

APPLICATION OF MONOALKYL METHANEPHOSPHONATES TO EXTRACTION OF SELECTED METALS

Alena TOKAROVA, Oldrich NAVRATIL and Petr SLADEK¹

Department of Special Chemistry, The Military College of Ground Forces, 682 03 Vyskov, Czech Republic; e-mail: ¹sladek@vvs-pv.cz

Received January 19, 1996

Accepted May 1, 1996

The distribution of scandium and hafnium between 0.1 or 1.0 mol l⁻¹ HNO₃ and solutions of monoalkyl methanephosphonates (HA; alkyl = methyl, propyl, butyl, isobutyl, pentyl, 2-methylbutyl, cyclohexyl, 1,2,2-trimethylpropyl) in chloroform and 1,1,2,2-tetrachloroethane has been studied. The organic solvents mentioned allow to obtain the optimum values of partition coefficients of the two metals. The corresponding extraction constants of the ScA₃(HA)_x and Hf(NO₃)₄(HA)₄ complexes have been calculated.

Key words: Liquid extraction; Scandium; Hafnium; Monoalkyl methanephosphonates.

In ref.¹ we showed that selected alkyl methanephosphonates RO(CH₃)P(O)OH (HA; R = methyl (Me), propyl (Pr), butyl (Bu), isobutyl (iBu), pentyl (Pen), 2-methylbutyl (iPen), cyclohexyl (cHex), 1,2,2-trimethylpropyl (iHex)) are acids of medium strength (pK = 0.53–1.48). These compounds serve as precursors in production of herbicides or are used in syntheses of some chemical warfare agents (CWA) paralysing the nervous system such as sarin or soman. HA can extract ScA₃(HA)₂, YbA₃, and EuA₃ complexes from aqueous phase media of 0.1 mol l⁻¹ HNO₃ or Hf(NO₃)_x(HA)_y complexes from 1 mol l⁻¹ HNO₃ into benzene. It was indicated¹ that for such extractions some chlorinated hydrocarbons can be better organic phases than benzene. Investigation of stability of the complex compounds mentioned can contribute to the determination of effects of the metals (or their cations) used on stability of CWA.

The aim of the present communication is to work out the optimum conditions of extraction of selected metals by HA. Chloroform and 1,1,2,2-tetrachloroethane proved to be the best organic phases for this purpose.

EXPERIMENTAL

Chemicals and Apparatus

The reagents were synthesized in Army Factory 072 in Zemianske Kostolany (Slovak Republic) according to refs^{2,3}. Their purity was checked by means of ³¹P NMR spectroscopy. The stock solutions were prepared by dissolving precise amounts of HA in chloroform, 1,1,2,2-tetrachloroethane (TCE),

benzene (B), *o*-dichlorobenzene (DCB), tetrachloromethane, heptane (H), and 1,1,2-trichlorofluoroethane (F-113). All the chemicals were of p.a. purity grade (Lachema Brno, Czech Republic and VEB Apolda, Germany).

The radioactive isotopes (Poland) were added to the aqueous phase as nitrates. Their concentrations (in $\mu\text{mol l}^{-1}$) and specific activities (in kBq ml^{-1}) in the working solutions were as follows: ^{46}Sc 1, 30; $^{175+181}\text{Hf}$ 8, 15.

The gamma activity of solutions was measured by means of an NA 3601 Gamaautomat (Tesla Liberec, Czech Republic) with a well-type NaI(Tl) detector. A pH Meter OP-208/I with OP-0808P combined glass electrode (Radelkis, Hungary) was used for pH measurements of aqueous phases; it was calibrated with the help of phthalate and citrate buffers. The ^{31}P NMR spectra of 50% solutions of HA in CDCl_3 were measured with the help of a WP 80 SY apparatus (Bruker, Germany) using H_3PO_4 as the external standard.

Procedures

The extractions were carried out with a rotary shaker of our own design and test tubes with glass stoppers. The organic and aqueous phases (5 ml + 5 ml) were mixed 60 min at 20 ± 1 °C. According to preliminary experiments, this time is sufficient for establishing of the extraction equilibrium. After separating the phases, 2 ml was withdrawn from each and placed into ampoules for the gamma activity measurements. Such a frequency of activity measurements in the well-type detector was chosen as to keep the mean quadratic error of each measurement below 2%.

