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**Mechanisms of Gas Generation from
Simulated SY Tank Farm Wastes:
FY 1995 Progress Report**

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July 1996

Prepared by the Georgia Institute of Technology for
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Richland, Washington 99352

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Summary

This report summarizes progress made at the Georgia Institute of Technology during fiscal year (FY) 1995. 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 tank farm waste mixtures. Topics reported are 1) long-term studies of the decomposition of HEDTA in simulated waste mixtures under an argon atmosphere at 90 and 120°C, including time profiles for disappearance of HEDTA and appearance of products, and the quantitative analysis of the kinetic behavior; 2) considerations of hydroxylamine as an intermediate in the production of nitrogen containing gases by HEDTA decomposition; 3) some thoughts on revisions of the global mechanism for thermal decomposition of HEDTA under argon; 4) preliminary long-term studies of the decomposition of HEDTA in simulated waste under an oxygen atmosphere at 120°C; 5) estimation of the amount of NH_3 in the gas phase above HEDTA reaction mixtures; and 6) further examination of the interaction of aluminum with nitrite ion using ^{27}Al NMR spectroscopy.

Long-Term Studies of the Decomposition of HEDTA in Simulated Waste Mixtures Under Argon

Three long-term studies of the decomposition of HEDTA in simulated waste have been completed; two of these studies were conducted under an argon atmosphere. The first of these, conducted at 90°C, was initiated in May 1994 and ran for 7003 hours. The second study was conducted at 120°C and ran for 4014 hours. The results of these studies have been used to develop 1) time profiles for loss of HEDTA and for formation and disappearance of products of the decomposition reaction and 2) a quantitative description of the kinetic behavior of HEDTA and of a primary product ED3A, which also decomposes. Finally, these results have been used to refine our earlier mechanism of fragmentation of HEDTA and for the production of H_2 , N_2 , N_2O and NH_3 under an inert atmosphere. An important observation from these studies, which has not been fully integrated into the mechanism, is that the nitrous oxide-to-hydrogen ratio, which is initially >30 at 120°C, decreases to 6-7 at 4000 hours. That this is a result of the change in composition of the species reacting is confirmed by an experiment in which a sample that had been heated until all of the HEDTA had reacted (~2000 hours) was heated for an additional 3500 hours under a fresh argon atmosphere. The ratio of nitrous oxide to hydrogen was 2.1 for this sample, which approaches the ratio observed for Tank 241-SY-101, 0.85. The mechanistic reasons for this behavior are not clear at this time. While HEDTA does not represent the present organic fraction of tank wastes well, these results suggest that the products of HEDTA aging do approximate the behavior of actual wastes.

Quantitative Analysis of the Kinetic Behavior of HEDTA Decomposition

Quantitative analyses of the kinetic behavior of HEDTA and ED3A decomposition in simulated waste under argon at 90 and 120°C are described in this report. These analyses are based upon the latest results obtained using stainless steel cylinders as reaction vessels, although some earlier results obtained using the glass-Teflon apparatus are included where appropriate. The quantitative description of the "rate law" for the disappearance of HEDTA is different at the two temperatures. At 120°C the disappearance of HEDTA is first-order in [HEDTA], but because of the large decrease in nitrite concentration during the reaction, a simple pseudo first-order kinetic treatment cannot be used. By using the experimentally determined variation of nitrite with time, the rate behavior of HEDTA is accounted for quantitatively and the pseudo first-order rate constant determined. At 90°C the disappearance of HEDTA is more complex. For purposes of analysis, the reaction is empirically described as zero-order until about one-half of the HEDTA is consumed, and thereafter first-order. The disappearance of ED3A, which is formed as a primary product of HEDTA decomposition, appears to be first order at both 90 and 120°C. The analysis of the data at 120°C suggests, however, that only about 85% of HEDTA decompositions yield ED3A.

Hydroxylamine as an Intermediate in the Thermal Decomposition of HEDTA

Formation of ammonia in simulated waste media from nitrite ion is expected to occur by the intermediate formation of hydroxylamine. We provided some theories on the microscopic mechanism of disproportionation of hydroxylamine to produce ammonia and molecular nitrogen and thermodynamic considerations of the potential for hydroxylamine to produce hydrogen in basic solution. Experiments were designed to detect the formation of hydrogen from hydroxylamine in basic solution. Hydrogen was not observed, and we conclude that this is not an important reaction of hydroxylamine. The failure to observe hydrogen also suggests that diimine, $\text{HN}=\text{NH}$, cannot be the precursor to the molecular nitrogen that is produced.

A Revised Mechanism for the Thermal Decomposition of HEDTA to ED3A in the Presence of Aluminate, Hydroxide, and Nitrite

Both product gas analyses and nitrite analyses indicated that the ratio of nitrite consumed to HEDTA reacting is greater than two. This is inconsistent with the mechanism that was proposed earlier by E. C. Ashby (WHC) for the HEDTA decomposition, which assumed a 1:1 nitrite to HEDTA stoichiometry. A modified mechanism allowed for an increased nitrite to HEDTA stoichiometry. The new mechanism also allowed for the possibility of autocatalysis, which was suggested as a possible explanation for the curvature in the plot of $\ln[\text{HEDTA}]$ versus time that was observed at 90°C.

Long-Term Studies of the Decomposition of HEDTA in Simulated Waste Mixtures Under Oxygen

The reaction of HEDTA in simulated waste was examined at 120°C under an oxygen atmosphere. The presence of oxygen markedly inhibits the rate of consumption of HEDTA and substantially inhibits the reaction of nitrite. The rates of production of nitrogen, nitrous oxide, and ammonia were all slower in the presence of oxygen, which was not unexpected, since these products are derived from nitrite. However, hydrogen was generated at a much faster rate in the presence of oxygen. The amount of data is limited, but the initial rates of the reactions in the presence and absence of oxygen appear to be about the same, with the rate of the reaction in the presence of oxygen slowing only after about 25 hours. No satisfactory mechanistic model is yet available to explain this behavior. That some redox active metal ion, rather than aluminum, could be responsible for activation of nitrite ion, and that in the presence of oxygen it is oxidized to an oxidation state in which it is no longer active, was ruled out.

Estimation of Ammonia in the Gas Phase Based on Henry's Law

The Henry's law constant for the solubility of ammonia in simulated waste, which was determined by Norton and Pederson (PNNL), was used to estimate that less than 2% of the ammonia produced is present in the headspace above reaction mixtures in the stainless steel cylinders. This supports our earlier assumption and justifies the determination of total ammonia by analysis of only the condensed phase portion of the reaction mixture.

The Role of Aluminum: ^{27}Al NMR Spectroscopic Data Suggesting Formation of Aluminum Nitrite Complexes in Acetonitrile

Aluminum-27 NMR spectroscopy was used to examine mixtures of AlX_3 ($\text{X}=\text{Cl}, \text{Br}$) and Bu_4NNO_2 in acetonitrile in an attempt to obtain evidence for the formation of aluminum-nitrite complexes. The ultimate objective was to isolate and characterize, especially with regard to reactivity, an aluminum-nitrite complex. New resonances have been observed in the ^{27}Al NMR spectra of mixtures of NO_2^- and AlCl_3 that are attributed to the formation of nitrite complexes. These are currently of unknown stoichiometry and structure, although the chemical shifts are consistent with a tetrahedral environment for the aluminum atom. Resonances for at least two different species were observed at low NO_2^-/Al ratios (≤ 5) for AlCl_3 , which were not observed with AlBr_3 . At a NO_2^-/Al ratio of 10, both aluminum salts displayed a resonance at about δ 23. This is consistent with either five- or six-coordinate aluminum, but again, the composition and structure are unknown.

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Acronyms and Abbreviations

ED3A	ethylenediamine 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, $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$
s-EDDA	ethylenediamine-N,N'-diacetic acid, $\text{HO}_2\text{CCH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CO}_2\text{H}$
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 241-SY-101
atm	atmosphere
e_{oxid}	electrons produced by oxidation
e_{red}	electrons produced by reduction
FY	fiscal year
GC	gas chromatography
IC	ion chromatography
NMR	nuclear magnetic resonance
rm temp	room temperature
SY1-SIM-91B	simulated waste
SY1-SIM-91B-NC	simulated waste without added carbonate
temp	temperature

1.0 Introduction

The objective of this work is 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 tank farm waste mixtures. This report summarizes the results of work done at the Georgia Institute of Technology in fiscal year 1995. Topics discussed are 1) long-term studies of the decomposition of HEDTA in simulated waste mixtures under an argon atmosphere at 90 and 120°C, including time profiles for disappearance of HEDTA and appearance of products and the quantitative analysis of the kinetic behavior; 2) considerations of hydroxylamine as an intermediate in the production of nitrogen containing gases by HEDTA decomposition; 3) some thoughts on the revision of the global mechanism for thermal decomposition of HEDTA under argon; 4) preliminary long-term studies of the decomposition of HEDTA in simulated waste under an oxygen atmosphere at 120°C; 5) estimation of the amount of NH_3 in the gas phase above HEDTA reaction mixtures; and 6) further examination of the interaction of aluminum with nitrite ion using ^{27}Al NMR spectroscopy.

Section 2 of this report describes the work conducted over the last three years at GIT. Section 3 contains a discussion of the kinetic behavior of HEDTA under argon; Section 4 discusses the role of hydroxylamine. Thermal decomposition of HEDTA to ED3A is the subject of Section 5, and decomposition of HEDTA in simulated waste mixtures under oxygen is covered in Section 6. In Section 7 we estimate ammonia in the gas phase; the role of aluminum is discussed in Section 8.

2.0 Long-Term Studies of the Decomposition of HEDTA in Simulated Waste Mixtures Under Argon

A major objective of the work done during the past two fiscal years was to develop a detailed model for the decomposition of HEDTA in simulated waste and the concomitant production of the gases H_2 , N_2 , N_2O and NH_3 . During fiscal year 1995, three long-term studies of the decomposition of HEDTA in simulated waste were completed. Two of these studies were conducted under an argon atmosphere. The first of these, conducted at $90^\circ C$, was initiated in May 1994 and ran for 7003 hours. The second study was conducted at $120^\circ C$ and ran for 4014 hours. The protocol used for both studies was described in Georgia Tech's 1993-94 annual report (Barefield et al. 1995). The results of these studies are used in this report to develop time profiles for loss of HEDTA and for formation and disappearance of products of the decomposition reaction, and to develop a quantitative description of the kinetic behavior of HEDTA and of a primary product ED3A, which also decomposes. Finally, these results were used to refine our earlier mechanism of fragmentation of HEDTA and for the production of H_2 , N_2 , N_2O and NH_3 under an inert atmosphere.

2.1 Reaction at $90^\circ C$ under argon

This report contains data on this reaction through more than 7000 hours (approximately 10 months). Two samples were obtained at each of nine reaction times over this period. Analytical results are given in Table 2.1. The data in Table 2.1 are based upon the measured initial concentration of HEDTA as determined by NMR (0.197 M). The total amount of gas produced by the reaction was measured manometrically as described in Barefield et al. (1995). A comparison of this value (total moles of gas) with the sum of the individual measurements of H_2 , N_2 , and N_2O is shown in Table 2.2.

