

Reactions of vanadium(IV) and (V) with s^2 metal-ion reducing centers † ‡

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The s^2 centers, Sn(II), Ge(II), and In(I) reduce VO_2^+ rapidly and quantitatively to VO^{2+} , and In(I) converts VO^{2+} (much more slowly) to V^{3+} . Sn(II) and Ge(II) react measurably with VO^{2+} only in chloride media in the presence of added Cu(II). Arguments are presented that the V(V) reductions are initiated by a two-unit reduction to V(III) (via a hydroxo bridge), followed by a rapid comproportionation ($\text{V}^{\text{III}} + \text{V}^{\text{V}} \rightarrow 2 \text{V}^{\text{IV}}$). The Cu(II)-catalyzed V(IV)–Sn(II) and V(IV)–Ge(II) reactions at high $[\text{Cl}^-]$ involve preliminary conversion of the catalyst to Cu(I), which then reduces V(IV), and kinetic profiles of the Ge(II) system point to participation of chloride-bound Ge(III) as well.

Introduction

The last two decades have seen a marked quickening of interest in the chemistry of vanadium species. This enlivening reflects, in large part, their versatility in binding to donor sites of biological importance,² resulting in roles for this metal in nitrogenases^{2ab,3} and haloperoxidases,⁴ as modulators of metabolic phosphoryl transfers,^{2c,5} and as insulin mimics in the treatment of diabetes.^{2ab,6}

Solutions of this element feature four accessible oxidation states separated by one unit. Early mechanistic studies of their interconversions contributed details to the current inorganic electron transfer picture,⁷ but, with rare exceptions,⁸ such transformations involved coreagents undergoing le^- changes. The recent availability of the p^0s^2 -ions, indium(I)⁹ and germanium(II)¹⁰ in workable concentrations allows us to examine reactions with soluble strongly reducing 2e^- reductants. However, since the resulting products, Ge(IV) and In(III), remain in solution mainly at very high or very low pHs, the interactions which we observe are only indirectly related to those in biosystems.

Experimental

Materials

All solutions were prepared from Millipore-Q water which had been boiled for two hours and then purged with pure argon for two hours more to remove dissolved oxygen. Indium metal, silver trifluoromethanesulfonate (silver triflate), germanium dioxide (Aldrich) and ammonium vanadate (Fisher) were used as received. Vanadium(IV) solutions were prepared from VO_2SO_4 and barium perchlorate; after removal of the BaSO_4 by centrifugation, these were standardized at 760 nm ($\epsilon = 17.2 \text{ M}^{-1} \text{ cm}^{-1}$).¹¹ Stock solutions of indium(I) triflate in anhydrous acetonitrile,⁹ Sn(II) solutions in HCl/NaCl,¹² and Ge(II) solutions in HCl¹⁰ were prepared and standardized as described.

Stoichiometric studies

Stoichiometric studies were carried out under argon with the oxidant in excess and were monitored at 280 (V^{V}) or 760 (V^{IV}) nm. Measured deficient quantities of each reductant were added to a known excess of the oxidant, and decreases in absorbance were compared to those resulting from addition of excess reductant.

† Electron Transfer. Part 156. For part 155, see ref. 1.

‡ Electronic supplementary information (ESI) available: Table S1 — reaction stoichiometries, Tables S2–S6 — kinetic data for redox reactions. See <http://www.rsc.org/suppdata/dt/b3/b306566a/>

Kinetic studies

All reactions were carried out under argon. Rates were evaluated from measurements of absorbance decreases associated with loss of V(V) or V(IV). The very rapid reductions of vanadium(V) were followed using a Durrum–Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system, whereas the much slower reductions of vanadium(IV) were monitored using a Shimadzu 1601 UV-visible spectrophotometer. Reductions of VO^{2+} by Ge(II) or Sn(II) proceeded inconveniently slowly unless carried out in at high concentrations of added chloride and with Cu^{2+} or CuCl added as a catalyst. Temperatures were 22.0 ± 0.5 °C. Ionic strength was maintained with NaCl/NaClO₄, with NaCl/NaClO₄/HCl, or (for In^I reactions) with NaClO₄/HClO₄. Concentrations were most often adjusted so that no more than 10% of the reagent in excess was consumed in a given run. Exponential profiles were monitored for at least five half-life periods, and rate constants were generally calculated by nonlinear least-squares fitting to the relationship describing first order decay.

