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SUMMARY

An oxidation-reduction balance of the products of the dissolution of plutonium metal and alloys in HNO_3-HF-N_2H_4 solution shows that the major reactions during dissolution are the reduction of nitrate to NH_3, N_2 and N_2O by the metal, and the oxidation of H free radicals to NH_3 by N_2H_4. Reactions between HNO_3 and N_2H_4 produce varying amounts of HN_3. The reaction rate is greater for delta-Pu than alpha-Pu, and is increased by higher concentrations of HF and HNO_3.

The low yield of reduced nitrogen species indicates that nitrate is reduced on the metal surface without producing a significant concentration of species that react with N_2H_4. It is conjectured that intermediate Pu valences and electron transfer within the metal are involved.

INTRODUCTION

Plutonium metal dissolves in HNO_3-HF solutions to yield a Pu^{4+} solution and a mixture of insoluble oxides.[1] The reaction evolves NO_2 and NO, and the reaction rate decreases as the Pu^{4+} ion complexes the fluoride catalyst and as the acid is consumed. When 0.5-1.0 M $N_2H_4 \cdot HNO_3$ is included in the dissolving solution, Pu metal dissolves cleanly to yield a blue Pu^{3+} solution with only traces of insoluble oxides.[2] The major product of the dissolving is NH_4NO_3, with small amounts of HN_3, N_2 and N_2O also produced. Since the Pu^{3+}-fluoride complex is much weaker than the Pu^{4+}-fluoride complex, the reaction is slowed only as the acid is consumed.

The HNO_3-N_2H_4-HF method of dissolving has been investigated in detail with the objective of deducing the chemical reactions that occur as Pu metal is dissolved. This paper reports the results of the study and discusses a probable mechanism for the dissolving chemistry.

EXPERIMENTAL

Alpha-phase and delta-phase plutonium metal, and plutonium alloys were obtained from the Rocky Flats Plant (Rockwell International, Golden, Colorado) and Los Alamos National Laboratory. Dissolvings used 5-10 g pieces of Pu metal and 50 mL of the dissolving solution.

The dissolving vessel was fitted with an o-ring seal connection that led through a gas sampling bulb to a water-filled flask. Evolution of gas during the reaction displaced water into a graduated cylinder for measurement. Gas volumes were corrected to STP after correction for the vapor pressure of water.

Analyses for H_2, N_2 and N_2O were performed by gas chromatography and the results corrected for the presence of air from an O_2 analysis. Hydrazine was determined by the iodate method. HN_3 was collected by sparging an aliquot of the solution with N_2 and collecting the evolved gas in 0.1 $\underline{M}$ NaOH. An aliquot was mixed with HNO_3-$Fe(NO_3)_3$ solution and the concentration of the $FeN_3{}^{2+}$ complex determined spectrophotometrically.[3] Ammonium ion produced during dissolving was determined by N_2-sparging a sample diluted 5x with 6 $\underline{M}$ NaOH. The NH_3 evolved was collected in a measured volume of 0.1 $\underline{M}$ HCl, and NH_3 determined either by back-titration or by an ammonia electrode (Orion Research, Cambridge, Mass).

RESULTS

The dissolution of plutonium metal and >90 wt % plutonium alloys in HNO_3-KF-$N_2H_4 \cdot HNO_3$ solutions is a smooth exothermic reaction with little gas evolution. The heat evolved was measured as 138 kcal/mole, to be compared with the reported value of 139.2 kcal/mole for the heat of dissolution in 2 $\underline{M}$ HCl.[4] Dissolving studies were done at constant temperature of 50°C to minimize the oxidation of hydrazine by HNO_3.[5]

The reaction rate depends on the type of plutonium metal or alloy, the acid concentation and the fluoride concentration. These effects are demonstrated (Table I) by the dissolving rates under different acid and fluoride concentration for specimens of alpha-phase Pu, delta-phase Pu, alloy A (6 wt % Na) and alloy B (3 wt % Ga). The reaction rate was unaffected by hydrazine concentration. From the data in Table I, the reaction rate for the α-phase Pu is about 1/3 the rate for delta-phase Pu.

The products of the reaction are NH_3, N_2, N_2O, HN_3 and traces of H_2. The yields of these products for different samples are shown in Table II. There is an appreciable variation in both the hydrazine consumed in the reaction and the NH_3 produced that is attributed to differences in the ratio of surface area of the metal to the volume of solution. This ratio was not studied systematically because of the small amount of material available.

