excess of the vinyl ether. The rate was followed spectrophotometrically by following the rate of disappearance of the colored R-TAD. The wavelength used varied from 526 to 544 nm (n → π*) depending on the solvent.

Metal Ion Oxidative Decarboxylations. 13.[1] Kinetics and Mechanisms of the Oxidation of N-Benzyliminodiacetic Acid with Cerium(IV) in Acidic Perchlorate and Acidic Sulfate Media[2]

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The Ce(IV)-mediated decarboxylation of N-benzyliminodiacetic acid (BIDA) produces benzaldehyde, formaldehyde, dimethylamine, benzylmethylamine, and N-benzylglycine in acidic perchlorate and acidic sulfate media. Spectrophotometric evidence of an intermediate Ce(IV)–BIDA complex is given. The data may be interpreted in terms of a mechanism which involves sequential reactions, the first of which is a reversible reaction: BIDA + Ce(IV) (k_1) ⇌ (k_{-1}) complex (k_2) → products. The rapid complex formation is followed by a slower oxidative decomposition to give a free radical capable of inducing free-radical polymerization. The free radical reacts rapidly with another Ce(IV) to give an iminium ion which undergoes either hydrolysis or decarboxylation. The rate constants k_1, k_{-1}, and k_2 were determined from kinetic data. At acidities between 0.10 and 2.0 M, the rates of both complex formation and complex decomposition are inversely dependent on [H+]. Activation parameters were determined in perchloric acid. Evidence is given to suggest $CeSO_4^{2+}$ as the reactive Ce(IV) species in acidic sulfate media.

In pursuing our studies of the oxidation and decarboxylation of hydroxy acids[3] and amino acids,[4] we have now chosen to investigate the mechanistic details of the cerium(IV)-mediated decarboxylation of N-benzyliminodiacetic acid (BIDA, 1). BIDA is a chelating agent which is used frequently, particularly in cross-linked polymer forms: Chelex 100 and Dowex A-1 ion-chelating resins. A knowledge of the compatibility of such agents with oxidizing metal ions prompted the present investigation. BIDA and the polymeric resins exhibit similar complexation behavior and are capable of forming 1:1 and 1:2 transition-metal complexes.[5] The thermodynamic properties of the resins can be identified with those of BIDA, and such information is useful in planning analytical separations with the ion-chelating resins.

In this paper we report the results of our investigation of the stoichiometry, products, kinetics, and mechanisms of the reaction of Ce(IV) with BIDA in acidic perchlorate and acidic sulfate media.

Experimental Section

Materials. Cerium(IV) perchlorate solution (0.5 M in 6 M perchloric acid), ferrous ammonium sulfate (reagent ACS), 70% perchloric acid (double distilled, reagent ACS), and sodium perchlorate (hydrated reagent) were obtained from G. Frederick Smith Chemical Co. N-Benzylglycine ethyl ester, N-benzyliminodiacetic acid (98%), benzylmethylamine (97%), dimethylamine (40% aqueous solution), and N-methylglycine (sarcosine, 98%) were obtained from Aldrich Chemical Co. Acrylamide, 5,5-dihydroxy-2,7-naphthalenedisulfonic acid (chromotropic acid; practical), and 2,4-dinitrofluorobenzene (2,4-DNFB) were from Eastman. Cerium(IV) sulfate (GR) and silica gel HF were from Merck. All other common reagents, indicators, and solvents were of the highest purity available from Fisher Scientific.

Synthesis. N-Benzylglycine, used as a standard for comparison, was prepared from N-benzylglycine ethyl ester through basic hydrolysis. The ethyl ester was heated with sodium hydroxide, poured over ice, and acidified with hydrochloric acid. White to off-white needlelike crystals formed immediately. The product was characterized by mass spectroscopy after recrystallization from water [mp 197 °C (lit.[6] mp 198–199 °C)].

Solutions. All solutions were made by using deionized water which was doubly distilled from an all-glass still. If the commercially available Ce(IV) perchlorate solution were found to contain polymeric cerium species,[7] it was first reduced with excess H_2O_2 and reoxidized electrolytically as described previously.[8] If the test for polymeric species were negative, the Ce(IV) solution was simply diluted and standardized.

The solutions used for kinetic measurements were made just prior to use. The BIDA solutions contained known weights of BIDA and calculated quantities of stock solutions of perchloric acid and sodium perchlorate. For the experiments done in acidic sulfate media, the solutions were prepared as mentioned above except that known weights of Na_2SO_4 were added just before the final dilution was made.

(1) Part 12: S. B. Hanna and M. E. Moehlenkamp, *Helv. Chim. Acta*, **63**, 1748 (1980).

(2) Results relating to portions of this work have been presented at the 5th IUPAC Conference on Physical Organic Chemistry, Santa Cruz, CA, Aug 17–22, 1980, the 2nd Chemical Congress of the North American Continent, San Francisco, CA, National Meeting of the American Chemical Society, Las Vegas, NV, Aug 24–29, 1980, the 6th IUPAC Conference on Physical Organic Chemistry, Louvain-la-Neuve, July 11–16, 1982, Belgium, and ref 1.

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Stoichiometry. The initial stoichiometry of the reaction was determined by potentiometric titrations (Sargent-Recording Titrator, Model D) of solutions containing known weights of BIDA with standardized Ce(IV) perchlorate solution. The stoichiometry was further investigated as a function of time by allowing known weights of BIDA to react with excess Ce(IV), quenching with ferrous ammonium sulfate, and back-titration with $K_2Cr_2O_7$ and barium diphenylamidosulfate as an indicator. The maximum amount of Ce(IV) consumed by reaction with BIDA was determined by heating the reaction mixture in boiling water for 30 min, quenching with Fe(II), and, after cooling, back-titration with $K_2Cr_2O_7$.

