

n-OCTYLPHENYLPHOSPHONIC ACID AS AN EXTRACTION AGENT FOR SCANDIUM AND HAFNIUM

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The extraction of Sc complexes with n-octylphenylphosphonic acid (HA) from HCl, HClO₄, HNO₃ and H₂SO₄ into benzene was studied and the effect of some tri-n-alkylphosphine oxides added was investigated. Scandium is extracted into the organic phase as the ScA₃(HA) complex from 2M mineral acids; when concentrated mineral acids, except for HNO₃, are employed, the extraction mechanism changes and ScX₃(HA)_n or Sc₂(SO₄)₃(HA)_n complexes, where X is a mineral acid residue, are extracted into the organic phase. The corresponding extraction constants were determined. The substances added did not cause synergistic extraction. The extraction of Hf from nitrate and sulphate media was studied analogously; with the former medium, only the solvation-mechanism extraction was observed. The IR and NMR spectra of the reagent were studied.

In a previous work¹ we dealt with the use of phenylphosphonic acid n-octyl ester, n-C₈H₁₇OC₆H₅P(O)OH, (further denoted as HA) for the extraction of Hf(IV) from chloride and perchlorate media and determined its dissociation constant and the dimerization and distribution constants for an ionic strength of *I* 2.0 and benzene, cyclohexane and n-octane organic phases.

The present work supplements some data on the reagent itself and on the Hf(IV) extraction and further deals with the scandium distribution between HA solutions in benzene and an aqueous phase with *I* 2.0.

EXPERIMENTAL

Chemicals and Apparatus

HA was prepared and purified using the procedure described earlier². The other chemicals were of reagent-grade quality. A radioactive solution of ¹⁷⁵⁺¹⁸¹Hf was prepared in the manner described in ref.¹. The Hf concentration in the working solutions was 6–7 · 10⁻⁶M and their activity was 1.8–7.4 · 10⁴ s⁻¹ ml⁻¹. Working solutions of ⁴⁶Ss were prepared from an ScCl₃ stock solution by evaporating excess HCl and dissolving in an appropriate mineral acid. The purity of both radioactive substances was checked spectrometrically using the single-channel spectrometer Vakutronik VAM 120 (GDR). The γ -activity of the samples was measured with a relative standard deviation of $s_r \leq 2\%$ on a VAM 15D instrument (GDR) with scintillation well-type crystal. The IR spectra were obtained on a Unicam SP 1000 instrument and the NMR

spectra on a Tesla BS 487 B instrument. If not stated otherwise, all measurements were carried out at $20 \pm 1^\circ\text{C}$.

Procedure

Equal volumes of the aqueous and organic phases (5 ml) were stirred for at least 4 hours. Preliminary experiments have shown that this time is quite sufficient for attainment of extraction equilibrium. The phases were then separated, 2 ml-aliqouts were taken and measured in glass ampoules in a well NaI(Tl) crystal. The aqueous phase acidity was adjusted (except for dependences of the studied metal distribution on the overall concentration of mineral acids) using $\text{HClO}_4 + \text{NaClO}_4$, $\text{HCl} + \text{LiCl}$ or $\text{HNO}_3 + \text{LiNO}_3$ solutions, so that the ionic strength always equalled 2.0. The IR spectrum was measured in a liquid film and the NMR spectrum in a 20% HA solution in CDCl_3 .

RESULTS AND DISCUSSION

The NMR and IR Spectra of the HA Reagent

The NMR spectrum of 20% HA in CDCl_3 at 25°C does not exhibit any pronounced impurity signals. The absorption minima correspond to the assumed groups of protons in the phenyl (2.25–2.70 τ), the methylene groups in n-octyl (6.11, 8.40, 8.82) and the methyl group (9.18).

