

## Thermal Decomposition of EDTA, NTA, and Nitrilotrimethylenephosphonic Acid in Aqueous Solution<sup>1</sup>

A. E. MARTELL,<sup>2</sup> R. J. MOTEKAITIS, A. R. FRIED, J. S. WILSON,  
AND D. T. MACMILLAN

Department of Chemistry, Texas A & M University, College Station, Texas 77843

Received December 23, 1974<sup>3</sup>

A. E. MARTELL, R. J. MOTEKAITIS, A. R. FRIED, J. S. WILSON, and D. T. MACMILLAN. *Can. J. Chem.* **53**, 3471 (1975).

The decomposition of ethylenediaminetetraacetic acid (EDTA) in water solution at 200 and 260 °C, nitrilotriacetic acid (NTA) at 260 and 293 °C, and of nitrilotrimethylenephosphonic acid (NTPO) at 260 °C was studied by n.m.r. as a function of time at pH 9.5 and decomposition rates and products were determined. The primary (fast) decomposition reaction of EDTA involves the hydrolytic cleavage of the ethylenic C—N bond to produce the relatively stable pair: *N*-(2-hydroxyethyl)iminodiacetic acid and iminodiacetic acid. NTA does not cleave below 260 °C but decomposes at about 290 °C and above through a stepwise decarboxylation reaction. NTPO cleaves hydrolytically at 260 °C at two C—N bonds to produce aminomethylenephosphonic acid and 2 mol of hydroxymethylenephosphonic acid. The further breakdown of the primary products of EDTA at higher temperatures occurs by the loss of carbon dioxide producing the corresponding methylamines, concomitantly with the hydrolytic cleavage of the remaining CH<sub>2</sub>CH<sub>2</sub>—N bond giving ethylene glycol. The pseudo first order rate constant  $k_{\text{obs}}$  for NTA decarboxylation at 293 °C and pH 9.3 is  $0.19 \pm 0.01 \text{ h}^{-1}$ . The value of  $k_{\text{obs}}$  for EDTA hydrolysis at 200 °C is  $1.4 \pm 0.2 \text{ h}^{-1}$ .

A. E. MARTELL, R. J. MOTEKAITIS, A. R. FRIED, J. S. WILSON et D. T. MACMILLAN. *Can. J. Chem.* **53**, 3471 (1975).

On a étudié, par r.m.n. en fonction du temps à un pH de 9.5, la décomposition de l'acide éthylènediaminotétraacétique (EDTA) dans des solutions aqueuses à 200 et 260 °C de l'acide nitrilotriacétique (NTA) à 260 et 293 °C et de l'acide nitrilotriméthylène phosphonique (NTPO) à 260 °C et on a déterminé les vitesses de décompositions et la nature des produits formés. La réaction de décomposition initiale (rapide) de l'EDTA implique un clivage hydrolytique du lien C—N éthylénique pour conduire à la paire relativement stable: acide *N*-(hydroxy-2 éthyliminodiacétique) et acide iminodiacétique. Le NTA ne se coupe pas en-dessous de 260 °C mais se décompose à environ 290 °C et plus haut par l'intermédiaire d'une série de réaction successive de décarboxylation. Le NTPO se coupe d'une façon hydrolytique à 260 °C à deux des liens C—N; il y a formation d'acide aminométhylène phosphonique et de deux moles d'acide hydroxyméthylène phosphonique. Des coupures ultérieures des produits initiaux de l'EDTA à des températures plus élevées se produisent par perte de CO<sub>2</sub> conduisant aux méthylamines correspondants; il y a un clivage hydrolytique concomitant du lien CH<sub>2</sub>CH<sub>2</sub>—N résiduel conduisant à l'éthylène glycol. La constante de vitesse du pseudo premier ordre ( $k_{\text{obs}}$ ) pour la décarboxylation de NTA, à 293 °C et un pH de 9.3, est de  $0.19 \pm 0.01 \text{ h}^{-1}$ . La valeur de  $k_{\text{obs}}$  pour l'hydrolyse de EDTA à 200 °C est  $1.4 \pm 0.2 \text{ h}^{-1}$ .

