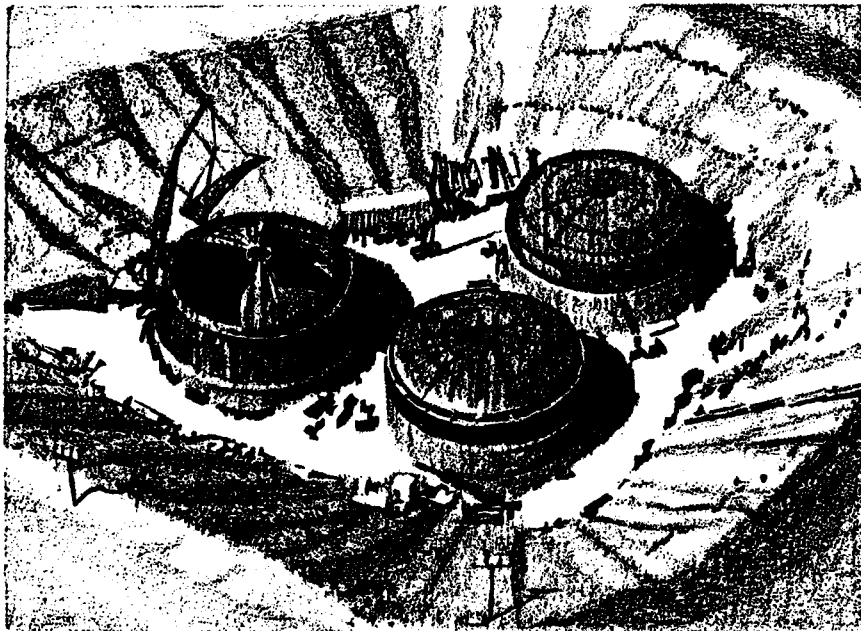


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Organic Tanks Safety Program Waste Aging Studies



November 1994

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**Pacific Northwest Laboratory
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Organic Tanks Safety Program
Waste Aging Studies

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Abbreviations

ANL	Argonne National Laboratory
DBP	dibutyl phosphate
DMF	<i>N,N</i> -dimethyl formamide
DMSO	dimethyl sulfoxide
DOE	Department of Energy
EDTA	ethylenediaminetetraacetate
EPR	electron paramagnetic resonance
GC	Gas Chromatography
Georgia Tech	Georgia Institute of Technology
FY	fiscal year
HEDTA	hydroxyethylethylenediaminetriacetate
hexone	4-methyl-2-pentanone
HPLC	high pressure liquid chromatography
mp	melting point
MS	Mass Spectrometry
NMR	nuclear magnetic resonance
NPH	normal paraffinic hydrocarbons
PNL	Pacific Northwest Laboratory
PUREX	Plutonium-Uranium Extraction (plant)
REDOX	Reduction-Oxidation (plant)
TBP	tributyl phosphate
TOC	total organic carbon
TWRS	Tank Waste Remediation Systems
WHC	Westinghouse Hanford Company

Summary

The underground storage tanks at the Hanford Complex contain wastes generated from many years of plutonium production and recovery processes, and mixed wastes from radiological degradation processes. The chemical changes of the organic materials used in the extraction processes have a direct bearing on several specific safety issues, including potential energy releases from these tanks. This report details the first year's findings of a study charged with determining how thermal and radiological processes may change the composition of organic compounds disposed to the tank. Our approach relies on literature precedent, experiments with simulated waste, and studies of model reactions. During the past year, efforts have focused on the global reaction kinetics of a simulated waste exposed to γ radiation, the reactions of organic radicals with nitrite ion, and the decomposition reactions of nitro compounds.

In our experiments with an "organic tanks" non-radioactive simulant (equi-molar amounts of dodecane, EDTA, tributyl phosphate (TBP), dibutyl phosphate (DBP), hexone, stearic acid, and citric acid in an inorganic matrix containing hydroxide, nitrate, nitrite, aluminum hydroxide, and a variety of alkali, alkaline earth, and transition metal cations), we found that gas production is predominantly radiolytically induced. The main gases found are hydrogen, nitrous oxide, and nitrogen. Concurrent with gas generation we observe the disappearance of EDTA, TBP, DBP and hexone. In the absence of radiolysis, the TBP readily saponifies in the basic medium, but decomposition of the other compounds required radiolysis. These findings appear consistent with mechanistic models found in the literature. They postulate that H_2 is partly formed via radiolytically produced H atoms abstracting H from organic donors, and that nitrogen and nitrous oxide result from organic radicals reacting with NO that is generated by radiolysis of nitrate and nitrite solutes. Our review of the literature uncovered precedent for organic radicals reacting directly with nitrite.

These mechanistic pathways have important implications for the Organic Tanks Safety Program. Key organic intermediates in the model are C-N bonded compounds such as oximes. As discussed in the report, oximes and nitro compounds decompose in strong base to yield aldehydes, ketones and carboxylic acids (from nitriles). Certain aldehydes can react in the absence of radiolysis to form H_2 , as reported in the literature. Thus, if the pathways are correct, then organic compounds reacting via these pathways are oxidizing to lower energy content. Because of the early stage of the work, our conclusions are tentative; additional work is needed.

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1.0 Introduction

The organic-containing underground storage tanks at Hanford are a safety concern because organic compounds react exothermically with inorganic oxidants in the tanks (nitrate, nitrite, multi-valent metal oxides, e.g. of Fe, Mn, U, etc.) (Burger 1993), and under certain conditions, reactions could be vigorous enough to break containment and release radioactivity to the environment (Kozlowski 1968; Beitel 1977). The U. S. Department of Energy's (DOE's) Organic Tanks Safety Program is charged with helping develop criteria for establishing whether an organic tank is a safety risk. The Waste Aging Task is one of several tasks in the Organic Tanks Safety Program that is supplying information for setting these criteria.

To assess the hazard and provide information needed to establish safety criteria, test programs must use simulants, at least until actual tank samples and hot cell test methods become available. Historical records can be used to identify the organics originally purchased and potentially present in the wastes, thus allowing experimental determination of the reactivity of mixtures of these materials with nitrates and nitrites as a first estimate of the hazard associated with these wastes. However, only postulated degradation products or analyses of individual tanks can be used to evaluate the current hazard associated with the organic wastes. To obtain more reliable knowledge of the degradation products, experimental studies are needed.

1.1 Objective

The purpose of the Waste Aging Task is to elucidate how chemical and radiological processes will have aged or degraded organic compounds stored in the tanks. This information will support energetics testing and development of organic analytical methods for analyzing actual tank wastes.

1.2 Background

Organic-containing wastes have been stored in Hanford underground storage tanks for tens of years and during that time have been exposed to radiation, temperatures of 20 to 140 °C, and to a reactive chemical environment having high concentrations of active chemicals, including hydroxide, nitrate, and nitrite, and in some cases, the oxides of manganese. In addition to the organics themselves, the tanks contain transition metals, including some noble metals, which could act as catalysts and affect the decomposition pathway.

Each of the 177 waste tanks at Hanford has a unique composition of organic, inorganic and radioactive elements. A number of studies (Allen 1976; Hall 1972; Jungfleisch 1984; Anderson 1990; Klem 1990) have been conducted to assess the inventory of chemicals added to the tanks as a result of chemical processes such as Uranium Recovery, Reduction-Oxidation (REDOX), PUREX, and Waste Fractionation and Encapsulation that were performed at Hanford. These studies were summarized by Gerber et al. (1992) in their assessment of concentration mechanisms for organic wastes in the tanks.

Table 1 lists the major organic compounds that were added to the tanks. The compounds consist of extraction solvents and complexants for di-, tri-, and tetravalent cations. The quantities of complexants, glycolic acid, citric acid, hydroxyethylethylenediaminetriacetic acid (HEDTA), and ethylenediaminetetraacetic acid (EDTA), were estimated by Allen 1976 (Gerber et al. 1992). The quantities of solvents, tributyl phosphate (TBP) and normal paraffinic hydrocarbons (NPH), come from a recent examination by Reddick (Sederburg 1994) of the PUREX plant material

balances from 1951 to 1990.^(a) 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 and dibutyl butyl phosphonate/carbon tetrachloride for extraction solvents. Considerable quantities of 4-methyl 2-pentanone (hexone) were used in the REDOX process as both extractant and solvent (Gerber et al. 1991). For example, 65 metric tons of hexone were retrieved from one storage tank, treated and disposed. 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 via evaporation, or, in the case of phosphate esters, have been saponified in the alkaline wastes (Burger 1955) is not known. Reddick (Sederburg 1994) has pointed out that during early operations of PUREX, the organic wash waste was combined with high level wastes that generated enough thermal heat to cause the tank wastes to boil.

Table 1. Major Organic Compounds and Quantities Added to the Tanks

Compound	Metric Tons
Normal Paraffinic Hydrocarbons	1310
Hydroxyethylenediaminetriacetic	745
Tributyl Phosphate	722
Glycolic Acid	684
Citric Acid	633
Ethylenediaminetetraacetic Acid	163

For complexants such as EDTA, HEDTA, glycolic acid, and citric acid, extensive studies of degradation mechanisms (aging) have been performed by Argonne National Laboratory (ANL) (Meisel et al. 1991a, 1991b, 1992, 1993), Georgia Institute of Technology (Georgia Tech) (Ashby et al. 1992), Pacific Northwest Laboratory^(b) (PNL) (Byran and Pederson 1994) and Westinghouse Hanford Company (WHC) (Delegard 1980, 1987). The purpose of these studies has been to determine the mechanisms by which organic wastes decompose and generate gases. Much of the work has focused on the role that chelators play in generating H₂, N₂, and N₂O in tanks such as Tank 241-SY-101. The Georgia Tech group has focused primarily on the thermal non-radiolytic pathways that degrade the complexants, mainly HEDTA and glycolate, and produce H₂ (Ashby et al. 1992). The ANL and PNL groups have explored direct and indirect radiation-induced pathways, as well as thermally activated pathways.

^(a)The amount of organic entrained in PUREX wash waste discharged to the tanks was estimated to be 655000 gallons. Assuming the composition of this waste was similar to the PUREX solvent (nominally 30 vol% TBP and 70 vol% NPH), then approximately 722 and 1310 metric tons of the respective solvents would have been discharged to the waste tanks.

^(b)Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

The simulants used in the above work did not include organic solvents, such as hexone, TBP, and NPHs, that were widely used in the processing plants, mainly because the flammable gas-producing tanks of greatest concern did not receive significant quantities of these compounds. Analyses of core samples from Tank 241-SY-101 have shown that a significant portion of the organic carbon is contained in chelators, chelator fragments, and low molecular weight carboxylic acid (*i.e.*, formic, acetic, glycolic, oxalic, succinic, and citric acids). The NPH components amounted to only 2 to 3 % of the organic carbon (Campbell et al. 1994). In contrast to Tank 241-SY-101, Tank 241-C-103 contains 15 to 21 kL of organic liquid composed primarily of TBP and NPH floating on the aqueous wastes (Huckaby and Story 1994; Pool and Bean 1994). Considering the large quantities and high energy content of the organic solvents disposed to the tanks, how they have aged and become distributed in the tanks is very relevant to the organic tanks safety issue.

As a precursor to the experimental studies described in this report, a literature review was performed to assemble a bibliography (Samuels et al. 1993) of literature relevant to understanding the chemical transformations that have occurred in the tanks (Babad et al. 1993). The bibliography focused on the hydrolytic, radiolytic, and free radical-mediated chemistry of normal paraffinic hydrocarbons (NPH), TBP, hexone, and other organic constituents. Aging mechanisms of ferri/ferrocyanides and the EDTA-type complexants were not addressed in the bibliography as they have been examined recently (Lilga et al. 1992; Meisel et al. 1991a, 1991b, 1993; Ashby 1994). The review found that few attempts had been made to understand mechanisms and products of waste aging under conditions similar to those in the Hanford tanks. Some work had been specifically targeted at degradation pathways in 3 M, or greater, nitric acid to understand the effects of processing conditions. The literature did not contain sufficient information needed to characterize how and to what degree these organics have changed while stored in the Hanford tanks. Much uncertainty exists regarding the pathways and products for radiolytic-mediated reactions of the organic solvents in alkaline conditions with high concentrations of nitrate and nitrite. Synergistic and inhibitory effects of oxide surfaces, metal ion catalysts, mass transfer, and solid-liquid interfaces have received little study.

1.3 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 present in the waste. Until sampling and analysis of the tank wastes become routine procedures, a viable approach to assessing the current organic content of the tanks is to simulate the chemical conditions of the tanks and elucidate mechanistic pathways that are key to knowing if the hazards have increased, decreased or remained constant with time. Accordingly, this project is using simulants in its studies of radiation-induced chemical aging effects. The work is proceeding in three sequential steps: 1) simulant selection and preparation, 2) scoping studies, and 3) long term aging studies. To facilitate studies of radiolytic-induced chemical aging, external radiation from a γ source rather than use of radioactive chemicals are used. Radiation doses and/or temperatures are selected to produce aging reactions over times ranging from a few days to several months. After being irradiated, the disappearance and appearance of detectable organic products in the simulant and evolved gases are determined. Details of this work are provided in section 2 of this report which is titled, "Irradiation of an Organic Tank Waste Simulant."

