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Ligand Capture in Reductions of Chromium(VI)

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The capture of ligands by Cr(III) in reductions of Cr(VI) has been investigated. The distribution of coordinated Cr(III) products has been determined as a function of proton and ligand concentrations. The results are interpreted in terms of probable fates of reactive Cr(IV) and Cr(V) intermediates.

The capture of ligands in the substitution-inert coordination sphere of Cr(III) is well known.[2-4] Reductions of Cr(VI) proceed through reactive Cr(IV) and Cr(V) intermediates both of which should be labile to ligand substitution; hence ligand capture is a direct result of the reduction steps producing Cr(III). A variety of mechanisms have been proposed for reductions of Cr(VI) involving combinations of one-, two-, and three-electron elementary processes.[5] One distinguishing feature of these alternative mechanisms is the extent to which Cr(IV) and Cr(V) participate as the immediate redox precursor of Cr(III). A study of ligand capture in Cr(VI) reductions, initiated under conditions favoring Cr(IV), Cr(V), or both, as the precursor of Cr(III), should provide a basis for distinguishing between several of the mechanisms.

Experimental Section

Analytical grade $Na_2Cr_2O_7 \cdot 2H_2O$ was used as a source of Cr(VI) and standardized iodometrically. Sodium perchlorate and sodium azide were recrystallized from water and hydrazinium perchlorate was prepared from $Ba(ClO_4)_2$ and $N_2H_5HSO_4$ and recrystallized from dilute perchloric acid following concentration on a vacuum solvent evaporator at 40°. Vanadium(IV) perchlorate was prepared from $VOSO_4$ and $Ba(ClO_4)_2$. Other reagents of analytical quality were used without further purification and standardized by well-known means.

Reactions were performed after separately deoxygenating measured quantities of reducing agents and Cr(VI) in a stream of N_2 before mixing the reagents. Where gas was a product, the completed reaction mixture was largely desaturated on a rotary solvent evaporator. Products were quantitatively diluted to a convenient volume and aliquots taken for separation. Separation was accomplished on BioRad resin columns (AG 50X-4 or AG 1X-4). Cation columns were prepared in a mixed Na^+-H^+ form to minimize Cr(III) complex aquation during separation and samples were pushed on the column with *ca.* 1 atm of excess N_2 pressure. Product complexes were eluted with discontinuously increasing concentrations of $NaClO_4$ doped with $HClO_4$ to $[H^+] = ca.\ 0.05\ M$; Cr^{3+} was eluted with acidified 4 *M* NaCl. Anion columns, used in the case of oxalate studies, were prepared in the Cl^- form. Complexes were eluted with NaCl doped with *ca.* 0.05 *M* HCl following an initial rinse with 0.15 *M* HCl to remove unreacted free oxalic acid. Complexes were identified by their absorption spectra and their column elution behavior. Total chromium analysis was performed spectrophotometrically, following alkaline peroxidation. Total phosphorus was determined photometrically[6] and coordinated P(III) was determined iodometrically following hydrolysis at pH 8.[3] In the presence of excess Cr(VI), stoichiometric consumption ratios were evaluated by measuring the CrO_4^{2-} absorption at 372 nm in dilute sodium hydroxide. Excess $N_2H_5^+$ in the presence of oxalate was estimated iodometrically.[7] Excess VO^{2+} in the presence of oxalate was estimated photometrically at 762 nm. To prevent oxalate oxidation by V(V), lead(II) perchlorate was used to precipitate the excess oxalate. The filtrate was placed on a fresh cation-exchange column and the VO^{2+} band was collected in dilute $HClO_4$ for analysis. Acid dissociation quotients for $NaHSO_4$ and H_3PO_3 were determined as described previously[3] at ionic strengths held constant with $NaClO_4$.

Results and Discussion

Generally, the ligands studied reduce Cr(VI) only slowly, if at all. Chromium(VI) reduction was initiated by addition either of VO^{2+}, a fast one-electron reducing agent,[8] or of $N_2H_5^+$, a fast two-electron reducing agent[9] for Cr(VI).

Stoichiometry. As shown in Table I, ligand oxidation occurs in the presence of oxidizable ligands. In the limit of equivalent or excess VO^{2+} initiator, the stoichiometric consumption ratio $Cr(VI):VO^{2+}$ is approximately 0.33 where N_3^-, $H_2PO_3^-$, and SO_4^{2-} are the ligands. In the presence of $C_2O_4^{2-}$, the stoichiometric ratio is considerably larger, indicating that $C_2O_4^{2-}$ competes effectively with VO^{2+} for at least one of the Cr intermediates. Using $N_2H_5^+$ as the reduction initiator, ligand oxidation occurs with all the oxidizable ligands tested.

