Preparation of aqueous solutions of hypovalent germanium; reactions involving germanium-(II) and -(III)

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Solutions 0.2–0.4 mol dm^{-1} in Ge^{II} and 6 mol dm^{-1} in HCl, generated by reaction of Ge^{IV} with H$_3$PO$_2$, are stable for more than three weeks and can be diluted 200-fold with dilute HCl to give GeCl$_4$$^{2-}$ preparations that may be handled by conventional techniques; kinetic profiles for the reduction of Fe^{III} by Ge^{II}, as catalyzed by Cu^{II} in this medium, implicate, for the first time, the odd-electron intermediate Ge^{III}, which is formed from Cu^{II} and Ge^{II} ($k = 30$ M^{-1} s^{-1} in 0.50 M HCl) and is consumed by reaction with Fe^{III} ($k = 6 \times 10^2$ M^{-1} s^{-1}).

Only a few accounts decribing the preparation and reactions of germanium(II) species in aqueous solution are at hand,[1–4] and no systematic redox studies of this unusual donor have yet appeared. This oxidation state ($E°_{IV,II} = -0.22$ V at pH 0) is described as unstable in aqueous media in the absence of halide.[5]

We here report the preparation of aqueous germanium(II) solutions which may be handled using conventional techniques. These have been used to compare the rates at which Ge(II) reacts with several oxidants in chloride media.
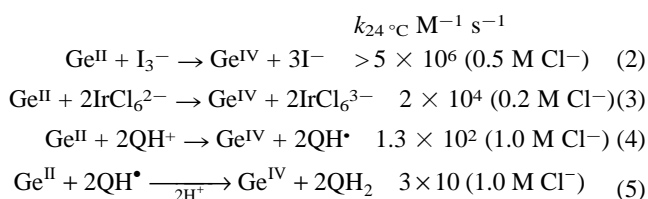
In a modification of the procedure of Jolly and Latimer,[1] all operations were carried out under high purity (99.99%) argon. 1.0 g of GeO$_2$ was dissolved in 5 ml of conc. NaOH, then reprecipitated and redissolved by adding 20 ml of 6 M HCl. The resulting Ge^{IV} solution was reduced with 7.5 ml of 50% H$_3$PO$_2$ at 100 °C for 5–6 h [eqn. (1)].

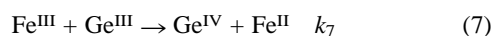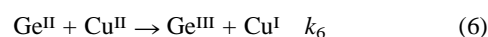$$Ge^{IV} + H_2O + H_3PO_2 \rightarrow H_3PO_3 + Ge^{II} + 2H^+ \qquad (1)$$

Germanium(II) hydroxide was precipitated from the cooled solution by addition of conc. NH$_3$, washed twice with 1 M HCl, then dissolved in 6 M HCl. Alternatively, crystalline GeCl$_2$ may separate slowly from the reduced solution and can be dissolved directly in 6 M HCl. Solutions 0.2–0.4 M in Ge(II) in 6 M HCl were unchanged after several weeks, but diluted solutions ([Ge^{II}] = 10^{-3} M, [Cl$^-$] = 0.08 M, [H$^+$] = 0.3 M) decomposed slowly ($t_{1/2}$ = 60 min). Germanium(II) hydroxide is not appreciably soluble in 4 M HClO$_4$. In analogy with the behavior of Sn(II),[6] Ge(II) may be taken to exist predominantly as GeCl$_4$$^{2-}$ at Cl$^-$ concentrations > 0.3 M.
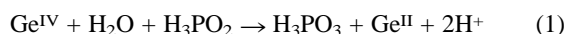
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Solutions of Ge(II) rapidly reduce I$_3$$^-$, IrCl$_6$$^{2-}$, and the quinoxalinium cation, QH$^+$,[7] first to its radical, QH$^•$, and thence to its dihydro derivative, QH$_2$:

$$k_{24 °C} \text{ M}^{-1} \text{ s}^{-1}$$

$$Ge^{II} + I_3^- \rightarrow Ge^{IV} + 3I^- \quad >5 \times 10^6 \text{ (0.5 M Cl}^-) \quad (2)$$

$$Ge^{II} + 2IrCl_6^{2-} \rightarrow Ge^{IV} + 2IrCl_6^{3-} \quad 2 \times 10^4 \text{ (0.2 M Cl}^-) \quad (3)$$

$$Ge^{II} + 2QH^+ \rightarrow Ge^{IV} + 2QH^• \quad 1.3 \times 10^2 \text{ (1.0 M Cl}^-) \quad (4)$$

$$Ge^{II} + 2QH^• \xrightarrow{2H^+} Ge^{IV} + 2QH_2 \quad 3 \times 10 \text{ (1.0 M Cl}^-) \quad (5)$$

