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Electron Transfer. 144. Reductions with Germanium(II)[1]

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Solutions 0.2−0.4 M in Ge(II) and 6 M in HCl, generated by reaction of Ge(IV) with H_3PO_2, are stable for more than 3 weeks and can be diluted 200-fold with dilute HCl to give $GeCl_3^-$ preparations to be used in redox studies. Kinetic profiles for the reduction of Fe(III) by Ge(II), as catalyzed by Cu(II), implicate the odd-electron intermediate, Ge(III), which is formed from Cu(II) and Ge(II) ($k = 30$ M^{-1} s^{-1} in 0.5 M HCl at 24 °C) and which is consumed by reaction with Fe(III) ($k = 6 \times 10^2$ M^{-1} s^{-1}). A slower direct reaction between Ge(II) and Fe(III) ($k = 0.66$ M^{-1} s^{-1}) can be detected in 1.0 M HCl. The reaction of Ge(II) with I_3^- in 0.01−0.50 M iodide is zero order in oxidant and appears to proceed via a rate-determining heterolysis of a Ge(II)−OH_2 species ($k = 0.045$ s^{-1}) which is subject to H^+-catalysis. Reductions of $IrCl_6^{2-}$ and $PtCl_6^{2-}$ by Ge(II) are strongly Cl^--catalyzed. The Ir(IV) reaction proceeds through a pair of $1e^-$ changes, of which the initial conversion to Ge(III) is rate-determining, whereas the Pt(IV) oxidant probably utilizes (at least in part) an inner-sphere Pt^{IV}−Cl−Ge^{II} bridge in which chlorine is transferred (as Cl^+) from oxidant to reductant. The $2e^-$ reagent, Ge(II), like its $5s^2$ counterpart, In(I), can partake in $1e^-$ transactions, but requires more severe constraints: the coreagent must be more powerfully oxidizing and the reaction medium more halide-rich.

Only a few accounts describing the preparation and reactions of germanium(II) species in aqueous solution have appeared,[2−7] and systematic redox studies of this unusual donor are even more sparse.[8,9] This oxidation state ($E°_{IV,II} = -0.227$ V at pH 0) is described as unstable in aqueous media in the absence of halide.[10] In line with our interest in reductions by hypovalent main group elements,[11] we here report the preparation of germanium(II) solutions which may be handled using conventional techniques and the examination of the reactions of this state with oxidants in aqueous halide media. The most novel facets of this study are (a) kinetic profiles which allow estimates of rates of reactions involving the odd-electron species, Ge(III), and (b) evidence for slow ligand substitution at a Ge(II) center. A preliminary communication[12] deals with a portion of these results.

Experimental Section

Materials. Solutions were prepared using Millipore water that had been boiled for 2 h and then sparged with N_2 for 2 h more to remove dissolved oxygen. Sodium perchlorate (used as a supporting electrolyte) was prepared in solution from $NaHCO_3$ and concentrated $HClO_4$. Iron(III) perchlorate, copper(II) perchlorate, germanium dioxide, hypophosphorous acid, and quinoxaline (Aldrich products), KI_3 solution and sodium iodide (Fisher), sodium hexachloroplatinate(IV) ($Na_2PtCl_6 \cdot 6H_2O$, ϵ_{262}^{max} $2.4 \times 10^4 = M^{-1}$ cm^{-1})[13] (Alfa), and hydroxocobalamin (B_{12a}) hydrochloride (Sigma) were used as received. Fresh solutions of sodium hexachloroiridate(IV) ($Na_2IrCl_6 \cdot 6H_2O$, $\epsilon_{489}^{max} = 4.07 \times 10^3$ M^{-1} cm^{-1})[14] (Aldrich) were prepared daily. Bromopentaamminecobalt(III) perchlorate ($[Br(NH_3)_5Co]^{2+}$ $[ClO_4^-]_2$) and its chloro analogue were prepared as described.[15] Concentrations of Fe(III) were determined iodometrically.

