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AUTHOR(S): T. W. Newton and V. L. Rundberg

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Los Alamos
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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DISPROPORTIONATION AND POLYMERIZATION OF PLUTONIUM(IV) IN DILUTE AQUEOUS SOLUTIONS

T. W. NEWTON AND V. L. RUNDBERG
Los Alamos National Laboratory, P. O. Box 1663, Los Alamos, NM 87545, USA

ABSTRACT

The rates of polymerization and disproportionation of Pu(IV) have been studied using low concentrations: $(1.7 - 10) \times 10^{-5}$ M Pu, $(0.8 - 12) \times 10^{-4}$ M HCl and 0.01M ionic strength. Osmium(II) complexes such as the tris-4,4'-2,2'-bipyridine complex were found to react rapidly with Pu(IV) but very slowly, if at all, with Pu(IV) polymer, Pu(III), or Pu(V). Thus, it is possible to determine unreacted Pu(IV) in the presence of reaction products by using Os(II) complexes. Disproportionation reaction products, Pu(III) and Pu(V), were determined using their reactions with Ce(IV) sulfate. We find $-d[Pu(IV)]/dt = k'[Pu(IV)]^2$ at constant pH. Log k' varies from about 4.25 at pH 3 to about 7.0 at pH 4.1 (units for k' are $M^{-1}min^{-1}$). The $[H^+]$ dependence varies from about -2 to -3 over the pH range studied. The measured rate is the sum of those for polymerization and disproportionation; the latter reaction amounts to about 75% of the total at pH 3 and 20% at pH 4. The second-order rate constants for disproportionation are very much larger than expected on the basis of extrapolation from 0.2 to 1.0M $HClO_4$ solutions. The products of the reaction do not affect the rate, but U(VI), aged Pu(IV) polymer, and CO_2 increase the rate.

INTRODUCTION

The chemistry of Pu(IV) in near-neutral solutions is poorly understood, which makes it very difficult to predict behavior in groundwaters such as those present at the proposed nuclear waste repository at Yucca Mountain in Nevada. In the absence of strongly complexing species, the principal reactions of Pu(IV) are hydrolysis, disproportionation, polymerization, and finally, precipitation. The first step in the hydrolysis of Pu(IV) becomes important at fairly high acid concentrations and satisfactory values for the first hydrolysis quotient are available [1]. The quotients for further hydrolysis are difficult to determine because of the reactions mentioned above, but apparently reasonable estimates have been given by Baes and Mesmer [1]. The rates of disproportionation of Pu(IV) in solutions of unit ionic strength and $0.2 \leq [H^+] \leq 1.0M$ have been reported by Rabideau [2]. These results may be extrapolated to higher pH values and lower concentrations. However, these estimates are quite uncertain and direct determinations would be very useful. The existence of polymers of Pu(IV) is well known, and important properties have been reviewed by Cleveland [3]. More recently, rates of polymer formation from fairly concentrated solutions have been studied [4,5], and some structural details have been elucidated [6]. The importance of the Pu(IV) polymer in understanding the behavior of plutonium

under environmental conditions was recognized by Rai and coworkers [7], who
have reported solubility as a function of pH for "aged" polymer. The pur-
pose of the work reported here is to determine the rates of disproportiona-
tion of Pu(IV) and the first step of polymerization in very dilute solutions
($\sim 10^{-4}$M Pu and pH $\geq$ 3) and to study some of the chemical properties of the
polymer formed under these conditions.

MATERIALS AND METHODS

Reagents

Plutonium(IV) stock solutions. Electrorefined plutonium-239 metal was
dissolved in 6M HCl. A portion of the Pu(III) formed was oxidized to Pu(VI)
with fuming HClO$_4$. One equivalent of the Pu(VI) was added to two equivalents
of Pu(III) to form Pu(IV) by the rapid reproportionation reaction. The final
HCl concentration was made 3M or greater to minimize disporportionation and
alpha reduction. The amounts of Pu(III) and/or Pu(VI) in the stock were
estimated by absorption spectrophotometry at 600 and 830 nm, respectively.