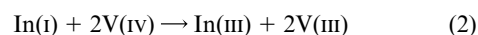
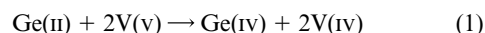
Kinetic studies of the $\text{V}^{\text{IV}}\text{--Ge}^{\text{II}}$ reaction as catalyzed by Cu^{II} were carried out with the oxidant in excess, for runs using excess Ge^{II} were frequently interrupted by transitory precipitation of solid CuCl. Since conversions under these conditions suffered progressively significant inhibition by the reaction product, V^{III} , initial rates were measured using the procedure of Chandler.¹³

None of the reductions of V(V) exhibited copper catalysis, nor did the V(IV)–In(I) reaction. None of the redox systems in this study showed perceptible signs of catalysis by Cr(III), Mn(II), or Co(II), (added as perchlorates at the 10^{-3} M level).

In addition to the various reactions involving vanadium, a limited study of the reductions of Cu(II) by Sn(II) in 0.8–4.0 M HCl was carried out ($\lambda = 880$ nm).

Results

In the acidic media taken, vanadium(V) exists preponderantly as VO_2^+ and vanadium(IV) as VO^{2+} . The monophasic kinetic profiles obtained, in conjunction with the close approach to the 2 : 1 stoichiometry observed throughout (Table S1 ‡) indicate that our individual kinetic runs feature single unit decreases for vanadium *e.g.*, (1) and (2),



without significant further reduction of the lower state on the same time scale.

Reductions of VO_2^+ ($E^\circ + 1.02$ V), monitored here *via* stopped-flow, are, not unexpectedly, several orders of magnitude faster than those of the much more weakly oxidizing cation, VO^{2+} (0.31 V).

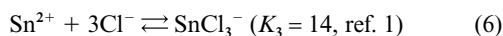
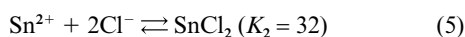
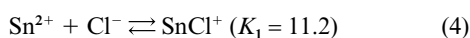
Reductions of vanadium(v)

The V(v)–In(i) and V(v)–Ge(ii) reactions at low pH values conform to the monomial rate law (3)

$$\text{rate} = -d[\text{V}^v]/dt = k [\text{V}^v][\text{red}] \quad (3)$$

$$(k_{\text{In}} = 2.5 \times 10^4; k_{\text{Ge}} = 1.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}, 22^\circ \text{C})$$

Neither exhibits a kinetic acidity dependence (in the range $[\text{H}^+] = 0.01\text{--}0.50$ M), and k_{Ge} is also independent of $[\text{Cl}^-]$ (in the range 0.5–1.0 M). Systematic variation of $[\text{Cl}^-]$ in the supporting electrolyte for the $\text{V}^v\text{--In}^i$ reaction is effectively ruled out by precipitation of InCl . Reaction with $\text{Sn}(\text{II})$ (Table S2 ‡) must take into account the partition of this reductant into four ligation levels.¹⁴



Rates for the V(v)–Sn(ii) reaction conform to expression (7)

$$-d[\text{V}^v]/dt = \frac{[\text{V}^v][\text{Sn}^{\text{II}}]k_3 K_3 [\text{Cl}^-]^3 [\text{H}^+]}{1 + K_1 [\text{Cl}^-] + K_2 [\text{Cl}^-]^2 + K_3 [\text{Cl}^-]^3} \quad (7)$$

in which the denominator reflects the partition of $\text{Sn}(\text{II})$ into chloro complexes. The numerator indicates that the predominant reaction path requires the trichloro reductant SnCl_3^- and an extra unit of H^+ (the latter doubtless associated with the oxidant). Refinement of data in terms of (7) yields the rate constant $(2.21 \pm 0.03) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ pertaining to reduction by SnCl_3^- . Alternate sequences, involving also the lower chloro complexes of $\text{Sn}(\text{II})$ as well, did not improve the fit. Calculated and observed rates are compared in the right-hand column of Table S2. ‡

