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Thermal Stability of Ethylenedinitrilotetraacetic Acid and its Salts

Part 3 - Oxygen Effect on the Thermal Decomposition of Tetrasodium Ethylenedinitrilotetraacetate in Aqueous Solutions

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13. ABSTRACT

The thermal decomposition of aqueous Na_4EDTA solutions containing varying amounts of dissolved oxygen was studied by a pmr technique. The presence of oxygen increases the rate of decomposition; at 200°C, the estimated time for one-half of the original $EDTA^{4-}$ to decompose increases from 4 to 5 hours for air-saturated solutions to 13 to 15 hours for degassed solutions. The pmr data are consistent with a postulated loss of a $-CH_2CO_2^-$ group from $EDTA^{4-}$ followed by the loss of a second group from the same nitrogen. The second-order kinetics of the first decomposition step show an increase in rate after an apparent induction period which is inversely proportional to the quantity of oxygen dissolved in solution. Apparently, dissolved oxygen causes the rapid formation of product(s) that, in turn, catalyze the decomposition of $EDTA^{4-}$. A chain-reaction mechanism is proposed for the thermal decomposition. The rapid rates of thermal decomposition observed for aqueous $EDTA^{4-}$ solutions suggest that stability studies are a necessary prerequisite to any high-temperature use of systems containing this chelating agent, especially if the aqueous solutions must be maintained at constant pH or in a high state of purity.

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ABSTRACT

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PROBLEM STATUS

This is an interim report on the problem; work is continuing.

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THERMAL STABILITY OF ETHYLENEDINITRILOTETRAACETIC ACID AND ITS SALTS

Part 3 - Oxygen Effect on the Thermal Decomposition of Tetrasodium Ethylenedinitrilotetraacetate in Aqueous Solutions

INTRODUCTION

The addition of the ethylenedinitrilotetraacetate ion ($EDTA^{4-}$) to boiler makeup water serves not only to control hardness but also to prevent the formation of iron-based sludge and other deposits on the internal heat-transfer surfaces. $EDTA^{4-}$ effectively maintains iron, calcium, and magnesium ions in a soluble form in the boiler water, thereby accomplishing the most significant step in the prevention of caustic corrosion in boilers: the elimination of internal deposits (1,2). Increasingly, $EDTA^{4-}$ is being advantageously used as a boiler water conditioning agent (3). However, data on the thermal stability of organic chelating agents in aqueous solution at high temperatures (200°C) have been reported only recently (4,5). Such information is necessary to elucidate the nature of the chelating agent, free or complexed, when it is present at high temperatures in aqueous solutions. If the decomposition of the organic chelating agent pollutes the boiler water and/or affects the pH control of the solution within the boiler, the inclusion of $EDTA^{4-}$ in the water treatment may not be advisable under certain conditions, and more stable materials should be substituted.

Our previous studies were based on $EDTA^{4-}$ solutions processed by several cycles of freeze-pump-thaw degassing (6) to eliminate dissolved oxygen before finally sealing the solution in thin-walled nmr tubes. For degassed water treated in this manner, approximately 0.08 ppm of oxygen was determined by a gas chromatographic method (7); this quantity of oxygen was attributed to gas absorbed by sample handling during the oxygen analysis. Consequently, thermal decompositions in solutions degassed as described above were considered to be taking place in the absence of dissolved oxygen.

Edwards and Merriman (8) report that temperatures near 180°C activate dissolved oxygen and cause an incomplete degradation of $EDTA^{4-}$, and that one part of oxygen equivalent causes 50 to 100 parts of $EDTA^{4-}$ to be nearly worthless in the prevention of deposits in a boiler. When oxygen-free water is used, however, free $EDTA^{4-}$ and its metal complexes are reported to be stable to temperatures of 251°C for a period of 2 hours (8). Because the use of $EDTA^{4-}$ as an oxygen scavenger is not economical, the addition of sodium sulfite to makeup water containing $EDTA^{4-}$ has been suggested to reduce the oxygen content of the boiler water and enhance the activity of the chelating agent (9).

Contrary to the above observations, our previous investigation (4) of degassed $EDTA^{4-}$ solutions (absence of dissolved oxygen) indicated a very rapid decomposition of the chelating material at 200°C. The purpose of this study is to compare the kinetics of the degradation of Na_4EDTA solutions containing varying quantities of dissolved oxygen and to elucidate, if possible, any observed differences in the rates of thermal decomposition.