[Traduit par le journal]

### Introduction

Among the many differing applications of the two organic chelating agents ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) are their use in aqueous solution at high temperatures for metal oxide solubilization (*i.e.*, scale removal) (1). To under-

stand the chemical processes that occur in such applications, it is essential to know the hydrolytic stabilities of these ligands, and to determine if the ligands present at the time of reaction are actually those introduced into the solution. Thus the determination of the breakdown of these ligands at high temperatures in aqueous solution is of considerable practical value, as well as being essential to a basic understanding of complexation reactions occurring at high temperatures. Indeed, it turns out that EDTA and NTA are not in fact stable in aqueous solution at high temperatures.

<sup>1</sup>This work was supported by a research contract G-9-2-D with the American Society of Mechanical Engineers, New York, N.Y.

<sup>2</sup>Author to whom correspondence should be addressed.

<sup>3</sup>Revision received July 2, 1975.

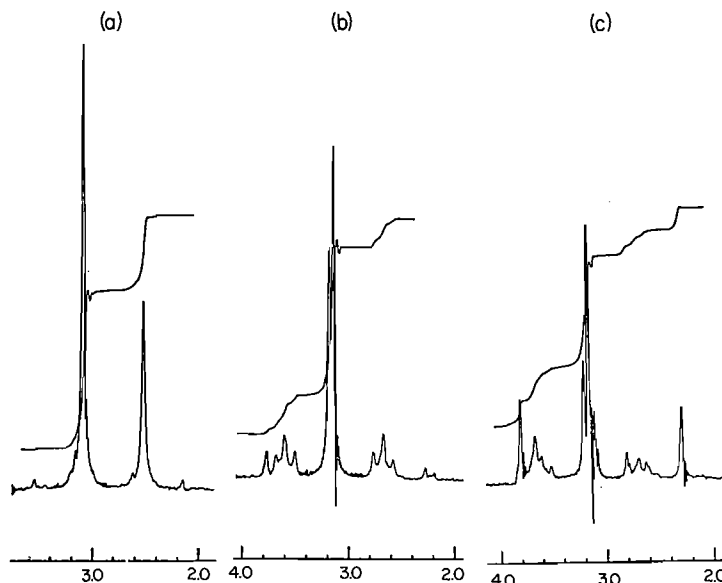


FIG. 1. Nuclear magnetic resonance spectra of EDTA samples heated at 260 °C at (a)  $t = 0$ , (b)  $t = 0.5$  h, (c)  $t = 7.5$  h. Solvent = 5% NaOD/D<sub>2</sub>O.

This work results from a program of synthesis and testing (2, 3) of organic chelating ligands of potential use for the removal of scale deposits on heat transfer surfaces of high pressure boilers.

It had been proposed (4, 5) that at 200 °C, EDTA<sup>4-</sup> decomposes stepwise through the sequential loss of acetate groups. Likewise, it was concluded (6, 7) that both Na<sub>3</sub>NTPA and Na<sub>2</sub>HNTA are exceptionally stable for at least 100 h at 200 °C. Later, the EDTA decomposition route was reinterpreted (8) to proceed through the hydrolysis of the ethylenic C—N link in agreement (2) with earlier findings in these laboratories.

This paper describes the sequential chemical reactions occurring in the aqueous decomposition of EDTA, NTA, and NTPO (nitrilotrimethylenephosphonic acid), and identifies the various decomposition products formed in each case. The pH of ~9.5 for this study represents a realistic working pH where the ligands would be efficient as scale removers yet at the same time the hydrolytic and boiler wall reactions would be kept reasonably low.

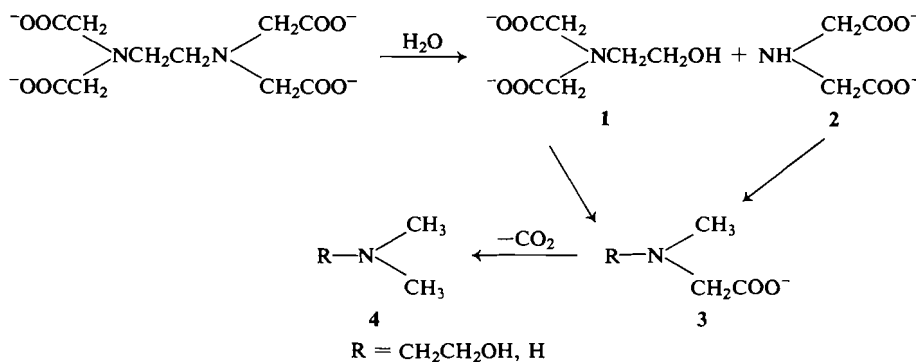
### Experimental

A 2-l titanium Parr stirred autoclave was charged with 1.00 l of 0.015 M deoxygenated (<1 p.p.m. O<sub>2</sub>) solutions of EDTA, NTA, and NTPO adjusted to pH ~ 9.5 with NaOH and was heated rapidly with