Reductions of vanadium(iv)

In contrast to the V(iv)–In(i) reaction, which may be monitored within a wide range of acidities, reductions by $\text{Sn}(\text{II})$ and $\text{Ge}(\text{II})$ proceed imperceptibly slowly but may be markedly accelerated by dissolved copper in chloride-rich media.

The In(i) reaction (Table S3 ‡) is favored by increases in pH and conforms to rate law (8)

$$-d[\text{V}^{\text{IV}}]/dt = [\text{V}^{\text{IV}}][\text{In}^i] \frac{k_b K_A + k_a [\text{H}^+]}{K_A + [\text{H}^+]} \quad (8)$$

which describes the operation of two paths at different protonation levels, with the protonated contributor (rate constant k_a) somewhat less reactive than the nonprotonated (k_b). Refinement yields $k_a = 0.73 \pm 0.03 \text{ M}^{-1} \text{ s}^{-1}$, $k_b = 6.1 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$, and K_A , relating the two levels, 2×10^{-4} .

The $\text{V}^{\text{IV}}\text{--Ge}^{\text{II}}$ reaction, as catalyzed by Cu^{II} , could be examined kinetically only with V^{IV} in excess, for transitory precipitation of CuCl was encountered with excess Ge^{II} . Kinetic data appear in Table S4. ‡ Rates are enhanced by increases in $[\text{H}^+]$ and $[\text{Cu}^{2+}]$, but neither trend corresponds to a simple first-order relationship. The $[\text{H}^+]$ dependency indicates contributions from a protonated (k_{H}) and a nonprotonated (k_0) path, whereas the convex $[\text{Cu}]$ profile (Fig. 1) is consistent with partial conversion

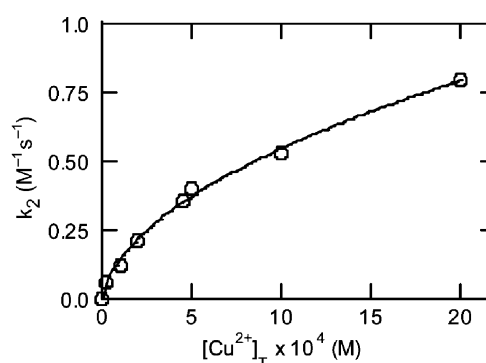


Fig. 1 Reduction of vanadium(iv) with germanium(ii), as catalyzed by copper(ii). Second order rate constants at varying values of $[\text{Cu}]$, $[\text{V}(\text{IV})] = 0.057$ M, $[\text{Ge}(\text{II})] = 8.0$ mM, $\mu = 2.0$ M HCl , $T = 22^\circ \text{C}$. The circles are experimental points, whereas the solid line has been calculated using eqn. (9) and the kinetic parameters listed in Table 1.

of the catalyst to an inactive dimer (see Appendix A), Superposition of these two effects generates expression (9):

$$(k)_{\text{obsd}} = (k_0 + k_{\text{H}}[\text{H}^+]) \frac{\sqrt{1 + 8K_{\text{D}}[\text{Cu}]_T} - 1}{4K_{\text{D}}} \quad (9)$$

where k_0 and k_{H} are rate constants associated with the two protonation levels, $[\text{Cu}]_T$ is the total concentration of added copper, and K_{D} is the dimerization constant of the catalyst. Refinement yields kinetic parameters listed in Table 1.