RESULTS AND DISCUSSION

Complexes of Reagents with Selected Metals

Figures 1 and 2 present the dependences of logarithm of distribution coefficient of scandium (and Figs 3 and 4 for hafnium) on the analytical concentration c_{HA} of the reagents. Chloroform (Figs 1 and 3) and TCHE (Figs 2 and 4) were used as the organic phases, the aqueous phases being 0.1 and 1 mol l^{-1} HNO_3 for Sc and Hf, respectively. Like for benzene¹, the extractability of both the metals into the organic phase used increases with increasing length of aliphatic chain in HA (Me < Pr < Bu < Pen) and decreases with its increased branching (Pen > iPen, Bu > iBu)

We also investigated the dependence of logarithm of partition coefficient of scandium upon the pH value of aqueous phase at constant ionic strength of 0.1 (adjusted by addition of HNO_3 and NaNO_3 solutions) and at constant concentration of the HA reagents: linear dependences with slopes of 3 ± 0.2 were obtained in the pH interval from 1 to 2, which means that the non-charged complexes are transferred to the organic phases according to the relation:

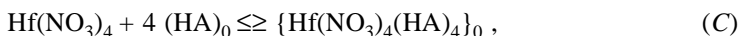


for which we can formulate the extraction constant $K_{\text{ex},1}$ as follows:

$$K_{\text{ex},1} = [\text{ScA}_3(\text{HA})_x]_0 [\text{H}^+]^3 / [\text{Sc}^{3+}] [\text{HA}]_0^{3+x} = D_{\text{Sc}} [\text{H}^+]^3 / [\text{HA}]_0^{3+x} \quad (\text{B})$$

The quantity x assumes the values from 0 to 1.

In contrast to scandium, the distribution coefficients of hafnium are independent of the acidity of aqueous phase within the initial HNO_3 concentration limits from 0.3 to 3 mol l^{-1} , which means that in this interval of acidity of aqueous phase hafnium is not extracted by a ion-exchange mechanism, e.g. according to (A), but most probably by the mechanism of solvation with nondissociated HA particles, e.g. according to the following relation:



for which it is possible to formulate the extraction constant $K_{\text{ex},2}$. A similar behaviour of hafnium complexes was described earlier⁴ in the context with its extraction into benzene solutions of 1-octanephosphonic acid.

$$K_{\text{ex},2} = [\text{Hf}(\text{NO}_3)_4(\text{HA})_4]_0 / [\text{Hf}(\text{NO}_3)_4] [\text{HA}]_0^4 = D_{\text{Hf}} / [\text{HA}]_0^4 \quad (\text{D})$$

We have not studied the solvation problem in any detail. The $K_{\text{ex},1}$ and $K_{\text{ex},2}$ values together with the x data are given in Table I for the individual HA.

From the distribution of scandium between the same aqueous phase and various organic phases at the ionic strength of 0.1 it follows that its extractability e.g. with HA ($\text{R} = \text{iPen}$) (Fig. 5) increases in the order $\text{H} < \text{F-113} = \text{CCl}_4 < \text{B} = \text{DCB} < \text{CHCl}_3 = \text{TCE}$, i.e., the

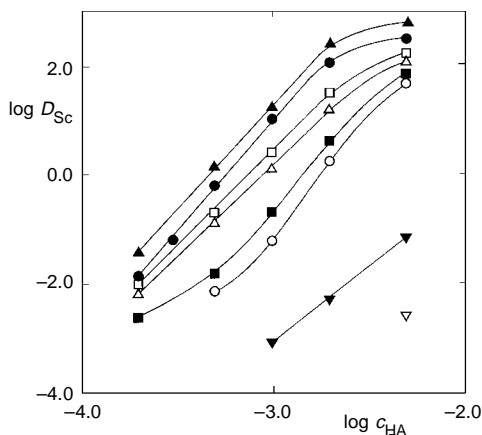


FIG. 1

Effect of analytical concentration of HA on distribution of scandium ($c_{\text{Sc}} = 1 \cdot 10^{-6}$ mol l^{-1}) between aqueous phase (0.1 M HNO_3) and CHCl_3 . R in HA: ∇ Me, \blacktriangledown Pr, \circ iBu, \blacksquare Bu, \triangle cHex, \square iHex, \bullet iPen, \blacktriangle Pen

