[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY CHEMISTRY DIVISION]

Anion Exchange Studies. III. Protactinium in Some HCl–HF Mixtures: Separation of Niobium, Tantalum and Protactinium[1]

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The anion exchange behavior of protactinium in HCl–HF mixtures has been studied and a number of conditions were found under which this element can be adsorbed. Since its adsorbability differs widely from that of niobium and tantalum, excellent separation of this triad can be achieved under a variety of conditions.

In previous papers of this series[2] the anion exchange behavior of niobium, tantalum and zirconium in HCl–HF mixtures was given. These studies have now been extended to protactinium and a number of conditions were found under which separation of all four elements is very effective. HCl–HF mixtures were chosen as eluents since they are excellent solvents even for highly insoluble compounds of these elements and since with them many difficulties can be avoided which might result from the unfavorable hydrolytic properties of these elements.

Experimental

The experiments were carried out with tracers of all elements (Zr^{95}–Nb^{95}, Ta^{182}, Pa^{233}) at 25 ± 1° using Dowex-1 columns of *ca.* 0.023 sq. cm. cross-sectional area. The preparation of the zirconium, niobium and tantalum tracers was described in I and II. Their purity was checked by decay and absorption measurements. Pa^{233} tracer (β-emitter, $T_{1/2} = 27.4$ days[3]) was prepared by neutron bombardment of thorium metal. After separation from thorium the Pa^{233} was shown to be of high purity through decay and β-absorption measurements. The elution rates were determined by monitoring the effluent and by direct scanning of the column. Each effluent band was identified radiochemically. Further details of the experimental procedure can be found in I.

Results and Discussion

Protactinium.—The results of the experiments are summarized in Table I. The data are given in terms of the elution constant E_{Pa} defined as $E_{Pa} = dA/V$ where d is the distance (cm.) the band maximum moves after passage of V ml. of eluent through a column of A sq. cm. cross-sectional area. In view of the symmetry of the bands it is believed that the columns were operated under equilibrium conditions. For comparison the ratio of elution constants $E_{Pa}:E_{Nb}:E_{Ta}$ have been included using the data from I and II.

As can be seen from this table protactinium is poorly adsorbed under most conditions studied with elution constants within a factor of two or three of the theoretical maximum (E *ca.* 2.4). Only at very low fluoride or low chloride concentrations is it fairly strongly adsorbed. This may be contrasted with the previous observation[4] that in 9 M HCl (in the absence of fluoride) protactinium is very strongly adsorbed (estimated E = *ca.* 10^{-3}). Thus addition of 4×10^{-3} M HF to a 9 M HCl eluent decreases the adsorbability of this element by a factor of approximately one hundred. This is similar to, though more extreme than, the behavior of niobium (see I) and a similar explanation is probably applicable.

TABLE I

ELUTION CONSTANTS OF PROTACTINIUM IN HF–HCl MIXTURES (FLOW RATES *ca.* 0.2 ML./SQ. CM./MIN.)

M HCl	M HF	$E_{Pa} \times 10^3$	$E_{Pa}:E_{Nb}:E_{Ta}$
9.0	0.0	*ca.* 1	
9.0	0.004	89	590:20 :1
9.0	0.02	810	165 :4 :1
9.0	0.1	1070	220:46 :1
9.0	0.5	1530	320:15 :1
3.0	0.1	1440	1200:160:1
3.0	0.5	1430	1300:160:1
3.0	2.0	1640	745:50 :1
3.0	5.0	1830	330:7.7:1
3.0	17.25	1200	33:0.7:1
0.5	0.05	490	....
0.5	0.1	380	1360:140:1
0.5	0.5	277	870:140:1
0.2	0.5	42	....

The strong adsorption of protactinium in 9 M HCl suggests (see I) that under these conditions it carries a charge of minus one (species 1). On addition of fluoride ions further complexing probably occurs, which could increase the negative charge to two or three (species 2) with a resulting decrease in adsorbability. The rapid decrease of E_{Pa} with decreasing hydrochloric acid concentration in fluoride solutions supports the assumption that species 2 has a charge more negative than minus one. In the lower hydrochloric acid range the slope of a log E_{Pa} *vs.* log (HCl) plot has a slope of two suggesting a charge of minus two. Since activity coefficients are unknown, a charge of minus three appears also possible.

