Hydrolysis and ammonolysis of EDTA in aqueous solution[1]

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The hydrolysis and ammonolysis of EDTA were studied in aqueous solution over a range of temperatures and at various pH values with the aid of nmr, gc, and gc – mass spectroscopic techniques. At high pH in the presence of ammonia, both ammonolysis and hydrolysis occur with the production of N-(2-aminoethyl)iminodiacetic acid (UEDDA), N-(2-hydroxyethyl)-iminodiacetic acid (HEIDA), and iminodiacetic acid (IDA) in molar ratios such that [IDA] = [UEDDA] + [HEIDA]. The first-order rate constant for the disappearance of EDTA at 175°C in dilute aqueous ammonia is 8.6×10^{-5} s^{-1} whereas in the absence of ammonia its hydrolysis constant is 4.2×10^{-5} s^{-1}. The value of ΔH° for this reaction is approximately 35 kcal/mol. When methylamine replaces ammonia, the UEDDA is replaced by N-(2-methyl-aminoethyl)iminodiacetic acid. The rate of hydrolysis is increased by the presence of a tertiary amine but the latter does not become incorporated into the reaction products. A reaction mechanism is proposed involving bimolecular S_N2 attack by base on a carbon atom of the ethylene bridge adjacent to a protonated nitrogen atom of EDTA with concomitant displacement of iminodiacetic acid.

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On a étudié l'hydrolyse et l'ammonolyse de l'AEDT dans des solutions aqueuses à diverses températures et divers pH en faisant appel à des techniques de rmn, de cpg et de spectroscopie de masse couplée à la cpg. A des pH élevés, en présence d'ammoniaque, il se produit une ammonolyse ainsi qu'une hydrolyse avec formation d'acides N-(amino-2 éthyl)iminodiacétique (AAEID), N-(hydroxy-2 éthyl)iminodiacétique (AHEID) et iminodiacétique (AID) dans les rapports molaires tels que [AID] = [AAEID] + [AHEID]. La constante de vitesse du premier ordre pour la disparition de l'AEDT à 175°C en solution dans l'ammoniaque dilué est égale à 8.6×10^{-5} s^{-1} alors qu'en l'absence d'ammoniac, la constante d'hydrolyse est égale à 4.2×10^{-5} s^{-1}. La valeur du ΔH° pour cette réaction est approximativement 35 kcal/mol. Si l'on remplace l'ammoniaque par de la méthylamine, il se forme de l'acide N-(méthylamino-2 éthyl)iminodiacétique au lieu de AAEID. La vitesse d'hydrolyse est accélérée par la présence d'une amine tertiaire; celle-ci n'est toutefois pas incorporée dans les produits de la réaction. On propose un mécanisme réactionnel impliquant une attaque S_N2 bimoléculaire par la base sur un atome de carbone du pont éthylène voisin de l'atome d'azote de ARDT protoné avec une substitution simultanée de l'acide iminodiacétique.

[Traduit par le journal]

Introduction

Since important applications of EDTA involve its use in aqueous solution at high temperature and pressure and possibly in the presence of ammonia or other basic compounds, it seemed that a study of the kinetics and mechanism of such reactions would be of importance. Earlier studies of EDTA hydrolysis at elevated temperatures (1–6) resulted in conflicting reports. These experiments were carried out at relatively high temperatures, which precluded ac-

curate determination of reaction rates. The present work describes hydrolytic measurements at more moderately elevated temperatures that allow the measurement of the rates of appearance of reaction products and the rates of disappearance of EDTA. The influence on reaction rate and product distribution resulting from the addition of basic substances such as ammonia and methylamine was also studied and was found to have mechanistic implications.

The pH was generally maintained at or near 9.3 by the addition of ammonia as a buffer as well as a reactant. The temperature range employed in this investigation, 145–175°C, was selected to provide a

convenient range of reaction rates for experimental measurements.

Experimental

Materials

EDTA, methylamine, and triethylamine were obtained from Eastman Chemical Company. Hydroxyethyliminodiacetic acid (HEIDA) and iminodiacetic acid (IDA) were obtained from Aldrich Chemical Company. Reagent grade ammonia and gaseous hydrogen chloride for esterification were obtained from Matheson, Coleman and Bell. Methanol and potassium carbonate were obtained from Baker Chemical Company. The water employed was distilled from glass and the methanol was dried over Linde Molecular Sieves. The 50% $NaOD/D_2O$ solution and 99.7% D_2O were obtained from Merck, Sharp and Dohme. Ethylenediamine-N,N-diacetic acid was synthesized by alkaline alkylation of N-acetylethylenediamine with bromoacetic acid, followed by alkaline hydrolysis of the amido group. N-Acetylethylenediamine was prepared by refluxing excess ethylenediamine with ethyl acetate for a 12-h period.

