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# Electron Transfer. 149. Reactions of Hypervalent Chromium With $s^2$ Metal-Ion Reducing Centers[1]

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Although the conversions of the $s^2$ reductants indium(I),[2] germanium(II),[3] and gallium(I)[4] to their $s^0$ counterparts may occur either by $2e^-$ transactions or by successive $le^-$ changes, the latter route is much more usual, even when the oxidant changes by two units.[2b,3b] Possible exceptions are oxidations by $Br_2$, $I_3^-$, and $PtCl_6^{2-}$, which may utilize bridged paths, allowing the transfer of halogenomium ($X^+$) ions.[5]

We here describe reactions of Sn(II), In(I), and Ge(II) with Cr(VI) and Cr(IV) species and present evidence for $2e^-$ changes, which almost certainly proceed via oxygen atom (oxo) transfer.

## Experimental Section

**Materials.** Reactions were carried out under nitrogen or argon in deaerated water. Tin(II) chloride, indium metal, and germanium dioxide (Aldrich) were used as received. The cobalt(III) complex $[Cl(NH_3)_5Co]^{2+}(ClO_4^-)_2$ and its fluoro-ligated analogue were prepared by the method of Wu,[6] and solutions of Cr(IV) stabilized by buffers of 2-ethyl-2-hydroxybutanoic acid (EHBA) were prepared by the procedure of Ghosh.[7] Solutions of In(I)[2a] and Ge(II)[3] were generated as described.

**Stoichiometric Studies and Trapping Experiments.** Stoichiometries of the reduction of Cr(VI) were determined at 350 nm by adding measured quantities of the reductant to excess $HCrO_4^-$ and measuring the resulting decreases in absorbances. Reactions were carried out both in solutions buffered (pH 3.2) by EHBA and its anion, and in 0.1 M HCl. Each mole of Cr(VI) expended 0.99 ± 0.03 mol of Ge(II) in the buffer and 1.49 ± 0.04 mol of Ge(II) in dilute HCl. The Cr(VI)−In(I) reaction featured 3/2 stoichiometry, irrespective of medium, and showed no irregularities attributable to the intervention of Cr(IV) on a time scale comparable to the principal reaction.

"Trapping" experiments with Cr(VI) and metal center reductants were carried out in the presence of $(NH_3)_5CoF^{2+}$ and were allowed to proceed for 5 min. The excess reductant was then destroyed by $Br_3^-$, and the Co(II) content was determined by nine-fold dilution with concentrated HCl, centrifuging, and measuring the absorbance of $CoCl_4^{2-}$ at 692 nm[8] in the supernatant.

**Kinetic Studies.** Reactions, under argon, were examined either at 350 nm ($\lambda_{max}$ for $HCrO_4^-$) or at 510 nm ($\lambda_{max}$ for Cr(IV)).[7] Temperatures were 22.5 ± 0.5 °C. Reduction of excess Cr(VI) with Ge(II) in EHBA buffer gave composite profiles comprising the growth and disappearance of Cr(IV). These were treated as combinations of two pseudo-first-order processes,[9] both of them first order in Cr(VI). Rates for the disappearance corresponded to those reported[10] for the oxidation of Cr(IV) by $HCrO_4^-$. The Cr(VI)−Ge(II) reaction was much more rapid in 0.2 M HCl in the absence of chelating ligand; such reductions were first order in Ge(II), but zero order in Cr(VI).

For reactions of stabilized Cr(IV), the oxidant was prepared by reduction of $HCrO_4^-$ with $H_3AsO_3$,[10] after which the reaction was monitored at 510 nm. The rapid Cr(IV)−In(I) reaction ($k = 2.2 \times 10^6$ $M^{-1}$ $s^{-1}$) required second-order conditions with both reagents at the $10^{-5}$ M level. Only a lower limit ($6 \times 10^7$ $M^{-1}$ $s^{-1}$) for the even more rapid In(I)−$HCrO_4^-$ reaction could be obtained, irrespective of medium.