EXPERIMENTAL PROCEDURE

$Na_4EDTA \cdot H_2O$ with a 99.0% purity was obtained from Matheson, Coleman and Bell and used without further purification. Li_4EDTA was prepared by reacting the acid, H_4EDTA, with lithium carbonate. Li_4EDTA solutions were prepared by dissolving the appropriate quantity of the solid, which was weighed in an nmr tube, in 1 ml of distilled H_2O. For Na_4EDTA samples, a 0.15M stock solution (pH = 9.9) was prepared, and the required amounts of solution transferred to an nmr tube. The pH of the solutions was determined prior to sealing the tubes (Table 1).

Table 1
Solutions, Sealed Under Reduced Pressure, used to Study the Thermal Decomposition of $EDTA^{-4}$ in Aqueous Solutions at 200°C

Sample	Salt	Solution Conc. (M)	pH	Solution Treatment before Sealing	Estimated $t_{1/2}$ (hr)*
A	Na_4EDTA	0.15	9.9	Air saturated	4
B	Na_4EDTA	0.15	9.9	Undegassed	5
C	Na_4EDTA	0.15	11.4	Degassed	15
D	Li_4EDTA	0.08	9.8	Air saturated	4
E	Li_4EDTA	0.10	9.8	Degassed	13

*Time estimated for one-half of the original $EDTA^{4-}$ to decompose.

The method used to degas and seal the solutions in the nmr tubes has been reported (4,5). Tubes containing solutions that were not degassed were solidified at liquid N_2 temperature and immediately sealed. Distilled H_2O through which air had been bubbled overnight was used to prepare the air-saturated solutions (approximately 4.2 ppm O_2). The distilled H_2O used to prepare the undegassed solutions contained approximately 3.5 ppm O_2. These solutions were immediately sealed after solidification at liquid N_2 temperature. The pressure within the tubes at the time of sealing was 10^{-4} to 10^{-5} torr; the degassed samples were sealed under the lowest pressures.

The sealed nmr tubes were placed in an iron protective jacket and then put in an oven set at 200°C ± 5°C. The time the tube was in the oven designated the length of the heating period. The proton magnetic resonance (pmr) spectrum of a sample was determined initially and following each period of heating.

The pmr spectra were recorded using a Varian HA-100 spectrometer, operating in the frequency-sweep mode. The H_2O peak was used as the locking signal. To facilitate quantitative measurements of spectral changes, a control sample was used to reset any variations in peak intensities between uses of the instrument. Electronic integration could not be employed because of the close spacing between peaks and the proximity to the lock signal. Consequently, signal heights were measured from the recordings and peak positions measured to ±1 Hz with a frequency counter.

RESULTS

The pmr spectrum (Fig. 1a) of Na_4EDTA solutions, like Li_4EDTA solutions (Fig. 4a), consists of two peaks (M and N in Figs. 1a and 4a), in a 2:1 intensity ratio corresponding to the two kinds of protons in the molecule (4). After the solutions were heated, the intensity of the peaks attributed to the $EDTA^{4-}$ protons decreased in intensity (Figs. 1 through 5). The rate of decrease appeared to be a function of the O_2 content but independent of the cation. Because the spectra were measured under identical conditions, the

decrease in height of the peak in the 200-Hz region should be a measure of the $EDTA^{4-}$ disappearance and should be useful in comparing the rates of decomposition. Figure 6 shows the relationship between the peak heights (normalized for comparison) and length of heating at 200°C of 0.15M Na_4EDTA solutions.

The rate of decomposition is observed to be greater for the air-saturated and undegassed solutions than for the degassed solution. For comparison, the estimated times that one-half of the $EDTA^{4-}$ in a sample is decomposed, $t_{1/2}$, are listed in Table 1. An approximately threefold increase in the rate of decomposition is noted for the samples which were not treated to remove O_2, thus, demonstrating the deleterious effect that the presence of dissolved O_2 has on the thermal stability of $EDTA^{4-}$ in aqueous solution. Also, as judged by the $t_{1/2}$ values, Li_4EDTA and Na_4EDTA solutions have comparable stabilities, although Li^+ has a pK which is 1.5 times greater than Na^+(10).

