# The Chemistry of Protactinium. X. A Study of the Effect of Chromium(II) on the Solvent Extraction of Protactinium(IV), Using *N*-Benzoyl-*N*-phenylhydroxylamine, Tri-*n*-octylamine and Thenoyltrifluoroacetone as the Extractants

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Cr(II) has been used for reducing protactinium in microquantities to the tetravalent state and for protecting it from re-oxidation. However, the effect of Cr(II) on the extraction behavior of Pa(IV) has not been taken into account by all of the previous investigators. On the basis of the above facts, the influence of Cr(II) on the extraction of Pa(IV) was studied by using such extractants as BPHA, TTA, and TOA. In every case, the distribution ratio of Pa(IV) decreased with an increase in the concentration of Cr(II) in the aqueous phase. One of the most reliable explanations for the phenomena is the possibility that a multi-nuclear complex between Pa(IV) and Cr(II) or Cr(III) is formed. However, the effect of Cr(II) on the absorption spectra of Pa(IV) could not be found, and many more experiments will be necessary to explain the effect of Cr(II) on the extraction behavior of Pa(IV).

Guillaumont[1)] investigated the behavior of Pa(IV) 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. The same author[2)] also studied the chloro-, sulfato-, and fluoro-complexes in aqueous solutions and calculated their stability constants. Muxart and Arapaki[3)] pointed out in their TOA-xylene extraction study that Pa(IV) formed an anionic ion in a sulfuric acid solution. Mitsuji[4)] investigated the behavior of Pa(IV) in perchloric, hydrochloric, and sulfuric acid solutions by means of TTA-benzene extraction in the pH range from 0.5 to 1.1, and suggested that $Pa(OH)_2^{2+}$ and $Pa(SO_4)(OH)^+$ were the most probable ionic species in perchlorate and chloride solutions and in the sulfate solution respectively.

In these experiments, Pa(V) was reduced to Pa(IV) by means of a liquid zinc amalgam in the presence of about $10^{-2}$ M Cr(III). Protactinium in microquantitites can not be reduced only by the liquid zinc amalgam method, even in an argon atmosphere, because the contact between protactinium and amalgam is not sufficient and because the Pa(IV) reduced is affected by any traces of oxygen which might remain in the solution. The role of Cr(III) is considered to be that the Cr(II) formed by the liquid zinc amalgam reduction mediates the reduction of Pa(V) and protects Pa(IV) from re-oxidation. In view of the above facts, Cr(III) has generally been used as a carrier for reduction in studies of the aqueous chemistry of Pa(IV).

Mitsuji[5)] reported that Pa(V) in the concentration range down to tracer level was readily reduced with a liquid zinc amalgam in the presence of more than $10^{-4}$ M of Cr(III), and that the co-precipitation with thorium fluoride was an excellent method for identifying the oxidation state of protactinium in a tracer concentration. It is very useful that the performance of the reduction of Pa(V) can be checked by the color change of the solution from green (Cr(III)) to light blue (Cr(II)). However, since the molar extinction coefficient of Cr(II) is only about 5 at its characteristic peak of 720 nm, about $10^{-2}$ M Cr(III) has been generally used in previous reports.[1—4)] Therefore, a fairly large amount of Cr(II) is always present in a solution of Pa(IV). Nevertheless, the influence of Cr(II) on the extraction behavior of Pa(IV) has not been taken into account in all of the experiments described above.

Guillaumont[6)] investigated the behavior of Pa(IV) in the perchlorate solution in detail by means of the TTA-benzene extraction method, and pointed out that TTA extracted not only Pa(IV), but also Cr(II). Therefore, the correction for the concentration of TTA, which chelates with Cr(II), was carried out, and it was found that the change in the distribution ratio of Pa(IV) was within the limits of experimental error for chromium concentration from $10^{-3}$ M to $10^{-1}$ M.