stirring to 200, 260, or 293 °C. Aliquots (10 ml) were withdrawn at periodic intervals and were evaporated to dryness under vacuum. The solvent was replaced by D<sub>2</sub>O several times, followed by evaporation, and finally the solution was made up to 0.50 ml with 5% NaOD in D<sub>2</sub>O. Precision n.m.r. tubes were employed and calibrated by integration of a standard EDTA solution. The n.m.r. spectra relative to TMS (trimethylsilylpropanesulfonic acid, sodium salt) were recorded and analyzed with a Varian T-60 n.m.r. spectrometer. The Varian HA-100 n.m.r. spectrometer was also used in earlier experiments on EDTA to identify and confirm the closely spaced peaks, but for routine measurements the T-60 resolution was found to be adequate.

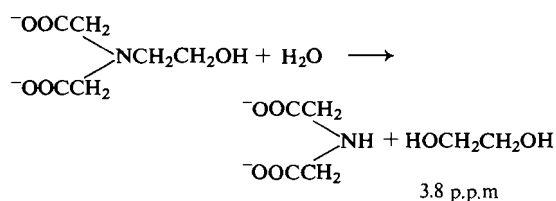
### Results and Discussion

Figure 1 shows that at 260 °C EDTA decomposes after about 30 min to its primary degradation products, *N*-(2-hydroxyethyl)iminodiacetic acid, 1, and iminodiacetic acid, 2. The two singlets in 2:1 ratio corresponding to the acetate methylenes and ethylene bridge protons of EDTA (Fig. 1a) have disappeared and were replaced by two closely spaced singlets at 3.1–3.2 p.p.m., and two triplets at 2.7 and 3.6 p.p.m. relative to TMS. At 200 °C, the  $t_{1/2}$  for this transformation at pH 11.4, 0.15 M Na<sub>4</sub>EDTA has been stated to be 15 h (6). Our calculations (Fig. 4) show that the half-life of EDTA at 200 °C under our conditions is ~0.5 h. The two singlets (Fig. 1b) are assigned to the acetate methylene protons of the cleaved



species **1** and **2**; their similar chemical shifts are caused by the difference in —H and —CH<sub>2</sub>—CH<sub>2</sub>OH substitution on the nitrogens. The two triplets represent the latter group with the absorption at 3.6 p.p.m. assigned to the methylene adjacent to the hydroxyl group. These assignments were confirmed by a direct comparison with the n.m.r. spectra of authentic samples of **1** and **2**.

After some time at 260 °C (Fig. 1c), the primary decay products of EDTA decarboxylate to the various substituted methylamines. This conclusion is reached both from the work on NTA and from an appreciation of the chemical shifts shown in Fig. 1c. The peak at approximately 2.3 p.p.m. is a methyl bound to nitrogen such as shown in **3** or **4**. The singlet that grows in at approximately 3.8 p.p.m. is indicative of further hydrolysis of *N*-(2-hydroxyethyl)iminodiacetic acid to ethylene glycol and iminodiacetic acid.



NTA apparently does not undergo hydrolytic cleavage, but does decompose at 293 °C via decarboxylation to *N*-methyliminodiacetic acid, **5**, methylsarcosine, **6**, and trimethylamine, **7**. Figure 2 shows the decay of NTA in 4 h, indicating a mixture of these products. The half-life of 4.0 h is appreciably longer than that associated with the initial decay of EDTA, but at this temperature is comparable to the decomposition rate of the primary decomposition products formed from EDTA. Indeed it

