

EXTRACTION OF HAFNIUM INTO BENZENE WITH TETRAPHENYL IMIDODIPHOSPHATE

Oldřich NAVRÁTIL^a, Miroslav CIGÁNEK^a and Eckhard HERMANN^b

^a Department of Inorganic Chemistry,

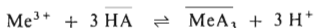
Purkyně University, 611 37 Brno, and

^b Section of Chemistry, Technical University, 8027 Dresden, GDR

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The distribution of hafnium(IV) was studied between aqueous solutions of perchloric, hydrochloric, or nitric acids (HX) and benzene solutions of tetraphenyl imidodiphosphate (HA). From perchloric and hydrochloric acids at concentrations $c_{\text{HX}} \leq 3 \text{ mol l}^{-1}$ hafnium is extracted as HfXA_3 complex. With the two acids present at higher concentrations or with nitric acid at concentrations $c_{\text{HNO}_3} \geq 1.5 \text{ mol l}^{-1}$ the initial ion exchange mechanism turns into a solvation mechanism associated with the formation of $\text{HfX}_4(\text{HA})_y$ complexes ($\text{X} = \text{ClO}_4, \text{Cl}$). The extraction constant values are given and the extracting agent is compared with other acid organophosphorus reagents.

Tetraphenyl imidodiphosphate $[(\text{C}_6\text{H}_5\text{O})_2\text{P}(\text{O})]_2\text{NH}$, (HA), has been used as an extracting agent only rarely¹⁻³. From aqueous solution of common mineral acids up to $c_{\text{HX}} \leq 4 \text{ mol l}^{-1}$, lanthanoids (Me^{3+}) are extracted by an ion exchange mechanism,



(the bar is used to label the organic phase). The central atom is coordinated *via* the oxygen atoms of the ligand. In perchloric acid the extraction mechanism turns into a solvation one if the acid concentration is higher than 6 mol l^{-1} ; this change is associated with an increase in the distribution ratio value.

Detailed study³ has shown that the reagent alone can be regarded as a monobasic acid, HA, forming H_2A_2 dimers in benzene solutions. The dimerization constant K_2 and the distribution constant of monomer $K_D(\text{HA})$ have been determined for this reagent; the values are $\log K_2 = 3.3 \pm 0.5$ and $K_D(\text{HA}) = 13 \pm 2$. The dissociation constant of the reagent K_a has been determined potentiometrically^{1,4}: $\text{p}K_a = (4.11 \pm 0.08) - (0.61 + 0.12) \sqrt{I}$ for the ionic strength (I) region of $0.1 - 1 \text{ mol l}^{-1}$ *

* Strictly speaking, this empirical relation for the defined dissociation constant cannot be extrapolated; still, regarding the error of determination of the experimental values for higher ionic strengths, we did perform the extrapolation, and used the values of $\text{p}K_a - 3.25$ and 3.05 for $I = 2.0$ and 3.0 , respectively.

In the present work the distribution has been studied of hafnium(IV) between solution of tetraphenyl imidodiphosphate in benzene and aqueous solutions of hydrochloric, perchloric, and nitric acids (occasionally with an addition of their sodium salts) with ionic strengths of 1–2.

EXPERIMENTAL

Chemicals and Apparatus

Tetraphenyl imidodiphosphate was prepared by direct condensation of diphenyl amidophosphate and chlorophosphate⁵. Its purity was checked by NMR spectroscopy on a Varian XL-100A spectrometer using H_3PO_4 ($w = 85\%$) as the external standard for phosphorus and by mass spectrometry on an AEI MS 902-S instrument. The remaining chemicals used were commercial products of reagent grade purity. Radioactive solutions of $HfCl_4$ were obtained by diluting the commercially available $^{175+181}HfCl_4$ preparation in 1M-HCl (Swierk Poland); for conversion to $Hf(ClO_4)_4$ and $Hf(NO_3)_4$ the solution was evaporated cautiously and diluted with the corresponding mineral acid. The concentration of hafnium in the working solutions was $0.3-7 \mu mol \cdot l^{-1}$, its specific activity was $(1-7) \cdot 10^4 Bq ml^{-1}$. The gamma radiation of the solutions was measured by means of a Nuclear Chicago 1185 automatic sample changer.

Procedure

Equal volumes (5 ml) of the aqueous and organic phases were agitated for a minimum of 4 h (as tentative experiments indicated, this time was fully sufficient for the extraction equilibrium to establish). After the phase separation, aliquots of either phase were taken and their activity was determined in a well-type crystal. The measurements were carried out at $20 \pm 1^\circ C$. The relative standard deviation of all measurements did not exceed 2%.

