Flammable Gas Safety Program

Mechanisms of Gas Generation from Simulated SY Tank Farm Wastes: FY 1994 Progress Report

Report Contributors:

E. Kent Barefield
David Boatright
Abhay Deshpande
Fabio Doctorovich

Charles L. Liotta
Henry M. Neumann
Sean Seymore

Prepared for Pacific Northwest Laboratories under contract
252368-A-F1

School of Chemistry and Biochemistry
Georgia Institute of Technology
Atlanta, Georgia 30332-0400

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Table of Contents

Table of Contents	ii
Acronyms and Abbreviations	iv
Summary	v
List of Tables	viii
List of Figures	ix
1.0 Introduction	1
2.0 Analysis of ammonia in the condensed phase	1
2.1 Experimental	3
2.1.1 Preparation of standard solutions	3
2.1.2 Estimation of ammonia after thermal degradation of HEDTA	3
3.0 Initiation of long term studies of HEDTA decomposition in stainless steel vessels	4
3.1 Results	5
3.1.1. Products of HEDTA decomposition	5
3.1.2. Redox Analysis	7
3.2 Experimental	7
3.2.1. Preparation of simulated waste solution (SY1-SIM-91B-NC)	7
3.2.2. Pretreatment of stainless steel vessels	8
3.2.3 Reactions of HEDTA in simulated waste ("C" runs)	8
3.2.4 Analysis of the samples by gas chromatography (GC)	9
3.2.5. Calculation of the amount of total gas produced	12
3.2.6. Calculation of the amounts of the individual gases produced	13
3.2.7 Analysis of samples by ion chromatography	14
3.2.8 NMR analyses	14
4.0 Development of kinetic models for decomposition of glycolate and HEDTA	15
4.1 A cage model for predicting ratios of gaseous products formed from glycolate	15
4.1.1 The cage effect	15
4.1.2 Lifetimes of intermediates	16
4.1.2a Trans-hyponitrite ion, $N_2O_2^{2-}$	16
4.1.2b Hyponitrite ion, $N_2O_3^{2-}$	17
4.1.2c Formohydroxamic acid	17
4.1.2d Hydroxylamine, NH_2OH	17
4.1.3 Quantitative applications of the model to glycolate decomposition	19
4.1.4 Implications of the cage model for HEDTA	21
4.2 Analysis of rate data for HEDTA	23
4.2.1 Equations applicable to consecutive first-order reactions	23
4.2.1a Application to data at 90 °C	24
4.2.1b Application to data at 120 °C	24
4.2.2 Case in which an additional product G is formed	26
4.2.2a Application to gases from HEDTA at 90 °C	28
4.2.2b Application to gases from HEDTA at 120 °C	30
4.2.3 Activation Energies	30
4.3 Analysis of the rate of reaction of HEDTA	35
4.3.1 Auto-catalysis mechanism	37
4.3.2 "Two-exponential" model	40

4.3.2a	Is there a possible "two-exponential" model for HEDTA?	40
4.3.2b	Preparation of HEDTA-lactone	41
5.0	^{27}Al NMR study of the composition of basic solutions of 1:1 mixtures of HEDTA and aluminum(III)	41
6.0	References	46

Acronyms and Abbreviations

ED3A	ethylene diamine triacetic acid, $\text{HO}_2\text{CCH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$
HEDTA	hydroxyethylethylenediamine triacetic acid, $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$
IDA	iminodiacetic acid, $\text{HN}(\text{CH}_2\text{CO}_2\text{H})_2$
S-EDDA	ethylenediamine-N,N'-diacetic acid, $\text{HO}_2\text{CCH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CO}_2\text{H}$
TMS	tetramethylsilane, $(\text{CH}_3)_4\text{Si}$
U-EDDA	ethylenediamine-N,N'-diacetic acid, $\text{H}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$
101-SY	waste storage tank SY-101
atm.	atmosphere
$e_{\text{oxid.}}$	electrons produced by oxidation
$e_{\text{red.}}$	electrons produced by reduction
FY	fiscal year
GC	gas chromatography
IC	ion chromatography
Meas.	measured
NMR	nuclear magnetic resonance
Ref.	reference
Ret. Time	retention time
r.t.	room temperature
S.M.	starting material
SY1-SIM-91B	simulated waste
SY1-SIM-91B-NC	simulated waste without added carbonate
Temp.	temperature

Summary

This is the final report for work done at Georgia Tech during Fiscal Year 1994. The objectives of this work were to develop a better understanding of the mechanism of formation of flammable gases in the thermal decomposition of metal complexants, such as HEDTA and sodium glycolate, in simulated SY waste mixtures. This project is a continuation of work begun under earlier contracts with Westinghouse Hanford Co. Three major areas are discussed: development of a reliable analysis for dissolved ammonia, the initiation of long term studies of HEDTA decomposition in stainless steel vessels and product analyses through 3800 h, and further consideration of product analyses and kinetic data reported in FY 1993 for decomposition of HEDTA and sodium glycolate in Teflon-lined glass vessels. A brief exploration was also made of the speciation of aluminum(III) in the presence of HEDTA as a function of pH using ^{27}Al NMR.

Analysis of ammonia in the condensed phase.

A protocol was developed for the analysis of ammonia produced in the thermal decomposition of HEDTA in simulated waste media. The procedure utilizes Nessler's reagent for the spectrophotometric determination of ammonia and is applicable in a concentration range of about 10^{-5} to 5×10^{-4} M using 1 cm cells. At higher concentrations the colloidal chromophore is unstable to precipitation. Nessler's reagent is easily prepared and is also commercially available.

Long term studies of HEDTA decomposition in stainless steel vessels.

Experimental limitations in prior studies at Georgia Tech of HEDTA decomposition in simulated waste media have restricted product analyses to either the gas phase or condensed phase in a given experiment. To remove the limitations on product analyses and to improve their statistics a new experimental setup was designed and constructed. The first experimental run, decomposition of HEDTA at 90 °C, was initiated on 4/20/94 with an anticipated run time of 7000 h. The new experimental setup, analytical procedures, methods of data treatment, and data through 1818 h for reaction of HEDTA at 90 °C under an argon atmosphere are given. Additional experiments at other temperatures have also been initiated; results from these will be reported in the next fiscal year. It is anticipated that when these studies are concluded the data may allow for a detailed kinetic description of the decomposition process and the calculation of more reliable activation energies than those that are presently available for both loss of HEDTA and for formation of the gaseous products.

Development of kinetic models for decomposition of glycolate and HEDTA.

Several models have been examined during the year to account for the kinetics of the reactions of both glycolate and HEDTA. Initially, these models were based upon data that was acquired during the latter part of the 1992-93 fiscal year and reported with minimal interpretation in the annual report for this period. The model for HEDTA was refined and modified in an effort to account for the experimental data obtained with the

stainless steel vessels described in Section 3 of the current report. The first model developed attempts to deal with the remarkable difference in the hydrogen/nitrogen gas (nitrogen and nitrous oxide) product ratio observed in the thermal decomposition of glycolate at 90 °C compared to the ratio observed at 120 °C. At 120 °C the major gas obtained is hydrogen, whereas at 90 °C the major gas is nitrogen. This difference is rationalized on the basis of a model that involves competition between the reaction of aldehyde (formaldehyde or glyoxalate) and NO^- within the solvent cage in which they are initially formed, while they still constitute a spin coupled singlet pair, and reactions of these species that occur after diffusion from the solvent cage. On the basis of this model, the primary difference in these systems at the two temperatures is the viscosity of the medium. Extrapolation of this model to 60 °C would predict that the amount of hydrogen formed from glycolate would be very small since the viscosity of the medium should be even higher. An evaluation of the probable lifetimes of the various nitrogen species that are predicted to be involved as intermediates in the reduction of nitrite, based upon the available literature data is included as part of this discussion.

The decomposition of HEDTA represents a more complicated situation and application of the cage model to its decomposition has not yet been attempted. Among the complications that limit the direct application of the model to HEDTA is that the initial fragmentation of the hydroxyethyl group involves production of two moles of formaldehyde to only one of NO^- . It should be noted, however, that the yield of hydrogen is still significantly lower than for glycolate. Never-the-less, there is a marked increase in the ratio of hydrogen to nitrogen gases upon increasing the temperature from 90 °C to 120 °C that must be accounted for by a satisfactory model.

An analysis of rate data for the decomposition of HEDTA at 90° C and 120° C has been made assuming that the decomposition of HEDTA is first-order in HEDTA with rate constant k_1 and that the decomposition of ED3A is first-order in ED3A with rate constant k_2 . This analysis allows the calculation of half-lives for HEDTA of 3,350 h and 587 h at 90 °C and 120 °C, respectively, and half-lives for ED3A of 13,000 h and 4472 h at 90 °C and 120 °C, respectively. Application of the Arrhenius equation to these data permit the calculation of activation energies of 16 kcal/mol for the decomposition of HEDTA and 10 kcal/mol for the decomposition of ED3A. From these activation energies, half-lives for the decomposition of HEDTA and ED3A of 3.0 y and 5.3 y, respectively, are calculated at 60 °C.

The analysis referred to above assumed that the decomposition of HEDTA in simulated waste was simply pseudo first-order in HEDTA, i.e., a plot of $\ln[\text{HEDTA}]$ vs time should be linear. However, in the two sets of experiments for which the most data are available, plots of $\ln[\text{HEDTA}]$ vs time show curvature. Two possible models that could account for this behavior, an auto-catalysis model and a two-exponential model, are considered from a mathematical point of view. One possible two-exponential model that would fit the data is one in which HEDTA exists in two interconvertible forms not distinguishable as such by the analytical methods used for its determination. From a practical point of view it is not clear what two forms of HEDTA might exist under tank or simulated waste conditions. In principle, HEDTA could be in equilibrium with its lactone although lactones are not normally found to be stable under basic conditions. That this

is also the case for HEDTA lactone was determined using ^1H NMR to monitor the stability of an authentic sample of the lactone in aqueous base.

^{27}Al NMR studies of HEDTA-aluminum(III) as a function of pH.

The possibility that a portion of the aluminum in waste mixtures is present as an HEDTA complex has been suggested on several occasions. To explore this possibility, ^{27}Al NMR spectroscopy has been used to examine the speciation of $\text{Al}(\text{NO}_3)_3$ under various pH conditions in the presence and absence of HEDTA. Although the broadness of the ^{27}Al resonance makes NMR a relatively insensitive method for detection of low concentrations of aluminum species, the similarity of the NMR spectra obtained at high pH values in the presence and absence of HEDTA suggests that little, if any, aluminum is present as an HEDTA complex under these conditions.

List of Tables

3.1	Reaction of HEDTA in simulated waste	5
3.2	Comparison of total moles of gas vs. $H_2+N_2+N_2O$	7
3.3	Redox calculation for the reaction HEDTA-1C	7
3.4	Reproducibility of the analysis of gas samples by gas chromatography (same sample, different runs)	12
3.5	Reproducibility of the analysis of gas samples by gas chromatography (different samples)	12
3.6	Gas responses and retention times for different gases	14
4.1	Estimated half-lives in 2 M NaOH at various temperatures	16
4.2	Effect of $[OH^-]$ on the ratio of N_2/N_2O formed from NH_2OH	18
4.3	Amounts of gases produced from thermal decomposition of glycolate in simulated waste at 90 °C under argon	20
4.4	Amounts of gases produced from thermal decomposition of glycolate in simulated waste at 120 °C under argon	20
4.5	Products from HEDTA decomposition at 120 °C	25
4.6	Value of t at which $(1-e^{-kt})-kt > 0.1(1-e^{-kt})$ for certain values of k	27
4.7	Activation energies and rate constants calculated at 60 °C	35
4.8	Comparison of measured and calculated concentrations of HEDTA at 120 °C using both two-exponential and auto-catalysis models	39
4.9	Comparison of measured and calculated concentrations of HEDTA at 90 °C using both two-exponential and auto-catalysis models	39