Table 2.1. Reaction of HEDTA in simulated waste at 90°C under argon
(experiment HEDTA-1C, SY1-SIM-91B-NC)^(a)

Time (h)	0	160		618		1123		1818	
SAMPLE	A, B	A	B	A	B	A	B	A	B
HEDTA (NMR) ^(b)	100	100.5	95.5	93.9	92.9	86.3	85.3	73.1	63.1
HEDTA (IC)	100	98.6±3.1	100.4±1.0	89.1±0.7	95.7±5.2	81.9±1.0	85.7±1.4	73.8±2.3	69.0±2.4
ED3A	0	1	2	7.1	9.1	18.8	15.8	21.6	28.2
s-EDDA	0	-	-	-	-	-	-	-	-
C ₂ O ₄ ²⁻	0	-	-	0.9±0.1	1.9±0.1	3.4±0.1	2.8±0.1	3.8±0.0	4.2±0.0
HCO ₂ ⁻ (NMR)	0	-	-	16.1	18.7	36.0	31.4	43.7	57.9
HCO ₂ ⁻ (IC) ^(c)	0	3.2±0.0	8.0±1.0	18.1±0.0	14.3±1.1	36.3±0.2	28.7±0.4	41.5±0.0	49.9±0.3
H ₂	0	0.05±0.00	0.03±0.00	0.18±0.00	0.12±0.00	0.25±0.01	0.20±0.00	0.35	0.54±0.02
N ₂	0	0.5±0.0	0.7±0.1	2.2±0.1	2.9±0.0	5.9±0.1	4.9±0.0	6.7	8.9±0.4
N ₂ O	0	1.4±0.0	1.7±0.1	4.4±0.1	5.0±0.1	11.5±0.2	8.7±0.1	13.3	21.1±0.7
NH ₃ (aq.)	0	1.0±0.2	1.4±0.2	4.8±0.1	5.9±0.6	15.3±0.5	11.3±0.5	17.7±0.3	20.4±0.3
NO ₂ ⁻ (M)	2.24	2.16±0.00	2.23±0.01	2.29±0.11	2.24±0.01	2.11±0.00	2.14±0.01	2.09±0.01	2.04±0.01

Table 2.1 (contd)

Time (h)	2707		3811		5207		7003	
SAMPLE	A	B	A	B	A	B	A	B
HEDTA (NMR) ^(b)	50.4	56.0	41.6	48.8	35.5	37.1	29.6	26.6
HEDTA (IC)	61.9±4.4	57.1±1.2	43.8±5.5	40.2±3.7	30.8±0.2	30.8±0.1	27.4±0.0	19.6±0.1
ED3A	42.1	36.7	45.9	52.5	56.6	57.6	50.3	67.5
s-EDDA	3	5	3	3	6	5	4	5
C ₂ O ₄ ²⁻	5.2±0.3	6.2±0.2	5.6±0.3	6.7±0.2	2.3±0.3	2.0±0.9	2.9±0.0	2.6±0.0
HCO ₂ ⁻ (NMR)	81.1	73.5	75.5	90.6	98.6	99.6	88.8	116.2
HCO ₂ ⁻ (IC) ^(c)	83.9±2.2	76.3±2.2	96.3±1.5	94.4±1.2	84.2±0.5	86.8±1.0	96.0±0.3	104.5±0.9
H ₂	0.61±0.01	0.79±0.01	0.93±0.02	0.78±0.02	1.21	0.99±0.01	0.89±0.05	1.39±0.01
N ₂	12.4±0.0	13.4±0.0	16.7±0.3	16.1±0.4	19.8	21.2±0.0	21.6±1.0	22.4±0.3
N ₂ O	22.0±0.3	28.0±0.5	37.2±0.8	32.1±0.8	39.8	38.0±0.13	40.5±2.6	51.0±0.5
NH ₃ (aq.)	34.4±0.7	35.2±0.1	41.3±0.8	40.8±0.3	44.6±1.0	56.0±0.8	53.0±1.2	64.3±1.0
NO ₂ ⁻ (M)	2.00±0.02	2.10±0.01	1.92±0.00	2.01±0.02	1.89±0.01	1.91±0.00	1.90±0.01	1.82±0.01

(a) All results in moles of product per 100 moles of starting HEDTA (except for nitrite).
(b) The initial concentration of HEDTA (as determined by ¹H-NMR) was 0.197 M.
(c) 6.1±1.4% of formate was detected at time = 0. All the values for HCO₂⁻ were corrected by subtracting that amount.

Table 2.2. Comparison of total moles of gas versus the sum of the individual amounts of H_2 , N_2 , and $\text{N}_2\text{O}^{(a)}$

Time (hours)	Total Moles of Gas	$\text{H}_2 + \text{N}_2 + \text{N}_2\text{O}$
160	0.87 ± 0.0	2.2 ± 0.2
618	6.2 ± 0.9	7.3 ± 0.7
1123	14.6 ± 1.4	15.7 ± 1.9
1818	28.4 ± 2.9	25.3 ± 5.1
2707	39.3 ± 4.4	38.7 ± 3.6
3811	46.8 ± 3.1	51.9 ± 2.9
5207	52.0 ± 2.6	60.5 ± 0.3
7003	66.0 ± 0.5	68.9 ± 5.9
(a) All results in moles of gas per 100 moles of starting HEDTA. Total moles of gas refers to the value measured manometrically. Plots of the temporal behavior of condensed phase reactants/products and of the appearance of gaseous products are given in Figures 2.1 and 2.2, respectively.		

Plots of the temporal evolution of condensed phase and gaseous products are shown in Figures 2.1 and 2.2, respectively. The total moles of gas determined manometrically (Table 2.2) is approximately coincident with the sum of the individual amounts of H_2 , N_2 , and N_2O determined by GC (most of the values overlap when the errors are considered). This indicates that no significant amounts of other products are present in the gas phase, and that the error introduced by the vapor pressure due to NH_3 is small. The latter point is discussed in some detail in Section 7.0 of this report.

Since all of the nitrogen atoms in the nitrogen-containing products are assumed to be derived from NO_2^- , the ratio $\Delta\text{NO}_2^-/\Delta\text{HEDTA}$ is of interest. A plot of $[\text{NO}_2^-]$ versus ΔHEDTA is shown in Figure 2.3. The solid line, which is based upon a least squares fit to the data, corresponds to a value of 2.5 for $\Delta\text{NO}_2^-/\Delta\text{HEDTA}$. The two dashed lines correspond to values of 2 (upper line) and 3 (lower line).

Redox analyses have been performed using the same method that was described in our 1993—94 annual report (Barefield et al. 1995) but with the modified set of oxidation half-reactions described in section 5.0. These results, which are recorded in Table 5.1, show that the difference between the amount of electrons produced by reductive and oxidative pathways is small, which suggests that the model accounts for the major reaction pathways.

Figure 2.1. Time evolution of condensed phase products from reaction of HEDTA in simulated waste at 90°C under argon (experiment: HEDTA-1C) (▲ = HEDTA, ◆ = formate, ■ = ED3A, x = oxalate, ● = s-EDDA)

Figure 2.2. Time evolution of gaseous products from reaction of HEDTA in simulated waste at 90°C under argon (experiment HEDTA-1C) (■ = NH₃, ◆ = N₂O, ● = N₂, ▲ = H₂) (NH₃ is included in this figure although it is actually contained in the condensed phase)

Figure 2.3. Concentration of nitrite ion versus percent HEDTA reacted in the decomposition of HEDTA at 90°C versus time (experiment HEDTA-1C). The solid line was computed by a least squares fit to the data and corresponds to a value of 2.5 for $\Delta[\text{NO}_2^-]/\Delta[\text{HEDTA}]$. The dotted lines are computed for values of 2 (upper line) and 3 (lower line).

2.2 Reaction at 120°C under argon

The reaction of HEDTA in simulated waste was monitored for 4014 hours (~5.5 mon) at 120°C under an argon atmosphere. The protocol used to obtain the data shown in Table 2.3 was identical to that used for the 90°C experiments. Data from two separate series of experiments (HEDTA-2C and HEDTA-3C) are recorded in Table 2.3. The first series (HEDTA-2C) showed very erratic gas analyses that were traced to leakage at the threads joining the stainless steel cylinder to the valve for some of the samples. The condensed phase data appeared to be unaffected, but the gas phase data were unusable. This problem was solved in the second series (HEDTA-3C) by applying greater torque to the valve when it was fitted to the cylinder. The analyses of the condensed phase in the first series did reveal, however, that the reaction had a rate that was more than twice that of earlier reactions conducted in Teflon-lined glass vessels for which a half-life of about 500 hours was determined (Barefield et al. 1995). This knowledge allowed us to set an accelerated schedule for removing samples from the oil bath for the second series so that the early phase of the reaction could be more closely examined.

Because it was determined rather early during the first series of experiments that a second series would be required, the sampling schedule and protocol were modified for the last samples in the series. At 2013 hours the remaining four samples were withdrawn from the oil bath. The gas phase of each was analyzed in the same fashion as the previous fourteen. One of the samples produced an extraordinary amount of gas, which was probably a result of an accidental addition of two aliquots of the initial reaction mixture. This sample was dropped from further consideration. Of the remaining three samples, two appeared to not have leaked. After the gas analysis was complete, the headspace of one of the two samples was evacuated in the same fashion as when the samples were originally prepared and a new atmosphere of argon established. This sample was again placed in the 120 °C bath and heated for an additional 3503 hours. The analyses of this sample will be discussed in a subsequent section. The condensed phases of the remaining two samples were analyzed according to the usual protocol and the results are included with those of the previous 14 in Table 2.4.

Plots of the temporal evolution of condensed phase and gaseous products are shown in Figures 2.4 and 2.5, respectively. Table 2.4 shows a comparison of the total amount of gas measured manometrically with the amount $H_2 + N_2 + N_2O$ (HEDTA-3C data).

The data in Table 2.4 indicate that the total moles of gas measured manometrically is approximately coincident with the sum of the quantities of H_2 , N_2 and N_2O determined by individual gas chromatographic measurements (most of the values actually overlap considering the errors). This indicates that no significant amounts of other products are present in the gas phase, and that the error introduced by the vapor pressure due to NH_3 is relatively small (see Section 7.0).

Table 2.3. Reaction of HEDTA in simulated waste: experiments HEDTA-2C (A) and HEDTA-3C (B)
(SY1-SIM-91B-NC, 120°C, argon atmosphere, stainless steel vessels)^(a)

Time (h)	0	30		77		99		149		247	
SAMPLE	A, B	A	B	A	B	A	B	A	B	A	B
HEDTA (NMR) ^(b)	100	91	88	70	74	65.7	67.5	53.5	58.0	44.2	47.8
HEDTA (IC)	100	89.3±0.2	87.8±0.2	70.2±0.7	69.5±0.2	73.5±1.9	68.2±2.9	51.7±0.1	58.8±0.9	39.9±0.9	44.1±0.0
ED3A	0	6.3	trace	21.8	20.4	33.2	35.9	34.9	30.4	45.7	47.5
s-EDDA	0	0	0	trace	trace	trace	trace	trace	trace	4	4
C ₂ O ₄ ²⁻	0	0.8±0.1	0.6±0.0	1.7±0.2	1.4±0.1	2.9±0.1	2.9±0.5	2.6±0.1	2.6±0.2	3.6±0.0	3.8±0.2
HCO ₂ ⁻ (NMR)	trace	11.2	10.9	36.0	33.1	46.2	48.6	57.3	53.4	74.6	70.7
HCO ₂ ⁻ (IC) ^(c)	0	10.7±0.0	10.1±0.0	40.8±0.9	37.5±0.1	41.1±0.2	45.8±0.7	61.8±6.6	61.2±0.5	81.6±0.1	82.2±4.8
H ₂	0	0.12±0.00	0.14±0.00	0.47±0.08	0.39±0.00			0.83±0.01	0.64±0.00	1.15±0.057	0.92±0.023
N ₂	0	1.48±0.01	1.17±0.03	4.53±0.12	4.24±0.09			8.30±0.15	7.08±0.02	11.49	11.17±0.20
N ₂ O	0	3.08±0.07	2.82±0.04	16.45±0.27	12.10±0.13			27.87±0.32	22.54 ±0.39	42.13	31.86±0.86
NH ₃ (aq.)	0	3.1±0.3	3.0±0.1	17.0±0.0	16.5±0.2	20.3±0.2	20.7±0.0	32.1±0.6	28.8±0.1	43.8±1.7	40.9±1.5
NO ₂ ⁻ (M)	2.24	2.23±0.0	2.21±0.0	2.08±0.00	2.13±0.03	2.15±0.00	2.18±0.00	2.00±0.0	2.03±0.0	1.95±0.04	1.92±0.00

Time (h)	261		405		504		603		913	
SAMPLE	A	B	A	B	A	B	A	B	A	B
HEDTA (NMR) ^(b)	39.2	39.5	23.9	20.9	17.2	17.4	11.3	19.8	10.4	5.6
HEDTA (IC)	36.3±1.3	31.0±0.2	23.1±0.2	23.7±0.7	11.8±0.3	12.7±0.4	13.3±0.1	15.6±0.1	8.0±0.1	5.0±0.1
ED3A	56.4	63.1	67.3	62.7	75.2	74.7	72.9	70.9	71.8	71.5
s-EDDA	4	4	5	6	8.1	7.7	6	6	9.8	10.8
C ₂ O ₄ ²⁻	7.2±0.9	5.0±0.1	8.2±0.0	8.1±0.0	5.3±0.1	7.3±0.8	11.0±0.0	6.5±0.1	9.7±1.0	5.1±0.2
HCO ₃ ⁻ (NMR)	96	107	115.1	111.5	121.1	120.7	130.8	129.2	137.9	134.0
HCO ₃ ⁻ (IC) ^(c)	90.7±0.5	93.4±0.2	137.3±0.2	135.9±2.3	119.1±0.2	120.2±0.5	154.8±0.7	139.2±0.8	145.6±0.3	148.1±0.2
H ₂					2.85±0.05	2.80±0.04			3.26±0.05	4.96±0.06
N ₂					17.14±0.26	16.42±0.13			19.25±0.34	21.23±0.31
N ₂ O					62.63±1.43	60.97±1.27			63.42±1.49	78.06±1.53
NH ₃ (aq.)	39.1±0.2	62.8±1.5	62.8±1.5	54.3±2.5	72.2±1.6	64.5±1.1	71.0±2.3	67.1±3.7	73.9±1.1	74.3±0.5
NO ₂ ⁻ (M)	2.06±0.01	2.02±0.01	1.89±0.00	1.85±0.01	1.76±0.01	1.73±0.00	1.79±0.00	1.82±0.01	1.76±0.00	1.69±0.00

