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The Oxidative Decarboxylation Of Polyaminocarboxylic Acids - I. A Study Of The Reaction Of Ethylenedinitrilotetraacetic Acid (EDTA) With Cerium (IV) In Acid Solution

Samir B. Hanna
Missouri University of Science and Technology

S. Al-Hashimi

William H. Webb
Missouri University of Science and Technology

William R. Carroll
Missouri University of Science and Technology

The Oxidative Decarboxylation of Polyaminocarboxylic Acids

I. A Study of the Reaction of Ethylenedinitrilotetraacetic Acid (EDTA) with Cerium (IV) in Acid Solution

S. B. Hanna, S. Al-Hashimi, W. H. Webb, and W. R. Carroll

Department of Chemistry, School of Science, University of Missouri-Rolla, Mo. (USA)

Summary. The reaction between Ce(IV) and EDTA was followed titrimetrically and spectrophotometrically, and was found to occur in stages. Four equivalents of Ce(IV) are reduced per mole of EDTA almost instantaneously at room temperature. With increasing temperature and reaction time an ultimate of about 14 equivalents of Ce(IV) is consumed per mole of EDTA. Carbon dioxide, formaldehyde, and other yet unidentified compounds are the products of oxidation of EDTA. The kinetics of the reaction in aqueous sulfuric acid was studied over the temperature range $11.7°—40°C$ by a spectrophotometric technique. The effects of the acidity of the medium and of added salts are reported.

Oxydative Decarboxylierung von Polyaminocarbonsäuren. I. Untersuchung der Reaktion von ÄDTE mit Ce(IV) in saurer Lösung. Die Reaktion zwischen Ce(IV) und ÄDTE wurde volumetrisch und spektroskopisch (UV) verfolgt. Dabei wurde gefunden, daß die Reaktion in Stufen verläuft. Bei Zimmertemperatur wurden vier Äquivalente Ce(IV) je Mol ÄDTE beinahe sofort reduziert. Mit zunehmender Temperatur und Reaktionszeit wurden bis zu 14 Äquivalente Ce(IV) je Mol ÄDTE verbraucht. Die Oxydationsprodukte von ÄDTE sind Kohlendioxid, Formaldehyd und andere noch nicht identifizierte Verbindungen. Die Reaktionskinetik in wäßriger Schwefelsäure wurde spektroskopisch (UV) im Temperaturbereich von $11,7°—40°C$ untersucht. Die Einflüsse der Acidität der Lösung und der zugefügten Salze werden angegeben.

Introduction

The study of Ce(IV) oxidations of organic compounds has become increasingly important in the past few years [11,14,17]. However, there are only a few reports in the literature on the oxidation of amino or polyaminocarboxylic acids by Ce(IV) or by other oxidizing agents. We have, therefore, initiated an extensive program to study the stoichiometry and the mechanisms of oxidation of polyaminocarboxylic acids commonly used as chelating agents. This work is primarily devoted to an investigation of the Ce(IV)-EDTA systems.

EDTA is known to form complexes with trivalent lanthanides, and such complexes have been the subject of detailed investigations [15,18,19]. On the other hand, very little is known about complexes with Ce(IV). In a limited acid range, the formation of an unstable Ce(IV)-EDTA complex, whose acid-catalyzed decomposition to Ce(III) and unidentified products, "within a few minutes of its formation", has been reported [2]. An earlier report on the reductive ability of EDTA showed that the chelating agent reacts with Ce(IV) in an acid medium in the ratio of 1:8, but only on heating [12]. Recently, a study of the stoichiometry of the reaction in question revealed that about 4 equivalents of Ce(IV) are consumed per mole of EDTA with the liberation of about 2.5 moles of CO_2, and N,N-dimethylethylenediamine in an unrecorded yield [7]. In this report we wish to relay the results of a more detailed investigation of the stoichiometry and the kinetics of the reaction between Ce(IV) and EDTA in acid medium, under a variety of conditions.

