# Thermal degradation of EDTA chelates in aqueous solution

RAMUNAS J. MOTEKAITIS, X. B. COX, III, PATRICK TAYLOR, AND ARTHUR E. MARTELL[1]
*Department of Chemistry, Texas A&M University, College Station, TX 77843, U.S.A.*

AND

BRAD MILES AND TORY J. TVEDT, JR.
*The Dow Chemical Company, Freeport, TX 77541, U.S.A.*

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The thermal degradation of Ca(II), Mg(II), Zn(II), Fe(II), and Ni(II) chelates of EDTA was investigated in alkaline aqueous solution at elevated temperatures (230–310°C). The kinetics of decomposition were followed by nmr, titrimetry, and spectrophotometry. Reaction products were identified through nmr and by gas chromatography. The relative order of degradation rates, as measured by the loss of EDTA, was found to be Mg(II) > Ca(II) > Zn(II) > Fe(II) > Ni(II). The main degradation products formed in the lower temperature range (~250°C) are iminodiacetic acid, hydroxyethyliminodiacetic acid, and ethylene glycol. Higher temperature products are primarily dimethylamine and carbon dioxide. The rates of degradation of Ca(II), Mg(II), and Zn(II) EDTA chelates are considerably enhanced when either phosphate is present or a glass-lined autoclave is employed.

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On a étudié la dégradation thermique, en solution aqueuse basique et à des températures élevées (230–310°C), des chelates entre l'EDTA et les ions CA(II), Mg(II), Zn(II), Fe(II) et Ni(II). On a déterminé les cinétiques de décomposition par la rmn, la titrimétrie et la spectrophotométrie. On a identifié les produits de la réaction par la rmn et la chromatographie en phase gazeuse. On a trouvé que l'ordre relatif des vitesses de dégradation, telles que mesurées par la perte de EDTA, est le suivant: Mg(II) > Ca(II) > Zn(II) > Fe(II) > Ni(II). Les principaux produits de dégradation formés dans le domaine de basses températures (~250°C) sont l'acide iminodiacétique, l'acide hydroxyéthyliminodiacétique et l'éthylène glycol. Les produits formés à une température plus élevée sont principalement la diméthylamine et le bioxyde de carbone. La présence du phosphate ou l'utilisation d'un autoclave tapissé de verre augmente considérablement les vitesses de dégradation des chelates de l'EDTA avec les ions Ca(II), Mg(II) et Zn(II).

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## Introduction

The numerous applications of ethylenediaminetetraacetic acid, EDTA, include its use in aqueous solutions at high temperatures for metal oxide solubilization and for maintenance of metal ions in a sequestered state in solution. This specific application is of particular interest to the power industry which employs EDTA formulation for the continuous treatment of boiler water in steam generators to prevent excessive build-up of scale. Since EDTA in this application is used at elevated temperatures, aqueous chemistry of EDTA and its chelates should be studied at high temperatures to understand the various reactions affecting the efficacy of this sequestering agent. Two preliminary publications describe the reactions of EDTA at elevated temperatures in aqueous solution (1, 2). At moderate temperatures, ~ 175°C in alkaline solution, EDTA was found to undergo hydrolytic C—N fission to give iminodiacetic acid (IDA) and hydroxyethyliminodiacetic acid (HEIDA) as the main reaction products (2). The half-life for this first order process at 175°C is 4.5 h at pH = 9.4. At somewhat higher temperatures (2) (200°C) this half-life is reduced to 0.5 h, while a concomitant consecutive reaction involving the further hydrolysis of HEIDA to ethylene glycol and IDA also takes place. At still higher temperatures decarboxylation reactions also occur. Thus at 265°C, the initial hydrolysis products decarboxylate to give *N*-methylglycine and dimethylamine.