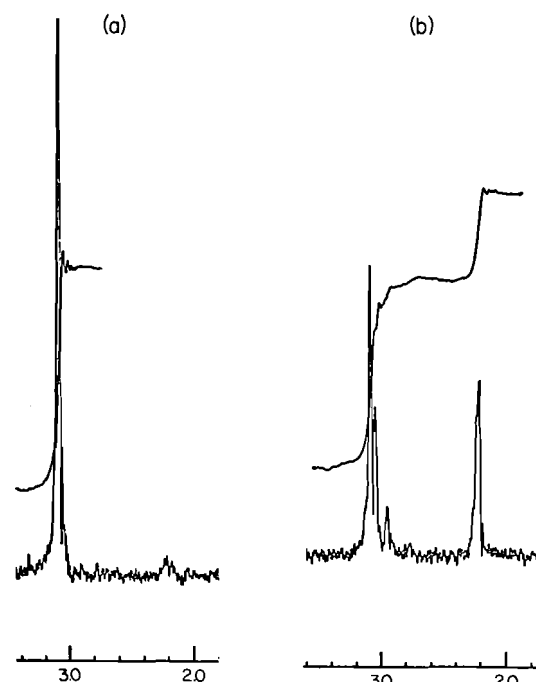


FIG. 2. Nuclear magnetic resonance spectra of NTA samples heated at 293 °C taken at (a)  $t = 0$ , (b)  $t = 4.0$  h. Solvent is 5% NaOD/D<sub>2</sub>O.

has been estimated that at the lower temperature of 200 °C, the half-lives of NTA<sup>3-</sup> and HNTA<sup>2-</sup> are both > 1000 h (7).

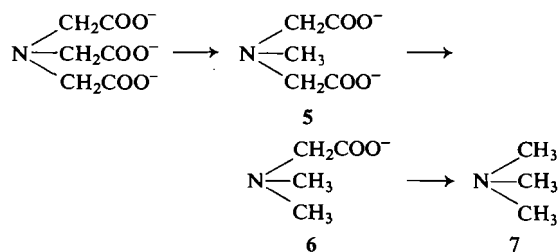


TABLE 1. Kinetic analysis of NTA decomposition at 293 °C and pH 9.3

Initial concentration of NTA ( <i>M</i> )	Time (h)	<i>F</i> Fraction remaining	1/ <i>t</i> ln <i>F</i> <sub>0</sub> / <i>F</i> (h <sup>-1</sup> )
0.0025	1.0	0.80	0.22
	2.5	0.62	0.19
	4.0	0.45	0.20
	6.0	0.22	0.25
		Average	0.21
0.0050	1.0	0.82	0.20
	2.0	0.71	0.17
	4.0	0.51	0.17
	6.0	0.26	0.22
		Average	0.19
0.010	0.75*	0.93*	0.10*
	2.0	0.73	0.16
	4.0	0.50	0.17
	6.0	0.28	0.21
		Average	0.18
0.020	1.0	0.83	0.19
	2.0	0.64	0.22
	4.0	0.46	0.19
	6.0	0.37	0.17
		Average	0.19

Mean of averages:  $k_{\text{obs}} = 0.19 \pm 0.01 \text{ h}^{-1}$

\*Discarded point.

The broadness of the 2.2 p.p.m. resonance (Fig. 2*b*) and the growth of closely spaced peaks at 3.0 p.p.m. support the composition of the mixture indicated in the equation above. Clearly, the 2.2 p.p.m. resonance represents three types of N—CH<sub>3</sub> groups (5–7), and the 3.0 p.p.m. peak shows the presence of three types of acetate methylenes (NTA, 5, 6).

Since the NTA decay rate at 293 °C was considerably slower than that of EDTA at the lower temperature investigated, a kinetic analysis for the initial NTA decomposition reaction was also undertaken in addition to the product analysis described above. Reaction kinetics was also obtained for EDTA hydrolysis within the limitation that a significant fraction of the starting substrate decomposes during heat-up time.

Table 1 summarizes the reaction conditions at four initial concentrations of NTA. It is seen that the observed rate constant does not vary with initial concentration. Thus the reaction rate at 293 °C and pH 9.3 for the decarboxylation of NTA follows pseudo first order kinetics with  $k_{\text{obs}} = 0.19 \text{ h}^{-1}$ .

