Pacific Northwest National Laboratory

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Organic Tanks Safety Program FY97 Waste Aging Studies

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February 1998

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

PNNL-11670

19980420 091

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under Contract DE-AC06-76RLO 1830

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Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401.

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MASTER

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Richland, Washington 99352

Summary

Uranium and plutonium production at the Hanford Site produced large quantities of radioactive by-products and contaminated process chemicals that are stored in underground tanks awaiting treatment and disposal. The aging of the organic compounds used in the extraction processes has a direct bearing on several specific safety issues, including hazards associated with fuel-nitrate combustion accidents. The purpose of this project is to understand the fate of organics species added to the tank wastes. We specifically are interested in learning the extent to which waste aging changes the energy content of organic species. Our approach subjects non-radioactive waste simulants to a range of temperatures and doses of γ -radiation and then performs chemical analyses for inorganic and organic species. Transforming the species data to carbon content and energy content allows for a quantitative description of the effects of temperature, radiation dose, and radiation flux on these key indices. This report details experimental progress towards these goals.

We studied the accelerated aging of a B-plant type waste simulant that contained the main complexants and the dominant non-radioactive inorganic species used or generated in Hanford processes. Aliquots of the simulant were exposed to conditions that caused aging to occur over a period of weeks or months rather than years, i.e., irradiation with a ^{60}Co gamma source at dose-rates of approximately a 1000 times higher than dose-rates of actual tank wastes. The effect of heating the simulant at temperatures of 40° to 90 °C with and without irradiation were also investigated. After exposure, the liquid and solid components of the aged simulant were quantitatively analyzed. The analytes included the original complexants (HEDTA, EDTA, glycolate, and citrate), oxalate, formate, carbonate, ammonia, nitrite, and nitrate. In some runs, the headspace gas was analyzed for H_2 , N_2O , N_2 , O_2 , and hydrocarbons. The results are generally consistent with and supportive of the concept that aging reduces the energetic content of the organic species. Significant amounts of carbonate, oxalate and formate were produced from organic complexant aging. Temperature and radiation were the main drivers of aging. When oxygen was in the headspace above the waste simulant, it was consumed and small effects were noted. HEDTA appeared to degrade ~25% faster under radiolytic conditions and carbonate was produced more rapidly under thermal conditions when O_2 was present. Also, yields of N_2O were enhanced under radiolytic conditions when O_2 was present. It is possible that with greater amounts of oxygen in the headspace and better mixing, greater effects might be observed. The effect of Fe(III) was surveyed in one run by leaving Fe(III) out of the simulant. The effects were modest. Approximately 25% more HEDTA was consumed when Fe was present than when it is absent (O_2 present in both cases). Headspace gas analyses showed increased consumption of O_2 , increased production of H_2 , and decreased production of N_2O . Taken together, the results suggest a synergistic effect of Fe and O_2 on the rate of HEDTA degradation and gas generation under radiolytic conditions.

To model tank waste aging and interpret tank waste speciation results, we began measuring the reactivity of organic complexants and related compounds towards radiation-induced oxidation reactions. Because of the high efficiency of scavenging of the primary radicals of water radiolysis by nitrate and nitrite ion, the major radiolytically-generated radicals in these solutions, and in Hanford tank wastes, are NO_2 , NO and O^- . Prior to this effort, little quantitative information existed for the reactions of these radicals with organic compounds such as those that were used in Hanford processes. Therefore, modeling of actual waste aging, or even simulated waste aging, was not feasible without measuring reactivities and determining reaction paths. We have made the first rate measurements of complexant aging and determined some of their degradation products.

The reactivities were measured relative to formate by irradiating binary mixtures of the complexant and ^{13}C -labeled formate in alkaline nitrate/nitrite solutions. The compounds divide into two classes: those with reactivity less than or equal to formate and those that are more reactive than formate. Compounds such as citrate and acetate make up the former class. They appear to be ~ 0.7 times as reactive as formate. Glycolate and nitrogen-containing complexants, hydroxyethyl-ethylenediaminetriacetate (HEDTA) and ethylenediaminetetraacetate (EDTA), and their fragments, nitrilotriacetate (NTA), iminodiacetate (IDA), ethylenediaminediacetate (EDDA), and glycine make up the more reactive class, being from 5 to 15 times more reactive than formate. The reactivities of ethylenediaminetriacetate (ED3A) and ethylenediaminemonoacetate (EDMA) have not been measured yet, but by analogy to related compounds already run, we expect they will have reactivities similar to the species that are more reactive than formate.

The EDTA-type complexants react by cleaving the $\text{N}-\text{CH}_2\text{CO}_2^-$ bond. How this happens is not clear. Glycolate, formate, oxalate and carbonate were all found. However, since these products were produced even when conversions were relatively low, at least two pathways may have been operating: one that produced carbonate and formate and another that produced oxalate. Glycolate also yielded mixtures of oxalate, formate, and carbonate, which suggests parallel pathways for its degradation.

Future work is planned to support development of an aging kinetic model. We plan to construct a kinetic model using the available data, while we validate measurements made this year and make relative rate measurements on other species needed to model aging reactions. Species for which rate constants remain to be measured include ED3A, EDMA, oxalate, DBP, butyrate, butanol, and succinate. ED3A and EDMA will be synthesized since they are not commercially available. Work is also planned to elucidate reaction paths from starting complexants to formate, oxalate, and/or carbonate. Experiments to determine effects of dose-rate, temperature, and other factors are recommended.

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Abbreviations

DBP	dibutyl phosphate
EDMA	ethylenediaminemonoacetate
EDTA	ethylenediaminetetraacetate
EDDA	ethylenediaminediacetate
ED3A	ethylenediaminetriacetate
EMSP	Environmental Management Science Program
GC	Gas Chromatography
FAI	Fauske & Associates, Inc.
FY	fiscal year
HEDTA	hydroxyethylethylenediaminetriacetate
hexone	methyl isobutyl ketone
HPLC	high performance liquid chromatography
IDA	iminodiacetate
IC	Ion Chromatography
IPC	Ion-Pair Chromatography
MS	Mass Spectrometry
NMR	nuclear magnetic resonance
NPH	normal paraffinic hydrocarbons
NTA	nitrilotriacetate
PUREX	Plutonium-Uranium Extraction
REDOX	Reduction-Oxidation
RSST	Reactive Systems Screening Tool
SST	Single-Shell Storage Tanks
TBP	tributyl phosphate
TOC	total organic carbon

1.0 Introduction

Uranium and plutonium production at the Hanford Site produced large quantities of radioactive by-products and contaminated process chemicals, which are stored in underground tanks awaiting treatment and disposal. Having been made strongly alkaline and then subjected to successive water evaporation campaigns to increase storage capacity, the wastes now exist in the physical forms of salt cakes, metal oxide sludges, and partially saturated aqueous brine solutions. The tanks that contain organic process chemicals mixed with nitrate/nitrite salt wastes may be at risk for fuel-nitrate combustion accidents.

To assess hazards and provide information needed to establish safety criteria, test programs have been restricted to use of simulants because tank samples were not readily available and hot-cell tests methods were not developed. Historical records (Allen 1996; Agnew 1996c) identify the organic compounds originally purchased and potentially present in the wastes, thus allowing experimental determination of the energetics of these starting materials with nitrates and nitrites as a first estimate of the hazard (Webb et al. 1995). Aging experiments with simulated waste have enabled us to identify the probable degradation products and evaluate the current hazard. Knowledge gained about the rates and pathways of degradation have facilitated prediction of how the hazard changes with time and/or altered storage conditions. Work with aged simulated waste has contributed to the development of analytical methods for characterizing actual wastes. Finally, the simulant data provide a baseline for comparing and interpreting tank characterization data.

1.1 Objective

The purpose of the Waste Aging Task is to elucidate how chemical and radiological processes will have aged or degraded the organic compounds stored in the tanks. Ultimately, the task has sought to develop quantitative measures of how aging changes the energetic properties of the wastes. This information directly supports efforts to evaluate the hazard as well as to develop potential control and mitigation strategies.

1.2 Approach

Hazards posed by uncontrolled exothermic oxidation of organic compounds by nitrate and nitrite relate directly to the energy content and oxidation kinetics of the various organic compounds in the waste. Because sampling and analysis of the tank wastes for aging characteristics were not routine procedures, our approach to assessing the probable current organic content of the tanks was to simulate the chemical conditions of the tanks and elucidate mechanistic pathways that would reveal whether the hazards have increased, decreased, or remained constant. Accordingly, this project has used simulants in its studies of chemical aging. The effects of radiation were simulated by irradiating simulants with an external ^{60}Co γ source rather than including radioactive isotopes in the simulant. The major radiation sources in tank wastes are ^{137}Cs and ^{90}Sr . These emit γ and β radiation. Since "there are no significant differences in the chemical effects of γ and β irradiation," (Meisel et al. 1991a), using an external γ source is a reasonable, cost-efficient, and safe alternative to using radioactive simulants. The dose-rates used were 100 to 1000 times greater than tank waste dose-rates so that tests could be run over periods of days or weeks rather than years. After

irradiation, the disappearance and appearance of detectable organic species in the simulant and evolved gases were determined.

1.3 Background

Waste aging is an integral part of the effort to understand and assess the organic-nitrate hazard. Each of the 177 waste tanks on the Hanford Site has a unique and uncertain composition of organic, inorganic, and radioactive elements (Agnew 1996a,b,c). Organic-containing wastes have been stored in underground storage tanks at Hanford for nearly half a century, during which time they have been constantly exposed to radiation and heated to temperatures of up to 140 °C (284 °F). The wastes contain hydroxide, nitrate, nitrite, aluminate, oxides of transition metals including noble metals, radioactive elements (e.g., uranium, plutonium, cesium, strontium), and many other substances that may catalyze or promote degradation of the original compounds. Many of the single-shell tanks have been sampled and total organic carbon (TOC) contents measured. However, knowledge of the TOC in a particular storage tank is insufficient to bound the safety risk because the organic compounds in the waste are uncertain. Because nitrate reaction energies of organic species vary widely, we also need some information about the identity and oxidation state of the organic carbon.

The organic compounds that were added to the tanks are divided into two main classes: complexants and extractants/solvents. The major organic complexants believed to have been added to the tanks are glycolate, citrate, hydroxyethylethylenediaminetriacetate (HEDTA), and ethylenediaminetetraacetate (EDTA). Allen (1976) estimated the following approximate quantities

- glycolic acid, 8.8×10^5 kg
- citric acid, 8.5×10^5 kg
- hydroxyethylethylenediaminetriacetic acid, 8.3×10^5 kg
- ethylenediaminetetraacetic acid, 2.2×10^5 kg

Lesser amounts of other complexants were used, but amounts that actually were discharged to the tanks are not known.

Process solvents of concern that were used in chemical processes and stored in the tanks are tributyl phosphate (TBP), normal paraffin hydrocarbons (NPHs), and methyl isobutyl ketone (hexone). Sederburg and Reddick (1994) examined material balances at the Plutonium-Uranium Extraction (PUREX) plant from 1955 to 1991⁽¹⁾; their findings indicate that 7.22×10^5 and 1.31×10^6 kg of TBP and NPH, respectively, went to the storage tanks. Other processes also used organic solvents and organic phosphate extractants, but less is known about the quantities that were added to the tanks. Di(2-ethylhexyl)phosphate diluted with hydrocarbon solvent was used in the waste fractionation and encapsulation process. The reflux solvent extraction process used TBP/carbon tetrachloride (Cleveland 1967) and dibutyl butyl phosphonate/carbon tetrachloride for extraction solvents (Kingsley 1965). Considerable quantities of hexone were used in the REDOX plant as both extractant and solvent. For example, 65000 kg (65 metric tons) of hexone were retrieved from one storage tank, treated, and sent off-site (Gerber et al. 1992).

⁽¹⁾The amount of organic entrained in PUREX wash waste discharged to the tanks was estimated to be 2,479 m³ (655,000 gal). Assuming the composition of this waste was similar to the PUREX solvent (nominally 30 vol% TBP and 70 vol% NPH), then approximately 7.22×10^5 and 1.31×10^6 kg of the respective solvents would have been discharged to the waste tanks.

The evidence suggests that the quantities of organic solvents added to the tanks rival the quantities of complexants. However, the fraction of organic solvents that have escaped the wastes through evaporation or, in the case of phosphate esters, been saponified in the alkaline wastes (Burger 1955) is not known. Sederburg and Reddick (1994) pointed out that during early PUREX operations, the organic wash waste was combined with high-level wastes that generated enough thermal heat to boil the tank wastes.

At the start of this project in FY94, little work had been performed on aging of organic solvent components. Therefore, we performed a series of aging studies on a simulant that contained both organic solvent compounds and complexants. This simulant was designated SY1-SIM-94C. Results of these studies were reported in FY95 and FY96 (Camaioni et al. 1995, 1996).

Energetics and reactivity tests performed by Fauske & Associates, Inc. (Fauske 1996, 1995, Webb et al. 1995, Fauske and Epstein 1995) have shown that complexants and organic salts pose the greatest risk of propagating reactions. Attempts to ignite sodium nitrate-organic solvent mixtures (Fauske 1995, Webb et al. 1995) in either a Reactive Systems Screening Tool (RSST) (Creed and Fauske 1990) or in a tube propagation device (Webb et al. 1996) did not lead to propagating reactions, despite the high potential energy content of test compounds, such as dodecane, mineral oil, tributyl phosphate and sodium di-2-ethylhexyl phosphate, calcium dibutyl phosphate and sodium stearate. Instead, the solvent components vaporized away from the ignition source. Although tributyl phosphate and dibutyl phosphate have low or negligible vapor pressures, they tend to decompose, liberating hydrocarbon gases, before ignition temperatures are attained. Presumably, the complexants and low molecular weight carboxylate salts (e.g., acetate, butyrate, and succinate) have sufficiently high thermal stability to keep them in contact with an ignition source until melt temperatures ($\sim 200^{\circ}$ to 250°C) are attained and propagating reactions ensue. Accordingly, these findings focused our concern on how aging affects the distribution of organic waste components that can sustain propagating reactions.

In FY96, we initiated a study of a neutralized PUREX Acid Sludge (PAS) simulant that contained HEDTA, EDTA, glycolate and citrate. Radiolytic aging was studied at 70°C . The change in distribution of organic carbon and average energy content was determined as a function of radiolytic dose. In FY97, we did similar experiments at 90°C in the absence of radiation to assess susceptibilities of organic species to thermal degradation, and we extended radiolytic aging studies to temperatures of 40° and 90°C with and without O_2 gas in contact with the simulant solution. Section 2 of this report describes these results.

New work started this year to measure relative reactivities of organic species and their reaction paths as a first step towards developing a chemical kinetic model of organic aging. Although an aggressive campaign to speciate a large number of representative tank wastes is underway to better understand the organic species that are now present, many tanks remain to be sampled and few tanks will have been extensively sampled. So, a new goal of the waste aging studies is to develop a model of waste aging that will enable distributions of species found in samples to be understood and matched with historical records of tank contents. Historical content information for many tanks may be quantitatively unreliable because of multiple waste transfers and evaporator campaigns. In these cases, use of the model to predict absolute concentrations of aging products for comparison with speciation data will not be possible. But, sampled distributions may be compared for consistency with reactivities of the original, as well as intermediate degradation products. Furthermore, with knowledge of the current species and waste conditions (temperature and dose-rate), the model may enable quantitative predictions of future aging necessary to assess safety of long term storage. For example, although much of the current waste inventory is probably too wet to sustain propagating reactions regardless of its energy content, unsafe

conditions could develop as the wastes dry out. Here, we place emphasis on radiolytic aging because thermally-activated aging reactions appear to have significant activation barriers and much of the waste is at relatively low temperatures (~20-60 °C).

2.0 Simulated Waste Aging Studies

Aging tests were performed using a simulant that was developed for FAI energetics and reactivity tests (Carlson and Babad 1996). The simulant, designated SIM-PAS-95-1c for FY96 studies and SIM-PAS-95-1d for FY97 studies, is a modified version of the SIM-PAS-94 simulant, which Scheele (1995) developed from B-plant chemical inventories and process flow sheets.

The simulant (Table 3.1) is a heterogeneous mix of metal oxide/hydroxide precipitates and aqueous solutions containing a variety of inorganic anions, but mainly nitrate, nitrite, and hydroxide, and the organic complexants, HEDTA, EDTA, citrate, and glycolate. The density is ~1.27 g/mL and the carbon content is 21 g/L or 4.5 wt% (dry basis). The SIM-PAS-95-1d simulant has the same components as SIM-PAS-95-1c, although the concentration of EDTA is lower and the concentration glycolate is higher.

Table 2.1 Target Composition of SIM-PAS-95-1c and -1d Simulants

Species	mg/g	Species	mg/g	Species	mg/g
HEDTA ⁻³	16.9	Al ⁺³	1.493	Ca ⁺²	0.080
EDTA ⁻⁴	3.1	F ⁻	1.281	Mn ⁺²	0.068
Citrate ⁻³	17.3	Pb ⁺²	1.066	Cr ⁺³	0.044
HOCH ₂ CO ₂ ⁻	11.3	PO ₄ ⁻³	0.507	Cl ⁻	0.004
NO ₃ ⁻	109	SO ₄ ⁻²	0.506	Pd ⁺²	0.003
Na ⁺	107	Bi ⁺²	0.419	Rh ⁺³	0.003
OH ⁻	39.3	Ce ⁺³	0.377	Ru ⁺⁴	0.003
NO ₂ ⁻	37.9	Ni ⁺²	0.099	H ₂ O	640
Fe ⁺³	2.61				

Aging tests were run over a variety of radiation doses, temperatures, and cover gas compositions of either pure Ar or 20/80 O₂/Ar. The simulant was also heated at 90 °C for up to 8 months under cover gases that started out as either pure Ar or 20/80 O₂/Ar. To foster reproducible results in our aging tests, the simulant was prepared before each irradiation by measuring exact quantities of 3 homogeneous stock solutions into the reactor vessel (see Section 3.3). The same vessel was used for each irradiation, and it was placed in the same location relative to the radiation source. The radiation flux was 3x10⁵ rad/h. After irradiation, the contents of the vessel were quantitatively transferred, and analyzed for organic compounds, carbonate, nitrate, and nitrite. In addition, a control simulant was mixed and then analyzed without having been irradiated. Additional information about experimental methods is in Section 3.3.