List of Figures

2.1	(a) Absorption spectrum of solution prepared by diluting 0.3 mL Nessler reagent to 10 mL with distilled water. (b) Absorption spectrum of solution prepared by diluting 5 mL 4.2×10^{-4} M ammonia and 0.3 mL Nessler reagent to 10.0 mL	1
2.2	Absorbance vs. $[\text{NH}_3]$ at (a) 450 nm, (b) 475 nm, and (c) 500 nm; 1st and 2nd runs refer to duplicate experiments described in text	2
3.1	Reaction of HEDTA in simulated waste. Products in solution (Trial: HEDTA-1C)	6
3.2	Reaction of HEDTA in simulated waste. Gaseous products (Trial: HEDTA-1C)	6
3.3	Apparatus for gas sampling	10
3.4	Gas sampling valve	11
4.1	Experimental yield of H_2 from glycolate in simulated waste at 90°C as a function of time (circles) compared to that calculated from the expression $P_t = P_\infty(1 - e^{-kt})$ where $P_\infty = 31$ and $k = 7.8 \times 10^{-4} \text{ h}^{-1}$	22
4.2	Experimental yields of H_2 (circles) and $(\text{N}_2 + \text{N}_2\text{O})$ (triangles) from glycolate decomposition in simulated waste at 120°C as a function of time compared to that calculated from the expression $P_t = P_\infty(1 - e^{-kt})$. For H_2 , $P_\infty = 60$ and $k = 2.5 \times 10^{-3} \text{ h}^{-1}$. The curve for $(\text{N}_2 + \text{N}_2\text{O})$ was calculated using the same value of k as for H_2	22
4.3	Experimental yield of H_2 from HEDTA in simulated waste under argon at 90°C as a function of time (circles). Curve A is the function $P_1(1 - e^{-k_1t})$ where $P_1 = 3.7$ and $k_1 = 2.07 \times 10^{-4} \text{ h}^{-1}$. Curve B is the function $P_1(1 - e^{-k_1t}) + P_2(1 - e^{-k_2t})$ where $P_1 = 1$, $P_2 = 10.5$, $k_1 = 2.07 \times 10^{-4} \text{ h}^{-1}$, and $k_2 = 5.3 \times 10^{-5} \text{ h}^{-1}$	29
4.4	Experimental yield of N_2 from HEDTA in simulated waste under argon at 90°C as a function of time (circles)	31
4.5	Experimental yield of H_2 from HEDTA in simulated waste under argon at 120°C as a function of time (circles)	32
4.6	Experimental yield of $(\text{N}_2 + \text{N}_2\text{O})$ from HEDTA in simulated waste under argon at 120°C as a function of time (circles)	33
4.7	Plot of $\ln[\text{HEDTA}]$ versus time for decomposition of HEDTA at 90°C under an argon atmosphere (lower plot) and 120°C under an air atmosphere (upper plot). Note that the time axis scales are different for the two plots	36
5.1	^{27}Al NMR spectra of solutions containing 0.5 M $\text{Al}(\text{NO}_3)_3$ and 0.52 M HEDTA and sufficient NaOH to adjust the pH to the desired range. The spectra shown as insets are recorded at 27 times the gain of the other spectra. The reference is external $\text{Al}(\text{OH}_2)_6^{3+}$. Measured values of the pH are shown for each spectrum.	43
5.2	^{27}Al spectra of solutions containing 0.5 M $\text{Al}(\text{NO}_3)_3$ and sufficient NaOH to adjust the pH to the desired range. The reference is external $\text{Al}(\text{OH}_2)_6^{3+}$. Measured values of the pH are shown for each spectrum	44
5.3	^{27}Al NMR spectrum taken on water versus an external $\text{Al}(\text{OH}_2)_6^{3+}$ standard. Both the full spectrum and the spectrum in the inset were taken at the same gain values as those in Figures 5.1 and 5.2. The broad resonance centered at ca. 50 ppm is due to the probe	45

1.0 Introduction

The objectives of this work are to develop a better understanding of the mechanism of formation of flammable gases in the thermal decomposition of metal complexants, such as HEDTA and sodium glycolate, in simulated SY waste mixtures. This report summarizes the results of work done at Georgia Tech in FY 1994, and is a continuation of work begun under earlier contracts with Westinghouse Hanford Co. Three major topics will be discussed: development of a reliable analysis for dissolved ammonia, the initiation of long term studies of HEDTA decomposition in stainless steel vessels and product analyses through 3800 h, and further consideration of product analyses and kinetic data reported in FY 1993¹ for decomposition of HEDTA and sodium glycolate in Teflon-lined glass vessels. A brief study was also made of the speciation of Al(III) in the presence of HEDTA as a function of pH using ²⁷Al NMR spectroscopy.

2.0 Analysis of ammonia in the condensed phase.

A critical aspect to the development of a mechanistic model for the formation of ammonia is the determination of the stoichiometry of its formation. To determine the stoichiometry, a reliable, preferably rapid, method for making a reasonably accurate estimation of the amount of ammonia formed is required. After consideration of several of the known methods for determination of ammonia, we focussed on the use of Nessler's reagent, basic HgI_4^{2-} , which is both easily prepared² or commercially available,³ for generation of a chromophore that can be detected by visible spectrophotometry. Ammonia reacts quantitatively with the Nessler reagent according to equation 2.1⁴ to produce an intensely colored colloid that absorbs in the 400-500 nm range⁵ (Figure 2.1),

Figure 2.1. (a) Absorption spectrum of solution prepared by diluting 0.3 mL Nessler reagent to 10 mL with distilled water. (b) Absorption spectrum of solution prepared by diluting 5 mL 4.2×10^{-4} M ammonia and 0.3 mL Nessler reagent to 10:0 mL.

Figure 2.2. Absorbance vs. $[\text{NH}_3]$ at (a) 450 nm, (b) 475 nm, and (c) 500 nm; 1st and 2nd runs refer to duplicate experiments described in text.

and whose absorbance follows the Beer-Lambert law at 450, 475 and 500 nm (Figure 2.2). Figure 2.2 shows plots of duplicate runs using independently prepared solutions of each concentration of ammonia. The method is very sensitive to small concentrations of ammonia $\geq 1 \times 10^{-5}$ M but is limited to about 5×10^{-4} M at the high end because of the instability of the colloid, which rapidly precipitates. Because of the colloidal nature of the chromophore, a protocol was utilized in which the absorbance of solutions was measured at a carefully determined time interval after generation of the colloid.

Extrapolation of the method to analysis of ammonia in HEDTA reaction mixtures must take into account the effects of unreacted HEDTA and its fragmentation products on the stability of both the Nessler reagent and the colloid formed with ammonia. Treatment of 1 mL of approximately 0.1 M solutions of HEDTA, glycine, IDA, and s-EDDA with 0.5 mL of Nessler reagent gave no color or precipitate. One species that will interfere is hydroxylamine. The Nessler method has been applied to the determination of hydroxylamine. The color of the product is very dark and is markedly different from that observed with ammonia. Since we suspect that hydroxylamine may be an intermediate in the formation of products derived from nitrite there is the potential for interference. However, nothing is known about the lifetime of hydroxylamine or the levels to which it might build up during these thermal reactions. Viewed more positively, the Nessler reagent may provide a means for detecting hydroxylamine if it persists.

Tests of reactions of Nessler reagent with standard solutions of ammonia in simulated waste mixtures indicated that Nessler reagent (HgI_4^{2-}) is destroyed by HEDTA and sufficient reagent must be added to samples such that enough remains to react with all of the ammonia that is present. Extensive tests of dilution and ratio of Nessler reagent to HEDTA required were performed to develop the protocol given below, which we believe gives reliable values. It should be emphasized that the procedure employs a calibration curve prepared using ammonia solutions of known concentration prepared in SY1-SIM-91B medium. The dilution factor of the simulated waste in the solutions used for preparation of the calibration curve is kept the same as that for the sample solution.

2.1 Experimental

2.1.1. Preparation of standard solutions. Solutions for the preparation of a calibration curve for determination of HEDTA in simulated waste reaction mixtures were prepared as follows: 5.0 mL of a SY1-SIM-91B solution (0.20 M in HEDTA) was diluted to 100 mL. Next, to 5.0 mL each of the ammonia solutions with varying concentrations (5.0×10^{-5} M, 1.0×10^{-4} M, 2.1×10^{-4} M, 4.2×10^{-4} M, 6.4×10^{-4} M, and 9.5×10^{-4} M) was added 1.0 mL of the diluted SY1-SIM-91B solution. Finally, 1.0 mL of Nessler reagent (prepared as described in reference 2) was added to each of these six solutions, and the total volume was made up to 10 mL. Absorbancies were measured at 450 nm, after allowing each solution to stand for 5.0 min following addition of the Nessler reagent.

2.1.2. Estimation of ammonia after thermal degradation of HEDTA. As described in section 3.2.7, after completion of gas analyses on an HEDTA sample, the reaction

mixture was rinsed from the reaction vessel and diluted to 100 mL to give a "stock solution". The following procedure utilized this stock solution. Five mL of the stock solution was further diluted to 50.0 mL. For absorbance measurements, 5.0 mL of this "doubly diluted" solution was combined with 1.0 mL of Nessler Reagent, and the total volume made up to 10.0 mL. This resulted in an overall dilution of the reaction mixture of 200 (a dilution of 125 had been used earlier⁶). Absorbancies were measured at 450 nm, and using the calibration curve described above, were converted to the amount of ammonia generated. This is expressed as moles formed per 100 mole of HEDTA.

3.0 Initiation of long term studies of HEDTA decomposition in stainless steel vessels.

Experimental limitations in prior studies of HEDTA decomposition have restricted product analyses to either the gas phase or condensed phase in a given experiment. To remove the limitations on product analyses and to improve their statistics a new experimental setup was designed and constructed. The first experimental run, decomposition of HEDTA at 90 °C, was initiated on 4/20/94 with an anticipated run time of 7000 h. The following sections describe the new experimental setup, analytical procedures, methods of data treatment, and reports the data through 1818 h for reaction of HEDTA at 90 °C under an argon atmosphere. Additional experiments at other temperatures have also been initiated; results from these will be reported at a later time. It is anticipated that when these studies are concluded the data may allow for a detailed kinetic description of the decomposition process and the calculation of more reliable activation energies than are presently available for both loss of HEDTA and for formation of the gaseous products.

The new experimental design for long-term decomposition studies employs 30 mL, 316 stainless steel cylinders as reaction vessels in place of the Teflon-lined glass reaction vessels used previously.⁷ The cylinders are fitted with a valve that allows attachment to a gas handling system and direct sampling for gas chromatography without the use of syringes (see Figure 3.3 in the experimental section). In earlier studies samples were taken from the reactor using a gas-tight syringe and injected into the GC. Contamination of the sample by air was frequently a problem that required correction of the measurements for nitrogen, a potential source of error. Also the temperature differences between various parts of the reactor required acquisition and analysis of multiple samples and the use of a complicated scheme to account for variations in gas composition in the various temperature zones. These problems are eliminated by the present system. Also the use of sealed cylinders as reaction vessels eliminates any loss of water from the reaction zone, which was an obvious problem with the Teflon-lined glass reaction vessels where water evaporated and then condensed between the Teflon liner and the wall of the container. This resulted in concentration of the reaction mixture and introduced an uncertainty in any analysis of the kinetics of the reaction. Thus, the accuracy and reproducibility of the determinations have been significantly improved. A possible disadvantage could be that reaction rates are affected by the presence of metal ions that are leached from the cylinder such that the new data might not be comparable with that obtained previously. A qualitative analysis of a 4 M NaOH solution kept in the vessel at 100 °C for 3 days showed the presence of iron.

3.1 Results

3.1.1. Products of HEDTA decomposition. Table 3.1 records the analytical results for decomposition of HEDTA at 90 °C through 1818 h. Each quantity is the average of two values measured on independent samples taken at each time. Measurements made by gas and ion chromatography were done in duplicate and the results averaged; those done by NMR spectroscopy were made from a single determination of the spectrum. Differences in values for the two independent samples were invariably much greater than the differences in the duplicate measurements and determine the errors indicated in the table. The total amount of gas produced was independently measured. A comparison of this value (total moles of gas) with the amount $H_2+N_2+N_2O$ is shown in Table 3.2. These values are in good agreement within the error limits of the measurements, except at 160 h. This indicates that all significant gas phase products have been accounted for by the individual analyses. Methane is not a detectable product. Plots of the production of products vs time are shown in Figures 3.1 and 3.2.

Table 3.1. Reaction of HEDTA in simulated waste
(Experiment HEDTA-1C: SY1-SIM-91B-NC,^a 90 °C, Ar, stainless steel vessels)^b

Time (h)	0	160	618	1123	1818
HEDTA (NMR) ^c	100	98.0±2.5	93.4±0.5	85.8±0.5	68.1±5.0
HEDTA (IC)	100	99.5±0.9	92.4±3.3	83.8±1.9	71.4±2.4
ED3A	0	1.5±0.5	8.1±1.0	17.3±1.5	24.9±3.3
$C_2O_4^{2-}$	0	trace	1.4±0.5	3.1±0.3	4.0±0.2
HCO_2^- (NMR)	0	trace	17.4±1.3	33.5±2.5	50.8±7.1
HCO_2^- (IC) ^d	0	5.6±2.4	16.2±1.9	32.5±3.8	47.2±5.7
H_2	0	0.04±0.01	0.15±0.03	0.22±0.02	0.44±0.09
N_2	0	0.6±0.1	2.5±0.4	5.4±0.5	7.7±1.1
N_2O	0	1.6±0.2	4.7±0.4	10.1±1.6	17.2±3.9
NH_3 (aq.)	0	1.1±0.3	5.3±0.6	13.3±2.0	19.1±1.3

^aSY1-SIM-91B-NC refers to the SY1-SIM-91B simulant described by Herting⁸ except that carbonate has been eliminated from the formulation. ^bAll results are expressed in moles of product per 100 moles of starting HEDTA. ^cThe initial concentration of HEDTA (as determined by 1H NMR spectroscopy) was 0.197 M. ^dA peak with the same retention time as formate (corresponding to 6.1±1.4% formate) was detected at time=0. All the ion chromatographic determinations of HCO_2^- were obtained by subtracting this amount.

As indicated previously this experiment is scheduled to run for a period of 7000 hours; at this time values at nine different times will have been determined. Upon conclusion of the experiment the data will be evaluated using a kinetic analyses similar to those described in a subsequent section.

Figure 3.1. Reaction of HEDTA in simulated waste. Products in solution (Trial: HEDTA-1C)

Figure 3.2. Reaction of HEDTA in simulated waste. Gaseous products (Trial: HEDTA-1C).

Table 3.2. Comparison of total moles of gas vs. $H_2+N_2+N_2O$.^a

Time (hours)	Total Moles of Gas	$H_2+N_2+N_2O$
160	0.8±0.3	2.2±0.2
618	5.8±1.2	7.3±0.4
1123	13.4±1.6	15.7±1.6
1818	29.2±3.5	25.3±3.9

^aAll results in moles of gas per 100 moles of starting HEDTA.