Another type of degradation reaction of EDTA chelates at elevated temperatures has been described recently (3). EDTA coordinated to Fe(III) or Cu(II) becomes oxidized to ethylenediamine triacetic acid (ED3A) and glyoxylic acid while the iron(III) is reduced to Fe(II) and copper(II) to Cu(0). The half life for Fe(III)–EDTA at pH 9.3 is about 3 h at 125°C. This redox reaction greatly destabilizes EDTA at temperatures just above the boiling point of water. However, the Fe(II) chelate formed was found to be stable at similar or higher temperatures even for periods exceeding several days.

The purpose of this present work is to determine the thermal stabilities and reaction sequences of representative metal chelates of EDTA under conditions of varying temperature, pH, and in the

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[1] To whom all correspondence should be addressed.

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presence and absence of catalysts. The metal ions employed are those that are not easily reduced, so that thermal degradation reactions would be expected to involve hydrolysis and decarboxylation, rather than redox reactions, in contrast to the reactions of the Fe(III) and Cu(II) chelates.

Very little work has been carried out previously on the thermal degradation of EDTA chelates and related compounds. Yakimets *et al.* (4) studied the thermal reactions of several EDTA chelates of reducible and non-easily reducible metal ions, and found a variety of products. By means of ir spectroscopy and gas chromatography, oxalic acid, formaldehyde, and hydrogen were found in the reaction mixture, but no major components were identified. An extensive study (5) of thermal degradation of NTA chelates of Fe(II), Fe(III), Ni(II), Co(II), and Cu(II) also yielded a wide variety of decomposition products.

## Experimental

### *Reagents*

All salts, solvents, and reagents were analytical grade materials and were obtained from various major chemical distributors. Doubly distilled, deionized water was used throughout. Solutions were deoxygenated by scrubbing with prepurified grade nitrogen gas which had been passed through an acidic chromous chloride solution. The metal ion – EDTA solutions were prepared from reagent grade $Ca(OH)_2$, $Mg(OH)_2$, $FeSO_4 \cdot 7H_2O$, MgO, ZnO, $Ni(OH)_2$, $Ni(OAc)_2$ (nickel acetate), $NaH_2PO_4$, and NaOH, as needed.

### *Kinetics*

The reactions were conducted under an inert atmosphere in a 2 L Parr all-titanium stirred bench autoclave equipped with temperature and pressure sensors and appropriate valves which were manipulated as needed to obtain samples either from the liquid or gaseous phase as the reaction proceeded.

### *Product analyses*

The constituents of the liquid phase were determined by nmr measurements of $D_2O$/NaOD solutions. For Ca(II) and Mg(II) chelates unreacted EDTA was generally determined by titration with standard 0.0200 *M* copper(II) solution in acetic acid-acidified solutions with pyrocatechol violet as an indicator. The products formed at high temperatures do not interfere with this determination.

### *Instrumentation*

Gas chromatograms were obtained with a microprocessor controlled Hewlett-Packard Model 5830A gas chromatograph equipped with dual TC and FI detectors. For gaseous sample analysis an 8-ft glass column packed with Chromosorb 101/4% was utilized, while liquid samples were run on a 1/8 in. × 10 ft. SS column packed with OV-1. The nmr spectra were recorded with a Varian T-60 spectrometer equipped with a variable temperature probe. The visible spectra were obtained on a Cary Model 14 spectrophotometer equipped with a Himamatsu photomultiplier tube.

## Results and discussion

In general, it was found that the EDTA molecule is considerably stabilized towards thermal and hydrolytic degradation through coordination to metal ions. Also, the decomposition pathways, the decomposition products, and the kinetics of the degradation of coordinated EDTA have been elucidated. Finally, it was found that phosphate and silicate catalyze this decomposition for some metal ions while not for others. In general, the reaction products at a given temperature were found to be the same for all metal ion tested at that temperature.

### *Kinetics of EDTA degradation*

Most of the decomposition rates were measured at the relatively high pH of 10.4 for several reasons. At this pH, the EDTA chelates of the divalent metal ions investigated are completely formed, and the species $ML^{2-}$ (where $L^{4-}$ is the $EDTA^{4-}$ anion) is the only major species present in solutions containing equimolar concentrations of metal ion and ligand. The fact that EDTA is used commercially at high pH to prevent scale build-up in steam generators also offers a practical incentive for determining degradation rates in alkaline solution.

