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ALPHA RADIOLYSIS OF PLUTONIUM (IV)-
NITRIC ACID SOLUTIONS

J. C. Sheppard

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NITRIC ACID SOLUTIONS

By

J. C. Sheppard

Applied Chemistry Section
Chemistry and Chemical Engineering Department

May 1968

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ABSTRACT

Some of the factors influencing the radiolytic generation of gases from plutonium-nitric acid solutions have been investigated. It has been found that small but significant amounts of oxygen and hydrogen are generated. The "G" values decrease with increasing nitric acid concentration, are independent of the temperature, and are slightly affected by the atmosphere over the solution. The influence of polyethylene, iron (111), and small concentrations of butyl alcohol have slight but measurable effects on the rate of radiolytic gas generation. It was found that a palladium catalyst can control the pressure buildup over a plutonium(IV)-4M nitric acid solution for about 4 weeks. Equations are given to calculate the pressure buildup as a function of free volume over the plutonium solution and the isotopic composition of the plutonium.

TABLE OF CONTENTS

ABSTRACT.	iii
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	4
RESULTS	5
Nitric Acid Dependence	5
Temperature Dependence	8
Effect of Argon and Oxygen on the Rate of Gas Generation	9
Effect of Iron(III) on the Rate of Gas Generation	10
Effect of Polyethylene	10
Organic Impurities	11
Catalytic Combination of Hydrogen and Oxygen	13
CONCLUSIONS	15
ACKNOWLEDGEMENTS.	16
APPENDIX A	A-1
REFERENCES	Ref-1
DISTRIBUTION	Distr-1

ALPHA RADIOLYSIS OF PLUTONIUM(IV)– NITRIC ACID SOLUTIONS

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INTRODUCTION

There have been reports of the pressurization and subsequent rupture of polyethylene shipping bottles containing nitric acid solutions of plutonium.⁽¹⁾ Radiolytic generation of gases is believed to be the source of the pressurization, but experimental evidence is conflicting.⁽²⁾ The aim of this study was to determine the "G" values for any gases, such as oxygen and hydrogen, which may be formed to provide quantitative means of predicting pressure buildup for a given set of conditions. The following section is a brief review of some important considerations with respect to the plutonium - nitric acid system and the radiolytic generation of gases.

Radiolytic reduction of the higher oxidation states has been observed for aqueous solutions of plutonium,^(3,4) americium,⁽⁵⁻⁸⁾ and neptunium.⁽⁹⁾ These studies indicated that the rate of reduction was proportional to the total metal ion concentration; therefore, all these reactions obey the relationship

$$\frac{-d[M(VI)]}{dt} = k[M]_{\text{tot}} \quad (1)$$

Presumably, these higher oxidation states are reduced by the H radical or hydrogen peroxide generated by the alpha radiolysis of water. The former generates hydrogen ion and the latter, oxygen. The respective reactions are shown below.

and

Several investigators⁽¹⁰⁻¹²⁾ have noted that oxygen is the principal gaseous radiolytic product of plutonium(VI) - nitric acid solutions. A small amount of hydrogen is also generated.

The source of H and H₂O₂ comes from the alpha radiolysis of water the primary reactions are believed to be

and to a lesser extent

This set of reactions suggests that some oxygen should be independently generated and some should come as a result of reaction three. As seen from reaction (2), the actinide ion has the potential to act as an H radical scavenger and thereby reduce the amount of molecular hydrogen gas evolved. Other radiolytic reactions will generate gaseous nitrogen and nitrous acid in nitric acid and they too must be considered.

Plutonium disproportion action reactions⁽⁴⁾ must also be considered because they are sources of plutonium(VI). These reactions are

and

High hydrogen ion concentrations favor the stabilization of the plus four oxidation state of plutonium, and it is further stabilized by complex formation with nitrate ion and other complex formation with nitrate ion and other complexing anions through reactions of the type

These reactions then must be considered as an integral part of the radiolytic reactions which give the final products because they play an important part in the generation of gaseous oxygen and hydrogen.

