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HYDROXYLAMINE NITRATE REDUCTION OF PLUTONIUM(IV):
IRON CATALYSIS

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ABSTRACT

The effect of ferric ion on the kinetics of the reduction of plutonium(IV) with hydroxylamine nitrate was examined. It was found that iron catalyzes the reaction, especially in the latter stages of the reaction. The effect of iron concentration was compared with other factors which influence the rate and was found to be less significant than temperature, acidity, or hydroxylamine nitrate concentration.

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INTRODUCTION

The kinetics of the reduction of plutonium(IV) to plutonium(III) by hydroxylamine nitrate (HN) have been studied in this laboratory⁽¹⁾ and by McKibben and Bercaw⁽²⁾ in order to determine the utility of HN as a reductant in the Purex solvent extraction process. Results of these investigations show that the reaction is relatively slow at the nitric acid concentrations which may be present in Purex extraction columns. Depending on residence time, acidity, temperature, Pu(IV) concentration and HN concentration, incomplete reduction of Pu(IV) may occur and cause poor uranium-plutonium partitioning in the column. McKibben and Bercaw⁽²⁾ have shown that the reaction is catalyzed by 0.1M ferric ion. Because of this catalysis, the utility of HN can be extended to the reduction of Pu(IV) at higher acidities at which the reaction is slow in the absence of iron.

The addition of iron to the Purex system must be carefully controlled since the radioactively contaminated iron waste must be stored indefinitely. Because of this, the iron addition must be kept to a minimum. This report contains data which show the effect of iron concentration on the reaction rate. Iron concentration is compared with other factors which also affect the rate (temperature, H^+ concentration, and HN concentration). All experiments were run in the absence of uranium since uranium is not expected to influence the reaction.

SUMMARY AND CONCLUSIONS

Iron catalysis of the reduction of plutonium(IV) to plutonium(III) by hydroxylamine nitrate was investigated under reaction conditions approximating those of the Purex solvent extraction columns. Data are presented which show the effect of iron concentration, acidity, HN concentration, and temperature on the rate of reaction. Because of the complex nature of this reaction, no attempt was made to reduce the rate data to a generalized rate equation. However, several general conclusions can be drawn from these data:

- The reaction is catalyzed by iron; the higher the iron concentration, the faster the reaction.
- The catalytic effect of iron is limited by the rate of reduction of Fe(III) to Fe(II) by HN.
- The effect of the catalysis is much greater near the latter part of the reaction. At the beginning, the rate is almost equal to the rate of the uncatalyzed reaction.
- The effect of adding iron (at the concentrations studied) is relatively small compared with changing other variables on which the rate depends. These variables are temperature, acidity, and HN concentration.

EXPERIMENTAL

REAGENTS

Reagent grade ferric nitrate (Baker and Adamson) and nitric acid (Mallinckrodt) were used throughout. All stock solutions were made using quartz-distilled water. A plutonium stock solution was prepared by loading Purex plutonium product solution (adjusted to 6M HNO₃) onto a column of 50 to 100 mesh Bio-Rex 9 anion exchange resin (Bio-Rad Laboratories) which had

previously been converted to the nitrate form. The column was washed with 6M HNO₃ and the plutonium then eluted with 1M HNO₃. The procedure was repeated and the resulting solution was adjusted to 3M HNO₃ in order to prevent the following disproportionation reaction from occurring:

Plutonium concentration in the stock solution was determined by standard alpha-counting techniques. A hydroxylamine nitrate stock solution was prepared by converting reagent grade hydroxylamine hydrochloride (Baker and Adamson) by ion exchange using 20 to 50 mesh Dowex 50W-X8 cation exchange resin (Dow Chemical Company) in the acid-form. Hydroxylamine was determined by the Raschig method.⁽³⁾ Ferrous sulfamate was obtained from Southwestern Analytical Chemicals, Inc., as a 3M Fe(NH₂SO₃)₂ solution.

PROCEDURE

The reaction was followed spectrophotometrically by measuring the absorbance at 476 nm [where Pu(IV) strongly absorbs] of the reacting solutions. Absorbance versus time curves were obtained with a Beckman Model DK-2A recording spectrophotometer. It was found that hydroxylamine and iron absorption at 476 nm was insignificant at the concentrations used in this study. A correction for Pu(III) absorption at 476 nm was applied to the data. Since temperature and HNO₃ concentration affect Pu(IV) absorbance at 476 nm, molar absorptivities for Pu(IV) were obtained for each temperature and HNO₃ concentration used in these experiments.

Plutonium solutions (with Fe³⁺ added) and HN solutions were placed separately in a thermostated water bath for about 20 minutes. After temperature equilibrium was reached, measured amounts of these two solutions were rapidly mixed and

the resulting solutions placed in the thermostated cell compartment of the spectrophotometer. The time required between mixing and the first absorbance measurement was about 15 seconds. Zero time was defined as the time at which one-half of the HN in a micropipet was added to the Pu(IV) solution. A circulating constant temperature bath maintained the cell compartment of the spectrophotometer to within ± 0.1 °C.

Rapid reactions were observed using an Aminco-Morrow stopped-flow apparatus (American Instrument Corporation) which was coupled to a Beckman DU monochromator (Beckman Instrument Company). The percent transmittance signal from an Aminco photometer was displayed versus time on a Hughes Memoscope storage oscilloscope (Division of Hughes Aircraft). This curve was then photographed on Polaroid film (Polaroid Corporation). The reagent solutions in the stopped-flow apparatus were maintained at the desired temperature ± 0.1 °C with a circulating temperature bath.

