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The Chemistry of Protactinium. VII. The Stability of Protactinium(V) in Perchloric Acid and TTA-Benzene Solutions

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With a view to understand the reasons for the confusion in published works as to the chemical behavior of protactinium(V) in a perchloric acid solution, the effect of the contact time and the stability of the perchloric acid solution of the pentavalent protactinium in the TTA-benzene extraction have been investigated in relation to the methods of preparing the solution. Four sample solutions, prepared by various methods, were used, and definite differences among them were observed. Two of them have been confirmed to be very stable and not to suffer a change in their distribution ratios with the time of standing, while the others are unstable–that is, their distribution ratios decrease with standing, thereby reaching a constant value which agrees with that of the former two. However, the value consistent with that obtained from backward extraction is not this constant value but the value obtained from fresh solutions of the latter type. Protactinium species in the TTA-benzene solution are also not stable, and their distribution ratios increase with standing. This increase in the distribution ratio is mainly due to the formation of unstrippable species. The mechanism of this irreversible change is assumed, from the indirect evidence of extraction experiments and absorption spectroscopy, to be the irreversible dehydration of $Pa(OH)_2T_3\cdot HT$ to form $PaOT_3\cdot HT$ in the organic phase. These unfavorable features of the extraction equilibrium should be taken into account in interpreting the results obtained by TTA extraction experiments.

As a result of an investigation by TTA-benzene extraction and by the ion exchange and filtration methods, of the chemical behavior of protactinium in a perchloric acid solution, it was concluded that $PaO_m(OH)_n^{5-2m-n}$ (where $2m+n=3$ and 4) was the predominant species present in a perchloric acid solution of 0.3—2.0M when the concentration of protactinium was lower than 10^{-6}M.[1] When the protactinium concentration was higher than 10^{-5}M, however, quite different behavior was observed. For example, when a perchloric acid solution which was made 10^{-7}M in protactinium by diluting a 10^{-5}M solution which had been prepared in advance was subjected to TTA extraction, the log-log plot of the distribution ratio and the TTA activity in the organic phase were different from those obtained with a solution which was directly made 10^{-7}M in protactinium concentration. In the former case, the distribution ratio decreased remarkably with the time. In the filtration experiments, the percentage of the removal of protactinium from a perchloric acid solution by membrane filters increased with a decrease in the pore sizes. However, this effect was especially noticeable when the protactinium concentration was as high as 10^{-5}M. In the same kind of experiments with Tōyō Roshi No. 5C filter paper (the finest filter for quantitative use), virtually no effect of aging was observed in the case of either carrier-free or 10^{-7}M protactinium solutions, while in the case of a 10^{-5}M solution the removal increased with the aging time, attaining a value of 45% after 80 days. The results can be understood in terms of the formation of colloidal aggregates to a great extent. These observations suggest that the method of preparation and the concentration of protactinium both affect the nature of protactinium in a perchloric acid solution. Much of the confusion in published works which has been pointed out previously[1] may be attributed to these facts. Furthermore, the contact time required to attain a constant distribution ratio in the TTA-benzene extraction system was different with different authors; that is, in a previous experiment by the present authors, only 30 min was long enough to attain a constant distribution ratio,[1] while Kolarich and his co-workers reported that a one-day contact was necessary to reach an extraction equilibrium.[2] This also constitutes one of the very important keys to solve the reasons for the discrepancies among the results obtained by various experimenters.[1]

The purpose of the present study is to investigate the effect on the TTA extraction behavior of the method of the preparation of the perchloric acid

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[1] S. Suzuki and Y. Inoue, This Bulletin, **39**, 1705 (1966).

[2] R. T. Kolarich, V. A. Ryan and R. P. Schuman, *J. Inorg. Nucl. Chem.*, **29**, 783 (1967).

solution of protactinium. In the course of the investigation, interesting results regarding the stability of the protactinium species in the TTA-benzene solution have been obtained.

Experimental

Reagents and Apparatus. *^{231}Pa and ^{233}Pa.* Stock solutions of these isotopes in hydrochloric-acid and hydrofluoric-acid mixtures were prepared by the methods reported previously.[3] The concentration of protactinium in the ^{231}Pa solution was determined by gravimetry by using protactinium pentoxide as a weighing form.