The purpose of the present study is to investigate the effect of the co-existence of Cr(II) on the extraction behavior of Pa(IV), using-*N*-benzoyl-*N*-phenylhydroxylamine (BPHA), tri-*n*-octylamine (TOA), or thenoyltrifluoroacetone (TTA) as an extractant.

BPHA is a weak acid ($pK_a=8.15^{7)}$) and has been widely used as a gravimetric or spectrophotometric reagent. Recently, it has also been used as an extracting agent for separation or purification; it is inclined to form chelate compounds with various metal ions, such as Ti(IV), Zr(IV), Hf(IV), Ta(V), Pa(V), and Pu(IV), but the extraction behavior of Pa(IV) or Cr(II) with BPHA has not yet been investigated. In this investigation we studied the BPHA extraction of Pa(IV) and Cr(II) in detail.

TTA[1,2,4)] and TOA[3)] have been widely used as extractants and also to investigate the behavior of Pa(IV). Taking account of the previously-reported information, we could define the experimental conditions without further study.

## Experimental

*Reagents.* The $^{231}Pa$ was purified by the method reported previously[8)], and its radiochemical purity was certified by α-ray and γ-ray spectroscopy. The concentration of protactinium in the $^{231}Pa$ solution was determined by gravimetry as $Pa_2O_5$ and by means of the absolute α-counting method. These two results agreed well within the limits of experimental error, so we can confirm that there was no contamination by non-radioactive impurities. The $^{233}$Pa was prepared by the method reported by Suzuki and Inoue[8].

The extraction behavior of Cr(II) and Cr(III) was examined using $^{51}$Cr as a tracer. $^{51}$Cr was obtained as a chemical form of $Na_2CrO_4$ and was reduced to the divalent state with a liquid zinc amalgam after adding some carriers of Cr(III). Cr(II) was readily oxidized to Cr(III) by exposure to air. After two cycles of reduction and oxidation, the Cr(III) thus prepared was used in this experiment. The radiochemical purity of $^{51}$Cr was certified by $\gamma$-ray spectroscopy. The water used was purified by distillation, followed by ion-exchange treatment. The TTA, BPHA, TOA, and 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 the previous report.[9] For the solvent-extraction procedure, an Iwaki universal mechanical shaker, Model V-S, was used. The $\alpha$- and $\gamma$-ray spectra were measured with an Osaka-Denpa gridded ionization chamber and with a 1 3/4 in × 1 in NaI(Tl) detector respectively, coupled with a Toshiba 800-channel pulse-height analyzer. A Hitachi Model SP-3 well-type NaI(Tl) scintillation probe coupled with a Kobe Kogyo Model SA-250 scaler was used for the $\gamma$-activity measurements. For measuring the absorption spectrum, a Hitachi Model EPS-3 recording spectrophotometer and a 1 cm quartz cell were used.

*Procedure.* Ten milliliters of a perchlorate or a sulfate solution which included $10^{-7}$M Pa(V) and a definite amount of Cr(III) were introduced into a reduction apparatus and thoroughly deoxygenated by bubbling with argon gas which had passed through a dilute sulfuric acid solution of ammonium metavanadate. By shaking the reduction apparatus for about 15 min, protactinium and chromium were reduced with a freshly-prepared liquid zinc amalgam. After the amalgam had been excluded from the apparatus, 10 ml of a TTA-benzene, BPHA-benzene, or TOA-xylene mixture was introduced. Then the solvent extraction was carried out with a mechanical shaker until the equilibrium was established. After the two phases had been completely separated, an aliquot of each phase was placed in a polyethylene test tube and its $\gamma$-radioactivity was counted. The distribution ratio ($D$) was calculated by the usual equation:

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

The ionic strength was kept constant by the use of $LiClO_4$, if needed. All the experiments were carried out in an argon atmosphere at room temperature, 17—20 °C.

## Results

*The Stability of Pa(IV).* After protactinium is once reduced to the tetravalent state, it is fairly stable in an oxygen-free atmosphere. For example, the reoxidation rate of Pa(IV) in a hydrochloric acid solution is 8% per 15 hr,[9] and Pa(IV) is more stable in a sulfuric acid solution.