The redox chemistry of Cr(V), apparently H_3CrO_4 in aqueous acid,[10] appears to be not unlike that of Cr(VI). Chromium(V) is subject either to one- or two-electron reduction depending on the specific reducing agent.[8,9] Chromium(IV) apparently may disproportionate[9]

$$2\mathrm{Cr(IV)} \rightarrow \mathrm{Cr(III)} + \mathrm{Cr(V)} \tag{1}$$

or may be oxidized by Cr(VI)[9,11]

$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \rightarrow 2\mathrm{Cr(V)} \tag{2}$$

or, in the presence of a one-electron oxidizable metal ion or ligand, may be reduced directly to Cr(III).[8,9] If the reducing agent is a ligand, radical intermediates may be produced

$$\mathrm{Cr(IV)} + \mathrm{L}: \rightarrow \mathrm{Cr(III)} + \mathrm{L}\cdot \tag{3}$$

Reactions initiated by $N_2H_5^+$ polymerize acrylonitrile in the presence of N_3^-, or $H_2PO_3^-$, but not in their absence, indicating radical-producing oxidation occurs. Failure to observe polymerization in the presence of oxalate has been interpreted by Hasan and Rocek[5c] in terms of a rapid oxidation of oxalate radicals by Cr(VI)

$$C_2O_4\cdot^- + \mathrm{Cr(VI)} \rightarrow \mathrm{Cr(V)} + 2CO_2 \tag{4}$$

This interpretation is substantiated by our failure to observe acrylonitrile polymerization in the rapid one-electron oxida-

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Table I. Cr(VI) Reduction Stoichiometry

		Cr(VI):initiator	
Ligand source	Concn, *F*	Initial	Consumption
	Initiator: VO^{2+}		
HSO_4^-	0.15	0.35	0.32
HN_3	0.15	0.34	0.32
H_3PO_3	0.15	1.02	0.36
	0.15	0.51	0.35
	0.15	0.40	0.34
$H_2C_2O_4$	0.15	0.40	0.66
	0.15	0.20	0.50
	Initiator: $N_2H_5^+$		
HSO_4^-	0.15	2.00	1.35
HN_3	0.15	1.80	1.52
H_3PO_3	0.15	1.80	1.44
$H_2C_2O_4$	0.15	0.55	1.54
	0.25	0.55	1.60
	0.40	0.55	1.68

Table II. Effect of Initiator on Ligand Capture[a]

Initiator	Ligand	% of product Cr(III)			
	SO_4^{2-}	Cr^{3+}	$CrSO_4^+$		
$N_2H_5^+$		80.2	18.2		
VO^{2+}		58.8	39.4		
	N_3^-	Cr^{3+}	CrN_3^{2+}	$Cr(N_3)_2^+$	
$N_2H_5^+$		73.9	14.6	10.9	
VO^{2+}		28.4	35.4	29.9	
	$H_2PO_3^-$	Cr^{3+}	$CrH_2PO_3^{2+}$	$CrH_2PO_4^{2+}$	
$N_2H_5^+$		49.4	24.5	9.1	
VO^{2+}		6.1	59.3	. . .	
	$C_2O_4^{2-}$	Cr^{3+}	$CrOx^+$	$CrOx_2^-$	$CrOx_3^{3-}$
$N_2H_5^+$		39.4	25.1	32.8	2.7
VO^{2+}		41.4	31.6	26.3	1.7
. . .		50.7	33.2	14.4	1.7

[a] Initial formal concentrations: Cr(VI), 0.01; H^+, 0.15; ligand source, 0.15; VO^{2+}, 0.053; $N_2H_5^+$, 0.018.

tions of oxalate either by Mn(III) or by Ce(IV), when Cr(VI) is present. In the absence of Cr(VI), either Ce(IV) or Mn(III) oxidizes $H_2C_2O_4$ with polymerization of acrylonitrile. Evidently Cr(IV) oxidizes N_3^-, $H_2PO_3^-$, and $C_2O_4^{2-}$ according to eq 3 under conditions of $N_2H_5^+$ initiation; under initiation with excess VO^{2+}, N_3^- and $H_2PO_3^-$ do not compete with VO^{2+} for Cr(IV).

Product Distributions. The extent of ligand capture depends on both the nature and the concentration of the ligand, on the reduction initiator, and to a lesser extent on the concentration of oxidizable metal ions that can trap Cr(V) or Cr(IV) intermediates. In dilute $HClO_4$ and fivefold ligand excess, initiation with $N_2H_5^+$ in the presence of weakly coordinating ligands such as NO_3^-, Cl^-, or CH_3COO^- results essentially in no ligand capture. In the presence of N_3^-, SO_4^{2-}, $H_2PO_2^-$, $H_2PO_3^-$, or $H_2PO_4^-$, significant fractions of the Cr(III) product are coordinated and chelating ligands, such as $C_2O_4^{2-}$ and $H_2P_2O_7^{2-}$, produce extensive ligand capture.