Benzene was purified by distillation, and doubly-distilled water was used throughout this experiment. The acidity of the solution was determined by titration with a standard sodium hydroxide solution. The other chemicals, such as the thenoyl trifluoroacetone (TTA), perchloric acid, hydrofluoric acid, and aluminum perchlorate, were of the highest purity. For the solvent extraction procedure, a Iwaki universal mechanical shaker, Model V-S was used. A Kōbe Kōgyō Model PS-400 well-type scintillation probe coupled with a Kōbe Kōgyō Model SA-400 scaler was used for the gamma-ray assay.

Procedures. All the experiments were carried out at room temperature. Ordinary separatory funnels made of glass were used for the solvent extraction. To eliminate distortions of the experimental results related to the adsorption on glass, the walls of the funnels were preliminarily saturated with protactinium by shaking the test solution for a time sufficient for adsorption equilibrium to be reached. Care was taken to ascertain the material balance in each experiment; each value given is the average of the results of at least two determinations. For all the solvent extractions except for Fomin's method,[4] 5-m*l* portions of the aqueous and organic phases were used, and after the separation of the two phases, a 2-m*l* aliquot of each phase was placed in a polyethylene test tube and its γ radioactivity counted; the distribution ratio was calculated by means of the usual relationship.

$$D = \frac{\gamma \text{ activity per m}l\text{ of the organic phase}}{\gamma \text{ activity per m}l\text{ of the aqueous phase}}$$

Forward Extraction. Four perchloric acid solutions of protactinium prepared by the various methods to be described below, were used. Examinations of the effect of contact time and of the stability of the solution, and analysis by Fomin's method, were carried out for each of the solutions.

No. 1: Aliquots of ^{231}Pa and ^{233}Pa stock solutions (total, 5 m*l*) and 30 m*l* of concentrated perchloric acid were transferred into a platinum dish and heated on a hot plate until the white fumes of perchloric acid appeared. Then the mixture was violently heated directly on a gas burner for five minutes. After cooling, 13 m*l* of concentrated perchloric acid were added. This solution was then diluted to 250 m*l* with distilled water. The concentrations of protactinium and of perchloric acid in this solution were 10^{-7} and 1.38 M respectively.

No. 2: Aliquots of ^{231}Pa and ^{233}Pa stock solutions (total, 5 m*l*) and a small amount of concentrated hydrofluoric acid were transferred into a platinum dish and evaporated almost to dryness, initially on a hot plate and finally on a water bath. The residue was then dissolved by heating it with 2.31 m*l* of 1.17 M hydrofluoric acid. Then 95 m*l* of a 5.28 M perchloric acid solution and 2.5 m*l* of a 3 M aluminium perchlorate solution were added, in this order, and the mixture was diluted with distilled water to 500 m*l*. The concentrations of protactinium, perchloric acid, fluoride ions, and aluminum ions in this solution were 5×10^{-8}, 1.05, 0.005, and 0.015 M respectively.

No. 3: Aliquots of ^{231}Pa and ^{233}Pa stock solutions (total, 5 m*l*), a few milliliters of concentrated hydrofluoric acid, and 2 m*l* of concentrated perchloric acid were placed in a platinum crucible, and the mixture was heated until the white fumes of perchloric acid appeared. Heating was then continued until the volume of the solution was reduced to about 1 m*l*. The residual solution was transferred to a polyethylene bottle, and 1 m*l* of concentrated perchloric acid was added to the crucible. The solution was then reduced to 0.5 m*l* by heating it on a hot plate; the residual solution was combined with the solution in the same bottle. The procedure was repeated until all the activity was removed from the crucible. The concentrations of protactinium and of perchloric acid in this solution were 8.7×10^{-6} and 8.48 M respectively. Before use, this solution was diluted to 10^{-7} M with respect to protactinium with perchloric acid of a suitable concentration, to make 1.00 M in acidity.

No. 4: Aliquots of ^{231}Pa and ^{233}Pa stock solutions (total, 5 m*l*) and a small amount of hydrofluoric acid were transferred into a platinum dish and evaporated almost to dryness, initially on a hot plate and finally on a water bath. The residue was dissolved out of the dish by heating it with concentrated perchloric acid until all the activity on the dish had been removed. The solution was then diluted to 250 m*l* with distilled water. The concentrations of protactinium and of perchloric acid in this solution were 10^{-7} and 0.998 M respectively.