2.1 Results

The results are divided into 4 sections. Sections 2.1.1-2.1.3 present analytical results showing how organic aging is affected by temperature, time, radiolytic dose, and O₂ in the cover gas. Section 2.1.4 uses the data to show how nitrate reaction enthalpies (ΔH_{rxn}) of the simulant change with radiation dose and thermal exposure. This latter treatment of the data is of particular interest because energy content and TOC are used to screen wastes for the likelihood of propagating reactions in tanks. For completeness, results for FY96 studies of radiolytic aging at 70 °C are included. Tables A1-A16 in Appendix A list the results of analyses performed. Species analyzed include HEDTA, EDTA, glycolate, citrate, oxalate, formate, carbonate, nitrate, nitrite and ammonia. Gases analyzed in the headspace above the aged mixtures include Ar, O₂, N₂, N₂O, H₂, CO, CO₂, and CH₄.

2.1.1 Effect of Radiation Dose on Aging

Figure 2.1 shows the disappearance of starting organic species and appearance of oxalate, formate, and carbonate as a function of radiation dose and time at 70° and 90 °C. The results show that all the complexants are susceptible to radiolytic degradation. The kinetic lifetimes obtained from fitting specie concentrations to an exponential decay function ($C=C_0e^{-t/\tau}$) suggest that the reactivities of the complexants decrease in the order: HEDTA > EDTA > glycolate > citrate.⁽¹⁾ Similar results were obtained for runs at 40 °C. The results also show that highly oxidized products grow in without delay. Nitrate decreases with increasing dose, while nitrite and ammonia increase (see Tables A1, A3, and A4). And, gaseous products, H₂, N₂O, and N₂ accumulate in the headspace above the aged simulant (see Table A10). These reaction products are all consistent with radiolysis-induced redox chemistry in which organic species are *reductants* and NO_x species are *oxidants*.

The species listed in Figure 2.1 represent a majority of the organic carbon present in the aged simulants. Figure 2.2 shows how radiolytic aging affects the concentrations of organic carbon in the simulants at 70° and 90 °C. The figure plots the concentrations of carbon in formate and oxalate, the starting species (glycolate, citrate, EDTA, and HEDTA), and unspciated or missing carbon, i.e., the difference of total carbon at start less total carbon at time, t. Tables A1- A7 contain the data used to generate these plots and provide similar data for other temperatures and conditions. This missing carbon is thought to largely be associated with chelator fragments, such as ED3A, NTA, IDA, and EDDA. These particular species were identified by GC-MS analyses of 70 °C runs and by ion pair-liquid chromatography of 90 °C runs, but amounts were not quantified. Acetic and succinic acids were detected by ion chromatography. Their concentrations were low in the 70 °C irradiation experiments.⁽²⁾ Concentrations in other experiments are being measured.

⁽¹⁾For example, half-lives determined from 70 °C data (Appendix A, Table A2) were HEDTA: 7.7 d; EDTA: 9.3 d; glycolate: 43 d; citrate: 66 d. To the extent that glycolate is a product of HEDTA, EDTA, and citrate degradations, glycolate may have greater reactivity. Results of Section 3 suggest EDTA and glycolate have comparable reactivities.

⁽²⁾For example, acetate reached a maximum concentration of 0.5 mg/mL (0.007 M) after 150 Mrad at 70 °C, and the concentration of succinate was 2.3 mg/mL (0.02 M).

Figure 2.1 Disappearance of Complexants and Appearance of Products in a Radiation Field of $\sim 3 \times 10^5$ rad hr⁻¹ at 70° and 90 °C. Scales on bottom of 70° graphs and top of 90° graphs are Dose (Mrad) and Time (days), respectively.

As shown in Figure 2.2, the amounts of missing carbon goes through maximum values of ~25% and ~15% at ~100 Mrad at 70° and 90 °C, respectively. The lower amounts of missing carbon at 90 °C is probably due partly to the fact that less EDTA is present in the simulant used for those runs, and also to faster rates of degradation for HEDTA and fragments at 90 °C. Note that carbonate production at 90 °C is nearly twice as fast as production at 70 °C (see Figure 2.1). The disappearance of carbon in starting species appears biexponential at 70° and exponential at 90 °C. This behavior may be due to a higher fraction of glycolate being present in the 90 °C simulant than was in the 70 °C simulant.

Figure 2.2 Plots of Carbon Content vs Dose for 70° and 90 °C Irradiations: (●) Organic Carbon, (■) Carbon in Organic Starting Compounds, (▲) Oxalate and Formate Carbon, (▼) Carbon in Other Organic Compounds, e.g., ED3A, NTA, IDA, etc.

2.1.2 Effect of Temperature on Radiolytic Aging

Radiolytic aging tests were run at 40°, 70° and 90° C to observe the effect of temperature on aging. Table 2.2 lists results for samples that received γ doses of ~40 to 50 Mrad. The effect seems small and may be masked by experimental scatter. The amounts of glycolate, citrate, HEDTA, and EDTA found at 40° and 70 °C are similar, indicating that rates of disappearance for the individual compounds are not strongly effected in this temperature range. More of HEDTA and glycolate are consumed at 90 °C, perhaps indicating a real increase in reaction rate with temperature. Formate, oxalate, and carbonate increased significantly on going from 70 to 90 °C as

well. It could be due to thermally-activated decomposition of intermediate products, i.e., the 2 to 5 mg C/g that are not accounted for by analytes (subtract total carbon values in lines 2, 3, or 4 from line 1).

Table 2.2 Effects of Temperature on Radiolytic Aging of Sim-PAS-95-1d

T, Dose (°C, Mrad)	Reactants/Products, mg C/g								Total
	Formate	Oxalate	Glycolate	Citrate	HEDTA	EDTA	CO ₃ ²⁻	Org C	
20°, 0	0.00	0.00	3.68	5.6	6.5	0.80	0.16	16.5	16.7
40°, 43	0.14	0.34	3.3	4.7	1.9	0.36	1.1	10.8	12.0
70°, 47 ^(a)	0.21	0.41	3.3	5.0	1.8	0.38	1.4	11.1	12.5
90°, 50	0.52	1.0	2.7	5.7	2.6	0.37	1.7	12.9	14.7

^(a)Average of two runs (see Table A1, A7 and A9)

Gas analyses show a corresponding increase in the yield of H₂ on going from 70° to 90 °C. These analyses are summarized in Figure 2.3 (see also Tables A7 and A8).

Figure 2.3 Effects of Temperature and Initial O₂ Concentration in Headspace Gas on Radiolytic Yields of Gases. (O₂): starting with 20/80 O₂/Ar; (no O₂): starting with 100% Ar; (no Fe): Starting with 20/80 O₂/Ar and simulant prepared by substituting water for Fe(III) solution (see Section 2.3 and Table 2.7).

The bar chart in Figure 2.3 shows the radiolytic yields (G) in molecules/100 eV of O₂, H₂, N₂O, and N₂ at 40°, 70° and 90 °C. Note that the yield of H₂ increases from G~0.03 at 40° to G~0.1 at 90 °C. We noted a similar trend for H₂ production from radiolytic aging of simulant SY1-SIM-94C (Camaioni et al. 1996, 1995). This trend may indicate that reaction paths to H₂-producing aldehyde intermediates are favored by higher temperatures. Formaldehyde and glyoxal degrade in alkaline solutions with irradiation producing H₂ (Ashby et al. 1993, 1994 ; Meisel et al. 1993; Karpoor et al. 1995). Finally, we mention that yields of H₂ are relatively unaffected by the either the presence or absence of O₂ in the headspace gas or Fe in the simulant. These results will be discussed in Section 2.1.4.

2.1.3 Results for Thermal Aging of the Simulant

Figure 2.4 shows how the organic composition of the simulant changes with time at 90 °C in the absence of γ radiation. Note that the time scale for thermal aging in Figure 2.4 is significantly longer than the time scale for radiolytic aging in Figure 2.1 (60 d in the former vs. 20 d in the latter). Even after heating for 2 months at 90 °C, negligible EDTA has reacted. *Thus, the degradation of organic species observed in Figure 2.1 is mainly caused, or initiated, by radiolysis.*

The relative reactivities of organic species towards thermal degradation are significantly different than those observed for radiolytic aging. Thermal rate constants for disappearance show the trend⁽¹⁾

Glycolate>HEDTA~citrate>>EDTA.

Whereas, radiolytic reactivities (see Section 2.1.1) decrease in the order:

HEDTA>EDTA>Glycolate>Citrate

Note that thermal reactivities of citrate and EDTA are the inverse of their radiolytic reactivities. Under actual tank waste storage conditions, radiolytic dose-rates are >100 times smaller than the dose-rate used to obtain the results shown in Figure 2.1. Tank waste storage times are about 100 (17 years = 6200 days) times longer than times shown in Figure 2.4. Thus, thermally activated processes may contribute to organic aging of tank wastes and cause complexants to age more uniformly than might be indicated by Figure 2.1. The results suggest that lifetimes and aging rates of organic complexants will be strongly dependent on radiolytic and thermal history of the wastes, and therefore, the degree of aging may vary from tank to tank.

⁽¹⁾Pseudo-first order lifetimes (τ) in solutions with 20/80 O₂/Ar cover gas: glycolate (~5000 h), HEDTA (7000 h), and citrate (8000 h).

Figure 2.4. Disappearance of Starting Organic Compounds and Appearance of Products vs. Time at 90 °C: Samples Unirradiated, headspace gas is initially 20/80 O₂/Ar.

2.1.4 Effects of O₂ and Fe on Radiolytic and Thermal Aging

The effects of O₂ on thermal and radiolytic aging were explored by running tests with and without O₂ cover gas. Thermal aging tests were run at 90 °C for times of up to 2 months. Radiolytic aging tests were run 70 °C with γ doses of ~50 Mrad. The initial compositions of the cover gas were either 20/80 O₂/Ar or 100% Ar. At the end of the experiments, the headspace gas was sampled (see Section 2.2, and Table 2.8) and analyzed for O₂, H₂, N₂O, N₂, and Ar.

2.1.4.1 Effects of O₂ and Fe on Radiolytic Aging

Table 2.3 shows organic and carbonate speciation results for radiolytically-aged samples. The results suggest that there are few discernible effects on the distribution of analytes when O₂ is initially present or absent in the headspace. HEDTA appears to be most affected; about 25% more reacted when O₂ was present.

Table 2.3. Effects of O₂ and Fe on Radiolytic Aging of Sim-PAS-95-1d at 70 °C^(a)

Conditions	Reactants/Products, mg C/g								
	Formate	Oxalate	Glycolate	Citrate	HEDTA	EDTA	CO ₃ ²⁻	Org C	Tot
Initial Amounts	0.00	0.00	3.7	5.6	6.5	0.64	0.16	15.3	15.5
20/80 O ₂ /Ar ^(b)	0.21	0.41	3.3	5.0	1.8	0.38	1.4	11.1	12.5
100% Ar ^(b)	0.36	0.39	3.5	5.1	2.3	0.36	1.2	12.0	13.2
No Fe ^(c)	0.40	0.38	3.5	5.0	2.4	0.32	1.4	12.0	13.4

(a)47 Mrad dose, 0.3 Mrad/h dose rate. (b)Average of two runs (see Table A4). (c)Simulant prepared by substituting water for Fe(III) solution (Solution 2 in Table 2.7); initial composition of headspace gas was 20/80 O₂/Ar.

The headspace gas analyses show O₂ was consumed when present initially (see Figure 2.3 and Tables A7 and A8). When O₂ was absent, small quantities were generated. Also, less N₂O was produced when O₂ was absent at start. Relatively more O₂ is consumed at 70° compared to 40° or 90°. However, the yield at 90° is based on data for a sample that was dosed with 146 Mrad. We observed in previous aging studies (Camaioni et al. 1996 and 1995) with SY1-SIM-94C that O₂ levels in the headspace reached steady state levels during irradiation that increased with temperature. The steady-state was achieved with a dose of 20 Mrad at 90 °C. So, yields derived from such a large dose might be artificially low.

The effects of Fe on radiolytic aging are modest. Approximately 25% more HEDTA is consumed when Fe is present than when Fe is absent (O₂ and other simulant constitutes present in both cases). Headspace gas analyses showed that leaving Fe out of the simulant caused increased consumption of O₂, increased production of H₂, and decreased production of N₂O (see Figure 2.3 and Tables A7 and A8). Taken together, the results suggest a synergistic effect of Fe and O₂ on the rate of HEDTA degradation and gas generation under radiolytic conditions.

2.1.4.2 Effects of O₂ on Thermal Aging

The organic species appear to be more reactive when O₂ is present initially. In Table 2.4, results are shown for analyses of thermally-aged samples in the presence and absence of O₂. These results show modest increases for glycolate, citrate, and HEDTA degradation rates. The effect on carbonate production is more pronounced, occurring nearly *twice* as fast in the presence of O₂. EDTA reactivity does not appear to be effected; although heated samples were routinely found to contain ~30% higher concentrations of EDTA than were measured in unaged samples of the simulant. Reasons for this anomalous behavior are unknown. One possibility is that degradation products of HEDTA interfere with EDTA analyses.

Results for headspace gas analyses are shown in Figure 2.5. Yields for 1330 h and 2330 h runs are normalized to 1000 h and 2000 h and charted in a bar graph for visual comparison. The analyses show that when O₂ is initially present, it is consumed by the aging reactions. However, it appears to be generated in small amounts when it is initially absent. Other notable effects of starting without O₂ present are: 1) N₂O generation is slightly faster than H₂ generation, and 2) both H₂ and N₂O generation are faster in the second 1000 h of reaction than in the first 1000 h. Similar observations have been reported by Barefield et al (1995, 1996).

Table 2.4 Effects of O₂ on Thermal Aging of Sim-PAS-95-1d(a)

Time h	Reactants/Products, mg C/g								Tot ^(b)
	Formate	Oxalate	Glycolate	Citrate	HEDTA	EDTA	CO ₃ ²⁻	Org C	
0			3.7	5.6	5.4	0.64	0.16	15.3	15.5
<u>20/80 O₂/Ar</u>									
675	0.00	0.19	3.01	5.2	5.1	0.80	0.85	14.2	15.1
1329	0.00	0.51	2.90	4.4	4.5	0.84	1.3	13.2	14.6
<u>100% Ar</u>									
666	0.00	0.12	3.8	5.1	5.3	0.78	0.36	15.0	15.4
1338	0.01	0.35	3.2	4.9	5.0	0.87	0.62	14.3	14.9
2300	0.43	0.59	2.4	4.3	3.7	0.76	1.04	12.5	13.5

(a)Data from Appendix A, Tables A5 and A6. (b)Total of Org C and CO₃²⁻ entries; Org C is sum of formate, oxalate, glycolate, citrate, HEDTA, and EDTA entries.

Figure 2.5 Effects of Initial Concentration of O₂ in Headspace Gas on Distribution of Gases Produced at 90 °C: (A) starting with 20/80 O₂/Ar; (B) starting with 100% Ar; ■ 1000 h, ■ 2000 h.

2.1.5 Effects of Waste Aging on Nitrate Reaction Energies

Having determined how the initial carbon redistributes as function of aging conditions, we now examine how the potential energy content of the simulant changes with aging. We define the potential energy content to be the heat that would be released from stoichiometric reaction of the organic species with nitrate on a dry weight basis, i.e., the mixtures have been concentrated to dryness. Since the starting and aged simulants all have excess nitrate and NaOH, we assume the products of reaction to be H₂O, Na₂CO₃, and N₂, and then calculate the reaction enthalpy of each species from ΔH_f data (Burger 1995). Table 2.5 lists the ΔH_f and ΔH_{rxn} data we used. The

contribution that each specie in the simulant makes to ΔH_{rxn} of the simulant is obtained by multiplying the concentration (mg/g dry mix) of the specie times the ΔH_{rxn} (kJ/g C) of the specie (Table 2.5). The ΔH_{rxn} for missing organic species is assumed to be the average of values for $\text{Na}_3\text{ED3A}$, Na_2EDDA , Na_3NTA , Na_2IDA , and sodium glycinate (aminoacetate).

Table 2.5 Nitrate Reaction Enthalpies (ΔH_{rxn}) for Organic Species

Compounds ^(a)	ΔH_f kJ/mol	ΔH_{rxn} ^(a)	
		kJ/mol	kJ/g C
Na_3HEDTA	-2247	-42423	-35.4
Na_4EDTA	-2715	-3846	-32.1
$\text{Na}_3\text{ED3A}$	-2052 ^(b)	-3239	-33.8
Na_2EDDA	-1389 ^(c)	-2633	-36.6
Sodium Glycinate	-765	-770	-32.1
Na_3NTA	-2022 ^(d)	-2050	-28.5
Na_2IDA	-1394 ^(e)	-495	-29.4
Sodium Glycolate	-901	-495	-25.5
Trisodium Citrate	-2260	-1446	-25.1
Disodium Oxalate	-1318	-269	-11.2
Sodium Formate	-667	-175	-17.9
Sodium Acetate	-709	-737	-30.7

(a) ΔH_{rxn} and ΔH_f from Burger (1995) except as noted.

(b) $[\Delta H_f(\text{EDTA}) + \Delta H_f(\text{EDDA})]/2$.

(c) $[\Delta H_f(\text{EDTA}) + \Delta H_f(\text{ethylenediamine})]/2$.

(d) $\Delta H_f(\text{NTA}) - 716$ kJ/mol, the correction for converting the free acid to the trisodium salt (Burger 1995).

