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# NITROUS OXIDE PRODUCTION FROM RADIOLYSIS OF SIMULATED HIGH-LEVEL NUCLEAR WASTE SOLUTIONS

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## ABSTRACT

Nitrous oxide gas ($N_2O$) is produced by the radiolysis of aqueous nitrate or nitrite solutions in the presence of organic compounds. When ethylenediaminetetraacetic acid (EDTA) or N-(2-hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA) is present, the G-value for hydrogen increases and $N_2O$ becomes the major gaseous product (G = 0.54). A survey of organic compounds indicates the amount of $N_2O$ formed depends on the structure of the organic. With highly oxidized organics (carbonate, formate, acetate and oxalate), little or no $N_2O$ is formed. Aromatic and aliphatic organics (sodium tetraphenylborate, benzene, phenol, n-paraffin, and tributylphosphate) produce small amounts of $N_2O$. Water soluble, easily oxidized organics (methanol, ethanol, isopropanol, *n*-butanol, acetone, and ethylene glycol) produce large amounts of $N_2O$ relative to the previous two categories. Nitrous oxide production is not greatly affected by pH between neutral and pH = 13, but increases significantly in acid solution. The G-value for $N_2O$ production in 10 wt % potassium tetraphenylborate slurries has been measured under process conditions important at the Savannah River Site.

## INTRODUCTION

High-level radioactive waste solutions resulting from processing nuclear materials are stored as aqueous slurries in large underground tanks. These solutions contain nitrates, nitrites, and in some cases organic materials. It is known that these solutions produce $H_2$ and $O_2$ by radiolysis of water, and nitrate is radiolytically reduced to nitrite. Recently, it has been found that $N_2O$ can be produced, but this has not been investigated in detail. This paper describes the initial results of our investigation into the radiolytic production of $N_2O$ from nuclear waste solutions.

The Savannah River Site (SRS) is planning to begin a new decontamination process for liquid high-activity wastes starting in 1992.[1] The process uses an organic precipitating agent, sodium tetraphenylborate, to remove cesium-137 from the wastes. The precipitate will be stored in a million-gallon, carbon steel waste tank until it is sent to the Defense Waste Processing Facility (DWPF) where it will be intentionally decomposed and the cesium-137 will be incorporated into borosilicate glass. During the storage period, sodium nitrite will be added to the precipitate to prevent tank corrosion. Due to the radioactive decay of the Cs-137, the slurry will undergo radiolytic decomposition. The nitrite reacts in the presence of the organic precipitate and the radiation to produce nitrous oxide gas. This reaction is important because it consumes the corrosion inhibitor and because it produces an oxidizing gas ($N_2O$). The tank in which the precipitate is stored is inerted with nitrogen gas to preclude inadvertent combustion of any dry precipitate on the walls of the tank. It is important to know how rapidly the nitrous oxide gas is produced since it can substitute for oxygen in the combustion of organics. For these reasons, the reaction of nitrite ion in the presence of organic compounds and radiation was studied.

## EXPERIMENTAL

Simulated nuclear waste solutions were prepared containing NaOH, $NaNO_3$, and $NaNO_2$. The solutions were placed in sealed bottles and irradiated with Co-60 gamma rays. The dose rate was determined with the Fricke dosimeter or with thin film dosimeters containing a radiochromic dye (Far West Technologies, Goleta, CA). The optical density of the the film dosimeters was measured on a Hitachi Model 200 UV/VIS spectrophotometer. The dose rates varied from $3\times10^4$ rads/hr to $3\times10^6$ rads/hr. Gases produced by the radiolysis were collected by the Van Slick apparatus or by sampling the void space above the solution with a syringe. The gases were analyzed by gas chromatography. Nitrous oxide was separated in a Varian Vista 6000 GC or a Varian Model 3400 GC using a Chromosorb-101 column(80/100 mesh, 2 meter x 1/8 inch). Other gases were separated in a Varian Model 3400 GC using a molecular sieve 13X column (45/60 mesh, 6 ft x 1/8 inch). Solutions were analyzed for nitrate and nitrite by ion chromatography using a Dionex Advanced Chromatography Module with an AS-4A separation column and AG-4A guard column. The samples were eluted with $NaHCO_3/Na_2CO_3$ solutions and nitrate and nitrite were detected by conductivity.