Determination of the organic aging products in actual or even waste simulants is non-trivial requiring many different analytical methods. Because of the complexity of the analyses, the simulant aging studies will be closely coupled with the Organic Methods Development Task to help

identify the aging products. The Organic Methods Development Task is charged with developing analytical methods for characterizing Hanford underground storage tank wastes. Consequently, this effort will provide information on the classes of compounds for which analytical methods should be developed. Also, information on the organic content of the aged simulants will support the Energetics and Reactivity Task which is determining how aging may effect the tendency of the tank wastes to undergo exothermic reactions.

Although simulant aging studies will provide global pathways for aging, they will not allow confident elucidation of how these reactions proceed on the molecular scale because of the complexity of the simulants. Therefore, in concert with and in support of the simulant aging studies, less complex reaction systems that are more readily probed and understood are being examined. In addition, this part of the aging studies is addressing specific safety/treatment questions. As these questions arise, the literature is consulted for pertinent information, and if insufficient information is available, then necessary experiments are designed and performed. Questions pertaining to the alkaline hydrolysis of nitrate and phosphate esters, effects of oxygen and radical initiators on degradation of nitroalkanes, production of organic nitro compounds via reaction of nitrite/aci anions with organic radicals, radiation-induced decomposition pathways of phosphate esters, and pathways for forming succinate have been or are being addressed. Section 3 of this report, entitled "Literature Review," summarizes literature precedents that bear on these questions.

In considering whether nitro compounds might be generated in the wastes, we found precedent for reaction of organic radicals with nitrite ion. A thorough review of the subject was performed (see Section 3). Insights gained from the review prompted experimental studies to elucidate the role this reaction might play in radiation-induced chemical aging. Details of these experiments are provided in Section 4 of this report, "Study of the Reaction of Radicals with Nitrite."

2.0 Irradiation of an Organic Tank Waste Simulant

Until sampling and analysis of the tanks become a routine procedure, hazard assessment must rely on information obtained from studies with simulants. As pointed in the Introduction, the Flammable Gas Safety Program has made extensive use of simulants to mimic the pertinent chemistry of the flammable gas-producing wastes. Their simulants did not include organic solvents, such as hexone, TBP, and NPHs, which were widely used in the processing plants. Thus, the Aging Studies Project is focusing on organic solvent aging and will integrate its findings with those of the Flammable Gas Safety Program's studies involving simulants.

The experimental plan called for developing an organic tanks simulant, performing scoping experiments, and then starting a series of long term aging experiments. The simulant composition was determined by consensus of PNL and WHC investigators involved with tank safety programs and having knowledge of the chemical process streams that were fed to the Organic Tanks. Scoping experiments were performed to optimize procedures and establish the range of conditions over which to collect data. The simulant was dosed with 0.6 MGy at 90 °C in an O₂/Ar atmosphere. In another experiment, the simulant was thermostatted at 90 °C for the same time (8 d) as the previous experiment except it was not irradiated. Gas and condensed phase samples were retrieved from the reactor and analyzed. Based on these results, sampling intervals and temperatures were selected for the long term aging studies. Experimental procedures and results are detailed in the following Experimental and Results Sections.

2.1 Experimental Section

All of the chemicals used in this study were purchased from Aldrich Chemical Company, Eastman Kodak, or Baker Chemicals. The purity of the chemicals was reagent grade or better. The chemicals used in this work were not further purified. A high-shear mixer (Poyltron™ PT6000, Brinkman Instruments Inc., Westbury, NY), was used to mix the simulant. The mixer speed was ~6000 rpm. Water used for preparing the simulant was deionized by a Milli-Q™ Deionization System (Millipore Corporation, San Francisco, CA). Specific details and procedures are given below.

2.1.1 Simulant Preparation

The simulant used in this portion of the study is designated SY1-SIM-94C. Its composition is listed in Table 2. The simulant was prepared by first dissolving the total amount of sodium hydroxide in 700 mL of water. Sodium aluminate was added slowly, with stirring. The remainder of the inorganic constituents were weighed out and added successively to the mixture with periodic mixing to homogenize the ingredients. The organic constituents, the first seven compounds in Table 2, were weighed out and added together. The remainder of the water was used to wash the organic residue into the mixture. The entire simulant mixture was mixed for an additional 10 min. The resultant light-green solution had the appearance and consistency of a milk shake. The simulant was stored in a tightly capped polyethylene jar at ~4 °C.

Table 2. Composition of SY1-SIM-94C Simulant.

	Molarity	Wt %
Na ₄ EDTA	0.10	2.24
Stearic Acid	0.10	1.43
Citric Acid	0.09	1.59
TBP	0.10	1.57
DBP	0.10	1.24
Hexone	0.10	1.01
Dodecane	0.10	1.01
Na ₃ PO ₄ • 12H ₂ O	0.11	2.42
NaNO ₂	3.65	14.90
NaNO ₃	2.46	12.33
Na ₂ CO ₃	0.84	5.26
Na ₂ SO ₄	0.07	0.56
NaF	1.0×10 ⁻⁴	<0.01
Ce(NO ₃) ₃ • 6H ₂ O	3.0×10 ⁻³	0.08
Ca(NO ₃) ₂ • 4H ₂ O	0.01	0.13
KNO ₃	0.13	0.80
ZnCl ₂	5.0×10 ⁻⁴	<0.01
CsNO ₃	2.0×10 ⁻⁴	<0.01
Sr(NO ₃) ₂	1.1×10 ⁻⁵	<0.01
NaOH	2.35	5.55
Cr(NO ₃) ₃ • 9H ₂ O	0.13	2.98
Fe(NO ₃) ₃ • 9H ₂ O	0.01	0.19
Ni(NO ₃) ₂ • 6H ₂ O	4.1×10 ⁻³	0.07
RuCl ₄ • 5H ₂ O	1.0×10 ⁻⁴	<0.01
Rh(NO ₃) ₃ • H ₂ O	1.0×10 ⁻⁴	<0.01
PdCl ₂	1.0×10 ⁻⁴	<0.01
Mn(NO ₃) ₂	0.01	0.11
Pb(NO ₃) ₂	0.01	0.20
Zr(citrate)	8.0×10 ⁻³	0.13
NaAlO ₂ • 0.21NaOH • 1.33H ₂ O	1.90	13.00
H ₂ O	29.0	30.70
Total	41.6	100.00
Total Organic Carbon		5.0

2.1.2 Irradiation

Sample irradiation experiments were performed within the γ -Irradiation Facility at PNL. The facility contains 37 stainless steel irradiation tubes positioned in a 2.13-m-diameter by 4.19-m-deep stainless steel tank. Two arrays of ⁶⁰Co sources with a combined inventory of 1.184×10¹⁶ Bq are

located near the bottom of the tank. For radiation shielding purposes, the tank is completely filled with water, and a concrete wall, 1.1 m in height, surrounds the top of the tank. The irradiation tubes, which are sealed on the bottom, vary in length from 4.9 to 5.5 m, and in diameter from 4.6 to 5.1 cm. The irradiation fluxes of the tubes range from 2 to 2×10^4 Gy/h. The uniform flux region varies from 15.2 cm for the tubes closest to the sources to greater than 30.5 cm for the tubes farthest from the sources. All flux measurements of the tubes are traceable to the National Institute of Science and Technology (Bryan and Pederson 1994).

Vessels of the simulant are manually lowered into the irradiation tubes to the desired flux where they are left in the tubes for a specific length of time to attain the required exposure. No nuclear activation products are associated with the γ irradiation, thus the samples and sample vessels can be transported to other facilities for examination after being removed from the tubes.

Other ancillary equipment at the γ -Irradiation Facility increases the repeatability of thermal control and sampling procedure. The gas manifold system is used to connect multiple reaction vessels to the initial headspace gas source, pressure monitoring equipment, and a port for headspace vapor removal. A gas sample is removed using an evacuated bulb sampler for analysis by mass spectrometry (MS) at another location. The data logger controls both the automated temperature and pressure measurements of the reaction vessels.

2.1.3 Reactor Vessel

The reactor vessel for this study was made from 1.59 cm inner-diameter 316 stainless steel pipe. One end of the pipe was sealed by welding a plate of 316 steel to the pipe. The other end was welded to a flange, 1.59 cm inner-diameter by 3.49 cm outer-diameter. The reactor cover has two openings. One opening was fitted with a 0.16 cm swagelok™ fitting (Swagelok Company, Solon, OH) to connect to the gas manifold via small-diameter stainless steel tubing. The other opening was fitted with a 0.32 cm swagelok™ fitting through which a K-thermocouple was inserted 15.2 cm into the body of the reactor from the top of the flange. The volume of the vessel to the top of the flange was approximately 30 mL.

The reactor vessel was heated to operating temperature by heating tape that had been wrapped around the outside of the vessel. The internal temperature of the reaction vessel was maintained by feedback control to minimize thermal gradient problems (Bryan and Pederson 1994). Reaction vessel temperatures and pressures were monitored using a data logger.

2.1.4 Filling and Placing the Reactor

The simulant was removed from storage at ~ 4 °C, equilibrated with room temperature, and re-suspended by mixing with the high-shear mixer. An aliquot of 15 mL was measured out and transferred to the reactor. The reactor was then sealed and transported to the γ -Irradiation Facility.

The staff at the γ -Irradiation Facility performed the irradiation experiments according to a set procedure. Table 3 lists individual steps in the experimental procedure. The identical procedure was used for each irradiation and control experiment. Valves and other equipment listed in Table 3 refer to features on the gas manifold system. The procedure involves purging the gas manifold lines, purging and venting the vessel, leak testing, heating the vessel to temperature, placing the vessel into an irradiation tube, monitoring pressure and temperature during the course of the reaction, sampling the reaction, and removing the reactor from the facility. This procedure is similar to the one developed by the Flammable Gas Safety Program (Bryan and Pederson 1994) with the

exception that the vapor was collected before the reactor was cooled to room temperature. A mixture of 79.5% argon and 20.5% oxygen was used as the gas phase, instead of air, to facilitate analyses of nitrogen gas.

Table 3. Procedure for Irradiating the Simulant and Collecting Gas Samples

1. Close vent, open purge valves, and turn on gas mixture(oxygen/argon) 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 O.K., 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 pit 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 before gas sample is collected.
28. Discontinue heating of the vessel and remove it from the γ irradiator.
29. Seal reactor and disconnect it from the gas manifold.
30. Remove the sample from the reactor and clean the vessel.

2.1.5 Gas Collection

The vapor phase of the reaction was removed at the end of the irradiation time via an evacuated bulb sampler at temperature. An evacuated bulb sampler that has a pressure of 2×10^{-6} to 5×10^{-7} atm was attached to the manifold. The bulb was filled by opening the gas sampling valve for 5

min, closing it, and then removing the bulb from the manifold. The vapor was later analyzed by PNL staff according to the procedure by Goheen (1988). Total moles of gases produced were calculated based on the measured pressure, temperature, and known volume of the gas phase of the reaction vessel. Concentrations (mol%) of individual components in the gas sample were determined using mass spectrometric analyses. The quantities of specific gases generated were calculated from the total moles of gas generated and the mole fraction data.

No attempt was made to extract product gases that were either dissolved in the simulated waste mixtures or present as gas bubbles. For all product gases except ammonia, this approach should result in negligible errors. Ammonia has significant solubility in the concentrated simulant mixtures (Bryan and Pederson 1994). Solubilities of gases such as H₂, N₂, and N₂O are known to be quite low in concentrated brines as compared to their solubilities in pure water (Schumpe et al. 1993; Bryan and Pederson 1994). Gas bubbles will contribute to the measured pressure in the test vessel, much as if the bubbles were brought to the slurry surface and eliminated, provided that simulant surface tension does not significantly compress the bubbles.

Bryan and Pederson (1994) estimated errors for measurements of H₂, N₂, and N₂O generated from simulated wastes. Several contributors to measurement error exist. Uncertainty in temperature can be a major contributor. Bryan and Pederson (1994) estimated that for an activation energy of 104.6 kJ/mol, approximately that reported for gas generation and related reactions (Delegard 1980, 1984; Schmidt et al. 1993; Meisel et al. 1993; Ashby et al. 1993; Person 1993), a 1 °C difference in temperature from 90°C would yield a 10% change in rate, a 2 °C difference would yield a 20% change in rate, and a 5 °C difference would yield a 60% change. For activation barriers of ~104.6 kJ/mol, this degree of precision leads to a 5% error. Other direct contributors to measurement uncertainties are mass spectrometry analyses and pressure measurements (Bryan and Pederson 1994). The precision in mass spectrometry measurements are approximately 2%, while the precision in pressure measurements are approximately 1%. Volumes of the reaction vessels and the quantities of simulant introduced into the reaction vessels are known to better than 1%. Bryan and Pederson (1994) estimated the combined errors for 30-ml reaction vessels to be approximately 20% (assuming a 104.6 kJ/mol activation barrier for gas generation). In their study they assumed a 1-2 °C drift in temperature. The errors for our work are thought to be ~15%, because the reaction vessels in our work were independently temperature controlled throughout the tests to within ±0.50 °C. The activation barriers for gas-producing reactions of the simulant being studied here are not known at this time. Activation energies smaller than 104.6 kJ/mol would give rise to smaller errors.