Instrumentation

The nmr spectra were recorded with a Varian T-60 nmr spectrometer which was found to be sufficiently accurate for quantitative determinations with the use of the sample preparation procedure described below. The gas chromatograms were obtained at 200°C on a Hewlett-Packard Model HP 5834a gas chromatograph equipped with a 12-ft, 3% OV-1 column and both FID and TC detectors. The gc mass spectrograms were measured with a Hewlett-Packard Model HP-5982-59-33, housed and operated by the Texas A&M Center for Trace Characterization, with the same chromatographic column but with linear temperature programming to shorten data collection time.

pH was measured at room temperature with a Beckman Research Model pH meter equipped with extension glass and calomel electrodes and was calibrated with standard strong acid and base to measure hydrogen ion concentration directly. The pH values cited in this paper were those measured at room temperature although the pH values at the high temperatures of the experimental runs may be estimated with known values of the heats of dissociation of water and heats of dissociation of the various bases used as buffers.
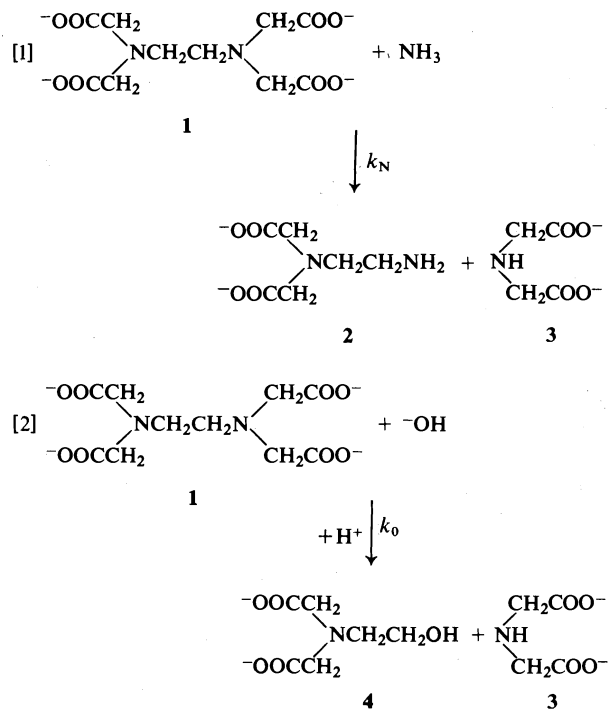
Procedure

Typical experimental runs were carried out as follows: a 2-L titanium glass-lined autoclave equipped with a titanium stirrer was charged with 1.50 L of 0.015–0.695 M EDTA, previously adjusted to the desired pH in the range 5.5–11, and was heated rapidly to the desired temperature in the range 145–175°C. Samples of the reaction solution were withdrawn at timed intervals and were analyzed either by nmr, gc, or gc – mass spectrometry. The nmr samples were prepared and measured in alkaline D_2O relative to TMS as an internal standard. The solvent was replaced by D_2O several times, followed by evaporation, and finally the solution was made up to 0.50 ml with 5% NaOD in D_2O. Precision nmr tubes were employed and calibrated by integration of a standard EDTA solution. Samples for gas chromatography were prepared through the use of a quantitative Fischer (7) methyl esterification procedure. Excess HCl was removed by vacuum evaporation followed by dilution to the desired concentration with dry methanol. Solid potassium carbonate was used to liberate the free esters from their hydrochloride salts immediately before

injection in the gas chromatograph. Samples for gc – mass spectrometer analysis were prepared in the same manner.

Results and Discussion

Product Identification

EDTA (**1**) was found to decompose in dilute aqueous ammonia solution at 145–175°C by the nucleophilic attack of ammonia (eq. [1]) on **1** to produce N-(2-aminoethyl)iminodiacetic acid (**2**) and iminodiacetic acid (**3**) and by a similar hydroxyl attack (eq. [2]) to give N-(2-hydroxyethyl)iminodi-

$$[1] \quad \begin{matrix} {}^-OOCCH_2 \\ \\ {}^-OOCCH_2 \end{matrix} NCH_2CH_2N \begin{matrix} CH_2COO^- \\ \\ CH_2COO^- \end{matrix} \quad +\ NH_3$$

1

$$\Big\downarrow k_N$$

$$\begin{matrix} {}^-OOCCH_2 \\ \\ {}^-OOCCH_2 \end{matrix} NCH_2CH_2NH_2 \ + \ \overset{}{N}H \begin{matrix} CH_2COO^- \\ \\ CH_2COO^- \end{matrix}$$