The absorption maxima found in the IR spectrum of HA in a range from 625 to 3800 cm^{-1} are summarized in Table I. The absorptions in a region of $2900\text{--}3100\text{ cm}^{-1}$ belong to C—H stretching vibrations in the alkyl and aryl groups. The very broad band around 1700 cm^{-1} is assigned in monobasic organophosphoric acids to the —OH group deformation vibration. The absorption in a region of 1205 to

TABLE I
IR Spectrum of HA

Band intensities: vw — very weak, w — weak, m — medium strong, s — strong, vs — very strong, S — shoulder. B — broad.

cm^{-1}	<i>I</i>	cm^{-1}	<i>I</i>	cm^{-1}	<i>I</i>	cm^{-1}	<i>I</i>
3 060	vw	1 466	w	1 140	vs	795	vw
2 960 S	m	1 458 S	w	1 068 S	s	766	vw
2 930	s	1 439	m	1 005	vs	754	m
2 860	m	1 388	vw	975 S	vw	737	w
2 370	vw	1 213	vs	931 S	vw	700	s
1 670 B	w	1 200 S	s	856	vw	675	vw
1 592	w	1 188 S	vs	810	vw		

1220 cm^{-1} corresponds to the P=O stretching vibration; the band width and its wavenumber indicate that this bond is very strong. The bands in the region around 1440 cm^{-1} are assigned to vibrations of the phenyl group directly bound to the phosphorus. Symmetrical and antisymmetrical deformation vibrations of the CH_3 and CH_2 groups in the alkyl are located in a region of 1385–1470 cm^{-1} , the bands of the CH out-of-plane deformation vibrations in the phenyl ring in a region of 700 to 760 cm^{-1} .

Scandium Extraction with HA

The effect of the initial Sc concentration. The dependence of the scandium distribution ratio, D_{Sc} , on its initial analytical concentration was studied in media of 2M-HCl, HNO_3 and H_2SO_4 with an initial analytical concentration of HA in benzene of $c_{\text{HA}} = 5 \cdot 10^{-4} - 1 \cdot 10^{-3}\text{M}$. The D_{Sc} value was constant over an interval of $c_{\text{Sc}} = 3 \cdot 10^{-7} - 1 \cdot 10^{-5}\text{M}$. In this interval of scandium initial concentrations, only monomeric complexes can be assumed.

The dependence of the scandium distribution on the aqueous phase acidity at a constant ionic strength. It was found that the dependence, $\log D_{\text{Sc}} = f(\log c_{\text{H}^+})$, is linear with a slope of -3.0 ± 0.1 in media of (H, Li)Cl, (H, Li) NO_3 and (H, Na). ClO_4 at a constant ionic strength of $I = 2.0$. Hence species Sc^{3+} can be assumed to be present in these aqueous phases, which is extracted into the organic phase in the form of an electroneutral complex with liberation of three protons. In contrast to the above media of three mineral acids it is difficult to obtain a medium with a definite ionic strength when using 1–2M- H_2SO_4 . The $\log D_{\text{Sc}}$ dependence on the log of the initial H_2SO_4 concentration in the aqueous phase in the region of 1–2M- H_2SO_4 without maintenance of a constant ionic strength is linear with a slope of -3.2 ; the HSO_4^- species is assumed to predominate in this region. This slope remains unchanged provided that the D_{Sc} value is corrected for the formation of sulphate-scandium complexes in the aqueous phase; the corresponding stability constants for these complexes were taken from ref.³. However, as the appropriate recalculation to the mean H_2SO_4 activities was not carried out, the calculation of the extraction constants was not attempted.

Dependence of the scandium distribution on the initial mineral acid concentration in the aqueous phase. The dependences of $\log D_{\text{Sc}}$ on the log of the mean activity of hydrochloric, nitric and perchloric acids are given in Figs 1–3 and these dependences on the log of the initial sulphuric acid concentration in the aqueous phase in Fig. 4 for various initial HA concentrations. These curves exhibit minima for 8–9M-HCl, 5–6M- HClO_4 and 8M- H_2SO_4 ; the minima shift somewhat to higher mineral acid concentrations with increasing analytical concentration of HA. It can be assumed that the ion-exchange extraction mechanism changes into a solvation mecha-

nism with increasing mineral acid concentration. Only the extraction from nitric acid medium (Fig. 2) proceeds differently than assumed and the shape of the reaction curve does not change even at 11M-HNO₃.