2.1.6 Condensed Phase Analyses

After the gas sample was removed, the reactor was cooled to below 35°C, removed from the manifold, sealed, and transported to another laboratory to retrieve the condensed phase. The lid was removed and the mixture was stirred with a spatula and separated into two samples of ~7.5 mL. One sample was combined with other washings from the reactor to a total volume of ~20 mL and stored at -2 °C. The other sample was analyzed for the organic constituents by PNL's Advanced Analytical Methods Development Group.

2.1.7 Sample Preparation for Condensed Phase Analyses

To prepare a sample, 1 gram of the irradiated simulated waste was weighed into a screw-topped glass test tube and 2.5 mL of CH₂Cl₂, and 10 mL of 2 N phosphoric acid were added as a precipi-

tate formed and the sample foamed. The tube was capped and shaken, carefully vented to release built up pressure, and then centrifuged for 15 min at 1500 rpm. The CH₂Cl₂ layer was removed and filtered through anhydrous Na₂SO₄ into a 50-mL volumetric flask. The aqueous and solid contents of the tube were extracted again, and the CH₂Cl₂ layer was combined with the previous fraction. To facilitate gas chromatographic analysis, 2 mL of a diazomethane solution was added to the combined CH₂Cl₂ extracts to methylate DBP and stearic acid. The volumetric flask was then filled to volume with CH₂Cl₂. A 1.5-ml portion of this solution was transferred to a gas chromatograph autosampler vial and 50 µL of a 3-µg/µL tridecane solution was added as an internal standard. The aqueous layer remaining in the test tube was prepared for ion chromatography by transferring it to a 10 mL volumetric to which was added 200 µL of 0.5 M CuSO₄ and water to volume.

2.1.8 Gas Chromatographic-Mass Spectrometric Analyses

Gas chromatography-mass spectrometry (GC-MS) was used to analyze for hexone, TBP, DBP, dodecane, and stearic acid in extracts from the simulated waste. Areas of peaks were obtained by integrating extracted-ion chromatograms. Table 4 lists chromatographic conditions and Table 5 gives extracted-ion chromatographic parameters used to quantify the analytes.

Table 4. GC-MS Conditions for Analyzing Dichloromethane Extracts of the Irradiated Simulant

Analytical Column: DB™-5 (J&W Scientific, Folsom, CA), 30 m×0.32 mm, 5 µm film thickness
 Head pressure: ~0.34 atm
 Mult. Voltage: 2031 (autotune nominal value)
 Zone temperatures: Injection, 260 °C; interface, 280 °C; source temp, 200 °C
 Oven Ramp: 40°C (1 min), 30 °C/min to 70 °C (4 min); 19 °C/min to 280 °C (19 min)

Table 5. Parameters Used for GC-MS Extracted-Ion Detection and Integration of Analytes

Compound	Extracted Ion Mass	Time Range, min
Hexone	43	9-10
Monobutyl Phosphate ^(a)	127	14-16
Dodecane	57	15-17
Tridecane (internal standard)	57	15-17
DBP	113	17-18
TBP	99	19-20
Methyl Stearate	74	29-31

^(a)Monobutyl phosphate was contaminant in the DBP.

2.1.9 Ion-Pair Chromatography

Ion-pair chromatography was used to analyze for EDTA. The samples were doped with copper(II) sulfate, as described, above to enhance ultraviolet absorption for detection. Table 6 lists analysis parameters.

Table 6. Ion Pair Chromatography Conditions for Analyzing EDTA in the Irradiated Simulant

Guard column:	Adsorbosphere® (Altech Associates, Deerfield, Illinois), C-8 cartridge
Analytical Column:	Adsorbosphere® C-8 (25 cm x 4.6 mm, particle size 5 µm)
Flow Rate:	1.5 mL/min.
Sample Volume:	15 µL
Detection:	UV detector set at 280 nm
Mobile phase:	0.002 M dodecyltrimethylammonium bromide, and 0.05 M potassium dihydrogen phosphate, pH 6.5

2.2 Results

2.2.1 Waste Composition

The simulant (composition shown in Table 2) was formulated with nonradioactive chemicals based on knowledge of tank waste composition and input from PNL and WHC staff involved with the Organic Tanks and Flammable Gas Safety Programs. Tank waste composition information was derived from process flow sheets and limited prior sampling. The organic components of the simulant were selected to make the simulant representative of the organic tanks. The level of 5% total organic carbon (TOC) was used because that level is part of the new criteria for placing waste tanks on the "watch" list. The organic components were limited to seven compounds to facilitate analyses of reactants and products in the condensed phase. Further, it was decided that each organic compound would be added to the simulant on an equi-molar basis. Stearate, a long chain carboxylate anion, and dibutyl phosphate were included in the simulant to reflect partial oxidation of NPH and hydrolysis of TBP under plutonium extraction (PUREX) process conditions. Glycolate and HEDTA, present in SY1-SIM-93C, were excluded to simplify analyses and because their breakdown has been well elucidated by Meisel et al. (1992, 1993).

The inorganic portion of Tank 241-SY-101 waste has been analyzed and results published (Reynolds 1993). It represents a typical inorganic waste for Hanford underground storage tanks. Sodium nitrate, nitrite, and hydroxide comprise the largest share of the mass of the inorganic and non-radioactive species (Reynolds 1993). Also, significant amounts of aluminum are present in the tanks, presumably, as sodium aluminate, not aluminum oxide, due to high levels of sodium hydroxide in the tanks. The simulant used in this study resulted from the waste simulant developed at WHC for the Tank Waste Remediation Systems (TWRS) program. SY1-SIM-94C was derived from SY1-SIM-93, with the addition of seven organic and four inorganic elements (Ce, Zr, Pd, Rh, and Ru and the reduction of the levels of Cl and F). The levels of the noble metals Pd, Ru, Rh (as nitrates or chlorides) were chosen from the data collected by Reynolds (1993). Cerium(III) was added so as to include an element from the lanthanide series. The concentration was

set at one third the level of Ca. The decision to add Zr and reduce the levels of halides was based on information (Scheele et al.) about the chemical compositions of Sr and Cs removal process waste streams.

2.2.2 Irradiation Schedule

The schedule of experiments is provided in Table 7. A radiation dose of 1 MGy approximates the average dose that an average underground storage tank would receive during its 30 years of existence (Gerber et al. 1992). Experiments 6, 13, 14, and 15 are duplicates. Experiments 2, B1-B3, and X1 serve as control experiments that test for the effects of thermal aging in the absence of radiation.

Table 7. SY1-SIM-94C Aging Experiments

Run #	°C	MGy	Days
1	90	0.6	8
2	90	0	8
3	50	1.0	14
4	70	1.0	14
5	90	1.0	14
6	90	0.6	8
7	50	0.6	8
8	70	0.6	8
9	90	1.25	17
10	90	0.8	11
11	50	0.8	11
12	70	0.8	11
13	90	0.8	11
14	70	0.8	11
15	50	0.8	11
B1	50	0	11
B2	70	0	11
B3	90	0	11
X1	50	0	90

2.2.3 Gas Phase Analytical Results

At the time of writing this report, 12 of the 18 experiments have been run. Results of head-space gas analyses have been received on samples up through August 16, 1994. Table 8 lists results of these analyses in terms of total gas produced and Table 9 lists the components that make up each of the gas samples. The data in Table 8 show that little gas is produced in the absence of radiation. Table 9 shows that gas produced in the absence of radiation is offset by the O₂ consumed. For example, with the initial gas composition of the headspace being 79.5/20.5 argon/oxygen, the amount of O₂ in experiments B1 and 2 started out at 188 μmol. After 11 days at temperatures of 58 and 90 °C, the total gas content changed negligibly. However, the amount of

O₂ fell to 155 and 86 μmmol for the respective experiments, which corresponds to decreases of 18 and 54% from the initial amounts of O₂.

Table 8. Moles of Gas Generated in Aging Experiments with SY1-SIM-94C

No.	T °C	Dose ^(a) MGy	Pressure atm	Gas mmol	%Increase
0	20	0	0.0	0.946	0.0
B1 ^(b)	50	0	0.1	0.947	0.1
B2 ^(b)	70	0	0.13	0.947	0.1
2 ^(b)	90	0	0.24	0.947	0.0
7	51	0.58	0.45	1.240	31.0
8	69	0.58	0.68	1.361	43.9
6	92	0.58	1.28	1.729	82.7
1	89	0.60	1.29	1.757	85.7
3	48	1.05	0.75	1.510	59.6
4	72	0.95	1.02	1.625	71.7
5	89	1.00	2.04	2.327	145.9

(a)0.6 and 1.0 MGy experiments correspond to 11 and 14 d in the γ Facility.

(b)Duration of experiment was 11 d.

Table 9. Headspace Gas Composition from γ -Irradiation Experiments with SY1-SIM-94C

Gas	Experiments ^(a)								
	B1	2	7	8	6	1	3	4	5
H ₂	0.1	2.5	109	178	672	288	185	225	432
N ₂	17.7	8.8	64.0	105	215	135	143	182	84.6
N ₂ O	0.1	0.4	112	200	500	356	299	331	206
NO _x	0.2	0.4	5.9	0.7	0.0	1.6	7.4	8.0	0.8
NH ₃	0.5	4.3	2.1	1.6	3.2	12.5	2.4	1.6	2.5
CH ₄	0.7	4.5	6.7	7.9	18.9	7.4	8.9	11.2	11.5
C ₂ H ₆	0.2	0.1	1.2	0.0	3.4	1.6	1.2	0.1	0.2
RH	9.4	8.5	8.2	13.9	31.8	19.3	11.8	17.6	22.8
CO	1.4	0.2	0.6	0.1	0.2	0.2	2.2	0.4	0.2
CO ₂	0.3	0.7	0.1	0.1	0.2	0.8	1.5	0.2	0.2
O ₂	155	86.3	110	74.8	76.8	75.0	73.4	77.1	73.8

(a)Quantities are in units of μmol . Initial composition is 729 μmol argon and 188 μmol oxygen.

In the presence of γ radiation, significant amounts of H_2 , N_2 , and N_2O are produced along with trace amounts of small hydrocarbons, CO , CO_2 , NO_x , and NH_3 . Yields of gases increase with temperature, as well. Evidently, these gases are produced from direct irradiation and thermal degradation of radiolytic products. Consumption of O_2 was marginally enhanced by γ irradiation. Interestingly, even though organic compounds in the simulant exceeded the amount of O_2 by a factor >50 (assuming dissolved O_2 is equal to the amount in the vapor phase), the amount of O_2 after irradiating the simulant was nearly constant at 73 to 77 μmol (roughly a 60% decrease) except for experiment 7, which involved the lowest dose, lowest temperature conditions.

Experiments have not yet been run to measure the gases generated by thermal and radiolytic treatments of SY1-SIM-94C without organic components. But, work with other simulants has shown that organics are required to generate nitrogen and nitrous oxide (Meisel et al. 1993; Byan and Pederson 1994; Strachan 1994). If this observation holds for our simulant, then attenuated gas yields are expected from the simulant absent organics, because these gases are significant products in the above experiments.

The composition of the gases listed as RH in Table 9 was found to be a mixture of butanol and hexone. The analysis was carried out with Hewlett/Packard GC/MS (5890/5870) instrumentation according to the procedure by Stromatt (1989) with the gas from experiment 4. Butanol was found present at 0.2 g/L, and hexone at 4.4 g/L, in the vapor phase. Butene and acetone, the respective products of hexone and TBP decomposition, which have been identified in the vapor of Tank 241-C-103 (Huckaby and Story 1994) were evidently below detection limits.

The generation of total gas appears to be linear with dose as shown in Figure 1. The behavior is consistent with a mechanism in which radiolysis of the simulant generates one or more steady-state intermediates that react via thermally-activated processes to liberate gases.

