September, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (9), 2213—2216 (1974) 2213

The Chemistry of Protactinium. XI. A Study of the Solvent Extraction of Protactinium(IV) Reduced with Europium(II) from a Perchloric Acid Solution, Using Thenoyltrifluoroacetone as the Extractant

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(Received February 19, 1974)

Europium(II) was found to be an excellent reductant for reducing protactinium in microquantities to the tetravalent state. The behavior of Pa(IV) in the perchloric acid solution was investigated by the TTA-benzene extraction method. It was found that the $PaOH^{3+}$ ion existed predominantly in a 0.03—3 M perchloric acid solution at the ionic strength of 3. The reaction of TTA extraction may proceed as:

$$PaOH^{3+} + 4HA = PaA_4 + H_2O + 3H^+$$

or

$$PaOH^{3+} + 4HA = Pa(OH)A_3(HA) + 3H^+$$

The distribution ratio of Pa(IV) in the system using Eu(II) as the reductant is about ten times as large as that in the system using Cr(II) as the reductant. It was considered that a non-extractable complex may be formed between Pa(IV) and Cr(III), while such a complex may not be formed when Eu(II) is used as the reductant.

Chromium(II) has been used for reducing protactinium in microquantities to the tetravalent state. Guillaumont[1] investigated the behavior of Pa(IV) reduced with Cr(II) in a perchlorate solution by means of the TTA-benzene extraction method and showed that Pa^{4+} was gradually hydrolyzed to $Pa(OH)_3^+$ in the pH range from −0.3 to 3.0 at the ionic strength of 3. Mitsuji[2] also investigated the behavior of Pa(IV) reduced with Cr(II) in a perchlorate solution by means of TTA-benzene extraction in the pH range from 0.4 to 1.1 at the ionic strength of 0.5; he suggested that $Pa(OH)_2^{2+}$ was the most probable ionic species in the perchlorate solution. However, in a previous report[3] we ourselves suggested that a multi-nuclear complex between Pa(IV) and Cr(II) or Cr(III) might be formed, because the distribution ratio of Pa(IV) decreased with an increase in the concentration of Cr(II). We also tried to measure the absorption spectra of Pa(IV), but could not find any influence of Cr(II) on it.

In the present experiment, we tried to use another reagent to reduce the protactinium in place of Cr(II); Eu(II) was found to be an excellent reductant. The standard oxidation-reduction potential of Pa(IV)–Pa(V) has been reported to be about −0.25 V,[4] and that of Eu(II)–Eu(III), −0.43 V.[5]

After ^{233}Pa in a perchloric acid solution was reduced to the tetravalent state by means of a liquid zinc amalgam in the presence of Eu(III), the oxidation state of protactinium was examined by the co-precipitation method with thorium fluoride reported by Mitsuji[6] and it was found that the complete reduction of ^{233}Pa(V) was readily attained. The chemical behavior of the ^{233}Pa(IV) thus obtained in the perchloric acid solution was investigated by the solvent extraction method, using TTA as the extractant.

In order to examine the difference in the extraction behavior of Pa(IV) caused by the difference in reductant between Cr(II) and Eu(II), experiments were also carried out on the extraction behavior of Pa(IV) reduced with Cr(II) under the same conditions as in the case of Eu(II).

Cr(II)[1,3] was extracted from a perchloric acid solution with TTA-benzene, but Eu(II) was not extracted from a 0.03—3 M perchloric acid solution at the ionic strength of 3. Therefore, Eu(II) can not act as a "holding reductant" in the organic phase. The present authors tried to measure the stability of the Pa(IV)–TTA chelate in the benzene solution by means of spectrophotometric measurements.