TABLE 2. Kinetic analysis of EDTA decomposition at 200 °C

EDTA initial concentration ( <i>M</i> )	Time (h)	<i>F</i> Fraction remaining	−ln <i>F</i>	<i>k</i> <sub>obs</sub> (h <sup>-1</sup> )	
0.0112	0.5	0.59	0.53	1.27	
	1.0	0.20	1.61		
	2.0	0.08	2.53		
0.0056	0.5	0.40	0.92	1.37	
	1.0	0.18	1.71		
	2.0	0.05	3.00		
0.0028	0.5	0.20	1.61	1.65	
	1.0	0.05	3.00		
	2.0	0.015	4.20		
				Average	1.43 ± 0.20

Similarly, over a fourfold initial concentration range (Table 2) the pseudo first order rate constant for EDTA hydrolysis is found to be rather invariant within  $\sigma = 0.2 \text{ h}^{-1}$  with a value of  $k_{\text{obs}} = 1.4 \text{ h}^{-1}$ .

The n.m.r. spectra of NTPO at 260 °C show the complete disappearance of the parent doublet ( $J_{\text{PCH}} = 12 \text{ Hz}$ ) after 0.25 h, replaced by two doublets with the same coupling constant and an intensity ratio of 2:1, both at lower field strength (Fig. 3*a*). The smaller doublet was determined to be aminomethylphosphonic acid (AMP) by the addition of an authentic sample

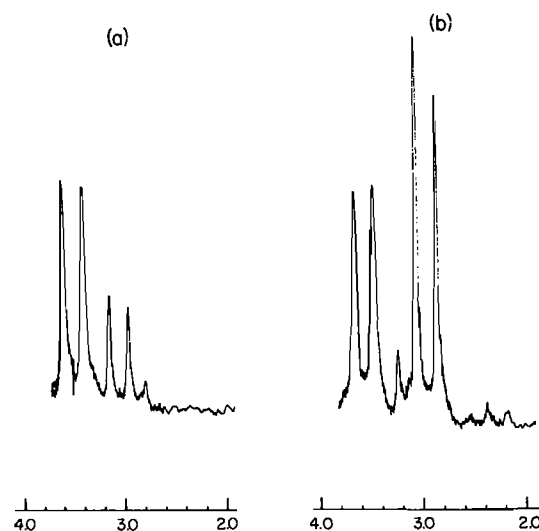
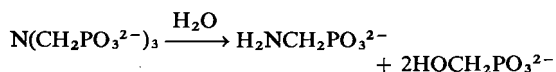


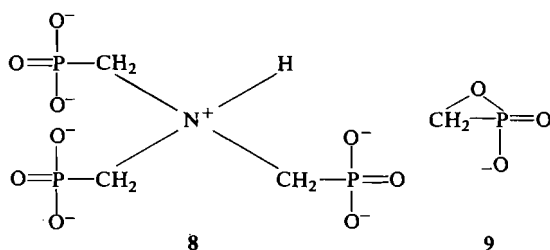
FIG. 3. Nuclear magnetic resonance spectra of NTPO sample at (a)  $t = 0.25$ , (b)  $t = 0.25$  h, with aminomethylenephosphonic acid added.  $T = 260$  °C, solvent = 5% NaOD/D<sub>2</sub>O.

of AMP to the n.m.r. tube (Fig. 3b). The larger doublet is therefore hydroxymethylphosphonic acid. Thus the fast hydrolytic reaction may be concluded to proceed as



This behavior is quite different from that found with NTA, which does not undergo carbon-nitrogen bond fission even at much higher temperatures. Since the presence of high negative charge resulting from the phosphonate groups would seem to repel hydroxide ions and thus decrease base-catalyzed carbon-nitrogen hydrolytic fission relative to what is observed in NTA, the question arises as to the special nature of the NTPO anion that would tend to promote hydrolytic splitting. In this connection, it should be noted that the basicity of the tertiary amino group in NTPO is at least two orders of magnitude greater than NTA (9). Hence, even at the high temperatures involved in these studies, a considerable proportion of the ligand must be in the *N*-protonated form, 8.

The positive charge on the nitrogen would be expected to assist carbon-nitrogen bond fission by transfer of the bonding electron pair to nitrogen.



There is also the possibility that hydrolytic fission of 8 may be assisted by the formation of an intermediate 9 which would be rapidly converted by hydroxide ion attack to hydroxymethylenephosphonic acid, which has been demonstrated to be one of the reaction products.