In some tests the effect of various organic compounds on the rate of production of $N_2O$ was investigated. In these tests, 20 mL of a solution containing 0.5 molar $NaNO_3$ and 0.5 molar organic was irradiated to a dose of 37 megarads in a 60 mL sealed vial. In some cases, a two-phase system was irradiated because of the low solubility of the organic compound in water (benzene, phenol, *n*-paraffin, and tributylphosphate).

## RESULTS AND DISCUSSION

### Radiolytic $H_2$, $O_2$, and $N_2O$ yields in the absence and presence of organics

When a simulated alkaline waste solution ($[NaNO_3]=2.8$ M, $[NaNO_2] = 2.2$ M, and $[NaOH] = 2.0$ M) was irradiated, $O_2$ and $H_2$ were produced with G-values (molecules produced per 100 eV of energy absorbed) of 0.068 and 0.031, respectively (Fig. 1). These results are consistent with published values for the radiolysis of nitrate solutions.[2] Hydrogen is produced by radiolysis of the water and oxygen by direct radiolysis of the dissolved nitrate ion. When an organic complexing agent such as EDTA or HEDTA was added (0.085 M), the G-value for $H_2$ increased to 0.062 and $N_2O$ was produced with a value of 0.54, making it the most abundant gaseous species(Fig. 2). This solution composition is similar to that expected from Hanford wastes containing complexant. When the organics were present, oxygen was not produced by radiolysis. In fact, oxygen was depleted from the gas phase, presumably by reaction with organic radicals produced in the solutions. The higher G-value for $H_2$ probably results from radiolytically produced H atoms reacting with the organic.

### Survey of organic compounds that produce $N_2O$ from the radiolysis of nitrate solutions.

Nitrous oxide is produced by the radiolysis of aqueous nitrate or nitrite solutions in the presence of a variety of organic compounds. A survey of organic compounds was made to determine the effect of the organic structure on the amount of $N_2O$ formed. The results are shown in Table I. All tests were run at the same initial nitrate and organic concentration (0.5 M) and were given the same dose in sealed vials. The results may be used as a coarse comparison between organic compounds but small differences may not be significant.

TABLE I. Nitrous Oxide Produced in Presence of Organics

| | | Concentration (vol %) | | | |
|---|---|---|---|---|---|
| Organic | N2O | H2 | O2 | CO | CO2 |
| $Na_2CO_3$ | 0.0 | 4.5 | 39.0 | 0 | 0 |
| NaFormate | 0.0 | 13.8 | 15.7 | 0 | 0 |
| $Na_2$Oxalate | 0.0 | 4.5 | 26.0 | 0 | 0 |
| $K_2$Oxalate | 0.03 | 5.6 | 27.0 | 0.6 | 0.7 |
| NaAcetate | 0.08 | 6.0 | 12.0 | 0.2 | 4.8 |
| NaTetraphenylborate | 0.30 | 6.8 | 7.8 | 0 | 0 |
| benzene | 0.60 | 7.2 | 6.0 | 0 | 0 |
| phenol | 0.20 | 6.4 | 6.1 | 0 | 0 |
| tributylphosphate | 0.42 | 14.2 | 1.0 | 0.7 | 4.3 |
| *n*-paraffin | 0.12 | 18.2 | 1.0 | 0.4 | 3.3 |
| acetone | 3.7 | 7.0 | 6.9 | 0 | 12.8 |
| methanol | 10.9 | 8.4 | 4.0 | 0 | 6.4 |
| ethanol | 4.3 | 11.9 | 6.9 | 0.2 | 1.3 |
| isopropanol | 0.75 | 15.6 | 9.1 | 0.05 | 0.05 |
| *n*-butanol | 3.5 | 14.5 | 4.8 | 0.3 | 0.1 |
| *tert*-butanol | 1.3 | 8.3 | 8.8 | 0.1 | 0.3 |
| ethylene glycol | 7.7 | 8.6 | 5.7 | 0.4 | 5.9 |
| EDTA | 1.9 | 24.3 | 9.8 | | |

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*All tests run at 0.5 M $NaNO_3$ and 0.5 M organic (or 2.0 g organic if the molecular weight was not defined) in water. The samples (20 mL) were placed in 60 mL serum vials, sealed, and irradiated to a total absorbed dose of 37 megarads at a dose rate of $4x10^5$ rads/hr.