Dependence of the scandium distribution on the HA equilibrium concentration in the organic phase. The equilibrium concentration of the HA monomer in the organic phase, $[HA]_{org}$, was calculated from the relationship, $[HA]_{org} = -(1 + K_D^{-1} + K_a/K_D[H^+]) + \{(1 + K_D^{-1} + K_a/K_D[H^+])^2 + 8K_2c_{HA}\}^{1/2}/4K_2$, where $K_a = [H^+][A^-]/[HA]$, $K_D = [HA]_{org}/[HA]$, $K_2 = [H_2A_2]_{org}/[HA]_{org}^2$, the square brackets without subscripts denoting the equilibrium concentrations in the aqueous phase and those with subscript org, the concentrations in the organic phase. The above constants were taken from ref.¹. The log D_{Sc} vs log $[HA]_{org}$ dependences for 2M mineral acid media are given in Fig. 5. They are linear with slopes of 3.8, 4.0, 3.9 and 4.8 for hydrochloric, nitric, perchloric and sulphuric acids, respectively.

Hence the formation of extractable scandium complexes can be expressed by the equations,

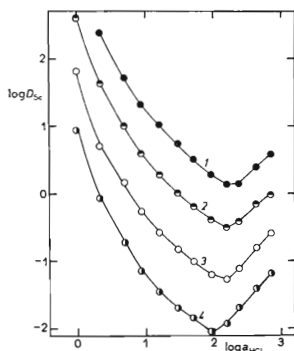
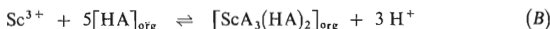
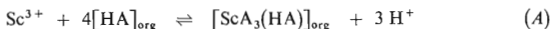


FIG. 1

The Effect of the Hydrochloric Acid Activity in the Aqueous Phase on the Scandium Distribution

c_{HA} : 4 $2.5 \cdot 10^{-4} M$, 3 $5 \cdot 10^{-4} M$, 2 $1 \cdot 10^{-3} M$, 1 $2 \cdot 10^{-3} M$.

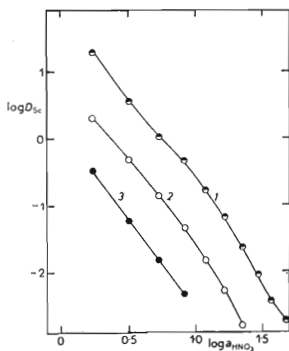


FIG. 2

The Effect of the Nitric Acid Activity in the Aqueous Phase on the Scandium Distribution

c_{HA} : 3 $2.5 \cdot 10^{-4} M$, 2 $5 \cdot 10^{-4} M$, 1 $1 \cdot 10^{-3} M$.

Eq. (B) expressing the equilibria in a sulphuric acid medium. The corresponding extraction constant, $K_{ex,1} = [\text{ScA}_3(\text{HA})]_{\text{org}}[\text{H}^+]^3/[\text{Sc}^{3+}][\text{HA}]_{\text{org}}^4$, must be calculated considering the formation of chloride and nitrate complexes of Sc and substituting the appropriate hydrogen ion activity³. The extraction constant equals $10^{17.2}$ for perchloric and hydrochloric acids and $10^{16.7}$ for nitric acid. The extraction constant corresponding to Eq. (B) could not be determined because the hydrogen ion activities in this medium are not known.

A loss of radioactive scandium was encountered in perchloric acid, probably due to the formation of its sparingly soluble complexes and their sorption in the interface or on the vessel walls. In the region of $-\log [\text{HA}]_{\text{org}} = 4.0-4.5$, the decrease in the activity did not exceed 10%; this region was considered in calculating $K_{ex,1}$.

