29 Jan 1993

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Recommended Citation

Linville, Audrey P., "Hypochlorite Oxidation of Nitrilotriacetic Acid" (1993). *Opportunities for Undergraduate Research Experience Program (OURE)*. 101.
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HYPOCHLORITE OXIDATION OF NITRILOTRIACETIC ACID

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The chemical degradation of nitrilotriacetic acid (NTA) by sodium hypochlorite is examined. Preliminary work indicates that NTA undergoes decarboxylation. In the second phase of this investigation (S92), the work was mainly concerned with the products from the reaction of NTA with hypochlorite. The product of decarboxylation has been found to be iminodiacetic acid. The decrease in concentration of hypochlorite per unit time was studied over a pH range of 7-14 and in the presence of lead, calcium, zinc, and copper ions.

Nitrilotriacetic acid (NTA) is found in many common household and industrial formulations: from shampoos to metal cleaning agents. Because of its widespread applications, studies have been performed to determine the carcinogenic nature of NTA. A study done by the United States Department of Health, Education, and Welfare found that NTA fed to rats and mice caused tumors of their urinary tracks[1]. However, researchers Greenblatt and Lijinsky dispute this claim. They found no increase in cancer incidence in Swiss mice given NTA in their drinking water[2]. Due to NTA's possible carcinogenicity, the removal of NTA from water is very important. Many different reagents have been used to oxidize NTA. Carr, et al. used the ferrate (VI) ion[3]; while Hanna used Ce(IV) in a $HClO_4$ media, MnO_4^-, and OCl^-[4]. However, no study has investigated the extent to which hypochlorite decarboxylates NTA nor the products of this reaction. Carr, et al. found the major product of ferrate oxidation to be iminodiacetic acid (IDA) with oxygen being the next most produced and glycine (GLY) and NH_3 being the minor products[3]. The hypochlorite ion, generated in most municipal water plants as a result of chlorination with Cl_2, is thus being investigated as a possible agent for the degradation of NTA. This study focuses on the products of the decarboxylation of NTA.

EXPERIMENTAL.

Reagents.

Sodium hypochlorite purchased from Sigma provided the hypochlorite ion. In order to measure the amount of available hypochlorite, excess KI was added to NaOCl generating I_2. The I_2 was titrated with sodium thiosulfate[5]. The amount of available hypochlorite is 7.8%. The NTA and IDA were purchased from the Eastman Kodak Company. Bis(trimethylsilyl)trifluoroacetamide (BSTFA) purchased, in 1 mL ampules, from Pierce provided the trimethylsilyl group for the derivation of the products. The metal ion solutions were atomic absorption standards (from the Fisher Company) which contain 1 mg of the metal for every 1 mL of solution. None of the reagents were purified.

Apparatus.

The apparatus used for the reaction between NTA and OCl is diagrammed in Figure 1. The vacuum flask containing $Ba(OH)_2$ pictured on the far right hand side of the picture is to insure carbon dioxide-free helium. The helium bubbles through the reaction flask containing a solution of NTA and OCl^-. A mixture of helium and carbon dioxide passes through the next three flasks which contain barium hydroxide.