Product Identification. The BIDA–Ce(IV) reaction was carried out in a 1:1 ratio in an acidic sulfate medium. The evolved gas was bubbled into a saturated $Ba(OH)_2$ solution, and when evolution had ceased, the reaction mixture was extracted with petroleum ether (for best extraction) or with cyclohexane (for easy GC/MS analysis). The organic layer was analyzed first by GC/MS on a JEOL D100 mass spectrometer equipped with a Varian Model 2700 gas chromatograph with a 6-ft, 3% SP 2100 DB column, temperature programmed (50–250 °C) at 10 °C/min. Since benzaldehyde was obviously present, as indicated by its characteristic smell, derivatization with (2,4-dinitrophenyl)-hydrazine of the carbonyl product(s) in the organic phase was carried out. The isolated 2,4-DNP derivative had a melting point of 241–243 °C.

The aqueous portion of the reaction mixture was neutralized with a slight excess of barium hydroxide and centrifuged to remove $BaSO_4$. Chromotropic acid was next used to test for the presence of formaldehyde.[9] Derivatization of the carbonyl product(s) in the aqueous phase was carried out with 2,4-DNP. The isolated derivative had a melting point of 164–166 °C.

It was suspected that if amines were formed that they may not be readily extracted by organic solvents. Therefore, the aqueous phase was subjected to TLC and GC analysis. TLC on precoated Brinkman Silplate-52 silica gel plates with two solvent systems was used: butanol–acetone–water–acetic acid (35:35:20:10) and phenol–water (4:1). Ninhydrin was used for visualization.[10] Standard reference compounds were used separately and as doping agents in the reaction product. For GC a Bendix 2500 (FID) equipped with a 6-ft Chromosorb 103 column (2 mm i.d.), temperature programmed (100–220 °C) at 8 °C/min, was used.

Further analysis of the components in the aqueous layer was attempted through derivatization. The 2,4-dinitrophenylamines, prepared by reaction with 2,4-DNFB,[11] were extracted in cyclohexane, concentrated, and subjected to TLC with hexane–ether (70:30) as the eluent.

Product Quantification. CO_2 was determined volumetrically as a function of the Ce(IV)/BIDA ratio. The total carbonyl content was determined gravimetrically as the 2,4-DNP derivatives.[12] Formaldehyde was determined at 570 nm by a spectrophotometric method using chromotropic acid.[13]

Test for Free Radicals. Several grams of acrylamide were dissolved in a small amount of water and divided into three portions. A small amount of BIDA was added to one portion, a small amount of Ce(IV) perchlorate was added to another portion, and a small sample of each of BIDA and Ce(IV) was added to the third portion. Gel formation was observed only in the solution containing both BIDA and Ce(IV).

Complex Formation. The molar ratio method[14] was used to determine the formula of the Ce(IV)–BIDA complex in acidic perchlorate media.
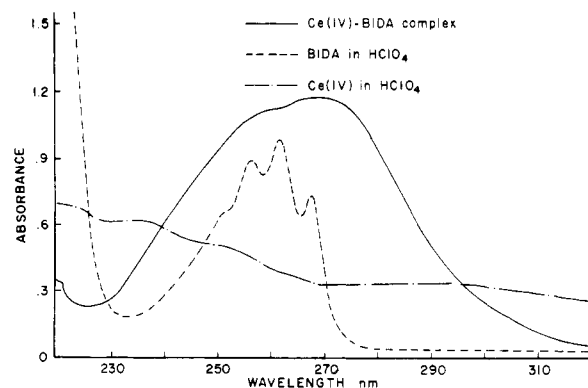

Figure 1. Spectra of BIDA, Ce(IV) in $HClO_4$, and Ce(IV)–BIDA complex.

Kinetic Measurements. Rate measurements in perchloric acid were made at 280 and 316 nm. The complex, which is formed very rapidly, has a strong absorbance at 268 nm. Unfortunately, both Ce(IV) and BIDA also have appreciable absorbances at that wavelength. The initial decrease in absorbance due to complexation of Ce(IV) was measured at 316 nm since Ce(IV) has appreciable absorbance at that wavelength, but the complex and BIDA do not (Figure 1). A Durrum-Gibson stopped-flow apparatus was used for these measurements.[8] The rates of decomposition of the complex in perchloric acid were made at 280 nm by using a Perkin-Elmer 552 UV–vis spectrophotometer equipped with a temperature-controlled cell.
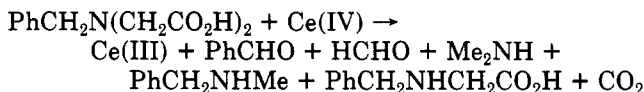
The reaction in acidic sulfate media was studied at three wavelengths: 316 nm, where Ce(IV) absorbs without interference from the excess BIDA or any of the reaction products; 268 nm, where the complex absorbs most intensely; 250 nm, where benzaldehyde absorbs strongly. These measurements were made on the Perkin-Elmer 552 spectrophotometer, except in cases where the reactions were quite fast and the stopped-flow apparatus had to be used.

Data Treatment. The steps of data collection and processing have been described previously.[8] For the slower reactions, and when the initial absorbance could not be determined accurately, the Guggenheim method of analysis was used to compute the pseudo-first-order rate constants[15] (see the paragraph at the end of the paper about supplementary material).

Results

Stoichiometry. The potentiometric titrations of BIDA with Ce(IV)/$HClO_4$ solution indicate that 2 mol of Ce(IV) were reduced almost instantaneously per mole of BIDA oxidized. However, with excess Ce(IV), up to about 7 mol of Ce(IV) were consumed rather slowly per mole of BIDA.

Products. Several products were identified in the BIDA–Ce(IV) reaction: CO_2, benzaldehyde (2), formaldehyde (3), N-benzylglycine (4), benzylmethylamine (5), and dimethylamine (6). Thus, the reaction between Ce(IV) and BIDA in acidic media may be represented by the following unbalanced equation:

$$PhCH_2N(CH_2CO_2H)_2 + Ce(IV) \rightarrow$$
$$Ce(III) + PhCHO + HCHO + Me_2NH +$$
$$PhCH_2NHMe + PhCH_2NHCH_2CO_2H + CO_2$$

When the Ce(IV) to BIDA ratio was about 2:1, the Ce(IV) reduction slowed markedly, and the Ce(IV) to CO_2 ratio was just slightly greater than unity.

