

EXTRACTION OF SILVER AND MERCURY WITH TETRAPHENYL IMIDOTHIODIPHOSPHATE

Oldřich NAVRÁTIL^a, Eckhard HERRMANN^b and Petr SLEZÁK^a

^a Department of Inorganic Chemistry,
Purkyně University, 611 37 Brno, Czechoslovakia and

^b Chemical Section, Luther University, 4 020 Halle-Wittenberg, G.D.R.

Received August 6th, 1986

The extraction of complexes of silver and mercury with tetraphenyl imidothiodiphosphate (HA) from HNO₃ and HCl solutions, respectively, into benzene was studied. The extraction from dilute aqueous solutions establishes within 10 min. The composition and stability of the complexes extracted, AgA(HA) and HgA₂, were derived from the dependences of the distribution ratios of the respective metals on the acidity of the aqueous phase and analytical concentration of reagent. Using HClO₄ solutions as the aqueous phase, silver is extracted by a double extraction mechanism, an appreciable fraction of the metal passing into benzene also in the absence of HA. Based on the distribution of HA between the aqueous phase and benzene, its distribution and dimerization constants were established; the dissociation constant of the reagent was determined potentiometrically.

The application of tetraphenyl imidothiodiphosphate, (C₆H₅O)₂P(O)NHP(S).(C₆H₅O)₂, (HA), to extraction purposes has been studied at a cursory level only^{1,2}. Still, we have found that the presence of sulphur brings about an increased selectivity of the reagent, particularly with respect to the extraction of silver and mercury; we lacked, however, some of the fundamental characteristics of the reagent such as the dissociation constant, K_a , distribution constant of monomer, K_D , and dimerization constant, K_2 . The present work is concerned with the determination of these data of the reagent and the distribution of silver and mercury between solutions of HA in benzene and aqueous phases at ionic strengths $I = 0.1, 1.0$ or 0.5 .

EXPERIMENTAL

Chemicals and Apparatus

Tetraphenyl imidothiodiphosphate was synthesized and purified following procedure³ and checked for purity by ³¹P NMR spectrometry on a Jeol FX-100 instrument⁴. The other chemicals used were of reagent grade purity (Lachema, Brno). Radioactive solutions were obtained from the Central Institute for Nuclear Physics in Rosendorf, G.D.R. Working solutions of ^{110m}AgNO₃ ($c_{Ag} = 1.2 \mu\text{mol l}^{-1}$) in 0.1M-HNO₃ had a specific activity of $(3-5) \cdot 10^3 \text{ s}^{-1} \text{ cm}^{-3}$, working solutions of ²⁰³HgCl₂ ($c_{Hg} = 0.6 \mu\text{mol l}^{-1}$) were prepared from a stock solution in 1M-HCl and their specific activity was $(2-3) \cdot 10^3 \text{ s}^{-1} \text{ cm}^{-3}$.

The pH values were measured at $25 \pm 1^\circ\text{C}$ with an MV 84 pH-meter (Clamann-Grahnert, Dresden, G.D.R.) equipped with a GA 50 glass electrode and a KE 10 saturated calomel electrode (both Forschungsinstitut Meinsberg, G.D.R.). The glass electrode performance was checked by means of phthalate and borate buffers. The relationship between the experimental potential and concentration of hydrogen ions was determined based on titrations of solutions of HClO_4 in similar conditions.

The gamma activity of the radioactive liquid samples was measured with a Nuclear Chicago Model 1185 automatic sample changer.

Procedure

5 ml of each of the aqueous and organic phases were agitated for 50 min which, as was found by preliminary experiments, was sufficient for the extraction equilibrium to establish. The phases then were allowed to separate, and 2 ml aliquots were taken and measured in glass ampoules in a well crystal. All measurements were performed at $20 \pm 1^\circ\text{C}$. The relative standard deviation of all measurements did not exceed 2%.

The dissociation constant of the reagent was determined potentiometrically in 75 vol. % acetone containing NaClO_4 in a concentration of 0.1 mol l^{-1} by titration with NaOH ($c = 0.1 \text{ mol l}^{-1}$) under argon. After each addition of titrant, solution of NaClO_4 in acetone was added so that the volume concentration of acetone and analytical concentration of perchlorate remained constant.