## Results and Discussion

When the reduction of Cr(VI) by Ge(II), Sn(II), or In(I) is carried out in solutions containing $(NH_3)_5CoF^{2+}$, this complex acts as a scavenger for chromium(II) ($Cr^{II} + Co^{III} \rightarrow Cr^{III} + Co^{II}$), for none of the other oxidation states of chromium will reduce this ammine-bound cobalt(III) species, nor will these $s^2$ reductants.[3b] Results of these trapping experiments are summarized in Table 1. Each reductant generates substantial Co(II), in contrast to the $le^-$ reagent, Fe(II), which produces none. The implication is that Ge(II), Sn(II), and In(I) reduce Cr(VI) mainly through two-unit transactions which, like formate[11] and an array of alcohols,[12] pass through Cr(IV); the latter state is then converted to Cr(II) ($Cr^{VI} \rightarrow Cr^{IV} \rightarrow Cr^{II}$). This path predominates in EHBA buffer (pH 3.5), which is known to stabilize tetrapositive chromium,[7] or in 0.15 M HCl in the absence of carboxylate ligands. The conclusion is most persuasive for In(I) in the buffered solutions, where conversions to Cr(II) are very nearly quantitative.

The increased recoveries of Co(II) at higher Co(III) concentrations (with the remaining systems) point to competition between the trapping reagent and a second oxidant, i.e., to sequence (1)−(3)

$$Cr^{IV} + \mathrm{Red} \xrightarrow{k_1} Cr^{II} \qquad (1)$$

$$Cr^{IV} + Cr^{II} \xrightarrow{k_2} 2Cr^{III} \qquad (2)$$

$$Cr^{II} + Co^{III} \xrightarrow{k_3} Cr^{III} + Co^{II} \qquad (3)$$

The value of $k_3$, pertaining to the $(NH_3)_5CoF^{2+}$−$Cr^{II}$ reaction, exceeds $2 \times 10^5$ $M^{-1}$ $s^{-}$,[6,13] and unless $k_1$ approaches $10^5$ $M^{-1}$ $s^{-1}$, the yield of Co(II) should be independent of $k_1$ but dependent upon the selectivity of Cr(II) toward the competing oxidants (i.e., the ratio $k_3/k_2$). Incorporation of sequence (1−3) into the KINSIM integration procedure[14] gives values for this

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**Table 1.** Reductions of Chromium(VI), Carried out with Added $[Co(NH_3)_5F]^{2+}$ (Trapping Experiments for Cr(II))[a]

| reductant (mM) | $[Co^{III}]$, mM | pH | % yield of $Co^{II}$ [f] | reductant (mM) | $[Co^{III}]$, mM | pH | % yield of $Co^{II}$ [f] |
|---|---|---|---|---|---|---|---|
| $Ge^{II}$ (4.8) | 1.0 | 0.85[b] | 48 (50) | $Sn^{II}$ (6.0) | 0.5[e] | 0.85[b] | 64 |
| | 2.0 | | 66 (65) | | 1.0[e] | | 71 |
| | 4.0 | | 85 (78) | | 2.0[e] | | 80 |
| | 0.5 | 3.5[d] | 33 (31) | | 0.5 | 3.5[d] | 28 (31) |
| | 1.0 | | 42 (44) | | 2.0 | | 54 (59) |
| | 2.0 | | 57 (59) | $In^{I}$ (5.0)[c] | 0.5 | 0.85 | 35 (33) |
| | 4.0 | | 70 (73) | | 1.0 | | 46 (47) |
| | | | | | 2.0 | | 56 (62) |
| | 0.5[e] | 0.85[b] | 53 (53) | | 1.0 | 3.5[d] | 91 |
| | 1.0[e] | | 69 (68) | | 2.0 | | 94 |
| | 2.0[e] | | 84 (80) | | 4.0 | | 98 |
| | | | | $Fe^{II}$ (5.0) | 1.0 | 0.85[b] | 0 |

[a] Reactions were carried out at 22.5 °C; $[Cr^{VI}] = 1.05$ mM, [Cl] = 0.15 M; $\mu = 0.5$ M ($ClO_4^-$). [b] Reactions in 0.15 M HCl. [c] Reactions in 0.15 M $HClO_4$. [d] Medium buffered by 0.1 M 2-ethyl-2-hydroxybutanoic acid and 0.1 M of its sodium salt. [e] Cobalt(III) trap was $[Co(NH_3)_5Cl]^{2+}$. [f] $[Co^{II}]_{found}/[Cr^{VI}]_{taken}$; parenthetical values were calculated from sequence 1−3 in text using the reactivity ratios in Table 2.

