
**EXTRACTION OF SCANDIUM WITH TETRAPHENYL
IMIDODIPHOSPHATE AND ITS SULFUR ANALOGUES,
AND THE RADIATION STABILITY OF THE REAGENT**Oldřich NAVRÁTIL^a, Eckhard HERRMANN^b, Gisbert GROSSMANN^c and Jiří TEPLÝ^d^a *Department of Inorganic Chemistry,**J. E. Purkyně University, 611 37 Brno, Czechoslovakia*^b *Chemistry Section, Martin Luther University, 4010 Halle-Wittenberg, G.D.R.*^c *Chemistry Section, Technical University, 8027 Dresden, G.D.R. and*^d *Institute of Nuclear Research, 250 68 Řež near Prague, Czechoslovakia*

Received April 17, 1989

Accepted June 26, 1989

Solvent extraction of scandium from perchloric or hydrochloric acid aqueous systems into benzene solutions of tetraphenyl imidodiphosphate, $(\text{PhO})_2\text{P}(\text{O})\text{NHP}(\text{O})(\text{PhO})_2$ (HA), and its sulfur analogues containing the $\text{P}(\text{O})\text{NHP}(\text{S})$ or $\text{P}(\text{S})\text{NHP}(\text{S})$ groups was studied. Behaving as weak acids in the aqueous phase, the reagents form complex extractable compounds ScA_3 with scandium. The extraction constants were measured and found lower for the sulfur analogues than for the oxygen reagent. The configuration changes induced in the reagent by gamma irradiation from a ^{60}Co source were studied by examining the extraction of scandium with it and by ^{31}P NMR measurements. Whereas the changes in the solid reagent are not very marked and appear only at doses in excess of 800 kGy, the reagent dissolved in benzene exhibits configuration changes even on the application of doses at the 10 kGy level. This fact is related to the presence of benzene and dissolved oxygen in the system.

Tetraphenyl imidodiphosphate, $(\text{PhO})_2\text{P}(\text{O})\text{NHP}(\text{O})(\text{PhO})_2$ (henceforth HA), is a white crystalline substance, m.p. 110–112°C, soluble in common organic solvents and very low soluble in water. It acts as a weak acid ($\text{p}K_a = 4.11$ at an ionic strength $I = 0$, ref.¹), and exhibits chelating properties. Owing to the tautomerization of the $\text{P}(\text{O})\text{NHP}(\text{O})$ group, it forms dimers in low polar organic solvents. The values of the distribution constant of the monomer, $K_D = [\text{HA}]_{\text{org}}/[\text{HA}]$, and the dimerization constant, $K_2 = [(\text{HA})_2]_{\text{org}}/[\text{HA}]_{\text{org}}^2$ (the subscript org denotes the organic phase, the unlabelled concentrations refer to the aqueous phase) have been determined indirectly by the radioactive tracer method; for benzene as the organic phase and at $I = 0.1$ they are¹ $\log K_D = 1.11 \pm 0.07$ and $\log K_2 = 3.3 \pm 0.5$. The use of this substance for solvent extraction has been so far confined to rare metals^{1–4}.

The selectivity of the reagent in solvent extraction increases if the oxygen in the $\text{P}(\text{O})$ group is replaced by sulfur: extraction of silver and mercury is thereby increased^{4,5} whereas that of scandium and rare earth elements is suppressed^{4,6}. The

K_D , K_2 and K_a values have been determined⁵ for $(\text{PhO})_2\text{P}(\text{O})\text{NHP}(\text{S})(\text{PhO})_2$ (henceforth HB) to be $\log K_D = 4.6 \pm 0.2$, $\log K_2 = 2.2 \pm 0.3$ (benzene) and $\text{p}K_a = 2.68 \pm 0.23$ in a medium of 75% acetone at $I = 0.1$ (for a comparison: for HA, the $\text{p}K_a$ value in the same system is 2.39 ± 0.14). Attempts to determine the values of these constants for $(\text{PhO})_2\text{P}(\text{S})\text{NHP}(\text{S})(\text{PhO})_2$ (HC) from its distribution between two solvent phases failed because of its insufficient solubility in the aqueous phase.

In the present work, the composition and stability of the extractable complexes of scandium are determined and, making use of the outstanding extractability of the complexes with HA, the configuration changes induced in this reagent by gamma irradiation are assessed.