Plutonium (IV) polymer. This material was prepared by diluting Pu(IV)
stock solution with water to give a final mixture ~0.008M in Pu and 0.05M in
HCl. This mixture was allowed to stand for about 1 week and ionic impurities
were removed by the use of a cation exchange column (Dowex 50 X-8). The
resulting green sol showed the visible absorption spectrum characteristic of
the polymer [6].

Osmium(II) complexes [8]. The tris-bipyridine and tris-4,4'-dimethyl-
2,2'-bipyridine complexes were prepared by published methods [9]. The formal
potential o the dimethyl bipyridine complex was determined to be ~0.09 V
less than that of the unsubstituted bipyridine complex, which is reported to
be 0.885 V. [10]. This was done using potentiometric titration with ceric
sulfate.

Other Reagents. Ce(IV) from the G. F. Smith Chemical Company was made
up in 8M H$_2$SO$_4$. Hydroquinone was vacuum sublimed and dissolved in distilled
water. Pyridine was repurified by distillation, and a 10% by volume solution
was made by dilution with distilled water.

Analytical Methods
   The plutonium concentrations encountered were too low for direct spec-
trophotometry, so indirect methods based on osmium(II) complexes were devel-
oped. These complexes react quite rapidly with monomeric Pu(IV) but very
slowly with the products of disproportionation or polymerization reactions.
For example, the apparent second order rate constant for the reduction of
Pu(IV) by the dimethyl bipyridine complex is about 1.5 x 10^4M^{-1}sec^{-1} at room
temperature and a pH of 3. The ligands on the osmium are essentially
nonlabile, and there is no evidence that they can dissociate and react with
the plutonium. Because the osmium(II) complexes have molar absorptivities of
about 1.3 x 10^4M^{-1}cm^{-1} in the visible region, compared with value <500M^{-1}cm^{-1}
for the corresponding Os(III) complexes, very dilute solutions of Pu(IV) can
be analyzed spectrophotometrically.
   An ion exchange method was used to identify the Pu(III) and Pu(V) formed
by disproportionation. This was done by means of small ion exchange columns
containing zirconium phosphate, as suggested by Gehmecker et al. [11]. In
this method, a sample is placed on the top of the column and eluted with
successive 2-ml portions of HCl of increasing concentration. Each portion is
collected separately from the bottom of the column, taken to dryness, heated
to about 300°C, and alpha-counted. Elution occurs in several distinct bands.

- ine total reducing agent formed in the experimental solutions was deter-
mined using Ce(IV) in dilute H_2SO_4. This reagent reacts rapidly with Pu(III)
and Pu(V) but only slowly, if at all, with Pu(IV) and the Pu(IV) polymer. A
small excess of Ce(IV) in $8M$ H_2SO_4 was added to the solution and back-
titrated spectrophotometrically at 320 nm with standardized Pu(III) solution.
The acid in the Ce(IV) reagent was chosen to make the final solution about
$0.5\underline{M}$ in H_2SO_4.

Procedure

Solutions for the kinetic experiments were prepared by adding small
measured volumes of Pu(IV) in $3\underline{M}$ HCl to much larger volumes (typically 60 ml)
of $0.01M$ HCl containing enough pyridine to give the desired pH. Unreacted
Pu(IV) was determined as a function of time by adding Os(II) complex to re-
duce the Pu(IV) and quench the reaction. The Os(III) complex that formed,
and hence, the Pu(IV) present at the time of quenching, was determined from
the increase in absorbance after adding excess hydroquinone, which rapidly
reduces the Os(III). For runs with pH values greater than ~3.5, it was
necessary to quench the reaction with 0.3 meq of HCl just before adding the
Os(II). This excess acid was neutralized with 0.3 meq of NH_4OH before adding
the hydroquinone. The reaction vessels were special 10-cm absorption cells
equipped with magnetically driven Teflon-covered stir bars. Absorbance was
determined at $23 \pm 1°C$ by using a Cary Model 17D spectrophotometer. After
essentially all the monomeric Pu(IV) had reacted, the total reducing agent
that formed was determined by using Ce(IV) as described above.