The apparent kinetic behavior of the copper-catalyzed $\text{V}^{\text{IV}}\text{--Sn}^{\text{II}}$ reaction depends on the ratio of reagents taken. With Sn^{II} in excess, reaction is first order each in V^{IV} , H^+ , and catalyst, with no noticeable falloff in catalytic activity when $[\text{Cu}]$ is raised to 2.0 mM, but rates are independent of $[\text{Sn}(\text{II})]$ in the range 0.016–0.13 M (Table S5). ‡ Moreover, the reaction is strongly accelerated by chloride at low $[\text{Cl}^-]$, but rates approach a maximum near 2.0 M. Data are consistent with expression (10), where $[\text{Cu}]_T$ is the total concentration of the catalyst. The denominator again mirrors the distribution between chloro complexes and, in this case, pertains to Cu^{I} .¹⁴

$$-d[\text{V}^{\text{IV}}]/dt = \frac{[\text{V}^{\text{IV}}][\text{Cu}]_T [\text{H}^+][\text{Sn}^{\text{II}}]^0 (k_2 K_2 [\text{Cl}^-]^2 + k_3 K_3 [\text{Cl}^-]^3)}{1 + K_1 [\text{Cl}^-] + K_2 [\text{Cl}^-]^2 + k_3 [\text{Cl}^-]^3} \quad (10)$$

When the same reaction is carried out with V^{IV} in excess, first order dependences on both copper and vanadium are again observed, but rates become proportional also to $[\text{Sn}^{\text{II}}]$. Dependences on $[\text{H}^+]$ and $[\text{Cl}^-]$ are also evident, but both are clearly more steep than those noted with Sn^{II} in excess.

In a brief examination of the related vanadium-free system, $\text{Sn}^{\text{II}} + \text{Cu}^{\text{II}}$, in a similarly high chloride medium (Table S6 ‡), rate constants for reduction were found to lie in the range $10^2\text{--}10^3 \text{ M}^{-1} \text{ s}^{-1}$. These reactions were acidity-dependent with a suggestion of kinetic saturation at high $[\text{H}^+]$.

Rate laws and kinetic parameters are summarized in Table 1.

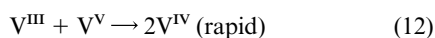
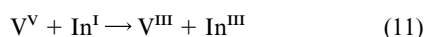
Discussion

The reactions in the present series, both uncatalyzed and catalyzed, involve two units of the vanadium oxidant to one of the s^2 reductant and thus require (at least) two redox transactions. The observed uniphase decay curves, and the absence of a quick absorbance drop immediately after mixing, point to a two-step sequence in which the initial step is rate-determining and the second step is rapid and therefore kinetically silent. For vanadium(v) two possibilities come to mind. The first is initiated by a two-unit reduction of V^{V} (11), followed by a III–V comproportionation (12)

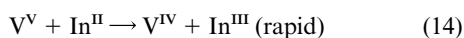
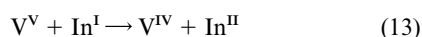
Table 1 Rate laws and kinetic parameters for the reductions of V(v) and V(IV) with s² metal reducing centers^a

Ox	Red	Rate law	Eqn.	Parameters
V ^V ^b	In ^I	$k[V^V][In^I]$	(3)	$k = (2.5 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$
V ^V ^c	Ge ^{II}	$k[V^V][Ge^{II}]$	(3)	$k = (1.10 \pm 0.04) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$
V ^V ^c	Sn ^{II}	$\frac{[V^V][Sn^{II}]k_3K_3[Cl^-]^3[H^+]}{1 + K_1[Cl^-] + K_2[Cl^-]^2 + K_3[Cl^-]^3}$	(7)	$k_3 = (2.21 \pm 0.03) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ $K_1 = 11.2, K_2 = 32; K_3 = 14$
V ^{IV} ^d	In ^I	$\frac{[V^{IV}][In^I](k_bK_A + k_a[H^+])}{(K_A + [H^+])}$	(8)	$k_a = 0.73 \pm 0.03 \text{ M}^{-1} \text{ s}^{-1}$ $k_b = 6.1 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$ $K_A = 2 \times 10^{-4}$
V ^{IV} ^e	Ge ^{II}	$k[V^{IV}][Ge^{II}](k_o + k_H[H^+])\sqrt{\frac{1 + 8K_D[Cu]_T - 1}{4K_D}}$	(9)	$k_o = (9.1 \pm 3.1) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ $k_H = (2.4 \pm 0.2) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ $K_D = 7.0 \pm 0.5 \times 10^6 \text{ M}^{-1}$
V ^{IV} ^f	Sn ^{II}	$\frac{[V^{IV}][Cu][H^+][Sn^{II}](k_2K_2[Cl^-]^2 + k_3K_3[Cl^-]^3)}{1 + K_1[Cl^-] + K_2[Cl^-]^2 + K_3[Cl^-]^3}$	(10)	$k_2 = 1.67 \pm 0.23 \text{ M}^{-2} \text{ s}^{-1}$ $k_3 = 2.9 \pm 0.1 \text{ M}^{-2} \text{ s}^{-1}$ $K_1 = 5.0 \times 10^2; K_2 = 1.0 \times 10^6$ $K_3 = 1.0 \times 10^6$ ^g

