Tr. J. of Chemistry
20 (1996) , 111 - 117.

Distribution of Ce (IV) Species in $HNO_3 - HClO_4$ Media and Determination of Stability Constants of the Nitrato Complexes

Seval BAYÜLKEN
Çekmece Nuclear Research and Training Center,
P. K. 1 Havaalanı, İstanbul-TURKEY
A. Sezai SARAÇ
İstanbul Technical University,
Sciences and Literature Faculty,
Chemistry Department,
80676 Maslak, İstanbul-TURKEY

Received 17.10.1995

In this paper, the distribution of cerium (IV) species depending on the charges of nitric acid-perchloric acid concentration at constant ionic strength (I=1.0) was investigated. Cerium (IV), being a strong oxidant, was utilized for investigating the oxidation kinetics of some amino acids. Knowing the distribution of cerium (IV) species is beneficial for better understanding this type of kinetics. Distribution of cerium (IV) species in aqueous media was studied by measuring the total optical absorbance of cerium (IV) species in different nitric acid-perchloric acid mixture solutions. The stability constants (K_1 and K_2) of the nitrato cerium complexes were determined spectrophotometrically from equilibrium data and from kinetic data concerning the ceric oxidation of amino acids. The magnitudes of the constants computed by these two separate methods were in accordance with each other.

Introduction

Cerium (IV) metal ion, being a strong oxidant, is widely used in the oxidation of organic substances, as well as of several inorganic substances. The basic advantage over other oxidants is its reduction to a single substance, cerium (III), without any intermediate reactions. The standard potential of the cerium (IV)-cerium (III) couple changes depending on the complex formation properties of the ligand and it is useful to know the distribution of cerium species in a given medium to explain more clearly the reaction mechanism in kinetic investigations.

The cerium (IV) species in perchloric acid medium [1-4] and sulfuric acid medium[5] have been established and equilibrium constants calculated. Although research involving the nitrato-cerium complexes started rather early, there is contradictory information about these complexes in the relevant literature [6-12]. It was found with potentiometry[8] that in aqueous nitrate medium, for $[NO_3^-] < 3.2$ mole/l, there is only one complex in the form of $Ce(NO_3)^{3+}$. Two other methods, namely as spectrophotometer[11] and extraction[12], revealed that the ligand number of nitrato cerium complexes may vary from 1 to 6.

In this work, the distribution of Cerium species with respect to the changes of nitric acid-perchloric acid concentrations was investigated, and the stability constants of the nitrato cerium complexes were calculated both from equilibrium data and from the data of the oxidation kinetics of amino acids.

Experimental

Materials

L-aspartic acid (Fluka, puriss), L-serine (Merck p.a.), ammonium iron (II) sulfate hexahydrate (Merck, p.a.), 70% perchloric acid (Merck, p.a.), 65% nitric acid (Merck, p.a.).

The stock solution is prepared by dissolving 0.1 M cerium (IV) ammonium nitrate (CAN) (Merck, p.a.) in 1 M nitric acid. Cerium (IV) in nitric acid- perchloric acid solutions were prepared freshly by dissolving ammonium cerium(IV) nitrate (Merck, p.a.) in acid solutions. Cerium solutions in nitric acid were titrated with ammonium iron (II) sulfate in the presence of N-phenyl antranilic acid indicator for their cerium(IV) content[13] and with standardized NaOH solution in the presence of methyl orange indicator for their acid content.

Instruments and methods

Spectrophotometric measurements were made by the Shimadzu UV-160 A UV-Vis recording spectrophotometer in quartz cells. To keep the temperature constant a Cps-240A thermoelectrically temperature-controlled cell were used. Absorbancy measurements of cerium (IV) were performed at λ=400 nm, t=25°C ±0.1°C, at constant ionic strength (I=1.0), for different concentrations of nitric acid-perchloric acid media.

Kinetic studies were made spectrophotometrically under conditions of excess of ligand. The time versus absorbancy data were processed by a linear least squares program. Pseudo first order rate constants were determined according to the following equation:

$$k^{I}_{abs} \cdot t = \ln(A_0 - A_\infty) - \ln(A_t - A_\infty), \qquad (1)$$

where A_0, A_∞ and A_t refer to the absorbancy at the start of reaction, at infinity and at time t, respectively. Rate constants were reproducible within ± 1%.