Solutions of Ge(II) were prepared by a modification of the procedure of Jolly and Latimer;[2] all operations were carried out under high-purity (99.99%) argon. Just 1.0 g of GeO_2 was dissolved in 5 mL of concentrated NaOH, then reprecipitated, and redissolved by the addition of 20 mL of 6 M HCl. The resulting Ge(IV) solution was reduced with 7.5 mL of 50% hypophosphorous acid at 100° for 5−6 h:

$$Ge^{IV} + H_2O + H_3PO_2 \rightarrow H_3PO_3 + Ge^{II} + 2H^+ \qquad (1)$$

Germanium(II) hydroxide was precipitated from the cooled solution by addition of concentrated NH_3, washed twice with cold 1 M HCl, and then dissolved in 6 M HCl. Solutions 0.2−0.4 M in Ge(II) and 6 M in HCl were unchanged after several weeks, but diluted solutions ($[Ge^{II}] = 10^{-3}$ M, $[Cl^-] = 0.08$ M, $[H^+] = 0.3$ M) decomposed gradually ($t_{1/2} = 60$ min at 25 °C). $Ge(OH)_2$ is slightly soluble in 6 M $HClO_4$; the reducing capacity of the resulting solution ($[Ge^{II}]$ ca. 0.03 M) slowly decreases, and hydrated GeO_2 eventually precipitates.

Stoichiometric Studies. Stoichiometric determinations were carried out under argon and monitored at or near the low-energy maximum of each oxidant. Measured deficient quantities of Ge(II) were added to a known excess of the oxidant. After fixed waiting periods (30 s for $PtCl_6^{2-}$ and $IrCl_6^{2-}$, 50 min for Fe^{III} in HCl) decreases in absorbance were compared to the initial known absorbance of the oxidant.

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Table 1. Stoichiometry of Reactions of Germanium(II) with Transition Metal Oxidants[a]

oxidant (M × 10^5)	medium	λ, nm	$10^5[\mathrm{Ge^{II}}]$, M	$10^5\Delta[\mathrm{Ox}]$, M	$\Delta[\mathrm{Ox}]/\Delta[\mathrm{Ge^{II}}]$
$\mathrm{PtCl_6}^{2-}$ (9.0)	1 M HCl	262	0.49	0.47	0.96
			1.46	1.45	0.98
			2.43	2.16	0.89
			3.4	2.8	0.83[b]
$\mathrm{IrCl_6}^{2-}$ (21.1)	0.5 M HCl	489	2.0	3.8	1.91
			4.0	7.7	1.94
			6.0	11.3	1.89
			8.0	14.8	1.86
Fe(III) (65.5)[c]	0.4 M HCl	350	6.8	13.2	1.94
			13.6	25.6	1.88
			20.4	39	1.91
			27.2	51	1.89

[a] Reactions were carried out at 23 °C. Waiting period: 0.5 min for $\mathrm{PtCl_6}^{2-}$ and $\mathrm{IrCl_6}^{2-}$; 50 min for Fe(III). [b] $\mathrm{PtCl_6}^{2-}$ experiments at higher $[\mathrm{Ge^{II}}]$ encountered precipitation. [c] Reactions catalyzed by 5.0×10^{-6} M Cu(II).

Reductions of $\mathrm{Fe^{III}}$ were inconveniently slow in the absence of catalytic quantities (5×10^{-6} M) of Cu(II). Results are summarized in Table 1.

Kinetic Studies. Reactions, under argon, were examined at or near $\lambda_{\max}$ of the oxidant, using either a Shimadzu-1601 instrument or a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. Temperatures were kept at 23.0 ± 0.5 °C throughout the entire series of experiments. Ionic strength was regulated by addition of ($\mathrm{NaClO_4} + \mathrm{HClO_4}$), (HCl + NaCl), or NaI.

A number of oxidants reacted imperceptibly slowly with Ge(II) under the conditions used. Among these were $\mathrm{UO_2}^{2+}$ and the chloro-, bromo-, and phenylglyoxylato derivatives of $(\mathrm{NH_3})_5\mathrm{Co^{III}}$. In contrast, the corrin-bound Co(III) complex, aquacobalamin (vitamin $\mathrm{B_{12a}}$), was rapidly reduced to a Co(II) species, whereas the quinoxalinium cation ($\mathrm{QH^+}$) was converted, in separable steps,[16] to the corresponding radical ($\mathrm{QH^\bullet}$), and thence to its dihydro derivative ($\mathrm{QH_2}$).