The $N_2O$ yields fall into three ranges which correlate with characteristics of the organic compounds. The lowest yields are obtained with highly oxidized organics, such as sodium salts of carbonate, formate, acetate, and oxalate. Under the test conditions, less than 0.1 vol % $N_2O$ was found in the vapor space of the sample container. This yield corresponds roughly to G-values smaller than 0.002 molecules per 100 eV.

Intermediate yields (0.1 to 0.7 vol %) were obtained with aromatic or aliphatic organics such as sodium tetraphenylborate (NaTPB), potassium tetraphenylborate (KTPB), benzene, phenol, *n*-paraffin, and tributylphosphate. These yields correspond to G-values of 0.002 to 0.02 molecules/100 eV. Except for the NaTPB, these compounds form two phase systems at the concentrations studied. The low yields of $N_2O$ may be due to poor contact between the insoluble organic and the aqueous nitrate phases during radiolysis. With phenol, it was possible to add sodium hydroxide to dissolve the phenol. The resulting alkaline, single-phase system yielded slightly less $N_2O$ than did the two-phase system, but this may be due to differences in pH (see below).

The highest $N_2O$ yields were obtained with easily oxidized, water soluble organics such as acetone, methanol, ethanol, isopropanol, *n*-butanol, *tert*-butanol, and ethylene glycol. Nitrous oxide was found at concentrations of 0.7 to 11. vol %, corresponding to G-values greater than 0.01 molecules/100 eV.

Ethylenediaminetetraacetic acid (EDTA) is not structurally similar to the previously mentioned groups, but it produced $N_2O$ in the high-yield range (1.9 vol %). Sodium hydroxide had to be added to the EDTA to dissolve it in water and form a single phase system. Although the pH was not measured, the solution may have been acidic which could significantly increase $N_2O$ production (see below). EDTA did not produce $N_2O$ when irradiated without nitrate or nitrite present.

**Effect of pH**

Acidic conditions increase the amount of $N_2O$ formed but strongly alkaline conditions do not appear to have much affect compared to neutral solutions. Table II lists some comparisons for solutions containing NaTPB or phenol. For both of these organics, little difference was observed between neutral solutions and 0.1 molar hydroxide. However, phenol in an acidic solution (0.1 M HNO3)

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TABLE II. Effect of pH on $N_2O$ Formation

| Organic | | Concentration (vol %)<br>N2O | H2 | O2 | CO2 |
|---|---|---|---|---|---|
| NaTPB | | | | | |
| | neutral | 0.21 | 8.0 | 8.3 | 00.1 |
| | 0.1 M NaOH | 0.17 | 8.3 | 4.1 | 0.0 |
| Phenol | | | | | |
| | 0.1 M $HNO_3$ | 2.4 | 3.2 | 7.1 | 0.3 |
| | neutral | 0.14 | 3.7 | 11.4 | 5.6 |
| | 0.1 M NaOH | 0.10 | 3.3 | 13.4 | 11.4 |

produced an order of magnitude more $N_2O$ gas than in neutral or alkaline solution. The reason for this increase is being investigated.

### $N_2O$ Production from Potassium Tetraphenylborate Slurries

At the Savannah River Site, the major interest in the $N_2O$ production rate is for slurries of potassium tetraphenylborate (KTPB) that contain Cs-137 precipitated from supernates in the waste tanks. The $N_2O$ yield for a nitrate and nitrite solution containing 10 weight percent KTPB slurry is shown in Figure 3. The G-value for $N_2O$ production from radiolysis of this slurry is 0.15 molecules/100 eV. $N_2O$ production at this rate in the actual SRS tanks will not create a hazard since they are already ventilated to reduce the concentration of radiolytically produced hydrogen.

### $NO_3^-$ and $NO_2^-$ Changes During Radiolysis of KTPB Slurries

Because this slurry will be present in two waste tanks at SRS, we investigated the radiolytically produced changes in nitrate and nitrite concentrations in the slurry. Results of typical experiments in the absence and presence of KTPB are shown in Fig.4. From the slopes of the lines at low doses it can be seen that the presence of the organic greatly increases the rate of disappearance of $NO_3^-$ and the production of $NO_2^-$. In the absence of organic, the rates of disappearance of $NO_3^-$ and the production of $NO_2^-$ are equal as expected. This still appears to be true at low doses in the presence of the KTPB. With larger doses in the presence of KTPB, the concentration of $NO_3^-$ goes to zero and the concentration of $NO_2^-$ begins to decrease linearly. It appears that the concentration of $NO_2^-$ also approaches zero. Determination of all the products has not been performed yet, but nitroaromatic compounds have been identified[3] as well as $N_2O$. In some recent tests we have also detected small amount of $NH_3$. Further tests are in progress.

