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OXIDATION OF PLUTONIUM(III) BY SODIUM NITRITE

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OXIDATION OF PLUTONIUM(III) BY SODIUM NITRITEI. INTRODUCTION

The oxidation of plutonium(III) to plutonium(IV) by nitrite has been studied by solvent extraction methods and found to be very rapid.^{(1) (2) (3)} The speed of the reaction has discouraged attempts to measure the reaction velocity constant by means of spectrophotometry and specific values of this constant were not available previously. Interest here is in the kinetics of the oxidation of plutonium(III) to plutonium(IV) in nitric acid solution containing ferrous sulfamate. The ferrous sulfamate yields sulfate ions when oxidized by the nitrite. The electrochemical potentials indicate oxidation of plutonium(IV) to be complete in the presence of sulfate.⁽³⁾ The velocity rate constant for the oxidation of plutonium(III) in this system has been determined to provide information for the design of equipment employing this reaction.

II. SUMMARY

The reaction velocity constant for the oxidation of plutonium(III) by nitrite in nitric acid solution containing ferrous sulfamate is given. The reaction rate was found to be measurable by means of spectrophotometry. The data indicate the reaction to be a pseudo first-order reaction in the region of nitric acid and nitrite concentration of interest. The reaction velocity constant, expressed as a first-order reaction with respect to plutonium, was found for several values of nitric acid and nitrite concentrations. The nitric acid-reaction velocity constant relationship is given.

The oxidation of the ferrous sulfamate-plutonium(III) solution proceeds successively through the sulfamate, ferrous, and plutonium(III) ions. An autocatalytic mechanism is associated with the oxidation of both ferrous and plutonium ions which obviates the possibility of simple calculations of constants based on nitrite concentration. An empirical relationship between the reaction velocity constant and the (added) nitrite concentration is given.

III. DISCUSSION

The Beckman DK-2 ratio recording spectrophotometer was used to follow the course of the reaction. A 1.6 M NaNO_2 solution was used to oxidize the ferrous sulfamate-plutonium(III) solution. The starting ferrous sulfamate concentration was 0.024 M in all experiments. The sodium nitrite solution was introduced into the reduced plutonium solution in the spectrophotometer cell and immediately stirred with a pipette. Care was taken not to introduce air while stirring. Absorbance readings were taken at 1/2 or 1 minute intervals until near completion of the reaction. The 600 m μ plutonium(III) absorbance peak was used to measure the reaction rate; however, several checks were made by measuring the growth of the 475 m μ plutonium(IV) peak. Only this part of the spectrum was scanned.

The reaction rate was determined at several acidity values within the range 0.4 M to 2.0 M HNO_3 . Starting concentrations from 0.04 M to 0.1 M were employed in determining the nitrite concentration effect.

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Timing of the spectrum scanning was done such that the indicated time lapse refers to the period from addition of the nitrite to the time indicated by the top of the 600 mμ plutonium(III) peak. Approximate plutonium(III) concentrations were calculated from absorbance at this wave length. Simultaneous values for plutonium(IV) formed in the oxidation were obtained by difference between the plutonium(III) values and starting (total) plutonium concentration. These plutonium(IV) concentrations and established plutonium(IV) molar absorbance values at 600 mμ were then used to calculate the contribution due to plutonium(IV) at the 600 mμ plutonium(III) peak. This plutonium(IV) contribution subtracted from the first plutonium(III) estimate gave the plutonium(III) concentration figures used in subsequent plots and calculations. Semilog plots of these data (C vs t) are shown. Convenient points were taken from these lines to calculate the rate constant k.

The disappearance (oxidation) of plutonium(III) is represented by the statement for a unimolecular reaction:

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

Values of k were calculated from the integrated form:

$$k = \frac{2.303}{t_2 - t_1} \log \frac{C_1}{C_2}$$

Constant values of k indicated the above expression to be satisfactory. This is also evident from the straight lines shown in semi-log plots, Figures 4 and 6. The effect of nitric acid variations is shown by sample spectra in Figures 1, 2, and 3. Figure 1 illustrates the delay period found at low acidity. The high general absorbance during the first three to four minutes is due to the continued liberation of nitrogen gas during the sulfamate oxidation.