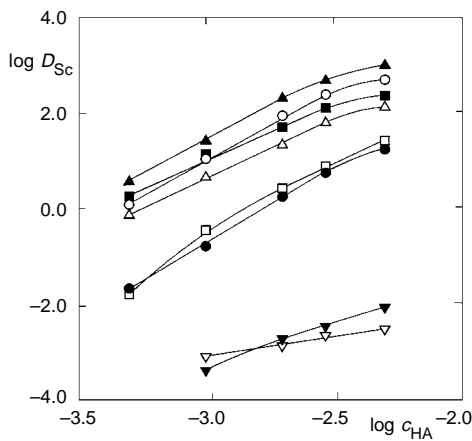


FIG. 2

Effect of analytical concentration of HA on distribution of scandium ($c_{\text{Sc}} = 1 \cdot 10^{-6}$ mol l^{-1}) between aqueous phase (0.1 M HNO_3) and 1,1,2,2-tetrachloroethane. R in HA: ∇ Me, \blacktriangledown Pr, \bullet iBu, \square Bu, \triangle cHex, \blacksquare iHex, \circ iPen, \blacktriangle Pen

last two solvents are more efficient than benzene, its chloro derivatives as well as tetrachloromethane and heptane as a representative of aliphatic solvents.

For distribution of hafnium and for ionic strength 1.0, we found a similar order of extractability: F-113 \ll B = CHCl₃ < TCE (Fig. 6), i.e., the differences in extraction

TABLE I
Values of extraction constants of Sc and Hf with RO(CH₃)P(O)OH reagents

R	CHCl ₃			TCE		
	Sc		Hf	Sc		Hf
	<i>x</i>	log <i>K</i> _{ex,1}	log <i>K</i> _{ex,2}	<i>x</i>	log <i>K</i> _{ex,1}	log <i>K</i> _{ex,2}
Pr	–	–	9.1	–	–	–
Bu	0	5.6	12.0	0	5.5	–
iBu	1	8.0	11.7	0	5.3	–
Pen	1	10.4	14.1	0	7.6	13.6
iPen	1	9.9	13.2	0	7.1	13.5
cH	0	6.2	14.0	0	6.8	13.6
iHex	1	9.5	14.8	0	7.3	14.4

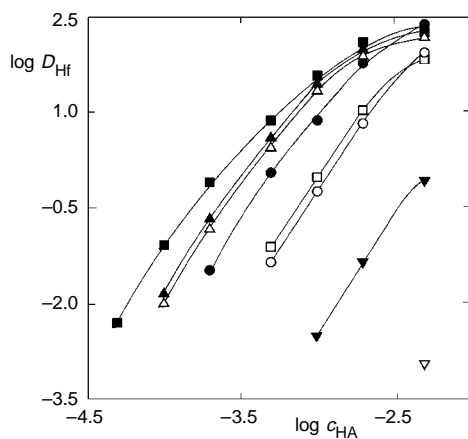


FIG. 3

Effect of analytical concentration of HA on distribution of hafnium ($c_{\text{Hf}} = 8 \cdot 10^{-6} \text{ mol l}^{-1}$) between aqueous phase (1.0 M HNO₃) and CHCl₃. R in HA: ∇ Me, \blacktriangledown Pr, \circ iBu, \square Bu, \bullet iPen, Δ cHex, \blacktriangle Pen, \blacksquare iHex