Fig. 1 - The pmr spectra of 0.15M aqueous, air-saturated solution of Na_4EDTA sealed under reduced pressure: (a) unheated; (b) heated 5 hours at 200°C; (c) heated 11 hours at 200°C; (d) heated 28 hours at 200°C; and (e) heated 296 hours at 200°C

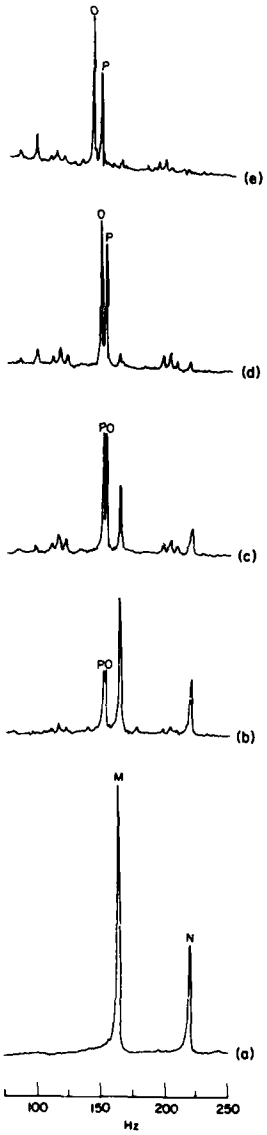


Fig. 2 - The pmr spectra of 0.15M aqueous, undegassed solution of Na_4EDTA sealed under reduced pressure: (a) unheated; (b) heated 5 hours at 200°C; (c) heated 11 hours at 200°C; (d) heated 28 hours at 200°C; and (e) heated 296 hours at 200°C

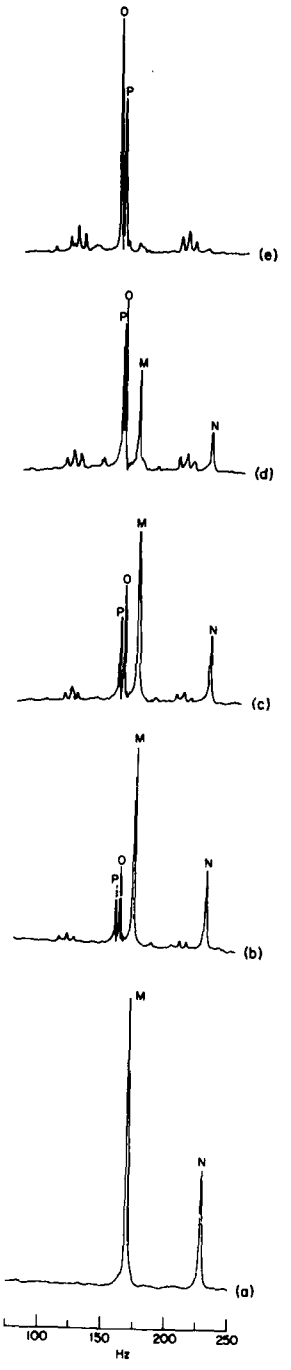


Fig. 3 - The pmr spectra of 0.15M aqueous, degassed solution of Na_4EDTA sealed under reduced pressure: (a) unheated; (b) heated 6 hours at 200°C; (c) heated 12 hours at 200°C; (d) heated 30 hours at 200°C and (e) heated 251 hours at 200°C