Backward Extraction. Aliquots of ^{231}Pa and ^{233}Pa stock solutions were transferred into a platinum dish and heated to dryness on a hot plate. The residue was dissolved in 0.64 m*l* of 1.17 M hydrofluoric acid, and then 0.948 m*l* of a 5.28 M perchloric acid solution and 1.7 m*l* of a 1.33 M aluminum perchlorate solution were added, in this order. The solution was diluted to 50 m*l* with distilled water. A protactinium solution in TTA-benzene was then prepared by extracting protactinium from 25 m*l* of this solution with 75 m*l* of a 0.1 M TTA-benzene solution for 25 min. The concentration of protactinium in the TTA-benzene solution thus prepared was 0.98×10^{-7} M. The backward extraction was performed by bringing into contact 5-m*l* portions of this solution and of the perchloric acid solution of definite concentration which had been pre-equilibrated with the 0.1 M TTA-benzene solution.

Fomin's Method.[4] The percentage of inextractable forms (P) which were not in rapid equilibrium with extractable forms, and the distribution ratio of extractable forms, D_t, were determined by Fomin's method. The essence of this method consists of the measurement of

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[3] S. Suzuki and Y. Inoue, This Bulletin, **39**, 490 (1966).

[4] V. V. Fomin, E. P. Mairova, M. I. Krapivin and V. G. Yudina, *Zh. Neorg. Khimiya*, **3**, 2113 (1958).

two or more distribution ratios in successive extractions:

$$D_t = \frac{D_n}{VD_{n+1}} + D_n - \frac{1}{V} \qquad (1)$$

$$P = \frac{D_t - D_n}{(1+VD_n)D_t} \qquad (2)$$

where D_n is the distribution ratio which is obtained in the nth extraction and where V is the ratio of the volumes of the organic and aqueous phases.

In practice 15-m*l* portions of both phases were first brought into contact. The $D_1(1/D_1)$ ratio was calculated, and then a 10-m*l* portion of the aqueous (organic) phase was placed in contact with 10-m*l* portion of the new organic (aqueous) phase to determine the $D_2(1/D_2)$ ratio. Finally, a 5-m*l* portion of the aqueous (organic) phase was shaken with a 5-m*l* portion of the new organic (aqueous) phase to determine the $D_3(1/D_3)$ ratio. From Eqs. (1) and (2), two sets of $D_t(1/D_t)$ and P values, one by using $D_1(1/D_1)$ and $D_2(1/D_2)$ and the other by using $D_2(1/D_2)$ and $D_3(1/D_3)$, were calculated. As an example, Table 1 shows one of these sets of results. The last column on the table (P_c) shows the P values, which should be in a $1/D_2-1/D_3$ couple, as calculated from the results of the $1/D_1-1/D_2$ couple. The experimental and calculated values agree within experimental error.

TABLE 1. FOMIN'S METHOD
Org. phase: C. F. ^{233}Pa in 0.1M TTA-benzene
Aq. phase: 1M $HClO_4$
12 days after the preparation

$1/D_1$	$1/D_2$	$1/D_3$	$1/K_t$	P (%)	P_c(%)
0.215	0.128		0.894	62.5	
	0.128	0.074	0.863	75.5	75.9
0.244	0.133		1.08	62.2	
	0.133	0.066	1.14	77.9	77.4

Results

The Results from Forward Extraction. *The Relation between the Method of Preparation and the Rate of Extraction.* The effect of the contact time on the distribution ratio is shown in Figs. 1 and 2. No significant difference in the curves with different methods of preparation is observed. In the case of No. 3, however, a contact time of only 1 min is sufficient to achieve a constant distribution ratio, while about 10 min is necessary in the cases of No. 1 and No. 4. As is clearly shown in Fig. 2, in the case of No. 2 the trend is slightly different: D reaches a maximum after a short contact time and then decreases with an increase in the contact time, finally reaching a constant. These tendencies hold irrespective of the aging time of the solution; Fig. 2 shows an example. From the above results, it can be said that 20 min of contact is sufficient to attain a constant distribution ratio in a forward extraction, regardless of the method of preparation.

