Kinetics and Possible Mechanisms of the Ce(IV) Oxidation of EDTA, CDTA, DTPA and NTA in Perchloric Acid Media*

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The rates of oxidation of four chelating agents with Ce(IV) in HClO_4 solutions, have been studied by the stopped-flow technique. The rates first increase with increasing acidity, reach maxima which are characteristic of the chelating agent and the medium, then progressively decrease with further increasing acid concentration. At their maximum reactivities, the tendencies for oxidation decrease in the following order: *trans*-1,2-diaminocyclohexane tetraacetic acid (CDTA) > ethylenedinitrilotetraacetic acid (EDTA) > diethylenetriaminepentaacetic acid (DTPA) > nitrilotriacetic acid (NTA). A mechanism for the oxidation of EDTA, involving Ce^{4+} and $\text{Ce}(\text{OH})^{3+}$ and both unprotonated and monoprotonated chelating agent, is proposed.

The complexation of polyaminocarboxylic acids – commonly used as chelating agents and recently as possible substitutes for phosphates in detergents – with trivalent lanthanides has been extensively investigated¹⁻³. On the other hand, the reactions of these polyaminocarboxylic acids with Ce(IV) have received little attention, apparently because oxidation rather than complexation is the observed reaction in such systems⁴.

The rates of oxidation of several chelating agents by alkaline ferricyanide $[\text{Fe}(\text{CN})_6]^{3-}$ were studied by LAMBERT and JONES⁵ who found that four moles of ferricyanide were consumed per mole of EDTA; the products then were reported to be iminodiacetic acid and glycollic acid. Recently, MUSHRAN *et al.* found that seven moles of chloramine-T were consumed per mole oxidation of EDTA⁶.

Our previous investigations on the Ce(IV) oxidation of EDTA, CDTA, DTPA, and NTA were carried out in aqueous H_2SO_4 ⁷⁻¹⁰, where Ce(IV) forms strong sulfato complexes¹¹. Such complexation only adds to the difficulties of formulating

possible reaction mechanisms. In aqueous HClO_4 , on the other hand, Ce(IV) exists mainly as the hydrolyzed species $\text{Ce}(\text{OH})^{3+}$ and $\text{Ce}(\text{OH})_2^{2+}$ along with the dimer $(\text{Ce}-\text{O}-\text{Ce})^{6+}$ ¹²⁻¹⁵. At high acidities, the non-hydrolyzed Ce^{4+} exists as a major fraction of the stoichiometric concentration of Ce(IV). Such a species is expected to be far more reactive than complexed Ce(IV) and would accordingly be a very efficient oxidizing agent. This paper deals with a study of the Ce(IV) oxidation of EDTA, CDTA, DTPA, and NTA in HClO_4 solutions.

Experimental

Reagents

Ceric perchlorate (perchlorato ceric acid), $\text{H}_2\text{Ce}(\text{ClO}_4)_6$, stock solution (0.5 M in 6 M HClO_4) was purchased from G. Frederick Smith Chemical Co., Columbus, Ohio. Perchloric acid solutions were made by dilution from 70% Fisher reagent which meets A.C.S. specifications. Monohydrated sodium perchlorate, and anhydrous sodium sulfate were analytical reagent grades. The primary standard was reagent-grade ferrous ammonium sulfate (Mohr's salt) $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$; *o*-phenanthroline was used as indicator.

The base indicator for Hammett acidity function determinations was *o*-nitroaniline ($\text{pK}_a = -0.29$). It was used after recrystallization from benzene.

The solutions of the chelating agents NTA, EDTA, CDTA, and DTPA (Merck, Eastman Kodak, and Geigy) were prepared by direct weighing. Except for EDTA, which is water soluble as the disodium

* This is part VII of a series on oxidative decarboxylation with Ce(IV). For part VI, see reference 10.

salt, dilute (0.1 N) NaOH solution was used for the other not readily soluble polyaminocarboxylic acids.