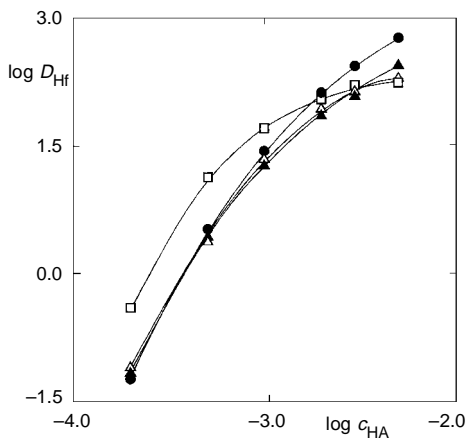


FIG. 4

Effect of analytical concentration of HA on distribution of hafnium ($c_{\text{Hf}} = 8 \cdot 10^{-6} \text{ mol l}^{-1}$) between aqueous phase (1.0 M HNO₃) and 1,1,2,2-tetrachloroethane. R in HA: \bullet iPen, \blacktriangle Pen, Δ cHex, \square iHex

efficiency are less distinct with regard to the higher ionic strength, but the values of distribution coefficients of the metals investigated unambiguously show the advantage of application of 1,1,2,2-tetrachloroethane.

If our results of extraction of scandium and hafnium with HA are compared with those obtained with analogous reagents, it can be stated that the application of octyl benzenephosphonate⁴ is more efficient obviously because of the phenyl group present. This group obviously causes (in contrast to the methyl group present in HA) a better interaction of the reagent with organic solvent, particularly that of aromatic type. Also the extraction of both the metals by dibutyl and bis(2-ethylhexyl) phosphates and by tetraphenyl imidodiphosphate into halogenated alkanes⁵ proceeds better. Our paper, however, does not want to investigate the efficiency of individual reagents, but deals with a particular reagent type possessing biological activity.

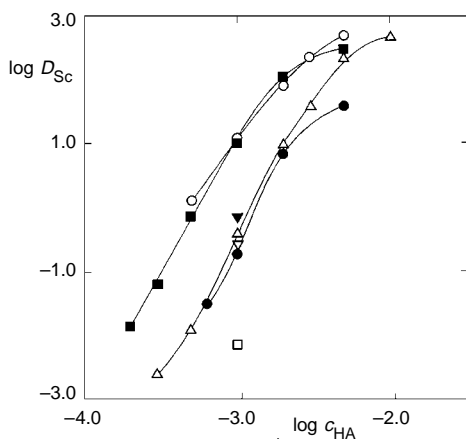


FIG. 5

Effect of analytical concentration of HA ($R = iPen$) on distribution of scandium ($c_{Sc} = 1 \cdot 10^{-6} \text{ mol l}^{-1}$) between aqueous phase (0.1 M HNO_3) and organic phase containing: \square H, \bullet F-113, ∇ CCl_4 , Δ B, \blacktriangledown DCB, \blacksquare CHCl_3 , \circ TCE

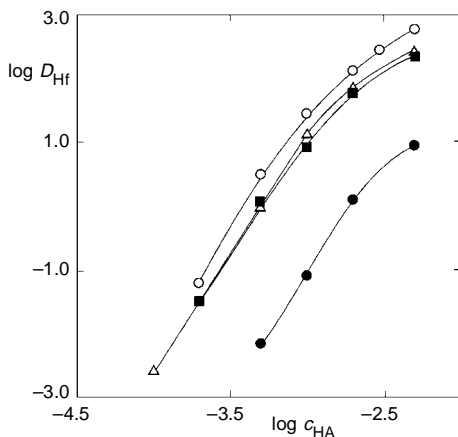


FIG. 6

Effect of analytical concentration of HA ($R = iPen$) on distribution of hafnium ($c_{Hf} = 8 \cdot 10^{-6} \text{ mol l}^{-1}$) between aqueous phase (1.0 M HNO_3) and organic phase containing: \bullet F-113, \blacksquare CHCl_3 , Δ B, \circ TCE

REFERENCES

1. Navratil O., Sladek P.: *Collect. Czech. Chem. Commun.* 59, 287 (1994).
2. Franke S., Franz P., Grummer G., Warnke W.: *Lehrbuch der Militärchemie*, Vol. 1, p. 418. Militärverlag der G.D.R., Berlin 1977.
3. Schrader G.: *Die Entwicklung neuer Insectizide auf Grundlage organischer Fluor- und Phosphor-Verbindungen*, p. 20. Verlag Chemie, Weinheim 1952.
4. Navratil O., Vykoupil J.: *Collect. Czech. Chem. Commun.* 42, 2126 (1977).
5. Sladek P.: *Ph.D. Thesis*. Military College, Vyskov 1992.