2   **3**

$$[2] \quad \begin{matrix} {}^-OOCCH_2 \\ \\ {}^-OOCCH_2 \end{matrix} NCH_2CH_2N \begin{matrix} CH_2COO^- \\ \\ CH_2COO^- \end{matrix} \quad +\ {}^-OH$$

1

$$+H^+ \Big\downarrow k_0$$

$$\begin{matrix} {}^-OOCCH_2 \\ \\ {}^-OOCCH_2 \end{matrix} NCH_2CH_2OH \ + \ \overset{}{N}H \begin{matrix} CH_2COO^- \\ \\ CH_2COO^- \end{matrix}$$

4   **3**

acetic acid (**4**) in addition to **3**. The aminolysis reaction (eq. [1]) is new and had not been described previously, while the hydrolysis reaction (eq. [2]) is consistent with previous studies (1, 4, 5, 8) which had been made at much higher temperatures in ammonia-free systems.

Originally, tentative product identification was made through nmr spectral analysis. Although it had been reported earlier that the hydrolytic cleavage of EDTA produces **4** and **3**, the similarity in the values of the chemical shifts between the respective protons in acetate groups of compounds **2**, **3**, **4**, and even **1** precluded an unequivocal determination by the nmr method that **2** had indeed been formed. As is also shown in Table 1, a similar ambiguity arose which was caused by the proximity of the ethylene proton chemical shifts in the starting material **1** and the ammonia cleaved product **2**.

TABLE 1. Nuclear magnetic resonance spectra (60 MHz) of reference compounds measured in 0.15 M D_2O solutions containing 5% NaOD; chemical shifts are reported in Hz relative to trimethylsilylpropanesulfonate (TMS*)

| | Chemical shifts[a] | |
Compound	Acetate	Ethylene
Ethylenediaminetetraacetic acid (**1**)	190(2)	160(1)
Ethylenediamine-N,N-diacetic acid (**2**)	185(1)	154(1)
Iminodiacetic acid (**3**)	186	
N-Hydroxyethyliminodiacetic acid (**4**)	191(2)	214(1)[b] 160(1)[b]
Glycine($NH_2CH_2COO^-$)	186	

[a]Relative integrated intensities in parentheses.
[b]Triplet.

A more direct confirmation of the new reaction product **2** was obtained through comparisons of the retention times shown in Table 2 from gas–liquid chromatograms of the methyl ester derivatives of the standard compounds with those obtained from the methyl esterified reaction mixture shown in Table 3. The gc technique also helped confirm the presence of the normal hydrolysis products, **3** and **4**, which had already been shown to form under the conditions of higher temperature even in the absence of ammonia. Table 2 contains a summary of the gc analytical data which were not only indispensable in fixing the reaction products but also provided evidence for the absence of any significant quantities of other side products. Thus, the reaction cleanly led only to the three products shown in [1] and [2].

To help appreciate the mechanism and the scope of these reactions, other reagents were substituted for dilute ammonia for adjusting pH, and representative samples of the results obtained are also presented in Table 3. All these reactions appear clean under a variety of reagent conditions as evidenced by the absence of gc peaks corresponding to the appearance of side products.

In the absence of ammonia, only the normal water-cleaved EDTA hydrolysis products were found. These experiments were carried out using NaOH, or TEA (triethylamine), or borax buffers. By contrast, ammonia was found to become incor-

TABLE 2. Retention times and relative intensities/unit concentration of gas chromatographic peaks representing the methyl ester derivatives of compounds encountered in this study of EDTA in dilute ammonia solutions at 145–175°C and pH 5.5–11.0

No.	Compound	Retention time (min)	Relative sensitivity[a]
1	EDTA	21.05	1.00
2	UEDDA	4.88	0.39
3	IDA	1.05	0.55
4	HEIDA	2.73	0.34

[a]Values depend on both yield of derivative and on detector (FID) response.
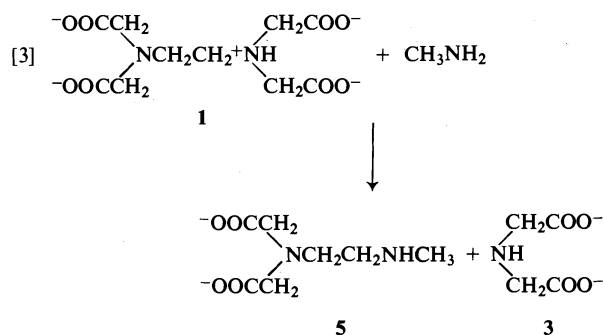
TABLE 3. The gas chromatographic determinations of the esterified reaction products formed in the employment of various buffers to achieve an initial pH of 9.3 on EDTA solutions which were subsequently heated at 175°C[a]

