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The Cerium(IV)/Cerium(III) Electrode Potential in Hydrochloric Acid Solution

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Introduction

Cerium(IV) is a popular oxidant in analytical[1] and organic[2] applications, because it is highly reactive, inexpensive, and readily available in high purity. Ce^{IV} has also been used as oxidant in studies of the homogeneously[3] and heterogeneously[4] catalyzed oxidations of H_2O to O_2 and Cl^- to Cl_2. These systems are convenient because the direct oxidations of H_2O and Cl^- by Ce(IV) are relatively slow. The Ce^{IV}/Ce^{III} potential is well established in aqueous H_2SO_4, HNO_3, and $HClO_4$.[5-7] In hydrochloric acid, however, much less information is available. The potential for Ce^{IV}/Ce^{III} in 1 M HCl was initially reported to be 1.28 V vs NHE,[7] but this result was later called into question.[8] Nevertheless, the 1.28-V value is still quoted, with the original reference, in electrochemical compilations.[9]

Our interest in the Ce^{IV}/Ce^{III} couple in HCl(aq) arises from reaction 1, which is known to proceed spontaneously in the forward

$$Ce(IV) + Cl^- \rightleftharpoons Ce(III) + {}^1/{}_2Cl_2 \qquad (1)$$

direction.[10,11] We recently discovered that the reaction is catalyzed by $ReCl_6^{2-}$.[12] In the course of studying this catalytic process, we attempted to measure the Ce^{IV}/Ce^{III} potential both by electrochemical means and by direct determination of the equilibrium quotient K_1 for reaction 1. The latter method proved to be successful; K_1 is 47 ± 13 $atm^{1/2}\ M^{-1}$ in 1 M HCl ($\mu = 1.2$ M), which yields a Ce^{IV}/Ce^{III} formal potential of 1.466 ± 0.008 V vs NHE.

Experimental Section

Instrumentation. Electronic absorption spectra were recorded by using an Aviv Model 14DS spectrophotometer. Cyclic voltammograms were recorded by using either a PAR Model 174A polarographic analyzer or a Wenking TS70/1 potentiostat with a home-built microcomputer interface. The cell contained a glassy-carbon working electrode (which was polished immediately before each measurement), a Pt counter electrode, and an aqueous Ag/AgCl (3 M NaCl) reference electrode.

Table I. Spectral and Equilibrium Data for the Reaction Ce(IV) + $Cl^- \rightleftharpoons$ Ce(III) + $^1/_2Cl_2$[a]

concn/M				spectral data for Ce(IV)				
H^+	Cl^-	Na^+	ClO_4^-	λ_{max} (ϵ_{max})	ϵ_{380}	ϵ_{400}	K_1[b]	$E°'(Ce^{IV}/Ce^{III})$[c]
1.00	1.00	0.20	0.20	287 (2510)	476	275	47 ± 13	1.466 ± 0.008
1.00	1.00	0.20	0.20	*d*	*d*	*d*	63 ± 7[d]	1.473 ± 0.003
0.20	1.00	1.00	0.20	291 (1990)	362	187	17 ± 4	1.443 ± 0.007
1.00	0.20	0.20	1.00	293 (2290)	330	178	123 ± 30	1.489 ± 0.006
				318 (5620)[f]				1.44[e]

[a] 24 ± 1 °C. Electronic absorption spectra: wavelengths/nm; extinction coefficients/$M^{-1}\ cm^{-1}$ (estimated uncertainties ±5% of Cl^--containing solutions, ±1% for 0.5 M H_2SO_4). [b] Equilibrium quotient/$atm^{1/2}\ M^{-1}$. Total Ce concentration 4.14×10^{-3} M unless otherwise noted. [c] In V vs NHE; calculated from K_1 and $E°'(Cl_2/Cl^-)$ (derived from data in rerf 16). See text for discussion. [d] Total Ce concentration 1.72×10^{-2} M. Maxima and extinction coefficients are the same as those in the more dilue solution; see Experimental Section. [e] Reference 6. [f] 0.5 M H_2SO_4.

Materials and Procedures. The molarity (M, or mol L^{-1}) scale was used for concentrations throughout this work, except that the estimation of activity coefficients (see below) required that some molalities (*m*, or mol (kg of $H_2O)^{-1}$) be determined.