Table 2.3 (contd)

Table 2.3 (contd)

Time (h)	913		1411		1710		2013		4014 ^(d)	
SAMPLE	A	B	A	B	A	B	C ^(d)	D ^(d)	A	B
HEDTA (NMR) ^(b)	trace	trace	0	0	-	-	0	0	-	-
HEDTA (IC)	4.9±0.4	4.1±0.1	2.8±0.1	1.3±0.0	1.2±0.3	0.9±0.1	0.6±0.0	1.4±0.0	trace	trace
ED3A	68.8	67.6	64.7	61.1	59.8	63.3	52.9	61.1	35.8	41.3
s-EDDA	6	6	8.1	11.4	14.1	15.0	15	12.7	18.5	19.7
C ₂ O ₄ ²⁻	5.6±0.9	9.1±0.0	5.5±0.6	6.5±0.1	7.1±0.5	4.7±0.0	5.8±0.0	15.3±0.0	8.2±0.5	10.8±0.2
HCO ₂ ⁻ (NMR)	143.5	145.3	142.9	149.6	154.4	155.5	158.7	157.5	186.5	177.0
HCO ₂ ⁻ (IC) ^(c)	154.5±2.1	148.8±0.3	153.2±4.2	158.2±0.7	172.7±1.0	167.4±0.5	167.2±0.7	165.0±0.6	230.5±1.5	213.9±0.8
H ₂					8.29±0.45	9.92±0.30			15.73±0.28	13.83±0.14
N ₂					29.69±1.58	30.58±0.95			44.91±0.06	45.22±0.82
N ₂ O					85.70±5.35	93.11±3.59			100.4±3.6	105.6±2.0
NH ₃ (aq.)	74.1±2.1	65.0±1.3	91.3±1.6	89.4±2.0	91.9±1.1	86.7±1.1	91.3±1.4	86.0±0.6	103.9±2.5	109.8±2.3
NO ₂ ⁻ (M)	1.73±0.0	1.72±0.1	1.68±0.1	1.59±0.1	1.61±0.01	1.59±0.00	1.58±0.0	1.62±0.1	1.46±0.01	1.63±0.00

(a) All results in moles of product per 100 moles of starting HEDTA (except for nitrite).
 (b) The initial concentration of HEDTA (as determined by ¹H-NMR) was 0.216 ± 0.003 M for HEDTA-3C and 0.224±0.004 M for HEDTA-2C.
 (c) 3.0 ± 0.4% and 4.6 ± 0.2% of formate was detected at time = 0 for HEDTA-3C and HEDTA-2C, respectively. All values for HCO₂⁻ were corrected by subtracting that amount.
 (d) No peaks due to u-EDDA were detected by ¹H-NMR (300 MHz). Acetate (2.4%) was observed in both A and B samples by ¹H-NMR.

Figure 2.4. Time evolution of condensed phase reactant/products from reaction of HEDTA in simulated waste at 120°C under argon (HEDTA-2C: Δ = HEDTA, $\diamond$ = formate, $\square$ = ED3A, $\times$ = oxalate, $\circ$ = s-EDDA; HEDTA-3C: $\blacktriangle$ = HEDTA, $\blacklozenge$ = formate, $\blacksquare$ = ED3A, $\times$ = oxalate, $\bullet$ = s-EDDA)

Figure 2.5. Time evolution of gaseous products from reaction of HEDTA in simulated waste at 120°C under argon (experiment HEDTA-2C: $\square$ = NH₃, $\diamond$ = N₂O, $\circ$ = N₂, Δ = H₂; HEDTA-3C: $\blacksquare$ = NH₃, $\blacklozenge$ = N₂O, $\bullet$ = N₂, $\blacktriangle$ = H₂)

Table 2.4. Comparison of total moles of gas versus sum of individual amounts H₂, N₂ and N₂O (experiment HEDTA-3C)^(a)

Time (hours)	Total Moles of Gas	H ₂ +N ₂ +N ₂ O
30	3.5±0.3	4.4±0.3
77	16.1±2.1	19.1±2.4
149	30.9±3.4	33.6±3.4
247	45.7±6.0	45.9±2.0
504	69.1±0.2	81.4±1.2
913	81.2±8.8	95.1±9.2
1710	123.3±4.9	128.6±5.0
4014	151.4±0.0	162.9±1.8
(a) All results in moles of gas per 100 moles of starting HEDTA. Total moles of gas refers to the value measured manometrically.		

The data in Table 2.3 indicate that approximately 3.3 equivalent of nitrite were consumed at 4014 hours per equivalent of HEDTA that reacted. This is the cumulative amount of nitrite that has reacted at this time and includes nitrite consumed by reaction with ED3A, s-EDDA, and any other fragments formed that may have reacted further.

Redox analyses have been also been performed for the 120°C reaction by the procedure described in the FY 1993-94 report (Barefield et al. 1995) but also using the modified reaction sequence described in Section 5.0. These results (see Table 5.2) show increasingly large differences in the amount of electrons produced by reductive and oxidative pathways as the reaction proceeds. This is not surprising, given the extent to which reaction of ED3A contributes to the products at the later times. There is also the possibility that HEDTA reacts to give undetected products. An analysis of the kinetic behavior of the decomposition at 120°C, which is presented in Section 3.1, suggests that only 85% of HEDTA decompositions lead to ED3A. Preliminary results suggest that additional products might be detectable by performing the NMR analyses at 600 MHz, which gives a significantly greater chemical shift dispersion (Figure 2.6). Capitalizing on this possibility will require the careful acquisition of a set of standard spectra of known/suspected products against which spectra of decomposition samples can be referenced. We have determined that the line widths, and thus the resolution, are significantly affected by concentration. The 600 MHz spectrum in Figure 2.6A was obtained on a sample that was only one-half the concentration of the one used for the normal 300 MHz NMR analyses (Figure 2.6B). To further improve the mass balance, an analytical technique for the quantitation of carbonate should also be developed.

Figure 2.6. Comparison of ^1H NMR spectra of sample 8A from series HEDTA-1C taken at 300 MHz (A) and 600 MHz (B)

2.3 Reaction of HEDTA product mixture (ED3A and s-EDDA) at 120°C under argon

As described, the atmosphere above one sample of experimental series HEDTA-2C was exchanged for fresh argon after the sample had been heated for 2013 hours; then the sample was heated at 120°C for an additional 3503 hours. At 2013 hours, the analysis of two other samples indicated that essentially all of the HEDTA originally present had reacted (Table 2.5) and that the identifiable, reactive, organic components were ED3A (~57% of the original amount of HEDTA) and s-EDDA (~14% of the original amount of HEDTA).

Some significant observations can be made based upon the data in Table 2.5. First, and perhaps most important, is that the ratio of N_2O to H_2 is about 2.1. The possibility that the true value is somewhat higher because of conversion of some of the N_2O to N_2 cannot be totally dismissed, but this does not appear to have occurred in earlier reactions conducted in stainless vessels. The value of 2.1 is much lower than the ratios obtained at earlier times in the reaction; the ratio is >30 at points early in the reaction but decreases to 6-7 at 4014 hours. This decrease in the N_2O to H_2 ratio is clearly a result of the change in the composition of the reactants. Measurements of the N_2O to H_2 ratio for Tank 241-101-SY prior to installation of the mixer pump gave a value of less than 1 (a value of 0.85 was used in DOE [1994]).

Analyses of the contents of tank 101-SY indicate that there is little HEDTA remaining and that ED3A is a major component (Campbell et al. 1995). Our data support the notion that HEDTA is not a good model for current tank compositions.

The results of this experiment confirm that s-EDDA is more reactive than ED3A this is also consistent with analyses of actual wastes, which contain relatively little s-EDDA. Whether there are detectable amounts of other large fragments derived from ED3A in our experiments is still an open question. Use of 600 MHz 1H NMR spectroscopy might permit the detection of some other species. Earlier results certainly suggest that u-EDDA is also formed (Ashby et al. 1994).

Table 2.5. Further reaction of HEDTA decomposition products in simulated waste (HEDTA-2C: SY1-SIM-91B-NC, 120°C, Ar atm, stainless steel vessels)^(a)

Time (h)	2013		5516	
SAMPLE	C ^(b)	D ^(b)	B ^(b)	B-(Avg) _{C,D}
HEDTA (NMR) ^(c)	0	0	0	0
HEDTA (IC)	0.6±0.0	1.4±0.0	0.2±0.0	-0.8±0.0
ED3A	52.9	61.1	22.6	-34.4±4.1
s-EDDA	15	12.7	18.5	4.6±1.2
C ₂ O ₄ ²⁻	5.8±0.0	15.3±0.0	13.1±0.1	2.5±4.7
HCO ₂ ⁻ (NMR)	158.7	157.5	217.6	59.5±0.6
HCO ₂ ⁻ (IC) ^(d)	167.2±0.7	165.0±0.6	223.6±1.6	57.5±1.6
H ₂			17.0±0.3	17.0±0.3 ^(e)
N ₂			36.2±0.5	36.2±0.5 ^(e)
N ₂ O			37.5±0.6	37.5±0.6 ^(e)
NH ₃ (aq.)	91.3±1.4	86.0±0.6	88.5±0.3	-0.1±2.6 ^(f)
NO ₂ ⁻ (M)	1.58±0.00	1.62±0.10	1.32±0.00	-0.28±0.02

(a) All results in moles of product per 100 moles of starting HEDTA (except for nitrite).
(b) At this time three samples were taken (B, C, D). Amounts of gases were determined for all samples by GC. B was evacuated, refilled with Ar and placed back in a 120° C oil bath. C and D were diluted and further analyzed.
(c) The initial concentration of HEDTA (as determined by ¹H-NMR) was 0.224 ± 0.004 M.
(d) 4.6 ± 0.2% of formate was detected at time = 0. All the values for HCO₂⁻ (IC) were corrected by subtracting that amount.
(e) The sample was evacuated before reheating, so the amount of gases present at that time was equal to zero.
(f) Part of the NH₃ produced initially was probably evaporated during the evacuation.

3.0 Quantitative Analysis of the Kinetic Behavior of HEDTA Decomposition Under Argon

The quantitative description of the "rate law" for the disappearance of HEDTA is different at 90 and 120°C. The behavior at 120°C is the simplest to understand and is presented first, followed by a discussion of the behavior at 90°C. All discussions use the data given in Tables 2.1 (90°C) and 2.3 (120°C).

3.1 Kinetic behavior at 120°C

A plot of $\log [\text{HEDTA}]$ versus time shows slight curvature (Figure 3.1), which is attributed to the change of $[\text{NO}_2^-]$ during the reaction. All related evidence suggests that $[\text{NO}_2^-]$ appears in the rate law, and the simplest assumption is that the reaction is first-order in $[\text{NO}_2^-]$.

To show quantitatively that the curvature can be accounted for by the change in $[\text{NO}_2^-]$ during the reaction, the following procedure was adopted. For a reaction that is first-order in A,

$$-d[A]/dt = k[A]$$

When k is constant with time, the integrated expression is

$$\ln[A] = \ln[A]_0 - kt$$

When k is a function of time, an effective k can be defined for each time t such that

$$\ln[A] = \ln[A]_0 - k_{\text{eff}}t$$

It follows that

$$k_{\text{eff}}t = \int_{t=0}^t k dt$$

and that

$$k_{\text{eff}} = \frac{1}{t} \int_{t=0}^t k dt$$

Figure 3.1. Plot of log [HEDTA] versus time for reaction of HEDTA in simulated waste at 120°C. Circles indicate data from HEDTA-2C, filled triangles from HEDTA-3C. Solid line is the curve calculated assuming that k_{eff} decreases with time from an initial value of 0.0041 h⁻¹; dotted line represents calculated change in [HEDTA] for an invariant k of 0.0041 h⁻¹.