^a Reactions carried out at 22.0 ± 0.5 °C. ^b μ = 0.50 M (HClO₄/NaClO₄). ^c μ = 1.0 M (Cl⁻/ClO₄⁻). ^d pH 1.8–4.7, μ = 0.20. ^e μ = 2.0 M (HCl/NaCl). ^f μ = 4.0 M (HCl/NaCl), reactions with Sn^{II} in excess. ^g K values refer to the Cu^I–Cl⁻ system (ref. 22).



Alternatively, reaction may entail a slow le⁻ transfer (13) forming an s¹ intermediate (a much stronger reductant than its s² precursor),¹⁵ which is then rapidly oxidized (14)

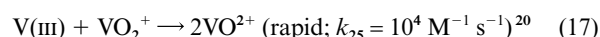
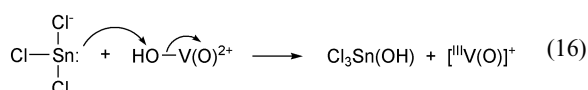


For reductions of V(IV), a sequence analogous to (11)–(12), passing through V(III), is effectively ruled out since the latter state is known to react rapidly with VO²⁺, forming a strongly absorbing (λ_{max} 425 nm) V–O–V intermediate.¹⁶

Although Sn(II), Ge(II), and In(I) are generally taken to be 2e⁻ reductants, In(I) is now recognized to be the most versatile of the trio, for it rapidly reduces a number of le⁻ oxidants derived from Fe(III)¹⁷ and Co(III)⁹ that react imperceptibly with Ge(II) or Sn(II) under comparable conditions. In this instance however, the Ge^{II}–V^V reaction ($k = 1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) is found to be nearly half as rapid as In^I–V^V ($2.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$), suggesting that Ge^{II} (and perhaps In^I as well) utilizes the alternate route analogous to (11)–(12), which bypasses the s¹ transient.

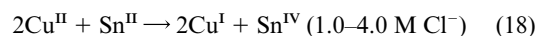
A similar conclusion probably applies to the Sn^{II}–V^V reaction, the kinetic picture of which is complicated by the presence of several chloro complexes of the reductant. The rate law [eqn. (7)] is remarkably like that for the reduction, by Sn^{II}, of the Co(III)-bound corrin, B_{12a}, to which a path initiated by reduction to the Co(I) complex, B_{12s}, has been assigned.¹⁸ As with B_{12a}, the predominant share of the redox burden is carried by the SnCl₃⁻ anion and the protonated form of the oxidant.