Results and Discussion

Both Poskozim[7] and Parshall[6] have reported the principal Ge(II) species in 3 M HCl to be the monoanion, $\mathrm{GeCl_3}^-$, but in analogy to the behavior of Sn(II),[17] partial further anation to the dianion, $\mathrm{GeCl_4}^{2-}$, in 6 M HCl would be expected.

Stoichiometric determinations (Table 1) indicate nearly complete conversion to Ge(IV) for oxidations by $\mathrm{PtCl_6}^{2-}$, $\mathrm{IrCl_6}^{2-}$, and Fe(III) (eqs 2−4), as has been reported[2] also for $\mathrm{I_3}^-$ (eq 5).

$$\mathrm{Ge(II)} + \mathrm{Pt(IV)} \rightarrow \mathrm{Ge(IV)} + \mathrm{Pt(II)} \quad (2)$$

$$\mathrm{Ge(II)} + 2\mathrm{Ir(IV)} \rightarrow \mathrm{Ge(IV)} + 2\mathrm{Ir(III)} \quad (3)$$

$$\mathrm{Ge(II)} + 2\mathrm{Fe(III)} \rightarrow \mathrm{Ge(IV)} + 2\mathrm{Fe(II)} \quad (4)$$

$$\mathrm{Ge(II)} + \mathrm{I_3}^- \rightarrow \mathrm{Ge(IV)} + 3\mathrm{I}^- \quad (5)$$

Oxidations by Fe(III). The very slow reduction of Fe(III) by Ge(II) is catalyzed markedly by Cu(II), even at the 10^{-7} M level, but by none of the other usual transition metal cations. With $[\mathrm{Cl^-}] < 0.2$ M, rates are proportional to $[\mathrm{Ge^{II}}]$ and $[\mathrm{Cu^{II}}]$ but *are independent of* $[\mathrm{Fe^{III}}]$, pointing to the slow formation of one or more active intermediates, the faster reactions of which are kinetically silent. At higher $[\mathrm{Cl^-}]$ and $[\mathrm{Ge^{II}}]$, the linear profiles become curved, most perceptibly near the end, indicating that the initial catalytic act and the loss of Fe(III) proceed at more nearly equal rates. The patterns strongly support sequence 6−8.

Table 2. Representative Kinetic Data for the Oxidation of Germanium(II) by Iron(III) as Catalyzed by Copper(II)[a]

$[\mathrm{H^+}]$, M	$[\mathrm{Cl^-}]$, M	$10^4[\mathrm{Ge^{II}}]$, M	$10^6[\mathrm{Cu^{II}}]$, M	k_6, M	$10^{-2}k_7$, $\mathrm{M^{-1}\,s^{-1}}$	$10^{-5}k_8$,[b] $\mathrm{M^{-1}\,s^{-1}}$
0.40	0.50	5.4	5.0	31	6.5	5.4
0.40	0.50	10.0	5.0	34	7.0	5.4
0.40	0.50	10.0	10.0	34	7.0	5.4
1.0	0.20	6.6	5.0	9.8	6.0	1.25
1.0	0.20	10.0	5.0	10.3	5.5	1.25
1.0	0.40	10.0	5.0	23	5.4	2.1

[a] Reactions were carried out under argon at 23 °C and at ionic strength 1.0 M ($\mathrm{Cl^-}$, $\mathrm{ClO_4}^-$). $[\mathrm{Fe^{III}}]_{\mathrm{initial}} = 1.0 \times 10^{-4}$ M throughout. Kinetic parameters k_6 and k_7 were obtained from the best fit of integrated forms of sequence 6−8 to experimental curves (see text and ref 18). [b] Values of k_8 were obtained from data of Orth and Liddell (ref 19).