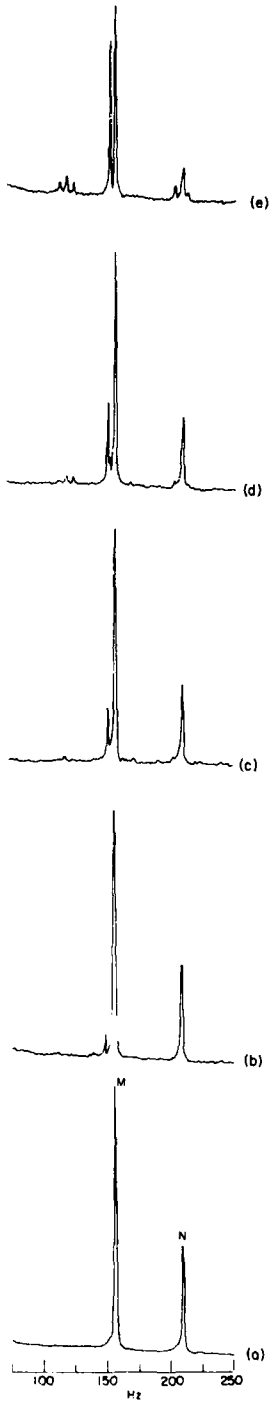


Fig. 4 - The pmr spectra of 0.08M aqueous, air-saturated solution of Li_4EDTA sealed under reduced pressure: (a) unheated; (b) heated 4 hours at 200°C; (c) heated 10 hours at 200°C; (d) heated 22 hours at 200°C; and (e) heated 37 hours at 200°C

Fig. 5 - The pmr spectra of 0.10M aqueous, degassed solution of Li_4EDTA sealed under reduced pressure: (a) unheated; (b) heated 5 hours at 200°C; (c) heated 45 hours at 200°C; (d) heated 137.5 hours at 200°C; and (e) heated 209.5 hours at 200°C

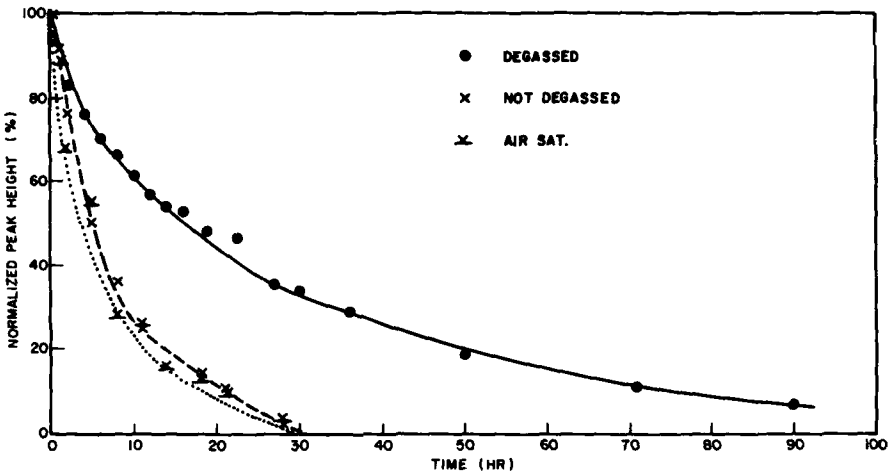


Fig. 6 - Change in normalized peak height (218 Hz) with respect to length of heating the sealed solutions of Na_4EDTA under reduced pressure. The solutions were heated to 200°C.

In all of the samples tested, decomposition of the $EDTA^{4-}$ was detected, after the first hour of heating at 200°C, by the formation of one or two peaks downfield from the intense peak M attributed to the methylene protons α to the carbonyl group. The position of the new peaks suggest that they too may be attributed to methylene protons α to a carbonyl group. Initially, the most intense of these two new peaks (O) (for example, Fig. 3b) appears closest to peak M and upfield from the less intense peak P. After prolonged heating, peak O shifts to the downfield side of peak P, Fig. 3e. Accordingly, some time during the heating periods, the two peaks are observed to overlap, and for the degassed (sample C in Table 1) and air-saturated (sample A in Table 1) solutions of Na_4EDTA, the peaks were often not clearly resolved and were difficult to identify. For the undegassed Na_4EDTA solution (sample B), shown in Fig. 2, peak O shifted from 150 Hz to 141 Hz, a change of 9 Hz after 296 hours of heating at 200°C, but the less intense peak P shifted only 3 Hz from 151 to 148 Hz. The growth of the peaks O and P indicates that peak O rapidly forms and then remains at a nearly constant height (Fig. 7), whereas peak P reaches a maximum and then gradually decreases (Fig. 8). Two triplets centered at 116 ± 2 Hz and 205 ± 2 Hz show the same growth characteristics as peak P and, apparently, are related to this peak.