Cerium(IV) was obtained in solution form (ca. 0.5 M in 6 M $HClO_4$) from GFS Chemicals. Other materials were reagent grade and were used as received. Acid solutions were standardized against NaOH(aq) (Merck Titrisol). The total cerium concentration in the stock solution was determined by inductively coupled plasma–atomic emission spectroscopy (Hazen Research Inc., Golden, CO), to be 0.518 ± 0.026 M.[13] This solution was diluted with water and $HClO_4$(aq) as needed to prepare "working solutions" of Ce(IV) (0.0207 or 0.0863 M) in 1 M $HClO_4$. "Working solutions" of Ce(III) with the same concentrations were prepared similarly, except that the Ce(IV) was first reduced to Ce(III) by treatment with H_2O_2(aq) and the solution boiled to destroy excess H_2O_2, before dilution.

Measurements of K_1 were carried out by mixing 0.60 mL of the above "working solutions" of Ce(IV) or Ce(III) with 2.40 mL of one of the following solutions: 1.00 M HCl/0.25 M NaCl, 1.25 M NaCl, or 1.00 M $HClO_4$/0.25 M NaCl. (These mixtures allowed us to vary [H^+] and [Cl^-] at a constant ionic strength of 1.20 M and gave a total Ce concentration of either 4.14×10^{-3} or 1.73×10^{-2} M; see Table I.) In each run, three solutions were used: one beginning with Ce(III), one beginning with Ce(IV), and one "blank" (i.e. of the same acid mixture, but without Ce). All three solutions were saturated with Cl_2(g) several times over the next 1–18 h. After the two Ce-containing solutions appeared to have reached equilibrium, their absorbances at 380 and 400 nm were recorded and (after "blank" subtraction) used to determine the equilibrium Ce(IV) concentration. (The wavelengths 380 and 400 nm were chosen so as to minimize interference from Cl_2(aq), which absorbs very strongly in the region of the Ce^{IV} absorbance maximum near 300 nm.) All experiments were performed in triplicate, and the resulting sample standard deviations for K_1 and $E°'(Ce^{IV}/Ce^{III})$ are reported as uncertainties in Table I. (The effects of other sources of error, including uncertainties in total Ce concentration and in extinction coefficients, on calculated values for K_1 and $E°'(Ce^{IV}/Ce^{III})$ are small compared to the variations between runs in measured [Ce^{IV}] at equilibrium.)

The extinction coefficients for Ce^{IV} in the above Cl^--containing solutions, which were needed for calculating K_1, could not be determined simply by measuring their spectra after a known dilution from the Ce(IV) stock solution. This is because significant loss of Ce(IV) occurs between the time the solutions are mixed and the earliest possible time a spectrum can be recorded. Instead, while the spectrum was being recorded, a 0.2-mL aliquot of the solution was withdrawn and the reaction was quenched by addition to 2.5 mL of 6 M H_2SO_4, followed by dilution to 5 mL with H_2O. (A similar procedure was used by Duke and Borchers to measure [Ce(IV)] in their kinetic studies of the oxidation of Cl^- by

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(11) For kinetic studies of the uncatalyzed reaction, see: (a) Duke, F. R.; Borchers, C. E. *J. Am. Chem. Soc.* **1953**, *75*, 5186–5188. (b) Alexiev, A. A.; Bontchev, P. R. *Z. Phys. Chem. (Leipzig)* **1969**, *242*, 333–340. The analogous reaction of Ce(IV) with Br^- has also been studied: (c) Wells, C. F.; Nazer, A. F. M. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 816–824.
(12) Maverick, A. W.; Henderson, L. J., Jr.; Yao, Q. Submitted for publication.
(13) The concentration of Ce^{IV} in the same stock solution was determined by titration to be 0.492 ± 0.001 M. However, for all of the equilibrium quotient calculations, it is the *total* concentration of Ce that is important, since the amounts of Ce(III) and Ce(IV) change during treatment with Cl_2 and HCl(aq).

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Ce(IV).[11a]) In separate experiments with solutions prepared from solid $(NH_4)_2Ce(NO_3)_6(s)$ (whose purity was established by titration), we found that $\epsilon_{316\ nm}$(Ce(IV)) = 6180 ± 80 $M^{-1}\ cm^{-1}$ in 3 M H_2SO_4.[14] This procedure enabled us to determine the Ce(IV) extinction coefficients for each different set of H^+ and Cl^- concentrations, and for two different Ce^{IV} concentrations differing by at least a factor in 4 in each case. The results are presented in Table I.

Partial pressures of Cl_2 over the solutions were obtained by subtracting the partial pressure of water vapor over the solution[15] from the current barometric pressure.