Experimental

Reagents

Ceric ammonium hexanitrate, $(NH_4)_2Ce(NO_3)_6$, ceric ammonium tetrasulfate, $(NH_4)_4Ce(SO_4)_4 \cdot 2 H_2O$, the disodium salt of ethylenedinitrilotetraacetic acid dihydrate, H_2EDTA, and the inorganic acids and salts used were reagent grade and were used without further purification. Solutions of Ce(IV) were prepared by direct weighing, and for the very dilute solutions, by dilution of standardized solutions. The primary standard used was reagent-grade ferrous ammonium sulphate (Mohr's salt, $FeSO_4 \cdot (NH_4)_2 SO_4 \cdot 6 H_2O$), and the indicator was o-phenanthroline prepared according to standard procedures.

Procedure for Determining Stoichiometry

Known volumes of standardized solutions of Ce(IV) were allowed to react with EDTA solutions under a variety of conditions. The concentrations of reactants and the acidity

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of the medium were varied. The temperature was varied from 25° to about 100°C (boiling solution), and the reaction was observed for periods of time ranging from a few seconds to a few days. The number of equivalents of Ce(IV) consumed per mole of EDTA was determined by titration with standard Fe(II) solution using o-phenanthorline as indicator. In a few cases, the stoichiometry was determined for the reaction between 1 M ceric ammonium hexanitrate solution in water and solid H_2EDTA at 25°C. This reaction is quite vigorous; actually it resembles the reaction of carbonates with acids in that CO_2 effervesces abundantly. The amount of CO_2 evolved was measured volumetrically.

Procedure for Following the Kinetics

The rates of reaction were followed spectrophotometrically at 316 nm where Ce(IV), but not EDTA, the medium, or the products, absorbs very strongly. The changes in absorbance were recorded automatically on a Beckman DK-2A spectrophotometer fitted with a time-drive attachment. The cells were placed in a thermostated cell-holder, and the temperature was regulated by a circulating Lauda Ultrathermostat, and was maintained at the desired temperature at better than $\pm 0.05°C$. The reference cell contained EDTA in H_2SO_4 of the same molarity as the reaction cell. The latter contained 3 ml of 10^{-4}—10^{-5} M Ce(IV) solution in H_2SO_4. To start a run, the time-drive device was switched on at the appropriate speed (usually 1 inch per minute), and 50 µl of an aqueous EDTA solution of a known concentration were injected in the Ce(IV) solution which was already thermostated in the cell compartment. The plunger of the delivering microliter syringe was worked up and down a few times to insure quick and thorough mixing. Separate trials with a solution of a colored indicator showed that mixing was efficient and was virtually complete within 1—2 seconds from injection time. In cases of moderately fast reactions, the recording pen was pulled across the chart by a constant-speed constant-tork motor. Uniform speeds of about one inch per second were easily achieved by this improvised device.

The absorbance of the reaction mixture, at 316 nm, decreased steadily with time, and within a few minutes approached zero. The percentage reaction [% Ce(IV) consumed] was readily calculable from the graph, and when the values were plotted versus time on one-cycle semi-log graph paper, straight lines were obtained over two to three half-lives for Ce(IV). The half-lives were read at the 50% line, and the first-order rate constants were computed from the equation:

$$k_1 = 0.693/t_{0.5}.$$

The EDTA was always in such an excess that its concentration did not vary by more than 1—2% at most when the Ce(IV) was already half-consumed, and the second-order rate constants, k_2, were obtained by dividing k_1 by the initial concentration of EDTA in any particular run. Rate constants were reproducible to better than $\pm 6\%$.