If the change of k is attributed to a change in $[\text{NO}_2^-]$ with time, and that k varies directly with $[\text{NO}_2^-]$ (i.e., that the reaction is first-order in $[\text{NO}_2^-]$), then

$$\frac{k}{k_0} = \frac{[\text{NO}_2^-]}{[\text{NO}_2^-]_0}$$

and

$$k_{\text{eff}} = \frac{k_0}{[\text{NO}_2^-]_0} \left(\frac{1}{t} \int_{t=0}^t [\text{NO}_2^-] dt \right)$$

To obtain numerical values of the integral, the data for $[\text{NO}_2^-]$ as a function of time were first fit to a function of the form

$$[\text{NO}_2^-] = U + Ve^{-Wt}$$

Then, using the values of U , V , and W in the equation

$$\frac{1}{t} \int_{t=0}^t [\text{NO}_2^-] dt = U + \frac{V}{Wt} (1 - e^{-Wt})$$

values of k_{eff} (based upon a value of k_0) and $[A]$ can then be calculated. The curve shown in Figure 3.1 is that so calculated for $k_0 = 0.0041 \text{ h}^{-1}$. The straight line corresponds to the behavior if k remained constant at this value throughout the reaction.

3.2 Kinetic behavior at 90°C

The behavior of HEDTA at 90°C is more difficult to describe. On the basis of the direct measurements of HEDTA by IC and NMR methods for reaction times less than 3000 hours, the reaction appears to be neither zero-order nor first-order. The data used in reaching this conclusion are shown in Figure 3.2, where the percent HEDTA remaining is plotted versus time. Two suggestions were made of kinetic models that would lead to the curvature corresponding to the data for these times, with an auto-catalytic model being favored (Barefield et al. 1995). Between 2000 and 3000 hours the curvature reverses, and thereafter it is consistent with a first-order description. The yields of product gases N_2 , H_2 , and N_2O may provide a more accurate measurement of the amount of HEDTA reacted. Points based on this line of reasoning, also shown in Figure 3.2, suggest a linear decrease in HEDTA corresponding to zero-order.

Figure 3.2. Percent HEDTA remaining for reaction in simulated waste under argon at 90°C. Diamonds indicate HEDTA concentrations determined by ion chromatography and ^1H NMR spectroscopy for reaction in stainless steel cylinders. Open squares indicate HEDTA concentrations determined using the yields of H_2 , N_2 , N_2O , and NH_3 for the reaction in stainless steel cylinders. Filled circle indicates the concentration of HEDTA determined by ion chromatography and ^1H NMR spectroscopy for a reaction in a glass-Teflon apparatus.

The following empirical description of the reaction at 90°C is thus made: the reaction is zero order until about half of the HEDTA is consumed; thereafter it is first-order. It is possible that the apparent linearity arises when curvature caused by an auto-catalytic effect is compensated for by an opposite curvature resulting from the effect of the decreasing $[\text{NO}_2^-]$, as observed at 120°C.

3.3 Sequential products from HEDTA

On the basis of our previous work, the reaction sequence

was assumed. If the two reactions are each first-order, with pseudo-first-order rate constants k_1 and k_2 , then the concentrations of HEDTA, ED3A, and C are given by known analytical expressions (Barefield et al. 1995). Previous estimates of k_2 at 90 and 120°C were made by fitting a small number of measurements of $[\text{B}]$ to the analytical expression for $[\text{B}]$.

The more extensive recent measurements provide new information about the reaction sequence. The results obtained at 120°C are more easily interpreted than those at 90°C and will be considered first. We have seen that k_1 varies with time, and we would expect that k_2 would also vary with time. But it was expected that the value for $[\text{B}]$ would correspond rather closely to that given by the analytical expression

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

if some appropriate average values for k_1 and k_2 were used. At sufficiently large values of t (in this case for $t \geq 1000$ hours) this expression reduces to

$$\frac{[\text{B}]}{[\text{A}]_0} = \left| \frac{k_1}{k_1 - k_2} \right| e^{-k_2 t}$$

A plot of $\log [\text{B}]/[\text{A}]_0$ versus time using measured values at four such times has the expected linearity (Figure 3.3), giving a value of $k_2 = 0.00020 \text{ h}^{-1}$. However, the intercept, which should correspond to $\log [k_1/(k_1 - k_2)]$, is less than 0. The simplest interpretation is that only 85% of the decompositions of HEDTA lead to ED3A. A reasonable fit

Figure 3.3. Plot of the log of the ratio $[\text{ED3A}]/[\text{HEDTA}]_0$ versus time for late times in the reaction of ED3A produced in the reaction of HEDTA in simulated waste at 120°C under argon. Filled diamonds indicate reaction HEDTA-2C; open squares indicate reaction HEDTA-3C; the line is a least squares fit to the data.

to measured values of ED3A is obtained using this percent in combination with $k_2 = 0.00020 \text{ h}^{-1}$ and $k_1 = 0.0039 \text{ h}^{-1}$. Since $k_1 = 0.0040 \text{ h}^{-1}$ at $t=0$, leading to $k_{\text{eff}} = 0.0039 \text{ h}^{-1}$ at about 200 hours, when about 50% of HEDTA has reacted. A comparison of calculated and measured values is shown in Table 3.1.

Predicting the behavior of ED3A in the reaction at 90°C is somewhat more complex. Furthermore, the reaction times do not extend into the region where k_2 can be determined in the direct way that it was at 120°C ; it can only be determined by attempting to fit the measured values of $[B]$. A reasonable fit was achieved using the assumption that all reactions of HEDTA give ED3A. Analysis is based on the empirical description of the behavior of HEDTA shown in Figure 3.2. For the shorter reaction times the sequential reactions are $A \xrightarrow{k_a} B$, which is zero-order with $k_a = 0.000156[A]_0 \text{ M h}^{-1}$, and $B \xrightarrow{k_2} C$, which is first-order. The analytical solutions are

$$\frac{[A]}{[A]_0} = 1 - \frac{k_a}{[A]_0} t \quad \text{and} \quad \frac{[B]}{[A]_0} = \frac{k_a}{[A]_0 k_2} (1 - e^{-k_2 t}).$$

For the longer reaction times, however, zero-order behavior persists only until time t_b , after which first-order behavior is assumed. At time t_b , the concentrations $[A]_b$ and $[B]_b$ can be calculated from the equations above.

After time t_b the concentrations of $[A]$ and $[B]$ are calculated using the equations applicable to first-order reactions in series

$$\frac{[B]}{[A]_0} = \frac{[A]_b k_1}{[A]_0 (k_1 - k_2)} (e^{-k_1 t'} - e^{-k_2 t'}) + \frac{[B]_b}{[A]_0} e^{-k_2 t'}$$

where $t' = t - t_b$.

A reasonable fit to measured values of ED3A is obtained using the following parameters:

$$\begin{array}{ll} k_a = 0.000156 [A]_0 \text{ M h}^{-1} & t_b = 3500 \text{ h} \\ k_1 = 0.000168 \text{ h}^{-1} & [A]_b/[A]_0 = 0.454 \\ k_2 = 0.000050 \text{ h}^{-1} & [B]_b/[A]_0 = 0.501 \end{array}$$

Comparisons of calculated and measured values for ED3A at 90°C are shown in Table 3.2.

Table 3.1. Comparison of calculated and measured values of ED3A at 120°C

Reaction	Time, h	ED3A (calc)	ED3A (meas)	
3C	30	9.4	6.3	trace
3C	77	21.9	20.4	21.8
2C	99	26.9	33.2	35.9
3C	149	36.9	30.4	34.9
3C	247	47.9	45.7	47.5
2C	261	53.2	56.4	63.1
2C	405	63.8	62.7	67.3
3C	504	68.5	74.7	75.2
2C	603	70.9	70.9	72.9
2C	913	72.1	67.6	68.8
3C	913	72.1	71.5	71.8
2C	1411	67.2	61.1	64.7
3C	1710	63.5	59.8	63.3
2C	2013	59.9	52.9	61.1
3C	4014	40.2	35.8	41.3

Table 3.2. Comparison of Calculated and Measured Values of ED3A at 90°C

Time, h	ED3A (calc)	ED3A (meas)	
160	2.5	1	2
618	9.5	7.1	9.1
1123	17.0	15.8	18.8
1818	27.1	21.6	28.2
2707	39.5	36.7	42.1
3811	51.6	45.9	52.5
4942	56.0	55 ^(a)	
5207	56.8	56.6	57.5
7003	60.4	50.3	67.5

(a) From a single reaction in a glass-Teflon apparatus.

3.4 Yields of N₂, H₂, N₂O, and NH₃

A comparison of the yields of the gaseous products H₂, N₂, and N₂O obtained in these 90°C experiments with the yields obtained in earlier experiments in Teflon-lined glass apparatus provides some important information. Attempts to explain the time dependence of the yields in the previous experiments¹ in terms of sequential first-order reactions were not successful.

Comparison of the yields of N₂, H₂, and N₂O obtained in the first 3000 hours are provided in Figures 3.4—3.7. The three experiments to be compared are

1. The experiment in stainless steel cylinders (HEDTA-1C).
2. The reaction performed in a Teflon-lined glass vessel with an argon atmosphere (Campbell et al. 1995). We concluded from results mentioned below that some air was present in the atmosphere.
3. The same as experiment 2, except that the atmosphere was an argon/O₂ mixture (Campbell et al. 1995).

The first conclusion arises from a comparison of the yield of N₂ in this experiment with the yields of N₂ in the other two experiments at 90°C (Figure 3.4). Within experimental error there is no difference in the yield of N₂ with time under the three different conditions, providing confidence in the reliability of the experimental procedure. The yield of N₂ is linear with time, but the semi-logarithmic plot is used for advantages in the display of the data for the other gases.

The yields of H₂ in the same three experiments (Figure 3.5) are quite different. This difference is attributed to the presence of O₂, which correlates with increase in the yield of H₂ (Campbell et al. 1995).

The yields of N₂O in the three experiments (Figure 3.6) are also quite different. It appears that N₂O is not formed in significant amounts until the O₂ in the system has been exhausted. Since N₂O is believed to form from the dimerization of NO[•], the effect of O₂ is most likely due to removal of NO[•] by reaction (1):

An explanation of why the yield of N₂ is not affected by O₂ is more difficult, since we believe that N₂ is formed from the disproportionation of hydroxylamine, and the latter is known to react with O₂.

Figure 3.7 shows the yield of NH₃ for experiment 1; similar data were not obtained for experiments 2 and 3. If the yield of a given gas (H₂, N₂O, or NH₃) is a constant

Figure 3.4. Semilogarithmic plots of the percent yield of nitrogen produced in decomposition of HEDTA at 90°C versus time (■ = stainless steel vessel under argon; ▲ = Teflon-lined glass vessel under oxygen contaminated argon atm; ● = Teflon-lined glass vessel under Ar/O₂ atmosphere); the curve was determined by a least squares fit to the three data sets.

Figure 3.5. Semilogarithmic plots of percent yield of hydrogen produced in decomposition of HEDTA at 90°C versus time (■ = stainless steel vessel under argon, ▲ = Teflon-lined glass vessel under oxygen-contaminated argon atmosphere, ● = Teflon-lined glass vessel under Ar/O₂ atm); the curve drawn through each data set is the same as Figure 3.4 but with vertical displacement.

Figure 3.6. Semilogarithmic plots of percent yield of nitrous oxide produced in decomposition of HEDTA at 90°C versus time (■ = stainless steel vessel under argon, ▲ = Teflon-lined glass vessel under oxygen-contaminated argon atm, ● = Teflon-lined glass vessel under Ar/O₂ atm). The curve drawn through the data set represented by the ■ is the same as Figure 3.4 but with vertical displacement. The curves through the other data sets have been displaced both vertically and horizontally.

Figure 3.7. Semilogarithmic plot of the percent yield of ammonia (condensed phase) produced in decomposition of HEDTA at 90°C versus time. The reaction was conducted in a stainless steel vessel under argon. The curve drawn is the same as Figure 3.4 but with vertical displacement.

multiple of that of N_2 at all times during the experiment, similar semilogarithmic plots for the individual gases should show the same curvature as that for N_2 (Figure 3.4) but with vertical displacement. The curves drawn through experiment 1 data in Figures 3.5—3.7 are such displaced curves and support the view that the ratios of gaseous products remain constant with time.

Figure 3.8 shows the yields of N_2 obtained over longer reaction times for two of the three conditions. At the longer reaction times the yields obtained from the glass-Teflon apparatus are consistently higher than those obtained from the separate stainless steel vessels; this could be due to small amounts of contaminant air being introduced into the glass-Teflon apparatus during the sampling procedure (samples for GC analysis were taken periodically through septa using a gas-tight syringe). The procedure used with the separate stainless steel vessels preclude this complication. For about 3000 hours the yield of N_2 in the HEDTA-1C experiments increases linearly with time. Although initial linearity of the N_2 yield would be expected if the decomposition of HEDTA were first-order (Barefield et al. 1995), the linearity shown in Figure 3.8 persists to longer times than predicted on this basis.