The decomposition rates of the chelates were measured by monitoring the concentration of the remaining EDTA. Ca(II) and Mg(II) EDTA rates were followed titrimetrically in acid solution with standard Cu(II) solution. The ferrous EDTA samples were dried, methyl esterified, and subjected to gas chromatographic analysis. Zinc(II)–EDTA sample solutions were evaporated and measured in $NaOD/D_2O$ by nmr. The nickel(II)–EDTA decomposition rate was likewise followed by nmr after pretreatment with excess $CN^-$ to convert the nickel(II) ion into the diamagnetic $Ni(CN)_4{}^{2-}$ ion.

Table 1 contains a summary of the first order rate constants for the decomposition of EDTA and its Ca(II), Mg(II), Fe(II), and Zn(II) chelates. The data in Table 1 show that metal chelate formation very strongly protects EDTA against hydrolytic degradation. Uncomplexed EDTA was found to decompose quite rapidly at 190°C ($k_{obs} = 0.37\,h^{-1}$), with a half-life at pH = 10.4 of 1.9 h. On the other hand, the Ca(II) chelate is inert under these conditions and requires heating at 310°C to achieve a similar rate of decomposition. Monitoring the reaction at 320°C showed that the rate of thermal decomposition is four times that measured at 307°C. In comparing the decomposition of the Mg(II) chelate at 307°C with that of the Ca(II) chelate at 310°C, it is seen that the Mg(II) rate is about a factor of two higher than the rate of Ca(II)–EDTA. The Fe(II)–EDTA and Zn(II)–EDTA degradation rates were found to be similar to that of Ca(II) after slight differences in temperature in Table 1 are taken into account. Nickel(II)

TABLE 1. First order rate constants for decomposition of EDTA and its metal chelates at $pH_0 = 10.4$ at various temperatures

| Metal ion | $t$ (°C) | $k_{obs}$ ($h^{-1}$) | Analytical method |
|---|---|---|---|
| None | 190 | 0.37 | Nmr |
| $Ca^{2+}$ | 310 | 0.27 | Titrimetric |
| $Ca^{2+}$ | 320 | 1.1 | Titrimetric |
| $Mg^{2+}$ | 307 | 0.50 | Titrimetric |
| $Fe^{2+}$ | 310 | 0.31 | Gas chromatographic |
| $Fe^{2+}$ | 310 | 0.30 | Spectrophotometric |
| $Zn^{2+}$ | 308 | 0.22 | Nmr |
| $Ni^{2+}$ | 310 | 0.075 | Nmr |

proved to be surprisingly inert, with only about one half the decomposition of the chelate observed at 310°C within the time limitation of the reaction employed.

The trend from the above results can be summarized in terms of a statement of relative rates in decreasing order:

$$\text{None (sodium salt)} > Mg^{2+} > Ca^{2+} \sim Fe^{2+} \sim Zn^{2+} \gg Ni^{2+}$$

The relative rates correlate approximately and inversely with the order of formation constants of the "normal" chelates, designated as $ML^{2-}$. These constants measured at room temperature for $Mg^{2+}$, $Ca^{2+}$, $Fe^{2+}$, $Zn^{2+}$, and $Ni^{2+}$ are respectively 8.8, 10.6, 14.3, 16.4, and 18.5 log units (6).

The inverse stability constant – rate correlation points to a mechanism whereby the predominant pathway near 310°C is a dissociation mechanism resulting in the liberation of the free EDTA anion. The resulting low concentrations of the free ligand may then undergo the type of degradation described previously (1, 2), as follows:

[1] $MEDTA^{2-} \rightleftharpoons M^{2+} + EDTA^{4-}$

[2] $EDTA^{4-} \rightarrow$ decomposition products

In [1] the very low concentration of $EDTA^{4-}$ formed is offered no protection and immediately undergoes rapid degradation. The degree to which equilibrium [1] is shifted is inversely proportional to the magnitude of the stability constant at 310°C. It would be very desirable to know precisely what these values are at 310°C but such information is not available and cannot be measured with techniques currently feasible. Therefore it is necessary to settle for the time being for equilibrium data taken at room temperature. The comparisons made above involve the assumption that the temperature coefficients of stability constants are sufficiently similar to maintain at high temperature the stability order observed at 25°C.