Vanadium(IV) initiation in the presence of a potential ligand generally results in more highly substituted Cr(III) products than does $N_2H_5^+$ initiation, as shown in Table II, the notable exception being oxalate. This increased yield of substituted products is consistent with different reduction mechanisms for these two initiators as indicated below.

Under VO^{2+} initiation, the immediate precursor of Cr(III) in the absence of ligand oxidation is Cr(IV). Thus the Cr(IV) ligand substitution equilibria govern the distribution of the Cr(III) product complexes. Chromium(V) can be ruled out as an immediate precursor of Cr(III) in the absence of evidence for two-electron oxidation of the ligand source; in excess VO^{2+}, Cr(V) is presumed to be reduced by VO^{2+} to Cr(IV) in the absence of ligand oxidation.

Hydrazinium ion has been shown to be ineffective as a one-electron reducing agent for Cr(IV);[9] therefore under $N_2H_5^+$ initiation, loss of Cr(IV) occurs through (i) disproportionation to Cr(III) and Cr(V) (eq 1), (ii) oxidation by Cr(VI) to Cr(V) (eq 2), and (iii) reduction in the presence of some one-electron oxidizable species (eq 3). In the first two cases, a Cr(V) intermediate is formed which is reduced to Cr(III) in a rapid two-electron step by $N_2H_5^+$; in the third case Cr(IV) is the immediate precursor of Cr(III). Differences in the substitution equilibria of Cr(IV) and Cr(V) are reflected in the different distributions of product Cr(III) complexes under the two reduction initiators.

In comparison with VO^{2+} initiation, the formation of Cr(III) products of lower substitution under $N_2H_5^+$ initiation is consistent with increased participation of Cr(V) as the precursor of Cr(III) under $N_2H_5^+$ initiation. It is expected that Cr(V), H_3CrO_4, is less extensively substituted in solution than octahedrally coordinated Cr(IV).[5b]

With oxalate as a ligand source, Cr(VI) reduction initiated by VO^{2+} results both in ligand oxidation and in slightly less substituted products than does $N_2H_5^+$ initiation. Srinivasan and Rocek[12] have shown that the rate of Cr(V) reduction by oxalate is only slightly faster than the rate of Cr(VI) reduction by oxalate, which is slow compared to the rate of Cr(VI) reduction by VO^{2+}. This result suggests that the product distribution under V(IV) initiation is shifted toward less extensive substitution due to the competition between $C_2O_4^{2-}$ and VO^{2+} for reduction of Cr(IV). The radical ligand formed, $C_2O_4\cdot^-$, is subsequently oxidized (eq 4), liberating 2 CO_2 and forming a Cr(III) product of reduced substitution.

Vanadium(IV) Initiation. The distribution of Cr(III) capture products has been determined as a function of ligand and of excess acid concentration in the presence of the ligand sources, HN_3, HSO_4^-, and H_3PO_3. Using excess VO^{2+} to eliminate ligand oxidation, the product distribution obtained is that due to the reduction of the Cr(IV) precursor of Cr(III) by V(IV). Under this condition, if the coordination equilibria between the ligand and both Cr(IV) and V(IV) are rapidly established relative to the redox reaction, the Cr(III) product distribution will reflect the relative rates of reduction of each coordinated Cr(IV) precursor. Thus if the equilibria involved are

$$\mathrm{Cr(IV)} + n\mathrm{L} \rightleftarrows \mathrm{Cr^{IV}L}_n; \quad Q_{\mathrm{c},n} = [\mathrm{Cr^{IV}L}_n]/[\mathrm{Cr(IV)}][\mathrm{L}]^n$$

then the $[\mathrm{Cr^{IV}L}_n]$ is determined in terms of the total Cr(IV), F_c

$$[\mathrm{Cr^{IV}L}_n] = F_\mathrm{c}Q_{\mathrm{c},n}[\mathrm{L}]^n/\{1 + \sum_m Q_{\mathrm{c},m}[\mathrm{L}]^m\}$$

and similarly for V(IV) and $\mathrm{V^{IV}L}$

$$[\mathrm{V(IV)}] = F_\mathrm{V}/(1 + Q_\mathrm{V}[\mathrm{L}])$$

$$[\mathrm{V^{IV}L}] = F_\mathrm{V}Q_\mathrm{V}[\mathrm{L}]/(1 + Q_\mathrm{V}[\mathrm{L}])$$

Each V(IV) species will reduce a coordinated $\mathrm{Cr(IV)L}_n$ with a specific rate constant, $k_{m,n}$

$$\mathrm{V^{IV}L}_m + \mathrm{Cr^{IV}L}_n \xrightarrow{k_{m,n}} \mathrm{V^{V}L}_m + \mathrm{Cr^{III}L}_n$$

where we have written that $\mathrm{V^{IV}L}_m$ reduces $\mathrm{Cr^{IV}L}_n$ without capture of the ligand coordinated to the V(IV). It is of

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[12] V. Srinivasan and J. Rocek, private communication.

course impossible to distinguish between the alternative steps

$$\mathrm{V^{IV}L}_m + \mathrm{Cr^{IV}L}_n \xrightarrow{k_{m,n}} \mathrm{V^{V}L}_m + \mathrm{Cr^{III}L}_n$$

and

$$\mathrm{V^{IV}L}_{m+1} + \mathrm{Cr^{IV}L}_{n-1} \xrightarrow{k_{m,n}} \mathrm{V^{V}L}_m + \mathrm{Cr^{III}L}_n$$

since they correspond to transition states of the same stoichiometry, leading to the same products.