The measured ratios of the products H_2 , N_2 , N_2O , and NH_3 in the 120°C experiments were examined next. The constancy of the ratios H_2/N_2 , N_2O/N_2 , and NH_3/N_2 during the first 3000 hours of reaction at 90°C described above was not unexpected since the reaction

is predominant in this time interval, whereas the reaction

occurs only to the extent of a few percent.

For times beyond 3000 hours, the second reaction occurs to a significant extent, and it was expected that the ratios would change with time. Contrary to expectation, the ratios remain constant. In Table 3.3 these values are shown along with values for C (defined by the reaction on p. 22), which provide a measure of the extent of the second reaction.

The ratio of each product to the amount of HEDTA reacted, $\Delta HEDTA$, is considered next. In Table 3.4 these ratios have been calculated using the average values of HEDTA obtained from the NMR and IC measurements. Although the lack of constancy and the trend with time for each ratio may be due to some as yet unknown complexity to the reaction, the most likely explanation is related to the accuracy of the measurements. In the earliest measurements there is considerable uncertainty in the

Figure 3.8. Percent N_2 versus time for reaction of HEDTA in simulated waste at $90^\circ C$ under argon. Filled diamonds indicate reaction conducted in a glass-Teflon apparatus; open squares indicate stainless steel cylinders. The line represents the least squares fit of the data through 2000 hours.

Δ HEDTA values since they are obtained as a small difference in measurements of HEDTA. The constancy for each ratio after 2000 hours is apparent. If it is assumed that these ratios are constant throughout the experiment, the values of Δ HEDTA and HEDTA can be calculated at the earlier times. (The numerical values used in the calculation are given in Table 3.7.) Values of HEDTA calculated this way fall within the limits of measured values obtained by the IC and NMR methods.

Table 3.3. Ratios of products at 90°C

Time, h	H ₂ /N ₂	N ₂ O/N ₂	NH ₃ /N ₂	[C]/[A] ₀
160	0.067±0.025 ^(a)	2.58±0.68	2.00±0.71	0.01
618	0.059±0.017	1.84±0.33	2.10±0.46	0.15
1123	0.042±0.007	1.87±0.36	2.46±0.51	0.48
1818	0.057±0.017	2.21±0.69	2.44±0.47	1.25
2707	0.054±0.009	1.94±0.28	2.70±0.13	2.73
3811	0.052±0.006	2.11±0.20	2.50 ±0.10	5.31
5207	0.054±0.007	1.90±0.09	2.45 ±0.34	9.11
7003	0.052±0.013	2.08±0.31	2.67 ±0.32	14.40
Average	0.055	2.07	2.42	
(a) Standard deviation.				

Table 3.4. Ratios of products to HEDTA reacted at 90°C

Time, h	H ₂ /ΔHEDTA	N ₂ /ΔHEDTA	N ₂ O/ΔHEDTA	NH ₃ /ΔHEDTA	ΣN/ΔHEDTA
160	0.032	0.48	1.24	0.96	3.50
618	0.021	0.36	0.66	0.75	2.79
1123	0.015	0.36	0.67	0.87	2.93
1818	0.015	0.26	0.57	0.63	2.29
2707	0.016	0.30	0.57	0.80	2.54
3811	0.015	0.29	0.61	0.73	2.53
5207	0.017	0.31	0.59	0.76	2.56
7003	0.015	0.30	0.62	0.79	2.63

It now appears that until at least 20% of the HEDTA has reacted, the gas measurements provide a more accurate measurement of the amount of HEDTA reacted and are the basis for the linearity shown in the first part of the plot shown in Figure 3.2.

The ratios of the products obtained at 120°C are shown in Table 3.5. Each ratio would be expected to remain constant only for the earlier times, when reactions of the sequential products are not important relative to the reaction of HEDTA. The measurements at the times 77, 149, and 247 hours provide information about the reaction at this stage. The ratio of each product to Δ HEDTA for reaction at 120°C is given in Table 3.6. Values for Δ HEDTA at each time were calculated from the value of HEDTA on the curve in Figure 3.1.

The yields of products formed in the reaction of HEDTA itself, in contrast to the yields that include contributions from later reactions in the sequence, are of importance in establishing the mechanism of the reaction. Values of the ratios at 90 and 120°C are compared in Table 3.7. In Tables 3.4, 3.6, and 3.7, ΣN is the sum of the nitrogen atoms in the three nitrogen-containing products. It should be noted that the value of 2.57 for $\Sigma N/\Delta$ HEDTA at 90°C is consistent with the decrease in $[\text{NO}_2^-]$ during the reaction (shown in Figure 2.3), and with the assumption that all of the nitrogen atoms in the products come from NO_2^- .

Table 3.5. Ratios of products at 120°C

Time, h	H_2/N_2	$\text{N}_2\text{O}/\text{N}_2$	NH_3/N_2
30	0.094	2.14	2.17
77	0.098	3.26	3.84
149	0.096	3.28	3.95
247	0.091	3.27	3.74
504	0.168	3.68	4.08
913	0.203	3.47	3.66
1710	0.302	2.97	2.96
4014	0.328	2.29	2.37

Table 3.6. Ratios of products to HEDTA reacted at 120°C

Time, h	H ₂ /ΔHEDTA	N ₂ /ΔHEDTA	N ₂ O/ΔHEDTAA	NH ₃ /ΔHEDTA	ΣN/ΔHEDTA
30	0.012	0.12	0.27	0.27	1.05
77	0.017	0.17	0.55	0.64	2.08
149	0.017	0.17	0.57	0.69	2.17
247	0.017	0.18	0.61	0.69	2.27
504	0.034	0.20	0.74	0.81	2.69
913	0.043	0.21	0.74	0.78	2.68
1710	0.092	0.30	0.90	0.90	3.30
4014	0.148	0.45	1.03	1.07	4.03

Table 3.7. Comparison of yields from reaction of HEDTA at 90 °C and 120°C

Temp.	H ₂ /ΔHEDTA	N ₂ /ΔHEDTA	N ₂ O/ΔHEDTA	NH ₃ /ΔHEDTA	ΣN/ΔHEDTA
90 °C ^(a)	0.016	0.30	0.60	0.77	2.57
120 °C ^(b)	0.017	0.17	0.58	0.67	2.17
(a) Average of the values at the last four times in Table 3.4.					
(b) Average of the values at 77, 149 and 247 h in Table 3.6.					

4.0 Hydroxylamine as an Intermediate in the Thermal Decomposition of HEDTA

It is well established that hydroxylamine decomposes in base at room temperature forming molecular nitrogen, nitrous oxide, and ammonia. In terms of stoichiometry the gaseous products can be accounted for by a combination of the following reactions:

That hyponitrite ion, $\text{N}_2\text{O}_2^{2-}$, is also a product under certain conditions has been established by isolation of salts of the ion (Nast and Foppl 1948). The stoichiometry for its formation is given by the reaction

It has been generally assumed that $\text{N}_2\text{O}_2^{2-}$ is a minor product. To our knowledge, molecular hydrogen has never been reported as a product from the disproportionation of hydroxylamine. The mechanism of hydrogen production from formaldehyde suggested there might be a possible parallel in the dianion of hydroxylamine under strongly basic conditions. Some thermodynamic considerations and experimental investigations of this possibility are given the following section. In the final section some speculations concerning the mechanism of formation of hydroxylamine and its disproportionation to give ammonia, nitrogen and nitrous oxide are presented.

4.1 Hydrogen as a possible product from hydroxylamine in highly basic media

On the basis of its reduction potentials, hydroxylamine is a good reducing agent, and the possibility of its forming H_2 needs to be considered. The reduction potential in aqueous base depends, of course, upon the oxidation product formed from NH_2OH . Although the thermodynamic prediction of possible reaction could be based on reduction potentials, it is more convenient in this case to base predictions on values of free energy of formation, ΔG°_f . Where possible the values for ΔG°_f were taken from the tabulation given by Maloy (1985). The value for $\text{H}_2\text{NO}^-_{(\text{aq})}$ was calculated from the values of ΔG°_f and the pK_a for H_2NOH . Values for singlet and triplet NO^- and singlet HNO are the estimates given by Stanbury (1989). (The specific assumptions used by Stanbury for these estimates are given in this article.) The calculated values for ΔG° for specific reactions are

Mechanistically, most of these reactions must occur via several steps, and individual steps could have positive values of ΔG° . Of these, the last reaction would be closest to having mechanistic simplicity, with NH_2O^- serving as a hydride transfer agent.

Experiments were performed with varying ratios and concentrations of hydroxylamine and NaOH in an attempt to detect hydrogen as a product. Reactions were conducted at room temperature, and both gas and condensed phases were analyzed. The results of five reactions are given in Table 4.1. Within the limits of the gas chromatographic analysis employed for the gas phase, no hydrogen was ever detected as a product.

Although hydrogen was not detected, the yields of the other products provide some information about the disproportionation and allow comparison with the behavior reported in the literature for this reaction. In reaction H3 (Table 4.2), the $\text{N}_2/\text{N}_2\text{O}$ ratio decreases as the decomposition proceeds; this coincides with the observation reported by Lunak and Veprek-Siska (1974). They attributed the decrease to increasing amounts of N_2O at later times resulting from decomposition of $\text{N}_2\text{O}_2^{2-}$. In an earlier review we projected the half-life of $\text{N}_2\text{O}_2^{2-}$ to be 600 hours at 25°C in 1 M NaOH (Ashby et al. 1992). Thus formation and decomposition of $\text{N}_2\text{O}_2^{2-}$ is a reasonable explanation for the trend in the $\text{N}_2/\text{N}_2\text{O}$ ratio.

Table 4.1. Yields of products from disproportionation of hydroxylamine (room temp)

Rxn. No.	[H ₂ NOH], M	[OH ⁻], M	Time, h	Product Yields, %				N ₂ /N ₂ O
				N ₂	N ₂ O	H ₂	NH ₃	
H3	1	2 ^(a)	30	32.0±4.0	2.0±0.2	<0.03	29.3±0.8	16±3
H4	0.009	10.9 ^(b)	24	18.8±0.4	0.8±0.2	<0.03	54.4±1.5	25±6
H5	0.008	11.4 ^(b)	24	10.0±0.2	0.4±0.1	<0.03	45.0±2.8	25±6
H7	0.1	9.5 ^(b)	24	3.7±0.2	0.1±0.01	<0.03	20.1±0.1	30±3
H10	0.07	7.9 ^(a)	24	29.0±6.0	1.4 ±0.1	<0.03	20.0±0.2	21±5

(a) Fisher ACS quality reagent.
(b) Fisher 19 M solution.

Table 4.2. Gas production as a function of time in decomposing hydroxylamine hydrochloride in the presence of base (reaction H3)^(a)

Time, h	% N ₂	%H ₂	%N ₂ O	% NH ₃	N ₂ /N ₂ O
1	12±5.0	<0.03	0.34±0.07	^(b)	35±16
2	17±6.6	<0.03	0.45±0.04	^(b)	38±15
3	24±5.6	<0.03	0.66±0.06	^(b)	36±9
4.5	29±3.6	<0.03	0.83±0.04	^(b)	35±5
6.5	20±1.6	<0.03	0.82±0.14	^(b)	24±5
20	31±3.0	<0.03	1.8±0.3	^(b)	17±3
25	32±3.0	<0.03	2±0.2	^(b)	16±2
30	32±4.0	<0.03	2±0.2	29.3±0.8	16±3
<p>(a) Reactions conducted at room temperature. (b) Ammonia was determined in the condensed phase after completion of the reaction.</p>					

The yield of NH₃ should approach 33% for a stoichiometry with N₂ as the only other product and 50% for a stoichiometry in which N₂O and/or N₂O₂²⁻ are the other products. The surprisingly high yields of NH₃ in experiments H4 and H5 could be accounted for by greater formation, and slower decomposition, of N₂O₂²⁻. The rate of decomposition of N₂O₂²⁻ is inversely proportional to [OH⁻] at high base concentrations (Hughes and Stedman 1963; Buckholz and Powell 1963).

The limited data in Table 4.1 suggest that the rate of disproportionation and the relative contribution of the two stoichiometries may depend upon impurities present in the base. ACS certified sodium hydroxide pellets have specified quantities of several metal ions, whereas the specifications for Fisher 19 M sodium hydroxide indicate only iron and silver as metallic impurities. The results are consistent with the suggestion of Lunak and Veprek-Siska (1974) that metallic cations catalyze the reaction. The data in Table 4.2 indicate a half-life of about 1.6 hours at 25°C when the initial NH₂OH concentration is 0.01 M. The only value for comparison at 2 M base concentration is the reported value of 3.4 hours at 20°C when the initial NH₂OH concentration is 2.79 M (Campbell et al. 1995). In the latter experiment the base was AR grade KOH.