The very slow reduction of Fe(III) by Ge(II) is catalyzed markedly by Cu(II), even at the 10^{-7} M level. With [Cl$^-$] < 0.2 M, rates are proportional to [Ge^{II}] and [Cu^{II}] but are *independent* of [Fe^{III}], pointing to a slow formation of one or more active intermediates, the faster reactions of which are kinetically silent. At higher [Cl$^-$] and [Ge^{II}], the linear profiles become curved, most perceptibly near the end of the conversions, indicating that the initial catalytic act and the loss of Fe^{III} proceed at more nearly equal rates. Such patterns strongly support the sequence (6)–(8)

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

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

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

Expression of this sequence as a trio of differential equations, and numerical integration using the program KINSIM[8] led, after slight adjustment for the slow unimolecular loss of Ge^{II} ($k = 2 \times 10^{-4}$ s^{-1}) to bimolecular rate constants k_6 and k_7 listed in Table 1. Values for k_8 (the Cu^I–Fe^{III} reaction) have been shown by Orth and Liddell[9] to vary with both [H$^+$] and [Cl$^-$] and have been taken from the report of these workers. A curved calculated in this manner is compared to a representative profile in Fig. 1. The constants k$_6$ and k$_7$, pertaining to the formation and oxidation of Ge^{III}, 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}, but not its oxidation, is proportional to [Cl$^-$]; neither rate is acid-dependent.

At [Cl$^-$] = 0.8–1.0 M and [Ge^{II}] > 3 × 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)[9] fit the observed curves

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Table 1 Representative kinetic data for the oxidation of germanium(II) by iron(III) as catalyzed by copper(II)^a

[H$^+$]/M	[Cl$^-$]/M	10^4[Ge^{II}]/M	10^6[Cu^{II}]/M	k_6/M^{-1} s^{-1}	10^{-2} k_7/M^{-1} s^{-1}	10^{-5} k_8^{b}/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 24 °C and at ionic strength 1.0 M (Cl$^-$, ClO$_4$$^-$). [Fe^{III}]$_{initial}$ = 1.0 × 10^{-4} M throughout. Kinetic parameters k_6 and k_7 were obtained from the best fit of integrated forms of the sequence (6)–(8) to experimental curves (see text and ref. 8). ^{b} Values of k_8 were obtained from data of Orth and Liddell (ref. 9).
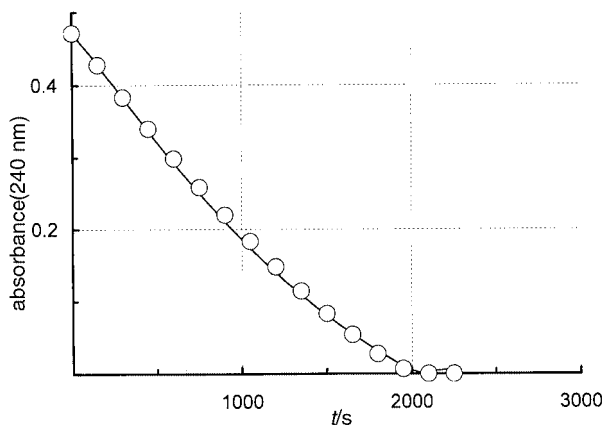

Fig. 1 Kinetic profile at 240 nm for the reduction of Fe(III) (1.0×10^{-4} M) by Ge(II) (6.6×10^{-4} M), as catalyzed by Cu(II) (5×10^{-6} M) in 0.20 M Cl$^-$ at 24 °C; [H$^+$] = 1.0 M. The solid line represents the experimental curve whereas the circles denote absorbances calculated from numerical integration of differential equations based on reaction sequence (6)–(8), taking k_6 as 9.8 M^{-1} s^{-1}, k_7 as 6×10^2 M^{-1} s^{-1}, and k_8 = 1.25×10^5 M^{-1} s^{-1} (ref. 9). The extinction coefficient used for Fe(III) is 4.7×10^3 M^{-1} cm^{-1}, and other species were considered to be negligibly absorbent. Optical path length = 1.00 cm.

only if an additional term (0.66 M^{-1} s^{-1}), pertaining to the uncatalyzed Ge^{II}–Fe^{III} reaction, is included in the treatment.

This non-complementary 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,[10] the odd-electron s^1 intermediate should be much more strongly reducing than the parent s^2 cation.

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