The correlation with inverse stability order described above is very rough and predicts considerably greater differences in decomposition rates of the Ca(II), Fe(II), and Zn(II) chelates on the basis of dissociation tendencies controlled by the stability constants alone (i.e., one would expect the chelates of the transition metal ions to be much more stable than the Ca(II) chelate). For the transition metal ions and the zinc(II) ion, the tendencies to liberate EDTA would be further increased by the tendencies of the metal ions to hydrolyze and precipitate from solution at pH 10. Thus the dissociation reactions may be written as in Table 2.

Through the use of the appropriate solubility products the logarithms of the equilibrium constants of reactions [3]–[5] at pH 10 show that there is considerable difference between the hydroxide precipitation tendencies of the Zn(II) and Fe(II)–EDTA chelates on one hand, and the Ni(II)–EDTA chelate on the other: a consequence of the much higher stability of the Ni(II) chelate. Thus metal hydroxide precipitation is expected to provide an additional driving force for EDTA chelate dissociation and on the basis of the proposed mechanism would increase the degradation rates of the Fe(II) and Zn(II) chelates much more than that of Ni(II), accounting more closely to the observed rate sequence, $Ca^{II} \sim Fe^{II} \sim$ Zn(II) $\gg$ Ni(II).

*Catalysis by glass surface and phosphate ion*

In early experimental runs the use of a Pyrex liner in the autoclave resulted in considerable rate enhancement for calcium(II) and magnesium(II) over those shown in Table 1. For example at 310°C, $k_{obs} = 1.0\ h^{-1}$ for Ca(II)–EDTA, which is almost four times greater than the rate constant determined after the glass liner was removed. For magnesium(II) the rate enhancement was even more dramatic. A measurable rate could not even be obtained near 310°C.

Further investigations revealed that the presence of phosphate ion also enhanced the rates of degradation of EDTA chelates of Mg(II), Ca(II), and Zn(II) but not those of the other metal ions tested. The only explanation for such catalytic behavior is the formation of insoluble Ca(II) and Mg(II) silicates (probably adsorbed on the glass surface) and of Ca(II), Mg(II), and Zn(II) phosphates. Such

TABLE 2. Dissociation reaction with hydroxide precipitation[a]

|  | Reaction | $\log k_{eff}{}^{M(OH)_2}$ |
|---|---|---|
| [3] | $FeL^{2-} \rightleftharpoons L^{4-} + Fe(OH)_2 + 2H^+$ | −8.0 |
| [4] | $ZnL^{2-} \rightleftharpoons L^{4-} + Zn(OH)_2 + 2H^+$ | −8.4 |
| [5] | $NiL^{2-} \rightleftharpoons L^{4-} + Ni(OH)_2 + 2H^+$ | −11.3 |

[a] Solubility products obtained from Smith and Martell (7).

insoluble phases would free more EDTA from its metal complexes resulting in enhanced reaction rates. Reaction [6] illustrates the postulated ion exchange process for glass

[6] $$\mathrm{CaL^{2-}} \xrightarrow[\text{glass}]{\mathrm{H_2O}} (\mathrm{CaSiO_4})\downarrow + \mathrm{L^{4-}}$$

Since phosphate ion may be studied over a range of conditions, some details of phosphate catalysis were investigated for Ca(II)–EDTA degradation. Table 3 lists the results of rate measurements under various conditions in the absence and presence of phosphate. The data for this table were obtained from kinetic plots obtained by titrimetric analysis of residual EDTA as a function of time. A typical example is illustrated in Fig. 1.

While the initial concentration of the Ca(II)–EDTA chelate was maintained constant at 0.0133 *M*, the phosphate concentration was varied sufficiently to produce a significant variation in the observed pseudo first order rate constants. Although the intended temperature for the comparison was 230°C, the data in Table 3 show some deviation from this value as well as deviations in pH values.