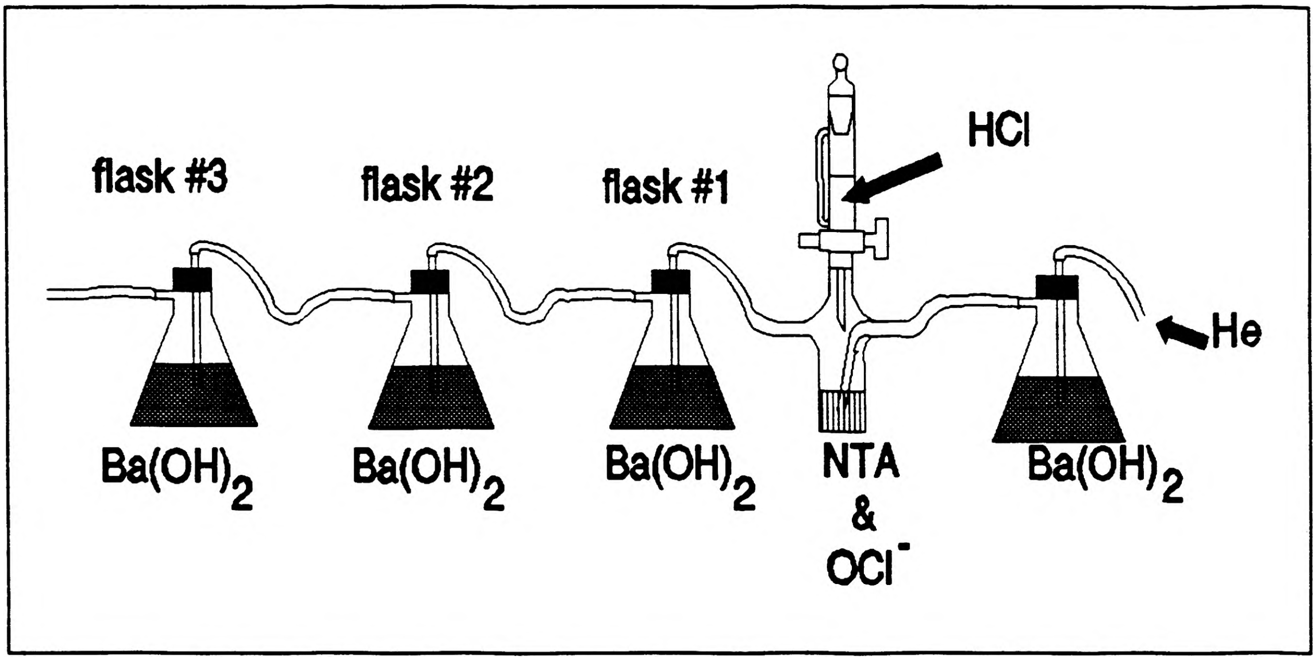

Figure 1. The apparatus used for the reaction between NTA and hypochlorite.

For product determination, gas chromatography was used. However, NTA and its products are not sufficiently volatile under normal conditions to be used in gas chromatography but the trimethylsilyl esters of these compounds are sufficiently volatile. For the derivation of the products, the silylation reaction tube was a screw-cap culture test tube made with standard pyrex glass. Since an oil bath was unavailable, a hot plate and an aluminum heating block provided the heat for making the derivative(see Figure 2).

Procedure.

NTA Decarboxylation Experiments.

Approximately 0.2 g of NTA was placed in the reaction flask and dissolved in sodium hydroxide due to its low solubility in water. The sodium hypochlorite was added and the mixture was allowed to sit for five minutes while helium bubbled through the solution. Hydrochloric acid was then added. An excess of NTA was used to prevent the necessity of eliminating unreacted hypochlorite.

Derivation of Products.

The procedure used for the formation of trimethylsilyl derivatives of the reaction products is the same as described by Gehrke and Leimer[6] except the samples were processed at 130 °C

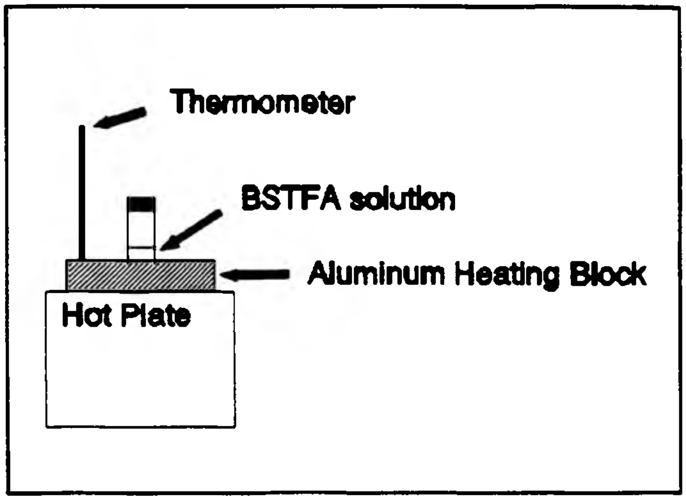

Figure 2. Apparatus used in derivatization.

during the removal of water and CH_2Cl_2 was used to aid in the azeotropic removal of water from the sample. BSTFA was used as both a solvent and a derivatization agent. Derivatives were made of the reaction products, NTA, IDA, and a mixture of NTA and IDA.

Gas Chromatography.

Each sample's chromatograph was obtained by keeping the oven temperature constant at 100 °C. The injector temperature was set to 220 °C. Approximately 1 μL of each solution (3 μL of the reaction mixture) was injected into a Hewlett Packard 5890A Gas Chromatograph with a Hewlett Packard 3390A Integrator.

Kinetics(pH).

For all rate measurements (both pH and metal ion experiments), the same amount and concentration of NTA and hypochlorite were used -- 10 mL of a 0.4484 M NTA solution and 10 mL of a 0.02298 M OCl^- solution. The 10 mL of NTA solution was placed in a beaker with a stir bar and 10 mL of a mixture of 1 M NaOH and 1 M HCl (See Table I). Upon the addition of the hypochlorite, stirring was started. At 30 s, 360 s (6 min), 1500 s (25 min), and 2400 s (40 min), 1 mL of the reaction solution was removed and quenched with 1 mL of 0.2298 M acidified KI. Due to the deep yellow color of the resulting solution, 0.5 mL was diluted to 25 mL. The absorbance spectrographs of the diluted solutions were recorded from 368 nm to 268 nm using a 1 cm quartz cell and a Perkin-Elmer 552 Spectrophotometer with a Perkin-Elmer 561 Recorder. Maximum peaks occurred at 348 nm and 287 nm.

TABLE I. Amount of NaOH and HCl used in each trial during pH experiments.