Original composition	Derivative retention time (min)	Product assignment
EDTA + NaOH	1.03	IDA
	2.67	HEIDA
	21.53	EDTA
EDTA + NH₃	1.04	IDA
	2.69	HEIDA
	4.85	UEDDA
	21.55	EDTA
EDTA + NH₃ + 7.2 atm O₂ at 145°C	1.16	IDA
	2.57	HEIDA
	20.86	EDTA
EDTA + TEA[b]	1.03	IDA
	2.62	HEIDA
	21.03	EDTA
EDTA + CH₃NH₂	1.03	IDA
	2.65	HEIDA
	4.04	N-CH₃-N',N'-EDDA
	20.47	EDTA
EDTA + borax	1.07	IDA
	2.85	HEIDA
	21.15	EDTA

[a]Unless stated otherwise.
[b]TEA = triethylamine.

porated into EDTA through the formation of UEDDA (**2**) and in an analogous way methylamine was found to react with EDTA according to [3] to give N-(2-methylaminoethyl)iminodiacetic acid (**5**) and the usual IDA (**3**). These assignments were made through the comparison of retention times listed in Table 3. In particular, the evidence for **5** was the appearance of a new single gc peak at 4.04 min replacing the 4.88 peak for UEDDA. The nmr spectrum (Fig. 1) of the product showed additional resonances at 2.26 and 2.92 ppm relative to TMS* (trimethylsilylpropionate), which are ascribable to

[3] $^-$OOCCH$_2$ CH$_2$COO$^-$
          \   /
           NCH$_2$CH$_2$$^+$NH   + CH$_3NH_2$
          /   \
       $^-$OOCCH$_2$ CH$_2$COO$^-$

1

$\downarrow$

    $^-$OOCCH$_2$ CH$_2$COO$^-$
       \   /
        NCH$_2$CH$_2$NHCH$_3$ + NH
       /   \
    $^-$OOCCH$_2$ CH$_2$COO$^-$

5   **3**

N—CH$_3$ and N—CH$_2$CH$_2$—N type proton groupings. The 2.26/2.92 peak ratio is $\sim 3:4$.

The chemical shift assignments were confirmed by comparison with the chemical shifts observed for an 'analogous' N-methyl compound measured under identical conditions. Thus for N,N'-dimethylethylenediamine the resonance for N—CH$_3$ appears at 2.28 ppm and the remaining resonance for the dimethylene bridge protons is at 2.63 ppm from TMS*.

The degradation experiment under added oxygen was performed at 145°C and confirms that EDTA is stable toward oxidation by molecular oxygen. However, the presence of UEDDA was not detected at this temperature indicating a higher temperature
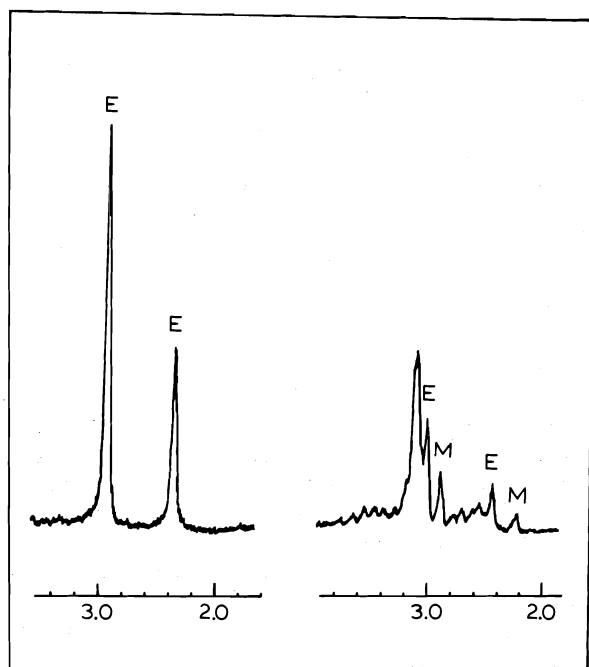

FIG. 1. Nuclear magnetic resonance spectra of two samples from the hydrolysis of EDTA at 175°C pH (25°C) 9.3 buffered with methylamine. Scale is in ppm relative to internal trimethylsilylpropionate: left, before heating; right, after 4.0 h of heating. Peaks marked M (see text) indicate the incorporation of methylamine through the formation of N-methylethylenediamine-N',N'-diacetic acid; E represents EDTA peaks.

reaction coefficient for ammonolysis as compared with the hydrolysis. For safety reasons, the reaction was not investigated under pressurized oxygen at higher temperatures.