3.1.2. Redox analysis. If all of the products of HEDTA decomposition have been accounted for, then the total moles of electrons available from oxidative processes should exactly equal those used in reductive processes.⁹ According to this procedure, the total moles of electrons produced by oxidation of known reactants (HEDTA and ED3A) can be calculated and compared to the total number of electrons consumed in formation of the reduction products. Table 3.3 shows the results obtained for reaction HEDTA-1C.

Table 3.3. Redox calculation for the reaction HEDTA-1C.

Time (h)	$e_{\text{oxid.}}$ (mol/ mol HEDTA)	$e_{\text{red.}}$ (mol/ mol HEDTA)	$\Delta(e_{\text{red.}}-e_{\text{oxid.}})$ (mol/ mol HEDTA)
160	0.17	0.17	0
618	0.61	0.56	-0.05
1123	1.24	1.53	0.29
1818	1.79	2.31	0.52

Table 3.3 indicates that there is an increasing discrepancy between the number of electrons utilized in reductive pathways and that produced by known oxidative processes. Thus it appears that some oxidation product(s) has not been accounted for. The identity of this product(s) is not clear at this stage, but carbonate is a possibility. The former has been proposed as a product of the reaction (see earlier global mechanism for the reaction of HEDTA in simulated waste¹⁰). A pathway for the formation of nitrate has not yet been proposed.

3.2 Experimental

3.2.1. Preparation of simulated waste solution (SY1-SIM-91B-NC). The simulated waste mixture used in these experiments differs from that used previously (SY1-SIM-91B) in that sodium carbonate has not been included. This component was deleted to facilitate dissolution of the components. The new composition has been designated SY1-SIM-91B-NC, where NC stands for "no carbonate". The waste mixture was prepared in a polypropylene Erlenmeyer flask with vigorous stirring by a Teflon coated

magnetic stirring bar at room temperature. For preparation of a 250 mL portion, 125 mL of distilled water was placed in the flask and the various solutes were added in the following order: sodium hydroxide (20.0 g), sodium aluminate (36.5 g),¹¹ sodium nitrate (55.0 g), sodium nitrite (38.6 g) and HEDTA (20.0 g, 52.5 mmol). The addition of each component was done only after the previous component had dissolved completely. Approximately 25 mL of water was added after the addition of sodium aluminate, and about 12 mL after the additions of sodium nitrite and of sodium nitrate. The solution was transferred to a 250 mL polypropylene volumetric flask and water added to the mark. Unless otherwise stated all solutions were prepared immediately prior to use.

3.2.2. Pretreatment of stainless steel vessels. New stainless steel vessels and valves were pretreated by immersing them in hexane at room temperature (r.t.) for at least one day to remove residual oil from the manufacturing process. They were removed from the hexane, drained, and allowed to dry at r.t. Then the cylinders were placed in a 2-propanol/KOH bath for at least one day at r.t., and the valves for 3-4 h. After removal from the bath all components were rinsed with water. The cylinders were then filled with 15 mL of 4 M NaOH and heated in an oil bath at 100 °C for at least two days. After that period of time they were washed with distilled water and allowed to dry at r.t. The NaOH solution, which was initially colorless, was green after the treatment. Addition of acidic KSCN solution to a portion of the basic wash solution produced a red color that is consistent with the presence of Fe(III).¹²

3.2.3 Reactions of HEDTA in simulated waste ("C" runs). Ten-mL aliquots of simulated waste were loaded into each of the stainless steel vessels by means of a polypropylene pipette (the total volume of each vessel was measured and was approximately 33 mL). Each cylinder was fitted with a stainless steel valve (see Figure 3.3) using Teflon tape as a sealant for the threads.

Each cylinder was connected in turn to a vacuum line ($\sim 10^{-1}$ mmHg) with a Swagelok fitting, evacuated for 10 to 15 sec, and then backfilled with argon. This procedure was repeated four times for each of the eighteen cylinders required such that two samples could be taken at each of nine reaction times (including zero time) over the anticipated 7000 h duration of the experiment. After the last argon filling, a valve connected to an oil bubbler was opened in order to vent excess argon and establish atmospheric pressure in the cylinder. After completion of this procedure the amount of air remaining in the headspace as determined by gas chromatography (following the procedure described below), was $\leq 0.5\%$ (mL of air per 100 mL of argon). This is a maximum value, since air could also be present in the gas sampling apparatus.

The samples were maintained at reaction temperature (90 °C) by immersing the stainless cylinders to 2/3 of their height in a Precision Scientific Co. constant temperature bath filled with approximately 25 L of Fisher high temperature bath oil. The bath was cubic with an inside dimension of ca. 15" and was heated by a 900 w resistance heater. The temperature was controlled by means of a 7500 Quick Set II adjustable thermoregulator, and measured with a mercury thermometer. The bath was stirred with a constant speed 1550 rpm motor equipped with a stainless steel propeller stirrer. The reactors were suspended by wires wrapped around the valves that were

hooked to metal rods laid across the top of the bath.

At each sampling time two cylinders were removed from the oil bath and allowed to stand at room temperature for two days in order to achieve equilibrium between the solution and the gas phase (this is particularly important for ammonia quantitation, since a good amount could be present in the gas phase at high temperature). After this time the samples were analyzed by gas chromatography, ion chromatography, and ^1H NMR spectroscopy by the procedures described below. The variability of the final value for each quantity that is reported in Table 3.1 is expressed as the absolute mean deviation D , defined by:

$$D = \frac{1}{n} \sum_{i=1}^n |x_i - \bar{x}|$$

where x_i is an individual value and $\bar{x}$ is the average of all values. For two data this expression reduces to $D = \frac{1}{2}(x_1 - x_2)$. In the cases where data were added (such as $\text{H}_2 + \text{N}_2 + \text{N}_2\text{O}$), the errors were approximated to the largest of the deviations.

3.2.4 Analysis of the samples by gas chromatography (GC). The cylinder valve is connected to the gas handling system (Figure 3.3) using a Swagelok fitting: After evacuation of the apparatus the cylinder valve is opened and the gas allowed to expand into the system. The sample can be expanded into gas sampling valves in either gas chromatograph by valves 3 and 4. Two different columns are being used in two different chromatographs as described earlier.^{13a} Valves 3 and 4 are connected to 0.25 mL sample loops in the chromatographs. The sample is introduced into the column by means of the gas sampling valve shown in Figure 3.4 (each chromatograph is outfitted with a valve). After each sample is taken the sample loop is filled with carrier gas (argon), and must be evacuated completely before performing the next analysis. This is done by opening valves 1 and 2. A complete step-by-step description of the procedure is provided below:

- 1 Connect cylinder to manifold by means of Swagelok union.
- 2 Turn vacuum pump on.
- 3 Open valves M, 3, 4, 5, 7, 8. The rest of the valves remain closed (keep 6 closed!).
- 4 After 1 or 2 minutes, close 7 and then M. Check for leaks by comparing the mercury level in the buret with the level in the left branch of the manometer. The mercury level should not go down noticeably after 5 minutes. If it does, a leak must be present (this generally happens in the Swagelok union from the cylinder to the tubing). Adjust the nut on the Swagelok union until no leak is observed.
- 5 Once the leak has been fixed, open valves 1, 2, M. Wait at least 5-10 minutes in order to allow the system to achieve good vacuum (0.1 mm Hg).
- 6 Close valves 1, 2, M. Open valve 6.

Figure 3.3. Apparatus for gas sampling.

- 7 Wait 5 minutes in order to achieve equilibration, close valve 5. At this point, determine the pressure inside the manifold by measuring the difference (in millimeters) between both branches of the manometer. This will be used for calculating the amount of total gas produced. Also, measure the gas volume shown by the level of mercury on the right side of the manometer (calibrated buret). This will be used for calculation of the total headspace volume.
- 8 Wait other 5 minutes in order to make sure that the GC loops are completely filled with sample.
- 9 Close valves 3 and 4.
- 10 Start GC runs. The valves will automatically turn on after 0.1 minutes and turn off after 1 minute. After that period of time, open valves 1 and 2 in order to evacuate the sample loops. Keep these valves open for at least 5 min.
- 11 Stop GC runs.
- 12 Close valves 1 and 2.
- 13 Open valves 3 and 4. Wait for at least 5-10 min in order to make sure that the sample loops are completely filled with gas sample.
- 14 Repeat steps 9 to 13 as many times as needed (usually two GC runs for each column are enough due to the high reproducibility of the method).

Figure 3.4. Gas sampling valve.

The reproducibility of the gas chromatographic method was tested several times. As an example, the areas of the sample peaks due to oxygen and nitrogen are shown for three different runs of the same air sample (Table 3.4). Table 3.4 indicates that the deviation of oxygen or nitrogen is less than 0.3%. The reproducibility was also tested for different air samples (Table 3.5). In this case, the deviation for oxygen is about 0.4 %, while the deviation for nitrogen is less than 0.1%. The amount of air present due to contamination, as determined for the cylinders at time = 0 by gas chromatography (following the procedure described below), was less than 0.5% (mL of air per 100 mL of

argon). As observed before, this is a maximum value, since part of that air could be due to contamination in the headspace of the reaction vessel.

Table 3.4. Reproducibility of the analysis of gas samples by gas chromatography (same sample, different runs).

Run #	O ₂ (area)	O ₂ (area, corrected) ^a	N ₂ (area)	N ₂ (area, corrected) ^a
1	97055	97055	279356	279356
2	94337	97167	272917	281104
3	91038	96692	263084	279357
Average		96971±186		279939±777

^aEach time the loop is filled the pressure in the apparatus decreases due to the amount of gas which has been used up for the analysis. Therefore, the area of the peak has to be corrected by the formula: area (corrected) = area(P_1/P_n), where P_1 is the pressure measured with the manometer for run #1, and P_n is the pressure measured with the manometer for run number n.

Table 3.5. Reproducibility of the analysis of gas samples by gas chromatography (different samples).

Sample #	O ₂ (area)	N ₂ (area)
1	96446	280114
2	96049	279681
3	97055	279356
Average	96583±356	279717±265

3.2.5. Calculation of the amount of total gas produced. The total volume of the cylinders was determined by completely filling two different cylinders with distilled water at r.t. and determining the mass of the contents. The volume was calculated by the formula $V_c = m/d$, where V_c is the volume of the cylinder (including the valve), m the weight of water, and d the density of water at r.t. (the density of the water used was approximated to that of degassed water). The determination performed with the two cylinders gave very similar values (33.25 ± 0.05 mL and 33.35 ± 0.05 mL) and the volume of all cylinders was assumed to be the average of these values. After the volume was determined, one of the two cylinders was filled with air at atmospheric pressure and then connected to the evacuated manifold (Figure 3.3), and the air allowed to expand into the apparatus. The total headspace of the manifold was calculated by the formula $V_m = P_a V_c / P_m$, where V_m is the volume of the manifold (headspace), P_a the atmospheric pressure (determined by using a Fortin barometer), V_c the volume of the cylinder, and P_m the pressure inside the manifold (measured with the mercury manometer). The headspace volume, V_o , defined as the volume of the manifold to the "zero" mark of the

buret (Fig. 3), was calculated by subtracting the buret volume, V_b , from V_m ($V_0 = V_m - V_b$). The calculation was done by using the equation:

$$G_{t(n)} = (P_{m(0)} - P_{m(n)})(V_0 + V_b - V_s)/RT$$

$G_{t(n)}$ = amount of total gas in moles for the sample at time= n

$P_{m(0)}$ = pressure (atm) inside the manifold for the sample at time= 0

$P_{m(n)}$ = pressure (atm) inside the manifold for the sample at time= n

R = gas constant (0.082 Latm/Kmol)

T = temperature (K)

V_0 = 88.8 ± 0.9 mL

V_s = volume of the reaction mixture (mL)

3.2.6. Calculation of the amounts of the individual gases produced. The gas chromatographic response (response factor) was obtained (in area/ μ mol) for each of the gases to be quantified. One of the calibrated cylinders was filled with the gas whose response factor was to be determined at a known concentration (such as 1% in helium) at atmospheric pressure and r.t., and allowed to expand into the manifold. The gas chromatogram was determined as described above and the response calculated by the formula:

$$Rp = (A)(R)(T)(H)/P_a V_L V_c [G]$$

Rp = response of the gas (area/ μ mol)

A = area of gas chromatographic peak

R = gas constant (0.082 L atm/mol K)

T = temperature (K)

H = total headspace volume ($V_0 + V_b$) (mL)

P_a = atmospheric pressure (atm)

V_L = volume of the GC sample loop (250 μ L)

V_c = volume of the cylinder (mL)

$[G]$ = concentration of the gas (mL/mL)

As an example, the calculation for nitrous oxide is as follows:

$$Rp = (1157 \text{ area})(0.082 \text{ L atm/K mol})(300 \text{ K})(118.9 \text{ mL}) / (0.965 \text{ atm})(250 \mu\text{L})(33.4 \text{ mL}) \\ (10^{-2} \text{ mL/mL}) = 41999 \text{ area}/\mu\text{mol}$$

The response factors used in all determinations of gaseous HEDTA decomposition products are shown in Table 3.6.^{13b}

The amount of each gas present in the samples, expressed in mole % of initial HEDTA, was calculated according to the formula:

$$\%G = ((V_0 - V_s + V_b) \cdot A) / (V_L \cdot R_p \cdot [\text{org}] \cdot V_s \cdot 10)$$

where %G is the amount of gas (moles/100 moles of starting organic material), V_s is the volume of the reaction mixture (mL), [org] is the initial concentration of the organic reactant (M), and the rest as described above. In calculating the total headspace ($V_0 - V_s + V_b$), it has been assumed that the reaction solution volume (V_s) is unchanged during the experiment.