Trial	Amount of NaOH (mL)	Amount of HCl (mL)
1	10	0
2	7.5	2.5
3	5	5
4	2.5	7.5
5	0	10

Kinetics(Metal ions).

Again, the 10 mL of the NTA solution was placed in a beaker with a stir bar and 35 mL of 1 M NaOH was added to insure a basic solution (NTA will precipitate out in an acidic solution). Stirring was begun and 25 mL of the metal solution was added. The mixture was stirred for 10 min to allow any chelating between the NTA and the metal ion to occur. The hypochlorite was added. The procedure is the same as described above except that no sample was taken after 30 s had elapsed due to the anomalous results at 30 s for the pH experiments.

RESULTS.

Product Identification.

Figures 3, 4, 5, and 6 are the gas chromatographs obtained from the BSTFA derivative of NTA, IDA, mixture of NTA and IDA, and the reaction mixture respectively. In the NTA, NTA + IDA, and reaction mixture graphs, a peak (which is absent in the IDA graph) occurs around a retention time equal to 1 min and 16 s. This suggests that the reaction mixture contains NTA (which should be correct since an excess of NTA was used during the reaction). A very broad peak with a shoulder occurs in the IDA chromatograph at 4 min 83 s which doesn't seem to occur in any other graph. Yet a peak does occur at 4 min and 23 s and 4 min 42 s in NTA + IDA and reaction mixture graphs respectively. Since the peak in the IDA graph is very broad, it covers the times where the peaks in the other two graphs occur. Therefore, the product (besides CO_2) of the reaction is IDA.

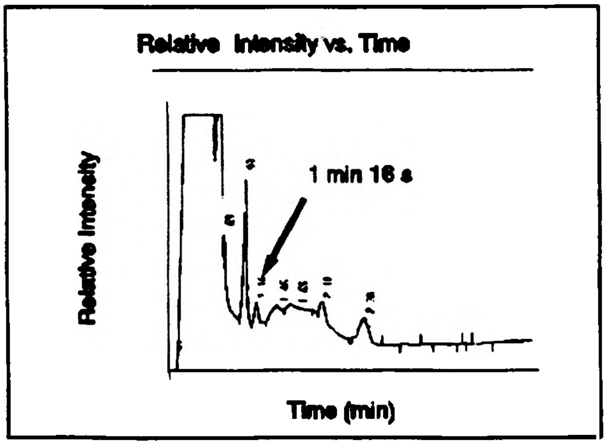

Figure 3. Gas chromatograph obtained from the BSTFA derivative of NTA.

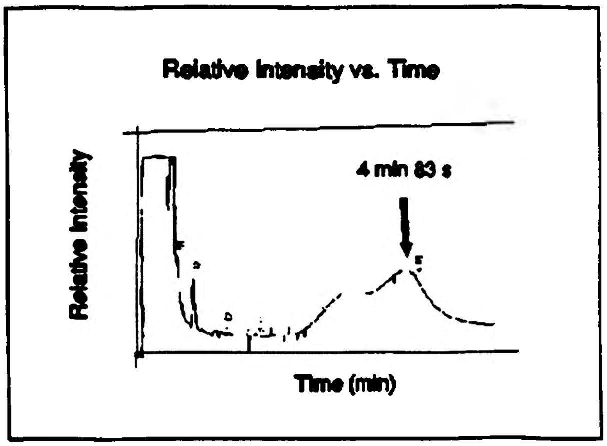

Figure 4. Gas chromatograph obtained from the BSTFA derivative of IDA.

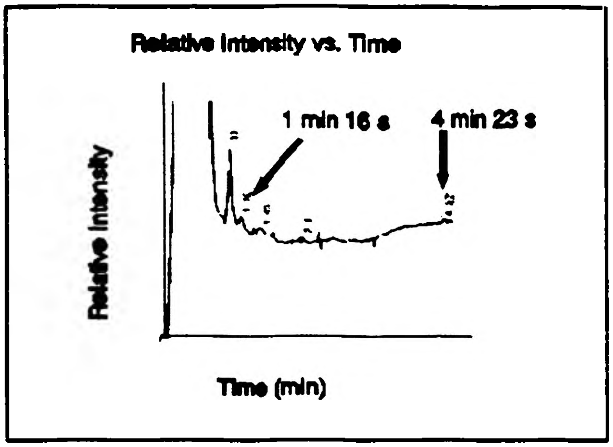

Figure 5. Gas chromatograph obtained from the BSTFA derivative of a mixture of NTA and IDA.

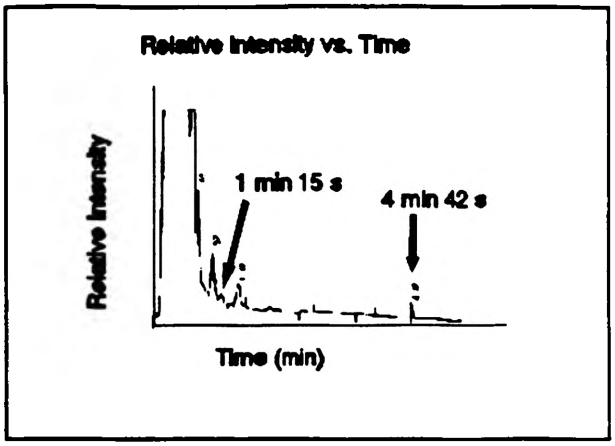

Figure 6. Gas chromatograph obtained from the BSTFA derivative of the reaction products.