These results are directly applicable to the storage of high level nuclear wastes containing organics in mild steel tanks. In these tanks, nitrite is necessary to inhibit the corrosion of the tank. If nitrite is consumed by radiolysis in the presence of the organic, then nitrite will have to be periodically replaced to continue to prevent tank corrosion.

## CONCLUSIONS

The results presented in this paper support the following conclusions:

- $N_2O$ can be produced by radiolysis of nuclear waste solutions when organics are present.
- The yield of $N_2O$ is dependent on the structure of the organic. Soluble aliphatic compounds produce the largest yields of $N_2O$.

- The presence of tetraphenylborate enhances the radiolytic reduction of both $NO_3^-$ and $NO_2^-$. At large radiation doses, both of these anions disappear from the solution.

## ACKNOWLEDGMENT

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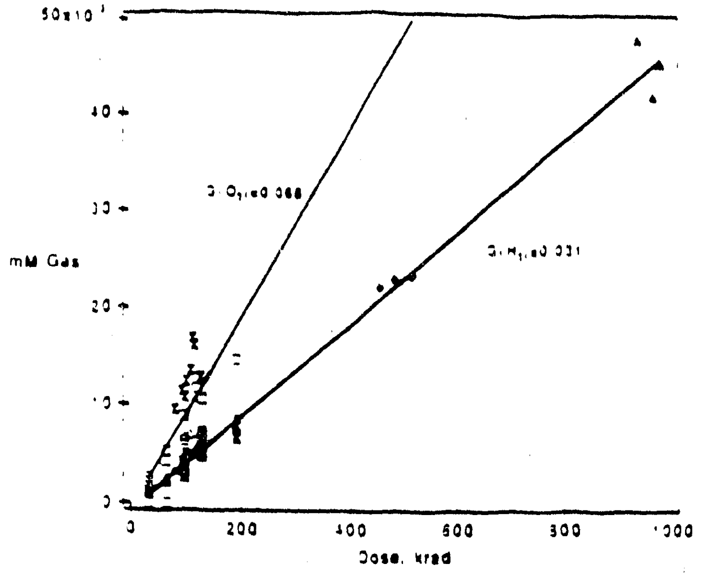
FIGURE 1. Hydrogen and Oxygen Production from Co-60 Gamma Radiolysis of a Simulated Nuclear Waste Solution. (NaOH=2.0 M, $NaNO_3$=2.8 M, $NaNO_2$=2.2 M, and $NaAlO_2$=1.3 M)

FIGURE 2. Nitrous Oxide and Hydrogen Production from Co-60 Gamma Radiolysis of a Simulated Nuclear Waste Solution Containing Organic. (NaOH=2.0 M, $NaNO_3$=2.8 M, $NaNO_2$=2.2 M, $NaAlO_2$=1.3 M and 0.085 M HEDTA and EDTA)

FIGURE 3. Nitrous Oxide Gas Yield from Co-60 Gamma Radiolysis of a 10 wt % Potassium Tetraphenylborate Slurry Containing 1.9 M $NaNO_3$, 1.6 M NaOH, and 0.75 M $NaNO_2$.

FIGURE 4. Nitrate and Nitrite Changes during Co-60 Gamma Radiolysis of a Simulated Nuclear Waste Solution in the Absence and Presence of 10 wt% KTPB Precipitate.
- - - , KTPB Absent; ------, KTPB Present.



