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Planning a Kinetic and Mechanistic Study with Cerium (IV)

Cerium(IV) is a strong oxidizing agent, and its oxidizing power can be varied widely by control of the type and concentration of acid used as the reaction medium. This is partly reflected in the Ce(IV)/Ce(III) electrode potential (versus the standard hydrogen electrode, SHE) which is markedly ligand dependent, e.g., the oxidation potentials are 1.28, 1.44, 1.61, and 1.70 V in 1 *N* hydrochloric, sulfuric, nitric, and perchloric acids, respectively (1). Increasing the perchloric acid concentration from 1*N* to 8*N* increases the potential from 1.70 to 1.78 V, whereas a corresponding change in sulfuric acid concentration lowers the potential to 1.42 V. This latter decrease is attributed to the formation of sulfato complexes, e.g., Ce(SO₄)²⁺, Ce(SO₄)₂ and Ce(SO₄)₃²⁻. In perchloric acid, Ce(IV) exists mainly as the hydrolyzed species Ce(OH)³⁺ and Ce(OH)₂²⁺ and the unhydrolyzed Ce⁴⁺ (2); two dimeric species, (Ce—O—Ce)⁶⁺ and (HO—Ce—O—Ce—OH)⁴⁺ have also been reported in HClO₄ (3).

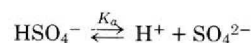
Despite the variety of tetravalent species of cerium, investigations of ceric oxidations frequently refer to the oxidant as “Ce(IV)” without specifying the particular form(s) involved in the reaction coordinate(s). This is particularly true for studies carried out in sulfuric acid media where the trisulfato complex, Ce(SO₄)₃²⁻, is the predominant species. The specification of reaction conditions, under which the concentrations of the different ceric species (unhydrolyzed, hydroxo, and sulfato) are controlled, and varied at will, is needed to formulate detailed mechanisms for many of the Ce(IV) oxidations. In this paper we first describe an acidic sulfate medium in which various concentrations of the possible Ce(IV) species can be prescribed. Secondly, we present the computations—based on the simultaneous solution of various equilibria—of the concentration distribution of the sulfato and hydroxo

species of Ce(IV). Lastly, the optimum planning of a kinetic study of a Ce(IV)-reductant system, based on the quantitative description of the medium is suggested.

Defining a Useful Acidic Sulfate Medium

Because working in a sulfuric acid medium presents the difficulties (1) of having a preponderance of the cerium(IV) trisulfato complex and (2) of varying the sulfate concentration independently of hydrogen ion concentration, we chose the system HClO₄-Na₂SO₄-NaClO₄ to define hydrogen, bisulfate, and sulfate ion concentrations and the ionic strength μ .

An ionic strength of two was chosen so as to coincide with the conditions established by Hardwick and Robertson (4) for evaluation of the sulfato complexes of Ce(IV). A knowledge of the sensitivity of the equilibrium constant K_a for the equilibrium



to ionic strength of the medium was essential to the success of our approach. We extrapolated the values of Reynolds and Fukushima (5) to an ionic strength of two using their equation

$$\log K_a = -1.991 + \frac{2.04\sqrt{\mu}}{1 + 1.7\sqrt{\mu}} + 0.0314\mu \quad (1)$$

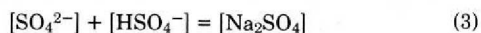
The different parameters of the system are defined as follows

- 1) The molar hydrogen ion concentration in solution is fixed to suit the concentration range of interest viz, 0.01–2.0 *M*.
- 2) Perchloric acid is assumed to be completely ionized in aqueous solution; thus

$$[\text{HClO}_4] = [\text{H}^+] + [\text{HSO}_4^-] \quad (2)$$

- 3) The concentrations of bisulfate and sulfate ions are determined by additions of known amounts ($10^{-3-0.6}$ *M*) of Na₂SO₄, and are related by eqn. (3).

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Substitution leads to eqn. (4)

$$\frac{[\text{Na}_2\text{SO}_4] - [\text{HSO}_4^-]}{[\text{HSO}_4^-]} = K_a/[\text{H}^+] \quad (4)$$

where $K_a = [\text{SO}_4^{2-}][\text{H}^+]/[\text{HSO}_4^-]$. The fixed values for hydrogen ion and sodium sulfate concentrations are defined (respectively) as c and m . Solving eqn. (4) for bisulfate ion concentration, we have

$$[\text{HSO}_4^-] = cm/(c + K_a) \quad (5)$$

The calculated values of bisulfate ion concentration can then be inserted in eqn. (2) to determine the concentration s of HClO_4 to be used.