Results and Discussion

When $[H^+]$ is kept constant between $[Ce(IV)] = 1.10^{-3} - 6.10^{-3}$M, the very high correlation coefficient of the relation between absorbancey and concentration proves that Lambert- Beer Law is valid, then there are no hydrolysis and polymerization reactions.

On the other hand, at constant $[H^+]$ = 1.0 M, variable $HNO_3 - HClO_4$ mixtures and constant total $[Ce(IV)] = 1.10^{-3}$M, absorbancy increases with increasing $[NO_3^-]$ and the wavelength of maximum absorbancy shifts to higher values (from 319 nm to 330 nm). This increase in the absorbancy may be attributed to the formation of nitrato-cerium complexes.

Spectrophotometric investigation of the Ce(IV) species distribution in $HNO_3 - HClO_4$ media

If only mono and dinitrato complexes are taken into account, one can write

$$Ce(4) + HNO_3 \overset{K_1}{\rightleftharpoons} Ce(NO_3)^{3+} + H^+ \tag{2}$$

$$Ce(NO_3)^{3+} + HNO_3 \overset{K_2}{\rightleftharpoons} Ce(NO_3)_2^{2+} + H^+, \tag{3}$$

where $Ce(4)$ is the free Ce^{4+} cation and all hydrolytic species. If $[Ce(IV)]_T$ is the total concentration of $Ce(4)$ and all nitrato complexes, one can obtain

$$\begin{aligned}
[Ce(4)] &= [Ce^{4+}] + [Ce(OH)^{3+}] + [Ce(OH)_2^{2+}] && (4)\\
[Ce(IV)]_T &= [Ce(4)] + [Ce(NO_3)^{3+}] + [Ce(NO_3)_2^{2+}] && (5)\\
&= [Ce(4)]\{1 + K_1 \cdot n + K_1 \cdot K_2 \cdot n^2,
\end{aligned}$$

where $n = [HNO_3]/[H^+]$.

On the other hand,

$$\begin{aligned}
A_T &= \varepsilon_0[Ce(4)] + \varepsilon_1[Ce(NO_3)^{3+}] + \varepsilon_2[Ce(NO_3)_2^{2+}]\\
&= [Ce(4)]\{\varepsilon_0 + \varepsilon_1 K_1 n + \varepsilon_2 K_1 K_2 n^2\} && (6)\\
A_T &= \varepsilon_T[Ce(IV)]_T. && (7)
\end{aligned}$$

Using the equations (5) and (6), the following equation for ε_T can be obtained:

$$\varepsilon_T = A_T/[Ce(IV)]_T = (\varepsilon_0 + \varepsilon_1 K_1 n + \varepsilon_2 K_1 K_2 n^2)/(1 + K_1 n + K_1 K_2 n^2). \tag{8}$$

In this equation, $\varepsilon_0, \varepsilon_1, \varepsilon_2, K_1$ and K_2 are the parameters to be calculated.

In order to find ε_0, the average molar absorptivity of Ce(4) species, the following equation should be used:

$$\varepsilon_0 = \varepsilon_0'.a_{Ce4+} + \varepsilon_1'.a_{Ce(OH)}3 + \varepsilon_2' \cdot a_{Ce(OH)_2^{2+}}, \tag{9}$$

where $\varepsilon_0', \varepsilon_1'$ and ε_2' are the molar absorptivity of $Ce^{4+}, Ce(OH)^{3+}$ and $Ce(OH)_2^{2+}$ species, respectively, and can be calculated using the following equation given in [4]:

$$A[H^+]^2 + A[H^+]K_3 + AK_3K_4 = \varepsilon_o'[Ce(4)][H^+]^2 + \varepsilon_1'[Ce(4)][H^+]K_3 + \varepsilon_2'[Ce(4)]K_3K_4. \tag{10}$$