Experimental

Reagents. ^{231}Pa was purified by a method reported previously,[7] and its radiochemical purity was certified by α- and γ-ray spectrometry. The concentration of protactinium in the ^{231}Pa solution was determined as Pa_2O_5 by gravimetry and by the absolute α-counting method. These two results agreed well within the limits of experimental error, so we could confirm that there was no contamination by non-radioactive impurities. ^{233}Pa was prepared by the method reported by Suzuki and Inoue.[7]

The extraction behavior of Cr(II) and Eu(II) was examined by the use of ^{51}Cr and ^{152}Eu respectively as the tracers. The radiochemical purity of ^{51}Cr or ^{152}Eu was certified by γ-ray spectrometry.

The lithium perchlorate was prepared by the method reported by Biedermann and Ciavatta.[8] The water used was purified by distillation, followed by ion-exchange treatment. TTA and the other reagents used in this experiment were of the highest purity.

Apparatus. Both the reduction and the extraction of protactinium were carried out in the reduction apparatus described in a previous report.[9] For the solvent extraction procedure, an Iwaki universal mechanical shaker, Model V-S, was used. The α-ray spectra were measured with an ORTEC silicon surface-barrier detector (active area: 450 mm^2; resolution: 30 KeV), coupled with a Tōshiba 4096-channel pulse-height analyzer. The α-ray counting was carried out by measuring the area of its energy peak and the counting efficiency of the detector with reference to the IAEA standard α-ray source (^{239}Pu+^{241}Am+^{244}Cm). The γ-ray spectra were measured with an ORTEC Ge(Li) coaxial detector (volume: 57 cc; resolution: 1.97 KeV), coupled with a Tōshiba 4096-channel pulse-height analyzer. For the γ-ray energy calibration, the IAEA standard γ-ray sources-^{60}Co,

^{57}Co, ^{137}Cs, ^{241}Am, ^{54}Mn, and ^{22}Na- were used. For the on-line data analysis, a Tōshiba TOSBAC-40 mini-computer was used. A Hitachi Model SP-3 well-type NaI(Tl) scintillation probe coupled with a Kōbe Kōgyō Model SA-250 scaler was used for the γ-activity measurements. For measuring the absorption spectrum, a Hitachi Model EPS-3 recording spectrophotometer and a 1 cm quartz cell were used.

Procedure. The Co-precipitation with Thorium Fluoride: Four milliliters of a perchloric acid solution of ^{233}Pa(V) containing a definite amount of Eu(III) were introduced into a reduction apparatus and thoroughly deoxygenated by bubbling with argon gas which had been passed through a dilute sulfuric acid solution of ammonium metavanadate. By shaking the reduction apparatus for about 15 min, the protactinium and europium were reduced with a freshly-prepared liquid zinc amalgam. After the amalgam had been excluded from the apparatus, 2 ml portions of a 0.05 M thorium chloride solution and of a 0.7 M potassium fluoride solution, which had been thoroughly deoxygenated, were added and thorium fluoride was precipitated. Then, the precipitate was separated by centrifuging the mixture for 3 min at 3000 rpm. The γ-activities of both the solution and the precipitate were measured, and the co-precipitation ratio was calculated.

The Absorption Spectra of the Pa(IV)–TTA Chelate: A sulfuric acid solution of ^{231}Pa was reduced by shaking with a liquid zinc amalgam for about 6 hr. After the ^{231}Pa(IV) had been extracted by shaking with a 0.5 M TTA–benzene solution for 10 min, the ^{231}Pa(IV)–TTA chelate in the organic phase was introduced into the quartz cell and the absorption spectrum was immediately measured with reference to a 0.5 M TTA–benzene solution.