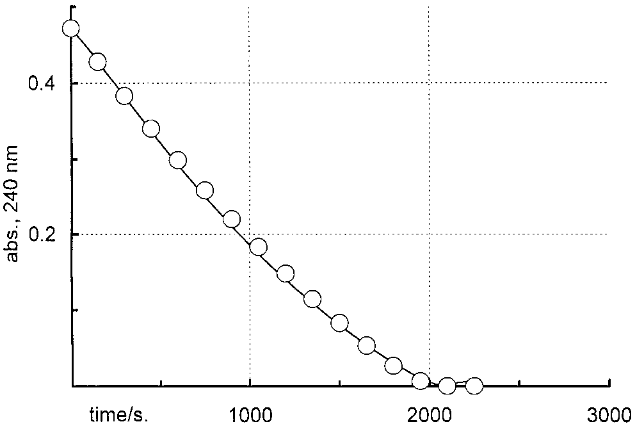

Figure 1. Kinetic profile at 240 nm for the reduction of Fe(III) (1.0×10^{-4} M) by Ge(II) (6.6×10^{-4} M), as catalyzed by Cu(II) (5×10^{-6} M) in 0.20 M $\mathrm{Cl^-}$ at 23 °C; $[\mathrm{H^+}] = 1.0$ M. The solid line represents the experimental curve whereas the circles denote absorbances calculated from numerical integration of differential equations based on reaction sequence 6−8, taking k_6 as 9.8 $\mathrm{M^{-1}\,s^{-1}}$, k_7 as 6×10^2 $\mathrm{M^{-1}\,s^{-1}}$, and $k_8 = 1.25 \times 10^5$ $\mathrm{M^{-1}\,s^{-1}}$ (ref 19). The extinction coefficient used for Fe(III) is 4.7×10^3 $\mathrm{M^{-1}\,cm^{-1}}$, and other species were considered to be negligibly absorbent. Optical path length = 1.00 cm.

$$\mathrm{Ge(II)} + \mathrm{Cu(II)} \rightarrow \mathrm{Ge(III)} + \mathrm{Cu(I)} \qquad k_6 \quad (6)$$

$$\mathrm{Fe(III)} + \mathrm{Ge(III)} \rightarrow \mathrm{Ge(IV)} + \mathrm{Fe(II)} \qquad k_7 \quad (7)$$

$$\mathrm{Fe(III)} + \mathrm{Cu(I)} \rightarrow \mathrm{Fe(II)} + \mathrm{Cu(II)} \qquad k_8 \quad (8)$$

Expression of this sequence as a trio of differential kinetic equations, and numerical integration using the program KINSIM,[18] leads, after slight adjustment for the slow unimolecular loss of Ge(II) ($k = 2 \times 10^{-4}$ $\mathrm{s^{-1}}$), to bimolecular rate constants k_6 and k_7 listed in Table 2. Values for k_8 (the Cu(I)−Fe(III) reaction) have been shown by Orth and Liddell[19] to vary with both $[\mathrm{H^+}]$ and $[\mathrm{Cl^-}]$ and have been taken from the report of these workers. A representative curve calculated in this manner is compared with the observed profile in Figure 1. The constants k_6 and k_7, pertaining to the formation and oxidation of a Ge-

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$$\mathrm{rate} = [\mathrm{Fe^{III}}][\mathrm{Cu^{I}}](a + b[\mathrm{Cl^-}]^2[\mathrm{H^-}]^{-1})$$

where $a = 9.7 \times 10^4$ $\mathrm{M^{-1}\,s^{-1}}$ and $b = 7.0 \times 10^5$ $\mathrm{M^{-2}\,s^{-1}}$ at 23 °C.

Table 3. Kinetic Data for Oxidation of Germanium(II) with I_3^-

$10^5[Ge^{II}]$, M	$[H^+]$, M	$[Cl^-]$, M	$[I^-]$, M	10^6(rate), M s^{-1} [b]
2.8	0.020	0.020	0.030	1.6 (1.7)
6.9	0.020	0.020	0.030	4.2 (4.1)
21	0.020	0.020	0.030	12 (12)
35	0.020	0.020	0.030	19 (20)
42	0.020	0.020	0.030	24 (25)
6.9	0.020	0.020	0.010	4.3 (4.1)
6.9	0.020	0.020	0.150	4.2 (4.1)
6.9	0.020	0.020	0.48	4.2 (4.1)
6.9	0.020	0.020	0.030	4.2 (4.1)
6.9	0.020	0.120	0.030	4.3 (4.1)
6.9	0.10	0.020	0.030	7.2 (7.9)
8.9	0.20	0.020	0.10	5.7 (5.3)
8.9	0.040	0.020	0.10	6.9 (6.6)
8.9	0.080	0.020	0.10	7.8 (9.0)
8.9	0.120	0.020	0.10	11 (11)
8.9	0.180	0.020	0.10	15 (15)
8.9	0.20	0.40	0.10	18 (17)
8.9	0.30	0.40	0.10	26 (23)