The product distributions are tabulated in terms of the fraction of the total Cr(III) obtained as each isolable product. For mononuclear Cr complexes, the ratio of yields of successively higher substituted products is of the form

$$\frac{[\mathrm{Cr^{III}L}_{n+1}]}{[\mathrm{Cr^{III}L}_n]} = \frac{k_{0,n+1} + k_{1,n+1}Q_{\mathrm{V}}[\mathrm{L}]}{k_{0,n} + k_{1,n}Q_{\mathrm{V}}[\mathrm{L}]}\,\frac{Q_{\mathrm{c},n+1}[\mathrm{L}]}{Q_{\mathrm{c},n}} \qquad (5)$$

For the ligand source, HSO_4^-, the product distributions were measured as a function of $[H^+]$ and $[HSO_4^-]$ at a constant ionic strength, $I = 0.53$, maintained with $NaClO_4$. The acid dissociation quotient of bisulfate was determined potentiometrically, $Q_a(HSO_4^-) = 0.050$, in reasonably good agreement with a previous report.[13] Hydrogen and sulfate ion concentrations were calculated from $Q_a(HSO_4^-)$ and the total concentrations of $HClO_4$ and HSO_4^- added. The ratio of Cr^{3+}:$CrSO_4^+$ in the product is a linear function of the $[SO_4^{2-}]^{-1}$, as shown in Table III: $Cr^{3+}:CrSO_4^+ = 1.09 + 0.0115/[SO_4^{2-}]$. The result corresponds to a negligible value of the $k_{1,1}Q_V[L]$ term relative to the $k_{0,1}$ term in eq 5. Evidently the transition state leading to the formation of $CrSO_4^+$ and containing 1 mol each of V(IV), Cr(IV), and sulfate is kinetically preferred to a transition state containing 2 mol of sulfate. This may be due to an intrinsically slow rate of formation of the transition state containing two sulfates, though it is more probably due to such a transition state leading preferentially to the formation of $Cr(SO_4)_2^-$, as would be the case if the SO_4^{2-} coordinated to V(IV) were bridged to the Cr(IV) in the electron-transfer step.

For the ligand source H_3PO_3, product distributions were measured at constant ionic strength, $I = 0.20$. The dissociation quotient of phosphorous acid was determined, $Q_a(H_3PO_3) = 0.087$ in reasonably good agreement with other reports.[14] The $[H^+]$ and $[H_2PO_3^-]$ were calculated from the Q_a and the total $HClO_4$ and H_3PO_3 added. The product ratio $Cr^{3+}:CrH_2PO_3^{2+}$ obtained is a linear function of $[H_2PO_3^-]^{-1}$ as shown in Table III: $Cr^{3+}:CrH_2PO_3^{2+} = 0.049 + 0.0023/[H_2PO_3^-]$. As in the case of the sulfate ligand, this result corresponds to a negligible value of the $k_{1,1}Q_V[L]$ term relative to the $k_{0,1}$ term and can be interpreted in the same way. In addition to the mononuclear $Cr(H_2PO_3)^{2+}$ product, other isolable species obtained in small amounts include another product of charge 2+ with an apparent P(III):Cr(III) ratio of 1.55 and a total P:Cr ratio of 1.53. Polymeric Cr^{III}–P^{III} species have been indicated previously,[15] and a dimer of the net stoichiometry $Cr_2(H_2PO_3)_2(HPO_3)^{2+}$ is consistent with this result although the exact structure cannot be specified. A species of charge 1+ and a P:Cr ratio of 2.0 was also found; a stoichiometry $Cr(H_2PO_3)_2^+$ while plausible is not unique. The negligible value of the $k_{1,1}Q_V \cdot [L]$ term for the product distribution in the phosphite system suggests that reduction of Cr(IV) *via* a transition state of the stoichiometry $V^{IV} \cdot Cr^{IV} \cdot 2P^{III}$ does not lead to significant amounts of monosubstituted $Cr(H_2PO_3)^{2+}$ but apparently results principally in $Cr(H_2PO_3)_2^+$.