Quantitative analysis of the carbonyl components in the reaction products indicated that approximately 3.0 mol of Ce(IV) were consumed for every 1 mol of 3 produced and that the ratio of 3 to 2 was nearly 1.5. The quantification of the other reaction products was not attempted.

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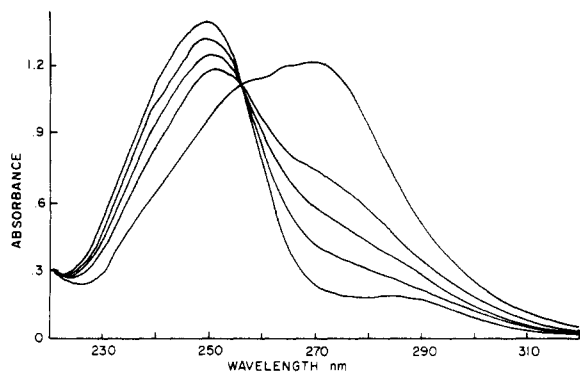
Figure 2. Spectra of a BIDA–Ce(IV) reaction mixture in HClO₄ run consecutively.

Table I. Rate Constants for Cerium(IV)–BIDA Complex Formation in Perchloric Acid at Various Concentrations of BIDA[a]

$10^3 \times$ [BIDA], M	k_{obsd}[b]	$10^3 \times$ [BIDA], M	k_{obsd}[b]
0.4	0.288	8.0	4.26
2.0	1.45	10	4.80[c]
4.0	2.69	20	7.62
5.0	3.33		

[a] [Ce(IV)] = 2.0×10^{-4} M, [H⁺] = 0.50 M, T = 25.0 ± 0.1 °C, μ = 2.0 (NaClO₄), λ = 316 nm. [b] Pseudo-first-order rate constants. [c] Standard deviation is less than 5.5%; all other standard deviations are less than 3.5%.

Table II. Pseudo-First-Order Rate Constants (s^{-1}) for Complex Formation and Complex Decomposition at Various Concentrations of Perchloric Acid[a]

complex formation[b]		complex decomposition[d]	
[HClO₄], M	k_{obsd}[c]	[HClO₄], M	$10^3 \times k_{obsd}$
0.10	10.2	0.040	12.7
0.25	4.79	0.050	12.7
0.50	2.11	0.060	13.1
0.75	1.26	0.080	12.4
1.00	0.913	0.10	11.5
1.25	0.741	0.25	8.95
2.00	0.405	0.50	4.97
		0.75	3.73
		1.00	2.92
		1.25	2.52[e]
		2.00	1.57

[a] [BIDA] = 3.0×10^{-3} M, [Ce(IV)] = 2.0×10^{-4} M, T = 25.0 ± 0.1 °C, μ = 2.0 (NaClO₄). [b] Recorded at λ = 316 nm. [c] All standard deviations are less than 1.5%. [d] Recorded at λ = 280 nm. [e] Standard deviation is 6%; all other standard deviations in this column are less than 2%.

Kinetic Measurements. Rate measurements were conducted in acidic perchlorate and in acidic sulfate media. In acidic perchlorate the effect of changes in [BIDA], [HClO₄], and temperature was investigated. In acidic sulfate media the effect of changing [BIDA] and [Na₂SO₄] was studied.

(a) **Acidic Perchlorate Media.** The mixing of Ce(IV) with BIDA brought about complex formation very rapidly, followed by decomposition at a slower rate. When several spectra (320–220 nm) were run consecutively, an isosbestic point was observed (Figure 2).

The dependence of the kinetics of complex formation on [BIDA] is shown in Table I. The rate constants for complex decomposition are independent of [BIDA]. The dependence of the rates of complex formation and complex decomposition on acidity is shown in Table II. Both sets of k_{obsd} values decrease as the acidity increases. For com-
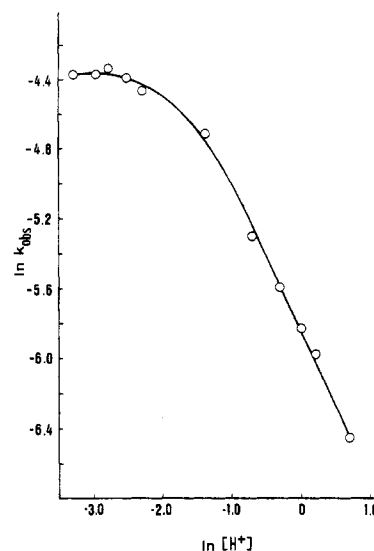

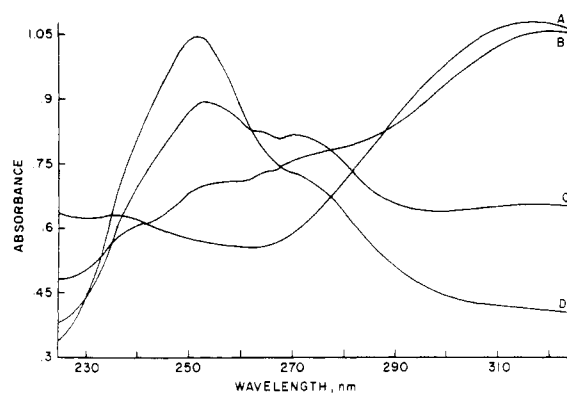**Figure 3.** Natural logarithm plot of reaction rate constant for complex decomposition vs. [H⁺].

Figure 4. Spectra of a BIDA–Ce(IV) reaction mixture in acidic sulfate media run consecutively.

plex formation, plot of ln k_{obsd} vs. ln [H⁺] is linear with a slope of about –1. For complex decomposition, a plot of ln k_{obsd} vs. ln [H⁺] yields a linear relationship for [H⁺] greater than 0.10 M (Figure 3). The slope of the linear portion is about –0.8.