[a] Reactions were run at 23.5 °C, $\mu = 0.50$ M ($HClO_4$/$NaClO_4$), $[I_3^-] = 3 \times 10^{-6}$ to 8×10^{-6} M. All profiles were linear. [b] Parenthetical values were calculated as $[Ge^{II}](k + k'[H^+])$, with $k = 0.045\ s^{-1}$ and $k' = 0.70\ M^{-1}\ s^{-1}$.

(III) center, appear to be the first reported kinetic parameters associated with this odd-electron state. Within the ranges examined, the rate of formation of Ge(III) ($= 50\ M^{-2}\ s^{-1}\ [Ge^{II}]\ [Cu^I]\ [Cl^-]$ at 23 °C), but not its rate of oxidation, is proportional to $[Cl^-]$. Neither rate is acid-dependent.

At $[Cl^-] = 0.8-1.0$ M and $[Ge(II)] > 3 \times 10^{-3}$ M, decay curves become exponential, and the unimolecular loss of Ge(II) is negligible. Combinations of parameters k_7, k_6, and k_8 (the latter two adjusted for $[Cl^-]$-dependence),[19] fit the observed curves only if an additional term ($0.66\ M^{-1}\ s^{-1}$) pertaining to the uncatalyzed Ge(II)−Fe(III) reaction is included in the integrated treatment. This noncomplementary redox change very probably passes through Ge(III) as well. As expected, the initial step is much slower than the Fe(III)−Ge(III) reaction ($k_7 = 6 \times 10^2\ M^{-1}\ s^{-1}$). In analogy to the In(I,III) system,[20] the s^1 intermediate should be much more strongly reducing than the parent s^2 cation.

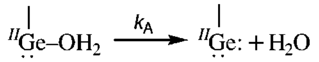
Oxidations by I_3^-. Reactions of this oxidant were carried out in 0.01−0.50 M iodide to minimize dissociation of I_3^- ($I_3^- \rightleftarrows I_2 + I^-$; $K = 1.4 \times 10^{-3}$ at 25°).[21] In analogy with reported speciations in Sn(II)−I^- systems,[22] we would expect partial conversion to GeI_3^- and GeI_4^{2-} in the solutions taken.

With Ge(II) in excess, *all profiles are linear* (i.e., rates do not vary with $[I_3^-]$). Slopes are proportional to [Ge(II)], are independent of $[I^-]$, and rise with $[H^+]$.

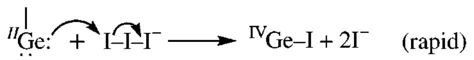
Kinetic data are listed in Table 3. Within the ranges studied, rates conform to binomial expression 9. Refinement yields $k = (4.5 \pm 0.2) \times 10^{-2}\ s^{-1}$ and $k' = 0.70 \pm 0.02\ M^{-1}\ s^{-1}$.

$$\text{rate} = [Ge^{II}][I_3^-]^0(k + k'[H^+]) \qquad (9)$$

The most unusual feature of this system, the zero-order dependence on I_3^-, requires that the oxidant enter the picture only after a pair of competing slow steps, both involving just the reductant. We are then almost certainly dealing with rate-determining heterolyses of Ge(II) centers at different protonation levels (the more protonated form the more reactive), yielding one or more coordinatively unsaturated intermediates. Since this reaction is not inhibited by added I^- but is accelerated by H^+, we infer that rates are being set by Ge(II)−O bond breakage. For the $[H^+]$-independent component we suggest sequence 10−11,



$${}^{II}Ge-OH_2 \xrightarrow{k_A} {}^{II}Ge: + H_2O \qquad (10)$$



$${}^{II}Ge: + I-I-I^- \longrightarrow {}^{IV}Ge-I + 2I^- \quad \text{(rapid)} \qquad (11)$$

and for the $[H^+]$-proportional contribution we suggest an analogous route (with protonation preceding scission). This duality of paths leads to rate law 12 (algebraically equivalent

$$\text{rate} = [Ge^{II}](k_A + k_{HA}[H^+]/K_{HA}) \qquad (12)$$

to eq 9), in which rate constants k_A and k_{HA} pertain to the two paths and K_{HA} pertains to the protonation preequilibrium. Our data allow calculation of the ratio k_{HA}/K_{HA}, but not individual values of these parameters. We do not observe kinetic saturation with respect to $[H^+]$, indicating that K_{HA} lies far above the acidity range examined.[23]