At higher acidities, this gas evolution is nearly instantaneous and is complete before scanning is started. It may be seen that the height of the 600 mμ plutonium(III) peak, above general absorbance, does not diminish nor is there a growth of the 475 mμ plutonium(IV) peak until liberation of gas is complete. Concentrations of plutonium(III) calculated from the spectra subsequent to gas liberation are shown at the right with a separate time axis in Figure 4. The first point does not fall on the straight line, indicating a slower reaction rate at first and a rate dependency on factors other than plutonium(III) concentration. Figure 5 is a plot of k vs nitric acid concentration. The nitric acid dependency of the reaction is linear in the range 0.5 M to 2.0 M acid and may be expressed:

$$k = 0.009 + 0.006 \text{ H}^+$$

Generalization of this expression beyond the conditions and range indicated are probably not warranted.

Figure 6 is a plot of data from the spectra shown in Figures 9 to 13 inclusive. The reaction at 0.04 M NaNO₂, Figure 8, is not measurable. The curves

representing the four highest nitrite concentrations again showed the rate to be mainly dependent on plutonium concentration. The shape of the curve representing oxidation with 0.053 M NaNO_2 would indicate that the specific reaction rate increased during the reaction. This is similar to the phenomena observed at low acidity. Both are explained on the bases of the autocatalytic mechanism of oxidation of iron and plutonium. Nitrogen dioxide has been shown to be the effective oxidant. (4) (5) (6)

The concentration of NO_2 is controlled by the following rapidly reversible reaction:

That the oxidation of plutonium(III) to plutonium(IV) actually results in an increase in oxidant may be seen from the following reactions:

Thus each plutonium atom oxidized adds one NO_2 molecule.

The reaction with iron and with plutonium are taken to be of identical mechanism. The above mechanism provides oxidant at high enough concentration to make the oxidation of plutonium appear dependent only on its own concentration. However, at low nitric acid and at low sodium nitrite concentrations there is a delay in establishing this condition, but even under these conditions, the reaction rate appears to become plutonium concentration dependent only.

The 0.024 M ferrous sulfamate requires an 0.048 M concentration of sodium nitrite for oxidation of the sulfamic acid only. The 0.04 M NaNO_2 , Figure 8, is, therefore, insufficient to oxidize the sulfamic acid, and oxidation of iron and plutonium is not accomplished. The 0.053 M added nitrite, Figure 9, is sufficient to oxidize the sulfamate and part of the iron, thus starting the autocatalytic mechanism, and effecting oxidation of iron and plutonium. The shape of the curve representing this concentration of added nitrite, Figure 6, indicates increasing reaction velocity during the first one and one-half minutes, which may be explained by the build-up of oxidant by the autocatalytic mechanism. The last three points of this curve form a nearly straight line, indicating the reaction has become mainly plutonium concentration dependent. The higher concentrations of added sodium nitrite, Figure 6, yielded unchanging values for the reaction velocity constant throughout the course of each reaction.

The values of k found at various added nitrite concentrations (M_{t_0}) produced a straight line when plotted on semilog paper (Figure 7). This graph is most convenient in evaluating the effect of added nitrite concentration on the reaction velocity. This graph indicates the reaction velocity constant may be related to the starting nitrite concentration by an expression of the type:

$$k = aC^{bC(\text{NaNO}_2)}$$

The slope and intercept of the line was used to obtain the expression

$$\log k = 6.41 (\text{NaNO}_2) + \log 0.004$$

where k is in sec^{-1} .

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Absorption Spectra

FIGURE 1

Pu 0.04 g/l
 HNO₃ 0.5 M
 NaNO₂ 0.08 M

FIGURE 2

Pu 1.9 g/l
 HNO₃ 1.0 M
 NaNO₂ 0.08 M

FIGURE 3

Pu 1.9 g/l
 HNO₃ 1.5 M
 NaNO₂ 0.08 M

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FIGURE 1
REACTION RATE ACID DEPENDENCY

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FIGURE 5

REACTION RATE - NITRITE OXIDATION OF Pu(III)
ACID DEPENDENCY

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FIGURE 6

OXIDATION OF Pu(III) BY NaNO_2
EFFECT OF NITRITE CONCENTRATION

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FIGURE 7

REACTION RATE NITRITE DEPENDENCY

Reaction Velocity Constant k sec^{-1}

0.020

0.015

0.010

0.06

0.08

0.10

0.12

M_{N} of NaNO_2

966

10

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ABSORPTION SPECTRA
NITRITE OXIDATION OF Pu(III)
EFFECT OF NITRITE CONCENTRATION

FIGURE 8

0.040 M NaNO_2

600m μ

FIGURE 9

0.053 M NaNO_2

FIGURE 10

0.072 M NaNO_2

All scans made at 1/2 minute intervals

FIGURE 11

0.080 M NaNO_2

FIGURE 12

0.098 M NaNO_2

FIGURE 13

0.107 M NaNO_2