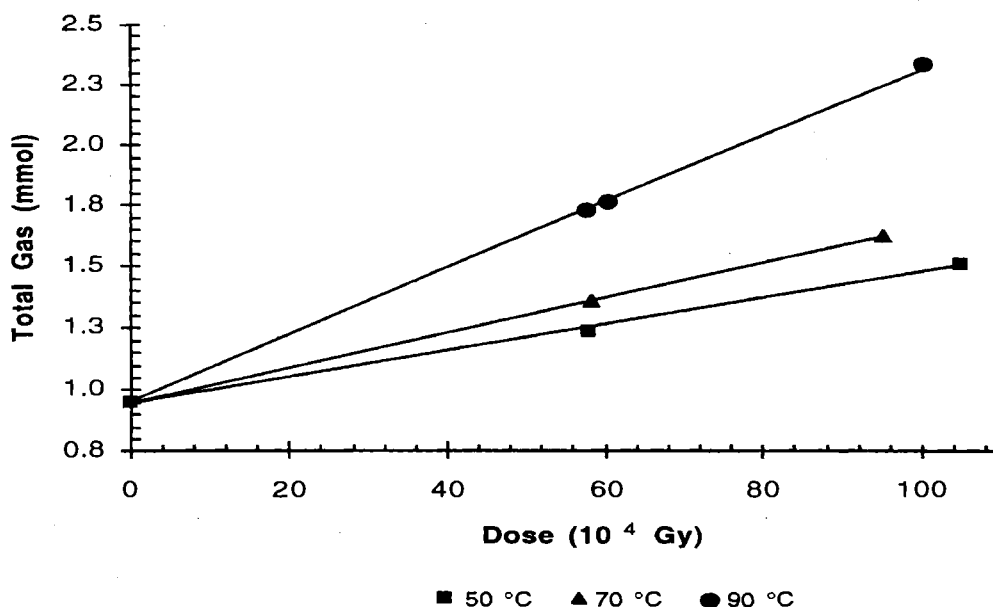


Figure 1. Gas Produced as a Function of Dose and Temperature at Constant Radiation Flux.

The data for individual gas yields may also be linear; however, scatter in the data preclude making this assertion at this stage of our study. More data including duplicates and smaller doses are required.

Figure 2 shows an Arrhenius plot of the radiolytic yields of total gases as function of temperature. Although only three data points are available at this time, the plot shows significant curvature with the slope or activation energy increasing with increasing temperature. This behavior is consistent with the above idea that a suite of reactions having a wide range of activation energies are involved in the production of gas. More data especially at lower doses and different dose rates will be required to determine how the activation barrier for gas production changes with temperature.

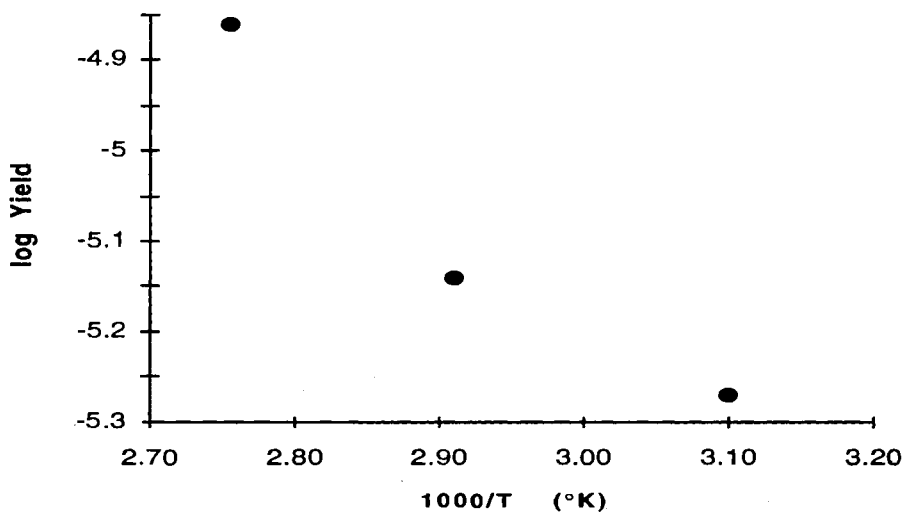


Figure 2. Arrhenius Plot of Radiolytic Yield of Gas for 50, 70, and 90 °C Irradiations of the SY1-SIM-94C.

2.2.4 Condensed Phase Analytical Results

Organic analyses for four of the irradiated samples have been performed. Table 10 shows recoveries of organic components from samples of experiments 1, 3, 4, and 5 and from an unirradiated control sample. Recoveries from the control experiment are quite variable. Additional controls, as well as repeat experiments, are planned to determine reproducibility and assess reasons for incomplete recoveries. Although recoveries are not 100%, some tentative interpretations are possible. Considerable destruction of EDTA, TBP, and hexone is observed. The data for EDTA is most consistent showing increased destruction with increasing dose and temperature. Destruction of TBP is near complete at all irradiation times. This observation is consistent with reported rates for TBP saponification to DBP (Burger 1955). DBP recoveries at 0.6 MGy, 90 °C and 1 MGy, 60 °C experiments are unchanged from the control but lower at more severe 1 MGy, 70 and 90 °C experiments. That DBP recoveries do not initially increase from the saponification of DBP suggests it must be aging, too. DBP is reported to be stable to subsequent saponification (Burger 1955), but is subject to radiolytic conversion to monobutylphosphate in the presences of water (Burger 1958). Therefore, radiolysis must be playing a role in its destruction. Dodecane appears to be relatively stable to thermal and radiolytic degradation.

Table 10. Percent Organic Components Recovered in SY1-SIM-94C before and after γ -Irradiation

Compounds	Control	0.6 MGy		1.0 MGy	
		90 °C	50 °C	70 °C	90°C
EDTA	77	24	32	22	5
TBP	89	1	0	0	0
DBP	48	48	49	24	36
Hexone	63	25	15	7	16
Dodecane	77	70	75	83	91
Stearic Acid	—	—	102	79	79

That dodecane recoveries increased with severity in the 1 MGy experiments is somewhat puzzling. Whether this trend is an artifact due to experimental uncertainties, or subtle changes in sampling or analysis procedures, or aging effects that improve the extraction of dodecane from the matrix is not known at this time. Our NPH in caustic increases up to 0.3% sodium hydroxide, but above 0.3% the reaction is retarded (Shcherbak and Mitskevich 1960). Therefore, the observation is supported by literature precedent.

Overall, the data show that EDTA, TBP, DBP, and hexone are more easily degraded by radiolysis than dodecane and stearic acid. Most of the EDTA and TBP is consumed before the first sampling event. This finding may explain why consumption of oxygen in the head space leveled out for the longer time/higher dose experiments. Oxygen was consumed probably via autoxidation reactions in which organic radicals that were generated thermally and/or radiolytically reacted with oxygen.



Radicals undergo other bimolecular reactions, including recombination, disproportionation, atom abstraction, and addition. As the oxygen levels are reduced these other reaction become more competitive. Oxygen is expected to be generated by direct radiolysis of nitrate and nitrite (Meisel et al. 1991a). Thus, steady state conditions may be reached under the more severe experimental conditions.

3.0 Literature Review

Prompted by specific questions concerning aging pathways and products, the chemical literature was searched for relevant prior work that might address the questions directly or provide insight to possible answers. This section summarizes these literature reviews which were performed this year on topics not covered in the annotated bibliography prepared in the previous year (Samuels et al. 1993).

3.1 Alkaline Hydrolysis of Butyl Nitrate and Nitroalkanes

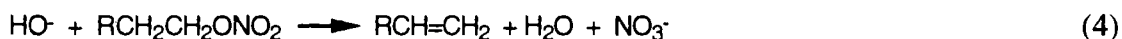
Concern that Hanford waste might contain nitroalkanes and/or organic nitrates that might be potentially more energetic than the original compounds led us to evaluate these classes of compounds. Nitro-containing derivatives may be formed either in the acidic PUREX process, or more directly by aging mechanisms in the alkaline wastes. Red oil, NPH that contains some amount of nitrated alkanes, has received considerable research into its formation since 1951 (Curtis), through this year (Watkins 1994). Watkins found only small amounts of nitro compounds in a study of their formation with acid present under conditions more drastic than encountered in the PUREX process (Watkins 1994).

We have recently examined the literature on hydrolysis of nitrate esters and nitroalkanes. Boschan et al. (1955) have reviewed the chemistry of alkyl nitrate esters. March (1992) reported on both of these reactions and cited leading references. The following three reactions dominate the alkaline hydrolysis of alkyl nitrates:

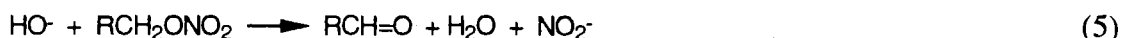
Nucleophilic substitution



Elimination of β -hydrogen



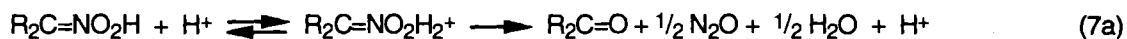
Elimination of α -hydrogen



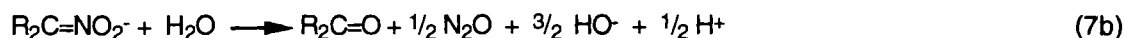
The rates for hydrolysis of alkyl nitrates are said to be relatively slow compared to the analogous alkyl halides, although solvent and alkyl structure effects are the same. However, the long exposure of wastes to alkaline conditions (10 to 30 years) in the Hanford storage tanks lessen concern that these materials are presently in the wastes. Thus, it seems that if butyl nitrate were produced during the PUREX process, then the long exposures to alkaline conditions during storage should have caused degradation. This point may be tested in experiments in which the rates of hydrolysis are measured in two-phase systems consisting of NPH/TBP/butyl nitrate and concentrated sodium hydroxide/sodium nitrate.

The hydrolysis of nitroalkanes is known as the Nef reaction (March 1992). Generally, it is performed by treating the nitroalkane with base to make the aci anion and acidifying with sulfuric

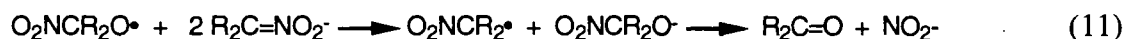
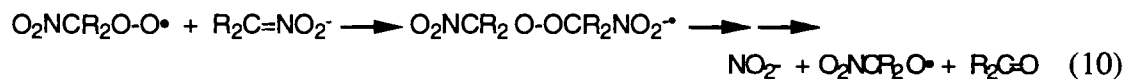
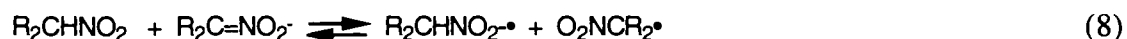
acid to obtain the aci form of the nitroalkane. Subsequent protonations by the strong acid lead to C-N bond scission and carbonyl products.



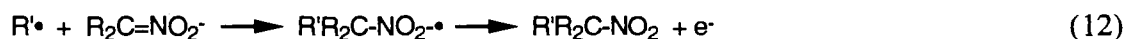
Whether equation 7b could proceed, or be catalyzed, in the alkaline wastes at kinetically significant rates remains to be examined.



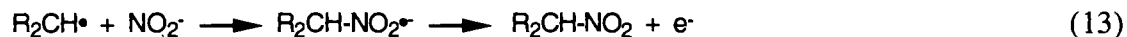
When oxygen is present, the aci anion is oxidized to ketone and nitrite ion (Russell 1967, 1987).



In the absence of oxygen, radicals add to the aci anion to give alkylation products.



In the absence of oxygen, alkyl radicals might also add to nitrite ion (*vide infra*) to produce nitroalkane aci anions via equation 13, then equation 6 (Garst 1973, and references cited below).



Nitro compounds having the nitro group attached to tertiary carbon (product of equation 12) are stable to hydrolysis, and therefore, could accumulate in the hydrocarbon phase, provided the above reaction mechanism is competitive with other reaction pathways. Thus, the exposure history of the NPH phase to air appears critical to assessing the possible presence of nitroalkanes. Experiments to assess better the relative importance of reactions leading to the formation and degradation of nitroalkanes seem warranted.

3.2 Radical Reactions of TBP

Bentrude's chapter (1973) on phosphorous radicals in *Free Radicals* provides insight to the reactions of alkyl phosphates with free radicals. Hydrogen atom and alkyl radicals readily add to the P=O bond to give a phosphoranyl radical intermediate. This intermediate subsequently cleaves one of the O-R bonds to reform the P=O bond. When R• is a long-chain hydrocarbon radical derived from NPH, the metathesis product would show surfactant properties.

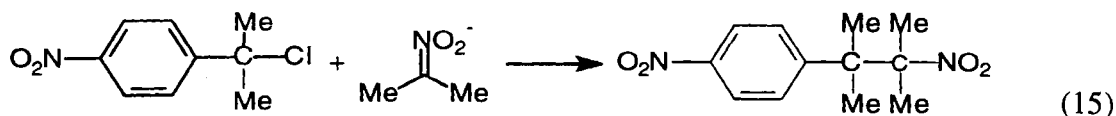


This pathway, with R=H, explains the formation of DBP during γ irradiation of TBP (Azzouz and Attou 1989). Also, it explains the formation of PUREX solvent by-products such as lauryl dibutyl phosphate (R=C₁₂H₂₅•), which was observed when the NPH solvent component was dodecane (Stielglitz and Becker 1985). Probably, analogous H-atom addition-alkoxy radical elimination reactions would proceed for DBP and monobutyl phosphate. And as such, they offer an viable pathway for radiolytically-induced decomposition of these hydrolytically stable phosphate esters.