RESULTS AND DISCUSSION

McKibben and Bercaw⁽²⁾ suggest that ferric ion catalyzes the reduction of Pu(IV) according to the following equations:

The kinetics of Reaction 1 in hydrochloric acid solutions has been examined by Mitchell.⁽⁴⁾ The reaction was found to be rapid near the beginning. The rate then fell off quickly, indicating that an inhibitor is produced during the course of the reaction. Mitchell also found that the rate was depressed by an increase in acid concentration. Similar observations have been made for the direct reduction of Pu(IV) with HN. The reactions, therefore, probably proceed in a similar manner.

Reaction 2 has been studied in perchloric acid medium by Newton and Cowan.⁽⁵⁾ They found the reaction to be first-order with respect to Pu(IV) concentration. From the values of rate constants which they obtained, the reaction can be considered fast. Under conditions of relatively high acid and ferrous concentrations which approximate those of the Purex 1BX extraction column (temperature = 40 °C, 2.30M H^+ , and 0.031M Fe^{2+}) the rate follows the equation

$$-\frac{d[\text{Pu(IV)}]}{dt} = k[\text{Pu(IV)}]$$

The rate constant, k , calculated from Reference 5 at the above reaction conditions, is 3.18 sec^{-1} . Since the rate is expected to vary according to the reaction medium, several kinetic runs were made in nitric acid, keeping all other reaction conditions the same as above. The results of a typical run are shown in Figure 1 in which $\ln(A_t - A_\infty)$ is plotted against time (A_t = absorbance at time, t , and A_∞ = absorbance at infinite time). Since the curve is linear, the reaction is first-order with respect to Pu(IV) concentration. The slope of the line (k) is 2.93 sec^{-1} . This rate constant is only slightly smaller than that calculated for the reaction in perchloric acid. The formation of Pu(IV)-NO_3^- complexes in HNO_3 may account for the small decrease in rate. Reaction 2, however, is rapid compared with Reaction 1 and therefore the catalytic effect of iron is limited by Reaction 1.

EFFECT OF IRON CONCENTRATION

In the absence of iron, reduction of Pu(IV) by hydroxylamine proceeds rapidly at the beginning of the reaction and then slows considerably near the end, as shown in Figure 2. The reaction is complex and does not conform to any simple rate law. There is a back-reaction occurring in which Pu(III) is reoxidized to Pu(IV) by some unknown species in the reacting solution.

Increasing the iron concentration speeds the reaction as shown in Figure 3. The percent Pu(IV) remaining versus time curves in this figure are presented as double logarithmic plots in order to show all the data. It can be seen that Fe(III) has the greatest catalytic effect near the end of the reaction. In the absence of Fe(III), this part of the reaction is slow. These curves also show that direct reduction of Pu(IV) by HN [without the Fe(II) intermediate] is important at the iron concentration studied.

EFFECT OF ACIDITY

The reaction rate was found to be extremely dependent on acid concentration. The reaction occurs much faster at low nitric acid concentrations. This is shown by comparing the curves in Figure 3, which were obtained at 2.30M HNO₃, with those of Figure 4. The data plotted in Figure 4 were obtained under conditions identical to those of Figure 3 except that the HNO₃ concentration was 1.75M. The rate is approximately proportional to [HNO₃]⁻⁴.

EFFECT OF HYDROXYLAMINE NITRATE CONCENTRATION

The effect on the reaction rate of doubling the HN concentration is shown in Figure 5. A large increase in the rate is observed when the HN concentration is increased. This observation is consistent with data obtained in this laboratory⁽¹⁾ for the reaction in the absence of iron which indicates that the rate of reaction is proportional to [HN]².

EFFECT OF TEMPERATURE

Temperature also has a large effect on the rate. Figure 6 shows concentration versus time curves for the reaction at 30, 40, and 50 °C. A rough approximation for the effect of temperature on the rate is that the rate increases by a factor

of five with each 10 degree (Celsius) increase in temperature. This is an unusually high temperature dependence.

No attempt has been made here to reduce the rate data to a generalized rate equation for the catalyzed reaction. The reaction, even in the absence of iron, is very complex--involving several steps and intermediates.⁽¹⁾ The additional variable, iron concentration, in the catalyzed reaction considerably complicates the rate. Because of this complexity, rate data were obtained under reaction conditions which approach those of the Purex plant so that the results can be directly used.

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FIGURE 1

PLOT OF $\ln(A_t - A_\infty)$ VERSUS TIME FOR THE REDUCTION
OF Pu(IV) WITH Fe²⁺ IN NITRIC ACID SOLUTION

FIGURE 2

PLUTONIUM(IV) CONCENTRATION VERSUS TIME FOR HN REDUCTION OF Pu(IV) [a] IN THE ABSENCE OF Fe^{3+} AND [b] IN 0.011M Fe^{3+}

FIGURE 3

EFFECT OF IRON CONCENTRATION ON THE RATE OF REDUCTION
OF Pu(IV) WITH HN AT 2.30M HNO₃

FIGURE 4

EFFECT OF IRON CONCENTRATION ON THE RATE OF REDUCTION
OF Pu(IV) WITH HN AT 1.75M HNO₃

FIGURE 5

EFFECT OF HYDROXYLAMINE NITRATE (HN) CONCENTRATION
ON THE RATE OF HN REDUCTION OF Pu(IV)

FIGURE 6

EFFECT OF TEMPERATURE ON THE RATE
OF HN REDUCTION OF Pu(IV)

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