Equations [7] and [8] describe the proposed rate law for Ca(II)–EDTA decomposition in these solutions and reaction [9] gives the concentration of the phosphate trianion in the experimental solution. Assuming that the phosphate does not become inaccessible to the reactants, then the slope of a plot of $k_{\mathrm{obs}}$ vs. phosphate levels can be obtained by combining eqs. [9], [10], and [8] to give eq. [11].

The numerical value of $k'$ calculated from a least-squares plot is 69 ± 12. The large scatter results from lack of precise temperature and pH control. In spite of the uncertainties involved, there does appear to be a direct correlation between reaction rate and phosphate anion concentration.

TABLE 3. Initial conditions and pseudo first order rate constants obtained as a function of phosphate concentration, temperature, and pH for the thermal degradation of Ca(II)–EDTA[a]

| Total phosphate | pH[b] | Temperature (°C) | $k_{\mathrm{obs}}$ (h$^{-1}$) |
|---|---|---|---|
| 0 | 10.40 | 250[c] | 0[c] |
| 0.00668 | 10.12 | 224 | 0.22±0.01[d] |
| 0.00667 | 10.85 | 226 | 0.31±0.01 |
| 0.00998 | 10.15 | 230 | 0.83±0.05 |
| 0.0133 | 10.17 | 229 | 0.86±0.07 |
| 0.0150 | 10.05 | 230 | 0.93±0.07 |
| 0.020[f] | 10.40 | 228 | 0.28[e] |
| 0.020[f] | 11.2 | 228 | 0.59[e] |
| 0.022[f] | 11.4 | 232 | >1.3[e] |
| 0.022[f] | 9.3 | 230 | 0.19[e] |

[a] $[\mathrm{CaEDTA}]_0 = 1.33 \times 10^{-2}\,M$; $\mathrm{PO_4^{3-}}$ added as $\mathrm{KH_2PO_4}$.

[b] pH measured at room temperature on the first sample collected for kinetic studies.

[c] No appreciable decomposition had occurred in 14 h at ~20° higher than the temperatures of other systems in this table.

[d] Standard deviations of slope obtained by least squares regression analysis.

[e] Error was evaluated only in terms of the regression coefficient which was > 0.998 in each case.

[f] Phosphate added as phosphoric acid.

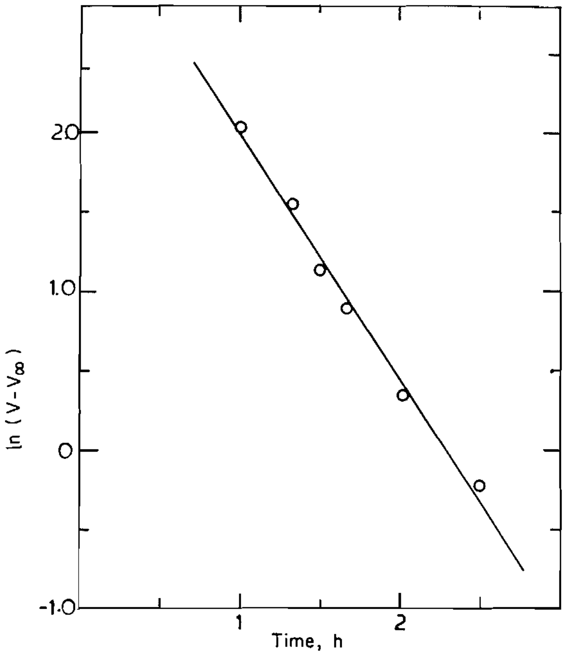


FIG. 1. Logarithm of volume of standard copper(II) solution titrated (measure of residual EDTA) vs. time of samples taken in the thermal degradation of Ca(II)–EDTA in the presence of phosphate at 230°C.