Ultimate identification of the reaction products shown in [1] and [2] was obtained through the comparison of gc – mass spectrometric data measured on the methyl esterified hydrolysis reaction products with those obtained on a set of methyl esterified known reference compounds. The mass patterns were identical in peak position, ratio, and number for corresponding pairs of compounds. The last four peaks and the strongest peaks are tabulated in Table 4.

An examination of the mass spectra indicates that EDTA and IDA esterify normally to yield the tetramethyl ester, 348 u, and the diester, 161 u, respectively, whereas UEDDA cyclizes during the acidic treatment with methanol to produce the monomethyl lactam, 172 u, while HEIDA forms a cyclic monomethyl lactone, 173 u. However, it is believed that under the experimental basic aqueous solution conditions, the actual products **2**, **3**, and **4** exist in their respective open forms.

Kinetics of EDTA Decomposition

For the chemical changes specified by [1] and [2], the overall rate of disappearance of EDTA through parallel solvolytic and ammonolysis paths was found to be proportional to the concentration of unreacted EDTA. Since the pH of the medium remained constant and a large excess of NH$_3$ was generally employed, first-order reaction conditions prevailed over a significant portion of the reaction time. Although the overlap in the nmr peak positions precluded the routine determination of the rates of formation of the three individual reaction products, the nmr method provided a very convenient means for following the rate of disappearance of EDTA itself.

The kinetic data listed in Table 5 were obtained from the slopes of plots of $\log_e I$ vs. t (I = integrated intensity of the —CH$_2$CH$_2$— resonance) reflecting the observed first-order kinetic expression shown in [4]. These rate constants were measured at two

[4] $-d[\text{EDTA}]/dt = k_{\text{obs}} [\text{EDTA}]$

concentrations and three temperatures as shown, yet appeared to be concentration independent within the scatter of the data. From a plot of $\log_e k_{\text{obs}}$ against reciprocal absolute temperature, the activation parameter $\Delta H_a^{\ddagger}$ was found to be 34.6 ($\sigma = 0.7$) kcal/mol.

With the fundamental rate law established for aqueous ammonia at pH 9.30 and 175°C and a firm

TABLE 4. Gas chromatographic – mass spectrometric data for EDTA-tetramethyl ester and esterified reaction products formed in ammoniacal solutions of EDTA at 145–175°C

No.	Compound	Mass (u)	Form	Last four peaks				Strongest peak
1	EDTA	348	Tetraester	317.1	348.2	349.2	350.2	174.1
2	UEDDA	172	Monoester lactam	157.1	163.0	172.1	173.0	113.1
3	IDA	161	Diester	130.0	146.1	161.1	162.0	102.0
4	HEIDA	173	Monoester lactam	171.0	173.1	174.1	175.1	114.0

TABLE 5. The pseudo-first-order rate constants for the disappearance of EDTA measured in aqueous NH_3 at pH 9.3 as a function of temperature and concentration

$[EDTA]_0$ (mol/L)	Time-averaged temperature	σ (°C)	k_{obs} (s^{-1})	σ (s^{-1})
0.015	174	4	7.8×10^{-5}	0.5×10^{-5}
0.065	175	1	8.8×10^{-5}	0.5×10^{-5}
0.015	162	1	2.5×10^{-5}	0.2×10^{-5}
0.065	163	1	2.8×10^{-5}	0.3×10^{-5}
0.015	149	1	7.5×10^{-6}	0.8×10^{-6}
0.065	149	1	8.1×10^{-6}	1.4×10^{-6}

proof of the reaction products formed, other reaction conditions were tried and the results of the variation in temperature, reagents, and pH are listed in Table 6. Thus, when ammonia is not present and NaOH is used to adjust the pH to 9.4, the value of the observed rate constant k_{obs} is reduced to about one-half of the original magnitude observed when NH_3 is present. Likewise, when pyridine was employed to effect 'neutralization' and just enough NH_3 was added to raise the pH, the value of the rate constant exceeded that of the NH_3-free run but was much lower than the NH_3-buffered solutions. Triethylamine in place of ammonia showed definite catalytic activity with a k_{obs} of 6.4×10^{-5} s^{-1}, yet only hydrolytic products were formed. Methylamine approached the reactivity of ammonia with a resulting k_{obs} of 7.8×10^{-5} s^{-1} with the reaction progressing according to [4].

Variation in pH on the ammonia system showed that at pH 6.01, which corresponds to about half neutralization of EDTA, the rate constant was about the same as in the absence of ammonia at pH 9.3, with $k_{obs} = 3.6 \times 10^{-5}$ s^{-1}. On the other hand, a very large excess of ammonia, pH 11.08, led to a pronounced increase of the rate with $k_{obs} = 1.1 \times 10^{-4}$ s^{-1}.