Results and Discussion

Stoichiometry

The reaction between Ce(IV) and EDTA proceeds in stages, and can be followed titrimetrically [back titration of unreacted Ce(IV) with Fe(II) using o-phenanthrolne as indicator] and spectrophoto-

metrically (at 316 nm). About 4 equivalents of Ce(IV) are reduced almost instantaneously at room temperature. Increased reaction time and temperature allows for the ultimate consumption of about 14 equivalents of Ce(IV) per mole of EDTA. The pertinent results are summarized in Table 1.

Table 1. *Stoichiometry of Ce(IV)-EDTA reaction. Progress of the reaction between ceric ammonium hexanitrate (25 ml, 0.098 M) and EDTA (1 ml, 0.1 M H_2SO_4). Equivalents calculated from back-titration with Fe(II). Temperature 25°C*

Time, min	Number of equivalents of Ce(IV) consumed per mole of EDTA
0.25	(4.10, 4.25, 4.19)[a]
1	5.0
5	5.1
15	5.3
30	5.6
60	6.1
120	6.2
240	7.1[b]
72 h	12.1
30 min at boiling temperature	13.9, 14.05, 14

[a] These determinations were carried out by fast mixing of solutions of reactants by injection, immediate quenching with Fe(II) solution, and back-titration with Ce(IV).
[b] In the reaction between solid H_2EDTA and 1 M ceric ammonium hexanitrate, 6 equivalents of Ce(IV) were consumed per mole of H_2EDTA in 10 min, 7 equivalents in 30 min

It is quite evident that the reaction exhibits variable stoichiometry and is thus an undesirable reaction from the quantitative analytical point of view (cf., however ref. [6]). It is also interesting to note that the stoichiometry obtained through titration of the EDTA with Ce(IV), to an end point stable for 10 min, varied with the acidity of the medium (Fig.1). The lower number of equivalents consumed in such titrations at high acid concentrations may be due to the preponderance of inactivated protonated EDTA species, H_5EDTA^+ and H_6EDTA^{2+} in highly acidic media.

The reaction proceeds with decarboxylation which is quite vigorous when solid EDTA is titrated with a 1 M solution of ceric ammonium hexanitrate. The relationship between the number of equivalents of Ce(IV) consumed per mole of EDTA and the number of moles of CO_2 produced per mole EDTA is depicted in Fig.2. The results confirm those obtained by Holzapfel and Dittrich [7], where it was shown that the consumption of 4 equivalents of Ce(IV) per mole of EDTA produced only slightly over 2 equiv-
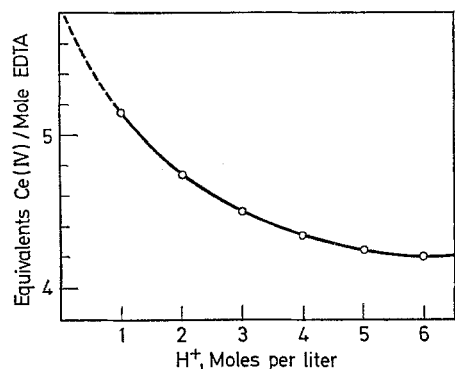
Fig. 1   Fig. 2

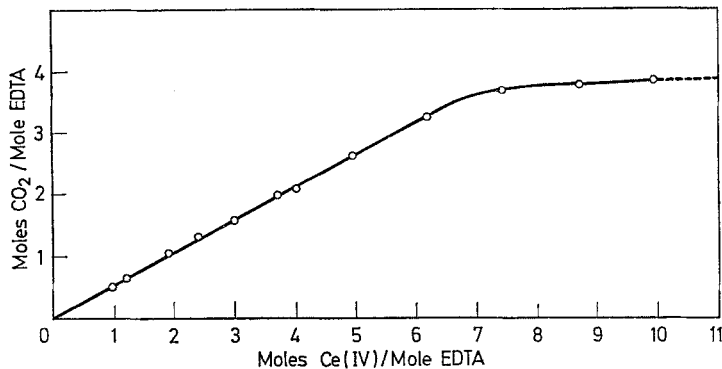Fig. 1. Change of stoichiometry of the Ce(IV)-EDTA reaction with changing the acidity of the medium

Fig. 2. Stoichiometry of decarboxylation of EDTA by Ce(IV)

alents of CO_2. The consumption of more than 4 equivalents of Ce(IV) per mole of EDTA does not produce CO_2 proportionately (Fig.2). The formation of formaldehyde was detected qualitatively by the positive Schiff's test on the reaction mixture. Thus one may write the following scheme.