**Table 2.** Selectivity of Cr(II) toward Co(III) and Cr(IV)[a]

| reductant | oxidant, $[(NH_3)_5CoX]^{2+}$ | medium | $k_{Co(III)}/k_{Cr(IV)}$ ($= k_3/k_2$) |
|---|---|---|---|
| Ge(II) | X = F | 0.15 M HCl | 0.087 |
| | | EHBA buffer[b] | 0.066 |
| | X = Cl | 0.15 M HCl | 0.20 |
| Sn(II) | X = F | EHBA buffer | 0.066 |
| In(I) | X = F | 0.15 M HCl | 0.076 |

[a] Reactions were carried out as described in Table 1. [b] Medium buffered by 0.1 M 2-ethyl-2-hydroxybutanoic acid and 0.1 M of its sodium salt.

**Table 3.** Kinetic Data for the Reaction of Cr(VI) with Ge(II) in 2-Ethyl-2-hydroxybutanoate Buffer[a]

| [Cr(VI)], mM | [LigH],[b] mM | $[Lig^-]$,[c] mM | pH | $k$, $s^{-1}$ [d] |
|---|---|---|---|---|
| 0.42 | 50 | 20 | 3.18 | 0.034 (0.030) |
| 0.62 | 50 | 20 | 3.16 | 0.045 (0.044) |
| 0.83 | 50 | 20 | 3.16 | 0.065 (0.059) |
| 1.25 | 50 | 20 | 3.17 | 0.089 (0.088) |
| 1.87 | 50 | 20 | 3.16 | 0.126 (0.131) |
| 0.99 | 6.3 | 2.5 | 3.15 | 0.206 (0.205) |
| 0.99 | 12.5 | 5.0 | 3.16 | 0.149 (0.152) |
| 0.99 | 25 | 10 | 3.16 | 0.110 (0.104) |
| 0.99 | 50 | 20 | 3.16 | 0.073 (0.070) |
| 0.99 | 75 | 30 | 3.16 | 0.059 (0.056) |
| 0.99 | 125 | 50 | 3.16 | 0.043 (0.043) |
| 0.99 | 100 | 20 | 2.84 | 0.060 (0.071) |
| 0.99 | 20 | 20 | 3.54 | 0.071 (0.071) |

[a] Reactions were run at 22.0 ± 0.5 °C; $\mu = 0.50$ M (NaCl); $[Ge^{II}] = 9.6 \times 10^{-5}$ M throughout. [b] 2-Ethyl-2-hydroxybutanoic acid. [c] 2-Ethyl-2-hydroxybutanoate. [d] Pseudo-first-order rate constants; parenthetical values were calculated using eq 7 in text, taking $k_{Cr} = 330$ $M^{-1}s^{-1}$, $k_{Lig} = 23$ $M^{-1}$ $s^{-1}$, and $K_f$, as 278 $M^{-1}$.

ratio that closely reproduce the yields of Co(II). Such selectivities are listed in Table 2. Calculated and observed yields are compared in Table 1.

Although both $k_2$ and $k_3$ should depend on the medium, dependencies must be similar since their ratio varies only slightly when the EHBA buffer is substituted for 0.15 M HCl. The ratio rises when the chloro-substituted Co(III) trap replaces the less reactive[6] fluoro. When $k_1$, pertaining to the conversion of Cr(IV) to Cr(II), exceeds $10^5$ $M^{-1}s^{-1}$, the trap becomes more efficient since Cr(IV) is consumed too quickly to compete effectively with the added Co(III). This is the case for reduction by In(I) ($k_1 = 2 \times 10^6$ $M^{-1}$ $s^{-1}$).