The two sets of triplets are in a 1:1 ratio, and the relatively weak peaks of the triplets are approximately in a 1:2:1 ratio with a coupling constant (J) of 5 ± 1 Hz. As the heating period of the Na_4EDTA solutions is lengthened, the intensity of the peaks increases to a maximum (Fig. 9) and then slowly decreases at a rate similar to that observed for peak P. The normalized peak heights plotted in Fig. 9 are actually the normalized sum of the six peak heights. During the heating, the triplets did not shift positions but the presence of dissolved O_2 appears to increase their rate of formation.

Although new peaks (Figs. 4 and 5) corresponding to methylene protons α to the carbonyl group are noted in the pmr spectra of Li_4EDTA solutions, the peaks, corresponding to peaks O and P of Na_4EDTA spectra, are difficult to resolve because of their

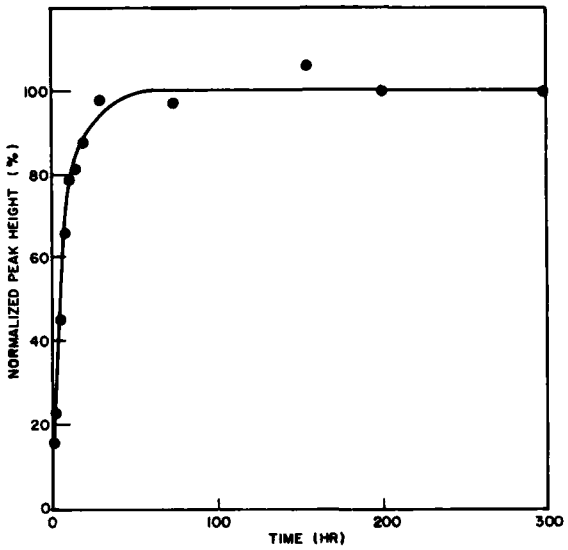


Fig. 7 - Change in the normalized peak height (peak O) with respect to length of heating, at 200°C, of the sealed, undegassed solution of Na_4EDTA under reduced pressure

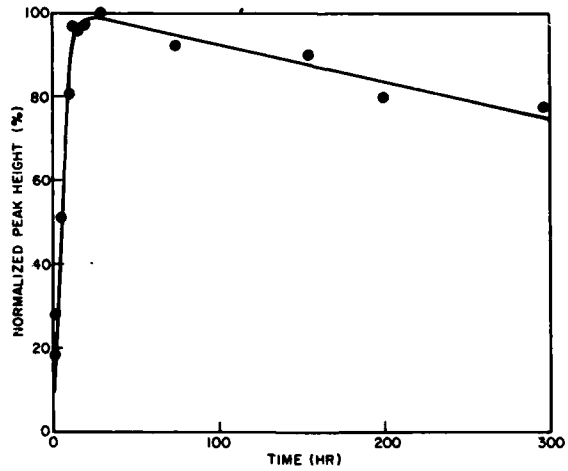


Fig. 8 - Change in normalized peak height (peak P) with respect to length of heating, at 200°C, of the sealed, undegassed solution of Na_4EDTA under reduced pressure

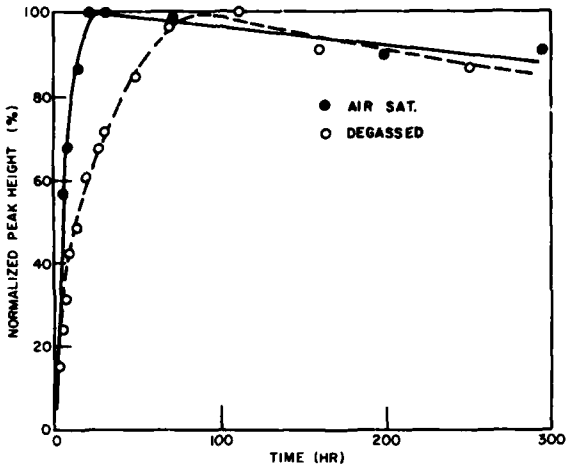
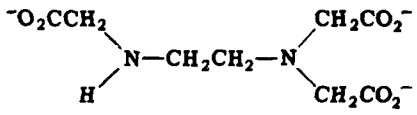


Fig. 9 - Change in normalized peak height with respect to length of heating, at 200°C, of sealed solutions of Na_4EDTA under reduced pressure. Heights are summed for the two triplets centered at 115 and 201 Hz.

superposition with the original peak M. Also, the center of the upfield triplet coincides with the position of peak N attributed to the ethylenic protons. In our previous studies (4), when Li_4EDTA and Na_2H_2EDTA were heated in D_2O, the peaks attributed to the protons α to the carbonyl group were not detected because of the rapid proton-deuterium exchange. The triplets noted in the reported regions were not affected when the solvent was D_2O; consequently, the triplets were attributed to a product molecule having non-equivalent methylene groups between the nitrogens.