Such products were reported for the anodic oxidation of EDTA at a potential difference of 4—6 V between shiny platinum electrodes at a current strength of 80 milliamps for 30—60 min [9].

The overall reaction in either path may thus be summarized as

EDTA $+ 4$ Ce(IV) $\rightarrow 2$ $CO_2 + ?CH_2O +$ organic oxidation products $+ 4$ Ce(III).
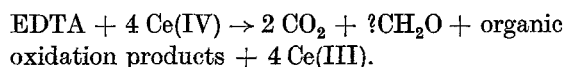
It is interesting to note that the addition of only 4 equivalents of Ce(IV)—as ceric ammonium hexanitrate in D_2O—to solid H_2EDTA has resulted in the complete disappearance of the sharp and simple NMR singlet peaks characteristic of H_2EDTA in
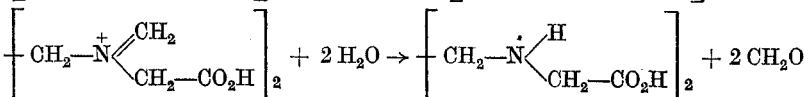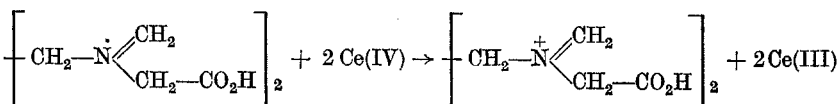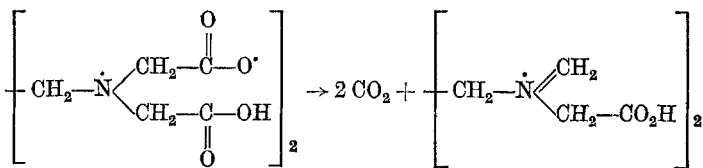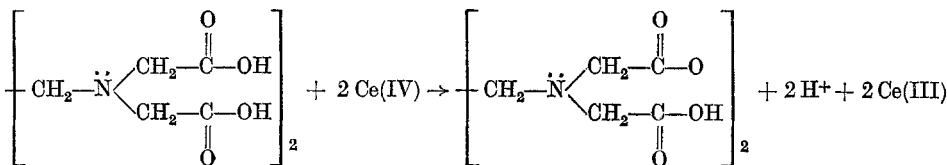
An alternative path may be depicted as follows:
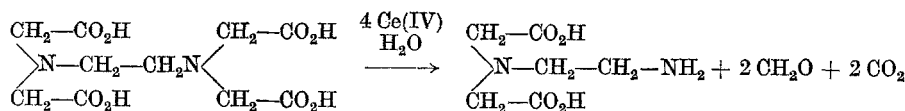
D_2O (3.75 and 4.0 ppm in the ratio of 1:2). This indicates that the reaction of EDTA with 4 equivalents of Ce(IV) is a complete reaction of its own. The further consumption of Ce(IV) is by the product(s) of such initial reaction and not by any EDTA left unreacted. In other words, EDTA is transformed into a less reactive, probably non-chelating, agent by its reaction with 4 and only 4 equivalents of Ce(IV). The results suggest that the chelating property of EDTA is essential for the first stage of oxidation by Ce(IV) leading to decarboxylation. In confirmation of this, the simple amino acid glycine does not undergo oxidative decarboxylation under the conditions used successfully with EDTA.