EXPERIMENTAL

Chemicals and Apparatus

The reagents HA, HB and HC were synthesized as described previously^{1,4}; their purity was checked by ^{31}P NMR spectroscopy. The other chemicals used were of reagent grade purity. For the radiation stability studies, benzene was dried and freed from oxygen by nitrogen purging.

The radioactive scandium isotope, ^{46}Sc (Poland), was added to the aqueous phase in the perchlorate or chloride form; its concentration in the working solutions was $0.1\text{--}3 \mu\text{mol l}^{-1}$, its specific activity was $1 \cdot 10^4$ to $5 \cdot 10^5 \text{ Bq cm}^{-3}$. Its purity was checked spectrometrically on an ICA-70 4096-channel analyzer (KFKI, Hungary) equipped with a Ge-Li detector (1 keV/channel). The gamma activity of the liquid samples was measured by using a Nuclear Chicago Model 1185 automatic sample changer.

The irradiation of the solid HA and its benzene solutions was accomplished at the State Textile Research Institute in Veverská Bítýška, using an AECL ^{60}Co source (16.9 PBq); the dose rate was 80 kGy/h for solid HA and 3.2 kGy/h for solutions. ^{31}P NMR measurements were performed on a Bruker MSL 300 instrument (F.R.G.).

Procedure

The aqueous and organic phases (5 ml each) were shaken on a rotary shaking machine in glass test tubes at $20 \pm 1^\circ\text{C}$ for 2 hours; this time was found sufficient for the extraction equilibrium to establish. After separation, 2 ml of each phase were pipetted into glass ampoules and their gamma activity was measured. The relative standard deviation of the measurements did not exceed 2%.

The acidity of the aqueous phase was adjusted with $\text{HClO}_4 + \text{NaClO}_4$ or $\text{HCl} + \text{LiCl}$ mixtures so that the ionic strength was held constant at $I = 0.1$ in all cases except for the measurement of the dependence of the distribution ratio of scandium on the starting concentration of the mineral acid.

RESULTS AND DISCUSSION

Study of the Composition and Stability of the Complex Compounds of Scandium with the Reagent and its Sulfur Analogues

Effect of hydrogen ion concentration. The dependence of the scandium distribution ratio D_{Sc} on the hydrogen ion concentration in the aqueous phase at $I = 0.1$ were measured for the $\text{HClO}_4 + \text{NaClO}_4$ and $\text{HCl} + \text{LiCl}$ systems. The lowest values of the slopes of the $\log D_{Sc} = f(\log c_{\text{H}^+})$ plots for the three reagents are -3.0 ± 0.2 (perchlorate system) and -3.0 ± 0.3 (chloride system). From this it can be inferred that at low acidities of the aqueous phase, where the ion exchange mechanism is assumed to operate, three protons are exchanged according to the reaction



where HA denotes the reagent in the monomeric form. The reactions of Sc^{3+} with HB and HC are alike.

Effect of starting concentration of inorganic acid. The dependence of the scandium distribution ratio on the starting concentration of HClO_4 or HCl was studied with HA and HB. While in the case of HCl , the D_{Sc} value decreases monotonically with the starting concentration of this acid⁷, in the case of HClO_4 a change in the extraction mechanism takes place (Fig. 1); the initial ion exchange mechanism in the less acid region is replaced by the solvation mechanism, where, e.g., the $\text{Sc}(\text{HA})_y \cdot (\text{ClO}_4)_3$ complexes are preferentially extracted. The fact that this is not observed with HCl is probably due to the formation of charged scandium chloro complexes in the aqueous phase.

Effect of starting concentration of reagent. The dependences of the scandium distribution ratio on the equilibrium concentrations of the reagents HA, HB or HC (in the monomeric form in the organic phase) at $c(\text{HClO}_4) = 0.1 \text{ mol l}^{-1}$ are shown in Fig. 2. The equilibrium concentrations of the monomers in the organic phase were calculated for $V_{\text{aq}} = V_{\text{org}}$ based on the known K_D , K_2 and K_a values, using the general relation

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

where HX stands for HA, HB or HC and c_{HX} is its analytical concentration. In our particular case, with respect to the c_{H^+} value (0.1 mol l^{-1}) and the K_a and K_D values, we have for HB

$$[\text{HX}]_{\text{org}} = \left[\left(1 + 8K_2c_{\text{HX}} \right)^{1/2} - 1 \right] / 4K_2. \quad (2)$$

Although the K_2 and K_a values are unavailable for HC, it is reasonable to assume that Eq. (2) will hold for this reagent as well.