Extrapolation of Disproportionation Data

Rabideau et al. [2b] have given a two-term rate law for the dispropor-
tionation of Pu(IV) at 25°C and $I = 1.0\underline{M}$. We have extrapolated the two rate
constants to $I = 0.01\underline{M}$ by using an extended form of the Debye-Hückel Equation
with parameters suitable for oxidation-reduction reactions [12]. The
resulting rate law is

$$-d[Pu(IV)]/dt = 2(7.1 \times 10^{-5}[H^+]^{-3} + 5.3 \times 10^{-5}[H^+]^{-4}) [Pu^{4+}]^2 M^{-1}sec^{-1}. \quad (1)$$

However, $[Pu^{4+}] = [Pu(IV)] (1 + \Sigma K_i [H^+]^{-1})^{-1}$, where the K_i are the hydrolysis
quotients. Using the values suggested by Baes and Mesmer[1] for $I = 0.01\underline{M}$,
we find $\log K_i = -0.76, -2.72, -5.82, -10.02,$ and -15.42 for $i = 1$ to 5,
respectively. These considerations lead to values for the apparent second-
order rate constant, expressed in $M^{-1}min^{-1}$, of $\log k' = 2.67, 2.03,$ and 0.34
at pH $= 3.0, 3.5,$ and $4.0,$ respectively. The relative concentrations of the
"reactive species," $PuOH^{3+}$ and $Pu(OH)_2^{2+}$, decrease with increasing pH, which
causes the calculated decrease in rate. The products of disproportionation
at pH ≥ 3 are predominantly Pu(III) and Pu(V) because the extensive hydro-
lysis of Pu(IV) causes the equilibrium in the reaction

$$Pu(III) + Pu(VI) = Pu(IV) + Pu(V) \quad (2)$$

to lie far to the right.

RESULTS

The kinetic data obtained indicate that the rate of disappearance of
monomeric Pu(IV) (that which reacts rapidly with Os(II) complexes) is pre-
dominantly second order in the concentration of unreacted Pu(IV). A typical
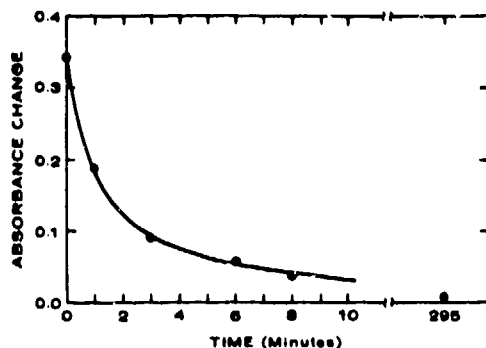plot of concentration vs time is shown in Fig. 1.

FIG. 1. Absorbance change vs time.
Solid curve for second-order rate law.

Apparent second-order rate constants were determined as a function of pH in the range from 2.9 to 4.1. A plot of the logarithm of the rate constant, expressed in $M^{-1}min^{-1}$, is shown in Fig. 2. The rate depends strongly on the pH; the slope of the curve increases from ~1.9 at Ph 3 to ~2.9 at pH 4. In most of the runs, the initial Pu(IV) concentration was in the range (1.7 to 2.0) x $10^{-5}M$, but in some runs, the concentrations were 3 x $10^{-6}M$ and 1.0 x $10^{-5}M$. The effect of varying initial Pu(IV) concentration was within the experimental error in the determinations.

The products of the reaction had no significant effect on the rate. A solution containing 4.2 x $10^{-5}M$ Pu(IV) at pH 4.3 was allowed to stand until the monomeric Pu(IV) had disappeared, principally by polymerization. More Pu(IV) was added and its rate of disappearance was determined as before. The rates in these experiments agreed within 5% with those of companion runs without product but at the same pH.