Stoichiometry

The stoichiometry of the reaction between Ce(IV) and EDTA in HClO_4 media was determined by allowing a known excess of a standardized solution (0.079 M) of Ce(IV) in HClO_4 to react with 1-ml samples of 0.1 M EDTA solution for a period of time ranging from a few seconds to several hours at room temperature. At recorded periods of time, the Ce(IV) consumed was determined by titrating the mixture against standard Fe(II) solution. When the reaction time was less than 30 minutes, the reaction was quenched by addition of a known volume of Fe(II) which was stored in the side arm of the reaction flask and by back titration against Cr(VI).

Rate measurements

The rates of reduction of Ce(IV) with EDTA, CDTA, DTPA and NTA, respectively, were studied spectrophotometrically at ~ 300 nm where Ce(IV) in HClO_4 absorbs strongly; neither Ce(III), nor the chelating agents or their reaction products interfere at this wavelength. The reactions were too fast to study by the ordinary techniques, and use was made of the commercially available Durrum-Gibson stopped-flow apparatus which allows measurements of half-lives in the millisecond region. Constant temperatures were maintained $\pm 0.05^\circ\text{C}$ by a circulating Lauda Ultrathermostat in combination with a cooling system. The solutions of Ce(IV) in HClO_4 and of the chelating agents of known molarities were injected by a pressure shock into a mixing chamber where mixing is complete within two milliseconds. The change in the percent transmittance with time, at the chosen wavelength, was displayed on the screen of an attached Tektronix storage oscilloscope. A permanent record of the display was photographed on a Polaroid film. A typical percent transmittance *vs* time sweep is shown in Fig. 1.

The concentrations of the chelating agents (Chel) and of Ce(IV) in the mixed reaction solutions were usually about 2.50×10^{-2} M and 3.50×10^{-4} M respectively, *i. e.*, $[\text{Chel}]_0 : [\text{Ce(IV)}]_0$ was about 70:1.

Fig. 1. Stopped-flow of three superimposed oscilloscope traces of Ce(IV)-NTA reaction.

The great excess of $[\text{Chel}]_0$ insured simple first-order variation in $[\text{Ce(IV)}]$. The half-life of $[\text{Ce(IV)}]_0$ was read directly from the oscilloscope screen. It was the time when the absorbance had reached half its initial value if the final reading was 100% transmittance, or at half the total change in absorbance when after 20 half-lives the transmittance was not 100%. The half-lives so obtained were translated to first-order rate constants; thus,

$$k_1 = 0.693/\tau_{0.5} \text{ sec}^{-1}$$

Second-order rate constants, k_2 , were calculated from the corresponding k_1 by dividing the latter by the initial concentration of the chelating agent $[\text{Chel}]_0$; thus,

$$k_2 = k_1/[\text{Chel}]_0 \text{ M}^{-1} \text{ sec}^{-1}.$$

Results and Discussion

a. Stoichiometry of the EDTA-Ce(IV) reaction

The reaction between Ce(IV) and EDTA in aqueous 1 M HClO_4 exhibits variable stoichiometry. In Table I evidence for the dependence of the

Table I. Stoichiometry of EDTA-Ce(IV) reaction as a function of time.

Time [min.]	Number of equivalents of Ce(IV) consumed per mole of EDTA
0*	4.10, 4.20, 4.30
0.3	5.90
1.0	6.60
5.0	7.30
10.0	7.80
30.0	8.90
140.0	11.80
630.0	13.70

* This was done by mixing the two reagents by injection and immediate quenching by Fe(II) which was stored in the side arm of the reaction flask.

stoichiometry on time is presented. An average of 4.2 moles of Ce(IV), recorded for three separate runs, represents the lowest amount of Ce(IV) found to react, almost instantaneously, per mole of EDTA. Ultimate consumption of about 14 equivalents of Ce(IV) per mole of EDTA was observed. In H_2SO_4 medium the stoichiometry ranged from a low of about 4 to a high of about 14⁷. In addition to CO_2 and formaldehyde⁷, various organic products have been detected by paper electrophoresis¹⁶. A summary of the possible Ce(IV) interactions in the system appears in Chart 1.