In the absence of a Co(III) trap, the Ge(II) reduction of excess Cr(VI) in EHBA buffer utilizes equivalent quantities of the redox partners, yielding preponderantly Cr(IV), since EHBA-stabilized Cr(IV) is reduced only slowly with Ge(II). In the absence of the Cr(IV) chelator, the reaction exhibits 3:2 stoichiometry, yielding Cr(III)

$$2\ \mathrm{Cr(VI)} + 3\ \mathrm{Ge(II)} \rightarrow 2\ \mathrm{Cr(III)} + 3\ \mathrm{Ge(IV)} \qquad (4)$$

This reaction again proceeds through Cr(IV), but the latter is not stabilized and is quickly reduced to Cr(II), which is consumed by excess Cr(VI)

$$\mathrm{Cr^{VI}} \xrightarrow{\mathrm{Ge^{II}}} \mathrm{Cr^{IV}} \xrightarrow[rapid]{\mathrm{Ge^{II}}} \mathrm{Cr^{II}} \xrightarrow[rapid]{\mathrm{Cr^{VI}}} \mathrm{Cr^{III}} + \mathrm{Cr^{V}} \qquad (5)$$

$$\mathrm{Cr^{V}} + \mathrm{Ge^{II}} \xrightarrow[rapid]{} \mathrm{Ge^{IV}} + \mathrm{Cr^{III}} \qquad (6)$$

The $Cr^V$ intermediate (also unstabilized) is then rapidly converted to $Cr^{III}$. The fast reduction of Cr(IV) (even when stabilized) by In(I) wipes out the differences in stoichiometry in the buffered and unbuffered solutions. Only the $2Cr^{VI}$:$3In^{I}$ reaction is perceived in both media.

Kinetic data for the Cr(VI)−Ge(II) reaction in EHBA buffer (yielding chelate-stabilized $Cr^{IV}$) are presented in Table 3. Rates are nearly invariant with pH, but reactions are inhibited by carboxylate, $Lig^-$. Data conform to rate law (7), which describes a reaction at two different ligation levels, the slower path ($k_{Lig}$) having one more ligand than the faster ($k$).

$$(k)_{obsd} = [\mathrm{Cr^{VI}}]\,\frac{k + k_{Lig}K_f[\mathrm{Lig}^-]}{1 + K_f[\mathrm{Lig}^-]} \qquad (7)$$

Refinement according to (7) yields $k = (3.3 \pm 0.3) \times 10^2$ $M^{-1}$ $s^{-1}$, $k_{Lig} = 23 \pm 5$ $M^{-1}$ $s^{-1}$, and $K_f$ (the formation quotient for ligation) $= (2.8 \pm 0.5) \times 10^2$ $M^{-1}$. It is likely that this partition involves Ge(II), rather than Cr(VI), since earlier $2e^-$ reductions of Cr(VI) in this media have been found,[15] in contrast, to be accelerated by this ligand.

When this reduction is carried out in 0.2 M HCl with chelator absent, it is much faster, and there is no spectral indication of formation and loss of a Cr(IV) species (although the eventual formation of Cr(II) points to its intervention). Moreover, the transformation proceeds at a rate independent of [Cr(VI)] whether the oxidant or reductant is in excess. This kinetic behavior corresponds closely to that for the Ge(II)−$I_3^-$ reaction in aqueous iodide.[3b] In both systems, the rate appears to be determined by an unexpectedly slow unimolecular heterolysis of a halo-substituted reductant to a coordinatively unsaturated

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(15) See, for example, Ghosh, M. C.; Gould, E. S. *Inorg. Chem.* **1991**, *30*, 491.

**Table 4.** Kinetic Data for the Reaction of Cr(IV) with Ge(II) in 2-Ethyl-2-hydroxybutanoate Buffers[a]

| [Ge(II)], mM | [LigH],[b] M | [Lig$^-$],[c] mM | pH | $10^2k$, s$^{-1}$ [d] |
|---|---|---|---|---|
| 0.71 | 0.20 | 7.4 | 2.12 | 0.67 |
| 0.71 | 0.15 | 5.6 | 2.11 | 0.90 |
| 0.71 | 0.10 | 3.9 | 2.11 | 1.40 |
| 0.71 | 0.075 | 2.9 | 2.13 | 2.1 |
| 0.71 | 0.050 | 2.08 | 2.16 | 3.2 |
| 0.71 | 0.025 | 1.02 | 2.15 | 8.1 |
| 0.71 | 0.020 | 0.85 | 2.16 | 9.2 |
| 0.35 | 0.10 | 3.9 | 2.11 | 0.85 |
| 0.73 | 0.10 | 3.9 | 2.12 | 1.73 |
| 1.12 | 0.10 | 3.9 | 2.11 | 2.7 |
| 1.51 | 0.10 | 3.9 | 2.12 | 3.6 |
| 1.90 | 0.10 | 3.9 | 2.12 | 4.6 |
| 0.71 | 0.025 | 6.4 | 2.96 | 0.86 |
| 0.71 | 0.050 | 6.4 | 2.65 | 1.00 |
| 0.71 | 0.10 | 6.4 | 2.45 | 1.24 |
| 0.71 | 0.20 | 6.4 | 2.08 | 1.92 |