We calculated formal potentials $E°'(Cl_2)$ on the molar scale for the $Cl_2/Cl_3^-/Cl^-$ electrode under our conditions (i.e. the emf of the cell $Pt|H_2(1\ atm)|HCl(aq)|Cl_2(1\ atm)|Pt$, including the effects of the formation of Cl_3^-). For this calculation, we used the formula $E°'(Cl_2) = E_m° + (RT/F)\ln((1 + K_{Cl_3^-})/(m_{H^+}m_{Cl^-}\gamma_\pm^2))$, derived from the work of Mussini et al.[16] In this formula, $E_m°$ is the standard molal electrode potential for the Cl_2/Cl^- couple (1.35952 ± 0.00003 V vs NHE at 24 °C), $K_{Cl_3^-}$ is the equilibrium constant for the reaction $Cl_2(g) + Cl^-(aq) \leftrightarrow Cl_3^-(aq)$ (0.0124 atm^{-1} at 24 °C), m_{H^+} and m_{Cl^-} are the molalities of H^+ and Cl^-, and $\gamma_\pm$ is the mean molal activity coefficient for HCl(aq). Values of $\gamma_\pm$ for these solutions were estimated using published activity coefficients for pure HCl(aq)[17] and Harned α coefficients[18,19] and the molalities of our solutions, which we determined from their known molarities by measuring their densities. The resulting values of $E°'(Cl_2)$ (μ = 1.20 M, with Na^+ and ClO_4^- balancing ions) are 1.3673 V (1.00 M H^+, 1.00 M Cl^-), 1.3703 V (0.20 M H^+, 1.00 M Cl^-), and 1.3654 V (1.00 M H^+, 0.20 M Cl^-) vs NHE. (These values are believed to be accurate within ca. 0.1 mV; the largest single source of error is likely to be the estimation of $\gamma_\pm$.)

Results and Discussion

Electrochemical Determination of $E(Ce^{IV}/Ce^{III})$. The Ce^{IV}/Ce^{III} potential has been measured successfully in $HClO_4$, H_2SO_4, and HNO_3 solutions by electrochemical methods.[6,7] Smith and Goetz[7] also attempted to measure the potential in 1 M HCl, reporting a value of 1.28 V vs NHE. We also attempted to determine the Ce^{IV}/Ce^{III} potential, by measuring the rest potential of a glassy-carbon electrode in various mixtures of Ce^{III} and Ce^{IV} in 1 M HCl (these were examined immediately after preparation, to minimize decomposition of Ce^{IV}). Our measurements suggested a Ce^{IV}/Ce^{III} potential of ≥1.5 V vs NHE. Unfortunately, both this result and the older 1.28-V value are likely to be in error, because (as pointed out in ref 8) the Cl_2/Cl^- couple is also electroactive under these conditions.

We also attempted to use cyclic voltammetry to obtain the half-wave potential for the Ce^{IV}/Ce^{III} couple. (We reasoned that voltammograms recorded using a glassy-carbon electrode, which shows a high overpotential for Cl_2 evolution, might yield a single wave attributable to Ce^{IV}/Ce^{III}.[20]) This attempt also failed: we found no waves attributable to Ce^{IV}/Ce^{III} at a variety of scan rates (10–500 mV s^{-1}).

Chemical Method, via K_1. Since several electrochemical methods had failed, we attempted a chemical approach. If equilibrium can be achieved in reaction 1, the Ce^{IV}/Ce^{III} potential can be calculated from K_1. We have now determined K_1 under several sets of conditions, by measuring spectrophotometrically the equilibrium concentration of Ce^{IV} in mixtures containing Ce, Cl^-, and Cl_2. The results of these experiments are presented in Table I.

We ensured that equilibrium was achieved in these experiments by passing Cl_2 into separate solutions initially containing only Ce^{III} or only Ce^{IV}. Over a period of 1–18 h (depending on the concentrations of H^+ and Cl^- chosen), the absorbances in the "Ce^{III}" and "Ce^{IV}" solutions converged to common values. Therefore, the mixtures must have arrived at equilibrium.

The Nernst equation applied to reaction 1, including activity effects (assuming unit activity coefficient for $Cl_2(g)$), is

$$E_1 = E_1° - (RT/nF)\ \ln\{a_{Ce^{III}}(P_{Cl_2})^{1/2}/a_{Ce^{IV}}a_{Cl^-}\} \qquad (2)$$

At equilibrium, E_1 is zero and

$$E_1° = (RT/nF)\ \ln\{a_{Ce^{III}}(P_{Cl_2})^{1/2}/a_{Ce^{IV}}a_{Cl^-}\} \qquad (3)$$