3.3 Organic Radical Reactions With Nitrite

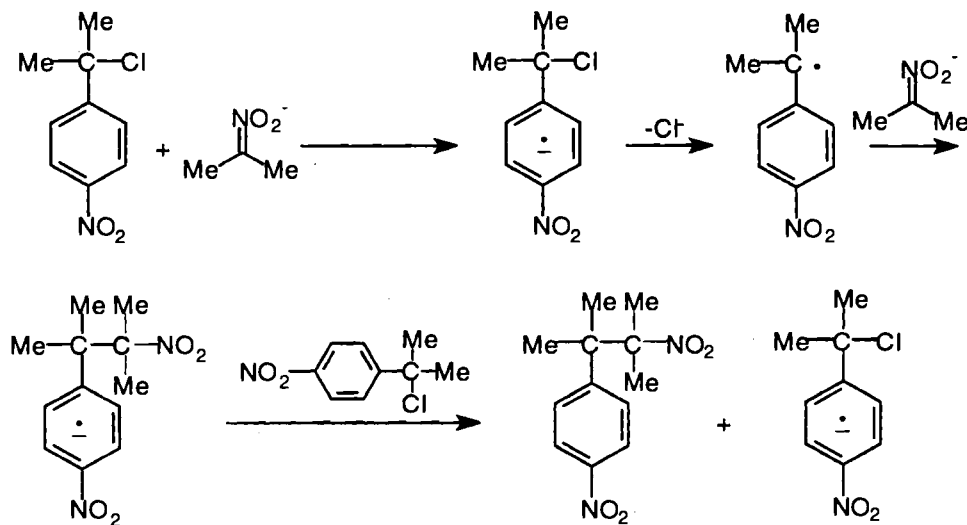
The annotated bibliography (Samuels et al. 1993) that was prepared last year did not cover the reactions of radicals with nitrite ion. After encountering literature precedent for this reaction while reviewing the chemistry of nitroalkanes, a thorough review of this subject was performed. The information indicates that radical reactions with nitrite could play a central role in the aging of organics in the tanks. Below is a summary of the relevant literature found on this topic.

In the early 1960s, Kornblum and coworkers discovered that carbon-alkylation of nitroalkane aci anions (equation 15) occurs via a free radical chain mechanism (now referred to as the S_{RN}1 mechanism) (Kerber et al. 1965, 1964).

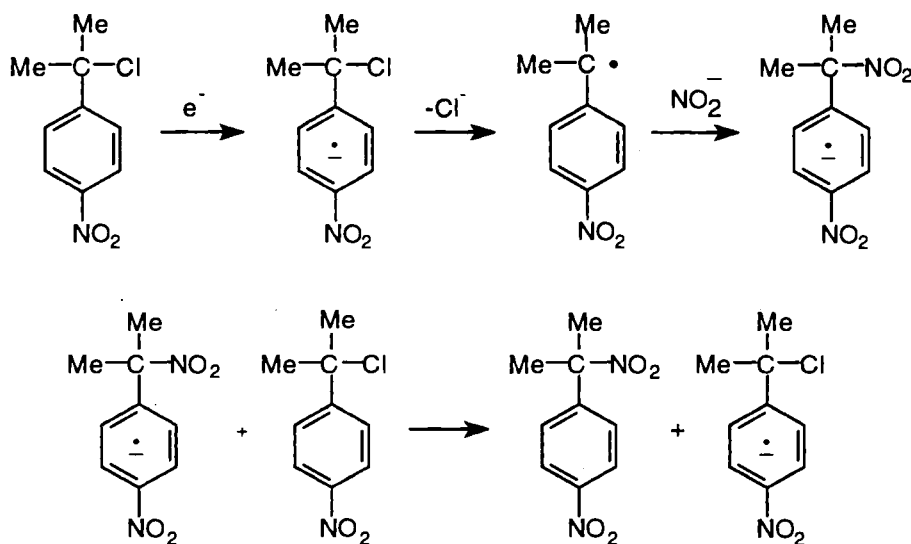


Studies of the reaction mechanism using the *p*-nitrocumyl system were particularly enlightening (Kornblum et al. 1975). The mechanism of the reaction (Scheme 1) invokes a dissociative electron attachment reaction of nitrocumyl chloride, followed by addition of nitrocumyl radical to the aci anion of 2-nitropropane. The radical anion intermediate then transfers an electron to nitrocumyl chloride to form product and propagate the chain reaction. An extensive set of experiments have been performed since the 1960s that support this mechanism.

Kornblum also found that the reaction mechanism is operable for many other nucleophilic anions, including nitrite ion (Scheme 2), in which case, *p*-nitrocumyl chloride yields α ,*p*-dinitrocumene (Kornblum et al. 1966, 1980).

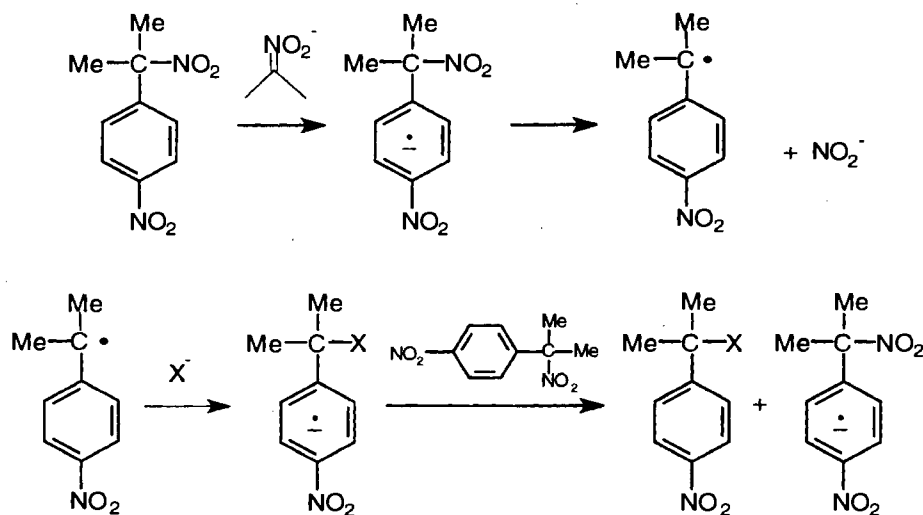


Scheme 1. $S_{RN}1$ Mechanism for Alkylation of 2-Nitropropane Anion



Scheme 2. $S_{RN}1$ Mechanism for Alkylation of Nitrite Ion.

Although good yields of α,p -dinitrocumene are obtained, the addition of p -nitrocumyl radical to nitrite is reversible. This was demonstrated by showing that other nucleophiles can displace the α -nitro group of α,p -dinitrocumene (Kornblum et al. 1987, 1988).

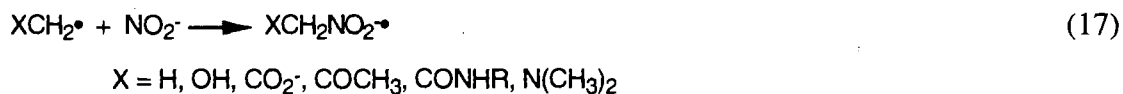


Scheme 3. Mechanism for Displacement of Nitrite from Dinitrocumene by Nucleophiles

The *p*-nitrocumyl system was particularly well suited to studying the $S_{RN}1$ mechanism which demonstrated that an organic radical may add to nitrite and other nucleophilic anions (Kornblum 1975). As mentioned above, ionic S_N1 and S_N2 displacement reactions are negligibly slow. Also, production of *p*-nitrocumyl radical via reductive electron transfer reactions in the initiation and chain propagating steps is facile. However, as revealed below, the chemistry is not unique to *p*-nitrocumyl systems. Since Kornblum's pioneering work with the nitrocumyl system, many examples of other radicals adding to nitrite ion have been reported. Evidence for a variety of functionalized alkyl radicals and phenyl radicals adding to nitrite now exists.



Although organic nitroanion radicals are transient intermediates, they are readily detected using electron paramagnetic resonance (EPR) spectroscopy. Zeldes and Livingston (1968) reported EPR spectra of aliphatic nitroanions that were generated by photolysis of aliphatic alcohols, ketones, acids, amides, and amines in solutions containing potassium nitrite and sodium hydroxide.



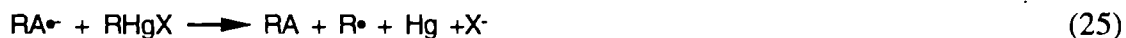
In addition, they observed that photolysis of nitromethane and nitroethane in alcoholic sodium hydroxide solutions yielded spectra for the respective methyl and ethyl nitroanions.



Using EPR techniques, Beckwith and Norman (1969) showed that phenyl radicals add to nitrite. They observed spectra for nitrobenzene radical anions when benzenediazonium salts were reacted with titanium(III). Russell and Metcalfe (1979) showed that sodium dithionite could also be used to generate nitroarene radical anions from arene diazonium salts.



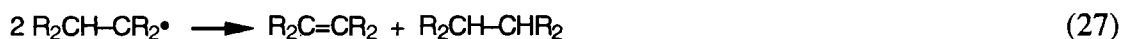
The work of Russell and Khanna (1979a,b) on $\text{S}_{\text{RN}}1$ reactions of *tert*-butylmercury chloride provides convincing evidence that even simple alkyl radicals readily add to nitrite and nitroalkane aci anions. Photolysis of *tert*-butylmercury chloride in the presence of nucleophiles initiates a radical chain reaction in which *t*-butyl radical adds to the nucleophile, forming a radical anion. The radical anion transfers an electron to *tert*-butylmercury chloride to regenerate *tert*-butyl radical and form nitro-*t*-butane in 71% yield.



Reactions performed in dimethylsulfoxide using nitrite ion and nitroalkane aci anions yielded nitroalkanes in good yield. The most reactive anion was the nitromethane anion. Nitrite reacts in good yield, but is slower by a factor of 100. Addition of *t*-butyl radical to 2-nitropropane is 2.4 times faster than addition to nitrite. Absolute rates for radicals adding to nitrite have not been measured, although we estimate the rate is moderately fast. Russell and Guo (1984) measured a rate of $10^5 \text{ M}^{-1}\text{s}^{-1}$ for 5-hexenyl radical adding to 2-nitropropane aci anion in dimethyl sulfoxide (DMSO) at 40 °C. Thus, we expect that reaction of *t*-butyl radical with nitrite ion should be in the range of 10^4 – $10^5 \text{ M}^{-1}\text{s}^{-1}$. Larger values for less stable alkyl radicals reacting in water may be expected, based on a report that methyl radical reacts with 2-nitropropane aci anion in water with a rate constant of $2.4 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ at room temperature (Veltwisch and Asmus 1982).

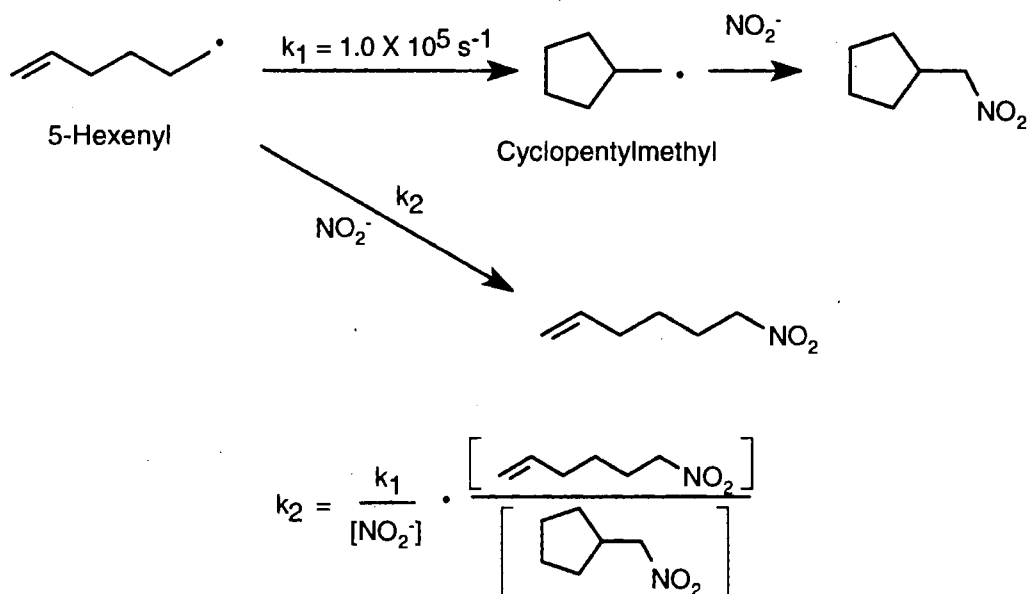
4.0 Study of the Reactions of Radicals With Nitrite

Literature precedent cited in the previous section suggests that organic radicals add to nitrite, thus producing a nitroanion radical intermediate. For this reaction to play a role in the radiolytic-induced aging of organics compounds in the tank wastess, its rate would have to be competitive with other bimolecular reactions that radicals undergo (*e.g.*, termination reactions with other carbon-centered radicals, nitrogen dioxide, or nitric oxide and reaction with O₂).