[7] $$d[\text{Ca–EDTA}]/dt = -k_{\mathrm{obs}}[\text{Ca–EDTA}]$$

[8] $$k_{\mathrm{obs}} = k'[\mathrm{PO_4^{3-}}]$$

[9] $$K^{\mathrm{H}} = [\mathrm{HPO_4^{2-}}]/[\mathrm{H^+}][\mathrm{PO_4^{3-}}]$$

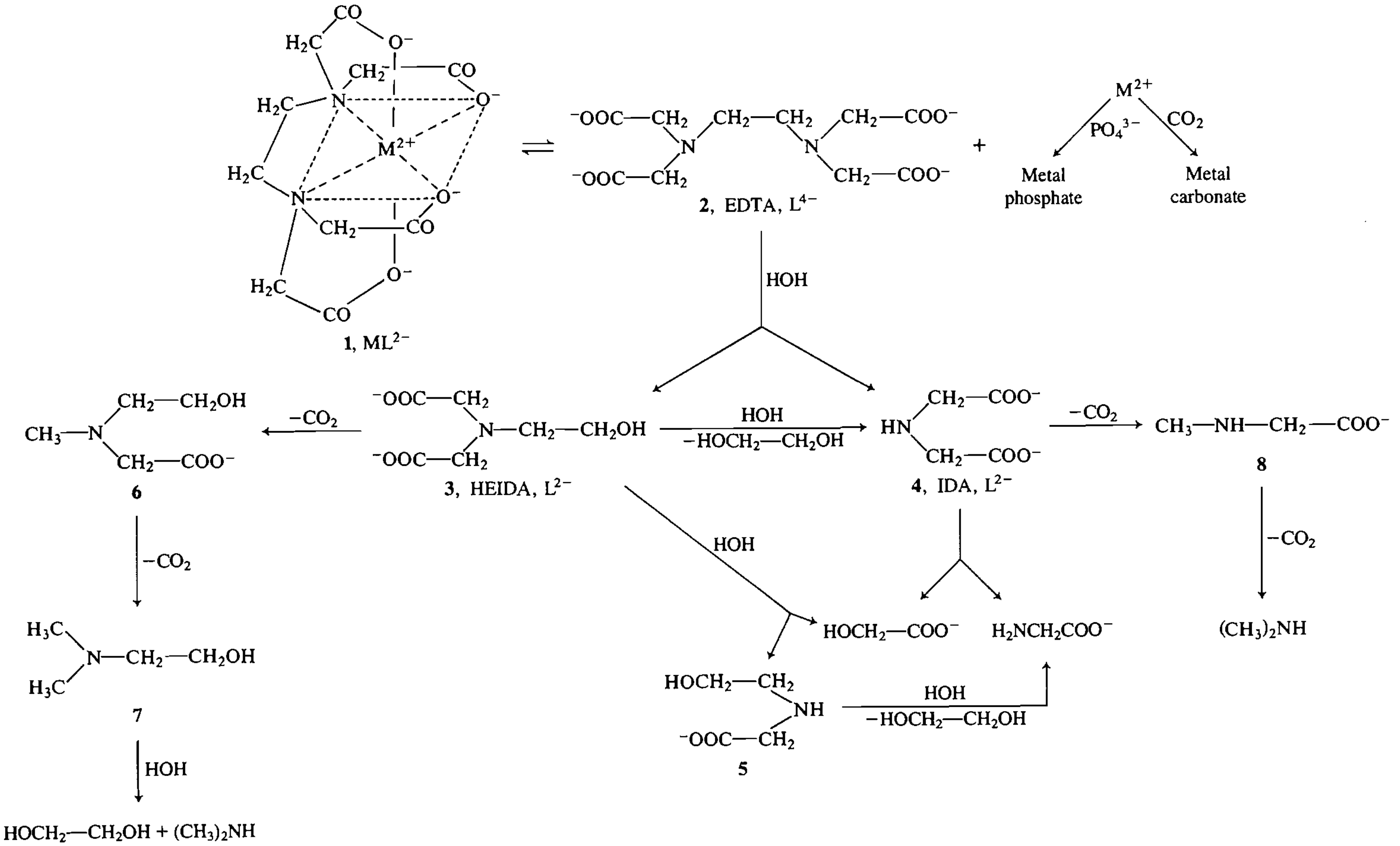
[10] $$T_{\mathrm{PO_4}} = [\mathrm{PO_4^{3-}}] + [\mathrm{HPO_4^{2-}}] \approx [\mathrm{HPO_4^{2-}}]$$