Some activity coefficients have been measured for solutions of Ce(III) in hydrochloric acid.[18] However, as far as we are aware, no such data are available for cerium(IV). Thus, we have carried out the remainder of our analysis using the formal potential $E_1°'$ on the molar scale, which is based on concentrations rather than activities:[21]

$$E_1°' = (RT/nF)\ \ln\{[Ce^{III}](P_{Cl_2})^{1/2}/([Ce^{IV}][Cl^-])\} = (RT/nF)\ \ln(K_1) \qquad (4)$$

Then, since $E_1°'$ is the difference between the formal potentials for the Ce^{IV}/Ce^{III} couple and the $Cl_2/Cl_3^-/Cl^-$ system[16] (see Experimental Section), the desired quantity $E°'(Ce^{IV}/Ce^{III})$, presented in Table I, is given by

$$E°'(Ce^{IV}/Ce^{III}) = (RT/nF)\ \ln(k_1) + E°'(Cl_2) \qquad (5)$$

The equilibrium quotient data in Table I show relatively large uncertainties (ca. ±25%).[22] Still, the corresponding uncertainties in the calculated Ce^{IV}/Ce^{III} formal potentials are less than 0.01 V, and as a result, the trends in $E°'(Ce^{IV}/Ce^{III})$ with $[H^+]$ and $[Cl^-]$ are clear.

$E°'(Ce^{IV}/Ce^{III})$ is smaller at $[H^+]$ = 0.2 M than at $[H^+]$ = 1 M. This suggests that Ce(IV) can be stabilized in these solutions by hydrolysis, i.e. by formation of hydroxo complexes. The higher value of $E°'(Ce^{IV}/Ce^{III})$ at $[Cl^-]$ = 0.2 M suggests that complexation by chloride ion also stabilizes Ce(IV). Both of these trends are consistent with previous work: Hydrolysis of Ce(IV) in $HClO_4$ solution has been studied by several other workers;[23,24] complexation of Ce(IV) by other ions, such as SO_4^{2-}, has also been demonstrated.[25] Thus, it is likely that $Ce^{IV}(OH)Cl_x^{x-3}$, or similar species, are important in the chemistry of cerium(IV) in hydrochloric acid.[26]

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(14) As a check, we also performed this procedure with the final solution 0.5 M in H_2SO_4. This gave an extinction coefficient of 5620 ± 50 $M^{-1}\ cm^{-1}$, in close agreement with the literature value of 5580 $M^{-1}\ cm^{-1}$: Medalia, A. I.; Byrne, B. J. *Anal. Chem.* **1951**, *23*, 453–456.

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(20) We recently used cyclic voltammetry to measure the $ReCl_6^{-/2-}$ half-wave potential, ca. 1.70 V vs NHE (also well beyond the Cl_2/Cl^- potential) in 1 M HCl.[12]

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(22) This variability may be due to differences in the efficiency of saturating the solutions with Cl_2: Runs in which the background absorbance due to Cl_2 was smaller also tended to show smaller net absorbance due to Ce(IV). However, more prolonged or more frequent saturation with Cl_2 did not improve the reproducibility of the data. There was no noticeable correlation between the temperature of a run, or the barometric pressure, and the measured [Ce(IV)] value.

(23) (a) Sherrill, M. S.; King, C. G.; Spooner, R. C. *J. Am. Chem. Soc.* **1943**, *65*, 170–179. (b) Hardwick, T. J.; Robertson, E. *Can. J. Chem.* **1951**, *29*, 818–822.

(24) Hardwick and Robertson[23b] also found evidence for dimerization of Ce(IV) complexes. Our data (see Table I) show little change in $E°'$ at higher total Ce concentration. This suggests that dimerization, if it occurs in our system, has little effect on redox properties.

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To summarize, we have used a chemical method to obtain the first reliable estimate for the Ce^{IV}/Ce^{III} redox potential in hydrochloric acid solution. Our results are consistent with previous reports of the reactivity of Ce^{IV} in HCl(aq), and they suggest that these solutions contain complexes of Ce^{IV} with Cl^- and OH^-.

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(26) Solutions of Ce(IV) in conc. HCl(aq) are orange-red,[11b] and the electronic spectrum of $CeCl_6^{2-}$ shows λ_{max} = 376 nm (Ryan, J. L.; Jørgensen, C. K. *J. Phys. Chem.* **1966**, *70*, 2845–2857). Both of these observations represent large red shifts relative to our spectra. Thus, we believe the number of chloride ions complexed to Ce(IV) under our conditions is small. (The equilibrium constants for binding of Cl^- to the isoelectronic Th^{4+} are all less than 2 M^{-1}: Waggener, W. C.; Stoughton, R. W. *J. Phys. Chem.* **1952**, *56*, 1–5.)