As mentioned above, it is the radiolysis of water that is the beginning of a chain of chemical reactions which ultimately results in the generation of the gaseous end-products. Furthermore, the amount of gaseous products formed should be directly proportional to the radiation dose, or energy absorbed by the system. The source of energy comes from the kinetic energy of the alphas emitted by the plutonium isotopes. The following equations result from the preceding discussion.

$$\begin{aligned} & (\text{Specific Activity of Pu}) \times (\text{grams of Pu}) \\ & \times (\text{Energy per disintegration.}) \\ & \times \frac{G_T}{100} = \text{rate of gas generation} = \frac{dn}{dt} \end{aligned} \quad (11)$$

where G_T is the total number of gas molecules evolved per hundred electron volts of energy absorbed by the system. In other words, G_T is an efficiency factor for the production of radiolytic gases under the conditions described above. For a constant volume system, such as a bottle containing a plutonium solution, the equation below applies if the gases behave ideally and their aqueous solubilities are small.

$$\frac{G_T}{100} \times g_{\text{Pu}} \times \frac{dE}{dt} \times t = \frac{P_t V}{RT} . \quad (12)$$

This equation can be rearranged to a more convenient form

$$P_t = \frac{G_T}{100} \times g_{\text{Pu}} \times \frac{RT}{V} \times \frac{dE}{dt} \times t, \quad (13)$$

where V is the volume over the solution; R , the gas constant; T , the absolute temperature; P_t , the pressure at time, t and $\frac{dE}{dt}$ the number of electron volts released per gram of plutonium

per unit time. For a given condition, a plot of P_t against t should yield a straight line having a slope

$$\frac{G_T}{100} \times g_{Pu} \times \frac{RT}{V} \times \frac{dE}{dt} \quad (14)$$

Since g_{Pu} , R , T , V , and $\frac{dE}{dt}$ are known, G_T can be obtained.

EXPERIMENTAL PROCEDURE

The reaction vessels for these experiments were calibrated bottles with an attached mercury manometer and side arms for the removal of gas samples. Experiments were performed in the following way. A known volume of a plutonium(IV) nitrate - nitric acid solution was added to the reaction vessel and the free volume was taken as the difference between the total volume of the vessel and the volume of solution added. The system was then closed and the pressure buildup was measured as a function of time (absorbed dose) with a cathetometer. As seen in Equation (12), a plot of P_t against time should yield a straight line

having a slope $\frac{RTg_{Pu}}{V} \frac{G_T}{100} \times \frac{dE}{dt}$. Since R , T , V , g_{Pu} and $\frac{dE}{dt}$ are known, G_T can be obtained. Gas samples were subsequently removed at the end of the experiment and analyzed by the use of mass spectrometer for O_2 , H_2 , N_2 , NO , CH_4 , CO , and CO_2 . Once the composition of the gas sample was known, individual G values were obtained for those gases present. Samples of the aqueous phase were taken to determine the plutonium concentration by coulometric analysis and nitric acid concentrations by standard titration techniques. Oxidation states were determined spectrophotometrically by the use of a Cary Model 14 Spectrophotometer.

Data for a typical run are shown in Figure 1. The curve is corrected for the volume change in the manometer and shows that Equation (12) is obeyed over the pressure range studied. Since the pressure can be measured to 0.1 mm of mercury, the major

FIGURE 1. *Pressure Buildup as Function of Time (Dose)*

RESULTS

NITRIC ACID DEPENDENCE

These experiments were done with the aim of determining the influence of nitric acid concentration on the rate of gas evolution. If the plutonium(IV) disproportionation equilibrium is important, the G value for oxygen should drop sharply with increasing nitric acid concentration. The results of these experiments are summarized in Table I and shown graphically in Figure 2.