Fig. 2 demonstrates that the slopes of the linear segments lie within the region of 3.0 ± 0.3 . This indicates that the composition of the extractable complexes at the used analytical concentrations of the reagents is ScX_3 , hence, the value of x in reaction (A) is zero. The extraction constants are expressed by the relation

$$K_{\text{ex,HX}} = ([\text{ScX}_3]_{\text{org}} [\text{H}^+]^3) / ([\text{Sc}^{3+}] [\text{HA}]_{\text{org}}^3), \quad (3a)$$

or

$$K_{\text{ex,HX}} = D_{\text{Sc}} [\text{H}^+]^3 / [\text{HA}]_{\text{org}}^3. \quad (3b)$$

From this, at $I = 0.1$ we obtain $\log K_{\text{ex,HA}} = 15.5$, $\log K_{\text{ex,HB}} = 8.8$ and $\log K_{\text{ex,HC}} = 5.4$ (the last, assuming that $\log K_{2,\text{HC}} = 2.2 \pm 0.3$). Thus, the reagent HA appears to be the most convenient of them for transferring scandium into benzene, the extraction being markedly suppressed by the presence of sulfur in place of oxygen in the molecule of the reagent.

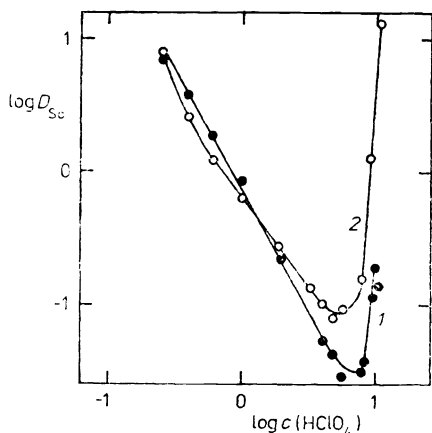


FIG. 1

Effect of the starting concentration of HClO_4 in the aqueous phase on the distribution of scandium between the aqueous phase and benzene solution of tetraphenyl imidodiphosphate, $c_{\text{HA}} = 0.01 \text{ mmol l}^{-1}$ (1) or imidodithiodiphosphate, $c_{\text{HB}} = 2 \text{ mmol l}^{-1}$ (2); $c_{\text{Sc}} (\mu\text{mol l}^{-1})$: 1 0.64, 2 0.4

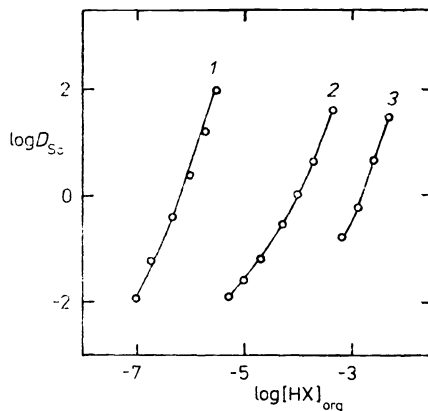


FIG. 2

Effect of the equilibrium concentration of reagent in the organic phase on the distribution of scandium between 0.1M-HClO_4 and benzene solution of the reagent; $c_{\text{Sc}} = 0.03 \mu\text{mol l}^{-1}$. Reagent: 1 HA, 2 HB, 3 HC

Effect of starting concentration of scandium. The dependences of the scandium distribution ratio on its starting concentration, for the three reagents and medium of 0.1M-HClO₄ or 0.1M-HCl, are shown in Fig. 3. While in the case of HA the scandium distribution ratio does not vary with its starting concentration, in the case of HB or HC the distribution ratio decreases with increasing starting concentration of scandium, regardless of the mineral acid used and even if the reagent is present in an excess. This indicates that the polymerization degree of the complex in the aqueous phase increases. This is rather surprising for scandium complexes, and sulfur in the reagents seems to take part in this effect. This behaviour was not studied in more detail; we suggest, however, that the formation of linear chains of the —P(S)—NH—P(O)—M—P(S)—NH—P(O)—... type in the aqueous phase may be involved. It is noteworthy that a similar concentration dependence has been observed⁷ for the extraction of silver with HC, while HA, and also HB, behaved in the normal manner.

Thus, it is imperative that for calculating K_{ex} according to Eq. (3), the starting concentration of scandium be held low enough. For important two-phase reaction the c_{sc} values used should always be reported.

Radiation stability of HA

Our previous results^{3,4,6} as well as the data shown in Fig. 2 demonstrate that the extraction of scandium into benzene with HA is very efficient. This fact was utilized for studying configuration changes in this reagent induced by gamma radiation, hence, for assessing the radiation stability of this substance.