Kinetics(pH).

In Trials 4 and 5, the NTA precipitated out before the hypochlorite was added and therefore no data was obtained for these trials. The sample obtained at 30 s produced anomalous results most likely due to lack of mixing within the first 30 s. The data obtained in this part of the experiment can be found in Table II. The absorbance is related to the concentration by Beer's Law:

$$A = \epsilon \times b \times c \tag{1}$$

where A is the absorbance, ϵ is the extinction coefficient, b is the path length of the cell, and c is the concentration of the solution. As the absorbance decreases, so does the concentration. Thus, as the absorbance decreases, the concentration of I_2 decreases which means the concentration of hypochlorite had also decreased. By comparing the absorbance at 6 min, one can see that in Trial 3 the concentration of the hypochlorite is less than the other two trials. The reaction proceeds at a greater rate in Trial 3. The next fastest rate occurs in Trial 2. Figures 7, 8, and 9 contain the absorbance spectrographs for Trial 1, 2, and 3 respectively.

TABLE II. Data obtained from the pH experiments.

Trial	Absorbance at 348 nm 6 min	25 min	40 min	Absorbance at 287 nm 6 min	25 min	40 min
1	0.540	0.414	0.354	0.817	0.629	0.539
2	0.529	0.411	0.260	0.790	0.611	0.389
3	0.298	0.235	0.225	0.454	0.360	0.345

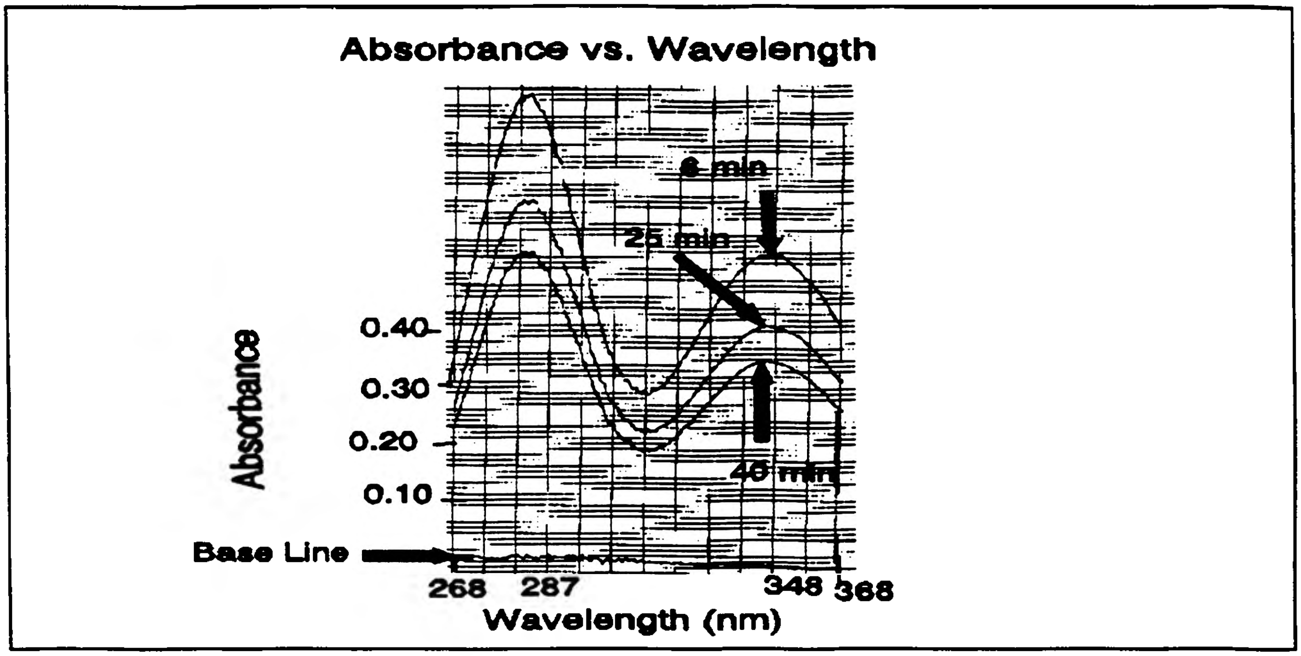

Figure 7. Absorbance spectrograph for Trial 1.