4.2 Experimental Section

Solutions of hydroxylamine were prepared by dissolving specific amounts of hydroxylamine hydrochloride (Aldrich) in distilled water to afford solutions of the desired

concentration. Solutions of NaOH were prepared either from Fisher Chemical ACS Certified Pellets (containing specified quantities of Fe, Cu, Ag, Hg, and Ni) or by diluting a 19 M solution (50% w/w, Fisher). All reactions were carried out at room temperature in Teflon-lined glass reaction vessels under an argon atmosphere. Product yields for gases were obtained by averaging triplicate measurements of each quantity. Nitrogen, nitrous oxide, and hydrogen gases were measured by gas chromatography as previously described. Ammonia (in aqueous medium) was measured in duplicate using the Nessler reagent (Barefield et al. 1994).

4.3 Postulations on the mechanisms of formation of hydroxylamine and its disproportionation to ammonia, nitrogen and nitrous oxide

In spite of the several studies of the kinetics of disproportionation of hydroxylamine, there have been few discussions of the microscopic mechanism by which it converts to products. The following reaction scheme presents an attempt to explain the origin of the nitrogen-containing gaseous products.

In reactions 4.1 and 4.2, the hydroxide ion reacts with hydroxylamine to form the two possible conjugate bases, since, in principle, a proton can be abstracted from the hydroxy group or from the amino group. It is proposed that the anionic species in which the negative charge is located on the nitrogen eliminates an hydroxyl group to form nitrene in the singlet state (reaction 4.3). It is well known that nitrene is a highly electrophilic reactive intermediate and we propose that it can abstract hydride from the anion of hydroxylamine (reaction 4.4) to form the amide anion and HNO, which then form

ammonia and NO^- in the singlet state (reaction 4.5). Reaction of the singlet NO^- with hydroxylamine (reaction 4.6) eventually produces molecular nitrogen. The possible alternative formation of molecular nitrogen from diimine, which might have been produced by addition of nitrene to hydroxylamine followed by loss of water, appears to be excluded since the decomposition of diimine would also produce hydrogen. Of course, dimerization of NO^- to give $\text{N}_2\text{O}_2^{2-}$ would lead to nitrous oxide. The competition between this reaction and reaction 4.6 will determine the relative amounts of nitrogen and nitrous oxide.

5.0 A Revised Mechanism for Thermal Decomposition of HEDTA to ED3A in the Presence of Aluminate, Hydroxide, and Nitrite

Redox analyses of the decomposition of HEDTA based upon the previously assumed mechanism indicate that a discrepancy exists between the electrons available from known oxidation products and those required to produce the known reduction products, even in the early stages of the reaction. The values for electrons produced by oxidation and consumed in reduction in this mechanism were based upon the following half reactions and assumptions:

Reductions:

Oxidations:

Assumptions:

- ED3A is converted to s-EDDA with production of oxalate.
- The remaining oxalate is derived from conversion of HEDTA to ED3A.
- Formate is derived from conversion of HEDTA to ED3A.

The fits of redox analyses to this model for HEDTA decomposition using data from Tables 2.1 and 2.3 are poor, suggesting that it is not an adequate model. This is further suggested by the ratio $\Delta NO_2^{-}/\Delta HEDTA$, which is observed to be >2 (Figure 2.3), and that $\Sigma N/\Delta HEDTA$ is >2 (Table 3.7), whereas the model predicts a ratio of only 1. A revised mechanism for the thermal decomposition of HEDTA that accommodates a value of $\Delta NO_2^{-}/\Delta HEDTA$ greater than 1 and gives a much improved redox balance is outlined below.

Nitrite ion is an ambident nucleophile that is capable of reaction at either oxygen or nitrogen. To generate an electrophilic nitrite, it is necessary to coordinate one of the oxygen atoms with a Lewis acid; upon coordination the nitrogen becomes an electrophilic center. The only species present in the simulated waste medium that can reasonably function as a Lewis acid is aluminate, $[Al(OH)_4]^{-}$. The following equilibrium was therefore postulated as the initial step in the thermal decomposition of HEDTA.

It is well known that alkyl nitrites undergo exchange with alcohols to produce mixtures of nitrite esters. By analogy it is postulated that the second step is the reaction of the nitrite complex of aluminate with HEDTA (reaction 5.9).

Fragmentation of the nitrite ester of HEDTA should produce NO^- , CH_2O and the methylene iminium salt of ED3A, **1** (reaction 5.10).

The NO^- and formaldehyde produced in reaction 5.10 are initially formed in a solvent cage as represented by the circle in Scheme 5.1. They may react to produce hydroxylamine as shown in Scheme 5.1, or they may escape from the solvent cage and react separately.

Scheme 5.1

From theoretical considerations alone, it must be concluded that NO^- formed in the solvent cage will be in the singlet state. As a consequence, its recombination with formaldehyde can readily take place to produce an adduct which can subsequently rearrange by 1,2-hydride shift to produce the anion of formohydroxamic acid. Hydroxide-promoted hydrolysis of this anion would produce formate and hydroxylamine anion (the conjugate base of hydroxylamine).

Conversion of excited state singlet NO^- to ground-state triplet NO^- within the solvent cage will facilitate the escape of this species from the cage to the bulk solvent, where it can react with radicals located therein. These radicals include molecular oxygen and NO^- in the triplet state. Reaction of NO^- with oxygen under basic conditions will produce nitrite, whereas dimerization of NO^- will produce $\text{N}_2\text{O}_2^{2-}$ and, eventually, nitrous oxide. Formaldehyde that escapes from the cage can react with hydroxide to produce formate and molecular hydrogen. Since only small amounts of molecular hydrogen are formed in the conversion of HEDTA to ED3A under argon at either 90 or 120°C, we believe that combination of NO^- with CH_2O within the cage must be an important process.

Iminium salt **1**, produced in reaction 5.10, can undergo several reactions, including reaction with hydroxide ion to form ED3A and formaldehyde (reaction 5.11) and reaction with nitrite ion (reaction 5.12).

Formaldehyde produced in reaction 5.11 would be expected to react with hydroxide to produce formate and molecular hydrogen. The nitrite ester from reaction 5.12 can serve as a nitrosating agent for HEDTA according to reaction 5.13.

That relatively little molecular hydrogen is produced in the conversion of HEDTA to ED3A suggests that production of formaldehyde by reaction 5.11 must be slower than reaction with nitrite ion. Loss of hydroxide from **3** would regenerate iminium ion **1** and provide a mechanism for autocatalysis, which could account for the acceleration in the rate of HEDTA (relative to first-order behavior) with time.

Nitrite ester **2** formed in reaction 5.12 may also react with hydroxide according to reaction 5.15 to form the N-formyl derivative of ED3A, **4**, NO^- and water.

Formylamide, **4**, can undergo several reactions, including reaction with hydroxide to form ED3A and formate (reaction 5.16) and with nitrite according to reaction 5.17.

Product **5** can subsequently react with hydroxide according to reaction 5.18 to form NO^- , water and the carbamate of ED3A, **6**.

Carbamate **6** can then react with hydroxide to eliminate carbonate according to reaction 5.19.

This mechanistic scheme accounts for several important observations:

- A ratio of $2 < \Delta\text{NO}_2^- / \Delta\text{HEDTA} < 3$.
- Generation of HCO_2^- from a variety of intermediates without the formation of molecular hydrogen.
- The sum of the moles of formate and carbonate is equal to 2.
- Autocatalysis of HEDTA decomposition via a reactive intermediate; i.e., the methyleneiminium salt of ED3A, 1.

Consideration of the above reactions leads to an additional oxidation process (reaction 5.20) that must be considered in the redox balance.

In addition to the half reactions 5.1-5.7 given above, the production of carbonate from HEDTA and the separation of formate produced into that arising by reactions 5.5 and 5.20 must be considered. This is done on the basis of the formate to HEDTA ratio. The $\text{HCO}_2^- / \Delta\text{HEDTA}$ ratio was required to be 2 in the "old" mechanism; in the new mechanism, it will be less than 2 only to the extent that the following oxidation reaction is operative. The following modifications to the previous assumptions are made:

- The formate produced through reaction 5.5 is determined by the expression {mol HCO_2^- produced - (2 - mol HCO_2^- produced/mol HEDTA consumed) x mol HEDTA consumed} and provides 3 mol e^- /mol formate.
- The remaining formate is presumed to be accompanied by an equal amount of carbonate, and together these provide 8 mol e^- /mol HEDTA reacting according to reaction 5.20.

Tables 5.1 and 5.2 give redox balances for the decomposition of HEDTA based upon the revised mechanism using the above oxidative and reductive half-reactions. Because the analysis only considers reaction of HEDTA and does not include any contribution from products arising from reaction of ED3A or s-EDDA, the imbalance in e_{red} and e_{oxid} must necessarily increase at later times. However, for the reaction at 90°C, the involvement of these fragments in the reaction is not important until the later times, and the agreement in the earlier stages is quite good. At 120°C the agreement is good for times through 247 hours, coincident with the constancy of the ratios of products to HEDTA reacted (Table 3.6). At later times the reactions of ED3A and s-EDDA contribute to increased product yields and the redox imbalance.

Table 5.1. Redox Calculation for the reaction of HEDTA at 90°C under argon (experiment HEDTA-1C)^(a)

Time, h	e _{red.}	e _{oxid.}	$\Delta(e_{red.}-e_{oxid.})$
160	0.17±0.02	0.01±0.03	0.16
618	0.66±0.06	0.49±0.09	0.18
1123	1.53±0.21	1.10±0.03	0.42
1818	2.31±0.30	2.38±0.27	-0.07
2707	3.88±0.18	3.25±0.10	0.63
3811	4.85±0.14	4.35±0.11	0.50
5207	5.83±0.35	4.97±0.07	0.85
7003	6.69±0.58	5.61±0.08	1.08
(a) All amounts in moles of electrons per mol of HEDTA.			

Table 5.2. Redox calculation for reaction of HEDTA at 90°C under argon (experiment HEDTA-3C)^(a)

Time, h	e _{oxid.}	e _{red.}	$\Delta(e_{red.}-e_{oxid.})$
30	1.04±0.06	0.38±0.02	-0.65
77	2.29±0.06	1.84±0.11	-0.45
149	3.49±0.27	3.31±0.24	-0.18
247	4.35±0.17	4.72±0.30	0.37
504	6.62±0.05	7.63±0.28	1.01
913	7.04±0.02	8.57±0.38	1.53
1710	7.17±0.07	10.93±0.03	3.76
4014	6.72±0.23	13.53±0.27	6.81
(a) All amounts in moles of electrons per mol of HEDTA.			

6.0 Long-Term Studies of the Decomposition of HEDTA in Simulated Waste Mixtures Under Oxygen

The reaction of HEDTA in simulated waste at 120°C under an oxygen atmosphere was examined to quantify the amounts of all products (gaseous and condensed phase) as a function of time and to compare these results with those for the reaction carried out under argon at 120°C. These experiments were conducted in stainless steel cylinders according to the protocol used for the experiments conducted under argon with the minor modifications described in Section 6.1. Because oxygen is consumed fairly rapidly, and the 20-mL headspace above the reaction mixture contains much less than is needed for complete reaction, these reactions were stopped before completion.

The analytical results for the reaction of HEDTA in the presence of oxygen are shown in Table 6.1. It is obvious from the small amounts of nitrogen products present in the reaction mixture and from the concentration of nitrite, which appears to have remained constant throughout the experiment, that the presence of oxygen markedly inhibits the reaction of HEDTA with nitrite. Figure 6.1 compares the rate of consumption of HEDTA in an argon atmosphere (HEDTA-3C) with the present experiment (HEDTA-6C); the rate of consumption of HEDTA is much slower in the presence of oxygen. Figures 6.2 and 6.3 are plots of the amounts of condensed phase and gaseous products as a function of time of the reaction under oxygen (HEDTA-6C). A comparison with reaction HEDTA-3C shows that, while the production of N_2 , N_2O , and NH_3 is slower in the presence of oxygen, H_2 is generated at a much faster rate. Although the number of data is too small for the curves to be well defined, Figure 6.1 might be taken to suggest that the initial rates of the reactions in the presence and absence of oxygen are the same and that the rate slows in the presence of oxygen only after 25 hours.

The inhibiting effect of oxygen on the rate of reaction of HEDTA in simulated waste media and the enhanced production of H_2 was observed earlier (Ashby et al. 1994), but the mechanistic basis for these phenomena has not received much consideration. There is still no satisfactory mechanistic model to explain this behavior. Some of the possibilities that must be considered include 1) the reaction of HEDTA in the absence of oxygen is a radical reaction that is largely inhibited by the presence of oxygen; 2) some redox active metal ion, rather than aluminum, is responsible for activation of nitrite ion, and in the presence of oxygen it is oxidized to an oxidation state in which it is no longer active; 3) oxygen intercepts some intermediate in the normal reaction such that the reaction is blocked or diverted along another pathway that does not consume nitrite.