In equation (9), a_i refers to the activity for the i^{th} species and is given by

$$a_i = \frac{Ci}{[Ce(4)]} \tag{11}$$

where C_i, the distribution of Ce^{4+} and hydroxo species, are given [14] as,

$$Ce^{4+} = 0.1224 \quad Ce(OH)^{3+} = 0.7836 \quad Ce(OH)_2^{2+} = 0.0940.$$

For the determination of $\varepsilon_0', \varepsilon_1'$ and ε_2', absorbancy measurements were performed in perchloric acid-sodium perchlorate medium for $I = 1.0, \lambda = 400$ nm and $[Ce(4)] = 1.10^{-3}$M. The values of K_3 and K_4, the stability constants of the mono and dinitrato species, respectively, are taken from [4] for $t = 25°$C and $I = 1.0$, as

$$K_3 = 6.4 \qquad K_4 = 0.12.$$

The calculations gave the following results:

$$\varepsilon_0' = 66 \quad \varepsilon_1' = 166 \quad \varepsilon_2' = 25.$$

The correlation coefficient of the curve fitting programme used for this calculation is given as $r^2 = 0.9996$.

As the hydroxo cerium species distribution were given in [14], and as only free Ce^{4+} cation and mono- and dihydroxo complexes are taken into account, for $[H^+]$=1.0 M, the average molar absorptivity value ε_0 is calculated as

$$\varepsilon_0 = 140.5 \; l.mol^{-1}.cm^{-1}$$

For the determination of ε_1 and K_1, absorbancies at 400 nm wavelength versus cerium (IV) concentration were measured at constant $[H^+] = 1.0$M and for $[HNO_3] = 1.10^{-3}M, /HClO_4] = 0.999$M solution medium. As the nitrate anion has no excess according to cerium cation, only Ce(4) and $Ce(NO_3)^{3+}$ species were supposed to be present in this medium. Using ε_0 already calculated, and by the help of an investigation done in H_2SO_4 medium[5], the following equation is resolved by the help of adequate computer programming:

$$Abs = \varepsilon_0.C_T + (1/2).(\varepsilon_1 - \varepsilon_0).\{[C_T + n_T + ([H^+]/K_1)] - [(C_T + n_T + ([H^+]/K_1))^2 - 4.C_T.n_T]^{1/2}\}. \quad (12)$$

This calculation gives ε_1 and K_1 as,

$$\varepsilon_1 = 817.4 \quad K_1 = 0.52.$$

The correlation coefficient of this equation is $r^2 = 0.9992$.

By using the measured absorbancy values for $[HNO_3] \leq 1.0M$, the equation (8) gives the values of ε_2 and K_2 as

$$\varepsilon_2 = 247 \quad K_2 = 0.65$$

with a correlation coefficient of $r^2 = 0.9997$.

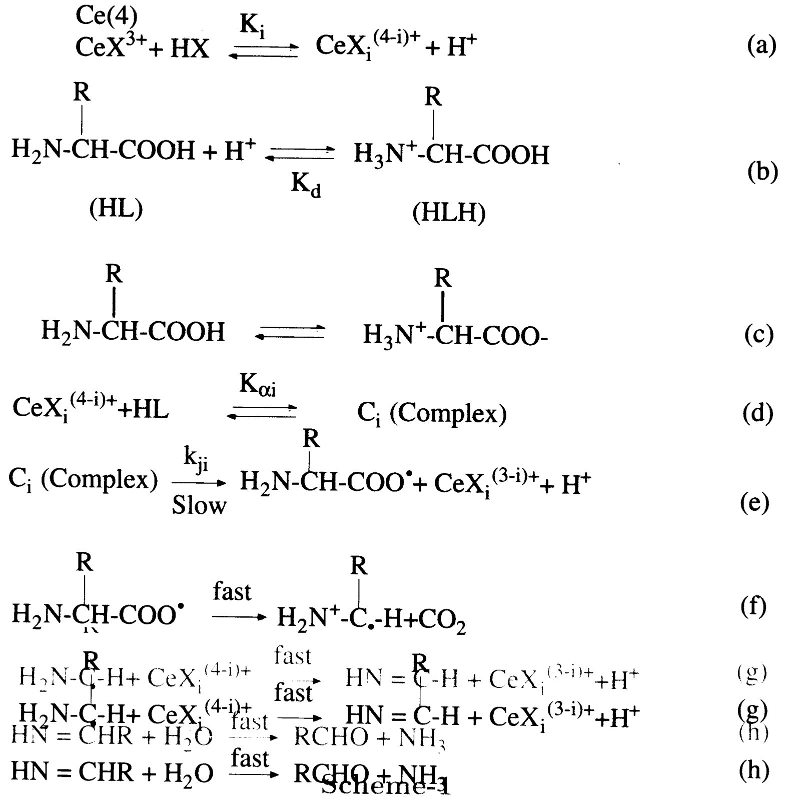
The cerium species distribution with respect to the change of $HNO_3 - HClO_4$ concentration at constant ionic strength (I=1.0) is calculated and given in Figure 1.