[a] Reactions were run at 22.0 ± 0.5 °C; $\mu = 0.50$ M (NaCl); $[\mathrm{Cr^{IV}}] = 7.0 \times 10^{-5}$ M throughout. [b] 2-Ethyl-2-hydroxybutanoic acid. [c] 2-Ethyl-2-hydroxybutanoate. [d] Pseudo-first-order rate constants.

species (eq 8); the latter is then consumed rapidly by the oxidant (eq 9)

$$[X_3Ge(H_2O)]^- \rightarrow [X_3Ge]^- + H_2O \; (X = Cl^-;\ k = 0.26\ s^{-1}) \qquad (8)$$

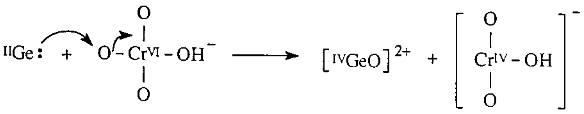
$$Cr(VI) \xrightarrow{X_3Ge^-} Cr(IV) \xrightarrow{Ge(II)} Cr(II) \quad (\textit{both rapid}) \qquad (9)$$

This conversion exhibits a rate constant (assigned to reaction 9) 0.26 ± 0.01 s$^{-1}$ in 0.20 M HCl (22 °C, $\mu = 0.5$ M), a value near that found for the Ge(II)$-$I$_3^-$ reaction (X = I$^-$, $k = 0.19$ s$^{-1}$).[3b] Since further reduction of (nonstabilized) Cr(IV) to Cr(II) is kinetically silent, we cannot say whether it too requires preliminary heterolysis of the reductant.

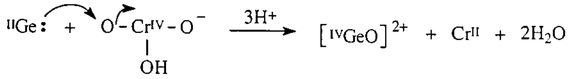
Rates for the Ge(II) reduction of stabilized Cr(IV), in EHBA buffers, are summarized in Table 4. Like the reduction of Cr(VI) in this medium, it is inhibited by added ligand anion (rates nearly inversely proportional to [Lig$^-$]). In addition to complexation of Ge(II), there is some ligation of Cr(IV) ($K_{CrLig} = 90\ M^{-1}$).[15] The system is further complicated by partial protonation of at least one of these ligation levels, and the data at hand do not allow estimates of the several equilibrium constants involved.

In summary, this study emphasizes the importance of Cr(II) formation in the reductions of Cr(VI) with s$^2$ centers, whether or not Cr(IV), which must intervene in such conversions, is sufficiently stabilized to allow its detection. With In(I), which partakes most readily in le$^-$ transactions,[2a] virtually all redox acts have been shown to operate through a VI$-$IV$-$II path in EHBA buffers, and the same is almost certainly true for the other s$^2$ systems as well.

Our reactions are thus predominantly two-unit conversions. For these, bridged paths must be assumed since outer-sphere routes for 2e transfers, reflecting exceptionally high Franck$-$Condon barriers, may be taken to be prohibitively slow.[16] The redox steps, in the absence of chelating ligand, may then be represented schematically as (10 and 11)



(10)



(11)

An analogous sequence operating in EHBA buffer must be modified to accommodate chelation of the Cr(IV) intermediate. Where in the sequence does the participation of this ligand occur? Note that reductions of Cr(VI) by hypophosphite[8b] and formate[11] were found to feature strong (second order) ligand dependencies, pointing to equilibria between ligand and oxidant established *before* the latter is consumed. No such dependencies are seen here for Ge(II); in this instance, attachment of the ligand must occur *after* the initial conversion.

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(16) See, for example: Lappin, G. *Redox Mechanisms in Inorganic Chemistry*; Ellis Horwood: New York, 1994; chapter 5.