One experiment has been performed in an attempt to test point 2. In this experiment the highest purity inorganic reagents that could be obtained commercially were used to prepare the simulated waste mixture. The rates of HEDTA reaction and product formation were measured (120°C, argon atmosphere) for comparison with those of the reaction in which the simulant was prepared with reagent grade chemicals:

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Time (h)	0	25		73		169	
SAMPLE	A, B	A	B	A	B	A	B
HEDTA (NMR) ^(b)	100	95.7	95.5	91	90.6	87	89.2
HEDTA (IC)	100	88.2±1.1	91.0±3.4	87.8±0.4	87.8±0.8	84.9±0.0	83.1±0.6
ED3A	0	trace	3.6	7.5	5.7	6.9	7.0
s-EDDA	0	0	0	0	0	trace	trace
C ₂ O ₄ ²⁻	0	1.8±0.1	0.5±0.1	1.7±0.0	1.9±0.1	5.4±0.1	7.5±0.2
HCO ₂ ⁻ (NMR)	trace	5.2	8.2	12.5	12.7	15.0	15.2
HCO ₂ ⁻ (IC) ^(c)	0	4.2±0.0	3.7±0.8	10.2±0.1	9.8±0.0	15.5±0.2	14.3±0.3
O ₂	45.8±1.2	39.5±0.2	40.0±0.9	27.1±0.4	29.4±0.5	16.6±0.2	14.8±0.2
H ₂	0	0.28±0.00	0.24±0.00	2.42±0.03	2.45±0.04	8.03±0.09	8.56±0.09
N ₂	0	trace	0.33±0.12	0.85±0.02	0.53±0.03	0.30±0.01	0.50±0.03
N ₂ O	0	0.69±0.05	1.00±0.01	2.12±0.28	1.15±0.03	0.34±0.03	0.81±0.01
NH ₃ (aq.)	0	1.9±0.2	2.2±0.2	3.9±0.1	3.6±0.3	3.8±0.1	4.9±0.1
NO ₂ ⁻ (M)	2.24	2.27±0.02	2.24±0.01	2.22±0.01	2.24±0.00	2.26±0.00	2.24±0.01

(a) All results in moles of product per 100 moles of starting HEDTA (except for nitrite).
(b) The initial concentration of HEDTA (as determined by ¹H-NMR) was 0.217±0.007 M.
(c) 5.2 ± 0.9% of formate was detected at time = 0. All the values for HCO₂⁻ (IC) were corrected by subtracting that amount.

Figure 6.1. Comparison of rates of consumption of HEDTA under oxygen (■ - HEDTA-6C) with that under argon (□ - HEDTA-3C) at 120°C

Figure 6.2. Reaction of HEDTA in simulated waste: formation of condensed phase products (HEDTA-6C) (● = formate, ■ = ED3A, ▲ = oxalate)

Figure 6.3. Reaction of HEDTA in simulated waste: formation/disappearance of gaseous reactants/products in solution (HEDTA-6C) (■ = oxygen, ● = H₂, ○ = NH₃, □ = N₂O, ▲ = N₂)

Table 6.2 gives the analytical results at three different reaction times. Figures 6.4 and 6.5 compare the rates of HEDTA disappearance and rates of product formation for these experiments (HEDTA-8C) with experiment HEDTA-3C, which was performed under otherwise identical conditions. Within experimental error, the results are identical, which suggests that the presence of metal ion impurities in the reagents used for all experiments performed in stainless steel cylinders have no effect on the reaction in the absence of oxygen. Therefore, it is unlikely that the presence of oxygen serves to circumvent the action of metal ions.

Although it is not possible to suggest a detailed mechanism for the reaction under oxygen, there are some potentially useful observations to be made that may guide future mechanistic considerations. Even though the yields of products are small, it is interesting to examine the data in search of stoichiometric relationships or trends. The yields of N₂ and N₂O are too erratic, but the reproducibility of the yields of other products is satisfactory for some analysis. The usual problem of determining the value of ΔHEDTA as the small difference of two large values also exists at the earliest time (25 hours). A resolution of this difficulty was based upon the ratio $\text{HCO}_2^- / \Delta\text{HEDTA}$, which can be determined from the average values of HCO_2^- and HEDTA to be 0.72 at 25 hours, 0.95 at 73 hours, and 1.08 at 169 hours. The values at the last two times suggest a value of 1 for the stoichiometric ratio of HCO_2^- to ΔHEDTA . If one assumes that this ratio also holds at 25 hours, then the measured value of HCO_2^- can be used to obtain a value for t

Table 6.2. Reaction of HEDTA in simulated waste prepared with high purity reagents at 120 °C under argon (exp. HEDTA-8C: SY1-SIM-91B-NC, stainless steel vessels)^(a)

Time (h)	0	77	165	244
HEDTA (NMR) ^(b)	100	68.8	58.4	45.2
ED3A	0	30.0	34.6	46.1
s-EDDA	0	0	2.5	3.6
HCO ₂ ⁻ (NMR)	0	35.0	59.4	72.3
H ₂	0	0.50±0.01	0.71±0.01	0.91±0.01
N ₂	0	3.07±0.37	7.05±0.47	8.87±0.65
N ₂ O	0	14.28±0.25	23.01±0.19	30.17±0.49

(a) All results in moles of product per 100 moles of starting HEDTA.
(b) The initial concentration of HEDTA (as determined by ¹H-NMR) was 0.222 M.

Figure 6.4. Reaction of HEDTA in simulated waste; comparison of rates of reaction/formation of condensed phase reactants/products in presence (HEDTA-3C, filled symbols) and absence (HEDTA-8C, open symbols) of metal ion impurities (□/■ = HEDTA, ○/● = formate, Δ/▲ = ED3A)

Figure 6.5. Reaction of HEDTA in simulated waste; comparison of rates of formation of gaseous products in the presence (HEDTA-3C, filled symbols) and absence (HEDTA-8C, open symbols) of metal ion impurities (O/● = N₂O, △/▲ = N₂, □/■ = H₂)

HEDTA at this point. This procedure gives a value of 94.7 for HEDTA, which agrees well with the value obtained by NMR. In the following discussion the value of Δ HEDTA will be taken as 5.3 at 25 hours.

An examination of the amounts of each nitrogen product relative to the amount of HEDTA consumed at each time provides some idea of the stoichiometry relative to these products. Because of the erratic nature of the measured values, the individual measured values from the duplicate runs were used to construct Table 6.3.

The behavior of NH₃ is quite regular; within experimental error the ratio NH₃/ΔHEDTA is constant at 0.35. This is a little more than one-half of the value found for the reaction done under argon at 120°C (Table 3.7). The ratio ΣN/ΔHEDTA, where ΣN is the sum of the nitrogen atoms in the three products, is erratic, but the value is almost certainly <1 and is much less than the value of 2.17 that was found for the reaction performed under argon at 120°C. That the value of ΣN/ΔHEDTA is <1 is deemed significant.

On the basis of the mechanism proposed for reaction of HEDTA (Barefield et al. 1995), at least one NO⁻ must be formed for each HEDTA that reacts. The ratio ΣN/ΔHEDTA should be greater than 1 if further reaction of NO⁻ resulted in the formation of only NH₃, N₂, or N₂O. That the ratio is less than 1 suggests that reaction of O₂ with

Table 6.3. Ratios of nitrogen products and hydrogen to HEDTA consumed for reaction of HEDTA under oxygen at 120°C (experiment HEDTA-6C)

Product	25 hours		73 hours		169 hours		Ar atm ^(a)
H ₂	0.28	0.24	2.42	2.45	8.03	8.56	
N ₂		0.33	0.85	0.53	0.30	0.50	
N ₂ O	0.7	1.00	2.12	1.15	0.34	0.81	
NH ₃	1.9	2.2	3.9	3.6	3.8	4.9	
ΣN	3.3	4.9	9.8	7.0	5.1	7.5	
H ₂ /ΔHEDTA	0.05	0.05	0.23	0.23	0.58	0.62	0.017
ΣN/ΔHEDTA	0.62	0.92	0.92	0.65	0.37	0.54	2.17
NH ₃ /ΔHEDTA	0.36	0.42	0.36	0.34	0.27	0.36	0.67
(a) Values taken from Table 3.7.							

some nitrogen-containing intermediate converts some nitrogen back to NO₂⁻. The literature suggests that peroxonitrite, ONOO⁻, which is undoubtedly formed by reaction of NO⁻ with O₂, decomposes in basic solution at least partially by the reaction (Edwards and Plumb 1994):

The significant yield of NH₃ means that NH₂OH must be produced as an intermediate and that disproportionation of NH₂OH, which leads to NH₃, must be competitive with its autoxidation. The formation of NH₂OH also means that reaction of NO⁻ with formaldehyde must also be competitive with its reaction with oxygen. The existence of a "cage effect" is strongly suggested. Among the products of autoxidation of NH₂OH are H₂O₂ and ONOO⁻, thought to arise in the sequence (Yagil and Anbar 1964; Hughes and Nicklin 1971)

The ratio H₂/ΔHEDTA rises dramatically with time and at all times is greater than the ratio under an argon atmosphere. The increased yield of H₂ may be associated with a build-up of H₂O₂ in the system since the reaction of formaldehyde with H₂O₂ in basic solution gives H₂ and HCO₂⁻.¹

6.1 General procedures

All analytical procedures and sample preparations were identical to those described in Barefield et al. (1995) except for reactions conducted under an oxygen atmosphere. Experiment HEDTA-2C, the first at 120°C, was stopped prematurely because it was found that several cylinders had leaked. This was determined to be a result of insufficient torque being applied to the valve when it was screwed into the cylinder. No problems with leakage were detected in subsequent experiments.

6.2 Procedure for reaction of HEDTA in simulated waste under an oxygen atmosphere

Reaction vessels were filled in the same fashion as for reactions under argon (Barefield et al. 1995) except that oxygen (Southeast Airgas, industrial grade, >99.5% purity) was used to fill the headspace of the stainless steel reaction vessels. All other procedures were the same. Whereas argon-atmosphere reaction mixtures were colorless, those produced under an oxygen atmosphere had a yellow-green color, most likely due to chromate ion (CrO_4^{2-}) formed from chromium, which was leached from the stainless steel.

6.3 Preparation of simulated waste employing highly purified reagents

The preparation was carried out as described previously (Hughes and Stedman 1963; Buckholz and Powell 1963) except for the following:

- Deionized water (Fisher DIUF Water) was used instead of distilled water.
- Sodium aluminate was not added as such. Instead, aluminum metal was dissolved in sodium hydroxide as follows: 2.08 g aluminum (99.999+%, pellets, 3-8 mesh) were placed in a polypropylene container to which 25 mL of deionized water and 3.08 g sodium hydroxide (99.99%, pellets) were added and stirred under a nitrogen atmosphere for a period of 8 hours at 80°C.
- All chemicals except HEDTA were replaced by the highest purity samples available from commercial sources.

The relative purities of the chemicals used in experiment 8C with those used in previous experiments are shown in Table 6.4. The HEDTA used for all experiments was in the form of the trisodium salt (Aldrich Chemical) which is stated to have a purity of 99%. Because of the high cost of the reagents, only three samples were prepared so that only one sample was available at each time. Values determined by gas chromatography are the average of two or more measurements. Values determined by ^1H NMR spectroscopy are based upon a single measurement of the spectrum.