DISCUSSION

Unfortunately, the nature of the pmr signals relative to other lines of the recorded spectra precludes a meaningful comparison of peak heights which would otherwise allow a calculation of the number of protons of each kind. Similarities between the observed spectra of Na_4EDTA and Li_4EDTA solutions (4), however, indicate that the primary decomposition product is the ethylenedinitrilotriacetate ion:



The amine hydrogens, being exchangeable, are presumably averaged in with the H_2O peak.

Since the spectra were measured under identical instrument conditions, the decrease with time in the height of peak N, which is attributed to the ethylenic protons, should be a measure of the rate at which $EDTA^{4-}$ disappears. The data obtained in this manner give nonlinear zero-order and first-order rate plots; however, a linear plot is obtained if second-order kinetics are assumed. Figure 10 compares the second-order kinetics of

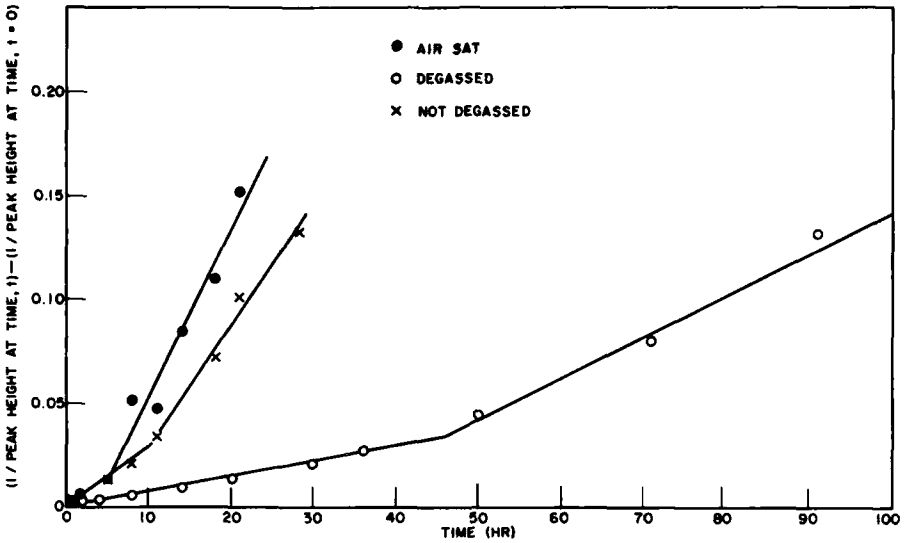


Fig. 10 - Second-order rate plot for the decomposition of 0.15M aqueous Na_4EDTA solutions

the various Na_4EDTA solutions. The striking feature of the curves is the change in the slope at times inversely proportional to the amount of dissolved O_2 in solutions. Thus, a more rapid rate is observed after a shorter heating period for the air-saturated solution A than for the undegassed solution B, which in turn shows the rate change at a time considerably sooner than the degassed sample C. A similar change is noted for the air-saturated Li_4EDTA solution (Fig. 11) but was not observed for the degassed solution. Although the uncertainty of the O_2 content in the solutions after the sealing operation prevents a quantitative analysis of this interesting relationship, the experimental results do aid in elucidating the mechanism by which $EDTA^{4-}$ decomposes under the conditions studied.