Following the first decarboxylation, several paths for further oxidation are available. These consecutive and concurrent reactions are expected to yield the observed time-dependent stoichiometry. Furthermore, the hydrolysis of the charged Schiff's base (Chart 1) yields formaldehyde which is oxidized by Ce(IV) readily¹⁷, and therefore is expected to contribute to the observed high consumption of the oxidant. However, because of the large difference in reaction rates, the formed formaldehyde does not interfere strongly with either the stoichiometry or the rate of Ce(IV) consumption at the early stages of the studied reactions.

b. Acidity dependence

The second-order rate constants for the oxidation of the four polyaminocarboxylic acids in HClO₄ media are shown collectively in Fig. 2. For each acid a maximum in the plot of log *k*₂ vs [HClO₄] is observed. When the acidity of the medium was varied but the ionic strength kept constant at μ = 5.0, a similar parabola for log *k*₂ vs [HClO₄] was obtained in the EDTA case. A similar bell-shape behavior was observed in H₂SO₄ media^{7,8}. However, it is hardly likely that one and the same explanation can be advanced for both media. In H₂SO₄, the Ce(IV) becomes heavily complexed, and therefore deactivated, as the SO₄²⁻ and HSO₄⁻ concentrations increase accompanying increases in [H₂SO₄]. With ClO₄⁻, where complexation is minimal¹⁸, the rates decrease rapidly with increasing [HClO₄] just the same as with increasing [H₂SO₄]. To the left of the maxima, the increase in rate with increasing acidity may be explained generally in terms of a model which portrays the Ce(IV) coordinated by both N and carboxylate ligands. The quality of Ce(IV) as

an electron sink is not fully sensed by the carboxylate as long as the electron pair of the N ligand occupies one of the positions available around the metal ion. With increasing acidity, H⁺ competes with Ce(IV) as an electron pair acceptor and when N is protonated, the Ce(IV) character as an electron sink is enhanced and electron transfer from a coordinated carboxylate takes place.

Fig. 2. Reaction rate constants as a function of Hammett acidity, stoichiometric concentration of HClO₄ and formal oxidation potential of Ce(IV)/Ce(III) couple.

To the right of the maxima, extensive protonation of the amino acid (and progressive sulfato complexation of Ce(IV) in H_2SO_4 solution) with increasing acidity is probably the main reason behind the observed decreased reactivity. Fully protonated polyaminocarboxylic acids, *e.g.*, $\text{H}_2\text{EDTA}^{2+}$ (H_6Y^{2+}), cannot conceivably coordinate with Ce(IV), and if complexation is a prerequisite for electron transfer¹⁹, the decreased reactivity with increasing acidity is to be expected. We will develop a quantitative description for the bell-shape behavior later in the paper under *Mechanism*.

c. Relative reactivities

At the respective maxima, the reactivities of the four polyaminocarboxylic acids as reducing agents towards Ce(IV) in aqueous HClO_4 decreases in the order $\text{CDTA} > \text{EDTA} > \text{DTPA} > \text{NTA}$. At a fixed acidity, the oxidation of these chelating agents by Ce(IV) follows an overall second-order rate equation, first order in each of the reagents. Thus,

$$-\frac{d[\text{Ce(IV)}]}{dt} = k_2[\text{Ce(IV)}][\text{Chel}].$$

The highest values for k_2 , in $\text{M}^{-1} \text{sec}^{-1}$ at 25°C , are 138×10^2 for CDTA at about 3–3.5 M HClO_4 ; 55×10^2 for EDTA at about 3–3.5 M HClO_4 ; 22×10^2 for DTPA at about 3 M HClO_4 ; and 17×10^2 for NTA at about 2.5–3 M HClO_4 .

The difference in reactivities of EDTA and CDTA may be explained in terms of their geometries and hexadentate coordinating abilities^{8,20}. DTPA, on the other hand, has enough centers for octadentate coordination which has been suggested for some tetravalent metal ions, *e.g.*, Th(IV) ²¹, and Ce(IV) ²². This is reflected in the fact that DTPA-M(IV) complexes are thermodynamically more stable than the EDTA analogues²¹. This, however, should not be taken to imply that DTPA complexes are formed faster. Actually, among the three chelating agents, EDTA, CDTA and DTPA, only the latter has a rate

of complexation with Ce(IV) slow enough to be measurable^{9,10}. This is probably a reflection of the need for octadentate coordination attainable through conformational adjustments and unfavorable entropy change.