Table 3.6. Gas responses and retention times for different gases.^{13b}

Gas	Ret. Time (min)	Response	% Error
H ₂	1.865	1326600±17600	1.3
O ₂	3.636	167600±600	0.4
N ₂	6.999	130600±300	0.2
N ₂ O	3.034	42480±410	1.0

3.2.7. Analysis of the samples by ion chromatography. The experimental procedure was very similar to that described earlier,¹⁴ and can be summarized as follows. Once the gas analyses for a sample were completed, the cylinder was removed from the manifold and the valve removed. The cylinder contents were transferred to a 100 mL volumetric flask and the cylinder was carefully washed several times with deionized water and the rinses added to the contents of the volumetric flask. The solution was then diluted to the 100 mL mark; this solution is referred to as the "stock solution" in the remainder of this report. Aliquots of the stock solution were further diluted in order to perform ion chromatographic analyses; 0.4 mL of the stock solution was diluted to 100 mL for analysis of the more concentrated species (formate, nitrite), and 3 mL of stock solution was diluted to 100 mL in order to quantify the species of lower concentration (HEDTA and oxalate). The solutions were analyzed using a Dionex DX-100 ion chromatograph equipped with an IONPAC AS10 4mm anion exchange column and an ASRS-I 4 mm anion self-regenerating suppressor. The eluent used was NaOH (8 mL of 50% NaOH diluted to 2 L with deionized water). Each ion was quantified by comparison of the peak area with that obtained with solutions of known concentrations of the ion. Since the concentration of nitrate is constant throughout the reaction (within experimental error), nitrate peak was used as an internal standard.

3.2.8. NMR analyses. The experimental procedure was very similar to that described earlier,⁹ and can be summarized as follows. A 10-mL aliquot of the stock solution was transferred to a round bottom flask and concentrated to dryness with a rotary evaporator at 60-70 °C (the evaporation time was close to 0.5 h). The solids were redissolved in D₂O and transferred to a 5 mL volumetric flask. The round bottomed flask was carefully washed several times with D₂O and the rinses added to the contents of the volumetric flask. The solution was diluted up to the mark, and a small amount (~0.6 mL) was transferred to an NMR tube provided with a concentric cell filled with a cyclohexane/CDCl₃ solution. The cell had been previously standardized by comparing the area of the peak due to cyclohexane with the area of the peak due to a known amount of HEDTA. The ¹H NMR spectrum was taken and the concentration of each compound was calculated by comparing its area with that of the peak due to cyclohexane (δ=1.38). This analysis assumes that the integrals for all species observed are proportional to their proton concentrations. This will be true if the nuclear spin relaxation times are approximately the same for all types of protons, or if not, the spectral acquisition parameters are set so that nuclear relaxation for all protons will be

complete before the next transient is collected. Discrepancies between the values for formate determined by ion chromatography and those determined by ^1H NMR spectroscopy suggested that the NMR values determined for formate might be in error. Further investigation determined that the relaxation time for the proton in the formate ion was significantly longer than those in HEDTA and ED3A so that new instrument parameters were chosen to ensure proportionality of the integrals of all resonances to the number of nuclei of each type.

4.0. Development of kinetic models for decomposition of glycolate and HEDTA.

Several models have been examined during the year to account for the kinetics of the reactions of both glycolate and HEDTA. Initially, these models were based upon data that was acquired during the latter part of the 1992-93 fiscal year and reported with minimal interpretation in the annual report for this period.¹ The model for HEDTA was refined and modified in an effort to account for the experimental data described in section 3 of the current report.

4.1. A cage model for predicting ratios of gaseous products formed from glycolate.

The following considerations result from an attempt to account for the striking difference in the temporal appearance of gaseous products at 90 °C and 120 °C from the reaction of glycolate in simulated waste media. For two years most of our experiments were done only at 120 °C, and in these experiments N_2 appeared as a product much later than H_2 and N_2O . We have suggested a reaction sequence, supported with experimental evidence, to account for the formation of gaseous products.¹ Important intermediates in this sequence are the anion of formohydroxamic acid formed according to reaction 4.1

and the conjugate base of hydroxylamine formed according to reaction 4.2.¹⁵

In contrast to the behavior at 120 °C, N_2 is the major product from both reactants at 90 °C, even at the earliest times. A simple model is developed below that accounts for this difference in behavior at the two temperatures.

4.1.1. The cage effect. We believe that the key to the difference in the behavior at 90 °C and 120 °C lies in the fact that the reactants shown in reaction 4.1 are formed adjacent to one another from a common intermediate (the nitrite ester of glycolate) in a medium of high viscosity. In a very viscous medium the NO^- and H_2CO formed in a single decomposition will be trapped by the so-called "solvent cage" and will have a high probability of combining with each other before they can diffuse away into the bulk of the solution. This is akin to the "geminate recombination" of radicals generated by homolytic cleavage, often by photochemical processes.¹⁶ The reaction of NO^- and

H₂CO produces the formohydroxamate ion (reaction 4.1), which ultimately undergoes base hydrolysis to give NH₂OH (reaction 4.2). Subsequent reactions of NH₂OH give N₂, N₂O, and NH₃.

Some H₂CO and NO⁻ will escape from the cage. It should be noted that the reactants in equation 4.1 are molecular H₂CO and singlet NO⁻, the same species formed from decomposition of the nitrite ester. Escape of a H₂CO molecule from the cage is rapidly followed by, or may be coincident with, its hydration to form the monoanion of the gem diol (reaction 4.3).

Subsequent formation of H₂C(O)₂²⁻ and its reaction with water to give H₂ should occur relatively rapidly. The NO⁻ that escapes should lead to formation of N₂O₂²⁻, N₂O, and possibly N₂O₃²⁻.

When the cage effect is large the amount of N₂ should be high relative to that of H₂ and N₂O. The behavior at 90 °C is consistent with this description. Alternatively, when the viscosity is less, as it would be at 120 °C, the early yields of H₂ and N₂O would be increased relative to N₂, because the amount of NO⁻ and H₂CO escaping the solvent cage will be greater. This is what is observed at 120 °C.

4.1.2. Lifetimes of intermediates. The lifetimes of various intermediates believed to be important in the formation of nitrogen gases have been estimated (Table 4.1) at 60 °C, 90 °C, and 120 °C, as indicated below, on the basis of information from the literature. These estimates are useful in quantitative application of the model (Part C), and as a guide to what intermediates may be detectable in later experiments.

Table 4.1. Estimated half-lives in 2 M NaOH at various temperatures

Compound	60 °C	90 °C	120 °C	Ref.
N ₂ O ₂ ²⁻	4 h	12 min	1.5 min	17,18
N ₂ O ₃ ²⁻	380 h	19 h	2.7 h	19,20
HC(O)NHO ⁻	-	min or s	-	
NH ₂ O ⁻	25 min	-	-	31

4.1.2a. *Trans*-hyponitrite ion, N₂O₂²⁻. The decomposition of *trans*-hyponitrite ion in neutral and alkaline solution is well understood as a result of rate measurements^{17,18} in the pH range 4-14. The stoichiometry and the rate data are consistent with reaction 4.4.

The dependence of rate on pH is consistent with a greater reactivity of HN₂O₂⁻ relative to H₂N₂O₂ or N₂O₂²⁻. Estimates of the pseudo first-order rate constants for

decomposition at higher temperatures (Table 4.1) are based on the value¹⁷ at 25 °C at pH 14, and a reported¹⁸ $\Delta H^\ddagger$ value of 23 kcal/mol. E_a is taken to be the same as $\Delta H^\ddagger$ in estimating the rates at the higher temperatures.

4.1.2b. Hyponitrate ion, $N_2O_3^{2-}$. The rate of decomposition of $N_2O_3^{2-}$ has been measured^{19,20} over the pH range 2-13 at 25 °C. Both sets of investigators agree that the stoichiometry is that shown in reaction 4.5 and that the rate determining step is reaction 4.6.

The dependence of rate on pH follows a pattern like that of $N_2O_2^{2-}$; hyponitrate is much less reactive in strongly alkaline solution. Estimates of the pseudo-first-order rate constant at higher temperatures (Table 4.1) are based on its value¹⁹ at 25 °C in 0.1 M KOH, and a value²⁰ of $\Delta H^\ddagger$ of 23.9 kcal/mol. E_a was again assumed to be equal to $\Delta H^\ddagger$ in estimating the values at the higher temperatures.

4.1.2c. Formohydroxamic acid (N-hydroxyformamide), $HC(O)NHOH$. No measurements of the rate of hydrolysis have been reported for this compound. However quantitative measurements of the rate of base catalyzed hydrolysis of benzohydroxamic acid (i.e., N-hydroxybenzamide) are available.²¹ For this relative of N-hydroxyformamide, the pseudo first-order rate constant in 2.18 M NaOH has a value of 0.0678 h⁻¹ at 88.6 °C. This corresponds to a half-life of 10.3 h.

To make an estimate of the rate for formohydroxamic acid, a comparison of the rates of hydrolysis of formamide and benzamide may be of some help. Second-order rate constants for the alkaline hydrolyses of both amides have been reported, although the experimental conditions were quite different for the two compounds. On the basis of experiments done with initial benzamide and OH^- concentrations of 0.1 M, a second-order rate constant of $7.33 \times 10^{-4} M^{-1} s^{-1}$ was determined for benzamide at 109 °C.²² On the basis of experiments in the pH range 1-9 under pseudo first-order conditions the second-order rate constant for formamide is $0.200 M^{-1} s^{-1}$ at 80 °C.²³ Even in the absence of activation energy data, it is clear that the hydrolysis of formamide is faster than the hydrolysis of benzamide by a factor of several powers of ten. Assuming that the ratio of the rate constants for the two hydroxamates is comparable, a half life of the order of minutes or seconds is expected for formohydroxamic ion in 2 M NaOH at 90 °C.

4.1.2d. Hydroxylamine, NH_2OH . Hydroxylamine may be present in aqueous solution as H_3NOH^+ , H_2NOH , or H_2NO^- . The pK_a values at 25 °C are 5.9 for H_3NOH^+ , and 13.7 for H_2NOH . The latter value²⁴ was determined on the basis of kinetic measurements of the autoxidation of NH_2OH (13.71) and a spectrophotometric measurement (13.74). Thus, in 2 M NaOH, 80% of the hydroxylamine is present as NH_2O^- , and 20% as NH_2OH . Disproportionation of hydroxylamine in concentrated alkali gives NH_3 , N_2 , and N_2O as gaseous products. In terms of stoichiometry the gaseous products can be accounted for by a combination of reactions 4.7 and 4.8.

Formation of hyponitrite ion, $\text{N}_2\text{O}_2^{2-}$, as a minor product has been established²⁵ by isolation of salts of the ion.

The ratio of N_2 to N_2O increases as the concentration of OH^- increases. Table 4.2 shows the dependence of the ratio of $\text{N}_2/\text{N}_2\text{O}$ based on data collected from several sources.^{26,27,28}

Table 4.2. Effect of $[\text{OH}^-]$ on the ratio of $\text{N}_2/\text{N}_2\text{O}$ formed from NH_2OH

$[\text{OH}^-]$	Temp./°C	$[\text{NH}_2\text{OH}]_0$	$\text{N}_2/\text{N}_2\text{O}$	Reference
0.02	25	0.153	1.6	27
0.32	25	0.153	6.2	27
1.7	?	~0.1	5.7	26
2.0	120	0.41	8	28
2.0	120	0.38	12	28
3.6	?	~0.1	11.5	26
4.4	?	~0.1	32	26

The relative importance of reactions 4.7 and 4.8 may also depend on the concentration of NH_2OH . Holzapfel²⁹ reports that in strongly alkaline solution the moles of NH_3 formed per mole of NH_2OH reacting varied from approximately 0.5 at the start of the reaction to approximately 0.33 at completion. The simplest interpretation of this result is that reaction 4.7 is more important than reaction 4.8 at low hydroxylamine concentration. On the other hand, Lunak and Veprek-Siska report³⁰ that the ratio $\text{N}_2/\text{N}_2\text{O}$ decreases as decomposition proceeds. This result is not necessarily inconsistent with the previous conclusion if significant amounts of $\text{N}_2\text{O}_2^{2-}$ accumulate during the early part of the reaction and then later decompose to N_2O .

That the disproportionation of hydroxylamine is reported^{29,30} to be first-order in NH_2OH is surprising since the reaction must occur by a complex mechanism. Lunak and Veprek-Siska give the rate law as³⁰

$$-d[\text{NH}_2\text{OH}]/dt = k[\text{OH}^-]^3[\text{NH}_2\text{OH}]$$

for reaction of $[\text{NH}_2\text{OH}]_0 = 2.79 \text{ M}$ at 20°C and $[\text{OH}^-]$ in the range 0.81-3.21 M. From the rate constant of $7 \times 10^{-6} \text{ M}^{-3} \text{ s}^{-1}$ a half-life of 3.4 h can be calculated for NH_2OH in 2 M OH^- under pseudo first-order conditions. These workers also report catalysis of the reaction by transition-metal cations with effectiveness in the order $\text{Fe(II)} > \text{Ni(II)} > \text{Cu(II)} > \text{Co(II)} > \text{Ag(I)} > \text{Zn(II)}$. They emphasize that the k reported is dependent on the purity of

the hydroxylamine and KOH used in their experiments. Extrapolation of a measurement²⁷ of the amount of gas produced in 49 h from 0.153 M NH₂OH at 25 °C at pH 13.5 suggests a half-life for the reaction of the order of 25 h in 2 M OH⁻, assuming first-order behavior of NH₂OH.