The acidic site involved in the protonation equilibrium in this system is uncertain. Our data are consistent with a pK_A below 0.0 for Ge(II)-bound H_2O, i.e., more than 4 units below that for the related Sn^{II}(aq) unit (ca. 4).[17] This is not unreasonable, for the acidities of aqua-substituted cations within group 14 are unusually sensitive to cationic size.[17] On the other hand, protonation at the unshared electron pair of Ge(II) cannot be excluded, since nucleophilic character associated with the analogous halide-ligated Sn(II) has been demonstrated.[24]

The proposed rate-determining scission at Ge(II) (eq 10) is not in accord with the general view[25] that sluggish bond-breaking at metal complexes in aqueous solution occurs only when activation entails a substantial loss in ligand field stabilization. There are, however, an array of reports of measurably slow substitutions at centers such as Ti(III),[26] Zn(II),[27] and Al(III),[28] which are conventionally considered to be substitution-labile. In addition, heterolysis (eq 10) may be considered unusual since it involves loss of a ligand from a tricoordinate species without compensation by attendant bond-making.

Reactions of $IrCl_6^{2-}$ and $PtCl_6^{2-}$. Reactions of both hexachloro-substituted oxidants were first-order each in the participating redox species. Conversions of the Ir(IV) center were run with Ge(II) in excess whereas transformations of Pt(IV) were carried out with excess oxidant to minimize complications resulting from formation of a Pt(II)−Ge(II) adduct.[29] Results are summarized in Table 4.

Both reactions are seen to be accelerated by chloride, pointing to the involvement of this anion in the activation processes.

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Table 4. Representative Kinetic Data for Oxidation of Germanium(II) with $IrCl_6^{2-}$ and $PtCl_6^{2-}$ [a]

A. $Ge^{II} + IrCl_6^{2-}$				B. $Ge^{II} + PtCl_6^{2-}$				
$10^4[Ge^{II}]$, M	$[H^+]$, M	$[Cl^-]$, M	$10^{-5}k_2$, $M^{-1}\,s^{-1}$	$10^6[Ge^{II}]$, M	$10^{-5}[Pt^{IV}]$, M	$[H^+]$, M	$[Cl^-]$, M	$10^{-2}k_2$,[b] $M^{-1}\,s^{-1}$
2.5	1.00	0.40	1.96	16.0	9.9	1.00	1.00	9.5 (9.1)
7.5	1.00	0.40	2.04	7.5	6.8	1.00	1.00	8.7 (9.1)
5.0	0.50	0.40	2.06	4.0	2.7	1.00	1.00	9.3 (8.1)
5.0	0.50	0.50	2.6	8.0	5.4	0.75	1.99	9.3 (9.1)
15.0	0.50	0.50	2.4	8.0	5.4	0.50	1.00	8.3 (9.1)
5.0	0.80	0.40	2.02	8.0	5.4	1.00	0.75	7.9 (7.7)
5.0	0.50	0.20	0.92	8.0	5.4	1.00	0.50	6.3 (6.2)
4.3	0.50	0.60	2.9	8.0	5.4	1.00	0.25	4.6 (4.8)
4.3	0.50	0.80	3.8					

[a] Reactions were carried out at 23.5 °C, $\mu = 1.0$ M ($HClO_4/NaClO_4$). [b] Parenthetical values were calculated as $(3.3 \times 10^2 + 5.8 \times 10^2[Cl^-])$ $M^{-1}\,s^{-1}$ (see text).