The ^{233}Pa(IV) Extraction: Ten milliliters of a perchloric acid solution of ^{233}Pa(V) containing a definite amount of Eu(III) were reduced with a liquid zinc amalgam. Then, the solvent extraction of Pa(IV) was carried out by shaking it with 10 ml of TTA–benzene solution for 10 min. We had confirmed previously that the equilibrium was established sufficiently in that time. After the two phases had been completely separated, an aliquot of each phase was placed in a polyethylene test tube and its γ-radioactivity was counted. The distribution ratio(D) was calculated by means of the usual equation:

$$D = \frac{\gamma\text{-activity per ml of the organic phase}}{\gamma\text{-activity per ml of the aqueous phase}} \quad (1)$$

As Cr(II) was extracted with TTA, we needed to correct the concentration of the TTA–benzene solution resulting from the co-existence of Cr(II). Therefore, the TTA extraction was carried out after ^{51}Cr had been added to the ^{233}Pa solution, and the distribution ratios of Cr(II) and Pa(IV) were obtained at the same time by measuring their γ-radioactivities at the characteristic energy peaks of 319.8 KeV and 311.9 KeV respectively. The concentration of TTA was corrected by means of a method reported previously.[3)]

The ionic strength was kept constant by the use of lithium perchlorate. All the experiments were carried out in an argon atmosphere at room temperature, 20—23 °C.

Results

The Co-precipitation with Thorium Fluoride. The co-precipitation of ^{233}Pa(IV) was almost complete in the presence of more than 10^{-3} M of europium, as is shown in Fig. 1. This means that protactinium can be reduced quantitatively to the tetravalent state on a tracer scale by the addition of europium. On the other hand, the co-precipitation of Pa(V) was about 15% when the concentration of europium was less than 3×10^{-4} M; this value then increased with an increase in the europium concentration when the concentration of europium was higher than 3×10^{-4} M; this was because of the contribution of Pa(V) co-precipitated with europium fluoride.

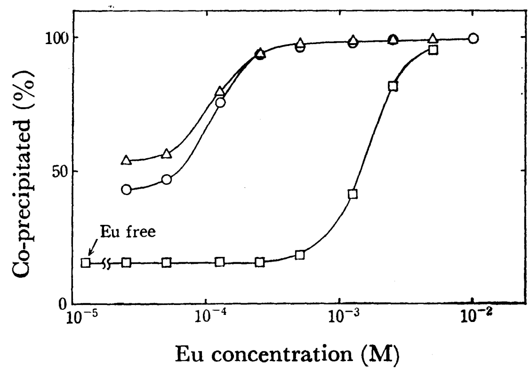

Fig. 1. Relation between Eu concentration and % co-precipitated with ThF$_4$
△: ^{233}Pa in 0.05 M HClO$_4$ reduced with Zn(Hg),
○: ^{233}Pa in 1 M HClO$_4$ reduced with Zn(Hg),
□: ^{233}Pa(V) in 0.3 M HClO$_4$.

The TTA Extraction of Europium. The extraction behavior of Eu(II) and Eu(III) was investigated using ^{152}Eu as a tracer. They were not extracted at all by the TTA–benzene solution from a perchloric acid solution when the acid concentration was 0.03—3 M at the ionic strength of 3.

The Stability of the Pa(IV)–TTA Chelate. The absorption spectra of the Pa(IV)–TTA chelate in benzene are shown in Fig. 2. The molar extinction coefficients at the main peaks of 730, 840, and 1980 nm were 1.50×10^3, 1.24×10^3, and 7.0×10^2 respectively. The molar extinction coefficient of the Pa(V)–TTA chelate was 1.76×10^4 at the characteristic peak of 418 nm. The stability of the Pa(IV)–TTA chelate was calculated on the basis of the decreasing rates of the intensities of the absorption peaks of the Pa(IV)–TTA chelate and the increasing rate of that of the