TABLE I. Effect of Nitric Acid Concentration

Experiment	$[\text{HNO}_3]$	$[\text{Pu}]_{\text{tot}}$	G_T^d	$G(\text{O}_2)$	$G(\text{H}_2)$	$G(\text{N}_2)$
1	1.0M	0.244M	0.56	0.21	0.28	0.06
2	2.4	0.487	0.264	0.12	0.13	0.01
3	4.2	0.466	0.096	0.030	0.059	0.004
4	4.2	0.466	0.088	a	-	
5	4.0	0.992	0.096	b	-	
6	6.6	0.470	0.073	0.017	0.057	
7	6.6	0.470	0.073	a	-	
8	8.0	0.467	0.039	0.009	0.024	0.005
9	10.0	0.496	0.021	c	-	

- a. Experiments 4 and 7 are repeats of 3 and 6. The duration of each experiment was for about one month.
- b. Ten times as much plutonium was used in this experiment as in experiment 3.
- c. The rate of pressure buildup was too low to collect a gas sample for analysis.
- d. The plutonium used in these experiments contained 7.5 to 8.4% ^{240}Pu and about 0.03% ^{238}Pu . These G_T values have been corrected for these contributions and represent those for pure ^{239}Pu . An equation for the calculation of pressure buildup as a function of isotopic composition appears in Appendix A.
- e. The sum of the individual G values compared to G_T give an indication of the material balance for a given experiment.

As seen in Figure 2, $G(\text{O}_2)$ does decrease with increasing nitric acid but not as rapidly as one would predict from reaction (4). This may be due to a combination of other reactions such as

FIGURE 2. G Values Versus Nitric Acid Concentration

The decrease of $G(\text{H}_2)$ with increasing nitric acid concentration may be attributed to H radical scavenging by nitrate ion. The reaction sequence may be

It is interesting to note that the $G(H_2)$ values reported in Table I agree with those found by Bakh, et al,⁽¹³⁾ while those for oxygen do not. The $G(N_2)$ values are very low but agree reasonably well with those of Sowden.⁽¹⁴⁾ With the exception of carbon dioxide, which was a contaminant, the only other gas noticed was nitric oxide and its yield was another order of magnitude lower than nitrogen.

Analysis of these solutions for plutonium and nitric acid before and after these experiments indicated that no appreciable change (less than 1%) took place in a period of two months. Spectrophotometric analysis of these solutions indicated the presence of only plutonium(IV), since the spectra obtained corresponded to those found by Ryan.⁽¹⁵⁾ Spectrophotometric evidence was not found for either plutonium(VI) or plutonium(III), indicating one or more of the following:

1. Very little plutonium(IV) had disproportionated,
2. Nitrate ion complexing further stabilizes plutonium(IV),
3. Radiolytically generated hydrogen peroxide is oxidizing plutonium(III) and reducing plutonium(VI).

In addition, these results suggest that plutonium(III) may be oxidized by radiolytically formed nitrous acid and hydrogen peroxide.

TEMPERATURE DEPENDENCE

The temperature dependence on the rate of gas generation was studied at three temperatures. The results shown in Table II indicate that there is essentially no temperature effect on either the rate of gas evolution or composition, and indicate that the rate determining step is the radiolysis reaction itself.

TABLE II. *Temperature Effect on the Rate of Radiolytic Gas Generation*

<u>Temperature, °C</u>	<u>4.0 M HNO₃</u>	
	<u>G(O₂)</u>	<u>G(H₂)</u>
10.5	0.033	0.054
25.0	0.030	0.059
34.0	0.027	0.058

EFFECT OF ARGON AND OXYGEN ON THE RATE OF GAS GENERATION

Oxygen is known to participate in many radiolytic reactions by acting as a radical scavenger,⁽¹⁶⁾ through reactions such as $H + O_2 = HO_2$. The HO_2 radical can then react with itself to form molecular oxygen and hydrogen peroxide. Two experiments were done to determine what effect changes in atmospheric composition over the plutonium-nitric acid solutions would have on the total G value. The first of these involved the substitution of argon for the normal air atmosphere, and in the second, a pure oxygen atmosphere was used. The results of these experiments are shown in Table III.