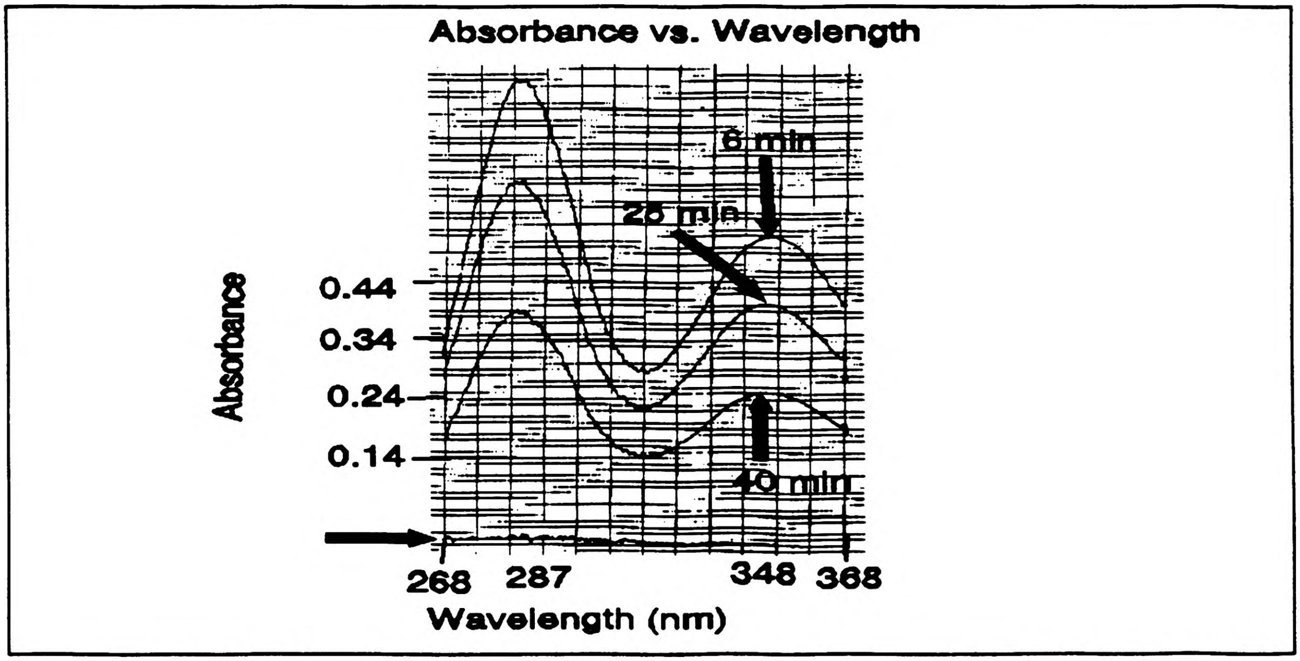

Figure 8. Absorbance spectrograph for Trial 2.

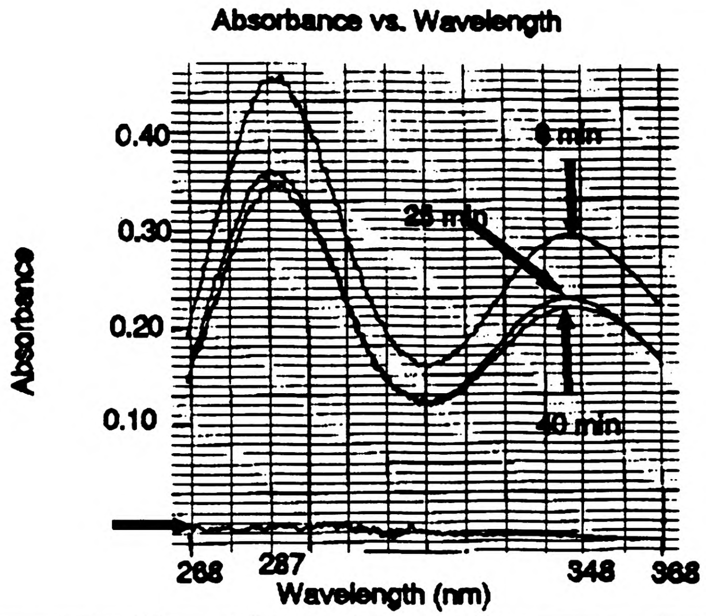

Figure 9. Absorbance spectrograph for Trial 3.

Kinetics(Metal ions).

Table III contains the data obtained in this part of the project. Again, by comparing the absorbance at 6 min, on can see that the reaction proceeds faster in the copper solution and the slowest in the zinc solution. This data suggests that NTA chelates the most with zinc, and the least with copper. The absorbance spectrographs for calcium, copper, lead, and zinc are contained in Figures 10, 11, 12, and 13 respectively.