When dissolved O_2 is present in solution, the kinetic data are consistent with a decomposition step proceeding through an initiation step. Furthermore, a two-step initiation process is suggested by the observed increase in rate that occurs after a heating period, the length of which depends on the dissolved O_2 content of the solution. The first reaction is assumed to be fast and followed by a second, much slower, reaction. The slow rate-determining reaction yields a product X that then participates in the propagation reaction. The scheme proposed for the ensuing chain reaction is

$$\left.\begin{array}{lll} O_2 + EDTA^{4-} \xrightarrow{k} W & \text{(fast)} \\ W + EDTA^{4-} \xrightarrow{k_1} X & \text{(slow)} \end{array}\right\} \text{initiation}$$

$$X + EDTA^{4-} \xrightarrow{k_2} X + Y \qquad \text{propagation}$$

$$X \xrightarrow{k_3} Z \qquad \text{termination}$$

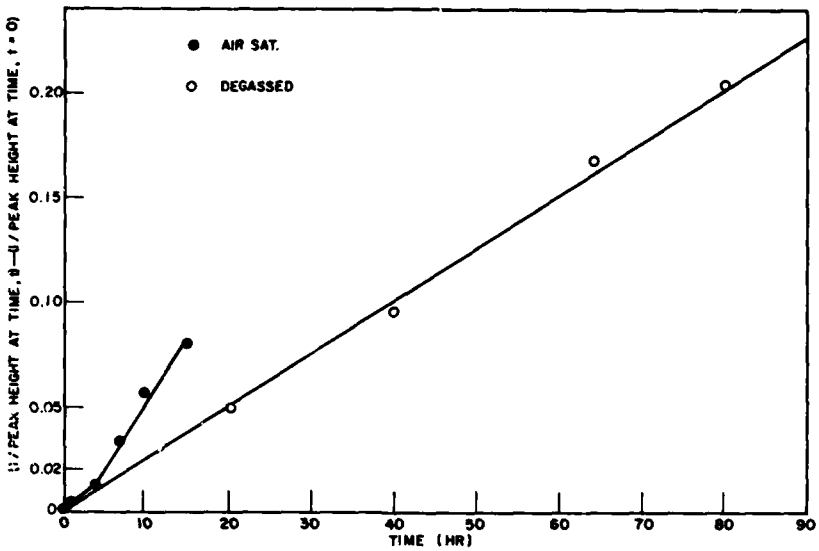


Fig. 11 - Second-order rate plot for the decomposition of aqueous Li_4EDTA solutions

A progressive accumlation of W will occur due to the inbalance between the two initiation steps, and after the initial period, a reasonable assumption is that $[O_2] = [W]$. Assuming steady-state conditions after initiation, we can write

$$\frac{dX}{dt} = k_1[W][EDTA^{4-}] - k_3[X] = 0$$

$$[X] = \frac{k_1[W][EDTA^{4-}]}{k_3} .$$

Consequently, the rate of decomposition r would be given by

$$r = \frac{-d[EDTA^{4-}]}{dt} = k_2[X][EDTA^{4-}]$$

$$r = \frac{k_2k_1}{k_3}[W]\ [EDTA^{4-}]^2$$

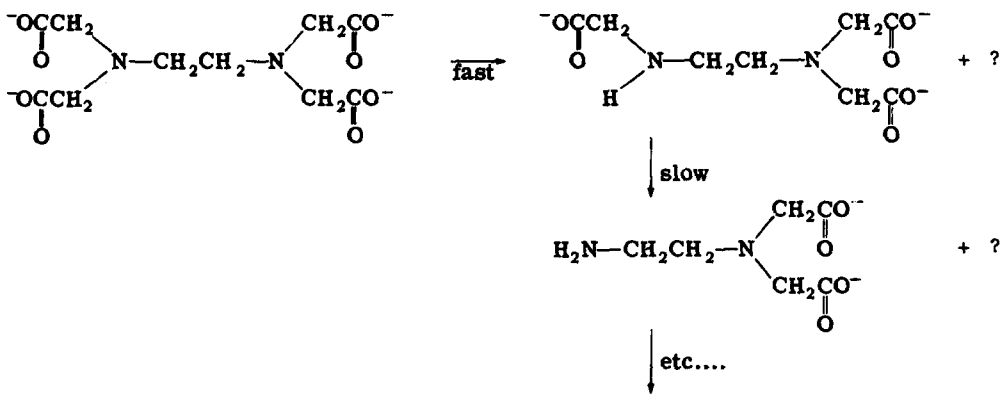
$$r = K[O_2][EDTA^{4-}]^2, \text{ where } K = \frac{k_2k_1}{k_3} .$$

Qualitatively, the expression is found to be consistent with the experimental data.