Protactinium seems to resemble niobium more than tantalum, since for both elements formation of species 2 occurs at very low fluoride concentration. Since niobium under these conditions is probably oxygenated, it is suggested that the same is the case for protactinium. The most probable formula of species 1 thus becomes $PaOCl_4^-$ (or $H_nPaOCl^-_{4+n}$). No evidence for the loss of the oxide ion at high concentration of hydrofluoric acid was found as was the case with niobium. Analysis of the data according to equation (17) of I suggests that, as with niobium and tantalum, two moles of hydrofluoric acid are involved in the formation of species 2 from species 1, although this conclusion can only be considered highly tentative. The formation constant $K_{12} = (2)/(1)(HF)^2$

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[1] This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory. Presented at the Chicago Meeting of the American Chemical Society, September, 1950.

[2] Part I: THIS JOURNAL, **73**, 9 (1951); Part II: *ibid.*, **73**, 13 (1951). Reference to these papers will be made by their Roman numerals. For a preliminary communication on the separation of niobium and tantalum see THIS JOURNAL, **71**, 3855 (1949).

[3] Information from "Tables of Isotopes," by G. T. Seaborg and I. Perlman, *Rev. Modern Phys.*, **20**, 585 (1948).

[4] K. A. Kraus and G. E. Moore, THIS JOURNAL, **72**, 4293 (1950).

where (1), (2) and (HF) are the molar concentrations of species 1 and 2 and of hydrofluoric acid, was estimated to be *ca.* 10^6 in 9 M HCl. The analogous formation constant for niobium was considerably smaller ($K_{12} = 1.5 \times 10^4$).

Separation of Niobium, Tantalum and Protactinium.—The ratios of the elution constants for these three elements (see Table I) are generally very large and their separation should be very effective with rather short columns and in many cases operation under break-through conditions with respect to the less strongly adsorbed component should be feasible. In all cases studied protactinium had the largest elution constant and hence should appear first in the eluent.

Two typical separations are illustrated in Figs. 1 and 2, the transcribed automatic records of the activity of the effluent (in Fig. 1 background was subtracted). For Fig. 1 the following conditions were used: 12.5 cm. Dowex-1 column with resin (200–230 mesh) in chloride form, 0.0226 sq. cm. cross-section, flow rate 0.3 ml./sq. cm./min., tracer Pa^{233}, tracer Nb^{95}, *ca.* 1 mg. Ta (with tracer Ta^{182}), eluent 9 M HCl–0.05 M HF throughout experiment. As can be seen from the figure, satisfactory separation of the three elements was achieved as predicted from the differences in the elution constants.

In Fig. 2 the results of an experiment are given where in the same run also zirconium was separated (using 1 mg. Zr and Zr^{95} tracer). The conditions were similar to the previous experiment except that a shorter column (6 cm.) with larger cross-sectional area was used (0.3 cm.^{2}). The composition of the eluent was changed several times during the experiment to permit elution of successive elements within more reasonable periods of time than would be attainable otherwise. Conditions were changed after the automatic record indicated that an element had been completely removed from the column. The following eluents were used: 9 M HCl–0.004 M HF (removed Zr(IV) and then Pa(V)); 9 M HCl–0.18 M HF (removed niobium); 4 M NH_4Cl–1 M HF (removed tantalum). Completeness of elution generally appeared satisfactory since scanning of the column showed no significant change in background activity.

