertheless, the kinetic data require chloride catalysis in the rate-determining step of the present systems. It may be that the presence of chloride ion in the solvation sphere of the organic azide promotes attack by chromium(II). If so, a Cr–Cl bond must not be formed prior to the initial electron-transfer reaction according to the proposed reaction scheme.

The kinetic results demonstrated a temperature dependence of $\bar{\epsilon}$ which was proportional to the dimer ($Cr(NR)Cr^{4+}$) yield. The reaction scheme requires (in the absence of Cl^-) that the various reaction paths for the $Cr(RNH)^{3+}$ intermediate, only one of which produces the dimer, be of the same order in Cr^{2+}. Therefore, the following equations should be valid:

$$\bar{\epsilon} = k(\text{reaction } 8)/k(\text{reaction } 9) = k_8/k_9 \quad (13)$$

and

$$\ln \bar{\epsilon} = A - B/T\ (\text{K}) \quad (14)$$

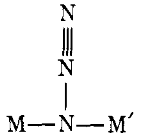
where $A = (\Delta S^*_8 - \Delta S^*_9)/R$ and $B = (E_{a,8} - E_{a,9})/R$. The observed linearity of plots of $\ln \bar{\epsilon}$ as a function of $1/T$ (K) is consistent with this prediction.

A very limited number of $Cr(RNH_2)^{3+}$ complexes have been previously synthesized.[4a,34] The present results indicate that the RN_3-Cr^{2+} reaction in 1–2 M HCl followed by an ion exchange separation holds promise as a general method of preparing solutions of these complexes. Apparently a Cr(III)/amine ratio of 2.0 is sufficient to establish the purity of the product thus isolated, though for new preparations the purity of the monoamminechromium(III) should be checked directly.

The azide ion is a very good bridging ligand in electron-transfer reactions.[35] It is widely assumed that structure I rather

$$M—N{=}N{=}N—M'$$

I



$$M—\overset{\overset{\displaystyle N}{|||}}{\underset{}{\overset{\displaystyle N}{|}}}{N}—M'$$

II

than II is the geometrical configuration. However, several structural studies on species containing the azido group as a bridge between two metal ions have shown that the bridging occurred through a single atom of the azide ligand.[36] In the present study, substantial evidence was presented that indicated attack of Cr^{2+} on the azide nitrogen adjacent to the organic group in the reduction of organic azides. These results suggest to us that structure II should be reconsidered as a possibility in azide bridging reactions.

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(27) $CrNH_3{}^{3+}$ was not observed previously[7a] as a product of the NH_3 OH^+–Cr^{2+} reaction. However, the detection of small amounts of this species in the presence of Cr^{3+} and $Cr(OH)_2Cr^{4+}$ requires a very slow ion exchange separation and could have been missed.

(28) We do not understand why this bond rupture is nearly complete in the $C_2H_5NH_2OH^+$–Cr^{2+} reaction, but it should be noted that C–N bond breaking in the azide systems was most extensive for $C_2H_5N_3$.

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