Aged polymer, however, caused a significant increase in the rate of disappearance of Pu(IV). The polymer was prepared as described above, aged at room temperature for 10 months and purified by ion exchange before use. Rates of disappearance of Pu(IV) in solutions containing 7.8 x $10^{-6}M$ of this polymer were compared with those from solutions with the same pH but without polymer. The rate in the presence of polymer was increased by a factor of 6.2 ± 0.5.

Toth et al. [5] reported that U(VI) reduced the rate of polymerization in their experiments at 50°C. The rate was decreased by about 30% by 0.5M U(VI) in a solution 0.05M in plutonium and 0.11M in HNO_3. We find that the effect is much different at lower temperatures and concentrations. Experiments were done at 23.5 ± 0.5°C by using 1.8 x $10^{-5}M$ Pu(IV) and 3.5 x $10^{-3}M$ U(VI) at pH values of 3.0 and 3.3. In both experiments, the observed second-order rate constants were about 40% larger than those expected without U(VI). Thus, at lower temperatures and concentrations the effect appears to be larger per M of U(VI) and of opposite sign.

Because both polymerization and disproportionation reactions were expected, we used the
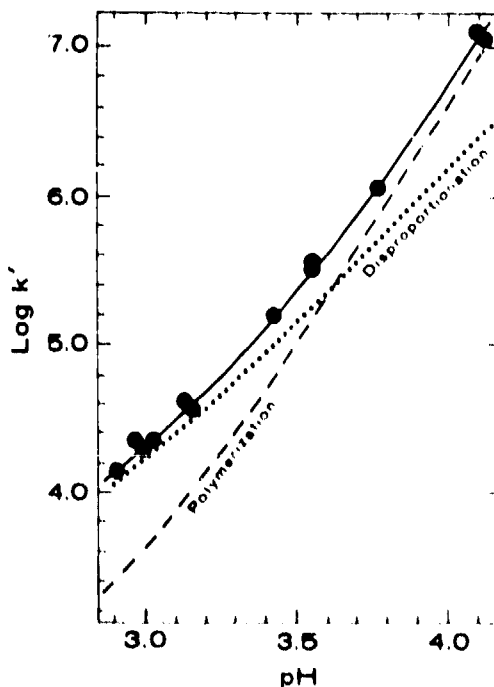

FIG. 2. Log apparent second-order rate constant vs pH.

zirconium phosphate method, described above, to find evidence for Pu(III) and Pu(V) among the reaction products in a typical experiment. The elution pattern was very similar to that obtained using an equimolar mixture of Pu(III) and Pu(V) at essentially the same pH. No evidence was found for a component resembling aged polymer, which is eluted only with great diffi-culty. Freshly formed polymer is difficult to identify because its elution pattern is much like that of Pu(IV), which, in turn, is formed from Pu(III) and Pu(V) on the zirconium phosphate, by reproportionation.

A more quantitative estimate of the fraction of the Pu(IV) that reacted by disproportionation was obtained by determining the total reducing agent formed using the Ce(IV) method described above. Values for the fraction of the initial Pu(IV) converted to reducing agent were more erratic than the corresponding values for the second-order rate constant, but they decreased with increasing pH. Average values and mean deviations were 0.75, 0.09; 0.52, 0.10; and 0.18, 0.02 at pH values of 3.0, 3.5, and 4.1, respectively. Uranium(VI) increases the fraction reducing agent formed as well as increasing the reaction rate. In the two experiments using $3.5 \times 10^{-4} \underline{M}$ U(VI), the fraction reducing agent was 0.99 and 0.90 at pH 3.0 and 3.3, respectively.

Replacing the air in the experimental solutions with argon or carbon dioxide influences the fraction of the Pu(IV) reduced. Experiments using purified argon showed small but significant increases in the fraction, whereas CO_2 at pH values of 3.3, 3.6, and 3.8 reduced the fraction essenti-ally to zero. Preliminary rate experiments at pH = 3.3 comparing CO_2 and air, both at about 0.77 atm, showed that Pu(IV) disappears more than 100 times faster in the presence of CO_2. A set of experiments using tank oxygen also gave anomalous results; the fractions reduced were very similar to those observed using argon. The argon effect can be explained by slow oxidation of Pu(III) and/or Pu(V) by the oxygen in the air, but the effect of the CO_2 can not yet be explained.