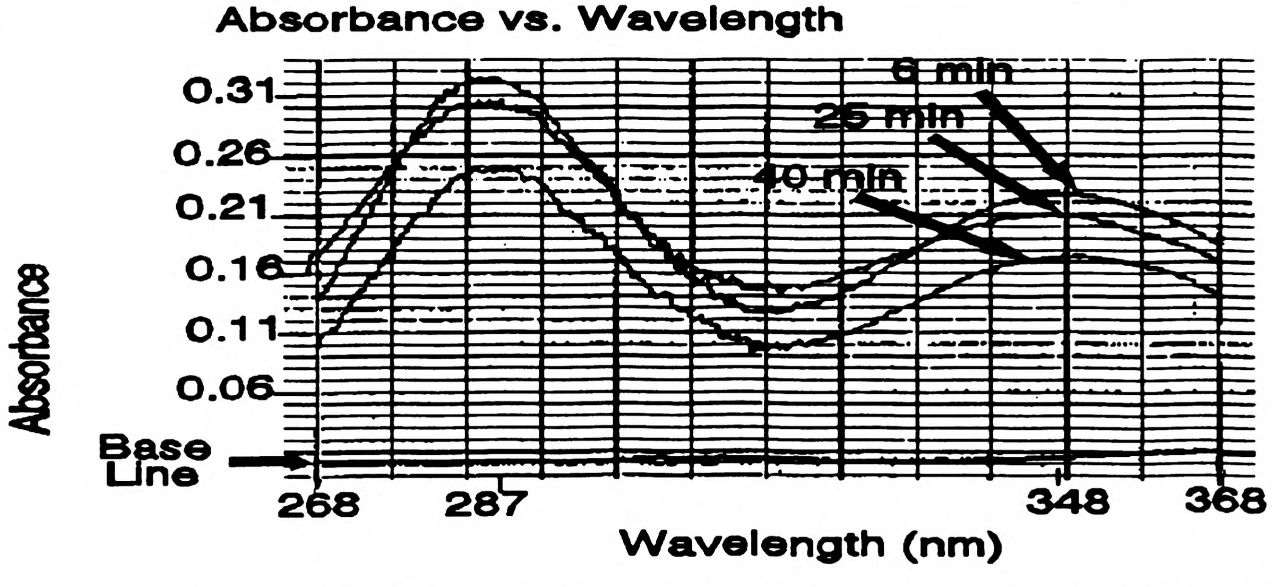

Figure 10. Absorbance spectrograph of calcium solution.

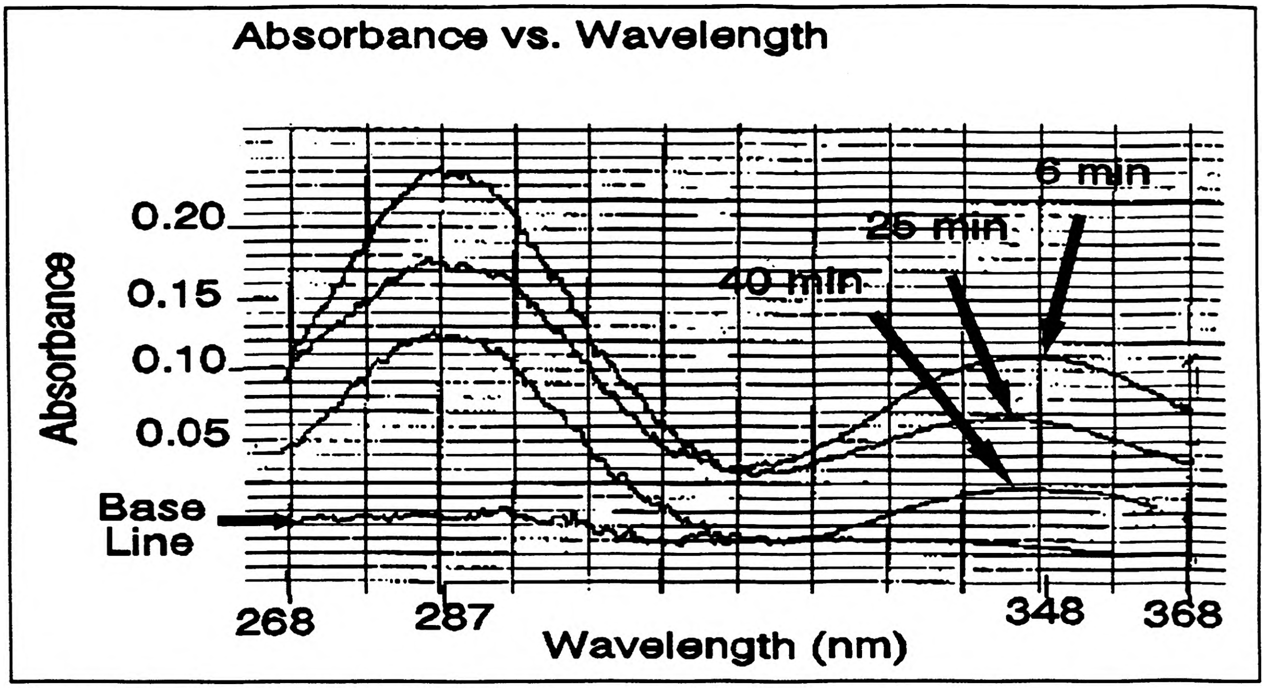

Figure 11. Absorbance spectrograph of copper solution.