[11] $$\text{Slope} = k'/K^{\mathrm{H}}[\mathrm{H^+}]$$

### *Reaction products*

*Ca(II)–EDTA degradation*. At the initial moderately high temperature, nonredox metal chelate reaction products are primarily the result of hydrolytic reactions, as has been clearly shown previously for uncomplexed EDTA (2). The calcium chelate, **1** (Scheme 1), in the presence of 1.5 equiv. of phosphate for example, after about four half-lives at 229°C undergoes the reaction sequence **1** → **2** → **3** + **4** indicated in Scheme 1, yielding predominantly a mixture of hydroxyethyliminodiacetic acid and iminodiacetic acid. A colorless solid found in the reaction mixture dissolves when treated with 6 *M* HCl, but without evolution of gas, and was identified as calcium phosphate (Fig. 2).

When phosphate is absent, the chelate solution must be heated at 300°C to induce decomposition,



SCHEME 1. Proposed degradation scheme for EDTA chelates of divalent metal ions in the vicinity of 300°C. Final reaction products: carbon dioxide, ethylene glycol; dimethylamine, glycine, glycolic acid (~300°C), **3**, hydroxyethyliminodiacetic acid (HEIDA); **4**, iminodiacetic acid (IDA) (200–230°C); intermediates (300°C) **3**, hydroxyethyliminodiacetic acid (HEIDA); **4**, iminodiacetic acid (IDA); **5**, *N*-hydroxyethylglycine; **6**, *N*-methyl-*N*-hydroxyethylglycine; **7**, *N*,*N*-dimethylethanolamine; **8**, *N*-methylglycine.

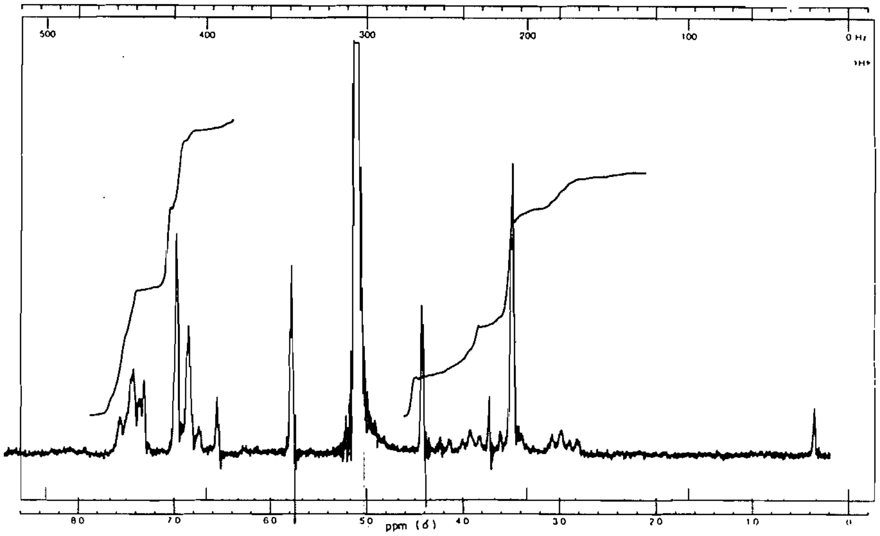


FIG. 2. Nuclear magnetic resonance spectrum of Ca(II)–EDTA solutions after thermal degradation showing the formation of IDA and HEIDA as sole reaction products at 230°C. The low field resonances belong to phenoxide which had been added as an internal standard.

and the degradation reactions proceed far beyond **3** and **4**. The predominant decomposition products found are: dimethylamine, ethylene glycol, and calcium carbonate. The carbonate was inferred from a test with dilute HCl, which produced the evolution of $CO_2$ from the colorless precipitate formed during the reaction. Ethylene glycol was detected by its nmr spectrum at 3.8 ppm, while dimethylamine was isolated in an acid trap from the volatile portion of the reaction. The acid solution was concentrated, made basic, and injected into a gc glass column. A peak at 1.0 min which was duplicated with standard dimethylamine confirmed the assignment.