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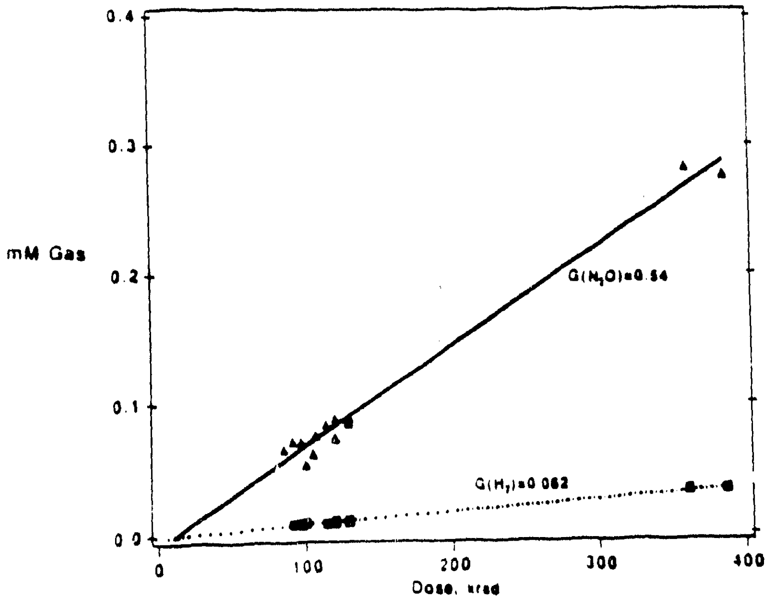

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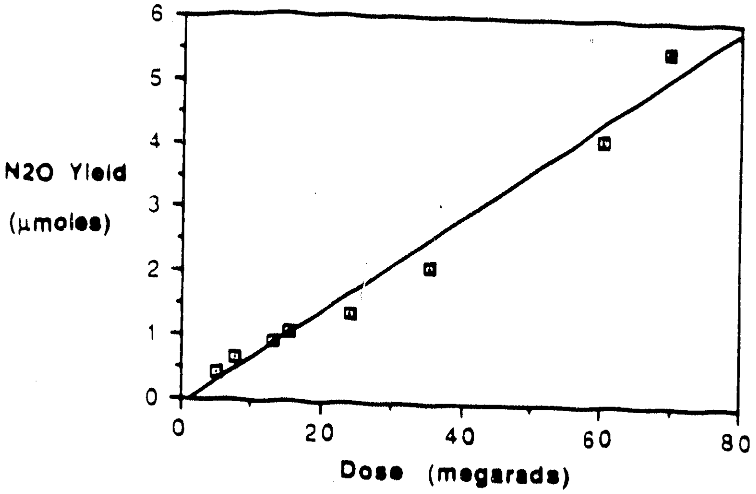

FIGURE 3. Nitrous Oxide Gas Yield from Co-60 Gamma Radiolysis of a 10 wt % Potassium Tetraphenylborate Slurry Containing 1.9 M $NaNO_3$, 1.6 M NaOH, and 0.75 M $NaNO_2$.

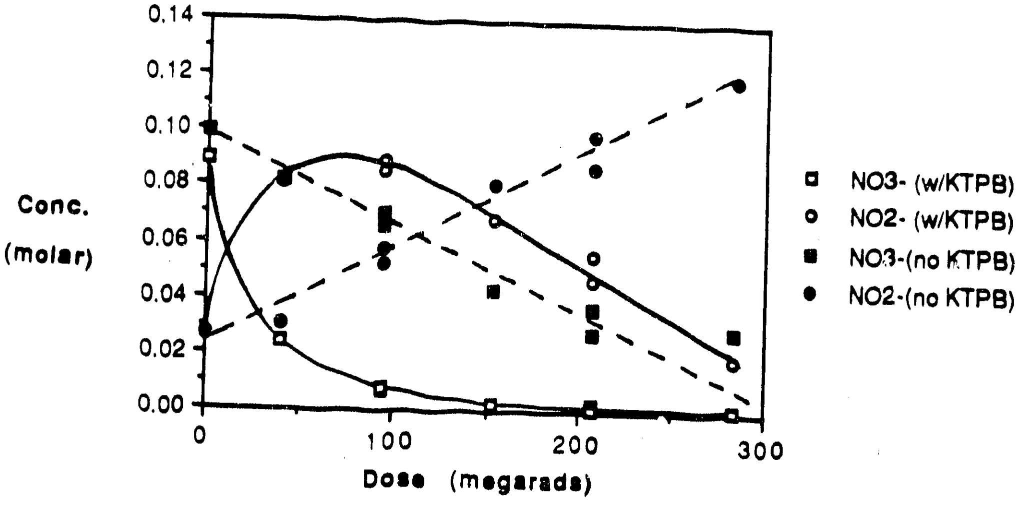

FIGURE 4. Nitrate and Nitrite Changes during Co-60 Gamma Radiolysis of a Simulated Nuclear Waste Solution in the Absence and Presence of 10 wt% KTPB Precipitate. - - - , KTPB Absent; ———, KTPB Present.

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