The theoretical and experimental absorbancy data are compared for 400 nm wavelength and it is seen that they are in accordance with each other.

The stability constants computed from the oxidation of some amino acids with Ce(IV)

The oxidation kinetics of some amino acids as, L-aspartic acid and L-serine with Ce(IV) in different nitric acid-perchloric acid media (I=1.0), at different substrate concentration [HL] are investigated and pseudo first order rate constants k^I) are computed.

For constant $[H^+]$ and ionic strength, the plot of $1/k^I$ versus $1/[HL]$ gives straight lines with positive intercept. This attitude shows the formation of an intermediate complex between the organic substance and the reactive cerium(IV) species [15]. The intermediate free radicals formation in the reaction mixture is demonstrated by acrylamide polymerization and the probable reaction mechanism is given in Scheme-1



Scheme-1

In these equations, $i = 0, 1, 2; [HX] = [HNO_3]; X = [NO_3^-]; K_{\alpha_i}$ =equilibrium constant for complex formation; and k_{ji}=rate constant for complex decomposition.

Since equation (e) can be taken as a rate determining step, the rate expression can be written as:

$$- d[Ce(IV)]_T/dt = k^I[Ce(IV)]_T = 2\sum k_{ji}[C_i] = 2\sum k_{ji}K_{\alpha i}[CeX_i^{(4-i)+}][HL]. \qquad (13)$$

$$- d[Ce(IV)]_T/dt = k^I[Ce(IV)]_T = 2\sum k_{ji}[C_i] = 2\sum k_{ji}K_{\alpha i}[CeX_i^{(4-i)+}][HL]. \qquad (13)$$

In this equation with the inclusion of

In this equation with the inclusion of

115

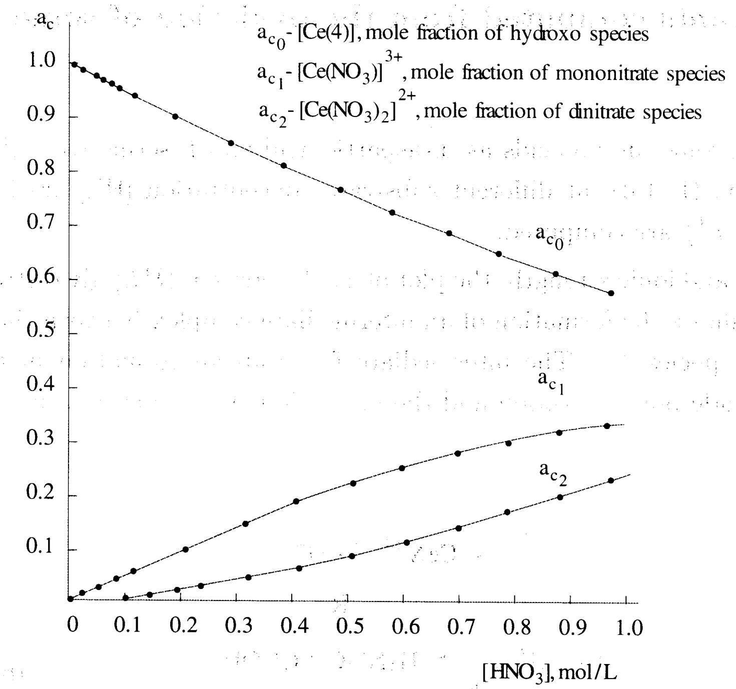


Figure 1. Distribution of Cerium (IV) Species

$$[Ce(IV)]_T = \sum[CeX_i^{(4-i)+}] + \sum[C_i] \tag{14}$$

and arrangement of the expression in the form of $1/k^I$, the following equation can be obtained (in the denominator, $(k_{j1}K_{\alpha1}K_1n)$ and $(k_{j2}K_{\alpha2}K_1K_2n^2)$ terms are neglected regarding the other terms):