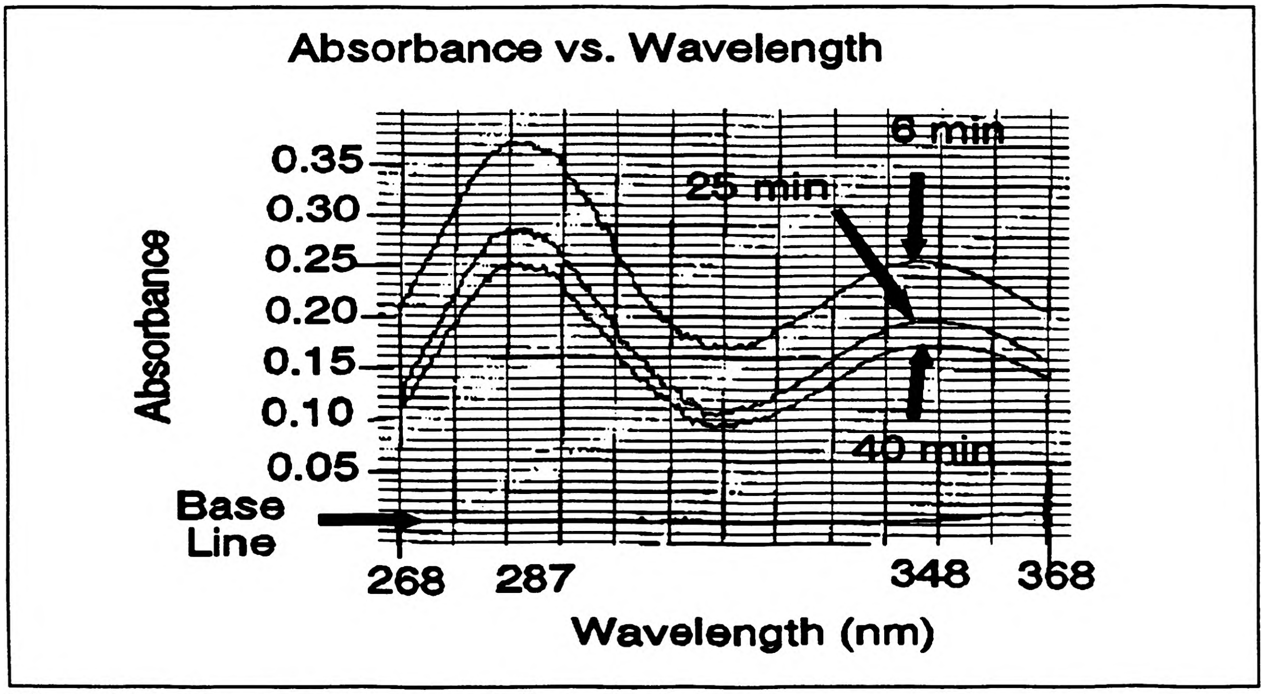

Figure 12. Absorbance spectrograph for lead solution.