Use of NH_4Cl–HF and NH_4Cl–NH_4F Mixtures for the Elution of Tantalum.—The NH_4Cl–HF mixture which was used for the removal of tantalum in the second experiment described in the previous section was introduced in an attempt to find a solvent which could rapidly remove tantalum from the column. All HCl–HF mixtures previously tested (see II and Table I) could move this element only relatively slowly and in some cases extremely slowly. It appeared that for rapid removal high chloride concentrations and high negative charge were necessary. The use of neutral or positively charged species seemed difficult in view of the danger of possible hydrolytic polymerization of the element followed by strong adsorption of the polymer (see II). An increase in negative charge should be attainable by a decrease in acidity since then possible acid complexes of the type $H_nTaX^-_{6+n}$ would "hydrolyze" to ions of the type $H_{n-m}TaX^{-1-m}_{6+n}$ or complexes of the type TaX_6^- might add further fluoride ions[5] to yield complexes of the type $TaX_6F^=$ and $TaX_6F_2^{\equiv}$. Using 4 M NH_4Cl–1 M HF instead of a similar HCl–HF mixture, a marked decrease in adsorbability was observed ($E = 0.016$ compared with an expected $E =$ *ca.* 0.002 for the HCl–HF mixture). This decrease in adsorbability became very dramatic when the acidity was further decreased by using 4 M NH_4Cl–1 M NH_4F as eluent. Under these conditions E becomes *ca.* 1.2, *i.e.*, 500 to 1000 times larger than in the corresponding HCl–HF mixture. Since the main decrease in adsorbability occurred on substituting NH_4F for HF (rather than where the over-all acidity was changed from strong to moderate), and since the acid complexes would most probably act as strong acids, it appears that of the two mechanisms proposed for an increase in negative charge, the formation of higher fluoride complexes is more probable.

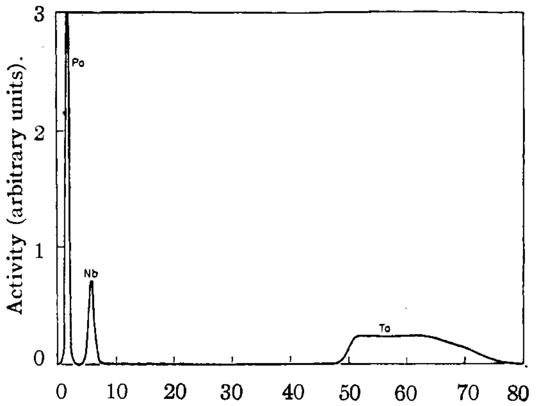

Fig. 1.—Separation of protactinium(V), niobium(V) and tantalum(V) by anion exchange: 12.5 cm. Dowex-1 column, 0.0226 sq. cm. cross-section, 0.3 ml. cm.$^{-2}$ min.$^{-1}$ flow rate, eluent 9 M HCl–0.05 M HF.

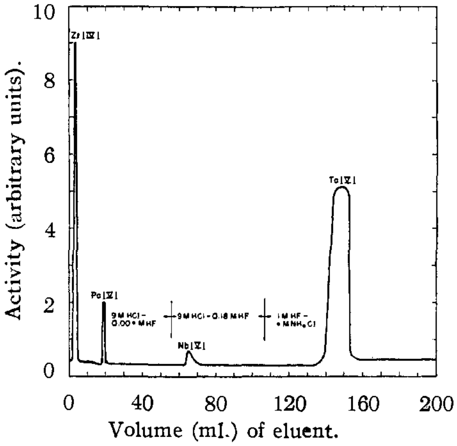

Fig. 2.—Separation of zirconium(IV), protactinium(V), niobium(V) and tantalum(V) by anion exchange: 6-cm. Dowex-1 column, 0.32 sq. cm. cross-sectional area, average flow rate 0.2 ml. min.$^{-1}$ cm.$^{-2}$.

General Discussion of Separations.—The separation efficiency in the triad niobium, tantalum

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[5] Since HF is a weak acid, the F^- concentration would increase rapidly with decreasing acidity.

and protactinium is, at first glance, surprisingly large considering the fact that these elements generally have very similar properties. Although the ion exchange data indicated that these elements may differ widely in their tendency to form oxygenated complexes, this cannot be considered the main reason for their ease of separation. Thus the apparently singly charged ions (species 1) existing at very low (and possibly zero) hydrofluoric acid concentration have very similar adsorbabilities. Their distribution coefficients D_1 (amounts per cc. of resin/amounts per cc. of solution) are in 9 M HCl-$NbOCl_4^-$, 420; TaX_6^-, 210; $PaOCl_4^-$, *ca.* 10^3.[6] These differences in distribution coefficients would at best permit separation by careful chromatography. The distribution coefficients D_2 of the various species 2, apparently formed by reaction of species 1 with two molecules of hydrofluoric acid, are also very similar, though less similar than those of the species 1 (calculated values of D_2: niobium, 1.0; tantalum, 27; protactinium, 0.2).