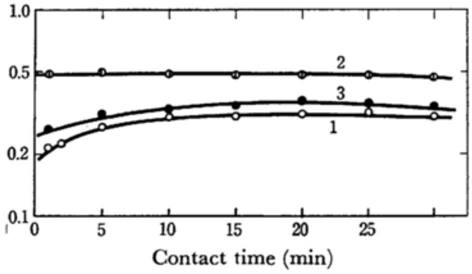

Fig. 1. The effect of contact time on the extraction of Pa. I.
Org. phase: 0.1M TTA-benzene
1: Sample No. 1
2: Sample No. 3
3: Sample No. 4

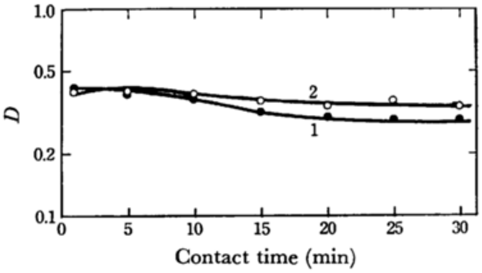

Fig. 2. The effect of contact time on the extraction of Pa. II.
Aq. phase: sample No. 2, Org. phase : 0.1M TTA-benzene
1: Immediately after the preparation
2: Aged for 48 days

The Effect of Aging Time on the Distribution Ratio. As is shown in Fig. 3, for some time after preparation Nos. 1 and 3 show constant distribution ratios which coincide with the values obtained from the backward distribution of a fresh solution of protactinium in TTA-benzene. The value from No. 1 begins to decrease 20 days after preparation and reaches a constant after 40 days of standing. The value from No. 3 begins to decrease 10 days after preparation and reaches a constant after 20 or 30

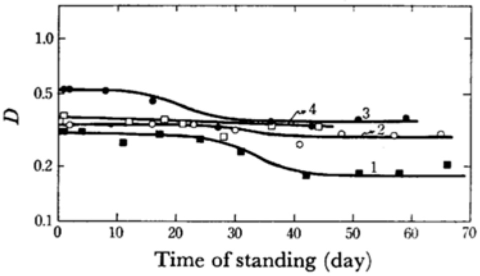

Fig. 3. The stability of Pa in perchloric acid solutions.
Org. phase: 0.1M TTA-benzene
1: Sample No. 1
2: Sample No. 2
3: Sample No. 3
4: Sample No. 4

days of standing. On the other hand, the Nos. 2 and 4 samples are stable for about 2 months and no change in distribution ratios beyond the limits of the experimental error are observed. Interestingly enough, these constant distribution ratios are nearly the same as those obtained from No. 3 and No. 1 after a long period of standing (if normalized to the value which will be obtained in 1 M perchloric acid).

The Results from Backward Extraction. *The Effect of the Contact Time.* The effect of the contact time on the distribution ratio from the backward extraction which was carried out by using a freshly-prepared protactinium solution in 0.1 M TTA-benzene was investigated; the results are shown in Fig. 4. The stripping solution was 1 M perchloric acid. It is apparent from Fig. 4 that the distribution ratio reaches a constant after 5 minutes' contact. The value of the distribution ratio coincides fairly well with that obtained by the forward extraction of a freshly-prepared No. 1 sample.

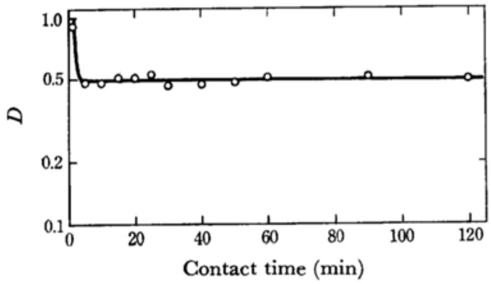

Fig. 4. The effect of contact time on the stripping of Pa.
Org. phase: 10^{-7} M Pa, 0.1 M TTA-benzene
Aq. phase: 1 M $HClO_4$

The Effect of Aging Time on the Distribution Ratio. A TTA-benzene solution of protactinium was stored in a brown bottle in the dark, and the change in the distribution ratio during standing was followed. The protactinium in a 0.1 M TTA-benzene solution was stripped by a 1 M perchloric acid solution. It is apparent from Fig. 5 that at first the distribution ratio decreases remarkably with standing; it shows a minimum at 30 min and then increases a little before reaching a constant. This constant value continues for about five hours. Then the distribution ratio increases continuously. After 2 weeks of standing, nearly all the protactinium becomes unstrippable. Essentially the same phenomenon is observed when carrier-free ^{233}Pa is used. When hydrochloric or sulfuric acid is used as the stripping reagent, virtually the same phenomenon is observed, as is shown in Fig. 6.