If, as we believe, these reductions of vanadium(v) are initiated by 2e⁻ transactions, we must infer that the first step utilizes a bridged activated complex since outer sphere two-unit transfers are considered to be exceedingly slow (mirroring a prohibitive Franck–Condon barrier).¹⁹ Sequence (15)–(17), featuring oxo-transfer from V(v) to Sn(II), is consistent with our observations:



Of the reductions of tetrapositive vanadium, only that by In(I) proceeds measurably without catalysis. In the absence of chloride, this conversion [rate law (8)] utilizes competing protonated ($k_a = 0.75 \text{ M}^{-1} \text{ s}^{-1}$) and deprotonated ($k_b = 6.1 \text{ M}^{-1} \text{ s}^{-1}$) paths, with the latter predominating. Since proton loss from a donor most generally makes it a more effective reductant, it is likely that the observed acidity pattern stems from an equilibrium (pK_A 3.7)²¹ involving In^I(aq) and the In⁺OH⁻ ion pair.

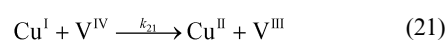
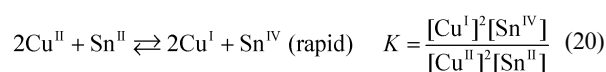
Copper catalysis of the V^{IV}–Sn^{II} and V^{IV}–Ge^{II} reactions may be assumed to involve a Cu(II,I) couple. In the chloride-rich media used in these systems, with other metal centers absent, the reduction of Cu^{II} by Sn^{II},



takes place much more rapidly (Table S6 ‡) than the V^{IV} reactions at hand.

$$\text{rate} = k [Cu^{II}][Sn^{II}][H^+], k_{Cu,Sn} = 2 \times 10^2 \text{ M}^{-2} \text{ s}^{-1} \quad (19)$$

Hence, a few seconds after mixing of the V^{IV}–Sn^{II}–Cu reaction, a major portion of the added Cu^{II} has been converted to Cu^I. The same applies when Sn^{II} is replaced by the more strongly reducing center, Ge^{II}. Moreover, the equilibria involving Cu(I/II) and the Sn(II/IV) centers may be taken to be established much more rapidly than the observed loss of V^{IV}. The two-step sequence (20)–(21), in conjunction with the conservation equation (22) for total copper, [Cu]_T, leads to rate law (23). At high initial concentrations of Sn^{II}, the half-power term in the denominator of (23) becomes negligible, and the dependence on [Sn^{II}] disappears, in accord with eqn. (10), which pertains to observed reactions with this reductant in excess.



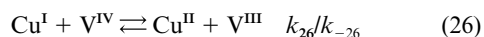
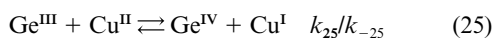
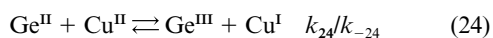
$$[Cu]_T = [Cu^I] + [Cu^{II}] = [Cu^I] \left[1 + \left(\frac{[Sn^{IV}]}{K_{20}[Sn^{II}]} \right)^{1/2} \right] \quad (22)$$

$$\text{rate} = \frac{-d[\text{V}^{\text{IV}}]}{dt} = k_{21} [\text{V}^{\text{IV}}][\text{Cu}^{\text{I}}] = \frac{k_{21}[\text{V}^{\text{IV}}][\text{Cu}]_{\text{T}}}{1 + \left(\frac{[\text{Sn}^{\text{IV}}]}{K_{20}[\text{Sn}^{\text{II}}]} \right)^{1/2}} \quad (23)$$

Additional features of rate law (10) are informative. The binomial numerator tells us that two kinetic paths at different chloro levels operate, and the $[\text{H}^+]$ -proportionality indicates that virtually all redox acts involve the protonated form of the oxidant. The speciation polynomial in the denominator applies not to Sn^{II} (which has become kinetically silent) but rather to Cu^{I} , which has been shown²² to form a series of chloro complexes, of which only CuCl_2^- and CuCl_3^{2-} appear to be significantly active in this case.

When the catalyzed $\text{V}^{\text{IV}}\text{-Sn}^{\text{II}}$ reaction is carried out with the oxidant in excess, dependence on $[\text{Sn}^{\text{II}}]$ (approximating first order)²³ reappears. However, we are now dealing with a system where speciation relationships involving two centers (Sn^{II} and Cu^{I}) apply. Inclusion of the various possible combinations of these chloro species would generate a rate expression too complex for meaningful refinement by our experiments.