TABLE I

Dissolving Rates at 50°C for Pu Samples

Sample	Dissolving Solution Conc, M HNO_3	KF	$N_2H_4 \cdot HNO_3$	Maximum Dissolving Rate, mg/cm^2-min
α-Pu	5	0.10	0.3	38
	5	0.10	0.4	35
	5	0.10	0.5	37
	3	0.10	0.3	22
δ-Pu	3	0.1	1.1	75
	3	0.05	1.1	40
Alloy A	2.5	0.05	1.1	23
	3	0.075	0.8	55
Alloy B	2.5	0.05	1.0	25
	3.0	0.075	1.0	30
	3.0	0.10	1.0	36

TABLE II

Reaction Products

Initial Conc, M				Mole Product/Mole Pu						
Sample	HNO_3	KF	N_2H_4	N_2H_4[a]	NH_3	HN_3	H_2	N_2	N_2O	HNO_3[a]
α-Pu										
	5	0.1	0.50	0.39	0.56	0.003	<0.01	nd	nd	3.2
	5	0.1	0.30	0.35	0.36	0.001	<0.01	nd	nd	3.1
δ-Pu										
	3	0.1	1.0	0.35	0.45	0.08	0.01	0.13	0.12	3.6
	3	0.1	1.0	0.50	0.43	0.13	0.01	0.12	0.04	3.8
Alloy A[b]										
	2.5	0.05	1.1	0.16	0.38	0.11	0.02	0.11	0.10	3.8
	3.0	0.075	1.0	0.31	0.45	0.09	0.02	0.10	0.04	3.7
Alloy B[b]										
	2.5	0.05	1.0	0.52	0.33	0.17	<0.001	0.07	0.04	3.7
	3.0	0.10	1.0	0.4	0.31	0.14	0.004	0.09	0.04	3.6

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a. Consumed in the reaction.

b. Data for products corrected to moles of trivalent metal.

DISCUSSION

The reduction products of the reaction offer a means for deducing the chemical reactions involved in dissolving plutonium in HNO_3-KF-$N_2H_4 \cdot HNO_3$. The oxidation of one mole of plutonium metal requires the reduction of three equivalents of oxidizing agents. The composition of the reduction products provides evidence for the chemical reactions that are involved in dissolving.

Since no reaction occurs unless fluoride is present, an initial attack on the metal by HF is assumed

$$Pu + 3\ HF \dashrightarrow Pu^{3+} + 3\ H + 3\ F^- \qquad (1)$$

The H free radical can then react by

$$2\ H \dashrightarrow H_2 \qquad (2)$$

and

$$2\ H + N_2H_5^+ + H^+ \dashrightarrow 2\ NH_4^+ \qquad (3)$$

The sum of the products of reactions 2 and 3 accounts for only 10-20% of the reduction products required for the oxidation of Pu metal based on the data in Table II.

The reduction of nitrate on the metal surface produces N_2, N_2O and NH_4^+ by

$$10\ Pu + 36\ H^+ + 6\ NO_3^- \dashrightarrow 10\ Pu^{3+} + 3\ N_2 + 18\ H_2O \qquad (4)$$

$$8\ Pu + 30\ H^+ + 6\ NO_3^- \dashrightarrow 8\ Pu^{3+} + 3\ N_2O + 15\ H_2O \qquad (5)$$

$$8\ Pu + 30\ H^+ + 6\ NO_3^- \dashrightarrow 8\ Pu^{3+} + 3\ NH_4^+ + 9\ H_2O \qquad (6)$$

HN_3 is produced by side-reaction between HNO_3 and $N_2H_5^+$

$$HNO3 + 2\ N2H5^+ \dashrightarrow HN_3 + 3\ H_2O + 2\ H^+ + N_2H_2 \text{ (two steps)} \qquad (7)$$

The diazine free radical further reacts with HN_3 and HNO_3 to produce N_2, NH_4^+ and HNO_2.[5] An approximate accounting of the reduction products will disregard the products of N_2H_2 reactions.

From reactions 1-6, the reduction products in units of moles per mole of Pu^{3+} can be fit to the expression

$$10\ N_2 + 8\ N_2O + 8(1-x)NH_4^+ + x\ NH_4^+ + 2\ H_2 = 3 \qquad (8)$$

where x is the fraction of NH_4^+ produced by reaction 3, and 1-x the fraction produced by reaction 6.

The amount of hydrazine consumed can be calculated from the contributions of reactions 3 and 7 as

$$N_2H_4 = x\ NH_4^+/2 + 2\ HN_3 \qquad (9)$$

The values calculated for x, the calculated N_2H_4 consumed, and the measured N_2H_4 consumption are shown in Table III for data taken from Table II.

TABLE III

Calculated N_2H_4 Consumption

		N_2H_4 Consumed, Mole/Mole Pu	
Sample	x	Experimental	Calculated
δ-1	0.90	0.35	0.36
δ-2	0.64	0.50	0.40
A-1	0.62	0.16	0.31
A-2	0.60	0.31	0.27
B-1	0.28	0.52	0.46
B-2	0.31	0.46	0.39

The experimental N_2H_4 and the calculated N_2H_4 agree within about 15%, disregarding the value for alloy A-1. (An experimental error is suspected in the data for alloy A-1.)

A discussion of the dissolving mechanism is necessarily speculative, but much can be made of the fact there is no appreciable yield of species that result from the reaction of hydrazine and intermediate nitrogen species, such as HNO_2. Since the reaction of hydrazine with HNO_2 is very fast,[6,7] it can be inferred that nitrate is reduced to the final products N_2, N_2O and NH_3 on the surface of the metal. It is reasonable also to presume that the transfer of electrons through the metal occurs, perhaps driven by the potential of a local cell created by an intermediate plutonium valence on the metal surface. It is hoped that some new experimental technique can lead to a better knowledge of the surface reactions in metal dissolving.

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