The rates of complexation between Ce(IV) and BIDA in 0.5 N perchloric acid were measured at five temperatures ranging from 4.6 to 29.8 °C. The energy of activation, E_a, calculated from the slope of an Arrhenius plot is 14.6 kcal/mol (61.1 kJ/mol). At 25 °C the enthalpy of activation is 14.2 kcal/mol (59.4 kJ/mol), and the entropy of activation is –9.3 eu (–38.9 J °C⁻¹ mol⁻¹).

The effect of temperature on the rates of complex decomposition was also studied. Measurements were made at five temperatures between 19.5 and 38.1 °C. The activation energy, E_a, obtained from the slope of a plot of ln k_{obsd} vs. T^{-1} is 16.0 kcal/mol (66.9 kJ/mol). The enthalpy of activation is 15.6 kcal/mol (65.3 kJ/mol), and tne entropy of activation is –17.3 eu (–72.4 J °C⁻¹ mol⁻¹) at 25 °C.

(b) **Acidic Sulfate Media.** A look at the spectrum of the BIDA–Ce(IV) reaction in these media revealed that complex formation occurred, but not to the extent observed in perchloric acid. In Figure 4, spectrum A is that of 2.0×10^{-4} M Ce(IV) in acidic sulfate medium ([Na₂SO₄] = 0.10 M, [H⁺] = 0.50 M). Spectra B–D are those of the BIDA–Ce(IV) reaction immediately after mixing, approximately 3 min after mixing, and approximately 7 min after mixing, respectively. Complex formation was slower and less complete in sulfate than in perchlorate media.

Table III. Pseudo-First-Order Rate Constants (s⁻¹) at Various BIDA Concentrations in Acidic Sulfate Media[a]

10³ × [BIDA], M	10³ k_{obsd}		
	λ = 316 nm	λ = 268 nm	λ = 250 nm
0.40	1.44[b]	1.36[c]	1.37[c]
1.0	3.46[d]	2.95[c]	3.37[d]
3.0	11.2[b]	5.14[b]	5.35[b]
5.0	15.2[c]	4.68[b]	4.59[b]

[a] [Ce(IV)] = 2.0 × 10⁻⁴ M, [H⁺] = 0.50 M, [Na₂SO₄] = 0.050 M, T = 25.0 ± 0.1 °C, μ = 2.0 (NaClO₄). [b] Standard deviation is less than 2%. [c] Standard deviation is less than 5%. [d] Standard deviation is less than 7%.

Table IV. Pseudo-First-Order Rate Constants (s⁻¹) at Various Sodium Sulfate Concentrations[a]

10² × [Na₂SO₄], M	[SO₄²⁻], M	10³ k_{obsd}		
		λ = 316 nm	λ = 268 nm	λ = 250 nm
0	0	2110	5.15	5.13
0.00200	0.0285	912	5.15	5.14
0.0100	0.142	182	5.09	5.20
0.0500	0.712	11.2	5.14	5.35
0.100	1.42	4.09	3.43	3.62
0.300	4.27	0.951	0.901[b]	0.931
0.600	8.54	0.437[b]	0.410[b]	0.447[b]

[a] [BIDA] = 3.0 × 10⁻³ M, [Ce(IV)] = 2.0 × 10⁻⁴ M, [H⁺] = 0.50 M, T = 25.0 ± 0.1 °C, μ = 2.0 (NaClO₄).
[b] Standard deviation is less than 6.5%; all other standard deviations are less than 3%.

One notices no isosbestic point for the reaction here.

The rates of disappearance of Ce(IV), decomposition of the complex, and production of 2 were studied as a function of [BIDA] (Table III). The observed rate constants for the disappearance of Ce(IV) are directly proportional to [BIDA]; a log–log plot has a slope of 0.9.

The effect of sulfato complexation with Ce(IV)[16] on the rate of the BIDA–Ce(IV) reaction was studied (Table IV). With increasing additions of Na₂SO₄, a drastic decrease in the rate of disappearance of Ce(IV) was observed. The rates of complex decomposition and product formation were much less sensitive to Na₂SO₄ additions.

Discussion

(A) Mechanistic Implications of Observed Stoichiometry and Reaction Products. The reaction of Ce(IV) with BIDA in acidic sulfate or perchlorate media leads to decarboxylation and to the formation of benzaldehyde, formaldehyde, dimethylamine, benzylmethylamine, and N-benzylglycine. The Ce(IV)/BIDA stoichiometry is initially 2:1 as determined by potentiometry. Surprisingly, however, the Ce(IV) to CO₂ ratio is just about unity. If BIDA were decarboxylated only oxidatively, one would expect the Ce(IV) to CO₂ ratio to be 2. A reconciliation of the observation and the expectation is evident from inspection of the mechanism portrayed in Scheme I. Electron transfer from the carboxyl group of 1 to Ce(IV) initiates decarboxylation and leads to the formation of a free radical (A). The presence of free radicals is supported by the formation of a polymer, when acrylamide was introduced into a reacting mixture of BIDA and Ce(IV).