(e) $[\Delta H_f(\text{NTA}) + \Delta H_f(\text{sodium glycinate})]/2$.

The concentrations (dry wt%) of organic species and their nitrate reaction enthalpies are tabulated in Appendix A, Tables A11-A16. Prior to aging, the reaction enthalpies of the simulants are 1340 J/g for SIM-PAS-95-1c and 1240 J/g for SIM-PAS-95-1d. In all cases, the nitrate reaction energies decline with the increasing severity of thermal and radiolytic aging. Figure 2.6 shows plots of $-\Delta H_{\text{rxn}}$ vs. dose for radiolytic aging at 70° and 90 °C. The slopes of the lines through the data points (3.1 and 4.1 J/g/Mrad for 70° and 90 °C, respectively) correspond to the rates of decrease in the simulant reaction enthalpies as a result of radiolytic aging. The actual rate of decrease depends somewhat on the energy of the missing carbon. Choosing a smaller average ΔH_{rxn} for the chelator fragments leads to a more curved line with a more rapid initial decrease in ΔH_{rxn} . Conversely, higher energy content fragments would result in slower initial decrease followed by a more rapid decline at higher doses. Estimates of ΔH_{rxn} after high doses will not be strongly dependent on the ΔH_{rxn} of missing species because the missing species make up small

Figure 2.6 Nitrate Reaction Enthalpy of Simulants vs. Dose at 70° and 90 °C.
 (●) SIM-PAS-95-1c, 70 °C; (■) SIM-PAS-95-1d, 90 °C.

Radiolytic aging reduces not only the organic carbon content and energy content of the simulant (see Appendix A, Tables A11, A14, and A15), it also reduces the average energy content per gram of carbon ($-\Delta H_{rxn}$ in kJ/g C).⁽¹⁾ The average energy content and organic carbon content of the simulants as a function of dose and temperature are shown in Table 2.6. The average energy content started out at ~30 kJ/g C. After a dose of 150 Mrad, the value had dropped to ~23-24 kJ/g C. An 150 Mrad dose at 70 °C reduced the organic carbon content of SIM-PAS-95-1c from 4.5 wt% C to 3.5 wt% C and at 90 °C, reduced SIM-PAS-95-1d from 4.3 wt% C to 2.9 wt% C. These results lend quantitative support to the idea that aging degrades the organic species in tank wastes to lower average energies and therefore results in safer storage conditions with respect to organic-nitrate reactions.

⁽¹⁾The average is calculated as the ΔH_{rxn} (kJ/g dry mix) divided by the TOC (mg C/g dry mix).

Table 2.6 Effect of Dose on Organic Carbon Content and Average $-\Delta H_{\text{rxn}}$ ^(a) of SIM-PAS-95-1 Simulants

40 °C ^(b)			70 °C ^(c)			90 °C ^(b)		
Dose (Mrad)	Org C (wt%)	$-\Delta H_{\text{rxn}}$ (kJ/g C)	Dose (Mrad)	Org C (wt%)	$-\Delta H_{\text{rxn}}$ (kJ/g C)	Dose (Mrad)	Org C (wt%)	$-\Delta H_{\text{rxn}}$ (kJ/g C)
0	4.3	29.1	0	4.5	29.8	0	4.3	29.1
28	4.1	28.6	30	4.3	28.5	22	4.2	28.4
43	4.0	28.0	50	4.2	27.8	50	4.0	26.3
			100	3.8	26.9	114	3.3	25.4
			150	3.5	24.1	146	2.9	23.1

^(a) ΔH_{rxn} (J/g dry simulant) divided by TOC (mg C/g dry simulant). ^(b)SIM-PAS-95-1d.

^(c)SIM-PAS-95-1c

2.2 Experimental Section

All of the chemicals used in this study were purchased from Aldrich Chemical Company, Eastman Kodak, or Baker Chemicals. Their purities were reagent grade or better, as defined by the American Chemical Society, and the chemicals were not further purified. Water used for preparing the simulant was deionized by a Milli-Q™ Deionization System (Millipore Corporation, San Francisco, CA).

The cylindrical bomb reactors used for this study were made from 316 stainless steel and were of two volumes, 500 mL and 30 mL. The larger one was used for radiolytic aging tests and the smaller one was used for thermal aging tests. Reaction temperatures were measured by a K-thermocouple that inserted through a port in the reactor cover to within 5 mm from the bottom. Another port was connected to the gas manifold via small diameter stainless-steel tubing.

The reactors were heated to operating temperatures by heating tape wrapped around the outside of the reactors. Reaction temperatures were maintained at set temperatures by feedback control (Bryan and Pederson 1994). Pressure and temperature in the vessel was monitored with a data logger. The gas volume of the reactors includes the reactor headspace, the tubing that connects the reactor to the manifold, and the portion of the manifold dedicated to the reactor. The tubing and manifold volume was measured to be 7.8 mL. The sample volumes were 130 mL for the large 500 mL reactor and 13 mL for the small 30 mL reactor. So, total headspace for the large reactor is 378 mL, and for the small reactor, 23 mL.

2.2.1 Simulant Preparation and Irradiation

The SIM-PAS-95-1c and -1d simulants are based on recipes published in the test plan (Carlson and Babad 1996) for tube propagation experiments (Fauske 1996). We noted that addition of solid ferric nitrate to alkaline solutions containing nitrite ion produced copious amounts of NO₂ gas. On varying the order and timing of addition, we found that if sufficient time (~2 h) were allowed for ferric nitrate to dissolve and hydrolyze to ferric hydroxide before addition of nitrite, then no gas was evolved. Therefore, due caution should be taken in mixing the reagents in proportions or orders different from that recommended here or in the test plan (Carlson and Babad 1996).

To avoid errors associated with dispensing aliquots of a heterogeneous simulant, the simulant was prepared in the reaction vessel before each irradiation by mixing together three homogeneous stock solutions (Table 2.7). These solutions were stored at approximately 4 °C and were allowed to warm to room temperature before volumetric transfers were made.

Simulant SIM-PAS-95-1d was prepared and dispensed as described above for SIM-PAS-95-1c, except that the quantities of all components were doubled to allow a greater number of tests. The three solutions were stored in 1 L plastic containers, sealed with tape, and refrigerated. Solution 1 which had a total volume of 2 L, was divided into two bottles.

For each test run in the large reactor, 100.0 mL of solution 1, 20.0 mL of solution 2, and 10.0 mL of solution 3 were added sequentially to the reactor. Test runs in small reactors used 10.0 mL, 2.0 mL and 1.0 mL of the respective stock solutions. No NO₂ gas was observed on mixing the solutions. Control runs were similarly mixed and analyzed without exposure to radiation. The measured density of the simulant was 1.27 g/mL. Water content is estimated to be 64%. The charged reactors were sealed and transported to the γ irradiation facility, where the irradiation experiments were performed according to the procedures described in Table 2.8. The gases generated during the irradiations were usually vented to the atmosphere, except for certain runs that were selected for gas analyses. In these cases, the gases were collected in an evacuated vessel and analyzed by mass spectrometry (Goheen 1988).

2.2.2 Solution Phase Analyses

The reactor was cooled to room temperature, removed from the gas manifold at the γ -irradiation facility, sealed, and transported to analytical facilities. The contents were diluted 3.85 fold (130 mL in 500 mL for large reactor and 13 mL in 50 mL for small reactor) with deionized water. Aliquots of this were used for IC, IPC, ammonia, and carbonate analyses. EDTA and HEDTA were quantified using IPC. Organic acid anions, including formic, glycolic, citric and oxalic acids were quantified by IC. Analyses of nitrate and nitrite were also performed by IC. Total inorganic carbon was performed with a carbon analyzer. The analysis of dissolved ammonia (NH₃)_{aq} was performed using an Orion 720A pH/ISE (ion selective electrode) meter equipped with an Orion 95-12 NH₃ ISE (Burt 1989).

Table 2.7 Approximate Compositions of Solutions Used to Prepare SIM-PAS-95-1 Simulants

COMPONENT	Mol. Wt. (g/mol)	Mass (g)	Conc. (M)
<u>Solution 1</u>			
NaOH	40	142	3.55
Al(NO ₃) ₃ •9H ₂ O	375.13	32	0.085
Na ₂ SiO ₃ •9H ₂ O	284.2	0.9	0.003
NaNO ₃	84.99	187	2.20
NaF	41.99	4.4	0.10
Na ₂ SO ₄	142.04	1.2	0.01
Na ₃ PO ₄ •12H ₂ O	380.13	3.1	0.01
Na ₃ HEDTA•2H ₂ O	344.18	36.2	0.11
Na ₄ EDTA•3H ₂ O	380.2	8.79	0.02
Na ₃ Citrate	294	35.8	0.12
Glycolic acid	76	23	0.30
H ₂ O	18	735	40.8
<u>Solution 2</u>			
Fe(NO ₃) ₃ •9H ₂ O	404	29.1	0.72
H ₂ O	18	64.8	36.00
<u>Solution 3</u>			
NaNO ₂	69	87.3	6.33
Cr(NO ₃) ₃ •9H ₂ O	400.15	0.5	0.01
Ni(NO ₃) ₂ •6H ₂ O	290.81	0.8	0.01
Mn(NO ₃) ₂	178.95	0.3	0.01
KNO ₃	101.1	0.4	0.02
Pd(NO ₃) ₂	230.41	0.012	0.0003
RuCl ₄ •5H ₂ O	332.96	0.02	0.0003
Rh(NO ₃) ₃ •2H ₂ O	324.93	0.019	0.0003
Ce(NO ₃) ₃ •6H ₂ O	434.23	1.8	0.02
Bi(NO ₃) ₃ •5H ₂ O	485.07	1.5	0.02
Pb(NO ₃) ₂	331.23	2.6	0.04
H ₂ O	18	162.5	45.1

Table 2.8 Procedure for Irradiating the Simulant and Collecting Gas Samples

1. Close vent, open purge valves, and turn on headspace gas mixture for 10 min
2. Close purge valves and turn off gas
3. Open vent
4. Hook up vessels; close vent
5. Open gas (oxygen/argon) inlet (2.7 atm)
6. Slowly open purge valves; let the vessel sit for 5 to 10 min; leak check fittings on the lid with leak detector solution
7. Take readings of temperature and pressure; close purge valves; open vent; let the vessel sit for 30 to 60 min
8. Take pressure readings to verify that the vessel does not leak
9. Slowly open each purge valve until bubbles are gone; close purge valves
10. Turn gas on and vent manifold; close vent
11. Slowly open purge valves; let the vessel sit for 5 to 10 min
12. Close purge valves; close gas inlet
13. Open vent
14. Repeat steps 6 to 10
15. Repeat 6; take readings, including pressure
16. Repeat 7 and continue at step 17
17. Open purge valves slowly and wait until the pressure reaches ~2.7 atm; let the vessel sit for 5 to 10 min
18. Take readings; close purge valves
19. Close gas supply; open vent. Shut off regulator
20. Leave vessel at pressure overnight
21. Check pressures
22. If pressures are OK, then open vent; slowly open each purge valve until bubbles are gone
23. Close purge valves
24. Connect thermocouple and heat tape to temperature controller; place vessel in the irradiator, if irradiating
25. Bring vessel up to temperature slowly; stabilize at temperature for 1 to 2 hours
26. Take readings and start data logging
27. Record time and pressure prior to discontinuing heating and removal of vessel from γ -irradiator.
28. Collect headspace gas sample after reactor has cooled to ambient temperature (~25 °C)
29. Close reactor valve and disconnect from the gas manifold
30. Remove solution and solids from the reactor and clean the vessel

2.2.2.1 Ion Pair Chromatography Analyses of EDTA and HEDTA

Using a volumetric pipet, 1 mL of the diluted aqueous solution was placed in a 10 mL volumetric flask to which 100 μ L of 0.5 M CuSO_4 was added and diluted to volume with water. The solution was analyzed using a Waters Associates high-performance liquid chromatography (HPLC) instrumentation with columns and conditions listed in Table 2.9.

Table 2.9 Columns and Conditions Used for IPC Analyses of EDTA and HEDTA

Guard column:	Adsorbosphere® C-8 cartridge
Analytical Column:	Adsorbosphere® C-8 (25 cm x 4.6 mm, 5- μ m particle size)
Flow:	1.5 mL/min
Sample Volume:	5 μ L
Detection:	UV, 280 nm, as copper complex
Mobile phase:	0.002 M dodecyltrimethylammonium bromide and 0.05 M potassium dihydrogen phosphate, pH 6.5

2.2.2.2 Ion Chromatography Preparation/Analyses of Organic Acids

Analyses were carried out using a Dionex model IC unit (Dionex Corp., Sunnyvale, CA, USA) equipped with a Dionex, Model CD20 conductivity detector. Analyses of formate, oxalate, and citrate were carried out using a Dionex AS-11 column. A Dionex AS-6 column was used for glycolate, acetate, and succinate analyses, since glycolate co-eluted with acetate on the AS-11 column. The standard concentrations bracketed the estimated concentrations of the samples. The AS-11 chromatographic conditions are listed in Tables 2.10 and 2.11. An aliquot of the simulant solution (see Section 2.2.2) was diluted 250-fold for these analyses.

Table 2.10 AS-11 IC Analysis Conditions

Guard column:	Dionex AG11
Analytical Column:	Dionex AS11
Anion Suppressor:	ASRS-I, 4mm
Flow:	2.0 mL/min
Sample Volume:	25 μ L
Column	Ambient
Temperature:	
Detection:	Conductivity

The mobile phase contained a gradient of deionized water and a weak solution of sodium hydroxide for the AS-11 column. Two solutions, 5 mM and a 100 mM NaOH, were prepared from 18.5 M NaOH stock solution. The water used to prepare the mobile phase and run the gradient was stirred under vacuum for over 12 hours, and then sparged with helium to avoid interference from dissolved carbon dioxide. Gradient conditions used for AS-11 column separation

32 are shown in Table 2. The column was allowed to equilibrate at initial conditions for at least 7 minutes before each run.

Table 2.11 AS-11 Analysis Mobile Phase Gradient

Time (minutes)	% Water	5 mM NaOH	100 mM NaOH
0.0	90	10	0
2.9	90	10	0
6.4	0	100	0
18.4	0	65	35

The mobile phase for the AS-6 column was made up of 0.4 mM heptafluorobutyric acid in deionized water. We used 5 mM tetrabutylammonium hydroxide as a suppression eluant. Further details for AS-6 column conditions are listed in Table 3. Concentrations were determined using a linear calibration curve. Quantification based on high dilution is not ideal, but is possible, as the plots of standard concentration versus response exhibit linear behavior down to 100 ppb for the key analytes.

Table 2.12 AS-6 Analysis Conditions

Guard column:	None
Analytical Column:	Dionex ICE-IonPac AS6 (9x250 mm)
Flow:	1.0 mL/min
Sample Volume:	25 µL
Mobile phase:	0.4 mM heptafluorobutyric acid
Detection:	Conductivity
Suppressor:	AMMS-ICE
Suppression eluant:	5 mM tetrabutylammonium hydroxide
Suppression eluant flow	3 mL/min
Column Temperature	Ambient

3.0 Relative Rate Constants for Radiolytic Aging of Organic Species

New work was initiated this year to measure relative rate constants and reaction paths of radiolytic aging of organic species as a step towards developing a kinetic model for organic aging. Although an aggressive campaign to speciate a large number of representative tank wastes is underway to better understand the organic species that are now present, many tanks remain to be sampled and few tanks will have been extensively sampled. So, a new goal of the waste aging studies is to develop a model of waste aging that will enable distributions of species found in samples to be understood, as well as to provide capabilities for predicting how distributions may evolve during interim storage.

3.1 Background and Approach

Although the reactions of water radiolysis intermediates with organic species have been extensively studied, little of this information applies to the radiolytic degradation of organic species in concentrated nitrate/nitrite solutions. Since last year, our understanding of the kinetics of aging has advanced significantly due to fundamental insights provided by Meisel and coworkers (1997). They point out that essentially all the primary radicals from water radiolysis are converted to NO_x radicals in the wastes because of the high rate constants⁽¹⁾ for reactions of e^- , $\text{HO}^\cdot$, $\text{O}^\cdot$, $\text{H}^\cdot$, and $\text{NO}_3^\cdot$ with nitrate and nitrite.

Electrons are rapidly scavenged by nitrate to make the reducing radical, NO_3^{2-} . But, it is short-lived, dissociating to NO_2 in less than 15 μsec (Meisel et al. 1991b, 1997).

A significant fraction of energy may be directly absorbed by nitrate ion in the concentrated waste solutions to produce $\text{NO}_3^\cdot$ radical. The redox couple of $\text{NO}_3/\text{NO}_3^-$ ($E^\circ = >2.3 \text{ V}$) (Neta and Huie 1986) is significantly more positive than that of $\text{NO}_2/\text{NO}_2^-$ ($E^\circ = 1.04 \text{ V}$), so the $\text{NO}_3^\cdot$ radical is expected to produce NO_2 , as well.

One expects a yield of $\text{G}(\text{NO}_2) \sim 6$ molecules per 100 eV and a yield of $\text{G}(\text{NO}) \sim 0.6$ molecule per 100 eV of deposited energy from the water radiolysis (Meisel et al. 1991b, 1993, and 1997). *Therefore, NO_2 must be the oxidant responsible for degrading organic species in the wastes and in our simulated aging experiments.*

The tank wastes are heterogeneous mixtures consisting of considerable solids and colloidal particles in contact with solution phases. The possible role that interfacial radiolysis may play is

⁽¹⁾All rate constants from Buxton et al. (1988).

just starting to be explored (Orlando et al. 1997; Meisel et al. 1997). Fundamental studies of electron beams interacting with NaNO_3 crystal surfaces in vacuum show that species that desorb from the surface are NO, O, O_2 , and NO_2 (Knutsen and Orlando 1997). The dominant species are NO and O. The O atoms react in part with NO_3^- to form O_2 and NO_2 . Extrapolating to NaNO_3 interfaces with tank waste aqueous supernatants, we expect that O atom would be scavenged by both NO_2^- and NO_3^- making O_2 and NO_2 , respectively. Therefore, interfacial radiolysis is expected to generate the same oxidants as solution phase radiolysis, with perhaps greater yields of NO. NO is not a good oxidizing agent of organic species, however, it is a ready scavenger of organic radicals, the products of which subsequently react to produce organic carbonyl compounds and N_2O (Meisel et al 1993).