These reactions all have rate constants that approach the diffusion limit of $>10^9 \text{ M}^{-1}\text{s}^{-1}$ (Ingold 1973). However, because these species are present in rather low concentrations, and nitrite concentrations are very high (in the aqueous phase), nitrite could conceivably compete even if rate constants for its reactions with radicals were less than diffusion limited. Thus, we initiated experiments to determine if the kinetics of this reaction are sufficiently fast for it to be considered a radiolytic aging pathway.

Our approach is based on competing the reaction of a radical with nitrite against a reaction of the radical for which an absolute rate is known. For example, competition against a radical rearrangement such as 5-hexenyl to cyclopentylmethyl, yields the desired rate constant from the ratio of the unrearranged and rearranged products, and the radical rearrangement rate constant.



Scheme 4. Competitive Kinetics Method for Determining Rate Constant for Radical Addition to Nitrite Using the 5-Hexenyl "Radical Clock Reaction"

Our experiments have, thus far, been aimed at finding reaction conditions that produce nitroalkanes when radicals are generated in the presence of nitrite. Observance of nitroalkane would be taken as proof that the radical reacted with nitrite.



Systems under study include generation of undecyl via thermal decomposition of lauroyl peroxide in heptane/water (two-phase solvent), and photolysis of 5-hexenylmercuric bromide and methylmercuric bromide in dimethyl sulfoxide solvent.

4.1 Experimental Section

Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Photolyses were performed using a BLAK-RAY B-100 A long-wave UV lamp with a 100 watt spot bulb 15 cm from the sample. Analyses were done using a Hewlett-Packard 5890 Gas Chromatograph with a Hewlett-Packard 5971 Mass Selective Detector. Proton (^1H) nuclear magnetic resonance spectra were recorded using a Varian VXR-300 nuclear magnetic resonance (NMR) spectrometer.

4.1.1 Procedure for Thermolysis of Lauroyl Peroxide in the Presence of Nitrite

A mixture of lauroyl peroxide (0.20 g, 0.5 mmol), sodium nitrite (0.69 g, 10 mmol), tetra-*n*-butylammonium chloride (0.14 g, 0.5 mmol) water (5 mL) and heptane (5 mL) was heated at ~ 70 to 80 $^\circ\text{C}$. The mixture was diluted with ether. After shaking and separating the layers, the organic phase was washed with water, dried over sodium sulfate, filtered, and analyzed using GC-MS.

4.1.2 Preparation of Undecane Aldoxime

Undecane aldoxime was prepared from undecanal by a method similar to that reported for the preparation of oximes (Lachman 1943). Sodium hydroxide (11.8 g, 294 mmol) was added to a mixture of undecanal (10.0 g, 58.7 mmol), hydroxylamine hydrochloride (6.1 g, 88 mmol), water (4 mL), and 95% ethanol (20 mL), one pellet at a time, during which the mixture became warm. It was refluxed 35 min, cooled, and poured into a mixture of water (200 mL) and concentrated HCl (30 mL). The mixture was cooled in ice, filtered, and rinsed with water. The filtrate, which produced a precipitate, was filtered again. The material was recrystallized from 95% ethanol to yield undecane aldoxime (4.43 g, 41%, mp 69 - 71 $^\circ\text{C}$ (literature, 71 - 72 $^\circ\text{C}$) (Lieberman 1955); ^1H NMR (CDCl_3): chemical shift (ppm), no. hydrogens, multiplicity, type; 0.9, 3H, triplet, CH_3 ; 1.2, 14 H, singlet, CH_2 ; 1.4-1.6, 2H, multiplet, CH ; 2.2, 1H, m, CH ; 2.4, 1H, multiplet, CH ; 6.7, 1H, broad singlet, OH ; 7.4, 1H, triplet, $\text{CH}=\text{N}$).

4.1.3 Thermolysis of Undecane Aldoxime

Undecylic aldehyde oxime (0.5 g, 2.7 mmol) was heated under nitrogen in a sand bath. At ~210 °C, a vapor appeared to be produced. It was heated at 210 to 230 °C for 10 to 15 min, after which the material was brown. Distillation at 7×10^{-4} atm yielded undecanenitrile that distilled at 100 °C (0.15 mg, 33%). Its infrared spectrum was identical to that of an authentic sample. Undecane aldoxime sublimed at 7×10^{-4} atm without decomposition.

4.1.4 Preparation of Nitroundecane

The preparation of nitroundecane and 6-nitro-1-hexene is similar to that reported for the preparation of nitroalkanes (Kornblum et al. 1956). A mixture containing 1-bromoundecane (3.00 g, 12.8 mmol) and sodium nitrite (1.50 g, 21.8 mmol) in N,N-dimethyl formamide (DMF) (26 mL) was stirred at room temperature for 8.5 h. It was poured into 75 mL of ice water, and extracted with five 5-mL portions of petroleum ether (bp 35 to 60 °C). The combined extracts were washed with four 4-mL portions of water, dried over sodium sulfate, filtered, concentrated in vacuo, and distilled at 5×10^{-4} atm. The fraction distilling at 82 °C (0.95 g, 37%) was 96% pure by GC-MS. IR (neat) 2922, 2852, 1549, 1457, 1429, 1372 cm^{-1} . NMR (CDCl_3): chemical shift (ppm), no. hydrogens, multiplicity, type; 0.88, 3H, triplet, CH_3 ; 1.4-2.0, 16H, multiplet, CH_2 ; 2.01, 2H, multiplet, $\text{CH}_2\text{CH}_2\text{NO}_2$; 4.38, 2H, triplet, CH_2NO_2 .

4.1.5 Preparation of 6-Nitro-1-hexene

6-Bromo-1-hexene was reacted with sodium nitrite in DMF, worked up, and distilled to obtain 6-nitro-1-hexene (0.17 g, 21%, bp 42 °C, 7×10^{-4} atm).

4.1.6 Preparation Cyclopentylmethanaldoxime

Cyclopentylmethanol, was oxidized to the corresponding aldehyde by a standard synthetic procedure (Corey and Suggs 1975) using pyridinium chlorochromate. The MS of the reaction product matched that of an authentic sample contained in the GC-MS library data base. Reacting the aldehyde with hydroxylamine by the method of Lachman (1943) produced an oil which consisted of two isomers in a 3:1 ratio by GC. Both exhibited the same MS showing a parent ion of 113 daltons corresponding to $\text{C}_6\text{H}_{11}\text{NO}$. Proton NMR spectra were consistent with cis- and trans-aldoxime structures, showing two vinyl-type and two methine resonances present in 7:3 ratios. NMR (CDCl_3): chemical shift (δ , ppm), no. hydrogens, multiplicity; 1.2-2.0, 8H, multiplet; 2.65, 0.7H, sextet (7.8 Hz splitting), 3.3, 0.3H, sextet (8.0 Hz splitting); 6.67, 0.3H, doublet (7.2 Hz splitting); 7.39, 0.7H, doublet (7.1 Hz splitting).

4.1.7 Preparation of 5-Hexenylmercuric Bromide

The procedure is similar to that reported for making alkylmercuric halides (Quirk and Lea 1976; Costa et al. 1977; Alnajjar 1985) by reacting a Grignard reagent with a mercuric halide. The Grignard reagent was prepared in a three-neck flask containing magnesium (0.72 g, 30 mmol) turnings and equipped with a magnetic stirrer, reflux condenser, and addition funnel. A solution of 6-bromo-1-hexene (2.16 g, 13.2 mmol) in 15 mL of ether was placed in the addition funnel, and a small portion of it was added to the magnesium with stirring. When the reaction began, the

bromide was added dropwise. When addition was completed, the solution was refluxed for 25 min, cooled to room temperature, and transferred via syringe to an addition funnel under nitrogen. The solution was added over a 7-min period to a stirred suspension of 4.76 g of mercuric bromide in 30 mL of ether at 0 °C. After stirring 17 h, it was carefully treated with 20 mL of water. The aqueous layer was separated and extracted with eight 10-mL portions of ether. The combined extracts were dried over sodium sulfate, filtered, and concentrated to a white solid. Recrystallization from methanol yielded 5-hexenylmercuric bromide (1.64 g, 34%, mp 99-101 °C). The material was recrystallized again from methanol (mp 102-104 °C).

4.1.8 Photolysis of 5-Hexenylmercuric Bromide

5-Hexenylmercuric bromide (36 mg, 0.10 mmol), sodium nitrite (69 mg, 1.0 mmol), and DMSO (1 mL) were added to a borosilicate glass tube. It was subjected to three freeze-pump-thaw cycles at 7×10^{-4} atm, using liquid nitrogen. It was then sealed under nitrogen, and photolyzed for 15.5 h, by which time it had become yellow, and mercury metal was visible. The mixture was worked up by adding the mixture to 5 mL of water containing 50 mg of sodium thiosulfate, extracting with six 5-mL portions of dichloromethane, drying over $MgSO_4$, and filtering to obtain a clear solution. The solution was analyzed by GC-MS.

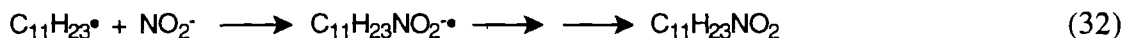
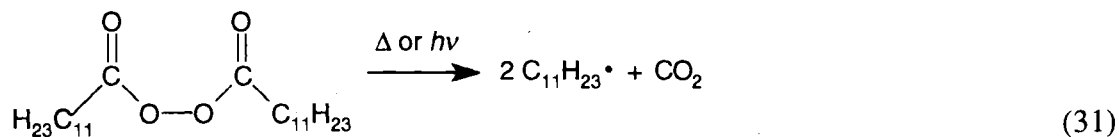
4.1.9 Photolysis of Methylmercuric Bromide in Deuterated Methyl Sulfoxide

A solution of methylmercuric bromide (15 mg, 0.051 mmol) and sodium nitrite (35 mg, 0.51 mmol) in deuterated DMSO (0.5 mL) was degassed by three freeze-pump-thaw cycles at 7×10^{-4} atm using dry ice-acetone. After photolysis in a 5-mm nmr tube under nitrogen for 5 h, the sample was analyzed using NMR. The 1H spectrum showed the methylmercuric bromide resonances had disappeared with the appearance of product resonances, none of which could be related to nitromethane. Observance of two doublets at 5.4 and 5.9 ppm with a 9 hz coupling constant and a broad peak at 10.4 ppm suggests the possible presence of formaldoxime.

4.2 Results

4.2.1 Thermolysis of Lauroyl Peroxide in the Presence of Nitrite

Lauroyl peroxide is a convenient source of primary alkyl radicals. Various experiments involving the reaction of undecyl radical in the presence of nitrite were performed to determine if nitrite could react with a lipophilic radical that would be formed in the organic phase of an "organic" tank.

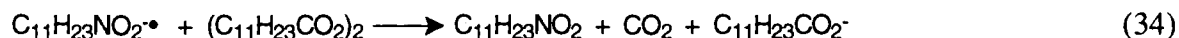


The results of a series of experiments are given in Table 11. In almost all cases, undecane, undecene, docosane and undecyl laurate were detected. Nitroundecane was not observed. The products all qualify as radical-radical termination and radical-solvent reaction products. Docosane

forms by dimerization of two undecyl radicals. Undecyl laurate is produced by geminant recombination (Koenig 1973; Koenig and Fischer 1973). Undecane and undecene may form by disproportionation of undecyl radicals, but this mechanism requires equal amounts of undecane and undecene. Because undecane is almost always formed in greater amounts than undecene, the excess undecane must be formed by abstracting hydrogen from solvent (heptane), or a portion of the undecene is consumed, possibly by adding undecyl radical to undecene to produce the docosyl radical, which terminates or abstracts hydrogen. While both explanations may apply, the former clearly happens in some cases, because the undecane concentration exceeds that of the docosane (see Table 11), which contradicts observations that recombination of primary radicals predominates over disproportionation (Ingold 1973).

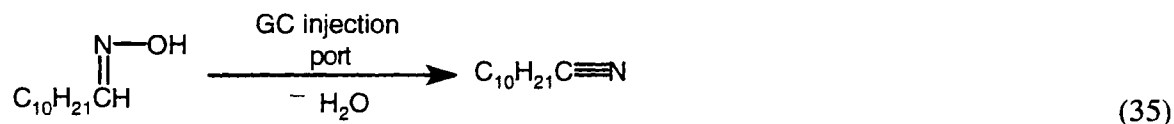


To obtain nitroundecane as a product would require the nitroanion to transfer an electron to an acceptor. Lauroyl peroxide could have functioned as the electron acceptor.