Except for the measurements of the dependence of the hafnium distribution on the total concentration of mineral acids, the acidity of the aqueous phase was adjusted by using mineral acids and their salts so that the ionic strength was 1.0 or $2.0 mol l^{-1}$ (exceptionally $3.0 mol l^{-1}$ for the $\log D_{Hf} - f(\log c_{H^+})$ dependence).

RESULTS AND DISCUSSION

Effect of the Initial Concentration of Hafnium

The dependence of the distribution ratio of hafnium D_{Hf} on its analytical concentration was examined in 2M-HCl and 2M- $HClO_4$ solutions applying the initial analytical concentration of the extracting agent in benzene $c_{HA} = 1 mmol l^{-1}$. The D_{Hf} value was constant over a region of $c_{Hf} = 0.3-10 \mu mol l^{-1}$; thus in this concentration region the system can be assumed to involve monomeric complexes only.

Effect of the Acidity of the Aqueous Phase

The $\log D_{Hf} = f(\log c_{H^+})$ dependences for solutions of $(H,Na)Cl$ or $(H,Na)ClO_4$ ($I = 2.0$ or 3.0) or $(H,Na)NO_3$ ($I = 2.0$) were found to be linear, with slopes of

-3.0 ± 0.1 (HCl), -2.8 ± 0.1 (HClO₄), and -0.9 ± 0.1 (HNO₃). Thus in HCl and HClO₄ the HfX³⁺ species can be assumed to be present and extracted into the organic phase as an electroneutral complex with a liberation of three protons. The experiments performed using higher ionic strengths also indicate that allowance for hydrolysis of hafnium⁶ essentially need not be made. Hence, in HCl or HClO₄ solutions in concentrations of 2–3 mol l⁻¹, mixtures of Hf(OH)³⁺ with HfCl³⁺ or Hf(ClO₄)³⁺ occur, the latter components obviously predominating. Similar results have been derived from a study of extraction of hafnium into benzene with some acid organophosphorus agents^{7–9}.

In nitric acid the situation will be somewhat different; not only the slope of the dependence is different, but differences are seen also in the extraction mechanism, as manifested by the $\log D_{\text{Hf}} = f(c_{\text{HNO}_3})$ plot. The assumption⁶ of the occurrence of the Hf(NO₃)₃⁺ species is reasonable, though it has not been verified.

The dependences of $\log D_{\text{Hf}}$ on the logarithm of the initial acid concentration for the three acids are shown in Figs 1–3. For perchloric and hydrochloric acids the curves display a minimum at $c_{\text{HClO}_4} = 3 \text{ mol l}^{-1}$ and $c_{\text{HCl}} = 4 \text{ mol l}^{-1}$, which shifts slightly to higher acid concentrations as the analytical concentration of the extracting agent

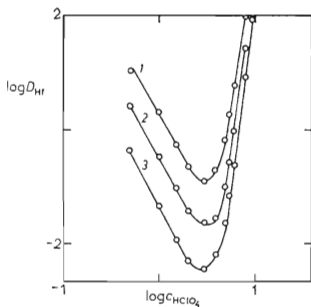


FIG. 1

Effect of the initial concentration of perchloric acid on the distribution of hafnium between the aqueous phase and solutions of tetraphenyl imidodiphosphate in benzene. Concentration of the extracting agent (mmol l⁻¹): 1 0.84, 2 0.34, 3 0.17

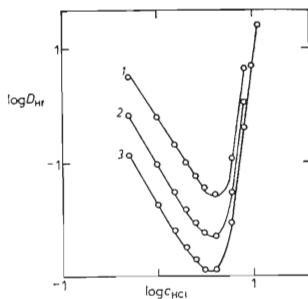


FIG. 2

Effect of the initial concentration of hydrochloric acid on the distribution of hafnium between the aqueous phase and solutions of tetraphenyl imidodiphosphate in benzene. Concentrations of the extracting agent as in Fig. 1

is raised. The ion exchange mechanism can be supposed to turn into a solvation mechanism as the mineral acid concentration increases. With nitric acid, a less pronounced minimum is observed at $c_{\text{HNO}_3} = 2-3 \text{ mol l}^{-1}$ and a maximum appears at $c_{\text{HNO}_3} = 6 \text{ mol l}^{-1}$, indicating an additional change in the extraction mechanism or a destruction of the reagent. Similar conclusions have been made based on experiments in which hafnium was extracted from nitric acid solutions with some dialkylphosphoric acids⁸ and octylphenylphosphonic acid¹⁰.