3.1.1 NO_2 Reaction Kinetics

Little information exists on the reactions of organic species with NO_2 . But, given that the reduction potential of NO_2 is less than the oxidation potentials of the organic species, reaction rates are expected to be well below diffusion limits. The hydrolysis reactions of NO_x radicals to nitrate and nitrite occurs with large bimolecular rate constants (Lee and Schwartz 1984) that are characteristic of radical-radical termination reactions.

For attack on organic species to be favorable in water, low rates of NO_x generation are required (Meisel et al. 1997). For example, a radiation field of $\sim 10^5$ rad/h generates $\sim 10^{-7}$ M/s NO_2 . In the absence of reducing agents, the steady-state concentration NO_2 will be $\sim 10^{-8}$ M⁽¹⁾ such that the lifetime of Reaction 3.5 is ~ 0.5 s. From this, we note that rate constants for attack on organic species need only be on the order of $1 \text{ M}^{-1}\text{s}^{-1}$ for 10% of NO_2 to oxidize organic species.⁽²⁾ Furthermore, the fraction of attack is inversely dependent on the steady-state concentration of NO_2 which has a square root dependence on dose-rate. With dose-rates common to tank wastes (for example, see Parra (1994)), steady-state concentrations of NO_2 are much lower so oxidation of organic species should be more efficient.

3.1.2 Kinetic Model for Radiolytic Aging

Aging studies of simulants show that the kinetic orders for disappearance of organic species are first order, e.g., EDTA and HEDTA in Figure 2.1. A generalized mechanism for radiolytic aging consistent with this observation and which takes into account the role of NO_2 is given in Scheme 3.1. It includes a step for generation of NO_2 (Meisel et al. 1991, 1993, 1997), steps for oxidation of the organic species (S_i), and self-reaction of NO_2 . Products, P_i , of reactions in Scheme 3.1 may subsequently reactant and therefore assume identities of species, S_j .

(1)Steady-state $[\text{NO}_2] \sim (10^{-7}/2k_5)^{1/2}$.

(2)Assume pseudo-first order lifetime for attack on organic species is 5 s, i.e., 10 times slower than self-reaction lifetime. If concentration of species is 0.01 M, then $1/5 = 2k[0.01]$, such that $k = 10$.

Scheme 3.1 General Mechanism for Radiolytic Aging

Although a general representation of the reaction steps and species involved, the rate law for this mechanism serves to show the major factors that control radiolytic aging of waste. Assuming steady-state approximations for oxidant concentrations yields the rate laws (Equations 3.8 and 3.9) for the disappearance of the organic species, S_i , in the presence of n organic species.

$$\frac{d[\text{S}_i]}{dt} \approx \frac{1}{2} G_{\text{NO}_2} (\text{DoseRate}) \frac{k_i [\text{S}_i]}{k_0 [\text{NO}_2] + \sum_{j=1}^n k_j [\text{S}_j]} \quad (3.8)$$

$$\frac{d[\text{S}_i]}{dt} \approx \frac{\frac{1}{2} G_{\text{NO}_2} \text{DoseRate}}{\frac{k_0 [\text{NO}_2]}{k_i [\text{S}_i]} + \sum_{j=1}^n \frac{k_j [\text{S}_j]}{k_i [\text{S}_i]}} \quad (3.9)$$

Inspection of the rate law shows that the reaction rate depends on 4 factors: dose-rate, radiolytic yield of NO_2 , reactivities (k_i/k_j) of S_i with NO_2 relative to each of the other species, and concentrations of S_i relative other reactive species. The reactions of organic radicals with NO_2 are not explicitly modeled in Scheme 3.1. These reactions are much faster than reactions of non-radicals with NO_2 . So, a factor of one-half in the numerator of Equation 3.8 accounts for the stoichiometry of two NO_2 per molecule of species consumed. The rate law cannot be solved analytically. However numerical methods are available for computer simulation of complex sequences of reactions, such as Scheme 3.1. What is needed to build the model is reaction path information and reactivities of organic species.

3.1.3 Kinetic Expressions for Relative Reactivities of Organic Species

From Equation 3.8, when two species degrade according to Scheme 3.1, the disappearance of one relative to the other is given by the rate law

$$\frac{d[\text{S}_j]}{d[\text{S}_i]} = \frac{k_j [\text{S}_j]}{k_i [\text{S}_i]} \quad (3.10)$$

Integrating and solving for the rate ratio, k_i/k_j , yields equation 3.11.

$$\frac{k_j}{k_i} = \frac{\ln \left(\frac{[S_j]_t}{[S_j]_o} \right)}{\ln \left(\frac{[S_i]_t}{[S_i]_o} \right)} \quad (3.11)$$

3.2 Results

Measurements of the relative reactivities of the complexants and several of their degradation products have now been made. The reactivities were measured relative to formate by irradiating binary mixtures of an organic species and ^{13}C -labeled formate in alkaline nitrate/nitrite solution. Conversions of organic species were measured by ^{13}C and proton NMR spectroscopies and corroborated by ion and liquid chromatography. Products are being identified, as well, to provide reaction path information. In addition, the absolute rate constant for reaction of NO_2 with formate has been estimated from the radiolytic yield of carbonate from formate in the absence of other organic species. These results are described in the following two sections. Data from these experiments are found in Appendix B.

3.2.1 Relative Reactivities of Organic Species

Formate degrades cleanly to carbonate during γ radiolysis. For this reason, we chose to measure reactivities of other organic species relative to it. And, we used formate- ^{13}C to avoid interference from formate and carbonate produced by degradation other organic species (*e.g.*, see Figure 2.1). Figure 3.1 shows ^{13}C NMR spectra of the formate/carbonate region before and after radiolysis. The ratio of the carbonate peak area to the formate peak area equals the conversion of formate to carbonate. Thus, for a binary competition between an organic specie and formate- ^{13}C , Equation 3.11 becomes

$$\frac{k_s}{k_{^{13}\text{CO}_3^{2-}}} = \frac{\ln \left(\frac{[S]_t}{[S]_o} \right)}{\ln \left(1 - \frac{[^{13}\text{CO}_3^{2-}]_t}{[^{\text{H}^{13}\text{CO}_2^-}]_o} \right)} \quad (3.12)$$

Figure 3.1 ^{13}C NMR Spectra of 0.024 M Sodium Formate in 0.1 M NaNO_3 , 0.03 M NaNO_2 , 2 M NaOH before and after γ Radiolysis.

Scouting experiments were first performed in which two ratios of EDTA/formate were irradiated for 5-11 days in γ -field of 8×10^4 rad/h. Figure 3.2 shows typical ^1H NMR spectra obtained from unirradiated and irradiated samples. Note products that appear in the irradiated sample: carbonate from formate- ^{13}C , and formate- ^{12}C and a variety of other products from EDTA.

Figure 3.2 ^1H NMR Spectra of Unirradiated (top) and Irradiated (bottom) EDTA/Formate- ^{13}C Solutions.

Figure 3.3 shows the observed dependence of radiolytic yield $G(^{13}\text{CO}_3^{2-})$ on initial formate and EDTA concentrations (see Table B1, Appendix B for data). Note that in the absence of EDTA, $G(^{13}\text{CO}_3^{2-})$ is greater at 0.1 M formate than at 0.05 M formate, and that at both concentrations, $G(^{13}\text{CO}_3^{2-})$ decreases as initial EDTA concentrations increase from 0 to 0.1 M. This behavior is entirely consistent with Scheme 3.1 in which formate and EDTA *compete* for radiolytically-generated oxidants. From measurements of the conversion of EDTA and formate, we obtain a relative rate constant, $k_{\text{EDTA}}/k_{\text{formate}} = 5 \pm 2$ using Equation 3.12.

Figure 3.3 Dependence of radiolytic Yield of Carbonate from Formate vs. Initial EDTA Concentration in a Solution of 3.75 M NaNO₃, 1.25 M NaNO₂, and 2 M NaOH. Dose-rate = 8×10^4 rad/h; irradiation times range from 5 to 11 days.

The uncertainty in $k_{\text{EDTA}}/k_{\text{formate}}$ measurements is larger than we expect, with values ranging from 2.1 to 9.3 (see Table B1). We estimate uncertainties in measurements of EDTA, formate and carbonate concentrations are ~5%. But, the relative rates are most sensitive to the measurement of formate conversion. For example, if EDTA conversions and the average relative rate constant are used to predict formate conversions,

$$\text{predicted formate conversion} = 1 - \exp\{5 \cdot \ln([\text{EDTA}]/[\text{EDTA}]_0)\} \quad (3.13)$$

then we find that the observed formate conversions are all within 15% the predicted ones. On the other hand, EDTA conversions predicted by the observed formate conversions differ from observed conversions by as much as 100%. Since our measurements of EDTA concentrations cannot suffer such large errors, we think it more probable that the spread in values is due to errors in measurements of carbonate/formate ratios. The significantly higher reactivity of EDTA causes these ratios to be small, even when significant amounts of EDTA are converted.

Subsequent experiments were run to measure relative rate constants for other organic species. The results are summarized in Table 3.1. The table lists starting concentrations, average fractions of formate-¹³C and organic species remaining after irradiation, and average k_{rel} . Standard deviations in the averages and number of measurements are listed, too. The values, C^s/C_o^s and

C^F/C_o^F , in Table 3.1 are the ratios of concentrations of species (superscript S) and formate- ^{13}C (superscript F) after irradiation to before irradiation. The variations in these values are in part due to samples receiving different doses depending on how they were located in the gamma irradiator.

Table 3.1 Rate Constants for Disappearance of Organic Species Relative to Conversion of Formate to Carbonate Caused by γ -Radiolysis of Nitrate/Nitrite/Hydroxide Solutions

Specie	C_o^S	C_o^F	$(C^S/C_o^S)^{(a)}$	$(C^F/C_o^F)^{(b)}$	$k_{\text{rel}}^{(c)}$	
u-EDDA	0.0120	0.0900	0.44 ± 0.01	0.94 ± 0.01	13.0 ± 0.3	(3)
s-EDDA	0.0206	0.0991	0.35 ± 0.02	0.92 ± 0.01	13 ± 2	(3)
IDA	0.0486	0.133	0.37 ± 0.06	0.92 ± 0.01	12 ± 3	(3)
NTA	0.0164	0.127	0.37 ± 0.08	0.090 ± 0.02	9.8 ± 0.5	(3)
HEDTA	0.0395	0.103	0.29 ± 0.05	0.92 ± 0.01	13.7 ± 0.5	(3)
HEDTA	0.088	0.10	$0.68 \pm 0.03^{(d)}$	0.93 ± 0.001	5.4 ± 0.4	(3)
Glycine	0.0549	0.111	0.49 ± 0.04	0.908 ± 0.006	7 ± 1	(3)
Glycolate	0.0401	0.101	0.45 ± 0.1	0.87 ± 0.04	6.1 ± 0.4	(2)
Glycolate	0.12	0.1	$0.7 \pm 0.1^{(d)}$	0.91 ± 0.02	4 ± 2	(3)
EDTA	0.0200	0.103	0.59 ± 0.04	0.91 ± 0.01	5.7 ± 0.7	(3)
EDTA			(d)		$5 \pm 2^{(e)}$	(13)
Formate					1 ^(f)	
Citrate	0.0047	0.0670	0.92 ± 0.05	$0.882 \pm 0.007^{(b)}$	0.6 ± 0.5	(3)
Citrate	0.0047	0.0670	0.62 ± 0.09	$0.52 \pm 0.06^{(b)}$	0.71 ± 0.09	(3)
Acetate	0.0078	0.0995	0.38 ± 0.06	$0.27 \pm 0.06^{(b)}$	0.72 ± 0.05	(3)

a) Measured by ^{13}C NMR. (b) Measured by ^1H NMR. (c) Number of measurements in parentheses. (d) Average of IPC and ^1H NMR measurements. (e) From experiments in Figure 3.3. (f) Defined value.

The species divide into two classes according to their reactivity relative to formate: those that are less reactive and those that are more reactive. Compounds such as citrate and acetate make up the less reactive class. Also, preliminary work on DBP, butyrate, and succinate suggest these will be part of this class, as well. Glycolate and nitrogen-containing complexants, HEDTA, EDTA, and their fragments, NTA, IDA, EDDA, and glycine, make up the more reactive class, being from 5 to 16 times more reactive than formate. The reactivities of ethylenediaminetriacetate (ED3A) and ethylenediaminemonoacetate (EDMA) have not been measured yet, but by analogy to related compounds already run, similarly high reactivity may be expected.

3.2.2 Products of Degradation

When possible products are identified from the chemical shifts of NMR peaks that appear after γ -irradiation. We note that formate is almost always a significant product. More than two moles of

formate are produced per mole of EDTA consumed, ~1 mole formate is formed per mole glycolate consumed, and for citrate, acetate, and HEDTA, ~0.5 mole formate is formed per mole of species consumed. Oxalate is also produced, and presumably carbonate (e.g., see Figure 2.1). Since we do not yet have authentic samples of ED3A, we have not yet determined to what extent EDTA and HEDTA degrade to ED3A. However, the pathway for NTA degradation is better understood. Figure 3.4 shows spectra taken before and after irradiation of an NTA solution. Readily identifiable products are IDA, glycine, and formate.

Figure 3.4 ^1H NMR Spectra Showing that NTA Degrades to IDA and Glycine During γ -Radiolysis in Nitrate/Nitrite/Hydroxide Solution. Top spectrum: unirradiated sample. Bottom spectrum: irradiated sample, ~8 Mrad dose.

In one experiment, 45% of starting NTA remained, 17% was IDA, and 29% was glycine. These products accounted for 91% of the nitrogen originally present in NTA. We presume the missing N is due to inorganic N resulting from oxidation of glycine. This progression of products is entirely consistent with the reactivities we measured for NTA, IDA, and glycine by competition with formate- ^{13}C (see Table 3.1). The yield of formate- ^{12}C was 83%. This high yield suggests that cleavage of the $\text{N}-\text{CH}_2\text{CO}_2^-$ may partly or wholly occur by oxidative decarboxylation.

3.2.3 Rate Constant for Reaction of NO₂ with Formate

Several experiments were run in which formate was radiolyzed in nitrate/nitrite/hydroxide solutions to learn the effect of starting concentration on the radiolytic yield of formate. Figure 3.5 shows results of these experiments, all of which were run in 3.75 M NaNO₃, 1.25 M NaNO₂, 2 M NaOH, and no organic species other than formate. They include 5 experiments from Figure 3.3 (0.05 and 0.1 M formate) that were run in 5 mm o.d. NMR tubes and 14 experiments that were run in 5 mL vials. The highest concentration of formate run was 1.1 M.

Figure 3.5 Radiolytic Yield (G in molecules/100 eV) of Carbonate from Formate in a Homogeneous Solution of 3.75 M NaNO₃, 1.25 M NaNO₂, and 2 M NaOH. (●) 100% formate-¹³C in these runs; (○) mixtures containing 0.1 M Formate-¹³C plus 0.25, 0.5 or 1.0 M Formate-¹²C.

As Scheme 3.1 and Equation 3.9 predict, the yield of carbonate increases with formate concentration. Since the radiolytic yield NO₂ is finite, the yield of carbonate should approach a limiting value that is determined by the yield of NO₂ and the stoichiometry of the reaction with formate. We do not observe a leveling of the yield, but with G(NO₂) ≈ 6 (Meisel et al. 1997) and a stoichiometry of 2 NO₂ consumed per CO₃²⁻ produced,

a limiting value of $G \approx 3$ is expected and we have only attained $G(\text{CO}_3^{2-}) \sim 2$ with 1 M formate. This fact suggests that reaction of NO₂ with formate is slow. Also, it clearly rules out highly reactive water radiolysis intermediates as dominant oxidants. Formate is an efficient scavenger of HO, O⁻, and H (Buxton et al. 1988).

Since the rate constant, k_5 , for hydrolysis of NO₂ is known, an absolute rate constant for

reaction of NO₂ with formate, k₁₄, can be derived from the data in Figure 3.5. The relative rate law for Reaction 3.14 competing with 3.5 is

$$\frac{d[\text{CO}_3^{2-}]}{\sqrt{d[\text{NO}_3^-]}} = \frac{k_{14}[\text{HCO}_2^-]}{\sqrt{k_5}} \sqrt{dt} \quad (3.15)$$

Integrating Equation 3.15 for the condition of small formate conversion and solving for k₁₄/√k₅ gives Equation 3.16.

$$\frac{k_{14}}{\sqrt{k_5}} = \frac{\Delta[\text{CO}_3^{2-}]}{\sqrt{\Delta[\text{NO}_3^-]} [\text{HCO}_2^-]_0 \sqrt{\Delta t}} \quad (3.16)$$

Since our experiments are run in 3.75 M NaNO₃ solutions and radiolysis interconverts NO₃⁻ and NO₂⁻ (see Equations 3.1-3.4), the change in NO₃⁻ due to Equation 3.5 cannot be directly measured. However, Δ[NO₃⁻] can be estimated from the Δ[CO₃²⁻], assuming G(NO₂) ~ 6 and the stoichiometry for Equations 3.5 and 3.14. The relationship is given by Equation 3.18

$$\frac{1}{2}G(\text{NO}_2) = G(\text{CO}_3^{2-}) + G(\text{NO}_3^-) \quad (3.17)$$

$$\Delta[\text{NO}_3^-] = \frac{1}{2}G(\text{NO}_2) \cdot \text{Dose} \cdot \rho / 965 - \Delta[\text{CO}_3^{2-}] \quad (3.18)$$

where G is in molecules/100 eV, dose is in units of Mrad, ρ is solution density in g/mL, and the 965 factor converts units to concentration in M.