Fomin's Method. As one of the methods for understanding the rather peculiar behavior observed in the stripping, Fomin's method was applied. The relation between the standing time and the percentage of unstrippable species (P) is shown in Fig. 7. The P value for a fresh Pa-TTA-benzene solution is only 2—3%. It increases remarkably with standing and reaches 80 or 90% after 2 months of standing, irrespective of the protactinium concentration or the kind of stripping reagent. The $1/K_t$ value decreases slowly with the time of standing, as is shown in Fig. 8. It is clear from these results that the reason for the decrease in stripping is mainly the formation of unstrippable species, but also partly the increase in the distribution ratio (K_t) of the strippable species.

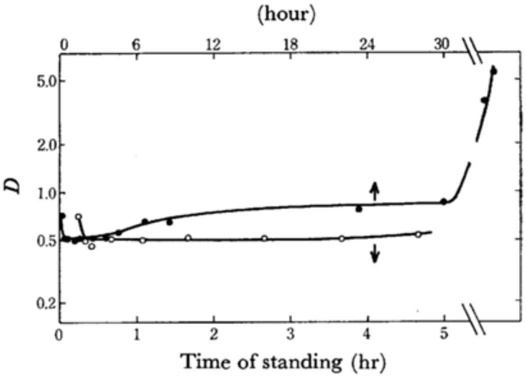

Fig. 5. The effect of time of standing on the stripping of Pa. I.
Org. phase: 10^{-7} M Pa, 0.1 M TTA-benzene
Aq. phase: 1 M $HClO_4$

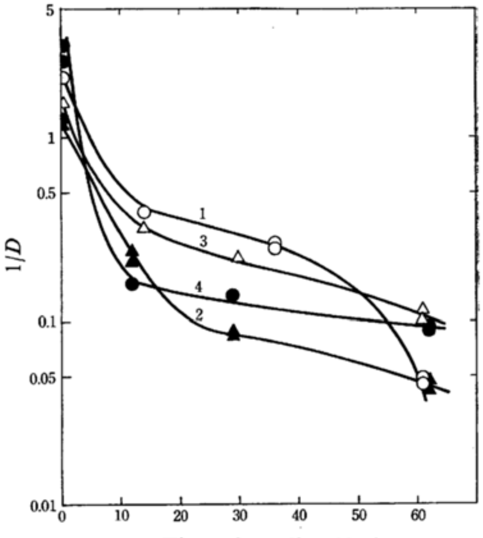

Fig. 6. The effect of time of standing on the stripping of Pa. II.
1: Aq. phase, 1 M $HClO_4$; Org. phase, 10^{-7} M Pa in 0.1 M TTA-benzene
2: Aq. phase, 1 M $HClO_4$; Org. phase, C.F. ^{233}Pa in 0.1 M TTA-benzene
3: Aq. phase, 0.4 N H_2SO_4; Org. phase, 10^{-7} M Pa in 0.1 M TTA-benzene
4: Aq. phase, 1 M HCl; Org. phase, 10^{-7} M Pa in 0.1 M TTA-benzene