To a first approximation, the equilibrium HA concentration in the organic phase can be assumed to equal the overall extractant concentration, c_{HA} , HA being present almost exclusively in the dimeric form in benzene. Hence the slope of $\log D_{\text{Sc}}$ vs the log of the analytical HA concentration actually corresponds to the number of dimeric units H_2A_2 which take part in the extraction. This reasoning was the basis for calculating the number of solvating particles in the strongly acidic aqueous phase (Fig. 6). The slopes of dependence $\log D_{\text{Sc}} = f(\log c_{\text{HA}})$ equal 2.0 ± 0.2 for

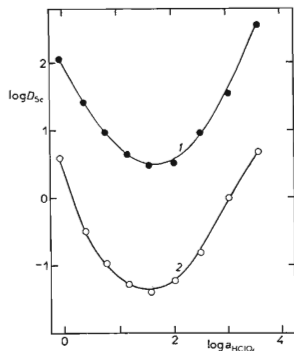


FIG. 3

The Effect of the Perchloric Acid Activity in the Aqueous Phase on the Scandium Distribution

c_{HA} : $2.1 \cdot 10^{-4}\text{M}$, $1.5 \cdot 10^{-4}\text{M}$.

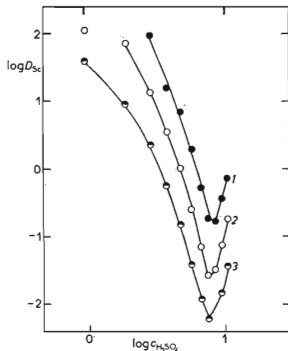


FIG. 4

The Effect of the Initial Sulphuric Acid Concentration in the Aqueous Phase on the Scandium Distribution

c_{HA} : $3.25 \cdot 10^{-3}\text{M}$, $2.5 \cdot 10^{-3}\text{M}$, $1.1 \cdot 10^{-2}\text{M}$.

11M-HCl and H_2SO_4 , 3.0 ± 0.2 for 9M- $HClO_4$ and 3.1 ± 0.2 for 11M- HNO_3 . As follows from the dependence presented in Figs 1, 3 and 4, $ScCl_3(H_2A_2)_2$, $Sc_2 \cdot (SO_4)_3(H_2A_2)_2$ and $Sc(ClO_4)_3 \cdot (H_2A_2)_3$ complexes are probably extracted. The extraction is more complicated in nitric acid medium; either the extraction mechanism does not change even in 11M- HNO_3 (Fig. 2), so that scandium could be extracted by the ion-exchange mechanism or the equilibrium concentration of free HA decreases owing to an increase in the nitric acid extraction as $(HNO_3)_n \cdot HA_m$ solvates starting at 6M- HNO_3 , so that an increase in the D_{Sc} value cannot play a role, even if $Sc(NO_3)_3(H_2A_2)_3$ complexes were involved.

Extraction of scandium in the presence of electroneutral organophosphoric reagents. In the presence of $10^{-4} - 10^{-2}$ M-tri-n-octylphosphine oxide and tri-n-butylphosphine oxide in benzene, no synergistic Sc extraction was observed in media of 2M-HCl, HNO_3 and H_2SO_4 . Addition of tri-n-butylphosphine oxide at an analytical concentration of $1 \cdot 10^{-3}$ M or higher had an antagonistic effect with a decrease in the D_{Sc} value by up to two orders of magnitude, probably due to interaction $(C_4H_9O)_3P=O \cdot HA$ causing the free HA equilibrium concentration to decrease.

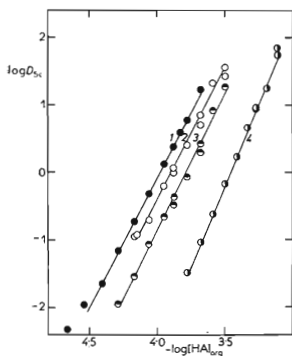


FIG. 5

The Effect of the Equilibrium Concentration of the HA Monomer in the Organic Phase on the Scandium Distribution between 2M Mineral Acids and Solution of HA in Benzene

Aqueous phase: 1 $HClO_4$, 2 HCl, 3 HNO_3 , 4 H_2SO_4 .

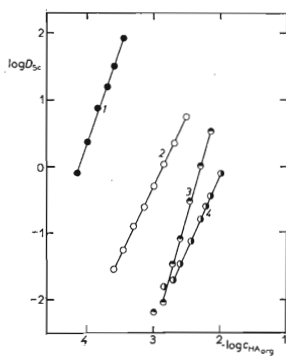


FIG. 6

The Effect of the Analytical Concentration of HA in the Organic Phase on the Scandium Distribution between More Concentrated Mineral Acids and HA Solutions in Benzene

Aqueous phase: 1 9M- $HClO_4$, 2 11M-HCl, 3 11M- HNO_3 , 4 11M- H_2SO_4 .