Application of Equations 3.16 and 3.18 to the data in Table B2 of the Appendix gives two average rate constants, 8.7±1.4 (9 measurements) and 2.4±0.3 (13 measurements). The former (larger) rate constant represents 5 measurements from the 0.05 and 0.1 M formate scouting experiments (runs in NMR tubes, Table B1) plus 6 repeat measurements obtained from deoxygenated solutions sealed in glass vials. The latter (smaller) rate constant represents 13 measurements for concentrations ranging from 0.35 to 1.1 M formate (see Table B2). The extent to which the results might be vessel-dependent and geometry-dependent is not known. However, the results clearly indicate that if NO₂ is the oxidizing specie, then the reaction rate constant with formate is on the order of 1 to 10 M⁻¹s⁻¹. By comparison, rate constants for HO, O⁻, H, (Buxton et al. 1988) and NO₃ (Neta and Huie 1986) reacting with formate are 1.4×10⁹, 4.3×10⁹, 1.2×10⁸, and <10⁵ M⁻¹s⁻¹, respectively.

3.3 Experimental Section

Organic Compounds were purchased from chemical suppliers with the exception of u-EDDA which was provided by J. Campbell (PNNL). Purity of all compounds established by ¹H NMR. The water used in these experiments was purified using a Millipore deionization system.

3.3.1 Sample Preparation

Samples for radiolytic experiments were prepared by adding aqueous stock solution to a weighed amount of solid substrate in a volumetric flask. The stock solution was made up to contain 3.75 M NaNO₃, 1.25 M NaNO₂, 2.0 M NaOH and either 0.1 M or 0.05 M ¹³C-labelled sodium formate. For all measurements in Table 3.1 except entries on lines 2, 4, and 8, the

prepared reaction solutions were purged with nitrogen and sealed in 2 ml glass vials fitted with a plastic lined screw cap. EDTA scoping experiments (Figure 3.3, Table 3.1 entry 2, and Appendix B, Table B1) were performed in 5 mm o.d. NMR tubes without N₂ purge. Scouting experiments for HEDTA and glycolate (Table 3.1 entries 4 and 8, respectively) were run in glass vials without N₂ purge, however, vials were filled to capacity. The vials or tubes were placed inside a reaction vessel at the PNNL γ Facility and irradiated for specified times. The samples were removed to the NMR facility for analysis. Selected samples were also analyzed by Ion-pair liquid chromatography (IPC) or ion chromatography (IC) to confirm the NMR results. The IC and HPLC methods are described in Section 2.3.2 (Camaioni et al. 1996, Campbell et al. 1996).

3.3.2 NMR Analysis

The relative rates of substrate molecules compared with formate were determined by ¹H and/or ¹³C NMR spectroscopies. A 0.50 ml aliquot of the homogeneous sample solution was transferred to a 5 mm o.d. NMR tube along with 0.10 ml of a caustic (2.0 M NaOH) deuterated water solution containing 0.667 M 2,2-dimethylmalonic acid (an internal chemical shift and integration standard).

¹H (300 MHz) and carbon (75 MHz) NMR spectra were recorded using a Varian VXR-300 NMR spectrometer. The following conditions for recording ¹H NMR spectra gave reproducible and quantitative results: 9° pulse, 5 second acquisition time, 2 second recycle time. The number of transients collected were dependent upon the concentrations of the species with the minimum number being 200. The spectra were carefully integrated to eliminate any contribution to the large ¹H signal between 5.5 and 4 ppm due to protonated water. The following conditions for recording ¹H decoupled ¹³C NMR spectra gave reproducible and quantitative results: 70° pulse, acquisition time of 1.8 s, and a recycle time of 60 s for a total of 360 transients. A line broadening of 1 Hz was used to process each spectrum. Increases in the recycle time to 90 s or 120 s did not change the ratios of carbonate to formate. The relative areas of the formate-¹³C and carbonate-¹³C peaks were used to calculate the conversion of formate-¹³C. The contribution to the NMR signal from natural abundance ¹³C from formate or carbonate produced by radiolysis of other organic species was negligible in all cases. The reproducibility between triplicate spectral collections of the same sample were $\pm 4\%$. Triplicate reintegration of the same spectrum routinely gave reproducibility of $\pm 1\%$. Product identification were made by comparing the ¹H NMR spectra of authentic samples of potential products collected in the same reaction medium as the radiolytic experiments.

3.3.3 Fricke Dosimetry

Dose rates were determined by Fricke dosimetry (Draganic and Draganic 1971; Spinks and Woods 1964) using the same reaction vials, inconel vessels, and irradiation methods used in aging experiments. The dosimetry solution contained 0.01 M Fe(NH₄)₂(SO₄)₂ and 0.001 M NaCl in 0.4 M H₂SO₄. The solution was purged with oxygen, sealed in glass vials, and the vials placed inside of inconel vessels. Vessels were placed in the gamma irradiation facility and removed after 15, 30, or 60 minutes. A control solution was handled identically, but was not irradiated. The concentration of Fe(III) formed was determined with use of a Cary 3E UV/Vis spectrophotometer. Doses absorbed by aging samples were calculated using appropriate corrections for solution density.

4.0 Conclusion

The Waste Aging studies task has shown that radiation promotes redox reactions between organic compounds (reducing agents) and nitrates/nitrites (precursors to oxidizing agents) in the wastes. We find that production of H_2 , N_2 , and N_2O by radiolysis is significant and occurs concurrent with the disappearance of organic species and appearance of highly oxidized fragments of the original species. The observations are consistent with progressive degradation to species with more C-O bonds and fewer C-H and C-C bonds, resulting in an overall lower energy content of the organic inventory.

4.1 Simulated Waste Aging Studies

The simulated waste aging studies using the PAS-95 simulants show quantitatively that energy content of the wastes should be expected to decrease due to aging (see Table 2.6). The theoretical energy content of the simulants declined steadily with increasing radiolytic dose, such that a radiation dose of 100 Mrad at 70 °C decreased the energy content of the waste simulant by ~25% from a starting value of ~1300 J/g dry simulant. Much of the remaining enthalpy is due to undegraded glycolate, citrate, and chelator fragments. We also established that the decline in energy content is temperature dependent, declining more rapidly at higher temperatures. Aging occurs at a much slower rate in the absence of radiation, but for long storage times at elevated temperatures, certain species, namely HEDTA, citrate, and glycolate, appear susceptible to thermal degradation (see also, Delagard 1987; Ashby et al. 1993; Barefield et al. 1995, 1996). Thus, it seems probable, that analogous actual wastes receiving similar doses may have even lower energy content due to contributions of both thermal and radiolytic aging. The results suggest that lifetimes and aging rates of organic complexants will be strongly dependent on radiolytic and thermal history of the wastes, and therefore, the degree of aging may vary from tank to tank.

TOC measurements have been obtained from a significant number of tank wastes. This database is used to screen for tanks that might be at risk to undergo propagating reactions (Webb et al. 1995). The assessment essentially converts TOC to enthalpy by assuming a proportionality factor, i.e.

$$\Delta H_{rxn} \text{ (kJ/g waste)} = \text{TOC (mg/g waste)} \times \Delta H \text{ (kJ/g C)} \quad (4.1)$$

Presently, the conversion factor is taken to be the reaction enthalpy of sodium acetate. Our PAS-95 simulants aging tests suggest that the actual conversion factor decreases with aging. Thus, as currently used, TOC is a conservative, and therefore a useful initial screen for problem tanks.

4.2 Relative Reactivities of Organic Complexants and Related Species

The organic species span a range of less than two orders of magnitude. Furthermore, the reactivities of citrate, glycolate, EDTA, and HEDTA are comparable to those observed in the more complex heterogeneous simulants studied in Section 2.0. This suggests that the same oxidant, or oxidants, are responsible for degrading the organic species. If NO_2 is the dominant oxidizing species, then we have made the first measurements of NO_2 reacting with these compounds. The absolute rate constant for formate is $\sim 10 \text{ M}^{-1}\text{s}^{-1}$. Using this value the absolute rates for attack on

organic species range from 1-200 M⁻¹s⁻¹. The distinguishing feature that seems to correlate with the reactivity of the compounds is the presence of hydroxyl or amino groups on carbons next to carboxylate groups.

Relative rate constants in Table 3.1 are very sensitive to the accuracy and precision of carbonate conversion measurements. Formate is an appropriate rate standard for competition reactions with the less reactive class of species. However, a faster reacting species is preferable for the more reactive class of species. For example, glycolate-¹³C may be better suited. In competitions with the nitrogen-containing species, relatively more of it will convert compared to formate, so experimental errors should be lower. The fraction reacted could be measured by either ¹H or carbon NMR as in the formate studies.

The nitrogen-containing complexants react by cleaving the N-CH₂CO₂⁻ bond. For example, the data shows that both NTA and IDA cleaved this bond. How this happens is not clear. Glycolate, formate, oxalate, and carbonate are all found. However, since these products are produced even when conversions are relatively low, at least two pathways may be operating: one that produces carbonate and formate and another that produces glycolate and oxalate. Glycolate which is less than or equal in reactivity to nitrogen containing species, yields mixtures of oxalate, formate, and carbonate which suggests parallel pathways for its degradation.

4.3 Future Plans and Recommendations

Future work is planned to support our objective to develop an aging kinetic model. Relative rate measurement made this year will be validated and measurements will be extended to other species needed to model aging reactions. These include ED3A, EDMA, oxalate, DBP, butyrate, butanol, succinate, and possibly others. Since rate measurements for the reactive organic species are very sensitive to measurements of formate conversion in the current methodology, other rate standards will also be used. For example, glycolate-¹³C seems well suited for the faster reacting species. Formate is appropriate for competition reactions with the less reactive class of species. Emphasis will be placed on determining initial products from each of the species for which we have rate constant data. Model development will ensue using available computer software for numerical simulation of chemical kinetics. The model will be tested against simulant aging data (Section 2.0). If satisfactory results are obtained, it will be used to interpret tank waste speciation data and make predictions about how distributions of species in tanks may change in the future.

Scheme 3.1 predicts an square-root dependence of organic degradation on dose rate. We think this relationship should be verified to lend credence to the model. Experiments that measure radiolytic yield of carbonate from formate (Figure 3.5) at higher and lower dose rates than we have run so far should suffice, since the model predicts the yield will be inversely dependent on dose-rate.

The effects of temperature on rate constants need to be investigated. Current rate data for radiolytically-induced degradation were measured at ~20 °C. Some experiments at elevated temperatures (40°-90°) should be run to learn just how dependent absolute rates and selectivities are on temperature. The effect on absolute rate constants may be obtained from measurements of radiolytic yields of carbonate from formate. Effects of temperature on selectivities may be surveyed by running competitive experiments with the slowest and fastest reacting compounds, e.g., citrate and EDDA. Also, some scoping of the effects of temperature and HO⁻ on rates of thermal degradation are warranted. For example, our simulant aging studies show that citrate is one of the more thermally reactive complexants. Ashby and coworkers (Ashby et al. 1994;

Barefield et al. 1995,1996) did not study citrate degradation in detail because citrate did not produce H_2 gas.

4.4 Acknowledgements

This work progresses in collaboration with projects on "The NO_x System in Nuclear Waste," at Argonne National Laboratory (ANL) and "Interfacial Radiolysis Effects in Tank Waste Speciation" at Pacific Northwest National Laboratory. These projects are funded by the DOE Environmental Management Science Program (EMSP). The EMSP work in progress on the kinetics and mechanisms of NO_x reactions complements and strengthens the work performed here. For example at PNNL, they examine reactions of NO_2 by contacting NO_2 gas with solutions of organic species to learn reaction products, gain mechanistic insights, and measure relative rate constants. At ANL, they use their pulse radiolysis capabilities to measure absolute rate constants which we cannot do in our γ Irradiation Facility. Since there is no ambiguity about the intermediacy of NO_2 in these experiments, finding products and rate constants similar to ours measured under radiolytic conditions will strengthen the hypothesis that NO_2 is the dominant oxidant of organic species in the tank wastes. The EMSP work on interfacial radiolysis provides us with insight to the role that solid surfaces and colloidal particles play in the generation of oxidizing intermediates.

We thank Phil Cappe, Associated Western Universities Summer Undergraduate Research Participant, for making NMR measurements of organic species conversions. We thank Dr. Leon Stock, consultant to Organic Tanks Safety Program, for helpful conversations and suggestions. And, we thank Dr. Harry Babad, formerly of Westinghouse Hanford Co., for guidance and unwavering support of these studies.

Dr. William D. Samuels led the simulant aging studies Task (Section 2). Amit Sharma, Scott Clauss, Dr. Karen Wahl and Dr. James A. Campbell provided analytical support for this task. Dr. John Linehan led the task to measure relative reactivities of organic species (Section 3). He developed the NMR analytical methods and collected and reduced much of the data. Michael O. Hogan and Dr. Michael A. Lilga provided technical support for this task by handling the preparation of samples and scheduling them in and out of the γ Facility. Dr. Donald M. Camaioni leads the Waste Aging Studies project. Inquiries and comments regarding this report or the Waste Aging Studies Task should be directed to him at 509-375-2739.

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APPENDIX A

Table A1. Analytical Results for Radiolytic Aging of PAS-95-1d Simulant at 90 °C Starting with 20/80 O₂/Ar Cover Gas

Dose		Reactants/Products, mg/mL									
MRad	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃	
0			14.8 ± 1.7	18.9 ± 1.7	16.0 ± 0.8	1.98 ± 0.15	0.8	56.2	154		
21.6	0.06 ± 0.1	0.49 ± 0.1	14.1 ± 1.6	19.6 ± 0.9	11.5 ± 1.8	1.69 ± 0.2	5.4	58.7	144		
50.2	2.54 ± 0.1	4.97 ± 0.4	10.9 ± 2.2	19.2 ± 1.1	7.7 ± 0.8	1.16 ± 0.8	11	53.8	121		
113.7	3.02 ± 0.7	6.17 ± 0.8	9.08 ± 1.0	13.4 ± 0.6	3.2 ± 2.7	0.54 ± 0.01	26.2	69.9	125	1.21	
146	5.09 ± 0	6.72 ± 0.2	9.25 ± 1.2	13.5 ± 0.6	0.7 ± 0.0	0.40 ± 0.01	36.7	73.7	113	1.39	

Dose		Reactants/Products, mg/g									
MRad	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃	
0	0.00 ±	0.00 ±	11.7 ± 1.3	14.9 ± 1.3	12.6 ± 0.6	1.6 ± 0.1	0.63	44.3	121		
21.6	0.04 ± 0.1	0.39 ± 0.1	11.1 ± 1.3	15.4 ± 0.7	9.0 ± 1.4	1.3 ± 0.1	4.25	46.2	113		
50.2	2.00 ± 0.1	3.91 ± 0.3	8.59 ± 1.7	15.1 ± 0.9	6.0 ± 0.6	0.9 ± 0.6	8.66	42.3	95.5		
113.7	2.38 ± 0.5	4.86 ± 0.6	7.15 ± 0.7	10.6 ± 0.4	2.5 ± 2.1	0.4 ± 0.0	20.6	55.1	98.6	0.95	
146	4.01 ± 0.0	5.29 ± 0.1	7.28 ± 1.0	10.7 ± 0.5	0.6 ± 0.0	0.3 ± 0.0	28.9	58.0	89.0	1.09	

Dose		Reactants/Products, M									
MRad	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃	
0	0	0.000	0.195	0.098	0.0575	0.0068	0.013	1.222	2.48		
21.6	0.001	0.005	0.186	0.102	0.0411	0.0058	0.090	1.275	2.32		
50.2	0.055	0.055	0.143	0.100	0.0276	0.0040	0.183	1.169	1.96		
113.7	0.066	0.068	0.119	0.070	0.0116	0.0018	0.436	1.520	2.02	0.071	
146	0.111	0.075	0.122	0.071	0.0026	0.0014	0.612	1.601	1.82	0.082	

Dose		Reactants/Products, mg C/g									
MRad	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	Org. C	Tot C		
0	± 0.00	0.00 ± 0.00	3.68 ± 0.42	5.58 ± 0.50	5.43 ± 0.27	0.64 ± 0.05	0.13	15.3	15.5		
21.6	0.01 ± 0.02	0.10 ± 0.03	3.51 ± 0.40	5.79 ±	3.89 ± 0.59	0.55 ± 0.06	0.85	13.8	14.7		
50.2	0.52 ± 0.03	1.04 ± 0.09	2.71 ± 0.55	5.67 ± 0.32	2.61 ± 0.28	0.37 ± 0.26	1.73	12.9	14.7		
113.7	0.62 ± 0.14	1.29 ± 0.17	2.25 ± 0.24	3.97 ±	1.09 ± 0.92	0.17 ± 0.00	4.12	9.4	13.5		
146	1.04 ± 0.00	1.41 ± 0.03	2.30 ± 0.30	4.00 ±	0.24 ± 0.01	0.13 ± 0.00	5.78	9.1	14.9		

Table A2. Analytical Results for Radiolytic Aging of PAS-95-1c Simulant at 70 °C Starting with 20/80 O₂/Ar Cover Gas