The free radical A loses an electron rapidly to another Ce(IV), thereby producing a resonance-stabilized Mannich-type iminium cation intermediate (B). The intermediate B is capable of undergoing hydrolysis or decarboxylation. The cationic intermediate B is expected to be
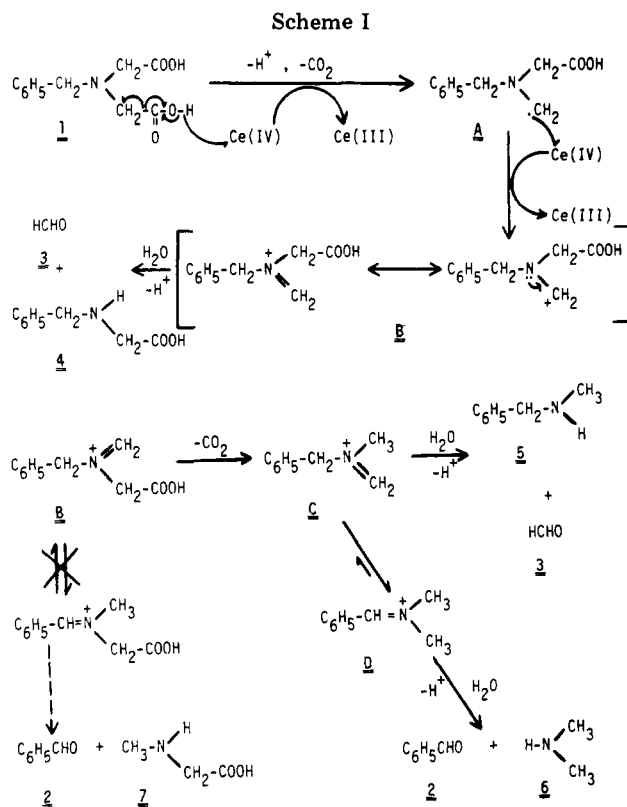
a strong electrophile[17] and is, therefore, readily susceptible to attack by water[18] to yield 4 in this case.

The alternative fate of B is decarboxylation which is due to the presence of a structural feature, >N⁺=CH₂, equivalent in its function as an electron-sink to the >C=O group in β-keto acids which are readily decarboxylated.

The product of decarboxylation (C) undergoes an α–γ proton shift to D to attain stability by establishing conjugation with the aromatic ring. Indeed, it is difficult to account for the formation of 2 and 6 without the intermediacy of a prototropically labile C. The alternative route of producing 2 from a rearranged B is ruled out because of the absence of 7 among the reaction products.

The nonoxidative decarboxylation of B is reminiscent of pyridoxal-mediated decarboxylations of α-amino acids.[19] Intermediates similar to B have been invoked in the carbonyl-assisted decarboxylation of sarcosine.[20]

This duality of decarboxylation pathways is also observed in the Ce(IV)–N-methyliminodiacetic acid (MIDA) and Ce(IV)–nitrilotriacetic acid (NTA) reactions[21] and may prove to be generally true for Ce(IV) oxidations of amino polycarboxylic acids.

It should be mentioned that whereas the initial stoichiometry of the BIDA–Ce(IV) reaction was found to be 2 mol of Ce(IV)/mole of BIDA, the amount of Ce(IV) consumed increased with time. This was not unexpected as several other aminopolycarboxylic acids have shown this behavior with Ce(IV)[22-25] and with Co(III).[26] When the

Scheme I

C₆H₅-CH₂-N(CH₂-COOH)(CH₂-C(O)-O-H) [1] →(-H⁺, -CO₂) (Ce(IV) → Ce(III)) → C₆H₅-CH₂-N(CH₂-COOH)(·CH₂) [A] →(Ce(IV) → Ce(III)) → [B] C₆H₅-CH₂-N⁺(CH₂-COOH)(CH₂) ↔ C₆H₅-CH₂-N(CH₂-COOH)(=CH₂)

HCHO [3] + C₆H₅-CH₂-N(H)(CH₂-COOH) [4] ←(H₂O, -H⁺) [B]

C₆H₅-CH₂-N⁺(CH₂)(CH₂-COOH) [B] →(-CO₂) C₆H₅-CH₂-N⁺(CH₃)(CH₂) [C] →(H₂O, -H⁺) C₆H₅-CH₂-N(CH₃)(H) [5] + HCHO [3]

[C] → C₆H₅-CH=N⁺(CH₃)(CH₂-COOH) [not formed, 7] ... C₆H₅CHO [2] + CH₃-N(H)(CH₂-COOH) [7]

[C] → C₆H₅-CH=N⁺(CH₃)(CH₃) [D] →(-H⁺, H₂O) C₆H₅CHO [2] + H-N(CH₃)(CH₃) [6]

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products were identified, it became evident why the reaction showed variable stoichiometry; both benzaldehyde[27] and formaldehyde[28] are oxidized by Ce(IV). The stoichiometry increases slowly; interference in the kinetic measurements by the oxidation of these two products is minimal since both are oxidized more slowly than BIDA and since BIDA is present in much larger quantities than either of these products.

(B) Complex Formation. When BIDA and Ce(IV) are mixed in acidic perchlorate media, there is a rapid increase in absorbance which is suggestive of complexation. The spectrum of the BIDA–Ce(IV) reaction mixture run immediately after mixing reveals a species which absorbs more strongly than Ce(IV) at 290 nm and which shows a maximum at 268 nm (Figure 1).

Spectral evidence for complexation has been recorded in other Ce(IV) oxidations. In the MIDA–Ce(IV) system in perchloric acid, a shift in the absorbance maximum from 295 to 310 nm was observed,[29] whereas the diethylene-triaminepentaacetic acid (DTPA)–Ce(IV) system in sulfuric acid showed a shift from 316 to 264 nm.[30]