Kinetics

Guided by the variation in the stoichiometry of the EDTA-Ce(IV) reaction with time and with temperature, we decided to look into the kinetics of this system. Only the initial stages of the reaction, where 4 equivalents of Ce(IV) are consumed per mole of EDTA, seemed interesting since the latter stages of the reaction are quite slow and of variable stoichiometry. At a 0.1 M concentration for reactants, the first stage was too fast to measure by any of the readily available techniques. However, at 10^{-4} M Ce(IV) where the absorbance at 316 nm is a maximum and is about unity, the reaction with excess (about 10^{-3} M) EDTA proceeds at such a rate that it could be followed spectrophotometrically conveniently. But first, it was necessary to evaluate the stoichiometry of the reaction in this low concentration region. When 5 millimols of Ce(IV) were mixed with one millimol of EDTA, in the region of concentrations allowable in UV spectrophotometry, the absorbance of the reaction mixture, after 15 min, pointed to the consumption of only 4 equivalents of Ce(IV).

The rates of consumption of Ce(IV) by EDTA were studied as a function of the medium. The influence of added salts and of varying the temperature were also studied.

Order of Reaction and Influence of Acidity of Medium

In the region of concentrations workable in UV spectrophotometry, and where one mole of EDTA reduces 4 moles of Ce(IV), the reaction is first order in each reactant (Table 2), and shows variable dependence on the concentration of hydrogen ions (Fig.3) in a fashion which may be summarized by the equation:

$$- \frac{d\,[Ce(IV)]}{dt} = k_2\,[Ce(IV)]\,[EDTA]\,[H^+]n$$

Table 2. *Half-lives for Ce(IV), and second-order rate constants for the reaction between Ce(IV) and EDTA in 6 N H_2SO_4; spectrophotometrically at 316 nm, at 30.1°C*

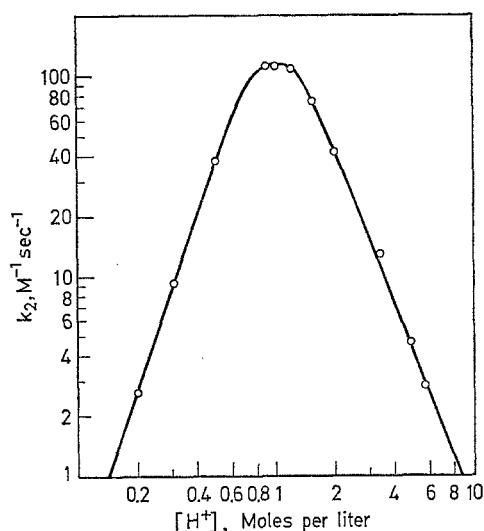| [Ce(IV)]₀ 10⁴M	[EDTA]₀ 10³ M	$t_{0.5}$ sec	k_2, M⁻¹sec⁻¹
1.64	1.64	53	7.9
1.06	1.64	55	7.7
0.53	1.64	54	7.8
1.64	0.82	96	8.8
1.64	1.64	50	8.4
1.64	3.28	37	8.2

Fig. 3. Logarithmic relationship of the Ce(IV)-EDTA second-order rate constants and the acidity of the medium

where n varies from about $+ 2.5$ to -2.5. The reaction rate is a maximum at about 1 M [H⁺], and decreases on either side. Evidently, the earlier report on the kinetics of the reduction of Ce(IV) with EDTA [2], which shows the rate to be directly proportional to [H⁺], is not a general one, but is valid only in a limited acid region, viz., below 1 M [H⁺].