The kinetic picture of the catalyzed $\text{V}^{\text{IV}}\text{-Ge}^{\text{II}}$ reaction is complicated by the reversal of the $\text{Cu}^{\text{I}}\text{-V}^{\text{IV}}$ step, for the reaction is perceptibly inhibited by V^{III} ,²⁴ particularly in its late stages. Rate law (9), which is based upon initial rates, measured before appreciable V^{III} had been formed, suggests that both the generation of Cu^{I} (from Ge^{II} and Cu^{II}) and its subsequent reaction with V^{IV} play a role in rate-determination. The sequence represented by eqns. (24)–(27) lists the various $1e^-$ conversions of this system:



Expression of this sequence as a series of differential equations and numerical integration using an adaptation of the program KINSIM,²⁵ yielded calculated absorbance curves which were compared to the observed kinetic profiles. Kinetic parameters giving optimal agreement between calculated and observed curves for a representative run (Fig. 2) are listed in Table 2. Note that the value of k_{24} ($32 \text{ M}^{-1} \text{ s}^{-1}$), referring to the $\text{Ge}^{\text{II}}\text{-Cu}^{\text{II}}$ reaction, is in reasonable agreement with an earlier

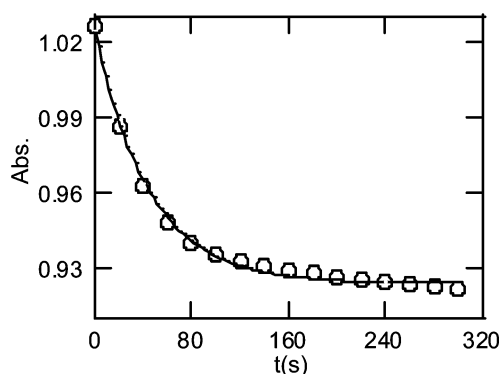


Fig. 2 Kinetic profile at 760 nm for the reduction of vanadium(IV) (0.057 M) by germanium(II) (2.5 mM), as catalyzed by copper(II) (1.0 mM) in 2.0 M Cl^- at 22 °C; $[\text{H}^+] = 1.7 \text{ M}$. The solid line represents the experimental curve whereas the circles were obtained by computerized treatment of differential equations based on reaction sequence (24)–(27), taking individual rate constants listed in Table 2. Extinction coefficients were $18.0 \text{ M}^{-1} \text{ cm}^{-1}$ for $\text{V}(\text{IV})$, and $11.0 \text{ M}^{-1} \text{ cm}^{-1}$ for $\text{Cu}(\text{II})$; other species were assumed to be negligibly absorbent. Path length 1.0 cm.

Table 2 Rate constants contributing to the reduction of vanadium(IV) by germanium(II) as catalyzed by added copper(II)^a

k_{24}	$32 \text{ M}^{-1} \text{ s}^{-1}$	k_{26}	$12 \text{ M}^{-1} \text{ s}^{-1}$
k_{-24}	$0.1 \text{ M}^{-1} \text{ s}^{-1}$	k_{-26}	$0.1 \text{ M}^{-1} \text{ s}^{-1}$
k_{25}	$10^3 \text{ M}^{-1} \text{ s}^{-1}$	k_{27}	$10^2 \text{ M}^{-1} \text{ s}^{-1}$
k_{-25}	$10^{-2} \text{ M}^{-1} \text{ s}^{-1}$	k_{-27}	$10^{-2} \text{ M}^{-1} \text{ s}^{-1}$