In the NTA case neither hexadentate nor octadentate coordination can be achieved through 1:1 interaction with Ce(IV). Recently, MALININA *et al.*²³, provided evidence for a 1:1 complex in sulfate media where Ce(IV) is strongly sulfato-complexed, and a 2 NTA:1 Ce(IV) complex in nitrate media where the Ce(IV) is not as strongly nitrato-complexed. Extrapolation to our perchlorate media, where perchlorato-complexation is minimal if not totally absent, would suggest the need for 2 NTA molecules for coordination prior to electron transfer; this would account – through entropy considerations – for a slower reaction rate with NTA. However, this suggestion is not supported kinetically.

It is interesting to note that while CDTA is almost 400 times more reactive than NTA in H_2SO_4 ⁸, it is only 7 times as reactive as NTA in HClO_4 at their points of maximum reactivities. This leveling effect in HClO_4 is true for the other chelating agents too, and may be explained in terms of the higher selectivity of a sulfato-complexed Ce(IV) *vs* the higher reactivity of a non-complexed Ce(IV) in HClO_4 solutions.

d. Salt effects and effect of ionic strength

Although the ionic strengths, μ , in the reaction media were too high to draw any quantitative conclusions from the application of the Brönsted-Bjerrum equation, we studied the effect of added salts in the hope of gaining some knowledge pertaining to the charges of the reacting species. With addition of NaClO_4 at an initial fixed $[\text{HClO}_4]$, k_2 increases steadily with μ (Table II). This increase cannot, however, be solely attributed to a primary kinetic salt effect. Previous investigators have shown that neutral salts have a marked effect on the protonating power of the medium as measured by the Hammett acidity function, H_0 ²⁴. In this work, we found that Na_2SO_4 and NaClO_4 have opposite effects on H_0 when added to HClO_4 solutions where the original H_0 was -0.25 (Table III). The effect of Na_2SO_4 may result from binding the protons of the medium to form the acid HSO_4^- , weaker than HClO_4 . With addition of NaClO_4 , however, a decisive increase in $-H_0$ is noted. This can be

Table II. Salt effects on EDTA-Ce(IV) reaction in HClO₄-NaClO₄ solutions at 25 °C.

Ionic strength [μ]	$\tau_{1/2}$ [msec]	k_2^a	k_2^b	Δk_2^c	k_2^d
			[M ⁻¹ sec ⁻¹]		
1.2	230	120	103	22	98
1.4	200	138	125	44	94
1.6	180	154	148	67	87
1.8	160	170	170	89	81
2.0	130	210	210	129	81
2.5	95	290	290	210	80

[EDTA]₀ = 2.5×10^{-2} M; [Ce(IV)]₀ = 3.5×10^{-4} M.
Hammett acidity function, -H₀, before salt additions = 0.25.

^a Observed second-order rate constants.

^b Second-order rate constants calculated for the increase in -H₀ accompanying salt additions.

^c The difference between (b) and k_2 at -H₀ = 0.25 (without added salt); this difference is due to the change of H₀. The value of k_2 at -H₀ = 0.25 is 81 M⁻¹ sec⁻¹.

^d Second-order rate constant corrected for change in H₀ and reflecting only changes in ionic strength due to salt addition.

Table III. Salt effects on Hammett acidity function. Original -H₀ = 0.25.

[Na ₂ SO ₄]	-H ₀	[NaClO ₄]	-H ₀
0.2	0.18	0.2	0.29
0.4	0.11	0.4	0.35
0.6	0.08	0.6	0.39
0.8	-0.01	0.8	0.45
1.0	-0.07	1.0	0.48
1.2	-0.09	1.5	0.56
		2.0	0.68

attributed to the decrease in water activity in the medium due to the solvation of the added salt.