The variation in k_{obs} measured under a variety of conditions indicates that the rate law may be a composite of both hydrolytic and ammonolysis terms with each term in turn depending on the degree of protonation of the EDTA anion itself. Therefore, in the most general case, the rate law may be expanded,

as shown in [5], to include all the individual EDTA

$$[5] \quad -d[EDTA]/dt = \{k_{NH_3}^{(1)}[L^{4-}]$$
$$+ k_{NH_3}^{(2)}[HL^{3-}] + k_{NH_3}^{(3)}[H_2L^{2-}]\}[NH_3]$$
$$+ \{k_{OH}^{(1)}[L^{4-}] + k_{OH}^{(2)}[HL^{3-}]$$
$$+ k_{OH}^{(3)}[H_2L^{2-}]\}[OH^-] + \{k_{H_2O}^{(1)}[L^{4-}]$$
$$+ k_{H_2O}^{(2)}[HL^{3-}] + k_{H_2O}^{(3)}[H_2L^{2-}]\}$$

species present in the pH range over which the measurements have been made. The pseudo-first-order kinetic expression shown in [4] becomes identical with [5] only under three conditions: (i) the reactive species of EDTA predominates to the virtual exclusion of the other species in equilibrium with it; (ii) only one form of EDTA is reactive, irrespective of its concentration, while the remaining species are sufficiently less reactive to be neglected; (iii) the very remote possibility that the rate constants of the various forms are equivalent for reaction with NH_3, OH, OH_2 (i.e., $k_{NH_3}^{(1)} = k_{NH_3}^{(2)} = k_{NH_3}^{(3)}$, $k_{OH}^{(1)} = k_{OH}^{(2)} = k_{OH}^{(3)}$, and $k_{H_2O}^{(1)} = k_{H_2O}^{(2)} = k_{H_2O}^{(3)}$. This possibility may be discarded since reactivities of differently charged species cannot possibly be equivalent. The fact that first-order kinetics have indeed been observed under a variety of conditions provides preliminary evidence that mechanism ii is most likely.

At this point, it is necessary to consider the detailed solution equilibria at 175°C, the temperature of the reaction. To accomplish this, the pK_a values for EDTA and NH_4^+ and K_W for water are needed at this elevated temperature. Although a direct measurement was not possible, an inverse temperature extrapolation technique was utilized to determine the ion product concentration constant for water and the proton association constants of EDTA at $\mu \simeq 0.100$ and $T = 175°C$. The values of $-\log K_W$ for water and $\log K_L^H$ for EDTA were measured at several elevated temperatures up to the boiling point of water and were then extrapolated to 175°C; $-\log K_W$ was found to be 10.72 while the successive log protonation constants for EDTA were determined to be 8.79, 5.62, 3.61, and 2.6. The pK_a for

TABLE 6. Smoothed values[a] of k_{obs} from Table 5 and k_{obs} values determined under other reaction conditions

System	Temperature (°C)	σ (°C)	pH	k_{obs} (s⁻¹)	σ (s⁻¹)
EDTA/NH₃	175		9.30	8.6×10^{-5}	0.6×10^{-5}
EDTA/NH₃	163		9.30	2.8×10^{-5}	0.3×10^{-5}
EDTA/NH₃	149		9.30	7.5×10^{-6}	0.3×10^{-6}
EDTA/NH₃	175	1.2	11.08	1.1×10^{-4}	0.1×10^{-4}
EDTA/NH₃	175	0.8	6.01	3.6×10^{-5}	0.3×10^{-5}
EDTA/NaOH	175	1.5	9.40	4.28×10^{-5}	0.08×10^{-5}
EDTA/Py/NH₃	175	2.0	9.39	5.0×10^{-5}	0.3×10^{-5}
EDTA/CH₃NH₂	175	0.9	9.45	7.8×10^{-5}	0.3×10^{-5}
EDTA/(C₂H₅)₃N	175	1.9	9.35	6.4×10^{-5}	0.3×10^{-5}

[a]First three entries; subsequent entries are results of individual experiments.

NH_4^+ was taken from the literature (9, 10) and corrected for ionic strength while that for boric acid was calculated from the work of Mesmer *et al.* (11). The final values of log K^H used in the calculation of the initial species concentration at 175°C shown in Table 7 were 6.19 for NH_4^+ and 8.26 for H_3BO_3.