TABLE III. *Effect of Atmosphere on Total G Values for Gas Evolution*

<u>Experiment</u>	<u>[HNO₃]</u>	<u>Atmosphere</u>	<u>G_T</u>
1	4.0	Air	0.097
2	4.0	Argon	0.12
3	4.0	Oxygen	0.06

These results indicate that there is significant contribution to the radiolytic gases which come through the reaction of the H radical with dissolved oxygen. Further experiments would be necessary to explain these results in detail.

EFFECT OF IRON(III) ON THE RATE OF GAS GENERATION

Iron salts catalyze the decomposition of hydrogen peroxide.⁽¹⁷⁾ Elson⁽¹⁸⁾ has also shown that 10^{-2} M iron(III) in plutonium(IV) - nitric acid solutions significantly increases the rate of the decomposition of hydrogen peroxide. One experiment was done to determine the effect of a 10^{-3} M iron(III) on the rate of gas evolution from a 1 M plutonium(IV) - 4.5 M nitric acid solution. The results of this experiment are shown in Table IV. These experiments indicate that there is no observable effect of 10^{-3} M iron(III), since the G_T 's are the same and the gas composition is close to that found for the 4.0 M conditions.

TABLE IV. *Effect of Iron(III) on rate of Radiolytic Gas Generation*

<u>Experiment</u>	<u>[Fe(III)]</u>	<u>[HNO₃]</u>	<u>G_T</u>	<u>G(O₂)</u>	<u>G(H₂)</u>	<u>G(N₂)</u>
1	-	4.5	0.074	-	-	-
2	10^{-3} M	4.5	0.074	0.022	0.043	0.007

EFFECT OF POLYETHYLENE

These experiments were performed to determine the influence of polyethylene on the rate and composition of the radiolytic gases. The results of these experiments are shown in Table V.

TABLE V. *The Influence of Polyethylene on the Rate and Composition of Radiolytic Gases*

<u>Experiment</u>	<u>[HNO₃]</u>	<u>Polyethylene Area, cm²</u>	<u>G_T</u>	<u>G(O₂)</u>	<u>G(H₂)</u>
1	4.0 M	0	0.093	0.030	0.059
2	4.0	570 ^{a,b}	0.072	-	-
3	4.0	500 ^{a,c}	0.093	0	0.090
4	4.0	550 ^{a,d}	0.084	0.007	0.071

- a. These areas are about twice that for a polyethylene bottle which might be used for these experiments
- b. Polyethylene tubes
- c. Polyethylene sheet
- d. Linear polyethylene tubes

The results of these experiments show that polyethylene significantly alters the composition of radiolytic gases and suggests that the polyethylene is behaving like a radical scavenger. Possible reactions are shown below:

and

The first reaction removes OH radicals which form H_2O_2 and ultimately react with plutonium(VI) to generate oxygen. Another explanation of these results is that the OH and H radicals are reacting with the water soluble part of the polyethylene binder.

ORGANIC IMPURITIES

Trace amounts of organic compounds dissolved in the plutonium - nitric acid solutions are potential sources of radiolytic gases and pressurization of vessels. Likely sources of these compounds are the hydrolysis and radiolysis products of tributylphosphate (TBP) and anion exchange resins. Butyl alcohol is the most likely hydrolysis and radiolysis product of TBP while primary, secondary, and tertiary amines will be the analogous products for the anion exchange resins. For one experiment a 4.4 M nitric acid—0.5 volume percent n-butyl alcohol-plutonium(IV) solution was used to determine the effect of an organic material. A rapid initial reaction, lasting about a day, evolved NO_2 , which indicates that nitric acid was being reduced by the butyl alcohol. The most likely net reaction is

After the initial reaction, the rate of gas evolution corresponded to a G_T of 0.060, which is lower than the 0.080 found for a 4.5 M nitric acid - plutonium(IV) solution. Mass spectrographic analysis of the gas yielded the information in Table VI.