Analysis of the results summarized in Table II suggests that the observed rate constants may be expressed in the form,

$$k_{\text{observed}} = k_0 + \Delta k_{\delta H_0} + \Delta k_{\text{salt}}$$

where k_0 denotes the rate constant at the initial acidity before salt addition, $\Delta k_{\delta H_0}$ denotes the increment in the rate constant due to the change of acidity (-H₀) caused by salt addition, and Δk_{salt} denotes the part of the rate constant due to salt effect apart from the effect due to changing H₀.

By referring to Table III we computed the change in H₀ due to addition of NaClO₄. From the dependence of k_2 on H₀ (Fig. 2) we calculated the value of k_2 expected for the increase accompanying salt addition. When the observed rate constants are corrected for the change in H₀, one finds that there

is no appreciable effect for increasing the ionic strength (Column d in Table II). This result may be taken to imply that one of the reactants has zero charge. Since Ce(IV) cannot exist as an uncharged species in HClO₄ solution, the results suggest that the reaction probably involves the unprotonated polyaminocarboxylic acid, H₄Y.

In confirmation of the proposal that the effect of added NaClO₄ merely enhances the acidity of the medium is the fact that on addition of NaClO₄ to the Ce(IV)-EDTA reaction mixture, k_2 decreased if the initial acidity of the medium was beyond its value at the inflection point, and increased if the acidity was originally below 3 M HClO₄.

e. Activation parameters

The oxidation of EDTA by Ce(IV) in 2.2 M HClO₄ was studied in the temperature range of 15–35 °C. The entropies of activation, $\Delta S^\ddagger$, are large and negative (−30.6 e.u. at 15 °C and −27.8 e.u. at 35 °C). This may be indicative of the occurrence of a free-radical process²⁵, and may also be a reflection of the conformational adjustments which the EDTA molecule must undergo to coordinate with Ce(IV) prior to electron transfer. In dilute HClO₄ solutions, the formation of an unstable Ce(IV)-EDTA complex has been reported²⁶. We have also observed complex formation even in H₂SO₄ solution (pH = 2)⁷.

f. Mechanism

The rate vs acidity reaction profiles observed in this work may be explained in terms of mechanistic pathways involving certain active species whose concentrations are controlled by the acidity of the medium in such a way as to produce the bell-shaped dependence of k_2 on [H⁺]. We propose a rate equation (at constant [Ce(IV)] and [Chel]) of the form

$$\text{Rate} = k_2' a_{\text{Ce}} \cdot a_{\text{Chel}} \quad (1)$$

where a_{Ce} and a_{Chel} represent the fractions of the stoichiometric concentrations of both reactants participating in the formation of the activated complex. The main species in HClO₄ are the unhydrolyzed Ce(H₂O)_n⁴⁺, the hydrolyzed CeOH(H₂O)_{n-1}³⁺, and Ce(OH)₂(H₂O)_{n-2}²⁺ 12–15. Although evidence for dimeric species, *e.g.*, (Ce–O–Ce)⁴⁺, (HO–Ce–O–CeOH)⁶⁺, *etc.* has been given²⁷, their importance can be ignored in solutions which are < 10^{−3} M Ce(IV). The concentrations of

the various species of Ce(IV) which may exist in HClO_4 are governed by the following equilibria:

The latest values for K_1 and K_2 are 6.4 and 0.12 respectively¹². In calculating the fraction of Ce(IV) which exists as the unhydrolyzed species at a particular $[\text{H}^+]$, use is made of the above equilibrium constants. Thus,

$$\frac{1}{\alpha_{\text{Ce}}} = 1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2} \quad (4)$$

where α_{Ce} refers to the unhydrolyzed Ce^{4+} species. Computations according to equation (4) indicate that α_{Ce} increases with acidity in HClO_4 solutions (Table IV). This unhydrolyzed species is probably

Table IV. Concentration distribution of Ce(IV) and EDTA species at different acidities.