When several spectra of the BIDA–Ce(IV) reaction are run consecutively (Figure 2), one notices that the absorbance at 268 nm decreases with time while the absorbance at 250 nm (benzaldehyde) increases. The isosbestic point observed in these spectra indicates that benzaldehyde arises *only* from the decomposition of the complex. These facts fit a typical consecutive reaction scheme (see below) where k_1 is much larger than k_2.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
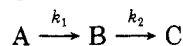
The study of the complex proved to be fraught with difficulties. No wavelength could be found where *only* the complex had considerable absorbance. At 280 nm BIDA does not absorb appreciably, but Ce(IV) does [ϵ_{280}(BIDA) $\doteq$ 0, ϵ_{280}(Ce(IV)) $\doteq$ 1900, ϵ_{280}(complex) $\doteq$ 5700], and allowance for such interference had to be made. Additionally, when an excess of Ce(IV) was used, the decomposition of the complex was rapid, and the initial absorbance, A_0, was difficult to measure. On the other hand, when the BIDA/Ce(IV) ratio was varied from 2:1 to 30:1, the initial absorbance did not change. Such an insensitivity to increasing concentrations of BIDA reflects virtually complete complexation even at a 2:1 BIDA to Ce(IV) ratio. The equilibrium constant (K) for such a complexation must be very large.
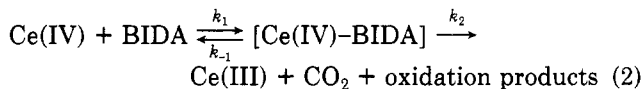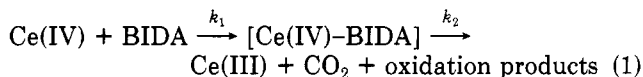
$$BIDA + Ce(IV) \overset{K}{\rightleftharpoons} complex$$
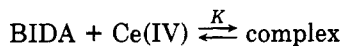
BIDA has been shown to form 1:1 and 2:1 ligand–metal complexes with a number of metal ions.[31,32] However, calculations with the molar ratio method for determination of the formula of the complex, while making allowances for the Ce(IV) absorbance, led to the conclusion that the complex has a 1:1 ratio of BIDA to Ce(IV).

(C) Mechanistic Implications of the Kinetics in Acidic Perchlorate Media. The facts about the Ce-

(IV)–BIDA reaction in perchloric acid are summarized here. (1) Rapid complex formation ($t_{1/2} \doteq$ 1–5 s) is followed by slow disappearance ($t_{1/2} \doteq$ 2 min) of the intermediate to products. (2) The decrease in the absorbance of the intermediate is paralleled by the simultaneous appearance of the spectrum characteristic of benzaldehyde; the changes exhibit an isosbestic point. (3) The rates of complex formation show a direct dependence on [BIDA] and an inverse dependence on [H$^+$]. (4) The rates of complex decay are independent of [BIDA] but still vary inversely with [H$^+$].

The two mechanistic pictures which emerge from the above set of facts may be summarized as eq 1 and 2. The

$$Ce(IV) + BIDA \xrightarrow{k_1} [Ce(IV)\text{–}BIDA] \xrightarrow{k_2}$$
$$Ce(III) + CO_2 + \text{oxidation products} \quad (1)$$

$$Ce(IV) + BIDA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ce(IV)\text{–}BIDA] \xrightarrow{k_2}$$
$$Ce(III) + CO_2 + \text{oxidation products} \quad (2)$$

reaction sequence consisting of two steps occurring in series (eq 1) fits facts 1 and 2. Under the conditions of the experiment where [BIDA] $\gg$ [Ce(IV)], the observed rate constants are pseudo first order, and, at a fixed [Ce(IV)], are given by $k_{obsd} = k_1$[BIDA]. It must be emphasized here that the intermediate Ce(IV)–BIDA complex is *not* a steady-state intermediate. Its concentration varies continuously with time. It attains a maximum concentration, [B]$_{max}$, at a given instant, t_{max}, given by eq 3 and 4, respectively.[33] In a reaction where [Ce(IV)]$_0$ = 2.0 × 10^{-4}

$$[B]_{max} = [A]_0 (k_2/k_1)^{k_2/(k_1-k_2)} \quad (3)$$

$$t_{max} = \frac{1}{k_2 - k_1} \ln (k_2/k_1) \quad (4)$$

M = [A]$_0$, [BIDA]$_0$ = 4 × 10^{-3} M, k_1 = 2.69 s^{-1}, and k_2 = 0.0050 s^{-1}, t_{max} = 2.34 s and [B]$_{max}$ = 1.98 × 10^{-4} M. In other words, the formation of the complex is rapid and complete (99%). A reaction quotient Q calculated at t_{max} is 2.6 × 10^4 (eq 5). Although Q is not an equilibrium

$$Q = \frac{[B]_{max}}{[Ce(IV)][BIDA]} =$$
$$\frac{1.98 \times 10^{-4} \text{ M}}{(0.02 \times 10^{-4} \text{ M})(3.8 \times 10^{-3} \text{ M})} = 2.6 \times 10^4 \quad (5)$$

constant, it serves to convey an idea about the magnitude of K.

The alternative mechanism (eq 2) portrays a reversible first step as the only difference from the simple consecutive reaction A → B → C. The solutions for the differential rate equations describing a consecutive reaction for the net transformation of A to C via reversible formation of intermediate B can be unwieldy,[34] unless the steady-state approximation is invoked. However, we know that our intermediate is *not* a steady-state intermediate. A solution to the differential equations has been proposed in Jencks' laboratory.[35] The time-dependence of the intermediate B in the suggested reaction sequence is given by eq 6 or,

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(35) A. R. Fersht and W. P. Jencks, *J. Am. Chem. Soc.*, **92**, 5432 (1970).

(36) The calculation of λ_1 as delineated by Jencks[35] was attempted. As A_B increased, the difference of terms on the right became negative and the natural logarithm could not be evaluated.

$$-\lambda_1 t = \ln \left[e^{-\lambda_2 t} - \frac{A_B(\lambda_1 - \lambda_2)}{\epsilon A_0 k_1} \right]$$

$$[B] = \frac{[A]_0 k_1}{\lambda_1 - \lambda_2}(e^{-\lambda_2 t} - e^{-\lambda_1 t}) \qquad (6)$$

in terms of the absorbance of B, A_B, by eq 7, where $[A]_0$

$$A_B = \frac{\epsilon [A]_0 k_1}{\lambda_1 - \lambda_2}(e^{-\lambda_2 t} - e^{-\lambda_1 t}) \qquad (7)$$

is the initial concentration of A, ϵ is the extinction coefficient of B, t represents time, and "λ_1 and λ_2 are kinetic constants which define the shape of the curve for the appearance and disappearance of B",[34] according to eq 8 and 9. Assuming, for simplification of eq 7, that λ_1 is at least

$$\lambda_1 = 0.5(k_1 + k_{-1} + k_2 + ((k_1 + k_{-1} + k_2)^2 - 4k_1k_2)^{1/2}) \qquad (8)$$

$$\lambda_2 = 0.5(k_1 + k_{-1} + k_2 - ((k_1 + k_{-1} + k_2)^2 - 4k_1k_2)^{1/2}) \qquad (9)$$