Figure 4 shows the relatively fast decomposition rate for EDTA, when compared to NTA. This, taken together with the above discussion, explains that the coordinating activity of aqueous solutions of EDTA at high temperatures (*i.e.*, above 200 °C) is due not to EDTA itself, but is primarily due to the complexing ability of the more thermally stable primary breakdown products 1 and 2. By virtue of its

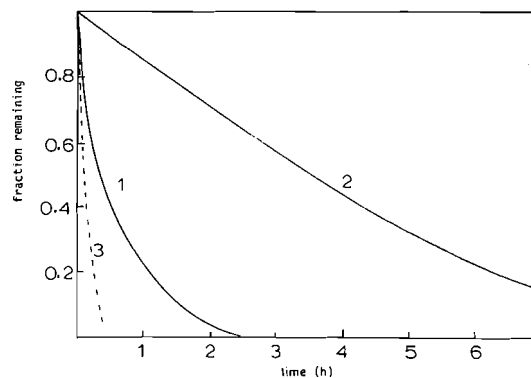


FIG. 4. Thermal decay plots of (1) EDTA at 200 °C, (2) NTA at 293 °C, (3) NTPO at 260 °C. The decay in (3) is so rapid as to be difficult to measure. The decay of (1) was measured at  $[\text{EDTA}]_0$  of 0.0112, 0.0056, and 0.0028 *M*; it showed no concentration dependence within the large experimental error induced by relatively long heat-up time compared to the rate of breakdown.

hydroxyethyl moiety 1 should be particularly suited for  $\text{Fe}^{3+}$  complexation, as is amply demonstrated in the literature and probably is the more active ingredient in such solutions. Both 1 and iminodiacetic acid, 2, would be effective toward divalent transition metal ions. Thus from an economic point of view, as well as for the purpose of maintaining maximum chemical effectiveness, it would probably be reasonable to use *N*-hydroxyethyliminodiacetic acid as a sequestering agent for transition metals at elevated temperature ( $\sim 200$  °C and above) in place of more rapidly-hydrolyzed substances such as EDTA. At the present time NTA is the least expensive organic sequestering agent available. Since its slower breakdown leads to *N*-methyliminodiacetic acid which still retains considerable effectiveness, and since NTA is itself an order of magnitude more stable than EDTA, it may very well be the chelating agent of choice at the present time.

The above argument is based on the relative stabilities of the ligands themselves, rather than the metal chelates. While this is logical from the point of view of maintaining an effective concentration of ligands for the purposes of scale removal, the abilities of the metal chelates to resist hydrolytic breakdown is also important to prevent redeposition of metal hydroxides in aqueous solution at elevated temperatures.

1. J. R. METCALF. Proc. 31st International Water Conference, Engineers Society of Western Pennsylvania, Pittsburgh, Pa. October, 1970.

2. A. E. MARTELL, R. J. MOTEKAITIS, and D. MACMILLAN. Fourth Quarterly Progress Report to the Contract Research Department, Texas Division, Dow Chemical Company, Freeport, Texas. August, 1972.
3. O. OSBORN, J. S. WILSON, A. R. FRIED, and W. H. PRYOR, JR. The development of a method for in-service high pressure boiler cleaning. Phase I - synthesis and screening program". Final Report to the American Society of Mechanical Engineers. March, 1973.
4. D. L. VENEZKY and W. B. MONIZ. NRL Report 6747 Naval Research Laboratory, Washington, D.C. August, 1968.
5. D. L. VENEZKY and W. B. MONIZ. Anal. Chem. **41**, 11 (1969).
6. D. L. VENEZKY. Proc. 32nd International Water Conference, Engineers Society of Western Pennsylvania, Pittsburgh, Pa. November, 1971.
7. D. L. VENEZKY and W. B. MONIZ. NRL Report 7192, Naval Research Laboratory, Washington, D.C. November, 1970.
8. P. J. SNIEGOWSKI and D. L. VENEZKY. J. Chromatogr. Sci. **12**, 359 (1974).
9. A. E. MARTELL and R. M. SMITH. Critical stability constants, Vol. 2. Plenum Press, Inc., New York 1975.