Effect of the Equilibrium Concentration of the Extracting Agent in the Organic Phase

The equilibrium concentration of monomeric HA in the organic phase was calculated as

$$[\text{HA}]_{\text{org}} = \left\{ -(1 + K_D^{-1} + K_a/K_D[\text{H}^+]_{\text{aq}}) + \right. \\ \left. + [(1 + K_D^{-1} + K_a/K_D[\text{H}^+]_{\text{aq}})^2 + 8K_2c_{\text{HA}}]^{1/2} \right\} / 4K_2,$$

where

$$K_a = [\text{H}^+]_{\text{aq}} [\text{A}^-]_{\text{aq}} / [\text{HA}]_{\text{aq}}$$

$$K_D = [\text{HA}]_{\text{org}} / [\text{HA}]_{\text{aq}}$$

$$K_2 = [\text{H}_2\text{A}_2]_{\text{org}} / [\text{HA}]_{\text{org}}^2$$

and c_{HA} is the initial analytical concentration of reagent. The brackets are used to designate the equilibrium concentrations. The values of the constants were taken from work^{3,4}. The $\log D_{\text{Hf}}$ values are plotted against $\log [\text{HA}]_{\text{org}}$ for the three

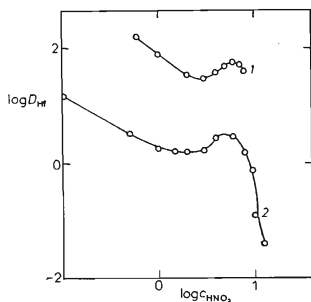


FIG. 3

Effect of the initial concentration of nitric acid on the distribution of hafnium between the aqueous phase and solutions of tetraphenyl imidodiphosphate in benzene. Concentration of the extracting agent ($10^{-5} \text{ mol} \cdot \text{l}^{-1}$): 1 50, 2 8.4

mineral acids in Fig. 4; the plots are linear and their slopes are 3.0 (1M-HCl), 3.2 (2M-HCl), 3.3 (1M-HClO₄), 3.0 (2M-HClO₄), and 2.7 (1M-HNO₃, 2M-HNO₃). Thus, in the range of the ion extraction mechanism the formation of the extractable hafnium complexes from perchloric and hydrochloric acids solutions can be represented as



In calculating the extraction constant

$$K_{\text{ex}} = [\text{HfXA}_3]_{\text{org}} [\text{H}^+]_{\text{aq}}^3 / [\text{HfX}^{3+}]_{\text{aq}} [\text{HA}]_{\text{org}}^3$$

allowance must be made for activity of hydrogen ions¹¹. The values of the constant for hydrochloric and perchloric acids are virtually identical, $\log K_{\text{ex}} = 10.5 \pm 0.2$.

As to nitric acid solutions, no detailed conclusions can be drawn from the slopes observed; it can only be admitted that in 1M to 2M-HNO₃ solutions, extractable complexes Hf(NO₃)₃A(HA) or Hf(NO₃)₃A(HA)₂ are present. The values of the extraction constants,

$$K_{\text{ex}} = [\text{Hf}(\text{NO}_3)_3\text{A}(\text{HA})]_{\text{org}} [\text{H}^+]_{\text{aq}} / [\text{Hf}(\text{NO}_3)_3^+]_{\text{aq}} [\text{HA}]_{\text{org}}^2$$

or

$$K_{\text{ex}} = [\text{Hf}(\text{NO}_3)_3\text{A}(\text{HA})_2]_{\text{org}} [\text{H}^+]_{\text{aq}} / [\text{Hf}(\text{NO}_3)_3^+]_{\text{aq}} [\text{HA}]_{\text{org}}^3$$

are $\log K_{\text{ex}} = 8.6 \pm 0.1$ and $\log K_{\text{ex}} = 12.8 \pm 0.1$, respectively.

Comparing the systems under study with analogous systems involving, *e.g.*, dialkylphosphoric acids as extracting agents^{7,8}, we find the extraction behaviour

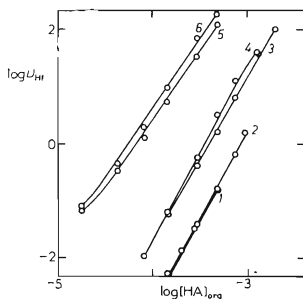


FIG. 4

Effect of the equilibrium concentration of tetraphenyl imidodiphosphate in the organic phase on the distribution of hafnium between the aqueous and the organic phases. Aqueous phase: 1 2M-HClO₄, 2 2M-HCl, 3 1M-HCl, 4 1M-HClO₄, 5 2M-HNO₃, 6 1M-HNO₃

nearly identical; this applies also to the extraction curve shapes including the positions of their minima and maxima. Only the numbers of the HA particles entering the reactions are different, probably on account of the different dimerization constants, monomer distribution constants, and dissociation constants of the reagents. We suppose that HA in HCl or HClO₄ solutions is bonded to hafnium as a bidentate ligand *via* the O=P—N=P—O⁻ grouping, hence analogously as to lanthanoids¹⁻³.

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