4) The amount of NaClO_4 to be added to obtain the desired ionic strength of two was calculated by using eqns. (6)–(8)

$$\mu = \frac{1}{2} \sum_i c_i z_i^2 \quad (6)$$

where c_i is equal to molarity of the ion and z_i is the charge of the ion.

$$\mu = \frac{1}{2} (c + [\text{HSO}_4^-] + 4[\text{SO}_4^{2-}] + 2m + s + 2[\text{NaClO}_4]) \quad (7)$$

$$[\text{NaClO}_4] = \mu - 3m + s - 2c \quad (8)$$

So now we have a system in which, at a prescribed ionic strength, the interdependent concentrations of hydrogen ion, bisulfate ion, and sulfate ion are calculable. We make use of such a system to calculate the concentration distribution of the sulfato complexes of Ce(IV) in acidic sulfate media.

Concentration Distribution of the Sulfato Complexes of Ce(IV) in the HClO_4 - Na_2SO_4 - NaClO_4 System

The study of Hardwick and Robertson (4) seemed the most suited for our calculations. They have reported three equilibrium constants, determined spectrophotometrically, for the mono-, di-, and tri-sulfato complexes

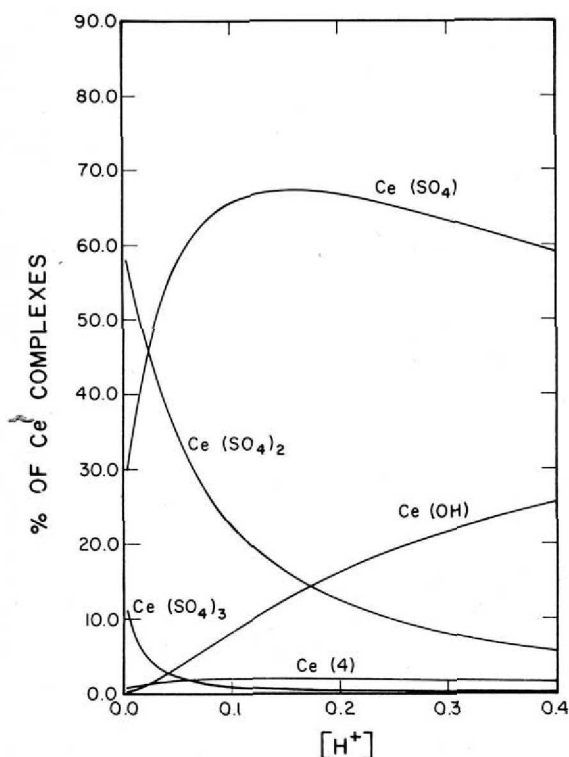
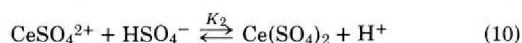
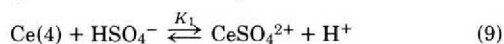


Figure 1. Percentage of Ce complexes versus $[\text{H}^+]$ at 0.001 M Na_2SO_4 concentration.

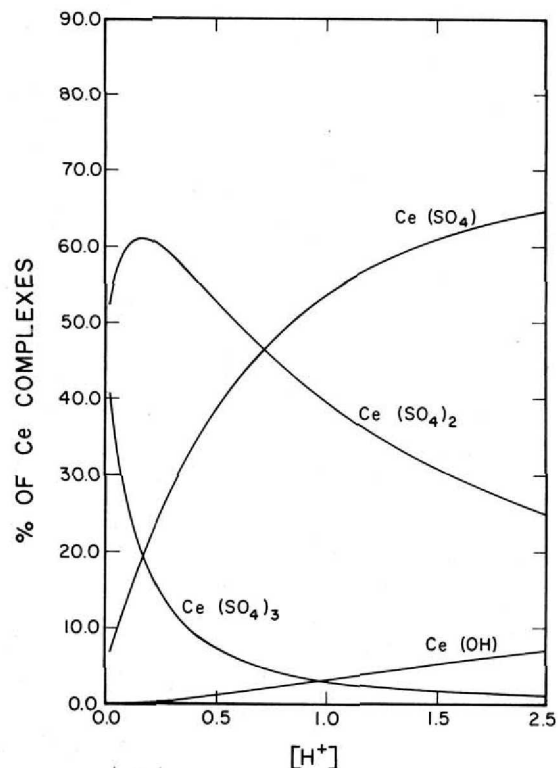


Figure 2. Percentage of Ce complexes versus $[\text{H}^+]$ at 0.004 M Na_2SO_4 concentration.