Thus, either the nitroanion did not form or the electron transfer reaction was too slow. In the latter case, the addition reaction would either reverse itself or termination reactions would convert the nitroanion to other products. The latter scenario may be plausible considering that the nitroanion would tend to migrate to the aqueous phase or the water-oil interface where electron transfer reactions with the peroxide would be disfavored.

A clue that the latter reaction may occur is provided by our finding that, in some cases, undecanenitrile is observed in the GC-MS analyses. The undecanenitrile is believed to result from dehydration of the aldoxime in the GC injection port, because gas chromatography of undecyl aldoxime prepared by an independent route also displayed the same retention time and mass spectrum of undecanenitrile. Also, thermolysis of undecyl aldoxime at 220 °C yielded undecanenitrile. Therefore, we believe that the aldoxime is formed initially, but undergoes dehydration in the GC injection port. Mechanisms for the production of oximes are discussed below in section 4.2.3.



Experiment numbers 24, 28, 29, 32, 41, and 42 gave undecanenitrile in the GC-MS analyses. Although experiment 24 gave undecanenitrile, other experiments done under similar conditions did not. The other experiments that showed evidence for undecanenitrile involved using metal catalysts or DMF as solvent. Experiments 41 and 42 show evidence for undecanol.

Table 11. Experimental Conditions for and Product Distributions from Decomposition of Lauroyl Peroxide in the Presence of Nitrite

Expt.	Peroxide (mmol)	NaNO ₂ (mmol)	Solvent	Other Reagents (mmol)	Time (h)	Conditions	Undecane	Undecene	Nitrile	Ester	Docosane
13	1	20	A	Bu ₄ NCl(1)	7	reflux	1.68	0.19	0	0.44	1
23	0.5	5	B	Bu ₄ NCl (0.5)	40	73 °C	2.27	0	0	0	1
24	0.5	10	B	Bu ₄ NCl (0.5)	40	73 °C	0	0	0.27	0.33	1
27	0.5	10	B	Bu ₄ NCl (0.5)	40	65-75 °C	0.70	0	0	0.33	1
28	0.5	10	B	CuCl (0.5) Bu ₄ NCl (0.5)	40	65-75 °C	0	0.54	0.93	0.27	1
29	0.5	10	B	FeCl ₂ (0.5) Bu ₄ NCl (0.5)	40	65-75 °C	0.25	0.12	0.25	0.40	1
30	0.5	10	B		40	70 °C	0.64	0.23	0	0.32	1
31	0.5	10	B	FeCl ₃ (0.025) Bu ₄ NCl (0.5)	40	70 °C	0.09	0.15	0	0.61	1
32	0.5	10	B	FeCl ₃ (0.5) Bu ₄ NCl (0.5)	40	70 °C	0.37	0.14	0.21	0.51	1
34	0.5	10	B	Bu ₄ NCl (0.5)	43	65-70 °C	1.55	0.31	0	0.38	1
35	0.5	5	B	Bu ₄ NCl (0.5)	43	65-70 °C	1.8	0.11	0	0.30	1
38	0.5	0	B	Bu ₄ NCl (0.5)	38	65-70 °C	2.04	0.06	0	0.29	1
39	0.5	5	B	Bu ₄ NCl (0.5)	38	65-70 °C	1.49	0.57	0	0.32	1
40	0.5	10	B	Bu ₄ NCl (0.5)	38	65-70 °C	0.92	0.19	0	0.45	1
41	0.5	10	C		22	65-70 °C	0	0.33	0.78	0.05	1
42	0.5	10	C	Bu ₄ NCl (0.5)	22	65-70 °C	0	0	1.53	0	1
43	0.5	10	E		22	65-70 °C	0	0.11	0	0.06	1
44	0.1	10	F	Na ₂ CO ₃ (1)	20	65-70 °C nitrogen	0.11	0.12	0	0.14	1
45	0.1	10	F	Na ₂ CO ₃ (1)	20	65-70 °C air	0	0.04	0	0.07	1

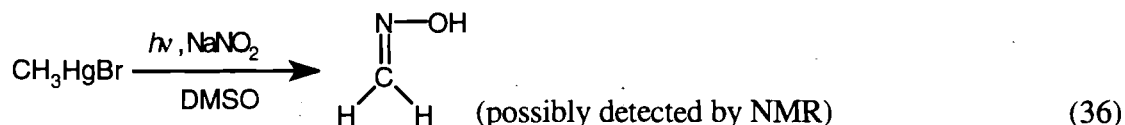
Table 11. cont'd.

Expt.	Peroxide (mmol)	NaNO ₂ (mmol)	solvent	Other reagents (mmol)	Time (h)	Conditions	Undecane	Undecene	Nitrile	Ester	Docosane
49	0.1	1	G	NaNO ₃ (1)	17	65-70 °C	0.40	0	0	0	1
50	0.1	1	G		17	65-70 °C	0.20	0	0	0	1

Solvent: A, 10 mL water, 10 mL heptane; B, 5 mL water, 5 mL heptane; C, DMF; E, DMSO; F, 5 mL TBP, 5 mL water; G, 10 mL 1:1 acetonitrile:water.

4.2.2 Alkylmercuric Bromide Photolyses

Our experiments with methyl and 5-hexenylmercuric bromide also failed to produce nitro compounds. In the case of methylmercuric bromide, the expected product was nitromethane, but $^1\text{H-NMR}$ analyses of the reaction mixture (in DMSO-d_6) did not show the resonance for nitromethane. However, resonances consistent with formaldoxime were observed (this is considered highly speculative at this time because it has not been confirmed against an authentic sample).



Photolysis of 5-hexenylmercuric bromide yielded several products by GC-MS analysis. The presence of nitrite ion was necessary for the products to form. Figure 3 shows a total-ion chromatogram for a typical experiment.^(a) The two major products with retention time 7.9 and 8.1 min have nearly identical mass spectra.

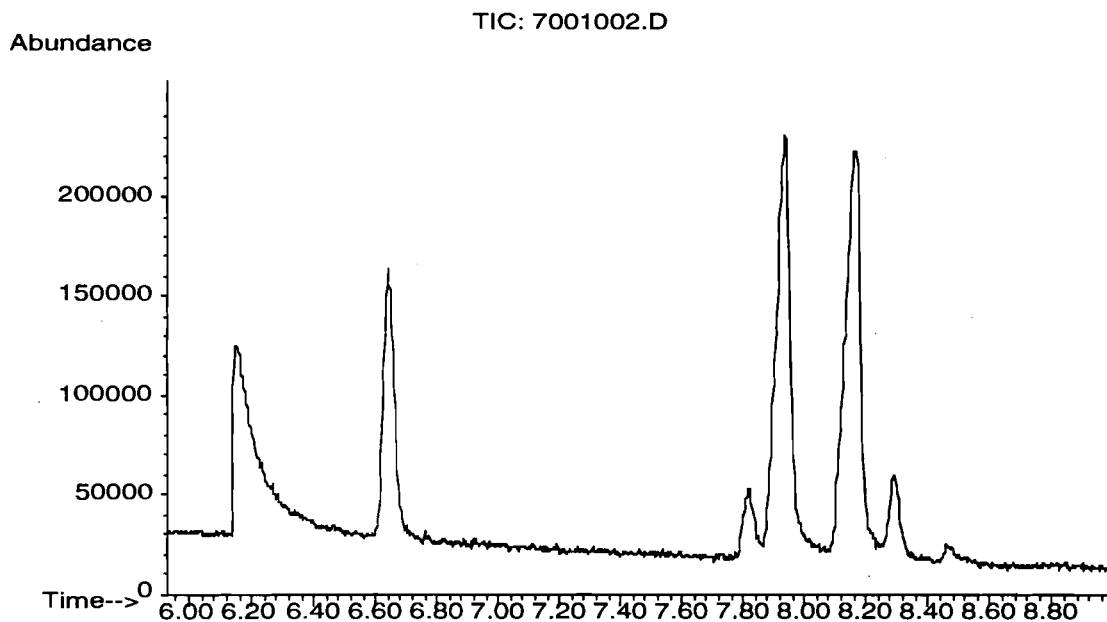


Figure 3. Total-Ion GC-MS Chromatogram of Products from Photolysis of 5-Hexenylmercuric Bromide with Nitrite Ion in DMSO. The peak at 6.2 min is DMSO.

^(a)Note added before printing: the peaks with retention times of 6.6 and 7.8 min are cyclopentylmethylcarbonitrile and methylmercuric bromide.

Figure 4 shows the spectrum obtained from the 7.9-min peak. The masses for the two compounds, 113 daltons, correspond to an empirical formula of $C_6H_{11}NO$, which is consistent with compounds being *cis*- and *trans*-aldoximes derived from either 5-hexenyl or cyclopentylmethyl radicals. An authentic sample of the cyclopentylmethanaldoxime was synthesized and found to match both GC retention times and MS cracking patterns for the reaction products. The 1H NMR spectrum of the cyclopentylmethanaldoxime showed resonances for both *cis* and *trans* isomers.

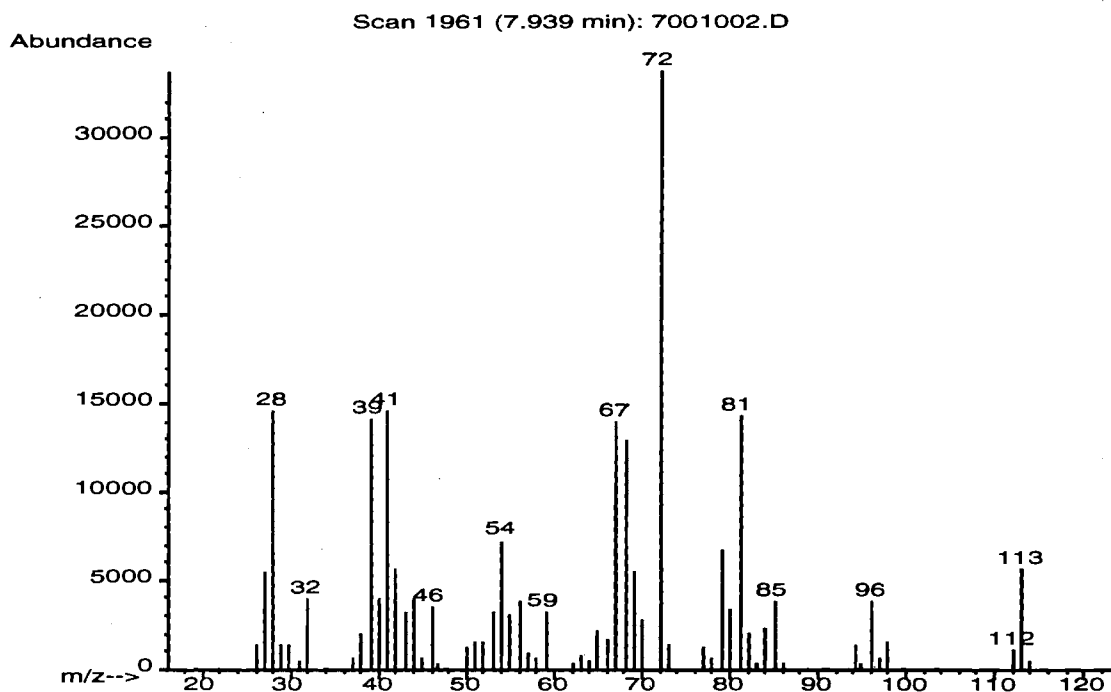


Figure 4. Mass spectrum for compound with 7.9-min retention time in Figure 3. The compound with 8.1-m retention time yielded a nearly identical spectrum.

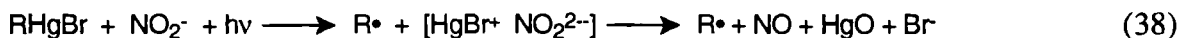
The lack of nitro compounds in the alkylmercuric bromide photolyses was, at first, surprising because photolysis of *t*-butylmercuric chloride in the presence of nitrite (Russell and Khanna 1985) and 5-hexenylmercuric chloride in the presence of 2-nitropropane anion (Russell and Guo 1984) had been observed to produce nitro compounds. However, a review of the $S_{RN}1$ chemistry of alkylmercuric halides (Barluenga and Yus 1988; Russell 1989) showed that bromides do not give as good a yield as chlorides and that the rates of electron transfer (radical anion to alkylmercuric chloride) decrease in the order tertiary > secondary > primary. Thus, it seems that production of nitroalkanes in these systems should not be as efficient as expected due to sluggish reaction rates for converting the nitroanion to nitroalkane via electron transfer. The production of cyclopentylmethanaldoxime requires that reaction of 5-hexenyl radical adding to nitrite is either reversible or much slower than the cyclization reaction of 5-hexenyl to cyclopentylmethyl. The latter case is feasible because nitroalkanes would have been produced, had electron transfer from the nitroalkane radical anion to 5-hexenylmercuric bromide been fast. Also, elimination of nitrite from nitroalkane radical anions has been documented in the literature (Kornblum et al. 1988).