Table 7 illustrates some very important observations concerning the changes in species distributions upon elevating the temperature from 25 to 175°C. In all cases, the pH at 175°C is lower than the original to different extents, depending mainly on the principal buffer present. For example, Table 6 contains an entry which shows that the rate of hydrolysis promoted by NaOH at pH 9.4 and 25°C is characterized by a $k_{obs} = 4.28 \times 10^{-5}$ s⁻¹. The use of material and electrobalance equations shows, in Table 7, that at 175°C, and pH 7.62, the hydroxide ion concentration rises some 20 times, while the predominating EDTA species, HL^{3-}, remains at ~93% of the total EDTA. Also the low pH solution dropped only ~0.8 pH units on heating while the free NH_3 concentration approached 10% of the total NH_3 added. The pK_a for NH_4^+ drops 2.94 log units in this temperature interval. In contrast, the borate buffered solution remained relatively alkaline, yet demonstrated a remarkably small k_{obs}. The remarkable catalytic effect of ammonia and the lack of catalysis by borate suggest an important role for low pH EDTA species in the hydrolysis reaction.

After calculation of high temperature initial distributions of the species under a variety of reaction conditions, the predominating species (*vide supra*, case *i*) model was tried both with and without k_{H_2O}. No satisfactory fit of the data could be obtained and the calculated results were inconsistent.

It was then assumed that only one protonated form of the EDTA was reactive while the remaining two were relatively unreactive. H_2L^{2-} was chosen as the reactive species because such a choice would be in conformity with several important observations. When HEIDA, or IDA, or NTA were subjected to the hydrolytic conditions described in this paper, no

decomposition was observed over several half-lives of EDTA hydrolysis. The property which sets EDTA apart is that its structure possesses two basic nitrogen atoms on adjacent carbon atoms capable of facile protonation. The increased localization of positive charge resulting from diprotonation contributes to the affinity for negatively charged nucleophiles and lone pairs on amine bases, thus greatly increasing the reactivity and rate of initial nucleophilic attack. Presumably, the other EDTA species (i.e., HL^{3-} and L^{4-}) can also react with the same nucleophiles but require higher temperatures (i.e., their reaction rates are much lower).

With H_2Y^{2-} as the reactive species, [5] may be simplified considerably to give [6]. Since $[H_2L^{2-}]$ is

$$[6] \quad -d[EDTA]/dt = \{k^{(3)}[NH_3] + k^{(3)}[OH^-] + k^{(3)}\}[H_2L^{2-}]$$

only a part of the EDTA present in solution, at each pH (175°C) a concentration correction is necessary to equate terms in [4] to corresponding terms of [6]. Thus

$$[7] \quad k_{obs} = \frac{K_1^H K_2^H [H]^2 k_{obs}'}{1 + K_1^H[H^+] + K_1^H K_2^H[H^+]^2}$$

and

$$[8] \quad k_{obs}' = k_{NH_3}^{(3)}[NH_3] + k_{OH}^{(3)}[OH^-] + k_{H_2O}^{(3)}$$

Equation [8] was analyzed in two ways. First, a regression analysis was performed which in addition to giving a very poor overall fit, provided a very large $k_{H_2O}^{(3)}$ which rendered the contributions from hydroxide attack and ammonia attack relatively unimportant. The actual values obtained in this way also do not make chemical sense ($k_{OH}^{(3)} = 3.2 \times 10^{-3}$ M^{-1} s⁻¹, $k_{NH_3}^{(3)} = 1.0 \times 10^{-2}$ M^{-1} s⁻¹, and $k_{H_2O}^{(3)} = 3.9 \times 10^{-3}$ M^{-1} s⁻¹ or 7.0×10^{-5} M^{-1} s⁻¹ for 55.5 M H_2O).

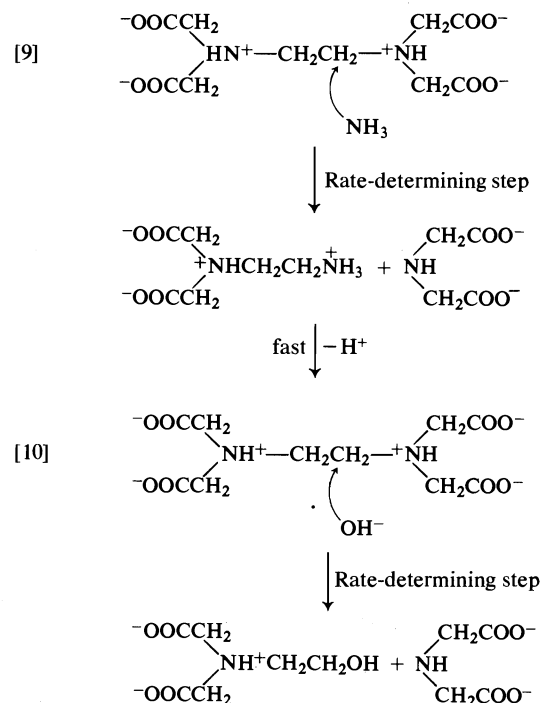Another analysis of [8] was made assuming that $k_{H_2O}^{(3)}$ is relatively unimportant and as such can be