### *Other metal chelates*

Thermal degradation of a sample of Zn(II)–EDTA produced a reaction mixture characterized by the nmr resonances tabulated in Table 4. It is interesting that one of the products appears to be glycolic acid (3.62 or 3.73 ppm). There are at least two types of acetate methylene resonances. Glycine with a —$CH_2$— resonance at 3.27 ppm, is definitely present. In addition ethylene diamine or substituted ethylenediamine may be present in view of the fact that a resonance was found at 2.80 ppm.

When the spectra of the Fe(II)–EDTA chelate and of the degradation products obtained were compared with those obtained from other metal EDTA chelates near 300°C, they were found to be generally similar, indicating that the distribution of reaction products does not vary much with the type of the metal ion present. A quantitative distinction has not been attempted from the experimental data available at this stage.

TABLE 4. Major nmr resonances of reaction products of Zn(II)–EDTA degradation at 300°C and pH 10

| Chemical shift (ppm)[a] | Assignment |
|---|---|
| 2.30 | N—$CH_3$ |
| 2.43 | EDTA, $NCH_2CH_2N$ |
| 2.80 | EN, $NCH_2CH_2N$ |
| 3.20 | EDTA, N—$CH_2COO^-$ |
| 3.27 | Glycine, N—$CH_2COO^-$ |
| 3.62 or 3.73 | O—$CH_2COO^-$ |
| 3.80 | Ethylene glycol |

[a] Measurements made in strongly basic $D_2O$ solution with a T-60 Varian nmr spectrometer. Chemical shifts relative to trimethylsilylpropanesulfonate.

In summary, tentative reaction pathways illustrated in the reaction scheme are suggested in order to provide a conceptual picture of the interrelationships of the various degradation products which have been shown to be formed in the present metal–EDTA chelate study.

In the complex reaction mixture formed, the metal ion probably distributes between the lower chelating ligands formed, principally IDA and HEIDA, and precipitated metal carbonate (or phosphate). The intermediate products **6** and **7** are inferred by consideration of the reactions known to take place in this system but have not directly been proved to be present in the reaction mixture. They do, however, lead to the known reaction products. The detection by nmr of the *N*-methyl and 2-hydroxyethyl groups provides some further support for their presence.

Work currently in progress is directed at obtaining further details about the complex degradation reactions of EDTA metal chelates reported for the first time in the present paper. These studies involve the quantitative determination of effects of temperature and pH on the stabilities of the chelates of the primary intermediates, IDA and HEIDA, further amplification of the chemistry of phosphate and silicate catalysis, and the exploration of the thermal stabilites in aqueous solution of other aminopolycarboxylic acids and their metal chelates.

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1. R. J. Motekaitis, D. Hayes, A. E. Martell, and W. W. Frenier. Can. J. Chem. **57**, 1018 (1979).
2. A. E. Martell, R. J. Motekaitis, A. R. Fried, J. S. Wilson, and D. T. MacMillan. Can. J. Chem. **53**, 3471 (1975) and references therein.
3. R. J. Motekaitis, A. E. Martell, D. Hayes, and W. W. Frenier. Can. J. Chem. **58**, 1999 (1980).
4. E. M. Yakimets, N. A. Berg, and N. I. Kuz'menko. Teploenergetica, **18**, 84 (1971).
5. M. Booy and T. W. Swaddle. Can. J. Chem. **55**, 1772 (1976).
6. A. E. Martell and R. M. Smith. Critical stability constants. Vol. 1. Plenum, New York. 1967.
7. R. M. Smith and A. E. Martell. Critical stability constants. Vol. 4. Plenum, New York. 1969.