Of more value in making an estimate of the life-time of NH₂OH at higher temperatures is the measurement of the rate of N₂O generation at 60 °C from a simulated waste solution containing 0.01 M NH₂OH reported by the Argonne Laboratory group.³¹ Their result suggests a pseudo-first-order rate constant of 2.8 x 10⁻² min⁻¹ for decomposition of NH₂OH, with a corresponding half-life of 25 min. Although the reaction of NH₂OH may occur by several pathways (see below), this rate constant is still a meaningful number provided all reactions contributing are first-order in NH₂OH.

A feature of the Argonne results that should be noted is what appears to be a mass-balance difficulty if NH₂OH undergoes reaction only by disproportionation. They obtained 6.7 mol N₂O and 30 mol N₂ per 100 mol of initial NH₂OH. If reactions 4.7 and 4.8 are the only ones that contribute to the disappearance of NH₂OH then 117 mol should be required. Viewed another way, the N₂/N₂O ratio of 4.5 is smaller than the values characteristic of 2 M OH⁻ solutions (Table 4.2). We note a similar difficulty with the results of some of our experiments that are analyzed in Section 4.1.3. A possible explanation is that in simulated waste media nitrite reacts with hydroxylamine according to reaction 4.9.

Formation of one molecule of N₂O by this route requires only one molecule of NH₂OH, compared to the four molecules required to generate an N₂O by disproportionation. This reaction has been extensively studied in acidic and neutral solution. Kinetic studies under these conditions suggest the reaction occurs by N-nitrosation of hydroxylamine; the terms in the rate law suggest that a variety of nitrosating agents are active. No studies of the reaction in alkaline solution have been reported but the possibility that nitrosation of NH₂OH could be achieved by an aluminum(III)-nitrite complex is reasonable. Evidence for participation of a reaction other than disproportionation will be sought in further studies by careful measurements of the yields of NH₃, N₂ and N₂O.

4.1.3. Quantitative applications of the model to glycolate decomposition. The data on the temporal appearance of products from glycolate at 90 °C and 120 °C that initiated these considerations are given in Tables 4.3 and 4.4. In analyzing the data we have begun with the simplest assumptions, and modified them as necessary. Inconsistencies, some qualitative and some quantitative, still exist, but important features of the reaction have been established.

If glycolate decomposes in a first-order manner, and the subsequent reactions that lead to products all occur rapidly relative to the time scale of the experiment, then the amount of a particular product produced at any time will be given by

$$P_t = P_\infty(1 - e^{-kt})$$

Table 4.3. Amounts of gases produced from thermal decomposition of glycolate in simulated waste at 90 °C under argon^a

Time/h	P_t^b		
	H ₂	N ₂	N ₂ O
24	0.1	0	0.2
73	0.4	2	0.8
168	0.8	5	1.7
243	1.2	5	2.6
384	1.9	8	4.1
625	3.0	12	6.4
1200	6.8	18	12.01
1922	13.1	24	20.3

^a0.21 M glycolate in SY1-SIM-91B under Ar. ^b P_t = mol of gas per 100 mol of initial glycolate

Table 4.4. Amounts of gases produced from thermal decomposition of glycolate in simulated waste at 120 °C under argon^a

Time/h	P_t^b		
	H ₂	N ₂	N ₂ O
25	2.4	0	3.9
73	8.5	3	13.2
146	17.6	4	24.5
217	25.1	7	32.5
361	37.5	13	43.5
580	44.4	21	45.9
915	54.1	-	44.6
1203	56.7	36	35.1

^a0.21 M glycolate in SY1-SIM-91B under Ar. ^b P_t = mol of gas per 100 mol of initial glycolate

where k is the pseudo-first-order rate constant for decomposition of glycolate, and P_{∞} is the percent of glycolate decompositions giving the particular product. This analysis assumes that P_{∞} is constant during the time of the experiment. Consequences of these assumptions are that all three gases have the same functional form with the same value of k , but with different values of P_{∞} ; and that the ratio of P_i values for any two gases are constant with time and equal to the ratios of the corresponding P_{∞} values.

At 90 °C, N_2 is the gas formed in largest amount and its variation with time fits the expected function rather well, with $P_{\infty} = 31$ and $k = 7.8 \times 10^{-4} \text{ h}^{-1}$ (Figure 4.1). The other two gases do not fit this form, and the ratios of the various gases do not stay constant throughout the experiment. The ratio of N_2/H_2 has a value of about 5.4 in the time interval 70-250 hours. This ratio in the early stages of the reaction, in combination with a P_{∞} value of 31 for N_2 , suggests a cage effect in which about 5% of the geminate pairs escape and 95% combine. The amount of N_2O is higher than expected, and formation by a reaction other than disproportionation of NH_2OH is required to explain this.

At 120 °C, H_2 is the gas formed in largest amount and its variation with time fits the expected function well with $P_{\infty} = 60$ and $k = 2.5 \times 10^{-3} \text{ h}^{-1}$ (Figure 4.2). The data for the gases N_2 and N_2O cannot be treated individually because of the complication of the thermal decomposition known to occur at this temperature (reaction 4.10).³²

Consequently, the ratios N_2/H_2 and N_2O/H_2 would not be constant but the ratio $(N_2+N_2O)/H_2$ should be. The calculated curve shown in Figure 4.2 for (N_2+N_2O) is one with the same value for k as for the hydrogen curve with the value of P_{∞} chosen to fit the experimental data at times less than 500 h. The $(N_2+N_2O)/H_2$ ratio is fairly constant over the first 500 h. The $P_{\infty} = 60$ for H_2 suggests a cage effect in which about 60% of the geminate pairs escape and 40% combine. As at 90 °C, the high yields of N_2O must be due to participation of an additional reaction that is even more significant at 120 °C than at 90 °C.

Using the values of k at 90 °C and 120 °C and the Arrhenius equation, a value of the rate constant for glycolate decomposition of $2.0 \times 10^{-4} \text{ h}^{-1}$ is calculated at 60 °C. This corresponds to a half-life of $3.5 \times 10^3 \text{ h}$ or 0.4 y. Assuming that the cage effect is even greater at 60 °C than at 90 °C, each glycolate decomposition should rapidly give one NH_2OH molecule and very little hydrogen should be produced. When steady-state conditions are attained the ratio $[NH_2OH]/[\text{glycolate}] = t_{1/2}(NH_2OH)/t_{1/2}(\text{glycolate}) = 1.2 \times 10^{-4}$.

4.1.4. Implications of the cage model for HEDTA. The decomposition of HEDTA represents a more complicated situation. There is a marked increase in the ratio of hydrogen to nitrogen gases upon increasing the temperature from 90 °C to 120 °C under argon but the yield of hydrogen is significantly lower than for glycolate. It must also be noted that the yield of hydrogen from HEDTA is considerably greater under oxygen-containing atmospheres than under argon. The present model does not account for this effect. We believe that it is time to consider experiments aimed at

Figure 4.1. Experimental yield of H₂ from glycolate in simulated waste at 90 °C as a function of time (circles) compared to that calculated from the expression $P_t = P_{\infty}(1 - e^{-kt})$ where $P_{\infty} = 31$ and $k = 7.8 \times 10^{-4} \text{ h}^{-1}$.

Figure 4.2. Experimental yields of H₂ (circles) and (N₂+N₂O) (triangles) from glycolate decomposition in simulated waste at 120 °C as a function of time compared to that calculated from the expression $P_t = P_{\infty}(1 - e^{-kt})$. For H₂, $P_{\infty} = 60$ and $k = 2.5 \times 10^{-3} \text{ h}^{-1}$. The curve for (N₂+N₂O) was calculated using the same value of k as for H₂.

specifically determining the manner in which oxygen is involved. A useful experiment might be to examine the decomposition of HEDTA under an oxygen-containing atmosphere in which the oxygen was enriched in O-18, whose distribution in the volatile and non-volatile products could be determined by mass spectrometry. Further consideration of the rate data for HEDTA decomposition are given in the next section.

4.2 Analysis of Rate Data for HEDTA

Consideration of the temporal appearance of products from the reaction of HEDTA begins with the recognition that a sequence of reactions must be occurring, with the formation of ED3A from HEDTA being the first reaction in the sequence. The initial assumptions are that the decomposition of HEDTA is first-order in HEDTA, and that the decomposition of ED3A is first-order in ED3A.

4.2.1 Equations Applicable to Consecutive First-Order Reactions. For a system of two consecutive first-order reactions

the following equations apply.³³

$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] = \frac{k_1 [A]_0}{k_1 - k_2} (e^{-k_2 t} - e^{-k_1 t})$$

$$[C] = [A]_0 \left\{ 1 + \left(\frac{k_2}{k_1 - k_2} \right) e^{-k_1 t} - \left(\frac{k_1}{k_1 - k_2} \right) e^{-k_2 t} \right\}$$

The concentration of [B] will go through a maximum. The time at which [B] is a maximum is given by

$$t_{\max} = \frac{1/n (k_1 / k_2)}{k_1 - k_2}$$

$$= \frac{t_{1/2}}{1/n \cdot 2} \left(\frac{R}{R - 1} \right) 1/n R$$

where $t_{1/2}$ is the half-time corresponding to k_1 , and $R = k_1 / k_2$. The value of [B] at the maximum is given by

$$[B]_{\max} = R^{\frac{1}{1-R}} [A]_0$$

For a three-step sequence

the previous equations hold, except for the equation for [C]. For the three-step sequence the correct equation is³⁴

$$[C] = \left\{ \frac{k_1 k_2}{(k_2 - k_1)(k_3 - k_1)} e^{-k_1 t} + \frac{k_1 k_2}{(k_1 - k_2)(k_3 - k_2)} e^{-k_2 t} + \frac{k_1 k_2}{(k_1 - k_3)(k_2 - k_3)} e^{-k_3 t} \right\} [A]_0$$

The equation for [D] can be derived readily by beginning with

$$[D] = [A]_0 - [A] - [B] - [C]$$

and substituting appropriately. Some estimates of the values of k_1 and k_2 at 90 °C and 120 °C can be made on the basis of measurements of amounts of HEDTA (A), ED3A (B), and s-EDDA (C) as shown in the following sections.

4.2.1a. Application to Data at 90 °C. Only one set of measurements was made at 90 °C. At 4942 hrs the amounts were: 36% HEDTA, 55% ED3A, and 6% s-EDDA.³⁵ Using the values for HEDTA and ED3A, and the equations for [A] and [B] above, gives $k_1 = 2.07 \times 10^{-4} \text{ h}^{-1}$ (corresponding to a half-time of $3.35 \times 10^3 \text{ h}$) and $k_2 = 5.3 \times 10^{-5} \text{ h}^{-1}$ (corresponding to a half-time of $13 \times 10^3 \text{ h}$). The value of R is 3.9, leading to $t_{\max} = 8.8 \times 10^3 \text{ h}$, and $[B]_{\max}/[A]_0 = 62.5\%$. The measurement was made at a time before the maximum was attained. The result suggests that consideration of a third step in the sequence is not important up to about 5000 h at 90°C.

Although mechanistic considerations suggest ED3A may decompose in several different ways, these measurements indicate s-EDDA is formed in the major reaction. For this reason s-EDDA is formally identified with C; but measured values of s-EDDA would be expected to be smaller than calculated values for C.

4.2.1b. Application to Data at 120 °C. At 120°C, measurements were made at different times in five different experiments (Table 4.5).³⁶ Use of trial values of k_1 and k_2 to fit these data gives $k_1 = 1.18 \times 10^{-3} \text{ h}^{-1}$ (corresponding to a half-time of 587 h) and $k_2 = 1.55 \times 10^{-4} \text{ h}^{-1}$ (corresponding to a half-time of 4472 h). Percentages calculated from these values are also given in Table 4.5. The value of R is 7.6, leading to $t_{\max} = 1980 \text{ hrs}$ and $[B]_{\max}/[A]_0 = 73.6\%$. The measurement made at 2038 h must be near the maximum.

Table 4.5. Products from HEDTA decomposition at 120° C.

Exp't.	Time, h	HEDTA (Meas)	A (Calc)	ED3A (Meas)	B (Calc)	s-EDDA (Meas)	C (Calc. 2-step)	C (Calc. 3-step)	D (Calc. 3-Step)
15A'	200	80	79						
15A	500	51	55	24	43	4	2	2	
22A	1000	35	31						
19B	2038	< 2	9	67	73	11	18	16	2
12B	4921	< 2	0.3	60	53	13	46	33	13

Values of $[C]/[A]_0$ calculated both for a 2-step and 3-step sequence are included in Table 4.5. For the 3-step sequence, the value of k_3 was taken to be $1.5 \times 10^{-4} \text{ h}^{-1}$. This is a reasonable value, being about the same as that for k_2 , and is consistent with a 14% decomposition of s-EDDA in 1000 h observed in a single experiment with it as the starting reactant at 120°C . Certainly at times beyond 2000 h, and possibly beyond 1000 h, a 3rd step in the reaction sequence is significant. In the early experiments in which products from HEDTA were identified by ^{13}C NMR, u-EDDA, IDA and glycine were observed at 732 h.³⁷

4.2.2 Case in Which an Additional Product G is Formed. We are interested in the case in which a gaseous product, indicated as G, is formed in all reactions in a sequence of reactions. We begin with the 2-step sequence

where f_1 is the fraction of decompositions of A yielding product G, and f_2 is the fraction of decompositions of B yielding product G.

$$[G] = f_1 \{ [A]_0 - [A] \} + f_2 [C]$$

and

$$\frac{[G]}{[A]_0} = f_1 (1 - e^{-k_1 t}) + f_2 \frac{[C]}{[A]_0}$$

Although this equation can be used for fitting data, a more convenient form can be obtained by substitution and rearrangement.

$$\frac{[G]}{[A]_0} = (f_1 + f_2) - \left(f_1 - \frac{f_2 k_2}{k_1 - k_2} \right) e^{-k_1 t} - \left(\frac{f_2 k_1}{k_1 - k_2} \right) e^{-k_2 t}$$

It is now convenient to define

$$P_1 = \left(f_1 - \frac{f_2 k_2}{k_1 - k_2} \right) \quad \text{and} \quad P_2 = f_2 \left(\frac{k_1}{k_1 - k_2} \right)$$

It follows that

$$f_2 = P_2 \left(\frac{k_1 - k_2}{k_1} \right)$$

$$f_1 = P_1 + P_2 \left(\frac{k_2}{k_1} \right)$$

$$P_1 + P_2 = f_1 + f_2$$

and

$$\frac{[G]}{[A]_0} = P_1 (1 - e^{-k_1 t}) + P_2 (1 - e^{-k_2 t})$$

Implicit in the use of this function is the assumption that f_1 and f_2 , and hence P_1 and P_2 , are constant throughout the time of the experiment.