$[\text{H}^+]$	$\alpha_{\text{Ce}^{4+}}$	$\alpha_{\text{Ce}(\text{OH})^{3+}}$	$\alpha_{\text{H}_4\text{Y}}$	$\alpha_{\text{H}_5\text{Y}^+}$
0.1	0.007	0.451	0.270	0.675
0.2	0.019	0.610	0.147	0.735
0.3	0.032	0.690	0.097	0.728
0.4	0.045	0.731	0.070	0.704
0.5	0.059	0.758	0.054	0.675
0.6	0.072	0.773	0.043	0.646
1.0	0.122	0.782	0.021	0.543
2.0	0.227	0.720	0.007	0.831
3.0	0.310	0.661	0.004	0.292
4.0	0.377	0.600	0.002	0.237
5.0	0.432	0.548	0.001	0.199

the most active Ce(IV) species in the reaction medium, and an increase in its concentration would lead to an increase in the observed rate according to equation (1).

Equation (5) was used to calculate the fraction of EDTA, $\alpha_{\text{H}_4\text{Y}}$, which exists as the non-protonated species at a particular $[\text{H}^+]$,

$$\frac{1}{\alpha_{\text{H}_4\text{Y}}} = 1 + K_5[\text{H}^+] + K_5 K_6 [\text{H}^+]^2 \quad (5)$$

where K_5 and K_6 denote the equilibria

With values of K_5 and K_6 of 25 and 0.8 respectively²⁸, one can see that $\alpha_{\text{H}_4\text{Y}}$ decreases from 0.27 at 0.1 M H^+ to 0.021 at 1 M H^+ and to 0.004 at 3 M H^+ . In other words, the concentration of the unprotonated species, H_4Y , decreases drastically with increasing acidity (Table IV).

In strongly acidic media, there are practically no anions of polyaminocarboxylic acids. Among the other possible species, the unprotonated form is the most amenable to loss of electrons and, therefore, to oxidation. If equation (1) represents the reaction between Ce^{4+} and H_4Y , the product $\alpha_{\text{Ce}} \cdot \alpha_{\text{Chel}}$ is observed to increase with increasing $[\text{H}^+]$ to a maximum at ~ 0.4 M H^+ and then declines rapidly (Fig. 3). A better fit with experiment is given by the dotted parabola in Fig. 3 which portrays a reaction path involving Ce^{4+} and H_5Y^+ . Using equation (1), one obtains a maximum rate for $\alpha_{\text{Ce}^{4+}} \cdot \alpha_{\text{H}_5\text{Y}^+}$ at 3.2 M H^+ ; the experimental maximum for the Ce(IV)-EDTA reaction is at 3–3.5 M HClO_4 . So, although salt effect studies suggest a reaction with H_4Y , a reaction path involving H_5Y^+ cannot be overlooked, and may indeed be the predominant path. Such a path is consistent with our explanation of the acid catalysis portrayed in section b. of the

Fig. 3. Simulated reaction rates as a function of acid concentration.

discussion. A third reaction path involving $\text{Ce}(\text{OH})^{3+}$ and H_5Y^+ exhibits a behavior similar to the $\text{Ce}^{4+}-\text{H}_4\text{Y}$ path, with a maximum at 0.42 M H^+ . It is quite possible that the reduction of $\text{Ce}(\text{IV})$ by EDTA takes place via the three mentioned reaction paths simultaneously and that the observed rate is best expressed by equation (8),

$$\text{Rate} = a(\text{ce}^{4+} \cdot \text{a}_{\text{H}_4\text{Y}}) + b(\text{ce}^{4+} \cdot \text{a}_{\text{H}_5\text{Y}^+}) + c(\text{ce}(\text{OH})^{3+} \cdot \text{a}_{\text{H}_5\text{Y}^+}) \quad (8)$$

where a , b and c are parameters whose magnitudes

determine the contribution of each term to the overall reaction rate.

Finally we wish to propose the reaction sequence shown in Chart 2, which is to be considered mainly as a guideline for future studies. Possibly, the intermediate charged Schiff's base (I) cyclizes to the corresponding lactone (II), which accounts for only 4 $\text{Ce}(\text{IV})$ reacting initially with the hydrolysis of (II) occurring afterward to give formaldehyde. Work with simpler amino acids is underway to test the proposed mechanism.

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