Table III. VO^{2+} Initiation–Ligand Capture Per Cent of Cr(III) Product Complexes

Ligand Source: HSO_4^-

$[H^+]$, *M*	$[SO_4^{2-}]$, *M*	% Cr^{3+}	% $CrSO_4^+$	$Cr^{3+}:CrSO_4^+$ Obsd	$Cr^{3+}:CrSO_4^+$ Calcd
0.069	0.060	54.2	42.7	1.27	1.28
0.090	0.054	54.5	42.5	1.28	1.30
0.114	0.044	54.9	41.7	1.32	1.35
0.187	0.032	58.8	39.4	1.49	1.45
0.328	0.021	61.9	36.0	1.72	1.64
0.187	0.021	61.3	37.5	1.63	1.64
0.187	0.0100	68.6	30.9	2.22	2.24
0.187	0.0060	74.1	25.6	2.89	3.01
0.187	0.0020	87.2	12.7	6.87	6.84

$$Cr^{3+}:CrSO_4^+ = 1.09 + 0.0115/[SO_4^{2-}]$$

Ligand Source: H_3PO_3

$[H^+]$, *M*	$[H_2PO_3^-]$, *M*	% Cr^{3+}	% $CrH_2PO_3^{2+}$	$Cr^{3+}:CrH_2PO_3^{2+}$ Obsd	$Cr^{3+}:CrH_2PO_3^{2+}$ Calcd
0.207	0.023	9.86	67.3	0.146	0.149
0.209	0.0436	6.09	59.3	0.103	0.102
0.208	0.0436	6.02	55.4	0.109	0.102
0.208	0.088	3.03	41.7	0.073	0.075
0.208	0.152	1.90	30.8	0.062	0.064
0.104	0.068	4.04	47.8	0.085	0.083

$$Cr^{3+}:CrH_2PO_3^{2+} = 0.049 + 0.0023/[H_2PO_3^-]$$

Ligand Source: HN_3

$[H^+]$, *M*	$[HN_3]$, *M*	% Cr^{3+}	% CrN_3^{2+}	$Cr^{3+}:CrN_3^{2+}$ Obsd	$Cr^{3+}:CrN_3^{2+}$ Calcd
0.169	0.0254	86.8	10.0	8.7	9.0
0.169	0.051	70.3	20.4	3.45	3.42
0.160	0.102	42.4	34.6	1.23	1.24
0.165	0.154	34.6	37.7	0.92	0.83
0.198	0.150	28.1	36.2	0.78	0.72
0.155	0.146	28.4	35.4	0.80	0.75
0.149	0.153	20.9	34.7	0.60	0.69
0.098	0.153	21.0	35.7	0.59	0.61
0.050	0.150	18.0	34.0	0.53	0.53

$$(Cr^{3+}:CrN_3^{2+})[HN_3] = \frac{0.38 + 0.085 \times 10^5[N_3^-]}{1 + 1.35 \times 10^5[N_3^-]}$$

For the ligand source HN_3, the product distribution was determined in solutions of ionic strength ranging from 0.2 to 0.35. The $Cr^{3+}:CrN_3^{2+}$ ratio is roughly inversely proportional to the $[HN_3]$ and dependent on the $[N_3^-]$ as shown in Table III: $(Cr^{3+}:CrN_3^{2+})[HN_3] = (0.38 + 8.5 \times 10^3[N_3^-])/(1 + 1.35 \times 10^5[N_3^-])$, where $[N_3^-]$ was calculated using $Q_a(HN_3) = 4.5 \times 10^{-5}$.[16]

The data in the N_3^- case are clearly less well fit than those in the sulfate or phosphite studies, due in part to the failure to maintain rigorous control of the ionic strength. Nonetheless, the form of the azide capture results differs in two significant ways from that of the SO_4^{2-} or $H_2PO_3^-$ results. First, transition states leading to formation of CrN_3^{2+} contain 1 mol of H^+. Azide is a much stronger base than either $H_2PO_3^-$ or SO_4^{2-} and the aquation kinetics for CrN_3^{2+} [17] contains a term first-order in the $[H^+]$, requiring a protonated Cr^{III}–N_3^- transition state for aquation. Second, in contrast to the results from SO_4^{2-} and $H_2PO_3^-$ capture, two transition states contribute to the formation of the monosubstituted product, CrN_3^{2+}, containing either 1 or 2 mol of N_3^-/mol of Cr. Evidently an elementary process of the net stoichiometry

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$\mathrm{Cr^{IV}\cdot V^{IV}\cdot 2N_3 \rightarrow CrN_3^{2+} + V^VN_3}$

occurs competitively with other modes of producing CrN_3^{2+}, whereas in the corresponding sulfate or phosphite cases a transition state of the same stoichiometry leads to the disubstituted $Cr^{III}L_2$ product if that transition state contributes at all