Since the data for a given gas is most conveniently shown by a plot of the amount of the gas versus time, the following feature of the function $(1 - e^{-kt})$ should be noted. For sufficiently small values of kt , the function is equal to kt , and a plot of the function versus t will be linear. For what length of time will linearity be observed? Table 4.6 indicates, for a given k , the value of t required for the difference between $(1 - e^{-kt})$ and kt to be greater than 10% of $(1 - e^{-kt})$.

Table 4.6. Value of t at which $(1 - e^{-kt}) - kt > 0.1(1 - e^{-kt})$ for certain values of k .

k	t at which Δ exceeds 10%
$k_1(90^\circ) = 0.000207 \text{ h}^{-1}$	970 h
$k_2(90^\circ) = 0.000053 \text{ h}^{-1}$	3600 h
$k_1(120^\circ) = 0.00118 \text{ h}^{-1}$	180 h
$k_2(120^\circ) = 0.000155 \text{ h}^{-1}$	1250 h

The value of 10% was chosen as a reasonable estimate of the experimental accuracy of a measurement. Another feature to be noted is that at greater times $(1 - e^{-kt}) < kt$ so that a plot of the function versus time always falls below the extrapolated line.

Extending these considerations to the function given above for $[G]/[A]_0$, it follows that, for small values of t ,

$$[G]/[A]_0 = (P_1 k_1 + P_2 k_2) t$$

and the plot of $[G]/[A]_0$ vs t will be linear with an initial slope of $(P_1 k_1 + P_2 k_2)$. The time at which deviation from linearity will be observed will be determined by the k of larger value, in this case k_1 . For given values of k_1 and k_2 , the slope provides limits on the possible values for P_1 and P_2 .

Since numerical results for $[G]/[A]_0$ are expressed in terms of percent rather than as a fraction, numerical values for f and P will also be given as percents for consistency. The numerical values for the slopes of plots of $[G]/[A]_0$ versus time will have the units of percent per hour.

The 3-step sequence

can be treated in similar fashion. Using the expressions for $[A]$, $[B]$, and $[C]$ given earlier, it can be shown easily that

$$\frac{[G]}{[A]_0} = P_1(1 - e^{-k_1 t}) + P_2(1 - e^{-k_2 t}) + P_3(1 - e^{-k_3 t})$$

where

$$P_1 = f_1 - \frac{k_2 f_2}{k_1 - k_2} + \frac{k_2 k_3 f_3}{(k_1 - k_2)(k_1 - k_3)}$$

$$P_2 = \frac{k_1 f_2}{k_1 - k_2} - \frac{k_1 k_3 f_3}{(k_1 - k_2)(k_2 - k_3)}$$

$$P_3 = \frac{k_1 k_2 f_3}{(k_1 - k_3)(k_2 - k_3)}$$

4.2.2a. Application to Gases from HEDTA at 90 °C. The data for H_2 at 90 °C³⁸ were examined in terms of the model. A plot of values of % H_2 versus time is shown in Figure 4.3. Qualitatively the behavior is as expected. As expected from the value of k_1 , deviation from linearity occurs after 970 h, and the measured values fall below the extrapolated line.

The initial slope is 7.85×10^{-4} . If this initial slope is interpreted as equal to $(P_1 k_1 + P_2 k_2)$ it follows that $P_1 \leq 3.79$ and $P_2 \leq 14.8$, using the values of k_1 and k_2 given earlier. Fitting the entire set of data quantitatively has difficulties. An excellent fit to the data through $t = 2618$ h can be obtained by taking $P_2 = f_2 = 0$. This can be seen from curve A

Figure 4.3. Experimental yield of H₂ from HEDTA in simulated waste under argon at 90°C as a function of time (circles). Curve A is the function $P_1[1-\exp(-k_1t)]$ where $P_1 = 3.7$ and $k_1 = 2.07 \times 10^{-4} \text{ h}^{-1}$. Curve B is the function $P_1[1-\exp(-k_1t)] + P_2[1-\exp(-k_2t)]$ where $P_1 = 1$, $P_2 = 10.5$, $k_1 = 2.07 \times 10^{-4} \text{ h}^{-1}$, and $k_2 = 5.3 \times 10^{-5} \text{ h}^{-1}$.

in Figure 4.3, which corresponds to $P_1 = f_1 = 3.7$. Attempts to include the points in the 3000-4000 hr range by using the two-term function were not satisfactory. Curve B is for the function with $P_1 = 1.0$ and $P_2 = 10.5$ ($f_1 = 3.7$ and $f_2 = 7.8$). Some variation in the P_1 and P_2 values gives essentially the same curve. Although the value of f_2 is in doubt, the value of f_1 must be about 3.7. This value would be consistent with the "cage model" suggested for glycolate at 90°C.

The data for N_2 at 90° C³⁸ (Figure 4.4) has a somewhat different pattern than that for H_2 . Initial linearity extends for a longer period, and the later deviation from linearity is in the opposite direction. The initial slope is 0.0048. If this initial slope is interpreted as equal to $f_1 k_1$ it follows that $f_1 = 23$. It would be easy to attribute the positive deviations to a lack of constancy of P_1 and P_2 during the reaction, but we have no explanation for why that would be so.

It is interesting to note that the amount of N_2 at the end of the experiment is 30%. Although the amount of NH_3 was measured much later, it was found to be 27.5%. These results would be consistent with both gases arising from the disproportionation of hydroxylamine with the stoichiometry

4.2.2b. Application to Gases from HEDTA at 120° C. The data for H_2 at 120° C follows the qualitative behavior expected (Figure 4.5). The initial slope is 0.0035 leading to $f_1 = 2.97$. The values for f_1 at the two temperatures (3.79 at 90° C and 2.97 at 120° C) are not significantly different. If k_1 at 90° C was 12% larger, and k_1 at 120° C was 12% smaller (well within the uncertainty of our knowledge of them), the value of f_1 would be 3.4 for both.

Since the reaction sequence in these experiments must go beyond two steps, it was expected that the data could not be fitted to a two-term expression. That expectation was verified. No attempts were made to fit a three-term expression.

Since the decomposition of gaseous N_2O into N_2 and O_2 is known to be significant at 120° C, the data for the individual gases N_2 and N_2O were not analyzed, but the sum of the two was. The data are shown in Figure 4.6. The initial slope is 0.0428, leading to $f_1 = 36.3$. Although the points at the very late times fall below the extrapolated line, the initial deviations are above the line, as was observed for the behavior of N_2 at 90° C. It is worth noting that, on the basis of the rate constants, the composition of the solution after 800 h at 120° C should be about the same as the solution at 90° C after 4500 h. Similar behavior might then be expected for the two solutions.

4.2.3. Activation Energies. Since extrapolation of rates to 60° C, the temperature of practical interest, is accomplished by use of the Arrhenius equation and the associated activation energy, E_a , some important distinctions related to E_a need to be considered.

Figure 4.4. Experimental yield of N₂ from HEDTA in simulated waste under argon at 90°C as a function of time (circles).

Figure 4.5. Experimental yield of H₂ from HEDTA in simulated waste under argon at 120°C as a function of time (circles).

Figure 4.6. Experimental yield of $(N_2 + N_2O)$ from HEDTA in simulated waste under argon at $120^{\circ}C$ as a function of time (circles).

As an example, for a reaction of the form

values of the rate constant k obtained from experiments at two or more temperatures, E_a can be used to calculate a value of E_a by use of the Arrhenius equation. Alternatively, a plot of $\ln k$ versus $1/T$ can be made. The evaluation of E_a follows from the slope of that plot:

$$\frac{d(\ln k)}{d(1/T)} = -\frac{E_a}{R}$$

Frequently, instead of measuring the rate constant at several temperatures, a particular rate is measured at several temperatures for solutions that have the same concentrations of reactants. For the example indicated above, either $\text{Rate}_A = -d[A]/dt$ or $\text{Rate}_G = d[G]/dt$ might be measured. From measurements of Rate_A

The plot of $\ln(\text{Rate}_A)$ versus $1/T$ gives E_a . But for measurements of Rate_G

$$\text{Rate}_G = d[G]/dt = f k[A]$$

$$\ln(\text{Rate}_G) = \ln f + \ln k + \ln[A]$$

$$\frac{d \ln(\text{Rate}_G)}{d(1/T)} = \frac{d \ln f}{d(1/T)} + \frac{d(\ln k)}{d(1/T)} = \frac{d(\ln f)}{d(1/T)} - \frac{E_a}{R}$$

If f has the same numerical value at all T , the $d(\ln f)/dt$ term equals zero, and the plot of $\ln(\text{Rate}_G)$ versus $1/T$ will be linear and will give the same value of E_a as that obtained from the Rate_A data. If f varies with temperature, two possibilities exist. If $d(\ln f)/d(1/T)$ is constant over the temperature range used, the plot of $\ln(\text{Rate}_G)$ versus $1/T$ will be linear and the value of the activation energy obtained, E_a' , will be different from E_a . If $d(\ln f)/d(1/T)$ varies with T , the plot of $\ln(\text{Rate}_G)$ versus $1/T$ will show curvature.

The rate constants obtained in the previous sections for HEDTA (k_1) and ED3A (k_2) at 90° C and 120° C, have been used in the Arrhenius equation to obtain values of E_a . These are given in Table 4.7, along with the rate constants and corresponding half-times calculated for 60° C. The values calculated for glycolate, in section 4.1. above are also given in Table 4.7.

In our FY 1993-94 final report³⁹ an activation energy of 17 kcal for decomposition of HEDTA, based on the rate of formation of H_2 at 60 °C, 90 °C, and 120 °C, was reported. In the analysis given in the previous section of this report, it was concluded that f_1 was the same, within experimental uncertainty, at 90° C and 120° C. The

linearity of the plot of the logarithm of the rate of hydrogen formation vs $1/T$, and the equivalence of the E_a values from the two methods, are consistent with a constant value of f_1 at the three temperatures.

For glycolate decomposition, however, f varies markedly with temperature, as described earlier in Section 4.1.3. Values, expressed as fractions, are ca. 0.05 at 90° C and 0.6 at 120° C. The slope of $d(\ln f)/d(1/T)$, based on these two points, has a value of -11.6, thus the E_a based on measurement of H_2 formation should be 23 kcal greater than the value given in Table 4.7, or 34 kcal. A value based on rate of H_2 formation of 30 kcal was reported earlier.⁴⁰

Table 4.7. Activation energies and rate constants calculated at 60° C.

Compound	E_a , kJ/mol (kcal/mol)	k_{60°	$t_{1/2}$
HEDTA	69 (16)	$2.65 \times 10^{-5} \text{ h}^{-1}$	3.0 y
ED3A	43 (10)	$1.49 \times 10^{-5} \text{ h}^{-1}$	5.3 y
glycolate	46 (11)	$2.0 \times 10^{-4} \text{ h}^{-1}$	0.4 y

4.3 Analysis of the Rate of Reaction of HEDTA

In previous attempts to treat quantitatively the rate of formation of gases from the decomposition of HEDTA we have assumed that the reaction is simply pseudo-first-order in HEDTA.

$$-d[\text{HEDTA}]/dt = k [\text{HEDTA}]$$

The corresponding integrated expression is

$$\ln [\text{HEDTA}] = \ln [\text{HEDTA}]_0 - kt$$

Thus a plot of $\ln[\text{HEDTA}]$ vs time should be linear. In fact, in the two sets of experiments in which we have most data, the plots show curvature. More instructive is a plot of $[\text{HEDTA}]$ vs time, which shows that the rate (defined as $-d[\text{HEDTA}]/dt$) increases with time in the earliest stages of the reaction.

This behavior was first observed in a reaction of HEDTA at 120 °C, conducted over a period of 500 h in glass apparatus with Teflon liner (but without Teflon cap) under an air atmosphere. The measured values under these experimental conditions are shown in a plot of $\ln[\text{HEDTA}]$ versus time (the points on the upper curve in Figure 4.7).

In our recent measurements of the reaction at 90 °C, conducted in stainless steel vessels under an argon atmosphere, the same kind of behavior was observed. The measured values under these experimental conditions are also shown (the points on the lower curve in Figure 4.7). Measurements with time are still continuing at these conditions.