10 times λ_2, an assumption which is justified by the magnitude of the observed k_1 (complex formation) and k_2 (complex decay), one finds the plot of $\ln A_B$ vs. t to be linear (correlation coefficient 0.9995) with a slope $= -\lambda_2$ $= -0.0054$ and an intercept equal to

$$\ln \frac{\epsilon[Ce(IV)]k_1}{\lambda_1 - \lambda_2} = 0.2506$$

when $[BIDA] = 2 \times 10^{-3}$ M. From the given values ($\epsilon = 5700$, $[Ce(IV)] = 2 \times 10^{-4}$ M, $k_1 = 1.45$ s^{-1}) one calculates $\lambda_1 = 1.29$.[35] As one might expect the calculated values of λ_1 and λ_2 are very close to the experimental values of $k_{1(obsd)}$ and $k_{2(obsd)}$ and were, therefore, replaced by $k_{1(obsd)}$ and $k_{2(obsd)}$ in eq 10 which is obtained by the addition of eq 8

$$\lambda_1 + \lambda_2 = k_2 + k_1[BIDA] + k_{-1} \qquad (10)$$

and 9, where $k_1[BIDA]$ now stands for k_1 in eq 1 and 2. A plot of the set of $(k_{1(obsd)} + k_{2(obsd)})$ vs. [BIDA] is linear up to 5.0×10^{-3} M BIDA (correlation coefficient 0.9993). The slope, k_1, is 656 whereas the intercept, which is $k_2 + k_{-1}$, equals 0.074. This gives a value of $k_{-1} \doteq 0.07$ and a value for the equilibrium constant $K = k_1/k_{-1} \doteq 10^4$. These calculations involve a number of approximations and should be viewed accordingly. Nevertheless, it is interesting to note the relative magnitudes of k_{-1} and k_2, which establish the second step, viz., the internal oxidation-reduction of the intermediate complex, as the rate-determining step in the overall oxidation process (see paragraph at end of paper about supplementary material).

An empirical rate expression for the process of complex formation is given by eq 11. When [H$^+$] and [Ce(IV)] are

$$\text{rate} = -d[Ce(IV)]/dt = k[BIDA]^x[H^+]^y[Ce(IV)] \qquad (11)$$

held constant and [BIDA] is varied and in excess, the observed rate constant, k_{obsd}, is given by $k_{obsd} = k'[BIDA]^x$. Therefore, a plot of $\ln k_{obsd}$ vs. $\ln$ [BIDA] should yield the order, x, as the slope. This plot, however, shows first-order dependence on [BIDA] (actual slope is 0.96 up to 5.0×10^{-3} M BIDA; correlation coefficient is 0.9996) only up to 5.0×10^{-3} M BIDA, after which the slope decreases progressively. This downward curvature may be due to the existence of dimeric or polymeric BIDA species which presumably cannot participate in complex formation. To correct for this, one needs the association constants which currently are not known for BIDA. One can imagine an association between two BIDAs via interaction between the π system of one BIDA and the aliphatic moiety of the other.

The effect of acidity on complex formation was studied for [H$^+$] up to 2.0 M at constant [BIDA] and [Ce(IV)]. For

0.10 M $\leq$ [H$^+$] ≤ 2.0 M the rate constants appear in Table II. The inverse relationship between k_{obsd} and [H$^+$] is not surprising; as the acidity increases, more of the BIDA becomes incapacitated by protonation, and, therefore, it becomes more difficult for it to act as a complexing agent. A plot of $\ln k_{obsd}$ vs. $\ln$ [H$^+$] between 0.10 and 2.0 M [H$^+$] is linear with a slope of about -1.

The decomposition of the complex formed in this system may be considered as a separate reaction:

$$\text{complex} \xrightarrow{k_2} \text{products}$$
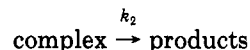
for which k_{obsd} appears to be independent of [BIDA] over a 50-fold change in initial concentration. This is to be expected for a system where complex formation is virtually complete in the first step, even at low [BIDA]. However, acidity has a marked effect on k_{obsd} (Table II). The rate constants at low acidities were difficult to measure because the reactions were somewhat slow for measurement by stopped-flow techniques but quite rapid for conventional techniques. A ln–ln plot of k_{obsd} vs. [H$^+$] (Figure 3) reveals a linear relationship only at [H$^+$] > 0.1 M with a slope of about -0.8. The decreasing slope (from 0 to almost -1) with increasing [H$^+$] observed in Figure 3 may be due to a sum of terms in the denominator of the rate expression,[37] which is expected to arise from a mechanism in which complexation, as expected, is accompanied by H$^+$ release and in which Ce(IV) participates probably as hydrolyzed species.