For determining the dimerization and distribution constants of HA monomer, the equilibrium concentration of HA in an aqueous phase containing HNO_3 in a concentration of 0.1 mol l^{-1} was determined by the radioactive tracer method⁴. After the distribution of HA between the two liquid phases, a small volume of the aqueous solution of $^{110\text{m}}\text{AgNO}_3$ in 0.1M- HNO_3 was added to an aliquot of the aqueous phase, and the latter was agitated again with pure benzene. The distribution of the tracer between the two phases then was determined, and the initial equilibrium concentration of HA in the aqueous phase was derived from a comparison with calibration curves.

The acidity of the aqueous phase was adjusted with HNO_3 and HClO_4 or with $\text{HNO}_3 + \text{LiNO}_3$ for silver and with HCl or $\text{HCl} + \text{LiCl}$ for mercury.

RESULTS AND DISCUSSION

Dissociation, Dimerization, and Distribution Constants of HA

Determination of the dissociation constant K_a of the reagent, which is a weak acid, is difficult because of its low solubility in water. The potentiometric titration was therefore performed in 75 vol. % acetone solutions. The $\text{p}K_a$ value obtained in a solution containing NaClO_4 in a concentration of 0.1 mol l^{-1} is 2.68 ± 0.23 (the confidence interval pertains to a set of 42 experimental values). For a comparison, the $\text{p}K_a$ value of the analogue, tetraphenyl imidodiphosphate, $(\text{C}_6\text{H}_5\text{O})_2\text{P}(\text{O})\text{NHP}(\text{O})\cdot(\text{OC}_6\text{H}_5)_2$, in 75 vol. % acetone at $I = 0.1$ is 2.39 ± 0.14 and in water ($I = 0$), 4.11 ± 0.08 (ref.⁵). From this it can be inferred that the $\text{p}K_a$ value of tetraphenyl imidothiodiphosphate in water shall not be lower than 3.0 (ref.⁶).

The dimerization constant $K_2 = [(\text{HA})_2]_{\text{org}}/[\text{HA}]_{\text{org}}^2$ and the distribution constant $K_D = [\text{HA}]_{\text{org}}/[\text{HA}]$, where HA and $(\text{HA})_2$ are the monomeric and dimeric species

of the reagent, respectively, the index org labels the species in the organic phase (the aqueous phase is unlabelled), and the brackets denote the equilibrium concentrations, were determined by using the relation

$$D_{\text{HA}} = ([\text{HA}]_{\text{org}} + 2[(\text{HA})_2]_{\text{org}})/[\text{HA}] = K_{\text{D}} + 2K_2K_{\text{D}}^2c_{\text{aq}}, \quad (1)$$

where D_{HA} is the distribution ratio of the reagent and $c_{\text{aq}} \equiv [\text{HA}]$. This equation holds for acidities of the aqueous phase $\text{pH} < 2$. Then, the plot of the dependence of D_{HA} on c_{aq} is a straight line whose intercept is K_{D} and whose slope can serve to determine the K_2 value. At $I = 0.1$ (HNO_3), the values of $\log K_{\text{D}} = 4.6 \pm 0.2$ and $\log K_2 = 2.2 \pm 0.3$ were thus obtained. These values, particularly that for K_{D} , are rather surprising in comparison with those for tetraphenyl imidodiphosphate, which are⁷ $\log K_{\text{D}} = 1.11 \pm 0.07$ and $\log K_2 = 3.3 \pm 0.5$. The differences are clearly due to the different nature and properties of the P(O)NHP(S) and P(O)NHP.(O) groupings.

Complex Compounds of HA with Silver

The composition of the extractable complex was determined from the dependences of the distribution ratio of silver on the initial analytical concentration of hydrogen ions and the initial analytical concentration of reagent. The latter can be transformed into the dependence of D_{Ag} on $[\text{HA}]_{\text{org}}$, provided that the values of K_{a} , K_{D} , and K_2 are known and that $V_{\text{aq}} = V_{\text{org}}$, by means of the general formula

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

In our particular case, with regard to the magnitudes of c_{H^+} (0.1 mol l^{-1}), K_{a} , and K_{D} , we can write

$$[\text{HA}]_{\text{org}} \approx \left[(1 + 8K_2c_{\text{HA}})^{1/2} - 1 \right] / 4K_2 \quad (3)$$