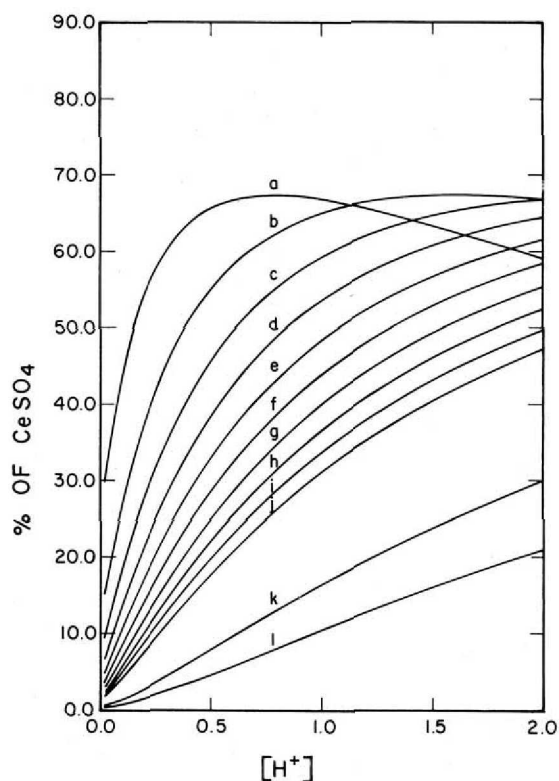


Figure 3. Percentage of CeSO_4^{2+} versus $[\text{H}^+]$ at varying concentrations of Na_2SO_4 .

The legend for sulfate concentration Figures 3, 4, and 5 is listed below in mole/l.

- | | | |
|-----------|-----------|-----------|
| (a) 0.001 | (b) 0.002 | (c) 0.003 |
| (d) 0.004 | (e) 0.005 | (f) 0.006 |
| (g) 0.007 | (h) 0.008 | (i) 0.009 |
| (j) 0.010 | (k) 0.020 | (l) 0.030 |

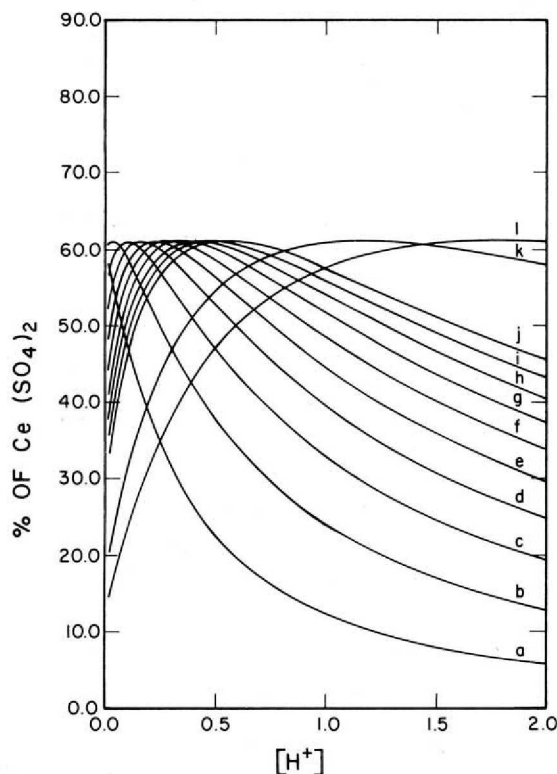


Figure 4. Percentage of $\text{Ce}(\text{SO}_4)_2$ versus $[\text{H}^+]$ at varying concentrations of Na_2SO_4 . See Figure 3 for legend.