DISCUSSION

The data indicate that Pu(IV) disappears by disproportionation and by an additional process. Although direct evidence for polymerization under our experimental conditions is lacking, the fact that polymer readily forms at higher concentrations makes it highly likely that the first stage of poly-merization is the additional process. The values found for the fraction of the initial Pu(IV) converted to reducing agent were used to estimate the rates of the individual processes, disproportionation and polymerization, as a function of pH (Fig. 2). Disproportionation is the predominant reaction for low concentrations of Pu(IV) and pH 3, but polymerization dominates at pH greater than about 3.5.

The determination of the rate constants involved the chemical analysis of separate very dilute solutions as a function of time and, therefore, was not very precise. The reproducibility and scatter of the data indicate an uncertainty in the logarithm of the overall rate constants of about $\pm$ 0.07.

A reliable extrapolation of the rate data to pH values considerably higher than the experimental range will require rate laws in terms of species present in the solutions. The hydrolysis quotients for Pu(IV), estimated for $I = 0.01\underline{M}$ [1], indicate that the predominant species is $Pu(OH)_3^+$ in the pH range from 3.1 to 4.2. The rate law for polymerization in terms of this species is

$$d[poly]/dt = (k_1[H^+]^{-1} + k_2[H^+]^{-2} + k_3[H^+]^{-4})[Pu(OH)_3^+]^2 , \qquad (3)$$

where three rate constants are approximately 12.9 min^{-1}, $6.4 \times 10^{-7} \underline{M}$ min^{-1} and $1.1 \times 10^{-9} \underline{M}^3$ min^{-1}, respectively. These rate constants show the first term is predominant at pH 3, whereas the third term is predominant at

pH 4 and above. The indicated hydrogen ion dependences and the values for the rate constants depend on the values assumed for the hydrolysis quotients and on the somewhat arbitrary choice of $Pu(OH)_3^+$ as the reactive species. However, completely equivalent rate laws could be written in terms of other species.

It is apparent that the nature of the plutonium(IV) polymerization reaction depends strongly on the plutonium and acid concentrations. This is seen when our results are compared with those of Toth et al. [5]. Those authors worked at much higher concentrations, typically $0.05\underline{M}$ Pu(IV) and 0.07 to $0.4\underline{M}$ HNO_3. They found that the rate of polymer formation is auto-catalytic, but after initial stages of reaction were complete, the rate is approximately proportional to $[Pu(IV)]^3$. In our much more dilute solutions, autocatalysis was not observed but catalysis by aged polymer was detected. The data in the high-concentration range indicate a much larger inverse $[H^+]$ dependence than is observed at low concentrations. These results are not directly comparable because the initial reactant species are different in the two pH regions and because the former results do not apply to the initial stages of reaction.

The rate law for disproportionation has the same form as that given above but with different rate constants: approximately 78 min^{-1}, $9 \times 10^{-}\underline{M}$ min^{-1}, and $2 \times 10^{-1}\underline{M}^3$ min^{-1}, respectively. The terms in this rate law were not observed in the work at higher acid concentrations [2], so it is not surprising that the observed rate constant is about 30 times greater at pH 3 and about 10^4 greater at pH 4 than the extrapolated values given in a previous section.

Our results show that studies of reactions such as the hydrolysis or complexation of Pu(IV) at pH values greater than 4 will require very dilute solutions and/or very short times. Of more direct importance to Pu(IV) in the environment, our work indicates that disproportionation to give Pu(III) and u(V) at pH values greater than about 3 occurs much more rapidly than earlier results would indicate. Although the Pu(III) would be rapidly re-oxidized to Pu(IV) and immobilized by adsorption or precipitation, the Pu(V) would probably remain in solution. In addition, at pH values greater than about 4, polymerization is very rapid, leading to material that is probably readily adsorbed.

ACKNOWLEDGEMENTS

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