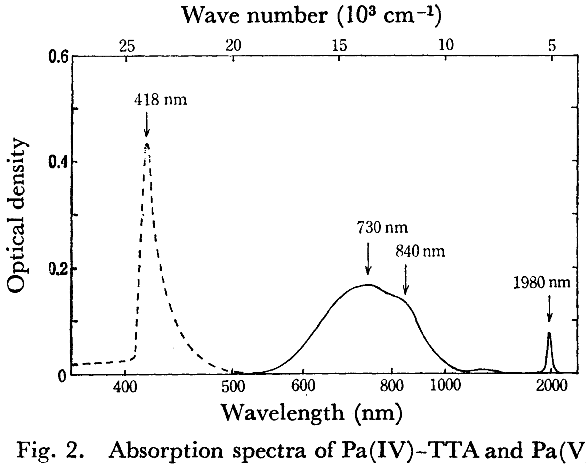

Fig. 2. Absorption spectra of Pa(IV)-TTA and Pa(V)-TTA chelates in benzene
----: Pa(V)-TTA chelate, ——: Pa(IV)-TTA chelate.

Pa(V)–TTA chelate as a function of the time. The oxidation rate of the Pa(IV)–TTA chelate was about 1%/hr, as is shown in Fig. 3. Therefore, we can confirm that Pa(IV) in a benzene solution is stable enough for us to carry out experiments without any effects of re-oxidation as long as all the atmospheric oxygen is excluded.

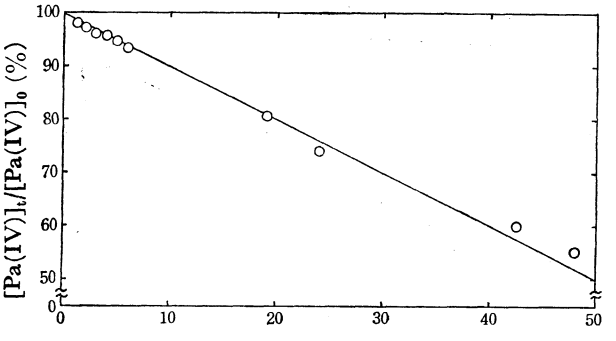

Fig. 3. Oxidation rate of Pa(IV)–TTA chelate in benzene

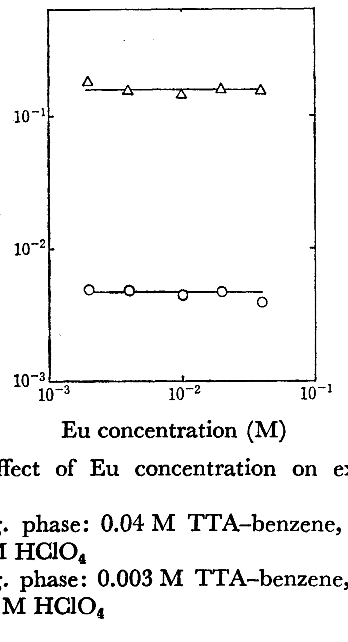

Fig. 4. Effect of Eu concentration on extraction of Pa(IV).

△: Org. phase: 0.04 M TTA–benzene, Aq. phase: I=2, 1 M $HClO_4$

○: Org. phase: 0.003 M TTA–benzene, Aq. phase: I=3, 0.1 M $HClO_4$

The Influence of the Europium Concentration on the TTA Extraction of Pa(IV). As is shown in Fig. 4, the log-log plot of the distribution ratio of Pa(IV) and the concentration of europium is constant within the limits of experimental error. This means that europium does not affect the TTA extraction of Pa(IV).

It is very useful that the performance of the reduction of Pa(V) can be checked by means of the color change of the solution. The absorption maxima of Eu(II) in the 1 M perchloric acid solution were at 250 nm ($\varepsilon = 2.6\times10^3$) and 322 nm ($\varepsilon = 7\times10^2$), and the color of the solution was yellow. About 2×10^{-2} M of europium is needed to observe the effective reduction of europium to the divalent state.

The Relation between the Distribution Ratio and the TTA Activity. The activity of TTA in the benzene phase at equilibrium is calculated from its initial concentration by means of the following equations:

$$\frac{(HA)_i}{(HA)_f} = 1.02 + \frac{10^{-8}}{(H^+)} \qquad (2)^{10)}$$

$$f_{HA} = 1 - 0.25(HA)_f^{0.48} \qquad (3)^{11)}$$

where f_{HA} is the activity coefficient of TTA in benzene; $(HA)_f$, the final concentration in benzene when equilibrated with an equal volume of an aqueous phase, and $(HA)_i$, the initial concentration.