$\mathrm{Cr^{IV}\cdot V^{IV}\cdot 2L \rightarrow Cr^{III}L_2 + V^V}$

Hydrazine Initiation. Qualitatively the dependence of the product ratios on ligand and acid concentration under $N_2H_5^+$ initiation is similar to the dependence observed under V(IV) initiation except for the substantially reduced extent of capture. The interpretation of the $N_2H_5^+$ capture results is hindered by two aspects of the chemistry: partial oxidation of the oxidizable ligands even in the presence of excess $N_2H_5^+$ and a lack of certainty as to the fate of the Cr(IV) not reduced by ligands. The approximate halving of the CrL yield in the case of $N_2H_5^+$ initiation, relative to that under VO^{2+} initiation, is consistent with Cr(IV) disproportionation (eq 1), which Haight, *et al.*,[9] have shown to be the dominant mechanism for sixfold excess $N_2H_5^+$ over Cr(VI) and *ca.* 10^{-4} *F* Cr(VI). For this mechanism 50% of the Cr(III) arises from a Cr(IV) precursor and 50% from Cr(V), which is assumed to be essentially unsubstituted in solution. It is not possible, however, to rule out unequivocally Cr(VI) oxidation of Cr(IV) to Cr(V) (eq 2) followed by a fortuitous substitution of Cr(V) sufficient to give approximately half the CrL yield obtained under VO^{2+} initiation.

In the case of HSO_4^- ligand source, the product distributions were obtained over a range of ionic strengths, $I = 0.34$–0.54. To evaluate capture of SO_4^{2-} by Cr(IV) the disproportionation mechanism (eq 1) is assumed. The product ratio was calculated by subtracting from the per cent Cr^{3+} obtained the 50% yield of Cr(III) presumed due to Cr(V) reduction by $N_2H_5^+$ and dividing by the per cent $CrSO_4^+$, as shown in Table IV.

$\mathrm{Cr(V) + {}^1\!/_2N_2H_5^+ \rightarrow Cr^{3+} + {}^1\!/_2N_2}$

The ratio, $R_S = (\%\ Cr^{3+} - 50)/\%\ CrSO_4^+$, is found to be linear in $[SO_4^{2-}]^{-1}$ similar to what was found under VO^{2+} initiation: $R_S = 0.79 + 0.030/[SO_4^{2-}]$. This result suggests that $Cr^{IV}SO_4$ can both reduce Cr(IV) and be reduced by Cr(IV) as provided by the disproportionation mechanism (eq 1)

$\mathrm{Cr^{IV}SO_4 + Cr(IV) \rightarrow CrSO_4^+ + Cr(V)}$

$\mathrm{Cr^{IV}SO_4 + Cr(IV) \rightarrow Cr^{3+} + Cr(V) + SO_4^{2-}}$

Analysis of the $H_2PO_3^-$ and N_3^- capture data under $N_2H_5^+$ initiation is complicated by the clear evidence of ligand oxidation. In the case of N_3^-, the oxidation product, N_2, does not remain coordinated and the $Cr^{3+}:CrN_3^{2+}$ ratio obtained is increased to the extent that ligand oxidation occurs

$\mathrm{Cr^{IV}N_3 \rightarrow Cr^{III}N_3\cdot}$

$\mathrm{2Cr^{III}N_3\cdot \rightarrow 2Cr(III) + 3N_2}$

Table IV. $N_2H_5^+$ Initiation–Ligand Capture Per Cent of Cr(III) Product Complexes

Ligand Source: HSO_4^-

$[H^+]$, *M*	$[SO_4^{2-}]$, *M*	% Cr^{3+}	% $CrSO_4^+$	R_S Obsd	R_S Calcd
0.426	0.018	84.8	14.4	2.42	2.46
0.328	0.022	84.3	15.0	2.29	2.15
0.231	0.027	82.6	16.6	1.96	1.90
0.184	0.031	80.2	18.2	1.66	1.76
0.140	0.038	79.6	19.3	1.53	1.58
0.099	0.048	79.4	19.3	1.52	1.42
0.092	0.051	77.6	20.4	1.35	1.38

$R_S = (\%\ Cr^{3+} - 50)/\%\ CrSO_4^+ = 0.79 + 0.030/[SO_4^{2-}]$

Ligand Source: HN_3

$[H^+]$, *M*	$[HN_3]$, *M*	% Cr^{3+}	% CrN_3^{2+}	R_A Obsd	R_A Calcd
0.046	0.155	68.4	14.5	1.27	1.33
0.052	0.152	70.7	15.0	1.38	1.39
0.099	0.152	72.8	13.8	1.65	1.56
0.104	0.151	70.8	13.3	1.56	1.59
0.152	0.154	76.5	15.1	1.75	1.74
0.156	0.150	73.9	14.6	1.64	1.78
0.207	0.159	77.8	14.3	1.94	1.87
0.151	0.025	94.8	2.4	18.6	17.0
0.153	0.051	91.6	6.6	6.3	6.5

$R_A[HN_3] = \{(\%\ Cr^{3+} - 50)/\%\ CrN_3^{2+}\}[HN_3] = 0.181 + 0.36[H^+] + 0.14 \times 10^{-5}/[N_3^-]$