Figure 4, curve 1, shows the dependence of the logarithm of the scandium distribution ratio on the logarithm of the starting concentration of HA in benzene in the

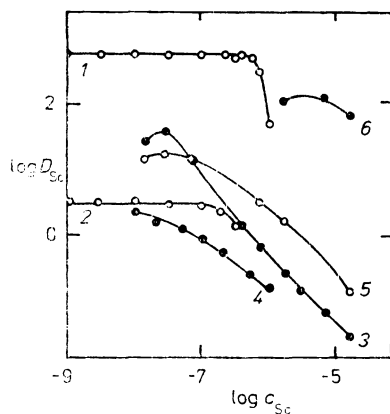


FIG. 3

Effect of the starting concentration of scandium on its distribution between 0.1M-HClO₄ (1–3, 5, 6) or 0.1M-HCl (4) and benzene solution of HA (1, 2), HB (3, 4) or HC (5, 6). Concentration of reagent (mmol . l⁻¹): 1 0.01, 2 0.001, 3 0.2, 4 0.2, 5 1.8, 6 18

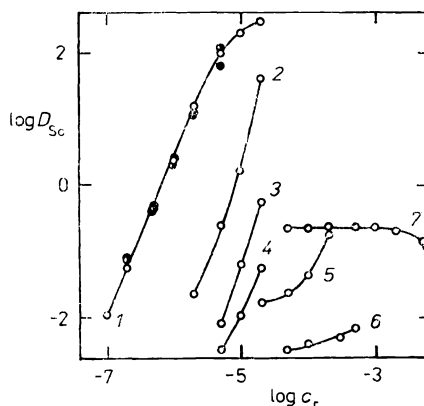
presence of the aqueous phase constituted by solution of Sc ($0.16 \mu\text{mol l}^{-1}$) in 0.1M-HClO_4 . This plot demonstrates that the extraction of scandium using the unexposed reagent and that exposed to a single 600 or 800 kGy dose and subsequently dissolved in benzene follows the same patterns. Hence, the reagent has undergone no deep destruction, to diphenylphosphoric acid or its amide for instance; otherwise the scandium distribution ratio would decrease, the two latter substances being considerably less powerful extracting agents for scandium (Fig. 4, curves 5 and 6).

For solutions of HA in benzene, on the other hand, it is sufficient to be irradiated by a dose of 10 kGy to extract scandium to a considerably lesser extent. Thus, some configuration changes promoted by the presence of the solvent must have taken place. Furthermore, the decrease in the scandium distribution ratio depends on the dose applied (Fig. 4, curves 2–4) unless oxygen has been removed by nitrogen purging (Fig. 5, curves 2–4); hence, this effect is apparently associated with the presence of oxygen in the system, and it can be assumed that peroxy compounds or phenol may be formed⁸. The fact that the extraction of scandium into benzene with HA is suppressed by phenol is documented by curve 7 in Fig. 4, although the antagonistic effect is not very marked.

A deeper insight into this effect was gained by ^{31}P NMR spectroscopic measurements. A solution containing HA in benzene in a concentration of 50mmol l^{-1} was freed from oxygen by nitrogen purging and subsequently exposed to a dose of 100 kGy. The mass balance of the components identified is given in Table I. It follows that at the concentration used, most of the reagent remains intact and the major compound formed is triphenyl imidodiphosphate. A next triaryl ester, containing a Ph-Ph-O- group, and triphenyl imididiphosphate-phosphonate are also identified. The last four compounds in Table I are present in fractions lower than 0.5 mole % P and their occurrence is not unambiguous.

FIG. 4

Effect of the starting concentration of reagent (c_r) on the distribution of scandium between 0.1M-HClO_4 and reagent solution in benzene; $c_{\text{Sc}} = 0.16 \mu\text{mol l}^{-1}$. Reagent: 1 HA unexposed to gamma radiation (\circ) and exposed to a dose of 600 (\bullet) and 800 (\blacklozenge) kGy in the solid state; 2–4 HA in benzene solution prior exposed to a dose of 10 (2), 50 (3) and 100 kGy (4); 5 diphenylphosphoric acid; 6 diphenylphosphoric amide; 7 phenol; $c_{\text{HA}} = 0.4 \mu\text{mol l}^{-1}$, $c_{\text{Sc}} = 0.02 \mu\text{mol l}^{-1}$



It can be concluded that HA in the solid state is highly resistant to gamma radiation. This stability, however, is disturbed by the presence of benzene as a solvent. In a simplified scheme, the formation of the radiolysis products of HA can be treated in terms of formation of excited molecules of benzene ($C_6H_6 \sim \rightarrow C_6H_6^*$), energy transfer ($C_6H_6^* + HA \rightarrow C_6H_6 + HA^*$) and decomposition ($HA^* \rightarrow$ products) (ref.⁸). Cundall and coworkers⁹ suggest that these reactions play a decisive role while the formation of radicals and the action of subexcited electrons are of minor importance.