The excellent separability of these elements is thus not primarily due to differences in adsorbability of their ions of like charge, as one might expect. It results more from the facts that ions of different charge have widely differing distribution coefficients under the experimental conditions and that the complex constants relating the various species differ greatly. Since the ratios of the distribution coefficients of ions of different (negative) charge depend strongly on the eluting conditions[7] and may even become unity—making separations impossible—at a cross over point P (see I), it is important to select eluting conditions where the ratio of the distribution coefficients is as large as possible. In the present case this is true at extremely high chloride concentrations since P is at a small chloride concentration. Fortunately, the apparently singly negatively charged complex ions of these elements have extremely high inherent adsorbabilities and hence can be adsorbed from solutions of very high ionic strength where distribution coefficients of ions of higher charge are small.

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[6] As mentioned earlier these formulas are only symbolic. They are probable but have not been proved in detail.

[7] As shown in I plots of log D *vs.* log (HCl) have different slopes for ions of different charge.

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Anion Exchange of Complex Ions of Hafnium and Zirconium in HCl-HF Mixtures

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The elution of complex ions of zirconium and hafnium from an anion exchange resin with mixtures of hydrochloric and hydrofluoric acids has been studied in two different concentration ranges. Differences in the dependence of the distribution coefficient upon the concentrations of chloride ion, hydrogen ion and hydrofluoric acid have been noted for the two ranges, and some possible ionic equilibria are discussed in connection with the data.

The separation of zirconium and hafnium by anion exchange of their complex ions containing fluoride and chloride has been reported by Kraus and Moore[1] and by Huffman and Lilly.[2] The former investigation made use of the resin Dowex-1 and an eluting solution composed of 1.0 M hydrochloric acid and 0.5 M hydrofluoric acid (referred to herein as high acid concentration); the latter investigation made use of the resin Amberlite IRA-400 and an eluting solution composed of 0.2 M hydrochloric acid and 0.01 M hydrofluoric acid (referred to herein as low acid concentration). Moore and Kraus have also presented data to show the dependence of the rate of elution of zirconium upon the hydrochloric acid and the hydrofluoric acid concentrations in the high acid concentration range,[3] though it is not clear from this work whether the rate of elution is dependent upon both the hydrogen ion concentration and the chloride ion concentration or only upon the latter.

Work in this Laboratory, principally with hafnium, has shown that the dependence of the elution rate upon the acid concentrations is not the same for the two different mixed acid concentration ranges. This paper presents the results of this work and discusses possible ionic species involved in the exchanges. Data have been obtained in the low acid concentration range to show the elution rate dependence upon chloride ion concentration, hydrogen ion concentration, and hydrofluoric acid concentration. Data have also been obtained in the region studied by Moore and Kraus,[3] but using lithium chloride as well as hydrochloric acid in order to obtain the effect due to chloride ion alone. The present data were obtained using macro quantities of zirconium and hafnium, and Amberlite IRA-400 in place of Dowex-1. Both of these resins are cross-linked quaternary amines and strongly basic.

Experimental

Preparation of the Adsorbent.—Amberlite IRA-400 resin, as received from the manufacturer, was in the chloride form. The air-dried material was ground and dry screened to obtain 200/325 mesh particles and washed free of fines by decantation with water in a beaker. Columns of 6.5 mm. i.d. were bored from 15 cm. lengths of lucite rod and threaded externally at both ends. The lower end was fitted with a lucite cap having a capillary tip and the upper end was fitted with a cap to which 6 mm. i.d. tygon tubing could be attached. Teflon gaskets were used to seal the fittings. A small cotton plug was inserted at the bottom of the column and the resin was washed in to give a bed length of 10.5 cm. after gentle tapping.

The free column volume was determined in the following

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[1] K. A. Kraus and G. E. Moore, THIS JOURNAL, **71**, 3263 (1949).

[2] E. H. Huffman and R. C. Lilly, *ibid.*, **71**, 4147 (1949).

[3] G. E. Moore and K. A. Kraus, Division of Physical and Inorganic Chemistry, American Chemical Society, Detroit, Michigan, April 18, 1950.