Ligand Source: H_3PO_3

$[H^+]$, *M*	$[H_2PO_3^-]$, *M*	% Cr^{3+}	% $CrH_2PO_3^{2+}$	R_P Obsd	R_P Calcd
0.196	0.139	28.4	29.4	0.97	0.93
0.196	0.0926	36.4	28.5	1.28	1.27
0.196	0.0465	47.8	25.1	1.90	1.96
0.196	0.0231	60.2	20.8	2.89	2.73
0.140	0.0578	45.7	25.0	1.83	1.94
0.079	0.0788	40.9	24.9	1.64	1.75

$R_P = \%\ Cr^{3+}/\%\ CrH_2PO_3^{2+} = 1/(1.15[H^+] + 6.1[H_2PO_3^-])$

Ligand Source: $H_2C_2O_4$

$[H^+]$, *M*	$[HC_2O_4^-]$, *M*	% Cr^{3+}	% $CrC_2O_4^+$	R_O Obsd	R_O Calcd
0.185	0.035	39.7	26.4	1.50	1.62
0.205	0.0545	33.7	28.9	1.17	1.17
0.230	0.080	30.0	31.7	0.95	0.91
0.276	0.0256	48.4	22.4	2.16	2.08
0.418	0.0180	52.1	18.7	2.79	2.80

$R_O = \%\ Cr^{3+}/\%\ CrC_2O_4^+ = 0.36 + 0.044/[HC_2O_4^-]$

Since both CrN_3^{2+} and $Cr(N_3)_2^+$ are found, it is not possible to attribute the excess Cr(VI) consumption exclusively either to $Cr^{IV}N_3$ or $Cr^{IV}(N_3)_2$. We assume that N_3^- coordination to Cr(V), like that to Cr(VI),[18] is quite small; hence 50% of the Cr(III) product is presumed derived from reduction of uncomplexed Cr(V) by $N_2H_5^+$ and is observed as Cr^{3+}. The product ratio formed from the balance of the Cr^{3+}, $R_A = (\%\ Cr^{3+} - 50)/\%\ CrN_3^{2+}$, corresponds to a mixed distribution formed both from disproportionation (eq 1) of Cr(IV) and from direct Cr(IV) reduction (eq 3) by N_3^-. The product distributions were obtained over a range of ionic strengths, $I = 0.19$–0.35, as a function of $[H^+]$ and $[HN_3]$ as shown in Table IV. The ratio, R_A, is inversely proportional to $[HN_3]$ as was found under VO^{2+} initiation and approximately linearly dependent on $[H^+]$ and $[N_3^-]^{-1}$: $R_A[HN_3] = 0.181 + 0.36[H^+] + 0.14 \times 10^{-5}/[N_3^-]$. This suggests that Cr^{3+} can be formed from disproportionation transition states involving either N_3^- or HN_3 or neither species of ligand; however, Cr^{3+} would also be formed from direct reduction (eq 3) of Cr(IV) by azide. The steady-state equations for Cr(IV) allowing both disproportionation (eq 1) and direct reduction (eq 3) are quadratic in Cr(IV). Qualitatively it is clear that disproportionation is necessarily second order in Cr(IV) whereas direct reduction is probably first order in Cr(IV); hence, conditions favoring low transient concentrations of Cr(IV) coordinated to azide should favor direct reduction over disproportionation. We have found that azide inhibits the reduc-

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[18] L. Settzo, J. Tonges, and J. Cooper, Bucknell University, unpublished results.

tion of Cr(VI) by $N_2H_5^+$, slowing the rate of Cr(IV) production. It seems plausible that either or both of the terms for Cr^{3+} production involving N_3^- or HN_3 may reflect direct reduction of Cr(IV).

The $H_2PO_3^-$ capture data under $N_2H_5^+$ initiation were obtained at constant ionic strength $I = 0.20$. Approximately 25% of the P(III) captured was oxidized to P(V); it is not possible unequivocally to assign this oxidation to Cr(IV) (eq 3) although we believe this to be the most plausible interpretation. The Cr(VI)-H_3PO_3 reaction is slow[19] and Cr(V) redox chemistry appears to be similar to that of Cr(VI),[5b] whereas the Cr(V)-$N_2H_5^+$ reaction is fast. Furthermore P(III) oxidation in this system is accompanied by the production of radicals that polymerize $CH_2{=}CHCN$, suggesting one-electron oxidation of P(III). In the absence of acrylonitrile, we assume that P(III) radical oxidation by Cr(IV) leads to a coordinated radical which is further oxidized in the presence of Cr(VI)

$$\mathrm{Cr^{IV}P^{III}} \rightarrow \mathrm{Cr^{III}P^{IV}\cdot}$$

$$\mathrm{Cr^{III}P^{IV}\cdot} + \mathrm{Cr(VI)} \rightarrow \mathrm{Cr^{III}P^{V}} + \mathrm{Cr(V)}$$

Thus 50% of the Cr(III) produced arises from a Cr(V) precursor, regardless of whether Cr(IV) disproportionates or is directly reduced.