When the perchloric acid concentration is 0.03—3 M at the ionic strength of 3, the log-log plot of the distribution ratio and the activity of TTA in benzene show a linear relationship, with a slope of 4 over a wide range of TTA activity, as is shown in Fig. 5.

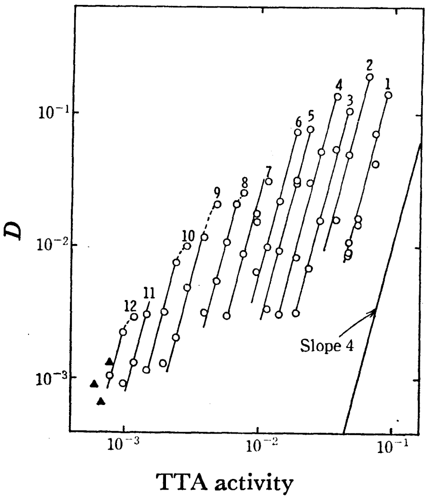

Fig. 5. Dependence of distribution ratio on TTA activity in benzene.
1: 3.0 M $HClO_4$, 2: 2.0 M $HClO_4$, 3: 1.5 M $HClO_4$, 4: 1.0 M $HClO_4$, 5: 0.7 M $HClO_4$, 6: 0.5 M $HClO_4$, 7: 0.3 M $HClO_4$, 8: 0.2 M $HClO_4$, 9: 0.1 M $HClO_4$, 10: 0.07 M $HClO_4$, 11: 0.05 M $HClO_4$, 12: 0.03 M $HClO_4$, ▲: 0.02 $HClO_4$; $[HClO_4]+[LiClO_4]=3.0$ M, $[Eu]=10^{-2}$ M.

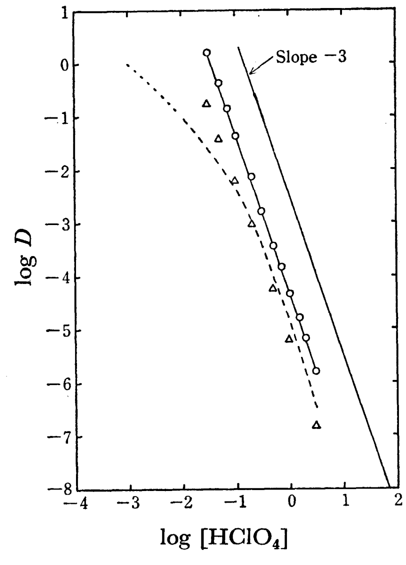

Fig. 6. Dependence of distribution ratio on $HClO_4$ concentration.

○: reduced with Eu(II), △: reduced with Cr(II), ----: by Guillaumont; TTA activity=5×10^{-3} M.

The Relation between the Distribution Ratio and the Perchloric Acid Concentration. The log-log plot of the distribution ratio and the perchloric acid concentration shows a linear relationship, with a slope of -3, as is shown in Fig. 6. The distribution ratios were calculated from the results shown in Fig. 5, and their values were normalized at the TTA activity of 5×10^{-3} M.

The relation between the distribution ratio of Pa(IV) reduced with Cr(II) and the perchloric acid concentration was examined under the conditions described above. The distribution ratio of Pa(IV) reduced with Cr(II) was about 1/10, compared to that of Pa(IV) reduced with Eu(II), as is shown in Fig. 6. The results obtained by Guillaumont[1] are also shown by a broken line in Fig. 6.