Table 6.4. Inorganic chemicals used in preparing simulated wastes

Chemical	Sodium Nitrite		Sodium Nitrate		Sodium Hydroxide		Aluminum	
Expt #	3C ^(a)	8C	3C ^(a)	8C	3C ^(a)	8C	3C ^(a,b)	8C
Vendor	Fisher	Fluka	Baker	Aldrich	Fisher	Aldrich	Strem	Aldrich
Quality	certified ACS	puriss. p.a.	Baker analyzed		certified ACS	semi-conductor		
% Purity ^(c)	100.0 (>97)	>99.0	100.1	99.995 ^(d)	98.2	99.99 ^(d)	99.9	99.999+
Cl ⁻	0.005%	<0.005%	<0.0005%		0.001%			
SO ₄ ²⁻	0.010%	<0.005%	<0.001%		0.0006%			
Fe	0.001%	<0.0005%	<1 ppm		0.0002%			
Ni		<0.0005%			0.0002%			0.2 ppm
Cr		<0.0005%						
Cu		<0.0005%			0.0002%			0.1 ppm
Mn		<0.0005%						
K	0.005%	<0.005%	<0.002%		0.003%	25 ppm		
Heavy metals	0.001% ^(e)		<3 ppm ^(e)		0.002% ^(f)			
<p>(a) The same materials were used for all other runs. (b) As sodium aluminate. (c) Actual analysis (catalog). (d) No impurities detected by ICP trace analysis. (e) As Pb. (f) As Ag.</p>								

7.0 Estimation of Ammonia in the Gas Phase Based on Henry's Law

Ammonia has been measured as a gaseous effluent from certain high-level waste storage tanks at Hanford since 1993 when measurements confirmed the observations by those working in the tank farms that NH_3 was probably present (LANL 1994). Although Delegard noted in his early work that there was a strong smell of NH_3 associated with the decomposition of HEDTA in simulated waste slurries (Delegard 1987), no determination of the stoichiometry with respect to HEDTA had been made prior to the work done at Georgia Tech in FY 1994 (Barefield et al. 1995). Ammonia has been included on plots of gaseous products in earlier sections of this report, but the analyses were actually made on the liquid phase, where the concentration of NH_3 *in solution* was estimated using a spectrophotometric method based on the reaction of NH_3 with the Nessler reagent (Barefield et al. 1995). All measurements of products were made at room temperature after the reaction mixture had been allowed to equilibrate for several days. The amount of NH_3 present in the head space above the solution in the cylinder was assumed to be small, and it was assumed that release of NH_3 during manipulation of the solution was negligible. Recent work by Norton and Pederson (1994) addressed the solubility of NH_3 in concentrated caustic mixtures and they determined Henry's law constants for the solubility of NH_3 in simulated waste mixtures and allows an assessment of the validity of these assumptions. The following analysis uses the Henry's law constant determined by Norton and Pederson (1994) for simulated waste SY1-SIM-91A (a slurry), which closely resembles the homogeneous solution used in our work, SY1-SIM-91B-NC (NC indicates that sodium carbonate has been eliminated).

According to Henry's law, $p = \gamma m / K_H$, where p is the partial pressure of the gas, γ its activity coefficient, m its molality, and K_H Henry's law constant. The simulated waste mixture SY1-SIM-91B-NC has a density of 1.39 g/mL and a water content of 51.0% (w/w). Using the expression $\ln K_H = -7.577 + 2571.3/T + 0.003076T$ given by Norton and Pederson (1994) a Henry's law constant of 7.16 is obtained, where K_H is actually defined as K_H/γ . The partial pressure of NH_3 , $p(\text{NH}_3)$, is then defined according to equation 7.1:

$$p(\text{NH}_3) = m(\text{NH}_3)/K_H \quad (7.1)$$

The moles of NH_3 present in the headspace is given by equation 7.2:

$$n(\text{NH}_3, g) = p(\text{NH}_3)V/RT = m(\text{NH}_3)V(\text{gas})/RTK_H \quad (7.2)$$

The moles of NH_3 present in solution is related to molality by equation 7.3, where $V(\text{sol})$ is the total volume of simulated waste solution and $f(\text{H}_2\text{O})$ is the mass of water (kg) in one liter of the solution:

$$n(\text{NH}_3, \text{sol}) = m(\text{NH}_3)V(\text{sol})f(\text{H}_2\text{O}) \quad (7.3)$$

The fraction of NH_3 in the gas phase is then given by equation 7.4:

$$f(\text{NH}_3) = n(\text{NH}_3, \text{g})/n(\text{NH}_3, \text{sol}) \quad (7.4)$$

Substitution into Equation (7.4) from Equations (7.2) and (7.3) gives Equation (7.5):

$$f(\text{NH}_3) = V(\text{gas})/RTK_HV(\text{sol})f(\text{H}_2\text{O}) \quad (7.5)$$

Using the values $V(\text{gas}) = 0.023 \text{ L}$, $T = 298 \text{ K}$, $V(\text{sol}) = 0.010 \text{ L}$, $K_H = 7.16$, and $f(\text{H}_2\text{O}) = 0.71$ gives a value of $f(\text{NH}_3) = 0.019$, or 1.9%. Were the gas to equilibrate with the full volume of the cylinder plus the gas handling manifold, a total of 0.079 L, the amount of NH_3 in the gas phase would be 6.4% of that in solution. This is considered to be very unlikely because the measurements require less than 30 minutes.

It is also of interest to consider the contribution of the partial pressure of NH_3 to the total gas pressure since, in calculations of total moles of gas produced, this contribution is ignored. For a sample in which 0.5 mol of NH_3 is produced per mol of HEDTA reacting, such as for HEDTA-2C after 400 hours, the molality of NH_3 is 0.146. Applying Equation (7.1) indicates that $p(\text{NH}_3)$ will be 0.02 atm. Given that the pressure of the expanded gases inside the manifold is approximately 0.5 atm, the contribution of NH_3 to the total pressure (expressed as percentage) is $0.02 \times 100 / 0.5 = 4\%$. Similar calculations for other samples indicate that neglecting the contribution of NH_3 to the total pressure does not introduce a significant error into estimating the total moles of gas produced.

There are two reasons for suggesting that the amount of NH_3 in the gas phase computed using this Henry's law constant is an upper limit. First, the electrolyte concentration is less in the SY1-SIM-91B mixture than in the mixture used by Norton and Pederson (1994), which should increase the NH_3 solubility. Second, the lowest temperature for which Norton and Pederson's constants are indicated to be valid is 25°C , whereas the measurements done at Georgia Tech were performed at $22\text{--}23^\circ\text{C}$, which will result in a slightly increased solubility and lower vapor pressure.

8.0 The Role of Aluminum: ^{27}Al NMR Spectroscopic Data Suggest Formation of Aluminum Nitrite Complexes in Acetonitrile

In the current mechanism for decomposition of metal complexants in simulated waste media, activation of nitrite is proposed to occur by complexation with aluminum. This nitrite complex, possibly $[\text{Al}(\text{OH})_3\text{ONO}]^-$, is presumed to nitrosate functional groups such as alcohols and amines to give intermediates that subsequently fragment. Cleavage of various aminoethanols by a mixture of tetraethylammonium tetrachloraluminate and sodium nitrite in acetonitrile provided indirect support for this hypothesis. However, no aluminum nitrite complex has yet been detected under any condition (Taylor 1987; Waste and Banister 1973). We now wish to report preliminary evidence of the formation and detection of aluminum nitrite complexes from the reaction of tetrabutylammonium nitrite with aluminum halides in acetonitrile using ^{27}Al NMR spectroscopy to monitor the reaction mixture.

8.1 Results

A series of reactions involving varying ratios of Bu_4NNO_2 and AlX_3 ($\text{X} = \text{Cl}$ or Br) were examined by ^{27}Al NMR spectroscopy. The results of the study with AlCl_3 are illustrated by the series of spectra shown in Figure 8.1, which were obtained for five NO_2^-/Al ratios ranging from 0 to 10. With no added Bu_4NNO_2 , the spectrum is consistent with that of the literature for AlCl_3 at about 0.1 M concentration (Werhli and Werhli 1981). The major species present is the AlCl_4^- ion ($\delta = 103.9$) with resonances due to several six-coordinate species at chemical shifts upfield ($\delta < 0$) of the reference peak. Adding one equivalent of Bu_4NNO_2 results in the disappearance of the resonances due to the six-coordinate species and the appearance of two resonances at $\delta = 89.1$ and 89.8 . Adding two additional equivalents of Bu_4NNO_2 ($\text{NO}_2^-/\text{Al} = 3$) results in an increase in the intensity of resonance at $\delta 89.1$ and 89.8 and the appearance of a new resonance at $\delta = 75.2$. The equal and invariant relative intensities of the resonances at $\delta 89.1$ and 89.8 suggest that they may result from a dinuclear species. That resonances corresponding to these are not observed with AlBr_3 suggests that chloride ion is also involved. The amounts of these species are clearly increasing relative to the amount of AlCl_4^- that remains. However, a comparison of the combined integrated intensities of the visible resonances with that of the resonance due to the external standard ($\text{Al}(\text{OH})_6^{3+}$) indicates that the amount of aluminum accounted for by these species (see Table 8.1) decreased as the nitrite concentration increased. When the NO_2^-/Al ratio is increased to 5, the only resonance observed in the spectrum is that of the external standard. The reason for the absence of any resonance is unknown but could be an exchange process that is rapid on the NMR time scale and/or the formation of a high molecular weight aggregate with a very long spin correlation time. However, at a NO_2^-/Al ratio of 10, a new resonance is apparent at $\delta = 23.0$. The integral of this resonance suggests that this species accounts for about two-thirds of the aluminum present in the sample.

Figure 8.1 ^{27}Al NMR spectra of mixtures of aluminum chloride and tetrabutylammonium nitrite in acetonitrile. All solutions are 0.12 M in AlCl_3 ; the molar ratio of nitrite to aluminum (x) is shown for each spectrum. The resonance at δ 103.9 in the first three spectra is due to the AlCl_4^- ion.

A similar series of ^{27}Al NMR experiments was performed on solutions that were 0.1 M in AlBr_3 . Three spectra from this series are shown in Figure 8.2. Addition of one equivalent of the nitrite salt resulted in the disappearance of the resonances due to six-coordinate aluminum species in the same manner as for the chloride salt, but no new resonances were detected. The integrated intensity of the resonance due to AlBr_4^- (δ 80.9) indicates that a significant portion of the aluminum is unobserved. Addition of 2–6 equivalents of nitrite resulted in the complete disappearance of all resonances from the spectrum except what is due to the standard. However, at a NO_2^-/Al ratio of 10, a resonance at $\delta = 23.2$ was visible. The similarity in chemical shift of this resonance to that observed with aluminum chloride suggests that they may arise from the same species, although the integrated intensity indicates that it accounted for less than one-third of the aluminum present in the bromide solution.

A complete interpretation of these NMR results cannot be given at this time, but we believe they offer compelling evidence for the formation of aluminum nitrite complexes, although of as yet unknown stoichiometry. We anticipate further experiments involving ^{15}N NMR spectroscopy that may help determine the composition of some of the species for which resonances are observed.

8.2 Experimental Section

Aluminum chloride (J. T. Baker) was sublimed prior to use. Aluminum bromide (Aldrich) and tetrabutylammonium nitrite (Fluka) were used as received. Acetonitrile (Fisher Chemical), which was the solvent for all the reactions studied, was distilled under nitrogen from calcium hydride prior to use.

All reactions and preparations of solutions were carried out in an inert atmosphere (argon) box. Reaction mixtures were monitored using ^{27}Al NMR spectroscopy at 104.2 MHz; chemical shifts and relative integrals were versus $\text{Al}(\text{OH}_2)_6^{3+}$ as an external standard.

Solutions of varying ratios of Bu_4NNO_2 to aluminum chloride in acetonitrile were prepared by combining the appropriate volume of 1.4 M nitrite solution with 0.4 mL of 0.6 M aluminum halide solution in a 5 mL volumetric flask and diluting to 5 mL with acetonitrile to give NO_2^-/Al ratios of 1, 2, 3, 4, 5, and 10. The final concentration of aluminum was 0.12 M. The reaction mixtures were allowed to stand for 23 hours prior to acquisition of the ^{27}Al NMR spectrum. Spectra taken after 48 hours were unchanged from those taken after 23 hours.

Figure 8.2. ^{27}Al NMR spectra of mixtures of aluminum bromide and tetrabutylammonium nitrite in acetonitrile. All solutions are 0.10 M in AlBr_3 ; the molar ratio of nitrite to aluminum (x) is shown for each spectrum. The resonance at δ 80.9 in the first two spectra is due to the AlBr_4^- ion.

Solutions of varying ratios of Bu_4NNO_2 to aluminum bromide were prepared in the same fashion as for the chloride except that the stock solution of Bu_4NNO_2 in CH_3CN was 1.35 M and 1 mL of 0.5 M AlBr_3 in CH_3CN was added to the 5-mL flask, giving a final concentration of aluminum of 0.1 M. The reaction mixtures were allowed to stand for 73 hours; then each mixture was analyzed by ^{27}Al NMR. Results are shown in Table 8.1.

Table 8.1. Ratio of integrated intensities of ^{27}Al NMR resonances to that of the reference signal in spectra obtained on samples containing various NO_2^-/Al ratios

Compound	NO_2^-/Al Ratio	Integral Ratio
AlCl_3	0	2.17
	1	1.5
	2	1.03
	3	0.55
	4	0.27
	5	(a)
	10	1.43
AlBr_3	0	2.01
	1	0.78
	2	(a)
	4	(a)
	10	0.48
(a) No resonances due to sample observed at these ratios.		

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