TABLE VI. *G Values for a 4.4 M Nitric Acid - 1 M Plutonium(IV) - 0.5 Volume Percent n-Butyl Alcohol Solution*

<u>G(O₂)</u>	<u>G(H₂)</u>	<u>G(N₂)</u>	<u>G(CO₂)</u>
-0.012	0.048	0.007	0.014

The G values for hydrogen and nitrogen are those found for a 4.5 M nitric acid - plutonium(IV) solution, but the negative $G(O_2)$ indicates that oxygen had been consumed either by radiolysis or by chemical reaction with plutonium(III), if present. Plutonium(III) may come from the reduction of plutonium(IV) by butyl aldehyde formed during the initial reaction. The appearance of carbon dioxide is indicative of the radiolysis or chemical degradation of n-butanol and its products. No mass spectrographic evidence was found for either methane or carbon monoxide. Methane is a likely radiolysis product of the terminal methyl group of all these compounds.

As mentioned above, aliphatic amines might be expected to behave chemically and radiolytically like anion exchange resin fragments. Since nitrous acid is formed from the radiolysis of nitric acid solutions,⁽¹⁹⁾ the following reaction is expected for primary amines:

Therefore the initial reaction should form nitrogen and an alcohol. Subsequent reactions involve the chemical oxidation of the alcohol to form an aliphatic acid, and finally the radiolytic degradation of the aliphatic acid. The distribution of reaction products should be those for the n-butyl alcohol experiment. Secondary and tertiary amines should not react

chemically with the nitrous acid, but the radiolysis products should be similar to those found in the n-butyl alcohol experiment.

CATALYTIC COMBINATION OF HYDROGEN AND OXYGEN

One exploratory experiment was done to determine if it is feasible to catalytically recombine the radiolytically generated hydrogen and oxygen gases, since it has been known^(20,21) for some time that platinum catalyzes this reaction at room temperature. Furthermore, Rosenblatt⁽²²⁾ has shown that palladium deposited on aluminum oxide or zirconium oxide catalyzes the recombination of hydrogen and oxygen. This catalyst is found in the "Deoxo" hydrogen gas purifier made by Englehart Industries. In this experiment 10 g of pellets from a "Deoxo" hydrogen gas purifier were placed in a chamber over a plutonium-nitric acid solution and the pressure buildup was followed for more than a month. Figure 3 shows the result of this experiment. The initial pressure increase is due to the vapor pressure of water and possibly also to the oxides of nitrogen in equilibrium with the nitric acid. The pressure then held steady for five days.

At this time the stopcock which separated the catalyst from the rest of the system was closed and the pressure was allowed to build up for ten days. On the seventeenth day the stopcock was opened and the catalyst was once again in contact with the radiolytic hydrogen and oxygen which had been produced. The pressure then fell to the initial steady state pressure in about 6 hr, and remained at this point until the twenty-sixth day. On the twenty-seventh day, the pressure began to increase, indicating that the catalyst had been poisoned, presumably because the palladium had been dissolved by the nitric acid vapor present in the reaction system. These results indicate that it would be worthwhile to investigate other catalysts since there is some

hope that catalysts can hold the pressure constant over plutonium solutions for a reasonable period of time.