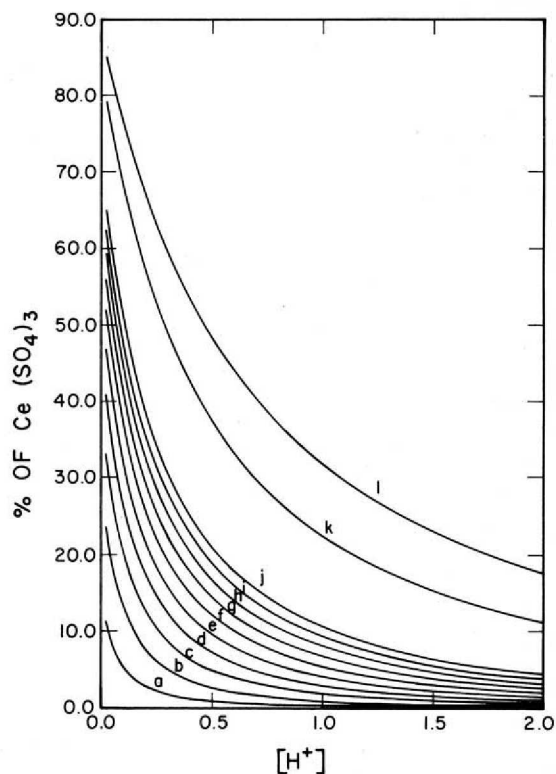


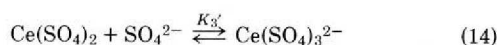
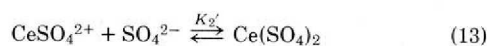
Figure 5. Percentage of $\text{Ce}(\text{SO}_4)_3^{2-}$ versus $[\text{H}^+]$ at varying concentrations of Na_2SO_4 . See Figure 3 for legend.

Half-Lives of Ce(IV) in the Ce(IV)-MIDA Reaction and the Percentage Distribution of the Ceric Species

$[\text{Na}_2\text{SO}_4], M$	Ce^{4+}	CeSO_4^{2+}	$\text{Ce}(\text{SO}_4)_2$	$\text{Ce}(\text{SO}_4)_3^{2-}$	$t_{1/2}, s$
$[\text{H}^+] = 0.3 M$					
10^{-3}	0.22	60	31	1.6	5.1
10^{-2}	0.004	193	58	30	6.1
10^{-1}	0.0000	0.31	16	84	39.9
$[\text{H}^+] = 0.8$					
10^{-3}	1.66	67	15	0.3	34.4
$4.1 \cdot 10^{-3}$	0.30	1.9	44	4	2.5
$7.1 \cdot 10^{-3}$	0.12	35	55	8.7	2.1

where $\text{Ce}(4)$ represents the concentration of non-sulfated Ce(IV) and includes the concentrations of the hydroxo complexes which will be evaluated later. The equilibrium constants K_1 , K_2 , and K_3 were determined at hydrogen ion concentration equal to 1 M and ionic strength of two for a range of sulfate ion concentrations equal to 10^{-3} –1 M; their values are 3500, 200, and 20, respectively.

For simplification we rewrite eqns. (9)–(11) as follows



where $K_1' = K_1/K_a$, $K_2' = K_2/K_a$ and $K_3' = K_3/K_a$. In spectrophotometric studies, the total concentration of Ce(IV) is usually about 10^{-4} M while the sulfate concentration is much larger and can, therefore, be considered as constant and equivalent to n . This leads to the following system of four equations, (15)–(18), and four unknowns

$$K_1' = [\text{CeSO}_4^{2+}]/[\text{Ce}(4)] \cdot n \quad (15)$$

$$K_2' = [\text{Ce}(\text{SO}_4)_2]/[\text{CeSO}_4^{2+}] \cdot n \quad (16)$$

$$K_3' = [\text{Ce}(\text{SO}_4)_3^{2-}]/[\text{Ce}(\text{SO}_4)_2] \cdot n \quad (17)$$

$$[\text{Ce}(4)] + [\text{CeSO}_4^{2+}] + [\text{Ce}(\text{SO}_4)_2] + [\text{Ce}(\text{SO}_4)_3^{2-}] = [\text{Ce}]_T = P \quad (18)$$

where $[\text{Ce}]_T$ is equal to the total concentration of the cerium present. The new solutions are given by eqns. (19)–(22)

$$[\text{Ce}(4)] = P/(1 + K_1' \cdot n + K_1' \cdot K_2' \cdot n^2 + K_1' \cdot K_2' \cdot K_3' \cdot n^3) \quad (19)$$

$$[\text{CeSO}_4^{2+}] = [\text{Ce}(4)] \cdot K_1' \cdot n \quad (20)$$

$$[\text{Ce}(\text{SO}_4)_2] = [\text{Ce}(4)] \cdot K_1' \cdot K_2' \cdot n^2 \quad (21)$$

$$[\text{Ce}(\text{SO}_4)_3^{2-}] = [\text{Ce}(4)] \cdot K_1' \cdot K_2' \cdot K_3' \cdot n^3 \quad (22)$$

Putting $P = 100$, one calculates the percentage distribution of the various species.