Dose	Reactants/Products, mg/mL									
Mrad	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	
0			10.6 ± 0.04	19.5 ± 0.1	19.2 ± 0.1	3.96 ± 0.1	1.81	49.8	137.5	
30	0.99 ± 0.1	2.2 ± 0	9.57 ± 0.14	18.9 ± 0.1	11.1 ± 0.2	2.64 ± 0.1	5.73	53.8	130.5	
50	2.2 ± 0.2	3.6 ± 0.3	8.60 ± 0.02	17.5 ± 0.1	6.4 ± 0.1	1.61 ± 0.1	8.33	56.4	125.6	
100	3.2 ± 0.1	4.5 ± 0.3	7.51 ± 0.01	15.9 ± 0.1	2.7 ± 0.1	1.10 ± 0.1	17.0	62.6	112.0	
150	5.7 ± 0.2	10.8 ± 0.2	6.73 ± 0.02	14.4 ± 0.1	1.2 ± 0.1	0.29 ± 0.1	22.0	28.2	110.6	
Dose	Reactants/Products, mg/g									
Mrad	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	
0	0 ±	0 ±	8.34 ± 0.03	15.4 ± 0.1	15.1 ± 0.1	3.1 ± 0.1	1.42	39.2	108.3	
30	0.8 ± 0.1	1.7 ± 0.0	7.54 ± 0.11	14.9 ± 0.1	8.7 ± 0.2	2.1 ± 0.1	4.51	42.3	102.7	
50	1.7 ± 0.2	2.8 ± 0.2	6.77 ± 0.02	13.8 ± 0.1	5.1 ± 0.1	1.3 ± 0.1	6.56	44.4	98.9	
100	2.5 ± 0.1	3.5 ± 0.2	5.91 ± 0.01	12.5 ± 0.1	2.1 ± 0.1	0.87 ± 0.1	13.36	49.3	88.2	
150	4.5 ± 0.2	8.5 ± 0.2	5.30 ± 0.02	11.3 ± 0.1	0.98 ± 0.1	0.23 ± 0.1	17.35	22.2	87.1	
Dose	Reactants/Products, M									
Mrad	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	
0	0.000	0.000	0.139	0.102	0.069	0.014	0.030	1.08	2.22	
30	0.022	0.024	0.126	0.098	0.040	0.009	0.096	1.17	2.10	
50	0.048	0.040	0.113	0.091	0.023	0.006	0.139	1.23	2.03	
100	0.070	0.050	0.099	0.083	0.010	0.004	0.283	1.36	1.81	
150	0.124	0.120	0.088	0.075	0.004	0.001	0.367	0.61	1.78	
Dose	Reactants/Products, mg C/g									
Mrad	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	Org. C	Tot C	
0	0.00 ± 0.00	0.00 ±	2.63 ± 0.01	5.76 ± 0.03	6.51 ± 0.05	1.28 ± 0.02	0.28	16.2	16.5	
30	0.20 ± 0.02	0.46 ±	2.38 ± 0.03	5.58 ± 0.03	3.75 ± 0.07	0.85 ± 0.02	0.90	13.2	14.1	
50	0.45 ± 0.04	0.76 ± 0.06	2.14 ±	5.17 ± 0.03	2.19 ± 0.02	0.52 ± 0.05	1.31	11.2	12.5	
100	0.66 ± 0.02	0.94 ± 0.06	1.87 ±	4.70 ± 0.03	0.92 ± 0.05	0.36 ± 0.02	2.67	9.4	12.1	
150	1.17 ± 0.04	2.27 ± 0.04	1.67 ±	4.25 ± 0.03	0.42 ± 0.02	0.09 ± 0.02	3.47	9.9	13.4	

Table A3. Analytical Results for Radiolytic Aging of PAS-95-1d Simulant at 40 °C Starting with 20/80 O₂/Ar Cover Gas

Dose		Reactants/Products, mg/mL									
MRad	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃	
0	0 ± 0	0 ± 0	14.8 ± 1.7	18.9 ± 1.70	16.0 ± 0.6	1.98 ± 0.15	0.99	55.9	155	0.054	
27.8	0.36 ± 0.25	0.07 ± 0.02	13.9 ± 0.1	18.2 ± 0.35	10.3 ± 0.2	1.70 ± 0.06	4.62	24.0	161	0.071	
42.7	0.67 ± 0.01	1.6 ± 0.3	13.4 ± 0.1	16.1 ± 0.20	5.6 ± 0.1	1.10 ± 0.10	7.10	54.3	171	0.141	
Dose		Reactants/Products, mg/g									
MRad	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃	
0	0 ± 0	0 ± 0	11.7 ± 0.3	14.9 ± 1.2	12.6 ± 0.5	1.56 ± 0.12	0.12	44.0	122	0.0008	
27.8	0.283 ± 0.2	0.06 ± 0.0	11.0 ± 0.1	14.3 ± 0.44	8.1 ± 0.2	1.33 ± 0.05	3.64	18.9	127	0.056	
42.7	0.528 ± 0.0	1.26 ± 0.2	10.6 ± 0.1	12.6 ± 0.20	4.4 ± 0.1	0.87 ± 0.08	5.59	42.8	135	0.111	
Dose		Reactants/Products, M									
MRad	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃	
0	0 ± 0.00	0.0 ± 0.0	0.195 ± 0.022	0.098 ± 0.009	0.0573 ± 0.002	0.0068 ± 5E-4	0.017	1.30	2.50	0.003	
27.8	0.008 ± 0.005	0.0008 ± 2E-4	0.183 ± 0.001	0.095 ± 0.002	0.0370 ± 0.001	0.0061 ± 0.006	0.077	0.52	2.60	0.0042	
42.7	0.015 ± 0.000	0.0178 ± 0.003	0.177 ± 0.001	0.084 ± 0.001	0.0199 ± 0.001	0.0039 ± 0.004	0.118	1.18	2.76	0.0083	
Dose		Reactants/Products, mg C/g									
MRad	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	Org. C	Tot C		
0	0.00 ± 0.00	0.00 ± 0.00	3.68 ± 0.09	5.58 ± 0.43	5.42 ± 0.19	0.64 ± 0.05	0.02	15.3	15.3		
27.8	0.07 ± 0.05	2E-2 ± 0.00	3.46 ± 0.02	5.37 ± 0.17	3.50 ± 0.07	0.55 ± 0.02	0.73	13.0	13.7		
42.7	0.14 ± 0.002	0.34 ± 0.06	3.34 ± 0.02	4.74 ± 0.08	1.88 ± 0.05	0.36 ± 0.03	1.12	10.8	11.9		

Table A4. Analytical Results for Radiolytic Aging of PAS-95-1d Simulant at 70 °C: Effects of O₂ Cover Gas and Fe in the Simulant

Dose		Reactants/Products, mg/mL													
MRad	Formic Acid	Oxalic Acid		Glycolic Acid		Citric Acid		HEDTA		EDTA		CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃
0					14.8 ± 1.7		18.9 ± 1.7		16.0 ± 0.6		1.98 ± 0.15	0.99	61.1	155	6E-05
47 ^(a)	1.26 ± 0.42		2.72 ± 0.68		13.2 ± 0.1		19.2 ± 2.83		5.0 ± 0.3		1.30 ± 0.10	9.80	57.0	149	0.338
48 ^(a)	0.74 ± 0.24		1.15 ± 0.15		13.4 ± 0.06		14.8 ± 2.21		5.2 ± 0.0		1.06 ± 0.17	8.30	25.9	120	0.126
47.6 ^(b)	0.73 ± 0.06		2.04 ± 0.16		13.6 ± 0.01		17.3 ± 0.49		5.6 ± 0.2		1.10 ± 0.10	7.90	52.7	138	0.083
45.6 ^(b)	1.58 ± 0.57		1.89 ± 0.45		14.0 ± 0.47		17.3 ± 1.62		6.5 ± 0.4		1.22 ± 0.28	6.70	49.4	120	0.262
46.2 ^(a,c)	1.94 ±		1.83 ±		13.9 ±		17.0 ±		6.9 ± 0.1		0.99 ± 0.03	9.05	45.1	155	0.046

Dose		Reactants/Products, mg/g													
MRad	Formic Acid	Oxalic Acid		Glycolic Acid		Citric Acid		HEDTA		EDTA		CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃
0					11.7 ± 1.34		14.9 ± 1.3		12.6 ± 0.45		1.56 ± 0.02	0.78	44.0	122	7.9E-4
47 ^(a)	0.99 ± 0.3		2.14 ± 0.5		10.4 ± 0.08		15.1 ± 2.2		3.93 ± 0.22		1.02 ± 0.10	7.72	44.9	117	0.266
48 ^(a)	0.58 ± 0.2		0.90 ± 0.1		10.6 ± 0.05		11.6 ± 1.7		4.07 ± 0.01		0.84 ± 0.15	6.54	20.4	94.3	0.099
47.6 ^(b)	0.57 ± 0.05		1.60 ± 0.13		10.7 ± 0.01		13.6 ± 0.4		4.38 ± 0.12		0.87 ± 0.10	6.22	41.5	109	0.066
45.6 ^(b)	1.24 ± 0.5		1.48 ± 0.4		11.1 ± 0.37		13.7 ± 1.3		5.09 ± 0.30		0.96 ± 0.30	5.28	38.9	94.2	0.206
46.2 ^(a,c)	1.53 ±		1.44 ±		11.0 ±		13.4 ±		5.40 ± 0.09		0.78 ± 0.03	7.13	35.5	122	0.036

Dose		Reactants/Products, M													
MRad	Formic Acid	Oxalic Acid		Glycolic Acid		Citric Acid		HEDTA		EDTA		CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃
0					0.195 ± 0.022		0.098 ± 0.009		0.0573 ± 2E-3		6.8E-3 ± 5E-4	0.017	1.22	2.50	5E-05
47 ^(a)	0.027 ± 0.009		0.030 ± 0.008		0.174 ± 0.001		0.100 ± 0.015		0.0179 ± 1E-3		4.4E-3 ± 3E-4	0.163	1.24	2.40	0.0199
48 ^(a)	0.016 ± 0.005		0.013 ± 0.002		0.176 ± 0.001		0.077 ± 0.012		0.0186 ± 7E-5		3.6E-3 ± 6E-4	0.138	0.56	1.93	0.0074
47.6 ^(b)	0.016 ± 0.001		0.023 ± 0.002		0.179 ± 0.000		0.090 ± 0.003		0.0200 ± 6E-4		3.8E-3 ± 3E-4	0.132	1.15	2.23	0.0049
45.6 ^(b)	0.034 ± 0.012		0.021 ± 0.005		0.185 ± 0.006		0.090 ± 0.008		0.0232 ± 1E-3		4.2E-3 ± 1E-3	0.112	1.07	1.93	0.0012
46.2 ^(a,c)	0.042 ±		0.020 ±		0.183 ±		0.089 ±		0.0246 ± 4E-4		3.4E-3 ± 1E-4	0.151	0.98	2.50	0.0027

Dose		Reactants/Products, mg C/g												
MRad	Formate	Oxalate		Glycolate		Citrate		HEDTA		EDTA		CO ₃ ²⁻	Org C	Tot C
0					3.68 ± 0.42		5.58 ± 0.50		5.42 ± 0.19		0.64 ± 0.01	0.16	15.3	15.5
47 ^(a)	0.26 ± 0.09		0.57 ± 0.14		3.29 ± 0.02		5.66 ± 0.84		1.69 ± 0.09		0.42 ± 0.04	1.54	11.9	13.4
48 ^(a)	0.15 ± 0.05		0.24 ± 0.03		3.33 ± 0.01		4.36 ± 0.65		1.76 ± 0.01		0.34 ± 0.06	1.31	10.2	11.5
47.6 ^(b)	0.15 ± 0.01		0.43 ± 0.03		3.38 ± 0.00		5.12 ± 0.14		1.89 ± 0.05		0.36 ± 0.04	1.24	11.3	12.6
45.6 ^(b)	0.32 ± 0.12		0.40 ± 0.09		3.49 ± 0.12		5.12 ± 0.48		2.20 ± 0.13		0.39 ± 0.12	1.06	11.9	13.0
46.2 ^(a,c)	0.40 ± 0.00		0.38 ± 0.00		3.47 ± 0.00		5.03 ± 0.00		2.33 ± 0.04		0.32 ± 0.01	1.43	11.9	13.4

(a)Started with 80/20 O₂/Ar in Headspace. (b)Started with 100% Ar in headspace. (c)No Iron in simulant.

Table A5. Analytical Results for Thermal Aging of PAS-95-1d Simulant at 90 °C Starting with Ar Cover Gas

Time	Reactants/Products, mg/mL										
Hr.	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃	
0	±	±	14.8 ± 1.7	18.9 ± 1.7	16.0 ± 0.6	1.98 ± 0.15	0.80	55.9	155	0.00	
336	0.0 ±	0.00 ± 1.6	12.2 ± 0.01	19.0 ± 1.72	16.9 ± 0.9	2.64 ± 0.15	2.88	21.5	125	0.10	
666	0.0 ±	0.55 ± 2.7	12.1 ± 0.02	17.6 ± 0.14	15.8 ± 0.6	2.58 ± 0.15	5.40	12.2	121	0.16	
1338	0.0 ±	1.67 ± 0.1	11.7 ± 0.19	14.8 ± 0.19	14.6 ± 0.4	2.69 ± 0.19	8.32	20.1	144	0.43	

Time	Reactants/Products, mg/g										
Hr.	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃	
0	0.00 ± 0	0.00 ± 0	11.7 ± 1.34	14.9 ± 1.34	12.6 ± 0.63	1.6 ± 0.16	0.78	44.0	122	0.000	
336	0.00 ± 0.0	0.00 ± 0.0	12.0 ± 0.09	14.7 ± 0.09	13.3 ± 0.94	2.1 ± 0.16	1.31	16.9	123	0.082	
666	0.00 ± 0.0	0.43 ± 0.0	12.1 ± 0.35	13.5 ± 0.12	12.4 ± 0.63	2.0 ± 0.16	1.80	9.6	135	0.126	
1338	0.00 ± 0.0	1.32 ± 0.3	10.2 ± 0.02	12.9 ± 0.27	11.5 ± 0.39	2.1 ± 0.20	3.08	15.8	129	0.339	

Time	Reactants/Products, M										
Hr.	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃	
0	0.00 ± 0.0	0.000 ± 0.00	0.195 ± 0.022	0.098 ± 0.022	0.057 ± 0.011	0.007 ± 0.003	0.017	1.21	2.50	3.2E-5	
336	0.00 ± 0.0	0.000 ± 0.00	0.201 ± 0.001	0.097 ± 0.002	0.061 ± 0.016	0.009 ± 0.003	0.028	0.47	2.52	6.2E-3	
666	0.00 ± 0.0	0.006 ± 0.09	0.201 ± 0.006	0.089 ± 0.002	0.057 ± 0.011	0.009 ± 0.003	0.038	0.27	2.76	9.4E-3	
1338	0.00 ± 0.0	0.019 ± 0.14	0.170 ± 0.000	0.086 ± 0.005	0.052 ± 0.007	0.009 ± 0.003	0.065	0.44	2.64	0.025	

Time	Reactants/Products, mg C/g										
Hr.	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	HEDTA	EDTA	CO ₃ ²⁻	Org C	Tot C		
0	0.00 ± 0.0	0.00 ± 0.0	3.68 ± 0.4	5.58 ± 0.5	5.42 ± 0.3	0.64 ± 0.06	0.16	15.3	15.5		
336	0.00 ± 0.0	0.00 ± 0.0	3.79 ± 0.0	5.50 ± 0.0	5.73 ± 0.4	0.85 ± 0.06	0.26	15.9	16.1		
666	0.00 ± 0.0	0.12 ± 0.0	3.81 ± 0.11	5.06 ± 0.04	5.37 ± 0.27	0.84 ± 0.06	0.36	15.2	15.5		
1338	0.00 ±	0.35 ± 0.07	3.22 ± 0.01	4.85 ± 0.10	4.96 ± 0.17	0.87 ± 0.08	0.62	14.2	14.9		

Table A6. Analytical Results for Thermal Aging of PAS95-1d Simulant at 90 °C Starting with 20/80 O₂/Ar Cover Gas

Time	Reactants/Products, mg/mL															
Hr.	Formic Acid		Oxalic Acid		Glycolic Acid		Citric Acid		HEDTA		EDTA		CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃
0	±		±		14.8 ± 1.7		18.9 ± 1.7		16.0 ± 0.6		1.98 ± 0.15		0.80	55.9	155	0.001
335	0 ± 0		2.34 ± 1.64		12.2 ± 0.01		19.0 ± 1.72		16.7 ± 0.07		2.36 ± 0.03		2.88	49.5	125	0.074
675	0 ± 0.1		0.90 ± 2.7		12.1 ± 0.02		17.6 ± 0.14		14.9 ± 0.11		2.49 ± 0.01		5.40	47.0	121	0.169
1329	0.69 ± 0.02		2.42 ± 0.09		11.7 ± 0.19		14.8 ± 0.19		13.2 ± 0.06		2.60 ± 0.11		8.32	57.7	144	0.508
Time	Reactants/Products, mg/g															
Hr.	Formic Acid		Oxalic Acid		Glycolic Acid		Citric Acid		HEDTA		EDTA		CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃
0	±		±		11.7 ± 1.34		14.9 ± 1.34		12.6 ± 0.4		1.6 ± 0.12		0.63	44.0	122	0
335	0.00 ± 0.0		1.84 ± 1.3		9.6 ± 0.01		15.0 ± 1.35		13.1 ± 0.1		1.9 ± 0.02		2.27	39.0	123	0.058
675	0.00 ± 0.1		0.71 ± 0.3		9.5 ± 0.02		13.9 ± 0.11		11.7 ± 0.1		2.0 ± 0.01		4.25	37.0	127	0.133
1329	0.54 ± 0.0		1.90 ± 0.1		9.2 ± 0.15		11.7 ± 0.15		10.4 ± 0.04		2.0 ± 0.09		6.55	45.4	127	0.400
Time	Reactants/Products, M															
Hr.	Formic Acid		Oxalic Acid		Glycolic Acid		Citric Acid		HEDTA		EDTA		CO ₃ ²⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₃
0					0.195		0.098		0.0575		6.8E-3		0.013	1.21	2.50	0.000
335	0.000		0.026		0.160		0.099		0.0599		8.1E-3		0.048	1.08	2.02	0.004
675	0.000		0.010		0.159		0.092		0.0534		8.5E-3		0.090	1.02	1.96	0.010
1329	0.015		0.027		0.154		0.077		0.0474		8.9E-3		0.139	1.25	2.32	0.030
Time	Reactants/Products, mg C/g															
Hr.	Formic Acid		Oxalic Acid		Glycolic Acid		Citric Acid		HEDTA		EDTA		CO ₃ ²⁻	Org. C	Tot C	
0	0.00		0.00		3.68		5.58		5.43		0.64		0.13	15.3	15.5	
335	0.00		0.49		3.03		5.62		5.66		0.76		0.45	15.6	16.0	
675	0.00		0.19		3.01		5.20		5.05		0.80		0.85	14.2	15.1	
1329	0.14		0.51		2.90		4.37		4.48		0.84		1.31	13.2	14.6	

Table A7 Headspace Gas Composition (mol%) vs. Radiolytic Dose, Temperature, and O₂ in Cover Gas (PAS-95-1d Simulant)

Starting Headspace Gas	20/80 O ₂ /Ar				Ar		20/80 O ₂ /Ar
Temperature, °C	40°		70°	90°	70°		70°
Dose/Time, Mrad (h)	47.2 (143)	64.9 (251)	47 (167)	146 (428)	47.6 (169)	45.6 (170)	46.2 (175.5)
Ar	74.8	75.3	73.5	65.4	90.40	90.55	77.2
O ₂	15.6	13.1	13.6	2.17	0.07	0.078	11.9
H ₂	1.48	2.38	2.74	12.6	3.14	2.9	4.6
N ₂ O	6.9	8.2	8.6	16.5	4.33	4.8	5.2
N ₂	1.13	1.08	1.57	3.29	2.01	1.66	1.04
CH ₄	0.004	0.003	0.009	0.035	0.06	0.047	0.005
NO _x	0.005	0.05	0.005	0.019	0.01	0.005	0.05

Table A8. Radiolytic Yield (G) of Gas from Simulant PAS-95-1d at 90 °C in a 10⁵ rad/h γ Field

Gas	Radiolytic Yield (G) vs. Temp and Starting Headspace Composition				
	40 °C, O ₂ /Ar ^a	70 °C, O ₂ /Ar ^b	70 °C, Ar ^c	90 °C, O ₂ /Ar ^d	70 °C, O ₂ /Ar ^e
O ₂	-0.086	-0.11	0.001	-0.11	-0.17
H ₂	0.033	0.058	0.058	0.097	0.095
N ₂ O	0.13	0.18	0.088	0.13	0.11
N ₂	0.020	0.033	0.036	0.025	0.021

^aAverage of 47 Mrad and 65 Mrad doses (Table A14). ^b46 Mrad dose. ^cAverage of 46 Mrad and 48 Mrad doses (Table A14). ^d146 Mrad dose (Table A14). ^eSimulant without Fe; 46 Mrad dose (Table A14).