TABLE 7. Initial concentrations of reactants and initial distribution of species calculated for 175°C from high temperature equilibrium constants[a,b,i]

[EDTA]$_T$	[NH$_3$]$_T$	pH (25°C)[c]	pH (175°C)[d]	[OH$^-$]	[NH$_3$]$_0$[d,e]	[H$_2$Y^{2-}][d,f]	[HY^{3-}][d,f]	[Y^{4-}][d,f]	k_{obs} (s^{-1})	k_{obs}' (s^{-1})
0.0150	0.0366	6.01	5.18	2.87×10^{-6}	2.62×10^{-3}	1.10×10^{-2} (73.3%)	3.98×10^{-3} (26.5%)	9.71×10^{-7} (<0.1%)	3.6×10^{-5}	4.9×10^{-5}
0.0150	0.120	9.30	6.53	6.53×10^{-5}	7.65×10^{-2}	1.62×10^{-3} (10.8%)	1.33×10^{-2} (88.7%)	7.40×10^{-5} (0.5%)	8.6×10^{-5}	7.9×10^{-4}
0.0150	2.20	11.08	7.94	1.65×10^{-3}	2.10	6.30×10^{-5} (0.4%)	1.31×10^{-2} (87.3%)	1.84×10^{-3} (12.3%)	11.0×10^{-5}	2.6×10^{-2}
0.0150[g]	[g]	9.40	7.62	7.97×10^{-4}	0	1.39×10^{-4} (0.9%)	1.39×10^{-2} (92.7%)	9.43×10^{-4} (6.3%)	4.28×10^{-5}	4.6×10^{-3}
0.0150[h]	[h]	9.20	8.24	3.28×10^{-3}	0	2.83×10^{-5} (0.2%)	1.17×10^{-2} (78.8%)	3.27×10^{-3} (21.8%)	2.0×10^{-5}	1.1×10^{-2}

[a] Corrections were not made for solution density.
[b] $-$Log $K_w = 10.72$; for EDTA, log $K_1^H = 8.79$, log $K_2^H = 5.62$, log $K_3^H = 3.61$, and log $K_4^H = 2.6$; for NH$_3$, log $K^H = 6.19$; for H$_3$BO$_3$, log $K^H = 8.26$; all at $\mu \approx 0.1$ and $T = 175$°C.
[c] Did not vary more than ~0.05 units during the course of any given kinetic run.
[d] 175°C values.
[e] As free ammonia, the remainder is NH$_4^+$.
[f] Y = EDTA^{4-} anion.
[g] Solution made up with NaOH instead of NH$_3$.
[h] Solution made up using borax buffer.
[i] Concentrations in mol/L.

eliminated from [8]. A linear least-squares regression computation was made which gave $k_{NH_3}^{(3)} = 8.5 \times 10^{-3} \, M^{-1} s^{-1}$ and $k_{OH}^{(3)} = 5.1 \, M^{-1} s^{-1}$ ($\sigma = 18\%$). This is a remarkable fit, which suggests that the kinetic model chosen is probably the correct one.

It appears then that the reaction pathways indicated by [1] and [2] may proceed by the attack of the respective nucleophiles (NH$_3$ or OH$^-$) on the diprotonated form of EDTA as shown in [9] and [10].

[9]

$$^-OOCCH_2 \quad\quad\quad CH_2COO^-$$
$$HN^+{-}CH_2CH_2{-}^+NH$$
$$^-OOCCH_2 \quad\quad\quad CH_2COO^-$$
$$NH_3$$

↓ Rate-determining step

$$^-OOCCH_2 \quad\quad\quad CH_2COO^-$$
$$^+NHCH_2CH_2\overset{+}{N}H_3 \;+\; NH$$
$$^-OOCCH_2 \quad\quad\quad CH_2COO^-$$

fast ↓ $-H^+$

[10]

$$^-OOCCH_2 \quad\quad\quad CH_2COO^-$$
$$NH^+{-}CH_2CH_2{-}^+NH$$
$$^-OOCCH_2 \quad\quad\quad CH_2COO^-$$
$$OH^-$$

↓ Rate-determining step

$$^-OOCCH_2 \quad\quad\quad CH_2COO^-$$
$$NH^+CH_2CH_2OH \;+\; NH$$
$$^-OOCCH_2 \quad\quad\quad CH_2COO^-$$

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