The change in the sign of the slope of log k vs. log [H⁺], may be explained in terms of the drastic changes which the reacting species suffer in changing the medium from 0.2—6 M H⁺. EDTA is primarily an α-amino acid, and the two nitrogens are basic enough to become protonated to different degrees in different acid media. Deactivated species such as H_5EDTA^+, and H_6EDTA^{2+}, where the reductive ability is expected to be reduced drastically if not totally inhibited, probably exist as substantial fractions of the stoichiometric H_2EDTA concentration in solutions where [H⁺] is above 1 M. The formation

constants for these two species have been determined recently [1], in solutions of unit ionic strength (NaClO$_4$), and found to be 25.1 and 0.76, respectively. Also, if complexation between Ce(IV) and H$_4$EDTA takes place as a first step towards the oxidation-reduction step which is observed, one would expect the concentration of the complex to decrease with increasing [H$^+$] in the medium, since

$$H_4EDTA + Ce(IV)^{4+} \rightleftarrows EDTA\text{-}Ce(IV) + 4H^+.$$
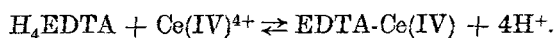
Actually, one would expect an inverse proportionality between the concentration of such a complex and the fourth power of [H$^+$] in the medium. The formation of a complex between Ce(IV) and EDTA has been reported [7], and has been confirmed in this work. Its momentary build-up, at 295 nm, and decay, was observed but only in solutions of low acidity ($\approx$ pH 2). If the reaction which finally leads to Ce(III) and oxidation products of EDTA takes place in two steps: complexation followed by electron transfer, and if the second step is catalyzed by H$^+$, one can see a possible explanation for the variable dependence on [H$^+$] depicted in Fig.3. Furthermore, Ce(IV) is known to exhibit an oxidative power which depends on the medium [10], particularly the acidity of the medium [16], and to exist in different forms in acidic solutions [5]. For example, it was estimated that in 2 M HClO$_4$, 28% of the Ce(IV) is present as aquated Ce^{4+}, the remainder predominantly as Ce(OH)$^{3+}$ and as a dimer such as (CeOCe)$^{6+}$ or (CeOCeOH)$^{5+}$ [4]. On the other hand, from electrical migration experiments in 0.5 to 20 N H$_2$SO$_4$, Ce(IV) was shown to exist in the form of anionic complexes which were believed to be Ce(OH) (SO$_4$)$_3{}^{3-}$ largely [8].

The Influence of Added Salts

Studies of the effect of changing the ionic strength, μ, on rates of ionic reactions are very important in formulating reaction mechanisms. In this study, rather high concentrations ($>$ 1 M) of salts had to be used since the media were already rich in ions (1—6 N H$_2$SO$_4$). Under such conditions the classical application of the Brönsted-Bjerrum equation, $k = k_0 \, 10^z A^z B \sqrt{\mu}$, may not be justified [3]. The graphical representation of the effect of added NaClO$_4$ to the reaction medium of *original* 0.5 N H$_2$SO$_4$ yields a straight line which shows a negative slope of $\approx$ 2 for the log k vs. $\sqrt{\mu}$ plot. This result, if meaningful, may be taken to imply that the reaction between EDTA and Ce(IV) in that acid region (1 N H$^+$) is between oppositely charged ions. There

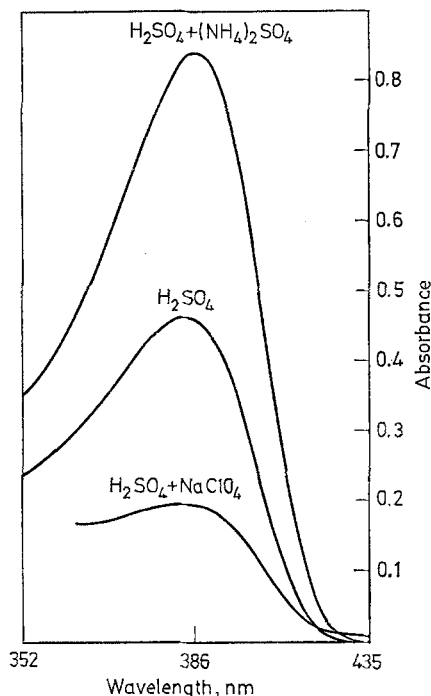Fig.4. Salt effects and acidity of medium absorbances of p-nitroaniline in H$_2$SO$_4$ alone and with added salts