The oxidation-reduction potential of the Pa(IV)-Pa(V) has been reported to be $-0.29\pm0.03$ V,[10] and that of Cr(II)-Cr(III), $-0.40$ V.[11] It was known from two reasons to be described below that Cr(II), which had been expected to be less stable than Pa(IV), was stable in both the aqueous and organic phases for 6 hr after the BPHA-benzene extraction was carried out. One of the reasons for this is that, if Cr(II), which is extracted with BPHA from a weak acid solution as will be described below, is re-oxidized to Cr(III), it should not be extracted with BPHA from an acid solution; another is that the aqueous phase still shows the light-blue color of Cr(II) after the two phases are separated. For the same reason, it was found that Cr(II) was also stable in both the phases during the TTA-benzene extraction and in the aqueous phase during the TOA-xylene extraction, by which Cr(II) was not extracted. Moreover, the distribution ratio of Pa(IV) with BPHA reaches a nearly constant value within 30 min, as is clearly shown in Fig. 1. It should be noted that there is a wide difference in the distribution ratio between Pa(IV) and Pa(V); for instance, the distribution ratio of Pa(V) under the same conditions as those of Pa(IV) is about two orders greater than that of Pa(IV),[12] as is shown in Fig. 1. For these reasons, it may be concluded that Pa(IV) is very stable during the solvent extraction in both the aqueous and organic phases.

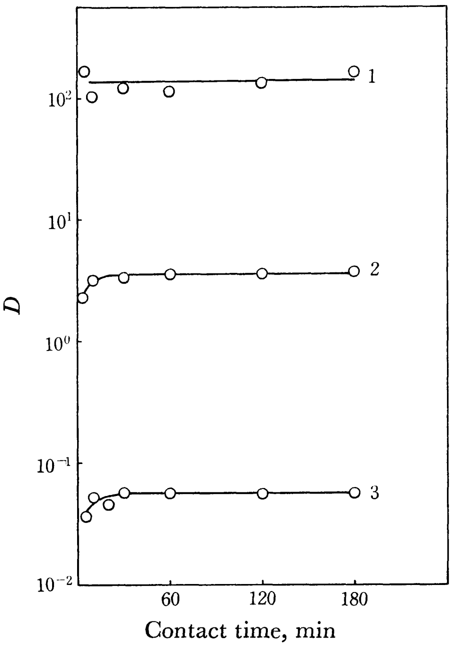

Fig. 1. Effect of contact time on distribution ratio of Pa.
Aq. phase: 0.125 M $H_2SO_4$, $6.22\times10^{-3}$ M [Cr], 1: Pa(V), 2,3: Pa(IV)
Org. phase: 1,2: 0.05 M BPHA-benzene, 3: 0.03 M BPHA-benzene

*BPHA Extraction.* *The Effect of the Contact Time*: From the results shown in Fig. 1, a 1-hr shaking was done in the case of the BPHA extraction of Pa(IV).

*The Relation between the Distribution Ratio and the BPHA Concentration*: The log-log plot of the distribution ratio of Pa(IV) in a sulfate solution and the concentration of BPHA shows a good linearity, with a slope of about 4; this value is independent of the concentration of Cr(II), as is shown in Fig. 2.

*The BPHA Extraction of Cr(II)*: Cr(II) is also extracted with BPHA from an acid solution when the acid concentration is lower than 0.1 M, as is shown in Fig. 3. As is shown in Fig. 4, the log-log plot of the distribution ratio of Cr(II) and the concentration