Extraction of Hafnium with HA

In order to supplement our previous work¹, the hafnium distribution from nitric and sulphuric acids was investigated. The $\log D_{\text{Hf}}$ dependence on the log of the analytical concentration of H_2SO_4 is shown in Fig. 7; Fig. 8 describes the analogous dependence of $\log D_{\text{Hf}}$ on the log of the nitric acid activity in the aqueous phase. While with H_2SO_4 the extraction mechanism again changes at $5\text{M-H}_2\text{SO}_4$, with HNO_3 a solvation extraction mechanism must be assumed from $c_{\text{HNO}_3} \geq 0.5\text{M}$, similar to Hf extraction with dialkylphosphoric acids⁴; the decrease in the D_{Hf} value in a region of 6M-HNO_3 and higher can be explained by increased formation of extractable solvates $(\text{HNO}_3)_n \cdot \text{HA}_m$.

The study of the $\log D_{\text{Hf}} = f(\log c_{\text{H}^+})$ dependences in 2M-(H, Li)NO_3 and $1-2\text{M-H}_2\text{SO}_4$ has shown that the value of the hafnium distribution ratio is independent of changes in the hydrogen ion concentration in nitric acid (for $I \geq 2.0$), while the ion-exchange mechanism must be assumed for sulphuric acid media without maintenance of the ionic strength, considering the formation of sulphate complexes of Hf (ref.⁵). The number of protons liberated was not determined for reasons analogous to those given in the study of the extraction of Sc.

The $\log D_{\text{Hf}} = f(\log [\text{HA}]_{\text{org}})$ dependences are straight lines with slopes of $2.0 \pm \pm 0.1$ for aqueous phases containing 2M-HNO_3 , 4.8 ± 0.2 for $2\text{M-H}_2\text{SO}_4$ and $2.0 \pm$

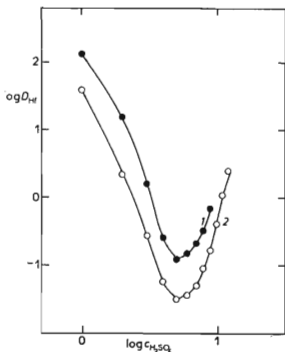


FIG. 7

The Effect of the Initial Sulphuric Acid Concentration in the Aqueous Phase on the Hafnium Distribution

$c_{\text{HA}}: 2.3 \cdot 10^{-3}\text{M}, 1.5 \cdot 10^{-3}\text{M}.$

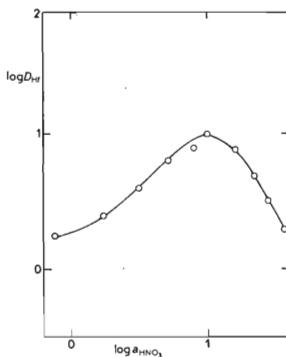
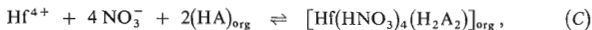


FIG. 8

The Effect of the Nitric Acid Activity in the Aqueous Phase on the Hafnium Distribution between the Aqueous Phase and a $1 \cdot 10^{-4}\text{M-HA}$ Solution in Benzene.

± 0.1 for $10M\text{-HNO}_3$ and $10M\text{-H}_2\text{SO}_4$. Hence it can be concluded that hafnium is extracted with HA from $2M\text{-HNO}_3$ according to the mechanism,



$K_{\text{ex},2} = [\text{Hf}(\text{NO}_3)_4(\text{H}_2\text{A}_2)]_{\text{org}} / [\text{Hf}][\text{NO}_3^-]^4[\text{HA}]_{\text{org}}^2 = 10^{8.0}$, and from $10M\text{-HNO}_3$ and H_2SO_4 in the form of extractable $\text{Hf}(\text{NO}_3)_4 \cdot (\text{H}_2\text{A}_2)_2$ or $\text{Hf}(\text{SO}_4)_2 \cdot (\text{H}_2\text{A}_2)_2$ complexes.

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