is reason to believe, however, that the decrease in the second-order rate constants with increasing neutral salt concentration is due to proportionate increases in the protonating power of the medium. Earlier work on the Hammett acidity function, H$_0$, has shown that the acidity of a medium increases with concentration of added neutral salts [13]. We confirmed this observation in our work by measuring the intensity of absorption of a colored indicator, p-nitroaniline, the protonated form of which is colorless, as a function of increasing salt concentrations. Fig.4 depicts absorbances for the said indicator in 0.5 N H$_2$SO$_4$ alone (middle curve), in 0.5 N H$_2$SO$_4$ + 2 M NaClO$_4$ (lower curve), and in 0.5 N H$_2$SO$_4$ + 2 M (NH$_4$)$_2$SO$_4$ (upper curve).

The lowering of the acidity with added ammonium sulfate, also accompanied by a decrease in k_2 (the inflexion point in Fig.3 occurs at just about 1 M H$^+$), may be explained by the common ion effect exerted by SO$_4{}^{2-}$ on the dissociation of H$_2$SO$_4$. The increasing acidity with added NaClO$_4$, also noticed in this work with NaCl, KCl, KNO$_3$ and LiClO$_4$, could be interpreted as a result of a decrease in the amount of solvation of protons in the medium due to clustering of the water molecules around the added salts. Schematically, one would expect the protonating power to increase steadily from I to III:
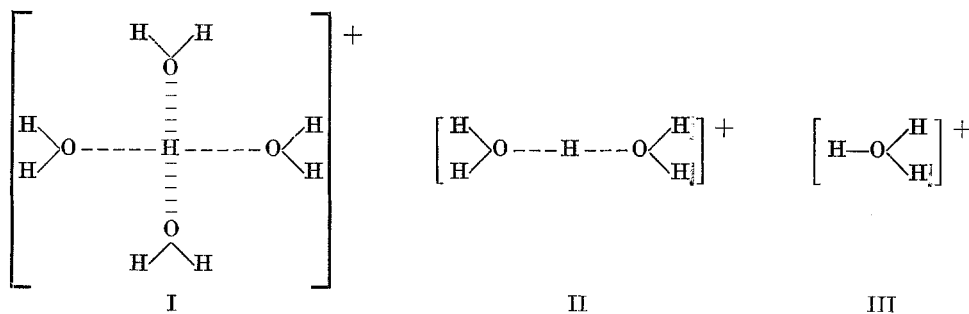
Influence of Temperature

The results of varying the temperature from 11 to 40°C on the rates of the reaction in question are summarized in Table 3. An Arrhenius plot of the rate constants gives an activation energy, E_a, of $17.6 \pm 0.2 \ k$ cal/mole.

Table 3. *Effect of temperature on the EDTA-Ce(IV) reaction. Reaction between ceric ammonium sulfate (1.64 $\times$ 10^{-4} M) and EDTA (1.64 $\times$ 10^{-3} M) in 5.85 N H$_2$SO$_4$*

Temperature °C	Half-life for [Ce(IV)], sec	k_2, M^{-1}sec^{-1}
11.7	570.0	0.74
20.7	150.0	2.82
31.5	49.5	8.53
40.2	22.5	18.78

Conclusion

Quadrivalent Ce is reduced by EDTA in acid medium. The reaction exhibits variable stoichiometry and is, therefore, undesirable analytically. Despite the variability in stoichiometry, the Ce(IV)-EDTA reaction lends itself to informative physicochemical studies. More comprehensive product analysis than is currently available is underway, and is essential for translating the kinetics presented in this work into a mechanism for the oxidation of EDTA by Ce(IV).

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Prof. Dr. S. B. Hanna
Techn. Chem. Lab. der Eidgen. Techn. Hochschule
CH-8006 Zürich, Universitätsstr. 6 (Schweiz)