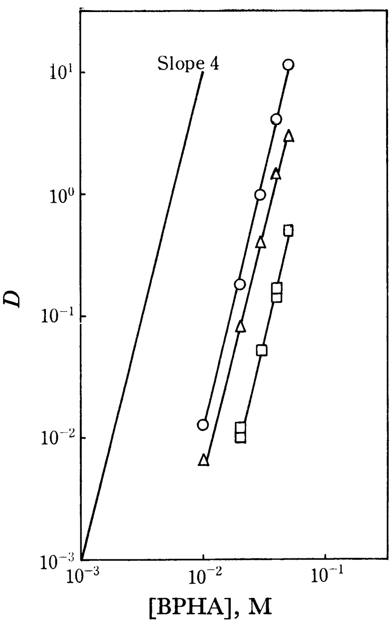

Fig. 2. Dependence of distribution ratio of Pa(IV) on BPHA concentration in benzene.
○: $I=2$ (adding $LiClO_4$), $1.7\times10^{-2}$ M [Cr(II)], 0.159 M $H_2SO_4$, △: $I=2$ (adding $Na_2SO_4$), $1.7\times10^{-3}$ M [Cr(II)], 0.159 M $H_2SO_4$, □: $I=2$ (adding $Na_2SO_4$), $8.5\times10^{-3}$ M [Cr(II)], 0.159 M $H_2SO_4$.

of BPHA shows a linear relationship, with a slope of about 2. This means that one atom of Cr(II) chelates with two molecules of BPHA, and that its chelating compound is extracted into the benzene phase, the color of which is green. The concentration of BPHA can be corrected by Eq. (2), but it is not necessary when the acid concentration is higher than 0.1 M. Cr(III) was not extracted with BPHA-benzene under the same conditions as Cr(II).

*The Influence of the Cr(II) Concentration on the BPHA Extraction of Pa(IV)*: As is shown in Fig. 5, the log-log plot of the distribution ratio of Pa(IV) and the concentration of Cr(II) shows a good linearity, and the distribution ratio of Pa(IV) decreases with an increase in the concentration of Cr(II).

*TTA Extraction.* *TTA Extraction of Cr(II)*: Cr(II) is extracted from a perchlorate or a sulfate solution with TTA-benzene. The log-log plot of the distribution ratio of Cr(II) and the concentration of TTA shows a linear relation, with a slope of about 2, as is shown in Fig. 4. This means that one atom of Cr(II) chelates with two molecules of TTA, and that its chelating compound is extracted into the benzene phase, the color of which is yellow. On the other

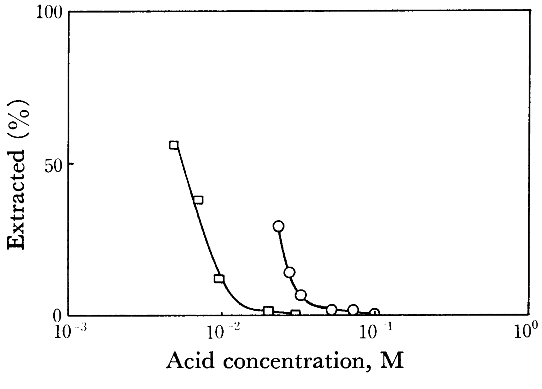

Fig. 3. Extraction of Cr(II) with 0.05 M BPHA-benzene from $H_2SO_4$ and $HClO_4$ solution.
○: $HClO_4$ solution, □: $H_2SO_4$ solution.