Figure 4.7. Plot of $\ln[\text{HEDTA}]$ versus time for decomposition of HEDTA at 90 °C under an argon atmosphere (lower plot), and at 120 °C under an air atmosphere (upper plot). Note that the time axis scales are different for the two plots.

To call attention to the similarity in the behavior at the two different conditions, time scales differing by a factor of four have been used for the two curves in Figure 4.7. Although this integral factor of four was initially chosen merely for convenience in making the plots, the reason that it is a good factor in showing the similarities will be presented in the next section.

Reactions, like these, which are initially very slow but which increase in rate with time, are often said to have an "induction period". This term is only a descriptive term, and the explanation for the phenomenon will be different from one reaction to another. Explanations of two types are being considered at this time, with the recognition that results of the experiment now in progress may alter the considerations.

The similarities of the behaviors under the two reaction conditions strongly suggest that the behavior, with its induction period, is not due to an effect caused by a reaction with the walls of the vessel, nor is it due to the presence of O₂. The latter point is important since O₂ is known to affect the amount and rate of formation of various gaseous products.⁴¹ Thus, the reaction(s) of O₂ occur after the initial rate-determining step.

4.3.1. Auto-catalysis Mechanism. Many reactions with "induction periods" are explained in terms of auto-catalysis, i.e., a product of the reaction acts as a catalyst for the reaction. A variety of mechanistic schemes fall into this general category. A specific example being investigated follows.

It is assumed that the stoichiometry of the reaction can be written as

where C is the product acting as a catalyst, and f is the fraction giving the stoichiometric relation between the amount of HEDTA and C. It is further assumed that the reaction occurs by an uncatalyzed path (with rate constant k_u) and a catalyzed path (with rate constant k_c). Thus

$$-d[A]/dt = k_u[A] + k_c[A][C]$$

where A represents HEDTA.

From stoichiometry: $[C] = f\{[A]_0 - [A]\}$

It should be noted that this statement implies that C does not decompose in a net way after being formed; it builds up continuously during the reaction of HEDTA.

The derivation of a useful expression for testing purposes follows:

$$\begin{aligned} -d[A]/dt &= k_u[A] + k_c[A]f\{[A]_0 - [A]\} \\ &= k_u[A] + fk_c[A][A]_0 - fk_c[A]^2 \end{aligned}$$

$$\begin{aligned}
 &= (k_u + f k_c [A]_o) [A] - f k_c [A]^2 \\
 &= k_o [A] - f k_c [A]^2 = (k_o - f k_c [A]) [A]
 \end{aligned}$$

where $k_o = k_u + f k_c [A]_o$

$$\begin{aligned}
 -d[A]/dt &= (k_o - f k_c [A]) [A] = k_o \{1 - (f k_c / k_o) [A]\} [A] \\
 &= k_o (1 - k' [A]) [A]
 \end{aligned}$$

where $k' = f k_c / k_o$

$$\int_{[A]_o}^{[A]} \frac{d[A]}{(1 - k' [A]) [A]} = -k_o \int_{t=0}^t dt$$

$$\ln \frac{[A]}{1 - k' [A]} - \ln \frac{[A]_o}{1 - k' [A]_o} = k_o t$$

$$\ln \frac{1 - k' [A]}{[A]} - \ln \frac{1 - k' [A]_o}{[A]_o} = k_o t$$

$$\ln \left(\frac{1}{[A]} - k' \right) = \ln \left(\frac{1}{[A]_o} - k' \right) + k_o t$$

The validity of the mechanism is tested by plotting $\ln (1/[A] - k')$ vs time for various assumed values of k' . If a straight line is obtained, the function may be a correct description for the reaction.

For data at 120 °C, a straight line is obtained for $k' = 4.30$. The slope, $k_o = 3.71 \times 10^{-3}$. These values lead to:

$$k_o = k_u + f k_c [A]_o = 0.00371 \text{ h}^{-1}$$

$$k' = f k_c / k_o = 4.30 \text{ M}^{-1}$$

$$f k_c = 4.30 k_o = 0.0160 \text{ M}^{-1} \text{ h}^{-1}$$

$$k_u = k_o - f k_c [A]_o = k_o - k_o k' [A]_o = k_o (1 - k' [A]_o)$$

$$= 3.26 \times 10^{-4} \text{ h}^{-1}$$

The upper curve in Figure 4.7 corresponds to values calculated with these constants. The excellence of the fit can be seen from Figure 4.7, or from comparison of

Table 4.8. Comparison of measured and calculated concentrations of HEDTA at 120 °C using both two-exponential and auto-catalysis models.

Time, h.	Measured	"Two-Exponential" Model	Auto-Catalysis Mechanism
0	0.212	0.212	0.212
112.5	0.203	0.205	0.203
191.0	0.194	0.195	0.194
303.0	0.179	0.176	0.179
408.5	0.161	0.157	0.161
500.5	0.144	0.142	0.143

calculated and measured values given in Table 4.8. The calculated values are given under Auto-Catalysis Mechanism.

At 90 °C the data through the first 1800 h gives a straight line for $k' = 4.55$. The slope, $k_o = 8.96 \times 10^{-4}$. These values lead to:

$$k_o = k_u + fk_c[A]_o = 8.96 \times 10^{-4} \text{ h}^{-1}$$

$$k' = fk_c/k_o = 4.55 \text{ M}^{-1}$$

$$fk_c = 4.55k_o = 4.55 \times 0.000896 = 4.08 \times 10^{-3} \text{ M}^{-1} \text{ h}^{-1}$$

$$k_u = k_o (1 - k'[A]_o) = 9.32 \times 10^{-5} \text{ h}^{-1}$$

Table 4.9. Comparison of measured and calculated concentrations of HEDTA at 90 °C using both two-exponential and auto-catalysis models.

Time, h	Measured	Auto-Catalysis Mechanism		"Two-Exponential" Model
		Model I	Model II	
0	0.197	0.197	0.197	0.197
160	0.194	0.194	0.194	0.194
618	0.183	0.183	0.183	0.181
1123	0.167	0.167	0.168	0.164
1818	0.137	0.138	0.142	0.139
2707	0.111	0.096	0.108	0.104

The lower curve in Figure 4.7 corresponds to values calculated with these constants. The excellence of the fit through the first 1800 h can be seen from Figure 4.7, or from comparison of calculated and measured values given in Table 4.9. The calculated values are given under Auto-Catalysis Mechanism: Model I.

The following comparisons at the two temperatures are informative:

$$k_u \text{ (at } 120^\circ \text{ C)} / k_u \text{ (at } 90^\circ \text{ C)} = 0.00033 / 0.000093 = 3.5$$

$$fk_c \text{ (at } 120^\circ \text{ C)} / fk_c \text{ (at } 90^\circ \text{ C)} = 0.0160 / 0.0041 = 3.9$$

$$k_o \text{ (at } 120^\circ \text{ C)} / k_o \text{ (at } 90^\circ \text{ C)} = 0.00371 / 0.000896 = 4.14$$

It is the fortuitous closeness of the last two values to the integer 4 that accounts for the similarity of the two curves in Figure 4.7.

The last point at 90° C , taken at 2707 hours, deviates from the value predicted by Model I, in a direction that suggests that C does not build up as rapidly as predicted by the model. A modification, designated Model II, that accomplishes this assumes that C is formed only in the uncatalyzed reaction. In Table 4.9, the results of a calculation according to Model II with $k_u = 9.32 \times 10^{-5} \text{ h}^{-1}$, $f = 1$, and $k_c = 6.0 \times 10^{-3} \text{ M}^{-1} \text{ h}^{-1}$ are given. Further refinement of this model is being suspended until data at later times are obtained.

4.3.2. "Two-Exponential" Model. A second possible explanation begins with the observation that data in each experiment fit a function of the form

$$[\text{HEDTA}] = Q_2 e^{-\lambda_2 t} - Q_1 e^{-\lambda_1 t}$$

reasonably well. In Table 4.8 are shown the values of [HEDTA] calculated with a function of this type to match data from the 120° C experiment. Values of the parameters are: $Q_2 = 0.264$, $Q_1 = 0.052$, $\lambda_2 = 1.21 \times 10^{-3} \text{ h}^{-1}$, and $\lambda_1 = 6.48 \times 10^{-3} \text{ h}^{-1}$. The fit is within the experimental error of the measurements.

A similar comparison for the data from the 90° C experiment is shown in Table 4.9. Values of the parameters in this case are: $Q_2 = 0.230$, $Q_1 = 0.033$, $\lambda_2 = 2.68 \times 10^{-4} \text{ h}^{-1}$, and $\lambda_1 = 0.00648 \text{ h}^{-1}$. Measurements that remain to be taken on this reaction should provide a good test for this model.

4.3.2a. Is there a possible "two-exponential" model? The time variation of the concentration of a species involved in a system of reversible first-order reactions in series will be given as a sum of exponential terms.⁴² A few systems of this type have been examined to see if curves of the kind shown in Figure 4.7 could be accounted for. A system that qualitatively gives a behavior with an "induction period" is

but with the additional requirement that A and B be different forms of HEDTA, which are not distinguished in the analytical procedures used to measure HEDTA. From a practical point of view it is not clear what two forms of HEDTA might exist under tank or simulated waste conditions. In principle, HEDTA could be in equilibrium with its lactone (reaction 4.12),

although lactones are not normally found to be stable under basic conditions. A sample of HEDTA lactone was prepared according to a literature procedure⁴³ and examined by NMR spectroscopy in both D₂O and in D₂O/OD⁻ solution. The spectrum of the lactone obtained in D₂O immediately after preparation of the solution (ca. 1 min prior to acquisition of the spectrum) consisted of six resonances assigned as shown on the structure in reaction 4.12. Additional spectra were recorded at intervals over 1 h during which time the spectrum due to the lactone was replaced by that of HEDTA (chemical shift assignments of the spectrum for HEDTA are shown on the structure in reaction 4.12). Attempts to record the spectrum of the lactone in basic solution were unsuccessful as only HEDTA was observed within one minute of preparation of the solution. We conclude that there is no likelihood that HEDTA can be in equilibrium with its lactone under such highly basic conditions.

4.3.2b. Preparation of HEDTA-lactone. HEDTA lactone was prepared according to Merciny.⁴³ A 0.600 g sample (0.216 mmol) of HEDTA contained in a tared, open ampule was placed into a Schlenk tube and was evacuated using a vacuum pump. The Schlenk tube was placed in a tube furnace; the furnace temperature was raised to 165 °C, and then maintained at 165-170 °C for five h. After cooling to room temperature the vacuum was broken and the sample removed. The tan sample had a melting point of 210 °C and a mass of 0.552 g; the mass loss of 0.0476 g corresponds to 0.26 mmol of water. The ¹H NMR spectrum of the compound obtained on a freshly prepared D₂O solution consisted of six resonances as described earlier; the compound hydrolyzed over ca. 1 h to HEDTA.

5.0. ²⁷Al NMR studies of HEDTA-aluminum(III) as a function of pH.

The possibility that complexation of HEDTA by aluminum was somehow responsible for its activation toward thermal decomposition in simulated waste mixtures was advanced during the earliest studies of this process.⁴⁴ The possibility that a portion of the aluminum in waste mixtures is present as an HEDTA complex has continued to receive consideration.⁴⁵ To explore this possibility, we have examined the ²⁷Al NMR spectra of solutions of Al(NO₃)₃ under various pH conditions in the presence and absence of HEDTA. Representative results are shown in Figures 5.1 and 5.2.

Figure 5.1 shows a series of spectra taken on 0.5 M Al(III) solutions containing 0.52 M HEDTA at the pH values indicated. At pH = 5.9 and at 6.7 there are broad resonances at ca. 36 ppm and a shoulder at lower fields whose maximum is estimated to be at ca. 50 ppm. The former resonance is assigned to an HEDTA aluminum complex based upon an earlier assignment by Iyer, et al.⁴⁶ Iyer and coworkers assigned a resonance at 32.8 ppm to $[\text{Al}(\text{HEDTA})(\text{OH}_2)]$, and indicate that the resonance broadens and moves to lower field as the pH is increased above 3. This is attributed to the formation of an hydroxo complex and a pK_a of 5.07 was determined for the aquo complex. We suggest that the 36 ppm resonance is due to $[\text{Al}(\text{HEDTA})\text{OH}]^-$. Although we believe that the resonance at ca. 50 ppm is also probably due to the presence of one or more aluminum species,⁴⁷ there is a contribution from a non-linear baseline that results from a resonance due to aluminum that is present in the probe materials.⁴⁸ This nonlinear baseline is shown at a comparable gain in Figure 5.3. As the pH is increased the intensity of the resonance at 36 ppm decreases and a resonance at 80 ppm due to $\text{Al}(\text{OH})_4^-$ begin to grow in; this is indicated by the spectrum at pH = 11.1. At pH = 12.2 there is no longer any evidence of a resonance for an HEDTA complex, and the resonance due to $\text{Al}(\text{OH})_4^-$ has increased in intensity. That all of the aluminum is not accounted for by this resonance is demonstrated by the further increase in intensity of the resonance (relative to that of the reference) at pH = 13. The ratio of the integrated intensity of this peak to that of the reference peak is 2.8.

The series of spectra shown in Figure 5.2 are for 0.5 M Al(III) solutions prepared in the same fashion as those shown in Figure 5.1, except that no HEDTA was added. At high gain there is again evidence for a broad resonance centered at ca. 50 ppm at all pH values. At pH = 10.2 the resonance for $\text{Al}(\text{OH})_4^-$ is detectable. The intensity of this resonance increases as the pH increases in the same fashion as for the spectra obtained with HEDTA. The ratio of the integrated intensity of this peak to that of the reference peak is 2.7.