Discussion

The TTA Extraction of Pa(IV). From the results shown in Figs. 5 and 6, the equation for the TTA extraction reaction can be written as:

$$\mathrm{PaOH^{3+}(aq.) + 4HA(org.) = PaO_{\mathit{p}}(OH)_{\mathit{q}}A_{4-2\mathit{p}-\mathit{q}}(HA)_{\mathit{r}}(org.)} \\ + (1-p-q)\mathrm{H_2O} + 3\mathrm{H^+(aq.)} \quad (4)$$

where HA and $\mathrm{A^-}$ are used to denote the TTA molecule and the dissociated TTA anion respectively. If the coefficient of water represented in Eq. (4) is not negative, and if the oxygen which does not coordinate with Pa(IV) in the aqueous phase does not coordinate with Pa(IV) in the organic phase, we can say that:

$$p = 0,\ q = 0 \text{ or } 1 \quad (5)$$

Therefore, Eq. (4) may be rewritten as:

$$\mathrm{PaOH^{3+}(aq.) + 4HA(org.)} \\ \mathrm{= PaA_4(org.) + H_2O + 3H^+(aq.)} \quad (6)$$

or

$$\mathrm{PaOH^{3+}(aq.) + 4HA(org.)} \\ \mathrm{= Pa(OH)A_3(HA)(org.) + 3H^+(aq.)} \quad (7)$$

The Difference between the Distribution Ratio Obtained by This Experiment and That Obtained by Guillaumont.[1] The distribution ratio obtained by Guillaumont becomes lower than that obtained by the present authors as the acidity decreases. This may be caused by two factors. One is the incomplete reduction of Pa(V); that is, the distribution ratio of Pa(IV) is higher than that of Pa(V) when the acidity is lower than 1 M at the ionic strength of 3.[1,12] The other is due to the Cr(II)–TTA chelate; its low distribution ratio, which is known by the fact that the aqueous phase is the yellow color of Cr(II)–TTA chelate after extraction, leads to the incomplete correction of the concentration of the TTA–benzene solution, because its correction was done on the supposition that the Cr(II)–TTA chelate is extracted quantitatively into the benzene phase.

The Chromium-Protactinium Complex. The distribution ratio of Pa(IV) in the system using Eu(II) as the reductant is about ten times as large as that in the system using Cr(II) as the reductant, as is shown in Fig. 6. Moreover, the distribution ratio of Pa(IV) decreases with an increase in the concentration of chromium, as has been reported previously.[3] One of the most reliable explanations of the above facts is the possibility that a multi-nuclear complex between Pa(IV) and Cr(II) or Cr(III) is formed. Taube *et al.*[13,14] reported that, when $\mathrm{Co(III)(NH_3)_5X}$ (X is a ligand; *i.e.* $\mathrm{Cl^-}$, $\mathrm{Br^-}$, or $\mathrm{H_2O}$) was reduced with Cr(II), a bridged activated complex for an electron-transfer reaction like $\mathrm{[Co(NH_3)_5\text{–}X\text{–}Cr]}$ was found. This reaction proceeds by means of an inner-sphere reaction mechanism. It has been established that when the actinoid ions are reduced with Cr(II) some binuclear intermediates are found. For instance, a 1 : 1 cationic complex[15] $\mathrm{[O\text{–}Np\text{–}O\text{–}Cr(H_2O)_5]^{4+}}$ was formed, and this inner sphere complex was fairly stable because of a sufficiently slow substitution reaction on Cr(III) when Np(VI) was reduced with Cr(II) in a perchloric acid solution; the binuclear intermediate[16] was also found in the investigation concerned with the reduction of U(VI) with Cr(II).

From the above facts, it may be considered that the Cr(III)–Pa(IV) complex, with the structure mentioned above, may be formed when Pa(V) is reduced with Cr(II) and that the complex is difficult to extract by an extractant. On the contrary, Pa(IV) forms no cationic complexes with Eu(III), because the ligand within the coordination sphere of Eu(III) is not so substitutional inert as that of Cr(III).

A part of the expenses for this investigation has been defrayed by a grant-in-aid from the Ministry of Education.

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