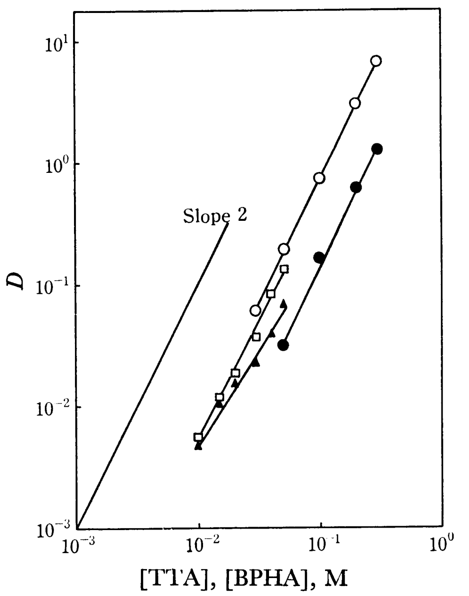

Fig. 4. Dependence of distribution ratio of Cr(II) on TTA and BPHA concentration in benzene.
Org. phase: ○,●: TTA-benzene, ▲,□: BPHA-benzene
Aq. phase: $I=2$, ○: 0.5 M $HClO_4$, $4.4\times10^{-3}$ M [Cr(II)], ●: 0.5 M $H_2SO_4$, $6.8\times10^{-3}$ M [Cr(II)], ▲: 0.033 M $HClO_4$, $2.2\times10^{-3}$ M [Cr(II)], □: 0.01 M $H_2SO_4$, $4.6\times10^{-3}$ M [Cr(II)].

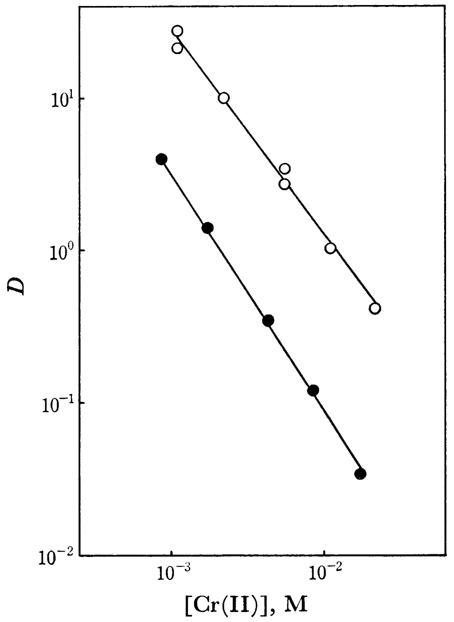

Fig. 5. Influence of Cr(II) concentration on extraction of Pa(IV) with BPHA.
Org. phase: ○: 0.01 M BPHA-benzene, ●: 0.03 M BPHA-benzene
Aq. phase: ●: $I=2$, 0.5 M $H_2SO_4$, ○: $I=2$, 0.5 M $HClO_4$.

hand, Cr(III) is not extracted under the same conditions.

The correction to the concentration of the TTA-benzene solution resulting from the co-existence of Cr(II) can be made by means of Eq. (2):

$$[\mathrm{HA}]_e = [\mathrm{HA}]_i - \frac{2D}{1+D}[\mathrm{Cr(II)}]_i \qquad (2)$$

where

$[\mathrm{HA}]_e$=effective TTA or BPHA concentration in equilibrium

$[\mathrm{HA}]_i$=initial TTA or BPHA concentration

$[\mathrm{Cr(II)}]_i$=initial Cr(II) concentration

$D$=distribution ratio of Cr(II)

It is well known that one atom of Pa(IV) chelates with four molecules of TTA.[1,4,6] Consequently, we can correct the distribution ratio of Pa(IV) on the basis of these values.

*The Influence of the Concentration of Cr(II) on the Extraction of Pa(IV) with TTA*: Taking account of previous information,[4,6] the contact time of 30 min was chosen. The log-log plot of the distribution ratio of Pa(IV) and the concentration of Cr(II) is shown in Fig. 6. The distribution ratio of Pa(IV) decreases with an increase in the concentration of Cr(II).