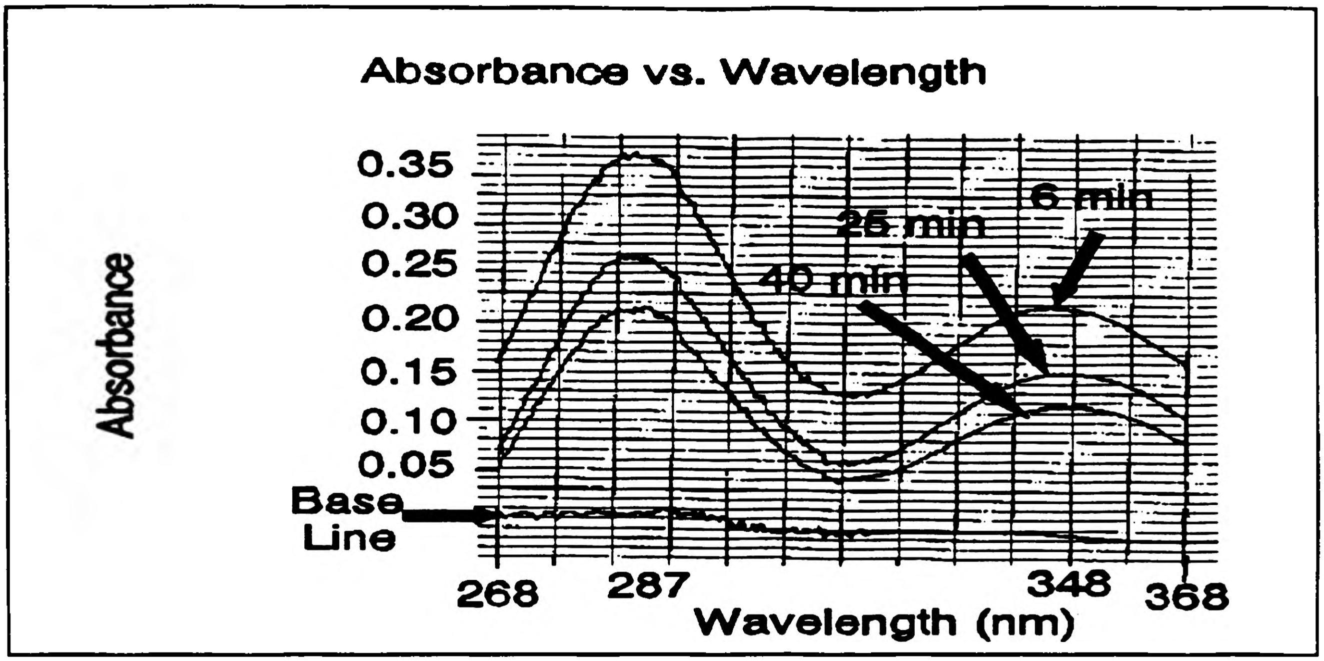

Figure 13. Absorbance spectrograph for zinc solution.

TABLE III. Data obtained from the metal ion experiment.

Metal	Absorbance at 348 nm			Absorbance at 287 nm		
	6 min	25 min	40 min	6 min	25 min	40 min
calcium	0.213	0.195	0.160	0.322	0.302	0.249
copper	0.130	0.086	0.037	0.240	0.175	0.126
lead	0.253	0.195	0.170	0.370	0.282	0.250
zinc	0.222	0.155	0.122	0.360	0.255	0.200

CONCLUSION.

The products of the reaction of NTA and NaOCl are CO_2 and IDA. The reaction proceeds faster at lower pHs. NTA chelates more with zinc than with lead, calcium, and copper. A mechanistic picture of the reaction was described by Hanna[4]. Figure 14 shows a revised mechanistic picture based on the results of this experiment. The hypochlorite attacks NTA providing IDA, CO_2, and formaldehyde. Through this project the presence of IDA and CO_2 has been confirmed. The logical step in proving this mechanism is to test for the presence of formaldehyde.

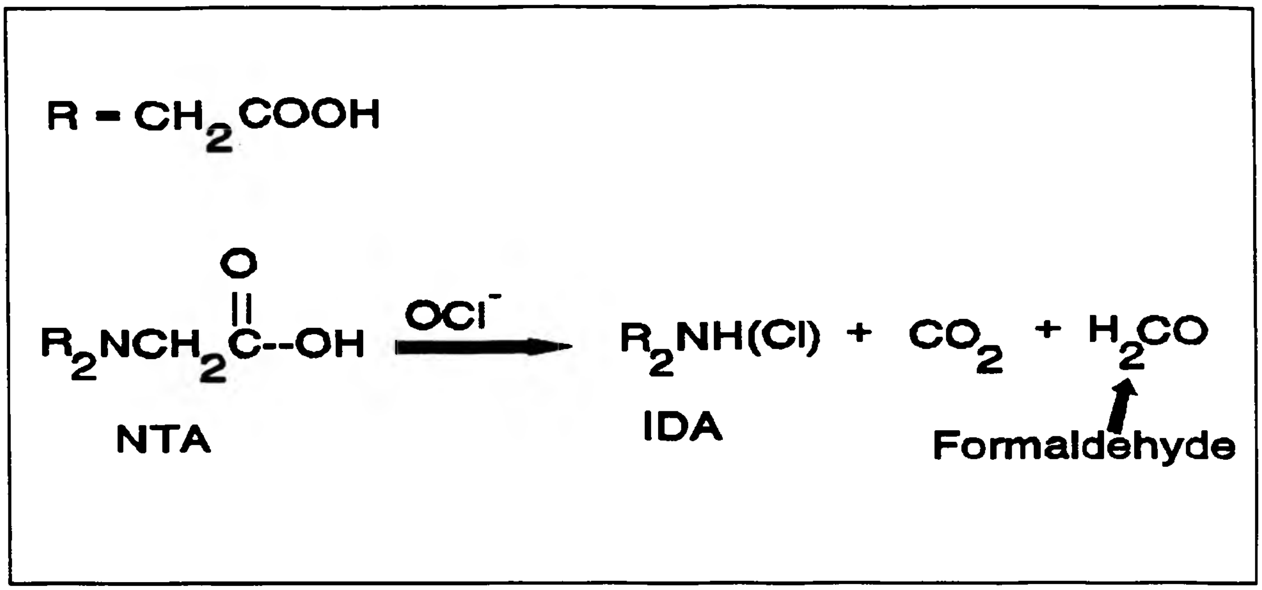

Figure 14. Mechanistic picture of the reaction between NaOCl and NTA.

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to Dr. Samir Hanna for his guidance and assistance during the entire project, Dr. Patricia Callahan for the use of the metal ion solutions, the Chemistry Department at the University of Missouri-Rolla for the use of the gas chromatograph and the spectrophotometer, and the Board of Directors of the Opportunities for the Undergraduate Experience Program (OURE) for the funding which made this project possible.

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