As stated above, product Y is postulated to be ethylenedinitrilotriacetate ion. The identity of products W, X, and Z are unknown, but W and X may be substances such as acidic protons originating from the $—CH_2CO_2—$ group lost from $EDTA^{4-}$. The relatively long initiation period noted for the degassed Na_4EDTA solution suggests that, in the absence of dissolved O_2, the formation of X proceeds by a more direct process than postulated. When the proper ratio of the reactants is established, the decomposition proceeds at a faster rate. In an effort to corroborate the above postulated mechanism, we are continuing work on this system.

CONCLUSIONS

The Li or Na cation does not influence the rate of thermal decomposition of the aqueous solutions of $EDTA^{4-}$ under the basic environment of our experiments. It should be noted that both Li^+ and Na^+ are weak Lewis acids and would not be expected to coordinate strongly with the $EDTA^{4-}$. Thus, the decomposition observed under our conditions at 200°C is postulated to proceed by a stepwise loss of $—CH_2CO_2—$ groups from the "free" $EDTA^{4-}$. The first loss appears to be relatively rapid and is followed by a slower, second-stage loss of $—CH_2CO_2—$ from the nitrogen which has the least number of remaining "acetate" groups.



Although the pmr spectra are consistent with such a stepwise reaction, the mechanism must be corroborated by the pmr study of the proposed intermediates singularly and in combination with each other. Methods of preparing these intermediates are under investigation.

The effect of O_2 on the thermal decomposition rate of Na_4EDTA and Li_4EDTA, that is, the fast reaction described above, is quite significant. The time for one-half of the original $EDTA^{4-}$ to decompose in the presence of dissolved oxygen (3-6 hr) is increased by a factor of approximately three (to 13-15 hr) by removing the dissolved O_2 from the solutions. The Na_4EDTA solutions showed an initial rate of decomposition which was followed by an increased rate of decomposition, the onset time of which is inversely proportional to the dissolved O_2 content. For a degassed Li_4EDTA solution, the data did not show a similar rate change, but the air-saturated solution did. Second-order kinetics, with respect to the $EDTA^{4-}$ concentration, appear to be followed in both the degassed solutions and solutions with dissolved O_2. Qualitatively, the experimental data are consistent with a proposed chain-reaction mechanism: an initiation step is followed by a propagation reaction involving reactants derived from the thermal decomposition of $EDTA^{4-}$.

We are currently studying the fate of the $—CH_2CO_2—$ *groups removed from the* $EDTA^{4-}$ and the effect of strong Lewis acids on the thermal stability of $EDTA^{4-}$. Although our investigation is not complete, the rapid thermal decomposition of $EDTA^{4-}$, observed at 200°C in sealed nmr tubes, suggests that stability studies are a necessary prerequisite to any high-temperature use of systems containing this chelating agent, especially if the aqueous solutions must be maintained at a constant pH or in a high state of purity.

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REFERENCES

1. Jacklin, C., "Waterside Failures in High-Pressure Boilers — A Field Survey," Am. Soc. Mech. Engrs. Paper 61-WA-271.

2. Klein, H.A., Combustion 34, No. 4, 45 (1962).

3. Venezky, D.L., "Thermal Stability of Ethylenedinitrilotetraacetic Acid and Its Salts, Part 1 — A Literature Survey." NRL Report 6674, Dec. 1967.

4. Venezky, D.L., and Moniz, W.B., Anal. Chem. 41 11, (1969).

5. Venezky, D.L. and Moniz, W.B., "The Thermal Stability of Nitrilotriacetic Acid and Its Salts in Aqueous Solutions," NRL Report 7192, Nov. 17, 1970.

6. Poole, C.P., Jr., "Electron Spin Resonance," Interscience, New York, 1967, p. 629.

7. Swinnerton, J.W., Linnenbom, V.J., and Cheek, C.H., Anal. Chem. 34, 483, 1509 (1962).

8. Edwards, J.C., and Merriman, W.R., Proc. Intl. Water Conf., Eng. Soc. of W. Pa. 24, 35 (1963).

9. Edwards, J.C. and Rozas, E.A., Proc. Am. Power Conf. 23, 575 (1961).

10. Sillén, L.G. and Martell, A.E., compilers, "Stability Constants of Metal-ion Complexes," Special Publication No. 17, The Chemical Society, Burlington House, London, 1964, p. 634.