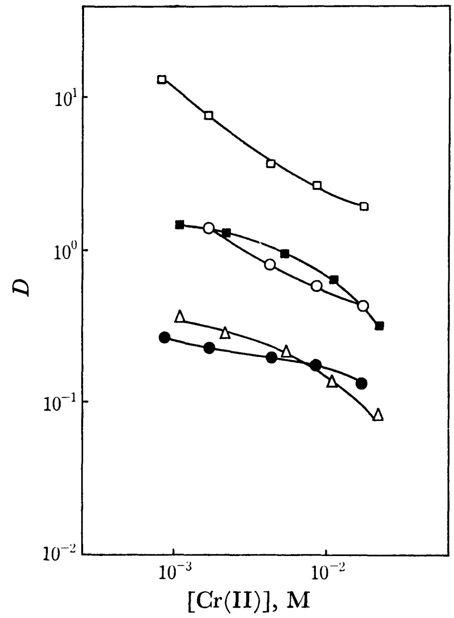

Fig. 6. Influence of Cr(II) concentration on extraction of Pa(IV) with TTA and TOA.
Org. phase: ●: 0.3 M TTA-benzene, ■,△: 0.1 M TTA-benzene, □,○: 5 v/v% TOA-xylene
Aq. phase: ●: $I$=2, 0.5 M $H_2SO_4$, ■: $I$=2, 0.5 M $HClO_4$, △: $I$=2, 1.0 M $HClO_4$, □: 0.236 M $H_2SO_4$, ○: 0.516 M $H_2SO_4$.

*TOA Extraction.* From the results of the previous paper,[3] the contact time of 30 min was chosen. As an anionic species of Pa(IV) is extracted with TOA, we investigated it only in a sulfuric acid solution, in which Pa(IV) was expected to form an anionic complex. The extraction of Pa(IV) from 0.263 and 0.516 M sulfuric acid solutions with 5 v/v % TOA-xylene was carried out; the log-log plot of the distribution ratio of Pa(IV) and the concentration of Cr(II) is shown in Fig. 6. The distribution ratio of Pa(IV) decreases as the concentration of Cr(II) increases, much as in the above results for the BPHA and TTA extractions. Under the same conditions, Cr(II) and Cr(III) were not extracted at all.

## Discussion

Chromium(II) has been used in the investigation of the aqueous chemistry of Pa(IV) in microquantities, and protactinium exists quantitatively in the tetravalent state in the presence of more than $10^{-4}$ M of Cr(II). However, there is no particular information about the influence of Cr(II) on the study of Pa(IV). The present authors, therefore, investigated the effect of Cr(II) on the extraction behavior of Pa(IV). The relations between the concentration of Cr(II) and the distribution ratio of Pa(IV) were examined by the use of such extractants as BPHA, TTA, and TOA, and it was found that the distribution ratio of Pa(IV) decreases with an increase in the concentration of Cr(II) in every case. It is considered that one of the causes leading to these results may be the re-oxidation of Pa(IV). However, Pa(IV) is fairly stable in an oxygen-free atmosphere. From the above experiments, it was found that Cr(II), which is less stable than Pa(IV), is sufficiently stable in both aqueous and organic phases after extraction. Moreover, in the BPHA extraction, if Pa(IV) is re-oxidized the apparent distribution ratio of Pa(IV) should be increased with an increase in the contact time, because Pa(V) has a larger distribution ratio than Pa(IV). The distribution ratio, however, becomes constant after about 30 min, as is shown in Fig. 1. In the TTA extraction, the distribution ratio must be increased because Pa(IV) has a larger distribution ratio than Pa(V),[13] but Fig. 6 shows the reverse of this, contrary to expectation. For these reasons, it is clear that protactinium is quantitatively in the tetravalent state during the extraction.

It is considered that one of the most reliable explanations of the results shown in Figs. 5 and 6 is the possibility that a multi-nuclear complex between Pa(IV) and Cr(II) or Cr(III) is formed. There is some previously-reported information on the Cr(III)–Np(V) complex[14] and Cr(III)–U(IV) complex[15] which is confirmed by the spectrophotometric measurement of the solution. The present authors also tried to measure the absorption spectra of Pa(IV), but could not find any influence of Cr(II) on it. However, it does not necessarily follow that the possibility of the Cr(II)–Pa(IV) complex cannot be denied, because the formation of a multinuclear complex does not always cause a change in the absorption spectrum. The influence of Pa(IV) on the absorption spectrum of Cr(II) could not be found because of its small molar extinction coefficient.

Much more investigations will be necessary to explain the direct interaction between Pa(IV) and Cr(II) completely.

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