Computation of the Concentration Distribution of the Ce(IV) Hydroxo Species in the Chosen Acidic Sulfate Media

In the previous section we referred to $\text{Ce}(4)$ as the concentration of non-sulfated Ce(IV) which includes Ce^{4+} , CeOH^{3+} ,

and $\text{Ce}(\text{OH})_2^{2+}$. Although evidence for dimeric species, e.g., $(\text{CeO}(\text{Ce}))^{6+}$, $(\text{HO}(\text{CeO}(\text{CeOH}))^{4+}$, etc. has been given (3), their importance can be ignored in solutions which are lower than $10^{-3} M$ in $\text{Ce}(\text{IV})$.

Everett and Skoog (6) have determined spectrophotometrically the hydrolysis constants (eqns. (23) and (24) at $\mu = 1$, and have shown that they are independent of ionic strength.

$$K_1'' = \frac{[\text{CeOH}^{3+}][\text{H}^+]}{[\text{Ce}^{4+}]} = 6.40 \quad (23)$$

$$K_2'' = \frac{[\text{Ce}(\text{OH})_2^{2+}][\text{H}^+]}{[\text{CeOH}^{3+}]} = 0.12 \quad (24)$$

Returning to eqn. (19), we carry out the following substitution

$$[\text{Ce}(4)] = [\text{Ce}^{4+}] + [\text{CeOH}^{3+}] + [\text{Ce}(\text{OH})_2^{2+}]$$

and solve for the concentrations of the different species. For the calculations described, a program was written for computation of the concentrations of the different sulfato and hydroxo complexes as well as Ce^{4+} , when the sodium sulfate concentration varies from 10^{-3} – $0.6 M$, and the hydrogen ion concentration varies from 10^{-2} – $2.0 M$ at a fixed ionic strength of two. The results were plotted to give two different types of graphs, Figures 1 and 2 and 3–5 representing, respectively

- 1) Variations of percentage ceric species versus hydrogen ion concentration for given concentrations of sodium sulfate.
- 2) Variation in percentage of each species with hydrogen ion concentration at various concentrations of sodium sulfate.

Planning a Kinetic Study

The oxidation of organic and inorganic substrate by $\text{Ce}(\text{IV})$ is usually much faster in perchlorate than in sulfate media (7). The competition between the SO_4^{2-} ion and the substrates' ligands for positions in the coordination sphere around the

metal-ion oxidant is responsible for the generally slower rates observed in sulfate media. Although a shift from perchlorate to a sulfate medium would ensure, in most cases, a reaction rate which can be followed by conventional techniques (as opposed to stopped-flow techniques), there are several problems (cf. section Defining a Useful Acidic Sulfate Medium) in working with $\text{Ce}(\text{IV})$ in H_2SO_4 . Working in the presently proposed acidic sulfate media (HClO_4 - Na_2SO_4 - NaClO_4) has the distinct advantage of ensuring (1) a defined and constant μ , (2) a H^+ ion concentration which can be varied independently from the SO_4^{2-} ion concentration, and (3) a defined and controllable distribution of ceric sulfato species.

The plan is simple. One chooses certain convenient H^+ ion concentrations, and at a fixed ionic strength introduces calculated amounts of Na_2SO_4 to produce controllable concentrations of the different ceric species, then studies the rate as a function of variations only in such species. The table shows the variation in $t_{1/2}$ for the $\text{Ce}(\text{IV})$ -oxidative decarboxylation of methyliminodiacetic acid (MIDA) at 0.3 and 0.8 M $[\text{H}^+]$. The variation in $t_{1/2}$, in this preliminary investigation, excludes the di- and tri-sulfato species as direct participants and suggests $\text{Ce}(\text{SO}_4)^{2+}$ (and possibly Ce^{4+}) as the main reactive species. For a complete kinetic analysis, the reducing substrate-proton equilibria also have to be taken into account (8).

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