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# The Oxidative Decarboxylation of Polyaminocarboxylic Acids

## II. A Comparative Kinetic Study of the Oxidation of NTA, EDTA, CDTA and DTPA with Cerium(IV) in Sulfuric Acid Media\*

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*Oxydative Decarboxylierung von Polyaminocarbonsäuren. II. Vergleichende kinetische Untersuchung der Oxydation von NTA, ÄDTA, CDTA und DTPA mit Ce(IV) in saurer Lösung.* Die Oxydationsgeschwindigkeiten von 4 Chelaten (NTA, ÄDTA, CDTA und DTPA) mit Ce(IV) in saurer Lösung wurden spektrophotometrisch mit Hilfe der „stopped-flow“-Technik bestimmt. Die Reduzierfähigkeit nimmt in der Reihenfolge CDTA > ÄDTA > DTPA > NTA ab. Der Einfluß verschiedener Säuregehalte in der Lösung wurde untersucht, und in jedem Fall wurde ein Maximum in der graphischen Darstellung der Geschwindigkeitskonstante gegen  $[H^+]$  beobachtet. Eine mögliche Erklärung des Reaktionsvermögens und des Säureinflusses wird gegeben.

*Summary.* The rates of oxidation of four chelating agents, NTA, EDTA, CDTA, and DTPA with Ce(IV), in sulfuric acid media, were determined spectrophotometrically by a stopped-flow technique. The reductive ability is in the order CDTA > EDTA > DTPA > NTA. The influence of varying the acidity of the medium was studied, and in each case a maximum in the rate constant vs.  $[H^+]$  plot was observed. A possible interpretation of the reactivities and the influence of acidity is advanced.

### Introduction

In part I of this series we reported [3] on the stoichiometry and the kinetics of the reaction of ethylenedinitrilotetraacetic acid (EDTA), in acid media, with Ce(IV). As a continuation of the previous work we wish to relay our results on the comparative case of oxidation, with Ce(IV) in sulfuric acid media, of several polyaminocarboxylic acids usually used as chelating agents, in the decontamination of living organisms, and recently involved in antipollution detergents.

### Experimental

*Reagents.* Ceric ammonium tetrasulfate  $(NH_4)_4Ce(SO_4)_4$ , ethylenedinitrilotetraacetic acid, EDTA (Titriplex III), nitrilotriacetic acid, NTA (Titriplex I), 1,2-cyclohexyldiaminetetraacetic acid, CDTA (Titriplex IV), and diethylenetriaminepentaacetic acid, DTPA (Titriplex V) were all Merck reagent grade chemicals of the highest purity and were used without further purification.

*Procedure.* The rates of reaction between Ce(IV) and the 4 chelating agents were studied spectrophotometrically at 316 nm by following the consumption of Ce(IV), using a Durrum-Gibson stopped-flow apparatus. The initial concentrations in the reaction mixture were  $1 \times 10^{-4}$  M Ce(IV)

and  $1 \times 10^{-2}$  M chelating agent for most of the studies. The acidity of the medium,  $[H^+]$ , was varied from a low of 0.04 M to a high of 5.0 M. Each rate measurement was repeated several times to insure reproducibility. The half-life of Ce(IV) was read directly from the oscilloscope screen displaying percentage transmission vs. time (Fig. 1). The first-order rate constants were calculated from the formula,  $k_1 = 0.693/t_{1/2}$ . The chelating agent was always in such an excess that its concentration did not vary by more than 1–2% when the Ce(IV) was already half consumed. The second-order rate

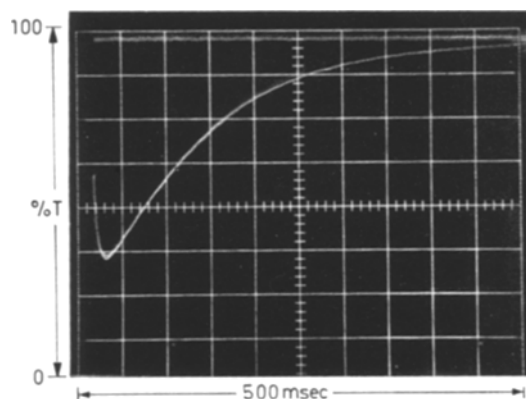


Fig. 1. Oscilloscope trace of the change in percent transmission vs. time for the Ce(IV)-CDTA system, recorded at 316 nm

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constants,  $k_2$ , were calculated by dividing  $k_1$  by  $[\text{Titriplex}]_0$  in any particular run. Second-order rate constants were reproducible to better than  $\pm 5\%$ .