Table A9. Rates of Production of Gas from Simulant PAS-95-1d at 90 °C in Absence of Radiolysis^a

Gas	Rate of Disappearance/Production		
	Starting with 20/80 O ₂ /Ar	Starting with Ar	
	mmol/1000 h	mmol/1000 h	mmol/2000 h
O ₂	-0.14	0.0036	0.049
H ₂	0.22	0.21	0.71
N ₂ O	0.22	0.30	0.88
N ₂	0.022	0.019	0.050
Total Products	0.46	0.52	1.69

^aDerived from Table A13

Table A10. Headspace Gas Composition vs Heating Time at 90° C: Effect of O₂

Rxn time, h	Headspace Gas Composition mole %				
	0	1338	2184	0	1239
Ar	100	62.90	44.5	80	59.80
Oxygen	0	0.26	0.127	20	4.44
Hydrogen	0	14.50	23.8	0	17.00
N ₂ O	0	21.00	28.5	0	17.10
Nitrogen	0	1.31	3	0	1.69
Methane	00	0.004	0.001	0	0.008

Table A11. Carbon Content and Heat Content of PAS95-1d Simulant vs. Radiolytic Dose at 90 °C Starting with 20/80 O₂/Ar Cover Gas

Dose Mrad	Formate	Oxalate	Glycolate	Citrate	HEDTA	EDTA	Chelator Fragments	Total
<u>dry wt% organic C</u>								
0	0.00	0.00	1.02	1.55	1.51	0.18	0.00	4.3
21.6	0.00	0.03	0.98	1.61	1.08	0.15	0.21	4.1
50.2	0.14	0.29	0.75	1.57	0.72	0.10	0.22	3.8
113.7	0.17	0.36	0.63	1.10	0.30	0.05	0.54	3.1
146	0.29	0.39	0.64	1.11	0.07	0.04	0.15	2.7
<u>-ΔHrxn. J/g mix</u>								
0	0	0	260	389	531	57	0	1238
21.6	1	3	249	404	380	49	68	1153
50.2	26	32	192	395	255	34	71	1005
113.7	31	40	160	277	107	16	172	802
146	52	44	163	279	24	11	50	622

Table A12. Carbon Content and Heat Content of PAS-95-1d Simulant vs. Time at 90 °C (No Radiation) Starting with 20/80 O₂/Ar Cover Gas

Time (h)	Formate	Oxalate	Glycolate	Citrate	HEDTA	EDTA	Chelator Fragments	Total
<u>wt% C</u>								
0	0.00	0.00	1.02	1.55	1.51	0.18	0.00	4.3
335	0.00	0.14	0.84	1.56	1.57	0.21	0.00	4.3
675	0.00	0.05	0.84	1.44	1.40	0.22	0.10	4.1
1329	0.04	0.14	0.81	1.21	1.25	0.23	0.25	3.9
<u>-ΔHrxn. J/g</u>								
0	0	0	260	389	531	57	0	1238
335	0	15	215	392	553	69	0	1243
675	0	6	213	362	493	72	32	1179
1329	7	16	206	305	438	75	80	1127

Table A13. Carbon Content and Heat Content of PAS95-1d Simulant vs. time at (No Radiation) 90 °C Starting with Ar Cover Gas

Time	Chelator							Total
Hrs	Formate	Oxalate	Glycolate	Citrate	HEDTA	EDTA	Fragments	
<u>wt% C</u>								
0	0.00	0.00	1.02	1.55	1.50	0.18	0.00	4.3
336	0.00	0.00	1.05	1.53	1.59	0.24	-0.18	4.2
666	0.00	0.03	1.06	1.40	1.49	0.23	-0.02	4.2
1338	0.00	0.10	0.89	1.35	1.38	0.24	0.17	4.1
<u>-ΔHrxn. J/g</u>								
0	0	0	260	389	530	57	0	1237
336	0	0	268	383	561	77	-59	1230
666	0	4	270	353	525	75	-6	1219
1338	0	11	228	338	485	78	55	1194

Table A14. Carbon Content and Heat Content of PAS-95-1c Simulant vs. Radiolytic Dose at 70 °C Starting with 20/80 O₂/Ar Cover Gas

Dose	Chelator							Total
Mrad	Formate	Oxalate	Glycolate	Citrate	HEDTA	EDTA	Fragments	
<u>dry wt% organic C</u>								
0	0.00	0.00	0.73	1.60	1.81	0.36	0.00	4.5
30	0.06	0.13	0.66	1.55	1.04	0.24	0.65	4.3
50	0.13	0.21	0.59	1.44	0.61	0.15	1.09	4.2
100	0.18	0.26	0.52	1.30	0.26	0.10	1.21	3.8
150	0.33	0.63	0.46	1.18	0.12	0.03	0.87	3.6
<u>-ΔHrxn. J/g mix</u>								
0	0	0	186	402	637	115	0	1340
30	10	14	168	389	367	77	208	1234
50	22	24	151	360	214	47	351	1169
100	33	29	132	328	90	32	388	1032
150	58	71	118	297	41	9	278	871

Table A15. Carbon Content and Heat Content of PAS-95-1d Simulant vs. Radiolytic Dose at 40 °C Starting with 20/80 O₂/Ar Cover Gas

Dose Mrad	Formate	Oxalate	Glycolate	Citrate	HEDTA	EDTA	Chelator Fragments	Total
<u>wt% C</u>								
0	0.00	0.00	1.02	1.55	1.50	0.18	0.00	4.3
27.8	0.02	0.00	0.96	1.49	0.97	0.15	0.46	4.1
42.7	0.04	0.09	0.93	1.32	0.52	0.10	0.95	4.0
<u>-ΔHrxn. J/g mix</u>								
0	0	0	260	389	530	57	0	1237
27.8	4	0	245	375	342	49	146	1161
42.7	7	10	237	330	184	32	305	1106

Table A16. Carbon Content and Heat Content of PAS-95-1d Simulant vs. Radiolytic Dose at 70 °C: Effect of O₂ in Cover Gas and the Presence of Iron in the Simulant

Dose Mrad	Formate	Oxalate	Glycolate	Citrate	HEDTA	EDTA	Chelator Fragments	Total
<u>dry wt% C</u>								
0	0.00	0.00	1.02	1.55	1.50	0.18	0.00	4.3
47 ^a	0.07	0.16	0.91	1.57	0.47	0.12	0.57	3.9
48 ^a	0.04	0.07	0.92	1.21	0.49	0.10	1.11	3.9
47.6 ^b	0.04	0.12	0.94	1.42	0.52	0.10	0.81	4.0
45.6 ^b	0.09	0.11	0.97	1.42	0.61	0.11	0.69	4.0
46.2 ^{a,c}	0.11	0.11	0.96	1.40	0.65	0.09	0.59	3.9
<u>-ΔHrxn. J/g dry</u>								
0	0	0	260	389	530	57	0	1237
47 ^a	13	18	233	395	166	38	182	1043
48 ^a	8	7	236	304	172	31	355	1112
47.6 ^b	7	13	239	357	185	32	260	1093
45.6 ^b	16	12	247	357	215	35	223	1105
46.2 ^{a,c}	20	12	246	351	228	29	189	1073

(a)Started with 80/20 O₂/Ar in Headspace. (b)Started with 100% Ar in headspace. (c)No Iron in simulant.

APPENDIX B

Table B1 Scoping Experiments Run with 0.049 M $\text{H}^{13}\text{CO}_2^-$ and 0 to 0.1 M EDTA

No.	Time h	Dose(a) Mrad	[EDTA] ₀ mM ^(b)	Final Concentration, mM				Radiolytic Yield, G (molecules/100 ev)		
				EDTA ^(b)	$^{13}\text{CO}_3^{2-}$	$\text{H}^{12}\text{CO}_2^-$	k_{rel}	$^{13}\text{CO}_3^{2-}$	EDTA	$\text{H}^{12}\text{CO}_2^-$
1	120	9.6	0		6.52			0.48		
2	192	15.3	0		12.3			0.57		
3	216	17.3	0		13.7					
4	0	0.0	22.5							
5	120	9.6	22.5	9.3	6.13	17.0	6.6	0.45	-0.97	1.25
6	216	17.3	22.5	5.6	9.67	26.7	6.4	0.40	-0.69	1.09
7	0	0.0	44.5	44.5						
8	192	15.3	44.5		9.02			0.41		
9	216	17.3	44.5	19.7	9.04	30.4	4.0	0.37	-1.01	1.24
10	0	0.0	93.1							
11	120	9.6	93.1	76.6	3.82	16.2	2.4	0.28	-1.21	1.19
12	192	15.3	93.1		7.06			0.32		
13	216	17.3	93.1	65.1	7.12	31.5	2.3	0.29	-1.14	1.28

^(a) γ dose-rate ~ 0.08 Mrad/h. ^(b) Average of determinations by NMR and ion pair chromatography.

Table B1 continued: Scoping Experiments Run with 0.099 M $\text{H}^{13}\text{CO}_2^-$ and 0 to 0.1 M EDTA

No.	Time h	Dose(a) Mrad	[EDTA] ₀ mM(b)	Final Concentration, mM			k_{rel}	Radiolytic Yield, G (molecules/100 ev)		
				EDTA(b)	$^{13}\text{CO}_3^{2-}$	$\text{H}^{12}\text{CO}_2^-$		$^{13}\text{CO}_3^{2-}$	EDTA	$\text{H}^{12}\text{CO}_2^-$
14	120	9.6	0		10.7			0.79		
15	264	21.1	0		24.2			0.81		
16	0	0.0	23.3							
17	120	9.6	23.3	13.3	7.72	14.3	6.9	0.57	-0.73	1.05
18	240	19.2	23.3	4.9	18.1	32.0	7.8	0.67	-0.68	1.18
19	264	21.1	23.3	3.8	18.8	33.9	8.6	0.63	-0.65	1.13
20	0	0.0	47.9							
21	120	9.6	47.9	28.8	7.72	17.7	6.3	0.57	-1.40	1.30
22	264	21.1	47.9	23.9	16.8	36.5	3.7	0.56	-0.80	1.22
23	0	0.0	99.0							
24	120	9.6	99.0	77.7	7.03	15.9	3.3	0.52	-1.56	1.17
25	264	21.1	99.0	56.9	13.7	37.4	3.7	0.46	-1.41	1.24

(a) γ dose-rate ~ 0.08 Mrad/h. (b) Average of determinations by NMR and ion pair chromatography.

Table B2. Conversion of Formate to Carbonate as a Function of γ -Dose/Time; Bimolecular Rate Constant for $\text{NO}_2 + \text{HCO}_2^- \rightarrow \text{CO}_3^{2-} + \text{NO}_2^-$

[Formate] ₀	% ¹³ C	Time h	Dose Mrad	¹³ CO ₃ ²⁻ mM	G(CO ₃ ²⁻)	k ^(a) M ⁻¹ s ⁻¹
0.049	100	120.0	9.60	6.5	0.48	9.9
0.049	100	191.7	15.34	12.3	0.57	13
0.049	100	215.8	17.26	13.7	0.56	13
0.050	100	120.0	7.89	6.4	0.57	10.
0.050	100	120.0	7.76	6.8	0.62	11
0.050	100	120.0	8.49	6.9	0.57	11
0.099	100	120.0	9.60	11.0	0.79	8.4
0.099	100	263.9	21.10	24.2	0.81	9.3
0.10	100	120.0	7.89	9.3	0.83	8.0
0.10	100	120.0	7.76	1.1	1.0	10.
0.10	100	120.0	8.49	1.2	1.0	11
0.35	28.6	143.9	10.96	5.0	1.1	3.5
0.35	28.6	288.9	20.89	9.8	1.2	3.6
0.35	28.6	143.9	10.02	6.7	1.6	5.8
0.35	28.6	288.9	20.81	9.5	1.1	3.5
0.35	28.6	143.9	10.09	5.5	1.3	4.3
0.35	28.6	288.9	19.95	1.0	1.3	4.0
0.60	16.7	143.9	11.91	3.5	1.2	2.4
0.60	16.7	288.9	21.85	6.9	1.3	2.6
0.60	16.7	143.9	10.87	6.0	2.3	7.1
0.60	16.7	288.9	21.66	7.8	1.5	3.1
0.60	16.7	143.9	10.39	3.8	1.5	3.1
0.60	16.7	288.9	20.26	7.8	1.6	3.4
1.1	9.09	288.9	21.85	4.9	1.7	2.1
1.1	9.09	288.9	21.66	5.5	2.0	2.6
1.1	9.09	288.9	20.26	5.3	2.0	2.7

^(a)From Equations 3.16 and 3.18, p.31: $p = 1.37$, assumes $G(\text{NO}_2) = 6$.