For the Ir(IV) reaction, which is very nearly first-order in halide, the Cl^--related step is preponderant, whereas the $PtCl_6^{2-}$ data conform to the binomial rate law (eq 13),

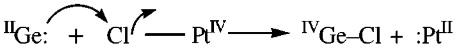
$$\text{rate} = [Ge^{II}][Pt^{IV}](k_1 + k_2[Cl^-]) \qquad (13)$$

where $k_1 = (3.3 \pm 0.4) \times 10^2$ $M^{-1}\,s^{-1}$ and $k_2 = (5.8 \pm 0.5) \times 10^2$ $M^{-2}\,s^{-1}$. The coordinatively saturated oxidants cannot accommodate an additional Cl^-, nor is it reasonable that a reaction between negatively charged redox partners be favored electrostatically by a third anion. The "extra" chloride then is almost certainly attached to the Ge(II) center where, in analogy with our observations of the Ge(II)−Fe(III) system, it would be expected to ease the formation of Ge(III).[30,31] This effect possibly reflects an increased conversion of $GeCl_3^-$ to $GeCl_4^{2-}$, which more closely resembles the probable Ge(III) intermediate ($GeCl_4^-$) and therefore may lower the Franck−Condon barrier to the initial electron transfer act.

The reaction with $IrCl_6^{2-}$ (a $1e^-$ oxidant) must pass through this odd-electron transient, but our exponential decay curves exhibit no irregularities attributable to its formation or destruction, indicating that initial conversion to the s^1 transient (designated noncommitally as $Ge^{III}(Cl^-)$, is rate-determining and its further oxidation is kinetically silent, as is the case with an array of reported reductions by In(I).[11]

$$Ge^{II} \underset{}{\overset{Cl^-}{\rightleftharpoons}} Ge^{II}(Cl^-) \xrightarrow{Ir^{IV}} Ge^{III}(Cl^-) \xrightarrow[\text{rapid}]{Ir^{IV}} Ge^{IV}(Cl^-) \qquad (14)$$

Two sequences come to mind for the reduction of $PtCl_6^{2-}$. The more direct is an inner-sphere $2e^-$ path proceeding via a chlorine bridge and involving net transfer of chloronium (Cl^+) from Pt^{IV} to Ge^{II}, in a manner similar to that demonstrated for a number of Pt(II)−Pt(IV) systems.[32]



$${}^{II}Ge{:} + Cl{-}Pt^{IV} \longrightarrow {}^{IV}Ge{-}Cl + {:}Pt^{II} \qquad (15)$$

Alternatively, and perhaps additionally, reaction may occur by a series of $1e^-$ transfers, in which the initial $Pt^{IV}-Ge^{II}$ step (eq 16) is rate-determining. If, as in the $IrCl_6^{2-}$ reduction, the

$$Pt^{IV} + Ge^{II} \xrightarrow{Cl^-} Pt^{III} + Ge^{III} \qquad (16)$$

$$Pt^{III} + Ge^{II} \rightarrow Pt^{II} + Ge^{III} \qquad \text{(rapid)} \qquad (17)$$

$$Pt^{IV} + Ge^{III} \rightarrow Pt^{III} + Ge^{IV} \qquad \text{(rapid)} \qquad (18)$$

conversion to Ge(III) is favored at high $[Cl^-]$, it is reasonable to associate the chloride-independent term in rate law 13 with the indicated bridged path and the $[Cl^-]$-proportional term to the stepwise route 16−18 involving a Pt(III) intermediate.[33]

In sum, this survey of the redox chemistry of Ge(II) tells us that this $2e^-$ donor, like its $5s^2$ counterpart, In(I), can partake in single electron transactions, but only under more stringent constraints. The coreagent should be a more powerful oxidant and/or the reaction medium must be halide-rich to facilitate initial conversion to Ge(III). The contrast is most vividly illustrated in reactions with an array of Co(III) oxidants which are reduced by In(I) (albeit sometimes slowly) but are inert to Ge(II). A possible exception is the Co(III)-bound corrin, B_{12a}; $2e^-$ reduction by Ge(II) may conceivably convert this to its Co(I) analogue, B_{12s} (cob(I)alamin), which is known to undergo rapid comproportionation with B_{12a} ($Co^I + Co^{III} \rightarrow 2Co^{II}$).[34]

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