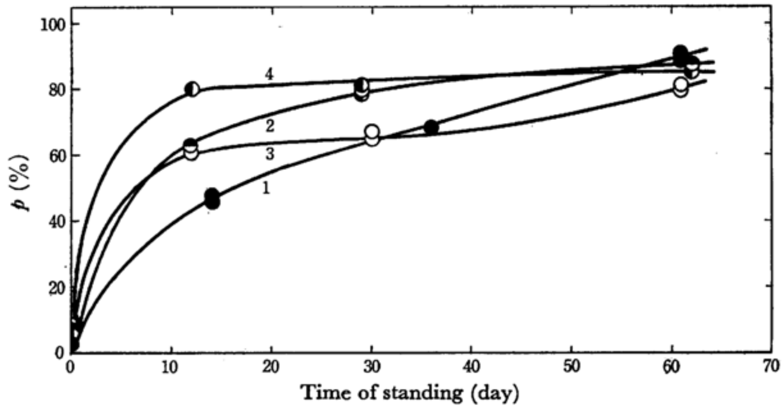

Fig. 7. The growth of unstrippable species of Pa in 0.1 M TTA-benzene.
1: Aq. phase, 1 M $HClO_4$; Org. pahse, 10^{-7} M Pa
2: Aq. phase, 1 M $HClO_4$; Org. phase, C.F. ^{233}Pa
3: Aq. phase, 0.4 N H_2SO_4; Org. phase, 10^{-7} M Pa
4: Aq. phase, 1 M HCl; Org. phase, 10^{-7} M Pa

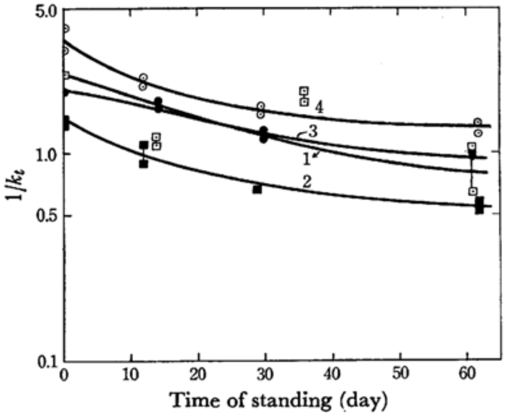

Fig. 8. The true distribution ratio of strippable species in 0.1 M TTA-benzene.
1: Aq. phase, 1 M $HClO_4$; Org. phase, 10^{-7} M Pa
2: Aq. phase, 1 M $HClO_4$; Org. phase, C.F. ^{233}Pa
3: Aq. phase, 0.4 N H_2SO_4; Org. phase, 10^{-7} M Pa
4: Aq. phase, 1 M HCl; Org. phase, 10^{-7} M Pa

The Relation between the Distribution Ratio and the Perchloric Acid Concentration as Determined by Backward Extraction. The distribution ratio was determined as a function of the perchloric acid concentration by using a fresh solution of protactinium in 0.1 M TTA-benzene. As is clearly shown in Fig. 9, the curve obtained was nearly the same as that shown in Fig. 6 of the second report of this series.[1] As has been described earlier, the values of the distribution ratio agree with those from the forward extraction which is made by using either a No. 1 or No. 3 solution.

Absorption Spectra of the Pa-TTA Complex. As another way to understand the peculiar behavior in stripping, the change in the absorption spectrum with standing was traced. The protactinium concentration was about 3×10^{-5} M. An absorption maximum was observed at 410 mμ. The spectrum did not change except for a slight decrease in absorbance with standing. As is shown in Table 2, the absorbance at 410 mμ decreases by 10% after 51 days of standing.

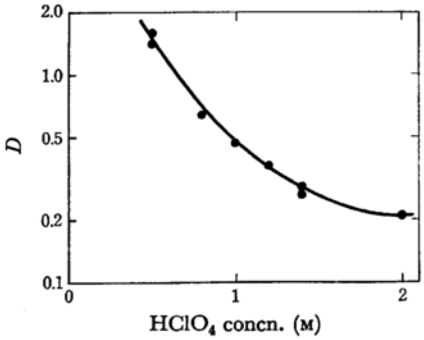

Fig. 9. Distribution ratios determined by stripping as a function of $HClO_4$ concentration.
TTA concn.: 10^{-1} M, Pa concn.: 10^{-7} M

TABLE 2. THE EFFECT TIME OF STANDING ON THE ABSORBANCE OF Pa IN TTA-BENZENE SOLUTION
TTA: 0.1 M Pa: *ca.* 3×10^{-5} M

Time (day)	Absorbance at 410 mμ
0	0.705
3	0.697
5	0.683
12	0.691
20	0.688
51	0.630

Discussion

In the equilibration experiment, it is obvious that a contact time of longer than half an hour makes no sense for the following reasons. In the forward extraction, the distribution ratio reaches a constant value within 20 min of contact time, irrespective of the method used to prepare the perchloric acid solution of protactinium. Five minutes' contact is long enough to get a constant value from backward extraction. Another important thing is the peculiar behavior of the stripping, which makes it impossible to establish a true equilibrium because of the unfavorable formation of unstrippable species.