4.2.3 Rationale for Production of Oximes

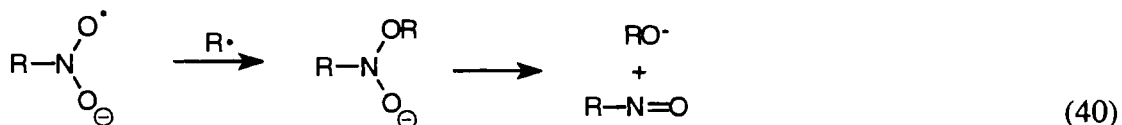
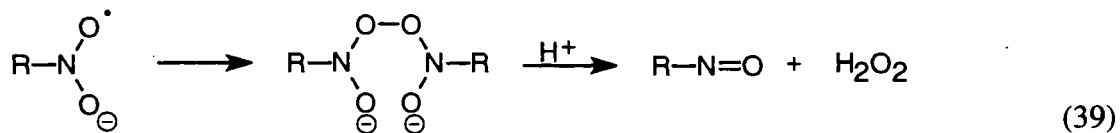
How the oximes form in these reactions is not completely understood, although they probably form from nitroso compounds. Primary and secondary nitroso compounds are unstable. They tautomerize to form oximes.



The nitroso compound can form more in than one way. Meisel et al. (1993) have discussed how a nitroso compound can form by combining an organic radical with nitric oxide. For this route to be operating in our experiments, nitrite ions would have to be reduced, perhaps by photo-excited organomercuric bromides.



Alternatively, photo-generated radicals might add to nitrite ions (equation 30) and then the resulting nitroanion radicals undergo further reduction to oximes, either by termination (equations 39 and 40), or other steps.



At this stage in the work, none these routes can be ruled out. Furthermore, the observation of mercury metal as a product (see Section 4.1.8) in the reaction indicates that additional mechanisms need to be considered.^(a)

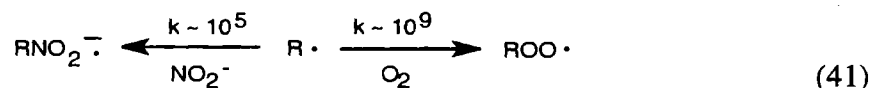
^(a)Note added before printing. Methyl-d₃-mercuric bromide has been detected in reactions run in DMSO-d₆. This finding indicates that DMSO and not organomercuric bromide reduces nitrite ion or the organic nitroanion radical in the above pathways.

5.0 Discussion

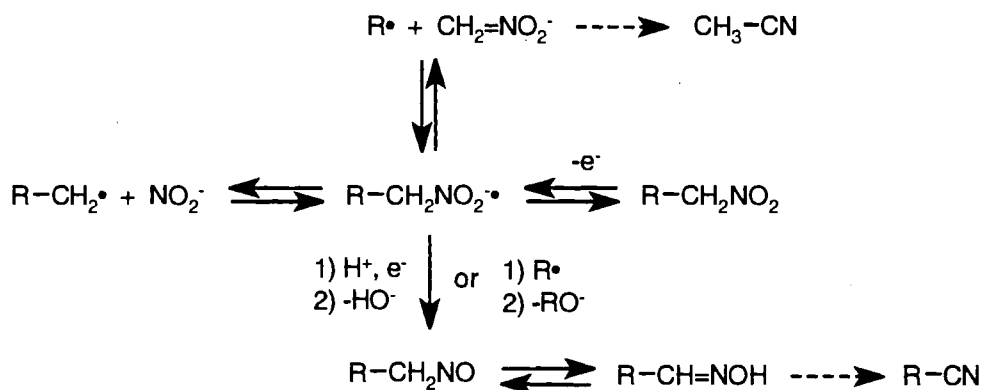
In this section of the report, experimental results presented in Sections 2,3, and 4 are integrated and discussed with respect to the insight they provide to waste tank safety issues.

5.1 Possible Role of Nitrite in Aging Mechanisms

Considering that nitrite is present in substantial concentrations in the tanks, the reaction of radicals with nitrite could play a dominate role in the initial steps of organic aging processes. As we pointed out in the bibliography, the O_2 concentration in the tank liquids is a key factor. If concentrations of nitrite are sufficiently high compared to O_2 concentrations, nitrite could be an effective trapping agent for free radicals. DBP and TBP can solubilize metal ions in hydrocarbon phases, carrying nitrite in along with the cation, so we expect that lipophilic radicals could be trapped by nitrite, too. Although trapping of radicals by O_2 is very fast ($\sim 10^9 M^{-1}s^{-1}$) (Thomas 1967), the concentration of O_2 is probably orders of magnitude lower than the concentration of nitrite such that trapping by nitrite could be competitive.



Thus, the subsequent reactions of the nitroanion become important in understanding the distribution of organic aging products. Electron transfer from the radical anion to O_2 , transition metals, or other electron acceptors would produce organic nitro compounds. Alternatively, further reduction of the nitroanion or combination/disproportionation with other radicals would produce oximes and aldoximes. Also, the nitroanion could scission a radical to produce the nitromethane aci anion and an n-1 carbon radical.

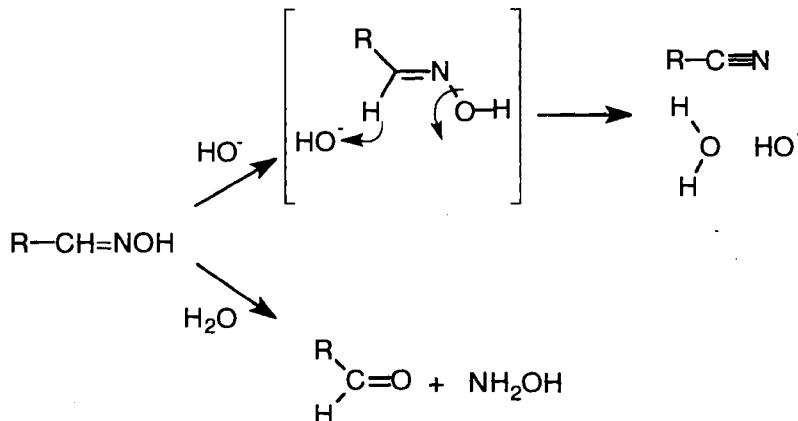


Scheme 5. Redox Chemistry of Organic Nitro Compounds

These various pathways all depend on the rate of electron transfer to an acceptor or from a donor. These rates depend both on the identities and concentrations of the various donor and acceptors that may be present in the tanks. Primary and secondary nitroalkanes are readily oxidized in alkaline media to carbonyl compounds and nitrite ion. So, if sufficient oxygen is present, then they should not build up.

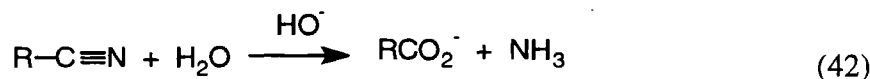
Meisel et al. (1993) have pointed out that the liquid phase of a tank should be oxygen depleted. Mass transfer between the head space and liquid phase of the tanks is thought to be too slow to replenish the oxygen that is consumed by radiolysis and redox reactions. Thus, under anoxic conditions, nitroanions formed by reactions of radicals with nitrite could, as we postulate in our model studies, suffer termination or disproportionation reactions leading to oximes.

Oximes and aldoximes hydrolyze, under alkaline conditions, to carbonyls and hydroxyl amines (March 1992). The possibility also exists that aldoximes could dehydrate to nitriles.



Scheme 6. Dehydration and Hydrolysis Reactions of Aldoximes

Nitriles are hydrolyzed in strong base to carboxylate anions and ammonia (March 1992). Although, being relatively volatile, they could escape hydrolysis in the vapor phase.



While the above scenario is speculative, it does provide a working hypothesis for explaining the mysterious origins of some gases and volatile organics emitted by the tank wastes.

In studies with simulated wastes, Meisel et al. (1993) reported that radiolytic production of N₂ and N₂O gas from nitrite required organics to be present. They postulated a multistep mechanism in which oximes, formed by reactions of radicals with NO, hydrolyzed to hydroxylamine and aldehydes or ketones. The hydroxylamine reacted with nitrite to produce N₂ and N₂O (Meisel et al. 1993). Our literature review and results from preliminary experiments suggest than reaction of

radicals with nitrite may provide an additional pathway to these gases, and ammonia as well.

In relation to Tank 241-C-103, nitriles have been observed in the tank vapor (Huckaby and Story 1994). We have seen that an oxime can decompose thermally to a nitrile. And, while nitriles hydrolyze in base to carboxylic acids and ammonia, their miscibility with hydrocarbons and volatility could allow for escape from the liquid phase. Accordingly, reactions of radiolytically generated radicals with nitrite or nitric oxide may explain the observation of small amounts of nitriles in the headspace of Tank 241-C-103 (Huckaby and Story 1994).

5.2 Relationship of Between Gas Production and Organic Aging

In our experiments with an organic tank simulant, gas production is predominantly induced radiolytically. Work with flammable gas simulants at ANL and PNL suggests that H₂ is, in part, from H atom abstracting H from organics and that production of N₂ and N₂O requires organic compounds to be present. Meisel et al. (1993) propose that these gases derive from reactions of organic radicals with NO which is generated by radiolysis of nitrate and nitrite. Radiolyses of our organic tank simulant generate predominantly N₂O, N₂, and H₂. Concurrent with gas generation we observed the disappearance of EDTA, TBP, DBP, and hexone. While disappearance of TBP would not have required radiation, it readily saponifies (Burger 1955), the other compounds probably reacted via radiolytic pathways. Thus, our product analyses are consistent with Meisel's mechanistic model.

We think that organic radicals may react directly with nitrite, as well, providing yet another route to oximes, nitro compounds, and possibly other C-N-containing compounds.

These mechanistic models have important implications for the Organic Tanks Safety Program. Key organic intermediates in the model are C-N bonded compounds such as oximes. As discussed above, oximes and nitro compounds decompose in strong base to yield aldehydes, ketones, and carboxylic acids (from nitriles). Thus, if the models are correct, then organic compounds reacting via these pathways are oxidizing to lower energy content.

6.0 Conclusions

Dodecane, a reasonable equivalent to NPH, appears to have degraded little under the conditions applied. Several explanations are possible, but at present it is most likely that these results are due to the relative greater susceptibility of the other organic compounds in the simulant to conditions of aging. The apparent order of "aging" is TBP>>EDTA, DBP, hexone>> dodecane, stearic acid. Perhaps as the more reactive organics are depleted, dodecane consumption will accelerate.

DBP is generated by the saponification of TBP within the first hours of any of the experiments run in this study. The DBP formed is not likely to saponify further to the monobutyl phosphate (Burger 1955). But the preliminary results from condensed-phase analyses suggest that radiolytically-induced decomposition occurs. Further, the lack of butenes in the vapor phase may show that radiolytic and radical-induced cleavage (see section 3.2) occurs at the phosphorus oxygen (O-P) bond rather than the carbon-oxygen bond (C-O).

Because of the early stage of the work, our conclusions are tentative; additional work is needed. The range of the experimental conditions of the γ irradiation experiments needs to be expanded to include reaction with both lower and higher total dose, radiation fluxes and temperatures. Also, experiments in which the distribution of organics in the simulant is varied should be examined. For example, are the organic solvents more or less reactive, if they are in a single phase atop the inorganic matrix? These additional data will increase our understanding of why dodecane is only marginally consumed in the experiments performed thus far.

The effect of the γ flux needs to be investigated. The assumption in this first set of irradiations was that the rate of irradiation would not change either the distribution or final products of "aging." Several experiments at lower dose rates need to be conducted to ascertain the validity of that assumption.

Experiments without any of the organic components need to be run to determine the rates and kinetics of H_2 generation for this simulant. The absence of N_2 , N_2O , and NO_x would confirm the results of others (Bryan and Pederson 1994; Meisel et al. 1993) that organic materials promote the formation of nitrogen-containing gases. Also, toward this end and establishing whether organic compounds are aging to more highly oxidized compounds, products formed in the irradiated simulant need to be identified. Additionally, irradiation experiments need to be performed in the absence of O_2 to understand the effect it has had on the experiments performed with it present in the head space above the simulant.

Experiments to determine the rate of reaction of nitrite with radicals have found oximes may be formed when radicals are generated in the presence of nitrite. While oximes are consistent with pathways in which radicals add to nitrite, additional work is needed to bolster this interpretation and obtain reaction rate data. Determining rates for the classes of radicals produced from the organics in the tanks would provide an understanding of the relative importance of this aging pathway. With this objective in mind, both competitive and absolute methods for measuring reaction rate constants should be pursued.

Under the TWRS program plan, this project will continue through FY 1996. We plan to address fully the above needs during this time, provided that funding levels for this project and the Organic Analytical Support project are maintained at the planned levels. By the end of FY 1996, we expect that a coherent picture of aging will emerge from the planned work, which will include integrating the results of all extant waste aging work (both complexants and solvents) at a programmatic level.

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