At high $[H_3PO_3]$, more than 50% of the Cr(III) product is coordinated to P(III) species indicating possibly some Cr(V) reduction occurs with P(III) capture. The extent of Cr(V) coordination

$$\mathrm{Cr^{V}P^{III}} + {}^1/_2\mathrm{N_2H_5^+} \rightarrow \mathrm{Cr^{III}P^{III}} + {}^1/_2\mathrm{N_2}$$

in H_3PO_3 solutions, like that of Cr(VI),[19] is expected to be relatively low, and the contribution to the product $CrH_2PO_3^{2+}$ from this source, relatively small.

The capture data correspond qualitatively to the results obtained with VO^{2+} initiation; the ratio $R_P = \%\ Cr^{3+}/\%\ CrH_2PO_3^{2+}$ is inversely related to $[H_2PO_3^-]$: $R_P = 1/(1.15[H^+] + 6.1[H_2PO_3^-])$, but a detailed interpretation of this result is probably not warranted, owing to the uncertainty in the extent to which the $CrH_2PO_3^{2+}$ produced reflects a Cr(V) or a Cr(IV) precursor.

Capture of oxalate ligands under $N_2H_5^+$ initiation was studied over a range of ionic strengths, $I = 0.18$–0.42. Hydrogen oxalate ion concentration was estimated using $Q_{1\,A}(H_2C_2O_4) = 0.057$. The product ratio, $R_O = \%\ Cr^{3+}/\%\ CrC_2O_4^+$, was found linear in $[HC_2O_4^-]^{-1}$ and essentially independent of $[H^+]$: $R_O = 0.36 + 0.044/[HC_2O_4^-]$. There is clear evidence of partial oxalate oxidation (*cf.* Table I) which increases with increasing oxalic acid concentration. Where oxalate is oxidized by Cr(IV), we have argued that the radical produced is further oxidized by Cr(VI) producing a Cr(III) species of reduced oxalate coordination

$$\mathrm{Cr^{IV}C_2O_4H} \rightarrow \mathrm{Cr^{III}C_2O_4H\cdot}$$

$$\mathrm{Cr^{III}C_2O_4H\cdot} + \mathrm{Cr(VI)} \rightarrow \mathrm{Cr^{3+}} + \mathrm{Cr(V)} + 2\mathrm{CO_2} + \mathrm{H^+}$$

The term in the ratio R_O corresponding to Cr^{3+} production from a transition state involving $HC_2O_4^-$ may reflect this effect, although it is not possible to exclude disproportionation steps of the form

$$\mathrm{Cr^{IV}C_2O_4H} + \mathrm{Cr(IV)} \rightarrow \mathrm{CrC_2O_4^+} + \mathrm{Cr(V)} + \mathrm{H^+}$$

from consideration.

Effects of Oxidizable Metal Ions. Ions such as Ce(III) and Mn^{2+} may influence both the stoichiometry and the product distributions of some $N_2H_5^+$-initiated reactions. Since neither is oxidized directly by Cr(VI), Cr intermediates must be involved. In the presence of Mn^{2+}, the consumption ratio, Cr(VI):$N_2H_5^+$, is reduced[9] to a limiting value of 0.67 corresponding to complete Mn^{2+} oxidation by Cr(IV) followed by the rapid one-electron oxidation of $N_2H_5^+$ by the Mn(III) produced

$$\mathrm{N_2H_5^+} + \mathrm{Mn(III)} \rightarrow \mathrm{Mn^{2+}} + {}^1/_2\mathrm{N_2} + \mathrm{NH_4^+} + \mathrm{H^+}$$

In the presence of HSO_4^- and excess Mn(II) the stoichiometry is reduced from 1.33 to 1.19 and the per cent $CrSO_4^+$ product increased from 18.2 to 21.1, qualitatively consistent with some trapping of Cr(IV) by Mn(II). Similarly excess Mn(II) reduced the consumption ratio in the presence of H_3PO_3 from 1.49 to 0.86 and increased the P(III) content of the 2+ product from 75 to 91%. With H_3PO_3 and traces of Ce(III) (2×10^{-5}–2×10^{-3} *F*) the consumption ratio is reduced from 1.48 to 1.3, and the P(III) content of the 2+ product is increased.

These qualitative results are consistent with Cr intermediate trapping by metal ions, in competition with ligands for the reduction of Cr(IV). The influence of metal ions depends on the ligand involved. Ce(III) is not effective in the presence of HSO_4^- and neither Ce(III) nor Mn(II) is effective in the presence of HN_3.

Registry No. Cr, 7440-47-3; H_2SO_4, 7664-93-9; HN_3, 7782-79-8; H_3PO_3, 13598-36-2; $H_2C_2O_4$, 144-62-7.

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(19) G. P. Haight, M. Rose, and J. Preer, *J. Amer. Chem. Soc.*, **90**, 4809 (1968).