FIGURE 3. Catalytic Recombination of H_2 and O_2 with "Deoxo" (Palladium Catalyst)

CONCLUSIONS

The results of these experiments indicate that small but significant volumes of radiolytic gases are generated by the alpha radiolysis of nitric acid. The principal gases evolved are oxygen and hydrogen with a small amount of nitrogen. Both $G(O_2)$ and $G(H_2)$ decrease with increasing nitric acid concentrations, but they do not obey the cube-root law.⁽²³⁾ This indicates the complexity of the nitric acid system coupled with the disproportionation equilibria of plutonium. The $G(H_2)$ values are in agreement with those of Bakh,⁽¹³⁾ and the 1 M nitric acid experiment is in fair agreement with Vladimirova, et al.⁽²⁴⁾ The $G(O_2)$ values are lower than those found by Bakh⁽¹³⁾ and suggest that their solutions had higher than equilibrium concentrations of plutonium(VI).

Pressure buildup in closed plutonium vessels can be minimized but not eliminated by increasing the nitric acid concentration as high as possible. The recombination of the radiolytically generated hydrogen and oxygen on a palladium catalyst shows some promise as a short-term means of controlling the pressure buildup. Other catalysts such as platinum should be investigated to determine if longer lived ones can be found. Platinum catalysts will be longer lived, expensive, but reusable. Another solution to the pressurization problem would be to have a platinum wire inserted into the cap of the plutonium container which could be heated periodically to convert the hydrogen and oxygen to water. This alternative should also be investigated in the future.

Although this work indicates that it is possible to minimize the pressure buildup, it still might not be enough to eliminate the cracking of the polyethylene bottles since the threshold pressure is not known at this time and any pressure tends to weaken polyethylene.

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APPENDIX A

EFFECT OF ISOTOPIC COMPOSITION
ON RATE OF PRESSURE BUILDUP

APPENDIX A
EFFECT OF ISOTOPIC COMPOSITION
ON RATE OF PRESSURE BUILDUP

Following is useful information concerning the calculation of pressure buildup. Rate of radiolytic gas generation is

$$g_{Pu} \times \frac{\text{Sp. Act.}}{6.02 \times 10^{23}} \times E_{\alpha} \times \frac{G^T}{1000}$$

$$= 1.73 \times 10^{-5} g_{Pu} G_T \text{ moles of gas per day}$$

where g_{Pu} = grams plutonium-239

Sp. Act. = disintegrations per day = 2.02×10^{14} d/day/g

E_{α} = plutonium-239 alpha energy = 5.15×10^6 eV

$G_T = G(H_2) = G(O_2) + G(N_2) + \dots$

The rate of pressure buildup will be

$$\frac{dP}{dt} = 2.09 \times 10^{-2} \left(\frac{273 + tc}{V_g} \right) g_{Pu} G_T \text{ psi day}^{-1}$$

$$= 1.08 \left(\frac{273 + tc}{V_g} \right) g_{Pu} G_T \text{ mm Hg day}^{-1}$$

$$= 1.42 \times 10^{-3} \left(\frac{273 + tc}{V_g} \right) g_{Pu} G_T \text{ atm day}^{-1}$$

where V_g = the free volume over the plutonium solution

t = the centigrade temperature.

An equation which takes into account the isotopic composition of the plutonium is given below. This equation is good for time periods of less than one year.

$$\frac{dp}{dt} = 2.0 \times 10^{-4} \left(\frac{273 + tc}{V_g} \right) g_{Pu} G_T \left([\% - 239] + 3.68 [\% - 240] \right. \\ \left. + 280 [\% - 238] + 31t [\% - \text{Am-241}] \right) \text{ psi day}^{-1}$$

The time, t , is in years from final plutonium separation. It should also be noted that this equation holds because the alpha

energies of these plutonium isotopes are nearly the same, so they should result in nearly the same G values for the generation of oxygen and hydrogen.

Figure A-1 graphically shows the influence of radiation history on the specific dose rate of plutonium with respect to irradiation exposure (isotopic composition). These data were calculated from Van Tuyl's data⁽²⁵⁾ for Shippingport fuel.

FIGURE A-1. Specific Dose Rate Versus Exposure (Shippingport Fuel)

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