### Results and Discussion

The rates of reduction of Ce(IV), in acid media by chelating agents which differ substantially in their complexing powers were studied spectrophotometrically. In the region of concentrations workable in UV spectrophotometry, variations in the initial concentrations of reactants at a fixed hydrogen ion concentration (Table) lead to a second-order kinetic equation

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

With fixed initial concentrations of reactants, the changing of the acidity of the medium had a remarkable influence on the rates of reactions. The variation

Table. *Second-order rate constants for the reduction of Ce(IV) by different chelating agents at a fixed  $(\text{H}^+) = 2.5 \text{ M}$  at  $25 \pm 0.05^\circ \text{C}$*

Chel. Agent	Run No.	$[\text{Ce(IV)}]_0$ $\text{M} \times 10^4$	$[\text{Titriplex}]_0$ $\text{M} \times 10^3$	$10^3 k_2$ $\text{M}^{-1} \text{sec}^{-1}$
NTA	261	1.00	2.50	2.20
	262	1.25	2.50	1.98
	277	1.00	5.00	1.98
	279	2.00	5.00	1.98
	240	0.75	10.00	1.93
	292	0.75	15.00	2.10
	295	2.00	15.00	1.89
EDTA	281	1.00	5.00	28.80
	282	1.25	5.00	28.80
	283	2.00	5.00	31.50
	248	2.00	10.00	31.50
	299	1.25	15.00	30.80
CDTA	271	2.00	2.50	44.00
	285	1.00	5.00	46.20
	251	1.00	10.00	45.60
	253	2.00	10.00	46.20
	302	1.00	15.00	44.00
DTPA <sup>a</sup>	272	0.75	2.50	33.80
	274	1.25	2.50	33.00
	286	1.00	5.00	33.80
	288	2.00	5.00	34.60
	257	1.25	10.00	33.00
	258	2.00	10.00	33.00
	307	1.25	15.00	35.60

<sup>a</sup> The higher  $k_2$  for DTPA compared to EDTA might seem inconsistent with the statement in the *summary* concerning the relative reactivities of the 2 chelating agents towards oxidation by Ce(IV). Those reported relative reactivities refer to the inflexions points in the  $k_2$  vs.  $[\text{H}^+]$  plot (Fig. 2). It is evident from that plot that, at  $[\text{H}^+]$  to the right of the inflexion points, the order of reactivity changes for these 2 chelating agents.

of  $k_2$  with  $[\text{H}^+]$  is shown in Fig. 2 for the 4 chelating agents. We observed an inflexion point for each of the chelating agents at a characteristic  $[\text{H}^+]$ : between 0.09 and 0.10 M for CDTA, about 0.8 M for NTA, about 1.5 M for DTPA, and between 1.0 and 1.5 M for EDTA. Similar behavior has been reported [1] in the oxidation of Fe(II) by Ce(IV), and recently in the oxidation of Sb(III) by Ce(IV) in perchloric acid medium [5].

The latter workers explained their results in terms of the various equilibria involving Ce(IV) in perchloric acid media. In view of the known increase in the oxidation potential of Ce(IV) with increasing acid concentration [6] we believe that the decrease in rate with increasing  $[\text{H}^+]$ , shown in Fig. 2, is probably mainly due to protonation of the polyaminocarboxylic acids which would render them inactivated towards complexation with Ce(IV) and towards oxidation. The lone pair of electrons on the nitrogen of the chelating agents is probably the source of the reductive ability of these agents. Protonation constants of 12.6, 25.1, and 52.5, for NTA, EDTA and CDTA respectively, recently reported by Anderegg [2], suggest that these chelating agents are heavily protonated at, and beyond, the particular inflexion points, and thereby deactivated in relatively strong acidic media.