Table B3. Spreadsheet Calculations for HEDTA Relative Rate Constant Determination (Table 3.1, Section 3.2.1)

Peak Areas From:								
Sample Name	PROTON NMR						¹³ C NMR	
	¹³ C Formate δ 8.76 ppm	¹³ C Formate δ 8.11 ppm	¹³ C Formate total	¹² C Formate δ 8.44 ppm	HEDTA δ 2.4 ppm	DMM δ 1.23 ppm	Formate	Carbonate
56198-49-2-c			184	3.76	648			
56198-49-2-1			212	32.6	565		0.937	0.063
56198-49-2-2			209	37.9	514		0.926	0.074
56198-49-2-3			54.6	8.19	142		0.938	0.062
56198-HEDTA-c	9.66	9.82	19.5	0.00	15.06	9.14		
56198-HEDTA-1	8.78	8.94	17.7	2.68	4.93	8.62	43.3	3.42
56198-HEDTA-2	9.06	9.16	18.2	2.90	4.06	9.75	64.5	5.26
56198-HEDTA-3	37.9	36.9	74.8	12.4	17.6	38.7	67.4	6.93
[DMM] = 0.00667								
Sample Name	Concentrations			[HEDTA] (IPC)	[HEDTA]/ [HEDTA] _o	[F]/[F] _o	k _{rel}	
	[¹³ C Formate]	[¹² C Formate]	[HEDTA]					
56198-49-2-c	0.100	0.002	0.088	0.105	1.000	1.000		
56198-49-2-1	0.094	0.014	0.063	0.072	0.698	0.937	5.53	
56198-49-2-2	0.093	0.017	0.057	0.074	0.676	0.926	6.13	
56198-49-2-3	0.094	0.014	0.061	0.076	0.708	0.938	5.40	
Average	0.0934	0.0151	0.0601	0.0740	0.694	0.934	5.68	
Standard Dev.	0.0007	0.0015	0.0029	0.002	0.017	0.007	0.39	
56198-HEDTA-c	0.1023	0.0000	0.0395		1.000			
56198-HEDTA-1	0.0986	0.0149	0.0137		0.347	0.93	13.9	
56198-HEDTA-2	0.0897	0.0143	0.0100		0.253	0.92	14.0	
56198-HEDTA-3	0.0929	0.0153	0.0110		0.277	0.91	13.1	
Average	0.0938	0.0148	0.0116		0.292	0.919	13.7	
Standard Dev.	0.0045	0.0005	0.0019		0.049	0.011	0.51	

Table B4. Spreadsheet Calculations for IDA Relative Rate Constant Determination (Table 3.1, Section 3.2.1)

Peak Areas From:								
PROTON NMR							¹³ C NMR	
Sample Name	¹³ C Formate δ 8.76 ppm	¹³ C Formate δ 8.11 ppm	¹³ C Formate total	¹² C Formate δ 8.44 ppm	IDA δ 3.16 ppm	DMM δ 1.23 ppm	Formate	Carbonate
56198-IDA-c	7.11	7.08	14.19	0.11	20.79	5.13		
56198-IDA-1	5.68	5.81	11.48	2.08	8.07	5.59	44.20	3.00
56198-IDA-2	6.53	5.77	12.30	2.64	8.42	6.50	50.71	4.94
56198-IDA-3	5.98	5.93	11.91	2.80	8.03	4.56	60.93	5.87
[DMM] = 0.00667								
Concentrations				[IDA]/				
Sample Name	[¹³ C Formate]	[¹² C Formate]	[IDA]	[IDA] _o	[F]/[F] _o	k _{rel}		
56198-IDA-c	0.1327	0.0011	0.0486	1.0000				
56198-IDA-1	0.0987	0.0179	0.0173	0.3570	0.94	15.69		
56198-IDA-2	0.0908	0.0195	0.0155	0.3199	0.91	12.39		
56198-IDA-3	0.1254	0.0294	0.0211	0.4351	0.91	9.05		
Average	0.1050	0.0223	0.0180	0.3707		12.38		
Standard Dev.	0.0181	0.0063	0.0029	0.0588		3.32		

Table B5. Spreadsheet Calculations for NTA Relative Rate Constant Determination (Table 3.1, Section 3.2.1)

Sample Name	Peak Areas From:						¹³ C NMR	
	PROTON NMR							
	¹³ C Formate δ 8.76 ppm	¹³ C Formate δ 8.11 ppm	¹³ C Formate total	¹² C Formate δ 8.76 ppm	NTA δ 3.08 ppm	DMM δ 1.23 ppm	Formate	Carbonate
56198-NTA-c	8.15	8.17	16.33	0.39	12.62	6.18		
56198-NTA-1	6.50	6.49	12.99	1.63	5.13	5.52	69.06	6.13
56198-NTA-2	6.18	5.91	12.09	2.14	2.90	5.29	60.01	8.22
56198-NTA-3	6.07	5.88	11.95	1.78	4.59	5.82	69.44	7.01
[DMM] =		0.00667						
Sample Name	Concentrations			[NTA]/	[F]/[F]o		k _{rel}	
	[¹³ C Formate]	[¹² C Formate]	[NTA]	[NTA]o				
56198-NTA-c	0.1269	0.0031	0.0164	1.0000				
56198-NTA-1	0.1129	0.0141	0.0074	0.4545	0.92	9.27		
56198-NTA-2	0.1097	0.0194	0.0044	0.2683	0.88	10.25		
56198-NTA-3	0.0985	0.0147	0.0063	0.3862	0.91	9.89		
average	0.1071	0.0161	0.0060	0.3697	0.90	9.80		
stdev	0.0075	0.0029	0.0015	0.0942	0.02	0.49		

Table B6. Spreadsheet Calculations for Glycine Relative Rate Constant Determination (Table 3.1, Section 3.2.1)

Table B0: Spreadsheet Calculations for Glycine Relative Rate Constant Determination (Table B-1, Section B-2.1)

	Peak Areas From:						¹³ C NMR	
	PROTON NMR							
	¹³ C Formate δ	¹³ C Formate δ	¹³ C Formate	¹² C Formate	Glycine	DMM		
Sample Name	8.76 ppm	8.11 ppm	total	δ 8.44 ppm	δ 3.15 ppm	δ 1.23 ppm	Formate	Carbonate
56198-Glycine-c	7.79	8.15	15.94	0.09	15.82	6.91		
56198-Glycine-1	6.99	6.92	13.92	2.17	7.79	7.04	62.25	6.49
56198-Glycine-2	6.50	6.79	13.29	1.64	7.23	6.92	63.65	5.88
56198-Glycine-3	6.74	6.36	13.10	1.71	7.04	5.68	61.35	6.48
[DMM] =		0.00667						
	Concentrations			[Glycine]/				
Sample Name	[¹³ C Formate]	[¹² C Formate]	[Glycine]	[Glycine]o	[F]/[F]o	k _{rel}		
56198-Glycine-c	0.1107	0.0006	0.0549	1.0000				
56198-Glycine-1	0.0949	0.0148	0.0265	0.4833	0.91	7.33		
56198-Glycine-2	0.0922	0.0114	0.0251	0.4564	0.92	8.88		
56198-Glycine-3	0.1108	0.0145	0.0298	0.5421	0.90	6.09		
average	0.0993	0.0136	0.0271	0.4940	0.91	7.43		
stdev	0.0100	0.0019	0.0024	0.0438	0.01	1.40		

Table B7. Spreadsheet Calculations for EDTA Relative Rate Constant Determination (Table 3.1, Section 3.2.1)

Sample Name	Peak Areas From:						^{13}C NMR	
	PROTON NMR						^{13}C NMR	
	^{13}C Formate δ 8.76 ppm	^{13}C Formate δ 8.11 ppm	^{13}C Formate total	^{12}C Formate δ 8.76 ppm	EDTA δ 2.42 ppm	DMM δ 1.23 ppm	Formate	Carbonate
56198-EDTA-c	11.41	11.03	22.44	0.00	17.39	10.42		
56198-EDTA-1	10.34	9.78	20.12	3.83	8.99	9.37	65.25	5.72
56198-EDTA-2	9.80	9.75	19.55	3.26	10.15	9.64	73.90	6.72
56198-EDTA-3	9.63	9.65	19.29	4.03	8.16	8.80	71.99	8.43
[DMM] = 0.00667								
Sample Name	Concentrations			[EDTA]/		k_{rel}		
	^{13}C Formate]	^{12}C Formate]	[EDTA]	[EDTA] _o	[F]/[F] _o			
56198-EDTA-c	0.1034	0.0000	0.0200	1.0000				
56198-EDTA-1	0.1031	0.0196	0.0115	0.5748	0.92	6.59		
56198-EDTA-2	0.0974	0.0162	0.0126	0.6310	0.92	5.29		
56198-EDTA-3	0.1052	0.0220	0.0111	0.5556	0.90	5.31		
average	0.1019	0.0193	0.0118	0.5871	0.91	5.73		
stdev	0.0041	0.0029	0.0008	0.0392	0.01	0.75		

Table B8. Spreadsheet Calculations for Glycolate Relative Rate Constant Determination (Table 3.1, Section 3.2.1)

	Peak Areas From:						
	PROTON NMR						
Sample Name*	¹³ C Formate δ 8.76 ppm	¹³ C Formate δ 8.11 ppm	¹³ C Formate total	¹² C-Formate δ 8.44 ppm	Glycolate δ 3.95 ppm	DMM δ 1.23 ppm	
56198-Glycolate-c	5.82	6.27	12.09	0.25	9.64	5.76	
56198-Glycolate-1	10.13	10.48	20.61	3.80	14.38	11.74	
56198-Glycolate-2	10.25	10.21	20.47	2.25	16.50	11.46	
56198-Glycolate-3	4.71	4.52	9.23	1.24	6.93	3.82	
56198-1-c	14.31	13.72	28.03	0.00			
56198-1-1			24.97	5.54	0.94	0.07	
56198-1-2			24.82	5.34	0.90	0.10	
56198-1-3			27.38	5.26	0.92	0.08	
56198-Glycolate-1b	26.05050	27.18360	53.23410	15.03290	20.26	35.36	
56198-Glycolate-2b	24.65030	21.58840	46.23870	8.30295			
56198-Glycolate-1b-D2O	20.82790	21.74290	42.57080	10.90370	14.89	24.08	
56198-Glycolate-2b-D2O	15.7425	15.7897	31.5322	7.0732	14.67	16.63	
[DMM] =		0.00667					
	Concentrations				[Glycolate]/		
Sample Name	[¹³ C Formate]	[¹² C Formate]	[Glycolate]	[Glycolate]	[Glycolate] _o	[F]/[F] _o	k _{rel}
56198-1-c	0.100	0.000	0.120	0.113	1.000	1.000	
56198-1-1	0.094	0.021	0.084	0.0850	0.727	0.935	4.74
56198-1-2	0.090	0.019	0.081	0.0895	0.734	0.900	2.93
56198-1-3	0.092	0.018	0.075	0.0641	0.595	0.920	6.23
Av.	0.092	0.019	0.080	0.080	0.665	0.910	4.58
s	0.002	0.002	0.005	0.014	0.099	0.014	2.33
56198-Glycolate-c	0.101	0.0021	0.0401		1.0000		
56198-Glycolate-1b	0.072	0.0204	0.0138		0.343	0.718	3.23
56198-Glycolate-1b-D2O	0.085	0.0217	0.0148		0.370	0.843	5.82
56198-Glycolate-2b-D2O	0.091	0.0204	0.0212		0.528	0.904	6.34
Av.	0.083	0.021	0.017		0.449	0.874	6.08
s	0.010	0.001	0.004		0.112	0.043	0.37

(a)Determined by ion pair chromatography.

Table B9. Spreadsheet Calculations for s-EDDA Relative Rate Constant Determination (Table 3.1, Section 3.2.1)

Peak Areas From:								
PROTON NMR							¹³ C NMR	
Sample Name	¹³ C Formate δ 8.76 ppm	¹³ C Formate δ 8.11 ppm	¹³ C Formate total	¹² C Formate δ 8.44 ppm	s-EDDA δ 2.62 ppm	DMM δ 1.23 ppm	Formate	Carbonate
56198-sEDDA-c	6.13	5.99	12.13	0.03	10.08	5.88		
56198-sEDDA-1	5.41	6.05	11.46	2.51	2.33	4.12	55.06	5.31
56198-sEDDA-2	6.21	6.04	12.24	1.87	3.41	5.75	41.23	3.04
56198-sEDDA-3	1.81	1.81	3.63	0.67	0.91	1.46	70.57	6.69
[DMM] = 0.00667								
Sample Name	Concentrations			[s-EDDA]/		k _{rel}		
	[¹³ C Formate]	[¹² C Formate]	[s-EDDA]	[s-EDDA] _o	[F]/[F] _o			
56198-sEDDA-c	0.0991	0.0003	0.0206	1.0000				
56198-sEDDA-1	0.1336	0.0292	0.0068	0.3300	0.91	12.05		
56198-sEDDA-2	0.1022	0.0156	0.0071	0.3453	0.93	14.95		
56198-sEDDA-3	0.1195	0.0219	0.0075	0.3644	0.91	11.14		
Av.	0.1184	0.0223	0.0071	0.3466	0.92	12.71		
s	0.0157	0.0068	0.0004	0.0172	0.01	1.99		

Table B10. Spreadsheet Calculations for u-EDDA Relative Rate Constant Determination (Table 3.1, Section 3.2.1)

Peak Areas From:								
	PROTON NMR						^{13}C NMR	
Sample Name	^{13}C Formate δ 8.76 ppm	^{13}C Formate δ 8.11 ppm	^{13}C Formate total	^{12}C Formate δ 8.44 ppm	u-EDDA δ 2.4 ppm	DMM δ 1.23 ppm	Formate	Carbonate
56198-uEDDA-c	38.62	39.81	78.43	1.66	41.80	41.80		
56198-uEDDA-1	26.71	29.44	56.15	7.74	14.32	32.69		
56198-uEDDA-2	22.95	27.76	50.72	4.84	9.45	28.62		
56198-uEDDA-3	24.46	26.74	51.20	4.15	10.00	26.43		
[DMM] = 0.00667								
	Concentrations			[u-EDDA]/				
Sample Name	[^{13}C Formate]	[^{12}C Formate]	[u-EDDA]	[u-EDDA] _o	[F]/[F] _o	k_{rel}		
56198-uEDDA-c	0.0901	0.0019	0.0120	1.0000				
56198-uEDDA-1	0.0824	0.0114	0.0053	0.4379	0.94	12.90		
56198-uEDDA-2	0.0851	0.0081	0.0040	0.3300	0.92	12.96		
56198-uEDDA-3	0.0930	0.0075	0.0045	0.3784	0.93	13.39		
average	0.0868	0.0090	0.0046	0.3821	0.93	13.08		
stdev	0.0055	0.0021	0.0006	0.0540	0.01	0.27		

Table B11. Spreadsheet Calculations for Citrate Relative Rate Constant Determination (Table 3.1, Section 3.2.1)

Peak Areas From:								
	PROTON NMR						¹³ C	
Sample Name	¹³ C Formate δ 8.76 ppm	¹³ C Formate δ 8.11 ppm	¹³ C Formate total	¹² C-Formate δ 8.44 ppm	Citrate δ * ppm	DMM δ 1.23 ppm	Formate	Carbonate
56198-Citrate-c	26.78	23.87	50.65	0.52	17.92	36.29		
56198-Citrate-1	18.40	18.40	36.79	1.49	14.29	31.13	41.34	5.95
56198-Citrate-2	17.21	15.22	32.43	0.00	12.26	28.72	42.84	5.60
56198-Citrate-3	16.23	15.84	32.07	0.36	13.79	28.64	42.96	5.40
56198-Citrate-c	26.78020	23.87290	50.65	0.52	5.23684	36.29		
56198-Citrate-1b	15.62060	17.77530	33.40	1.16	3.97673	52.18		
56198-Citrate-2b	9.87393	12.85980	22.73	1.08	2.86669	28.14		
56198-Citrate-3b	14.0468	13.5356	27.5824	1.3106	3.48041	38.13	32.68	8.91667
*peaks at 2.46, 2.52, 2.68, and 2.73 ppm								
[DMM] =	0.00667							
	Concentrations			Citrate]/	(Proton)	(C13)		
Sample Name	[¹³ C Formate]	[¹² C Formate]	[Citrate]	[Citrate]o	[F]/[F]o	[F]/[F]o	k _{rel}	k _{rel} (¹³ C)
56198-Citrate-c	0.06700	0.00069	0.00474	1.00				
56198-Citrate-1	0.05674	0.00229	0.00441	0.93	0.847	0.87	0.441	0.546
56198-Citrate-2	0.05419	0.00000	0.00410	0.86	0.809	0.88	0.690	1.191
56198-Citrate-3	0.05375	0.00061	0.00462	0.98	0.802	0.89	0.114	0.213
average	0.05489	0.00097	0.00438	0.92	0.819	0.88	0.718	0.650
stdev	0.00161	0.00119	0.00027	0.06	0.024	0.01	0.093	0.498
56198-Citrate-c	0.1		0.00520					
56198-Citrate-1b	0.03072	0.00106	0.00274	0.53	0.458		0.819	
56198-Citrate-2b	0.03878	0.00184	0.00367	0.71	0.579		0.637	
56198-Citrate-3b	0.03472	0.00165	0.00329	0.63	0.518	0.79	0.697	1.899
average				0.62	0.51848			
stdev				0.09	0.06015			

Table B12. Spreadsheet Calculations for Acetate Relative Rate Constant Determination (Table 3.1, Section 3.2.1)

Peak Areas From:						
PROTON NMR						
Sample Name	¹³ C Formate δ 8.76 ppm	¹³ C Formate δ 8.11 ppm	¹³ C Formate total	¹² C-Formate δ 8.44 ppm	Acetate δ 1.90 ppm	DMM δ 1.23 ppm
56198-Acetate-c	25.58	24.91	50.49	0.00	11.87	24.37
56198-Acetate-1	14.03	14.37	28.40	0.00	7.98	16.12
56198-Acetate-2	14.43	15.32	29.76	1.35	8.48	28.83
56198-Acetate-3	11.55	10.40	21.95	0.00	6.20	13.68
56198-Acetate-1b	14.55	14.08	28.64	2.05	8.75	43.48
56198-Acetate-2b	10.51	8.98	19.50	0.93	7.13	47.19
56198-Acetate-3b	12.08	12.39	24.47	2.99	8.81	42.13
[DMM] =	0.00667					
Concentrations				[Acetate]/		
Sample Name	[¹³ C Formate]	[¹² C Formate]	[Acetate]	[Acetate] _o	[F]/[F] _o	k _{rel}
56198-Acetate-c	0.0995		0.0078	1.000		
56198-Acetate-1	0.0846		0.0079	1.017	0.850	
56198-Acetate-2	0.0495	0.0022	0.0047	0.604	0.498	0.72
56198-Acetate-3	0.0770		0.00726	0.931	0.774	0.28
56198-Acetate-1b	0.0316	0.00227	0.00322	0.413	0.318	0.77
56198-Acetate-2b	0.0198	0.00094	0.00242	0.310	0.199	0.73
56198-Acetate-3b	0.0279	0.0034	0.00335	0.429	0.280	0.66
average	0.0264	0.0022	0.00299	0.384	0.266	0.72
stdev	0.0060	0.00123	0.00050	0.065	0.061	0.05

Figure B1. NMR spectra of citrate and formate-¹³C solution before (top) and after (bottom) γ irradiation at 20 °C.

Figure B2. NMR spectra of s-EDDA and formate-¹³C solution before (top) and after (bottom) γ irradiation at 20 °C.

Figure B3. NMR spectra of u-EDDA and formate- ^{13}C solution before (top) and after (bottom) γ irradiation at 20 °C.

Figure B4. NMR spectra of EDTA and formate- ^{13}C solution before (top) and after (bottom) γ irradiation at 20 °C.

Figure B5. NMR spectra of glycine and formate- ^{13}C solution before (top) and after (bottom) γ irradiation at 20 °C.

Figure B6. NMR spectra of glycolate and formate- ^{13}C solution before (top) and after (bottom) γ irradiation at 20 °C.

Figure B7. NMR spectra of HEDTA and formate-¹³C solution before (top) and after (bottom) γ irradiation at 20 °C.

Figure B8. NMR spectra of IDA and formate-¹³C solution before (top) and after (bottom) γ irradiation at 20 °C.

Figure B9. NMR spectra of NTA and formate- ^{13}C solution before (top) and after (bottom) γ Irradiation at 20 °C.

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