(D) Mechanistic Implication of the Kinetics in Acidic Sulfate Media. The BIDA–Ce(IV) reaction in acidic sulfate media differs in some respects from that conducted in acidic perchlorate media: (1) The overall reaction rates in sulfate media are considerably slower than those observed in perchloric acid, presumably due to deactivation of Ce(IV) through sulfato complexation. (2) Complexation between Ce(IV) and BIDA occurs but with severe limitations on the rate and extent of complexation. (3) Contrary to the situation in HClO$_4$, no isosbestic point is observed in acidic sulfate media.
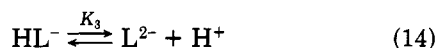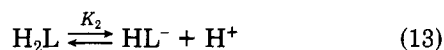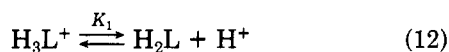
Inspection of the rate constants for the disappearance of Ce(IV) (at 316 nm) and the formation of 2 (at 250 nm) in Table III suggests that a mechanism involving intermediate complex formation followed by slower oxidative decomposition is operative. With increasing [Na$_2$SO$_4$], the rate constants recorded at 316 and 250 nm approach the same value (Table IV) and become almost identical at [Na$_2$SO$_4$] ≥ 0.30 M. This could have been interpreted as a direct redox reaction not involving intermediate complex formation. This interpretation, suggestive of a duality in mechanism, is supported by the lack of an isosbestic point between the decay of the intermediate and the formation of benzaldehyde. However, the rate constants for the decay of the intermediate (at 268 nm) and for the formation of benzaldehyde (at 250 nm) are almost identical at *all* concentrations of Na$_2$SO$_4$.

One is left, then, with a mechanism involving complexation, which becomes more and more difficult as BIDA tries to displace SO$_4^{2-}$ from heavily sulfated Ce(IV) species. It is possible that at high [Na$_2$SO$_4$] the BIDA–Ce(IV) complexes may still retain some sulfato ligands and thereby exhibit a reactivity different from that shown by complexes formed at lower Na$_2$SO$_4$ concentrations. Such a hypothesis may be invoked in explaining the changes in the rate constants observed at 250 nm (Table IV). This may be interpreted in terms of an initial state for Ce(IV) which has orderly primary and secondary coordination

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(37) J. P. Birk, *J. Chem. Educ.*, **53**, 704 (1976).

spheres which have to be disrupted in the process of complex formation.

(E) Kinetic Identification of Reactive Species. (See paragraph at the end of paper about supplementary material.) In perchloric acid, k_{obsd} for the formation of the complex decreases from 10.2 to 0.405 s^{-1} as [H$^+$] increases from 0.10 to 2.0 M. Inspection of data regarding the distribution of the major species of Ce(IV) in HClO$_4$ media reveals that whereas Ce^{4+} and CeOH^{3+} concentrations increase with increasing [H$^+$], Ce(OH)$_2^{2+}$ concentrations decrease. If these were the only changes in the system reflecting changes of acidity, one might have been tempted to draw a parallelism between the decreases in k_{obsd} and Ce(OH)$_2^{2+}$ and to propose that Ce(OH)$_2^{2+}$ is the kinetically significant species in Ce(IV)–BIDA reaction. However, BIDA also undergoes drastic changes with changes in [H$^+$] (eq 12–14, where H$_2$L represents BIDA as a neutral

$$H_3L^+ \overset{K_1}{\rightleftharpoons} H_2L + H^+ \qquad (12)$$

$$H_2L \overset{K_2}{\rightleftharpoons} HL^- + H^+ \qquad (13)$$

$$HL^- \overset{K_3}{\rightleftharpoons} L^{2-} + H^+ \qquad (14)$$

species). With pK_1 = 1.49,[32] significant fractions of BIDA exist as a H$_3$L$^+$ species which is not readily amenable to complexation. For example, at 1.0 M [H$^+$], over 96% of BIDA exists as H$_3$L$^+$. This will cause substantial reduction in the concentration of H$_2$L, HL$^-$, and L^{2-}, the species which are most readily complexed. It is conceivable, therefore, that a complexation between BIDA and Ce(IV) might involve Ce(OH)$^{3+}$ and even Ce^{4+} with H$_2$L, HL$^-$, and L^{2-}. Such complexes are expected to suffer drastic reduction in concentration with increasing acidity.

In acidic sulfate media, which consisted of HClO$_4$, Na$_2$SO$_4$, and NaClO$_4$ (to allow for the independent variation of [H$^+$] and [SO$_4^{2-}$]),[16] k_{obsd} decreased by a factor of about 2100 as the sodium sulfate concentration increased from 0.002 00 to 0.600 M. Data on the distribution of Ce(IV) species in these media show a decrease by a factor of about 2700 in the concentration of CeSO$_4^{2+}$ as opposed to an increase in concentration for each of the other sulfato species of Ce(IV). This strongly suggests that in these media, CeSO$_4^{2+}$ is kinetically the most significant species.

(F) Temperature Effects. These were investigated for the BIDA–Ce(IV) reaction only in perchloric acid media. For the formation of the complex, $\Delta H^\ddagger$ is 14.2 kcal/mol, and $\Delta S^\ddagger$ is –9.3 eu. For complex decomposition $\Delta H^\ddagger$ is 15.6 kcal/mol, and $\Delta S^\ddagger$ is –17.3 eu. While a large negative $\Delta S^\ddagger$ is expected for the formation of the complex, the observed $\Delta S^\ddagger$ is small. On the other hand, one might expect to see a positive $\Delta S^\ddagger$ for the decomposition of the complex; instead, a $\Delta S^\ddagger$ which is even more negative than that for complex formation was observed. This could be indicative of a free radical process.[38] The interactions of all the product molecules with solvent could also be a contributing factor.

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Linear Solvation Energy Relationships. 24. Solvent Effects on the Transition State of the Addition Reaction of the p-Aminobenzenethiyl Free Radical to Styrene

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The solvatochromic equations have been successfully applied to the rate constants for the reversible addition of the p-aminobenzenethiyl radical to styrene, the relative equilibrium constants, and the electronic absorption spectra of the thiyl radical in 21 solvents. The resultant dissection of this data into solvent dipolarity and hydrogen bond acceptor basicity has been used in conjunction with literature substituent effect studies to provide a detailed picture of the transition state and its cybotactic environment.

Earlier studies of solvent effects on free-radical reaction rates[1] have generally found that the influence of solvent is usually small compared to that in analogous heterolytic reactions, since large differences in charge separation between the initial state and the transition state are not to be expected.[2] The small effect of solvent on reaction rate has invoked explanations ranging from similar solvation of the initial state and transition state, which have about

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