The much higher reductive ability of CDTA as compared to the other chelating agents may be readily explained in terms of the favorable and fixed geometry of the nitrogen ligands in CDTA which allows for easy interaction with Ce(IV). The hindered rotation around  $\text{C}_1-\text{C}_2$  in 1,2-cyclohexyldiaminetetraacetic acid in contrast to the freely rotating EDTA, apparently endows the CDTA molecule with the most favorable geometry for complexation. We are inclined to believe that such complexation, which may be a necessary step in the oxidative decarboxylation process, involves the 2 nitrogens primarily, and that CDTA provides the ideal needed stereoelectronic environment.

Attempts to measure rates of formation of a Ce(IV) complex with EDTA failed with the available instrumentation. Complex formation, detected spectrophotometrically with EDTA but not with CDTA, was too fast to measure by the ordinary stopped-flow technique. However, with DTPA, where conformational adjustments are probably needed for complexation with Ce(IV), the rates of such complexation and of the decay of the complex to Ce(III) and DTPA oxidation products have been measured conveniently at room temperature. At  $[\text{H}^+] = 0.6 \text{ M}$

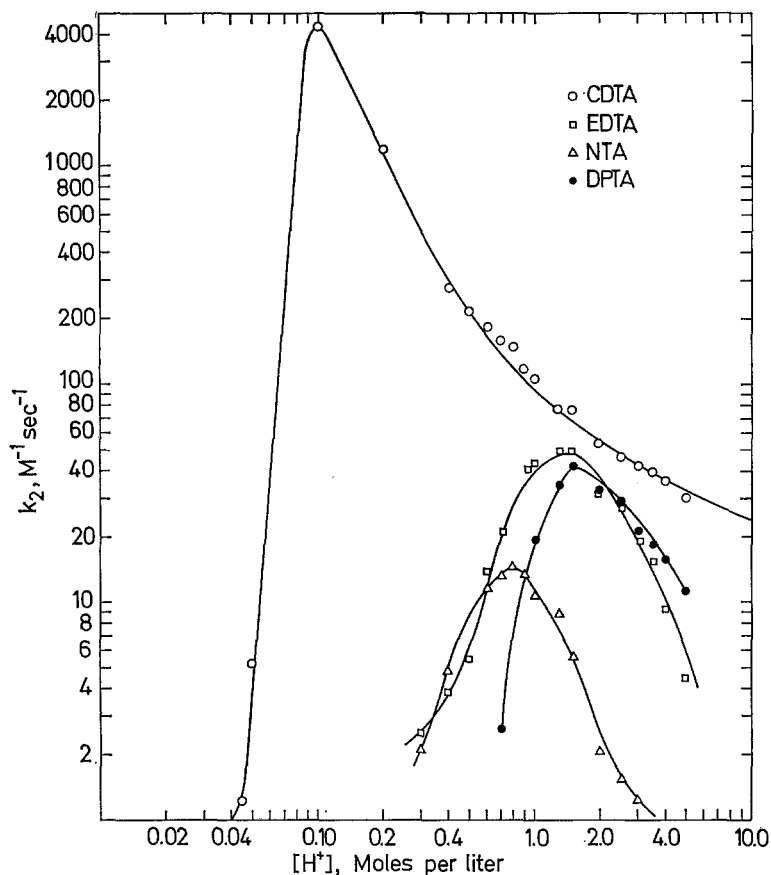


Fig. 2. Logarithmic relationship of the Ce(IV)-Titriplex second-order rate constants and the acidity of the medium

the half-life of complex formation between  $10^{-4}$  M Ce(IV) and  $10^{-2}$  M DTPA is 35 msec; the half-life for complex decay is 76 sec. The details of this study at different  $[H^+]$  and different temperatures are reported elsewhere [4].

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