^a Parameters pertain to sequence (24)–(27) in text. Reactions were run at 22 °C; $\mu = 2.0 \text{ M}$ (HCl/NaCl); $[\text{H}^+] = 1.7 \text{ M}$; $[\text{V}^{\text{IV}}] = 0.057 \text{ M}$; $[\text{Ge}^{\text{II}}] = 2.5 \text{ mM}$; $[\text{Cu}^{\text{II}}] = 1.0 \text{ mM}$; $\lambda = 760 \text{ nm}$. Values listed are those giving optimum agreement between calculated and observed absorbances for duplicate runs. Extinction coefficients were $18.0 \text{ M}^{-1} \text{ cm}^{-1}$ for $\text{V}(\text{IV})$ and $11.0 \text{ M}^{-1} \text{ cm}^{-1}$ for $\text{Cu}(\text{II})$; other species were assumed to be negligibly absorbent. Path length 1.00 cm.

estimate ($34 \text{ M}^{-1} \text{ s}^{-1}$ at 24 °C)¹⁰ pertaining to the $\text{Ge}^{\text{II}}\text{-Fe}^{\text{III}}\text{-Cu}^{\text{II}}$ system. Extension of this procedure to runs at various acidities indicates that both k_{24} and k_{26} increase with $[\text{H}^+]$, but the values are not precise enough to justify a correlation with the observed binomial $[\text{H}^+]$ -pattern.

The convex $[\text{Cu}]$ -dependence perceived for this reaction indicates the partial conversion of the catalyst to an inactive dimeric form (presumably featuring chloro bridging). No evidence for this dimerization is observed for the catalyzed V^{IV} reaction with excess Sn^{II} , which was examined under strongly reducing conditions; here virtually all added copper was in the unipositive state.

In sum, the catalysis, by copper, of the reductions by Sn^{II} and Ge^{II} reflects the ease with which these s^2 centers, ordinarily $2e^-$ reagents, undergo single electron oxidations by Cu^{II} in chloride-rich media, in contrast to their inactivity toward the stronger oxidant VO^{2+} . The initial reduction of Cu^{II} almost certainly proceeds through a chloro bridge of the type $\text{Cu}^{\text{II}}\text{-Cl-Sn}^{\text{II}}$ or $\text{Cu}^{\text{II}}\text{-Cl-Ge}^{\text{II}}$, and the high chloride content probably serves further to stabilize the metastable Sn^{III} or Ge^{III} intermediate by polychloro ligation as suggested by Higginson²⁶ and by Babich.¹⁰

The oxidations of $\text{Ge}(\text{II})$ and $\text{Sn}(\text{II})$ to the tetrapositive states, and $\text{Ga}(\text{I})$ and $\text{In}(\text{I})$ to the respective tripositive species, entail partial or complete removal of the pair of outer s -electrons, often designated as the “inert pair”.²⁷ In each case involving p -block elements, the lighter of the two group co-members is oxidized the more readily, *i.e.*, its inert pair is less inert than that in its heavier congener. This trend in reactivity is most frequently observed for hydroxo- or halo-ligated systems. It has been attributed in part to more effective stabilization (*via* multiligation) of the oxidized state of the lighter atom. Such a picture, although simplified, is consistent with the direction of trend.

Appendix

Derivation of eqn. (9)

Two paths are indicated for this reaction. Both the protonated path (designated $k_{\text{H}}[\text{H}^+]$) and the non-protonated (k_{o}) utilize one unit of the monomeric $\text{Cu}(\text{II})$ catalyst, Cu_{M} :

$$(k)_{\text{obsd}} = k_{\text{o}}[\text{Cu}_{\text{M}}] + k_{\text{H}}[\text{H}^+][\text{Cu}_{\text{M}}] \quad (\text{A1})$$

Total copper(II), Cu_{T} , is partitioned into the dimeric (Cu_{D}) and monomeric (Cu_{M}) forms.

$$[\text{Cu}]_{\text{T}} = [\text{Cu}_{\text{M}}] + 2[\text{Cu}_{\text{D}}] = [\text{Cu}_{\text{M}}] + 2 K_{\text{D}}[\text{Cu}_{\text{M}}]^2 \quad (\text{A2})$$

where K_{D} is the dimerization constant. Solving for $[\text{Cu}_{\text{M}}]$ and substitution into eqn. (A1) yields eqn. (9) in the text.

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