Although the broadness of the ^{27}Al resonance makes NMR a relatively insensitive method for detection of low concentrations of aluminum species, the similarity of the NMR spectra obtained at high pH values in the presence and absence of HEDTA suggests that little aluminum is present as an HEDTA complex under these conditions. The high stability of Al-HEDTA referred to in reference 45, 45 is relative to uncomplexed Al(III) which is equivalent to $\text{Al}(\text{OH}_2)_6^{3+}$. In strongly basic solution the concentration of the hexaquo complex is extremely small because of the equilibrium $\text{Al}(\text{OH}_2)_6^{3+} + 4 \text{OH}^- \rightleftharpoons \text{Al}(\text{OH})_4^- + 6 \text{H}_2\text{O}$. The equilibrium constant for this reaction is very large.⁴⁹ Thus the concentration of an HEDTA complex may be much larger than the concentration of the hexaquo complex but both concentrations are very much lower than the concentration of $\text{Al}(\text{OH})_4^-$ in strongly basic solution. Of course, the fact that the concentration of any HEDTA complex that does exist is very low cannot be used to rule out its participation as an intermediate in the thermal decomposition reaction.

Figure 5.1. ^{27}Al NMR spectra of solutions containing 0.5 M $\text{Al}(\text{NO}_3)_3$ and 0.52 M HEDTA and sufficient NaOH to adjust the pH to the desired range. The spectra shown as insets are recorded at 27 times the gain of the other spectra. The reference is external $\text{Al}(\text{OH}_2)_6^{3+}$. Measured values of the pH are shown for each spectrum.

Figure 5.2. ^{27}Al spectra of solutions containing 0.5 M $\text{Al}(\text{NO}_3)_3$ and sufficient NaOH to adjust the pH to the desired range. The reference is external $\text{Al}(\text{OH}_2)_6^{3+}$. Measured values of the pH are shown for each spectrum.

Figure 5.3. ^{27}Al NMR spectrum taken on water versus an external $\text{Al}(\text{OH}_2)_6^{3+}$ standard. Both the full spectrum and the spectrum in the inset were taken at the same gain values as those in Figures 5.1 and 5.2. The broad resonance centered at ca. 50 ppm is due to the probe.

References

- (1) E. C. Ashby, A. Annis, E. K. Barefield, D. Boatright, F. Doctorovich, C.L. Liotta, H.M. Neumann, A. Konda, C.-F. Yao, K. Zhang and N. G. McDuffie, *Synthetic Waste Chemical Mechanism Studies*. WHC-EP-0823, 1994.
- (2) Treadwell, F.P.; Hall, W.T. "Analytical Chemistry", Vol. I, 9th Edition; John Wiley, Inc.: New York, NY, ; p. 91.
- (3) Aldrich Chemical Co.
- (4) Nichols, M.L.; Willits, C.O. *J. Am. Chem. Soc.*, **1934**, *56*, 769.
- (5) Burns, E.A. in "The Analytical Chemistry of Nitrogen and Its Compounds"; Streuli, C.A.; Averell, P.R., Editors; Wiley-Interscience: NY, 1970; Chapter 3.
- (6) Georgia Tech progress report, February 1994.
- (7) Reference 1, p 90, Figure E.1.
- (8) Herting, D. April 30, 1991 memorandum, "Final word on simulated waste recipe. Strachen, D. letter to E. C. Ashby, May 28, 1992, indicates the nomenclature adopted for designation of the various simulated wastes developed by Herting.
- (9) Application of a redox analysis to HEDTA decomposition was described in the Georgia Tech FY 1992-93 final report, p 83.
- (10) Reference 1, p 58.
- (11) Based on the analysis of the sodium aluminate used for this preparation, which contains 8% by weight H₂O and 5% NaOH as impurities, the final concentration of aluminum is 1.55 M. Also, the final concentration of NaOH in the solution is 2.2 M.
- (12) Treadwell, F.P.; Hall, W.T. *Analytical Chemistry* **1937**, Vol 1, John Wiley & Sons, New York.
- (13) (a) Reference 1, p 86.

(b) Hydrogen, oxygen and nitrogen were determined using a 0.25 in x 12 ft, 60/80 mesh, 5Å molecular sieve column. Nitrous oxide was determined using a 0.53 mm x 25 M HP Chromopack Poraplot Q capillary column.
- (14) Reference 1, Experimental Section.
- (15) It should be noted that there is an alternative fragmentation of glycolate and the hydroxyethyl group of HEDTA that leads initially to HC(O)CO₂⁻ (glyoxalate) and then to oxalate. Although not explicitly included in the following discussion, glyoxalate must also be formed simultaneously with NO⁻ in a solvent cage. We

assume that glyoxalate behaves in a similar fashion to formaldehyde and that the analysis given here also applies to it.

- (16) Wayne, R.P., "Photochemistry", American Elsevier Publ. Co., 1970, p. 76.
- (17) Buchholz, J.R.; Powell, R.E., *J. Am. Chem. Soc.* **1963**, *85*, 509.
- (18) Hughes, M.N.; Stedman, G., *J. Chem. Soc.*, 1239, (1963).
- (19) Bonner, F.T.; Ravid, B., *Inorg. Chem.* **1975**, *14*, 558.
- (20) Hughes, M.N.; Wimbledon, P.E., *J. Chem. Soc., Dalton Trans.* **1976**, 703.
- (21) Berndt, D.C.; Fuller, R.L., *J. Org. Chem.* **1966**, *31*, 3312.
- (22) Bender, M.L.; Ginger, R.D. *J. Am. Chem. Soc.* **1955**, *77*, 348.
- (23) Hine, J.; King, R.S.M.; Midden, W.R.; Sinha, A. *J. Org. Chem.* **1981**, *46*, 3186.
- (24) Hughes, M.N.; Nicklin, H.G.; Shrimanker, K. *J. Chem. Soc., (A)* **1971** 3485.
- (25) Heiber, W.; Nast, R.; Proeschel, E., *Z. Anorg. Chem.* **1948**, *256*, 159.
- (26) Kurtenacker, A.; Werner, F., *Z. Anorg. Allgem. Chem.* **1927**, *160*, 387.
- (27) Bonner, F.T.; Dzelkalns, L.S.; Bonucci, J.A. *Inorg. Chem.* **1978**, *17*, 2487.
- (28) Georgia Tech monthly report, April 1993.
- (29) Holzapfel, H.; Wiss. Z. *Karl Marx Univ. Leipzig, Math.-Naturwiss. Reihe* **1959-60**, *9*, 17. *Chem. Abst.* **1960**, *57*, 387h.
- (30) Lunak, S.; Veprek-Siska, J. *Collect. Czech. Chem. Commun.* **1974**, *39*, 391.
- (31) Meisel, D.; Johah, C.D.; Kapoor, S.; Matheson, M. S.; Sauer, M.C. *Radiolytic and Radiolytically Induced Generation of Gases from Synthetic Wastes*, ANL 93/43, Oct. 1993, p. 37.
- (32) Reference 1, p. 72.
- (33) The equations for the 2-step sequence can be found in many chemical kinetics textbooks; e.g., Moore, J. W.; Pearson, R. G., *Kinetics and Mechanism*, John Wiley and Sons, 3rd Ed., 1981, p. 290-292.
- (34) Systems of consecutive first-order chemical reactions are mathematically identical to radioactive-decay chains, and equations for n-step chains are found in many radiochemistry or nuclear chemistry textbooks; e.g., *Introduction to Nuclear Physics and Chemistry*, Prentice-Hall, 1962, p. 37-38. The equations were first obtained by Bateman, H.; *Proc. Cambridge Phil. Soc.*, **15**, 423 (1910)

- (35) Reference 1, p. 2.
- (36) Table 4.5 is a corrected version of the table given in the Georgia Tech March 1994 report. The original data are taken from tables 1.1 (exp'ts 12B and 19B), 1.8 (exp't 15A), 1.9 (exp't 15A'), and 1.10 (exp't 22A). It should be noted that the column headings HEDTA-15A and HEDTA-16A are reversed in table 1.8 from reference 1 and this error was propagated in the March monthly report. Also the trial names HEDTA-15A and HEDTA-16A in table 1.9 from reference 1 should have been HEDTA-15A' and HEDTA-16A'. This error was also propagated in the March monthly report.
- (37) Reference 1, p. 34.
- (38) Reference 1, p. 4; Table E.4.
- (39) Reference 1, p. 3.
- (40) Reference 1, p. 11.
- (41) Reference 1, p. 23.
- (42) See, for example, J. W. Moore and R. G. Pearson, "Kinetics and Mechanism", John Wiley and Sons, 3rd edition, 1981, p. 296.
- (43) Merciny, E. *Anal. Chim. Acta* **1967**, 37, 542.
- (44) Delegard, C. Informal Report, RHO-LD-124, 1980.
- (45) Westinghouse Hanford Co. internal memo 28120-91-087; T. Cooper to G. Johnson.
- (46) Iyer, R.K.; Karweer, S.B.; Jain, V.K. *Magn. Reson. Chem.* **1989**, 27, 328.
- (47) The speciation of aluminum in aqueous base has received a great deal of attention (see Singhal, A.; Keefer, K.D.; *J. Mater. Res.* **1994**, 9, 1973 for a recent review); however, most studies have examined solutions of much lower pH than those studied here. One exception is a report by Akitt, et al. who mentions that only 1/6 of the aluminum present in concentrated sodium hydroxide solutions is observed as $\text{Al}(\text{OH})_4^-$ (Akitt, J.W.; Gessner, W. *J. Chem. Soc., Dalton* **1984**, 147).
- (48) This is a well known phenomenon, see Akitt, J.W. "Aluminum, Gallium, Indium and Thallium," in *Multinuclear NMR*, Mason, J., Ed., Plenum Press, New York, 1987.
- (49) An old estimate gives $K = 10^{33}$ but this neglects more recent information concerning the complexity of speciation in Al(III) solutions. Clifford, A.F. *Inorganic Chemistry of Qualitative Analysis*, Prentice-Hall, New York, 1961, p. 235.

Distribution

**No. of
Copies**

**No. of
Copies**

OFFSITE

- S. Agnew
Los Alamos National Laboratory
MS-C345, Group INC-4
P.O. Box 1664
Los Alamos, NM 87545
- 2 Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
Attn: D. Meisel
L. Stock, Chemistry Division
- E. K. Barefield
225 North Avenue
Boggs Chemistry Building
Georgia Institute of Technology
Atlanta, GA 30332
- D. O. Campbell, MS 6268
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6268
- B. S. Hudson
Lawrence Livermore National Laboratory
P.O. Box 271
Lindsborg, KA 67456
- L. Kovach
NUCON
P.O. Box 29151
Columbus, OH 43229
- 2 SAIC
20300 Century Blvd.
Germantown, MD 20874
Attn: R. Daniels
P. Hogroian

- W. W. Schulz
727 Sweetleaf Drive
Wilmington, DE 19808
- 16 School of Chemistry and Biochemistry
Georgia Institute of Technology
Atlanta, GA 30332-0400
Attn: E. K. Barefield (10)
D. Boatright
A. Deshpande
F. Doctorovich
C. L. Liotta
H. M. Neumann
S. Seymore
- 3 U.S. Department of Energy
Trevion II
Washington, DC 20585-0002
Attn: P. Bryns, EM-35
C. O'Dell, EM-36
D. Pepson, EM 36
- 2 Westinghouse Savannah River
P.O. Box 616
Aiken, SC 29802
Attn: N. E. Bibler, Bldg. 773A, Rm 108
P. d'Entremont, Bldg. 703-H

ONSITE

- 6 DOE Richland Operations Office
R. F. Christensen	S7-54
R. E. Gerton	S7-54
J. M. Gray	S7-54
M. F. Jarvis	S7-54
G. Rosenwald	S7-54
Reading Room	A1-65

**No. of
Copies**

31 Westinghouse Hanford Company

H. Babad	S7-30
W. B. Barton	R2-11
R. J. Cash	S7-15
K. A. Gasper	G3-21
D. L. Herting	T6-09
J. D. Hopkins	R2-11
J. Jewett	T6-09
G. D. Johnson (5)	S7-15
N. W. Kirch	R2-11
J. W. Lentsch	S7-15
R. M. Marusich	H5-65
N. G. McDuffie (10)	S7-15
D. M. Ogden	H0-34
M. A. Payne	S7-14
J. C. Person	T6-09
D. A. Reynolds	R2-11
D. J. Sherwood	S7-15
R. J. Van Vleet	H4-63

49 Pacific Northwest Laboratory

Z. I. Antoniak	K7-15
J. L. Bates	K2-45

**No. of
Copies**

J. W. Brothers (10)	K5-22
S. A. Bryan	P7-25
L. L. Burger	P7-25
D. M. Camaioni	K2-38
J. A. Campbell	P8-08
P. A. Gauglitz	P7-41
S. C. Goheen	P8-08
R. J. Hall	K8-28
R. T. Hallen	P8-38
J. D. Hudson	K7-15
M. A. Lilga	P8-38
L. R. Pederson (10)	K2-44
H. C. Reid	K7-15
W. D. Samuels	K2-44
R. D. Scheele	P7-25
G. F. Schiefelbein	P8-38
A. Shekarriz	K7-15
C. W. Stewart	K7-15
R. W. Stromatt	P7-22
J. M. Tingey	P7-25
D. S. Trent	K7-15
H. H. Van Tuyl	P7-22
Information Release Office (7)	K1-06