$$1/k^I = \{(1 + K_1n + K_1K_2n^2)/2k_{j0}K_{\alpha0}\}.1/[HL] + \{K_{\alpha0} + K_{\alpha1}K_1n + K_{\alpha2}K_1K_2n^2\}/2k_{j0}K_\alpha \tag{15}$$

The plots of $1/k^I$ versus $1/[HL]$ give straight lines. By the help of the slope and intercept values of these lines and using a non linear regression analysis computer program, this equation is computed and the constant for complex formation $K_{\alpha i}$, the rate constants for complex decomposition k_{ji}, and the equilibrium constants for the formation of nitrato cerium complexes K_1 and K_2 are obtained and given in Table 1.

As it is observed from this investigation, the K_1 and K_2 values

Table 1. K_1 and K_2 values obtained from kinetic and spectrophotometric results

	From Kinetic Study of L-Aspartic Acid	From Kinetic Study of L-Serine	From Spectrophotometric Method
K_1	0.59	0.56	0.52
K_2	0.60	0.56	0.65
Corr. Coeff.(r^2)			0.9992

In the relevant literature [16], for $I = 3.5$ and $t = 23°$C, the value of K_1 has been given as $K_1 = 2.09$ (log $K_1 = 0.32$) for cerium mononitrato complex. In our research, the experimental conditions were $I = 1.0$ and $t = 25°$C and this explains the difference between the two values. With the same exxperimental conditions ($I = 1.0$ and $t = 25°$C), stability constants for nickel, cobalt and manganese mononitrate complexes were given [17] as $K_1 = 0.60$, K_1=0.35 and $K_1 = 0.37$, respectively.

References

1. M. S. Sherill, C. B. King and R. C. Spooner, J. of the Amer, Chem. Soc. vol 65, pp. 170-179, (1943).
2. T. C. Hardwick and E. Robertson, J. Canadian, of Chemistry, vol 29, pp. 818-827, (1951).
3. H. G. Offner and D. A. Skoog, Anal Chem. vol. 38, No. 11, pp. 1520- 21, (1966).
4. K. G. Everett, D. A. Skoog, Anal Chem. vol, 43, No 12, p. 1541, (1971).
5. T. J. Hardwick, E. Robertson, J. Canadian of Chem., vol. 29, pp. 828- 837, (1951).
6. F. R. Duke, A. A. Forist, J. of the Am. Chem. Soc, vol 71, pp. 2790- 2792, (1949).
7. B. D. Blaustein, J. W. Gryder, J. of the Am. Chem. Soc, 79, pp. 540- 547, (1957).
8. I. M. Batyaev, et all; Ffiziko-khimiçeskie svoystva rastvorov, Izd. Leningrad Gos. Univ., pp. 148-156, (1964).
9. B. Krishna, K. C. Tewari, J. Chem. Soc., pp. 3097-3100, (1961).
10. Z. Amjad, A. McAuley, part 17, J. of Chem. Soc. Dalton, pp. 304-308, (1977).
11. V. I. Levin et al.; Atomnaya energiya, vol. 15, p. 138, (1963).
12. V. S. Smelov, Yu. I. Vereşçagin Neorgan, Khimii, vol. 9, p. 2775 (1964).
13. A. I. Vogel, "Quantitative Inorganic Analysis" 3 rd. ed., Longman, London, p. 319, (1961).
14. S. B. Hanna et all; Z. Naturforsch., vol 306, p. 532, (1975).
15. M. Ardon, J. Chem. Soc. pp. 1811-1815, (1957).
16. R. Phillps, P. Eisenberg, P. George and R. J. Rutman J. Biol. Chem., vol 240, p. 4393, (1965).
17. R. Smith and A. E. Martell, Critical Stability Constants, vol. 4, Plenum Press., New York (1976).