The method of preparing No. 3 corresponds in protactinium concentration to that shown in Fig. 5b of the second report of this series,[1] but the method used to prepare the stock solution is different. From this comparison it may be concluded that a protactinium solution with a concentration as high as 10^{-5}M is unstable. Besides, the solution prepared by such method as No. 1 is unstable regardless of the protactinium concentration.

The change in the absorption spectrum of protactinium(V) in a hydrochloric acid solution has been ascribed to the onset of hydrolysis, which is accompanied by the disappearance of solvent extractability.[5] The extractability of protactinium from a nitric acid solution decreases with standing, a fact which has been ascribed to the formation of inextractable species.[6,7] Even in the case of a fresh solution, the amount of protactinium in inextractable forms comprises 3%.[7] These phenomena have been ascribed to the formation of colloidal aggregates in the aqueous phase, which is not in rapid equilibrium with monomeric forms. Similar behavior was observed in our previous experiment in perchloric acid solution. About 17% and 44% of protactinium in 0.5 and 3.1M perchloric acid solutions respectively were unadsorbable species on cation exchange resin, and consistent results were obtained in the filtration experiments. No such phenomenon could, however, be observed in the TTA extraction.[1]

The same kind of investigation was undertaken in this experiment with relation to both the methods of preparing the protactinium solutions and their aging. It is evident that, in all the cases examined, the distribution coefficient remains unchanged in successive extraction. Therefore, the change in the distribution ratio with the time of standing is directly related to the change in K_t value. This difference between TTA extraction and other methods can be explained by the existence of a dynamic equilibrium in the TTA extraction; this in turn destroys the colloidal aggregates to some degree by means of the strong chelating action of TTA. It is obvious from these results that the extraction behavior differs greatly with the method of preparation, even in such a dilute solution as 10^{-7}M; nearly the same distribution ratio is obtained regardless of the method of preparation when the solution has been aged for longer than a month. However, the value consistent with that obtained from back extraction is not this value but the value obtained from fresh No. 1 and No. 3 samples. These observations suggest that the method of preparing either No. 1 or No. 3 is suitable from the standpoint of extraction equilibrium; however, No. 3 can not be considered to be very appropriate because of its unique behavior, discussed in a previous report. From the above considerations, about a 30-min contact of a fresh No. 1 sample with a TTA-benzene solution is most suitable for the investigation. It should be noted, however, that this statement of experimental conditions takes no cognizance of the thermodynamically-stable state of protactinium in a perchloric acid solution.

In any case these difficulties should be taken into account in interpreting the results.

There are many possibilities for interpreting the interesting behavior observed in stripping. One possibility is the polymerization of the extracted Pa-TTA chelate in the organic phase. However, this may be rejected on the basis of the fact that this phenomenon is observed irrespective of the protactinium concentration. Besides, the rate of the formation of the unstrippable species is faster in carrier-free ^{233}Pa than in 10^{-7}M protactinium. This obviously mitigates against this possibility. Another possibility is the decomposition of the chelate by some such means as thermal or radiation decomposition. This possibility is not warranted either because the rate of decrease in absorbance is too slow to interpret the rather drastic increase of unstrippable species. The last possibility is a minor and irreversible change of the extracted compounds in the organic phase. If the TTA chelate of protactinium is assumed to be absent in the aqueous phase, the extracted species should be $Pa(OH)T_4$, according to the second report of this series.[1] Strictly speaking, though, this form is not general enough; as alternate forms species like $Pa(OH)_2T_3 \cdot HT$ and $PaOT_3 \cdot HT$ are possible. If we consider that the first form participates in the extraction equilibrium and irreversibly undergoes dehydration to form the second form, which is naturally assumed to be more hydrophobic than the first form, the peculiar stripping behavior may be understood. Of course, there is no direct evidence for this hypothesis. Further study to support this hypothesis is being undertaken and will be reported on in the near future.

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[6] C. J. Hardy, D. Scargill and J. M. Fletcher, *J. Inorg. Nucl. Chem.*, **7**, 257 (1958).

[7] V. I. Spitsyn, R. A. D'yachkova and V. P. Khlebnikov, *Radiokhimiya*, **7**, 257 (1965).