TABLE I

Compounds identified by ^{31}P NMR spectroscopy in a solution of HA in benzene, $c_{HA} = 50 \text{ mmol l}^{-1}$, after its nitrogen purging and exposure to a 100 kGy gamma dose

| Compound | $\delta(^{31}P)$ ppm | $^2J/PP$ interaction constant, Hz | x^a % |
|--------------------------------|-------------------------|--------------------------------------|------------|
| $(PhO)_2P(O)NHP(O)(PhO)_2^b$ | -9.5 | — | 86 |
| $(PhO)(OH)P(O)NHP(O)(PhO)_2$ | -5.3, -8.6 | 8.7 | 10 |
| $(PhPhO)(OH)P(O)NHP(O)(PhO)_2$ | -5.1, -8.6 | 8.9 | 1.4 |
| $(PhO)(H)P(O)NHP(O)(PhO)_2$ | 0.7, -8.0 | 11.6-12 | 0.6 |
| $(PhO)(Ph)P(O)NHP(O)(PhO)_2$ | 6.4, -8.3 | 11.2-11.8 | <0.5 |
| $(PhO)_2P(O)NH_2$ | 1.7 | — | <0.5 |
| $(PhO)(OH)P(O)NHP(O)(PhO)(OH)$ | -4.4 | — | <0.5 |
| $(PhO)_2P(O)NPhP(O)(PhO)_2$ | 8.8 | — | <0.5 |

^a Mole fraction, calculated with respect to the P content; ^b starting substance (HA).

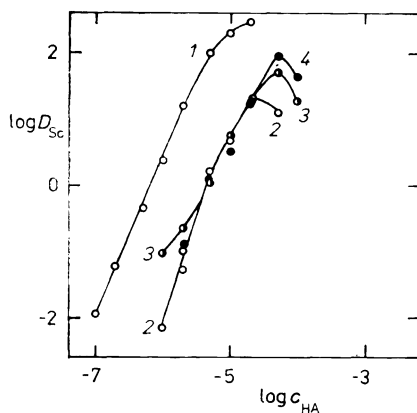


FIG. 5

Effect of the starting concentration of HA on the distribution of scandium ($c_{Sc} = 0.16 \mu\text{mol l}^{-1}$) between $0.1M\text{-HClO}_4$ and solutions of HA in benzene prior nitrogen purged and exposed to gamma radiation. Dose (kGy): 1 0, 2 10, 3 50, 4 100

REFERENCES

1. Herrmann E., Navrátil O., Hoang ba Nang, Smola J., Friedrich J., Příklad J., Dreyer R., Chalkin V. A., Kulpe S.: *Collect. Czech. Chem. Commun.* **49**, 201 (1984).
2. Navrátil O., Cigánek M., Herrmann E.: *Collect. Czech. Chem. Commun.* **48**, 2009 (1983).
3. Herrmann E., Navrátil O.: *6th International Symposium High Purity Materials in Science and Technology. Dresden, G.D.R., May 1985*, Poster Abstracts I, p. 128 (D 81).
4. Navrátil O., Fofana M., Smola J.: *Z. Chem.* **24**, 30 (1984).
5. Navrátil O., Herrmann E., Slezák P.: *Collect. Czech. Chem. Commun.* **52**, 1708 (1987).
6. Navrátil O., Herrmann E.: *Proceedings of the 43th Congress of the Czechoslovak Chemical Society, Ústí nad Labem, July 1987*; p. 123, Poster V-162.
7. Fofana M.: *Thesis*. J. E. Purkyně University, Brno 1985.
8. Czeper G., György I., Roder M., Wojnárowits L. in: *Radiation Chemistry of Hydrocarbons* (G. Földiák, Ed.), p. 397. Akademiai Kiadó, Budapest 1981.
9. Cundall R. B., Robinson D. A., Pereire L. C.: *Advances in Photochemistry*, p. 147. Wiley, New York 1977.

Translated by P. Adámek.