The dependence of the distribution ratio of silver on the concentration of hydrogen ions in the aqueous phase, at a constant ionic strength of $I = 0.1$ ($\text{HNO}_3 + \text{LiNO}_3$) and concentration of HA in benzene $25 \mu\text{mol l}^{-1}$, is linear with a slope of $-1.0 \pm \pm 0.1$. The dependence of the distribution of silver on the initial concentration of reagent in the presence of HNO_3 is presented in a logarithmic form in Fig. 1. The plot is linear with a slope of 2.0 ± 0.1 . Using Eq. (3) we find that at $c_{\text{HA}} = 5 - 100 \mu\text{mol l}^{-1}$, virtually all reagent in the organic phase is present in its monomeric form. The above dependences thus indicate the occurrence of the equilibrium



hence, the extracted species is $\text{AgA}(\text{HA})$. The logarithm of the corresponding extraction constant $K_{\text{ex}} = [\text{AgA}(\text{HA})]_{\text{org}}[\text{H}^+]/[\text{Ag}^+][\text{HA}]_{\text{org}}^2$ is $\log K_{\text{ex}} = 9.7 \pm 0.1$ at $I = 0.1$ or 1.0 , taking into account the activity of hydrogen ions at $c_{\text{HNO}_3} = 0.1$ or 1.0 mol l^{-1} (ref.⁸).

The use of dilute aqueous perchloric acid is a particular case. The dependence of $\log D_{\text{Ag}}$ on the initial concentration of this acid, in the presence of HA ($25 \mu\text{mol} \cdot \text{l}^{-1}$) in benzene, is shown in Fig. 2. It is clear that the initially ion exchange extraction mechanism, expressed, *e.g.*, by equilibrium (A), alters at $c_{\text{HClO}_4} \geq 7 \text{ mol l}^{-1}$. By studying the dependence of D_{Ag} on the initial concentration of HNO_3 or HClO_4 in the absence of HA we found that whereas the amount of silver passing into benzene in the presence of HNO_3 is negligible ($\log D_{\text{Ag}} \leq -3.0$), this is not true in the presence of HClO_4 (Fig. 2, curve 2). Thus, the minimum in curve 1 (Fig. 2) is due to the solubility of AgClO_4 itself in benzene⁹, although conversion of the initial extraction mechanism (Scheme (A)) into the solvation mechanism leading to $(\text{Ag}(\text{HA})_x^+, \text{ClO}_4^-)_{\text{org}}$ is not impossible.

The use of organic phases of different kind is illustrated in Fig. 3. The distribution ratio of silver extracted from 0.1M-HNO_3 increases in order benzene \approx methylbenzene $<$ CCl_4 $<$ cyclohexane. The nature of the extraction into cyclohexane, in relation to the change in the slope of the plot of $\log D_{\text{Ag}}$ vs $\log c_{\text{HA}}$, was not examined; it can be associated with the K_{D} and K_2 values.

Complex Compounds of HA with Mercury

Since HgCl_2 is a covalent compound, very low dissociated in water, we examined its solubility in benzene. The dependence of the distribution of mercury(II) between benzene and hydrochloric acid of various concentrations is shown in Fig. 4. This distribution is not negligible and is affected by the formation of the unextractable HgCl_3^- and HgCl_4^{2-} species in the aqueous phase. The initial concentration of $c_{\text{HCl}} = 0.5 \text{ mol l}^{-1}$ was chosen as the optimum for further experiments.

Of interest is the dependence of the mercury distribution ratio on the initial concentration of mercury(II) in the aqueous phase (Fig. 5). The corresponding curve for $c_{\text{HCl}} = 0.5 \text{ mol l}^{-1}$ has a maximum at $c_{\text{Hg}} \approx 0.05 \mu\text{mol l}^{-1}$. This shape was found both in the presence (0.5 mmol l^{-1}) and in the absence of HA in benzene, which indicates that the system is rather complex and cannot be treated in terms of the occurrence of polydentate species solely.

For establishing the composition of the complex extracted with HA into benzene, the dependences of $\log D_{\text{Hg}}$ on c_{H^+} and c_{HA} were investigated at a constant ionic strength of $I = 0.5$ or 1.0 (adjusted with HCl and LiCl) because here the extraction of HgCl_2 itself can be neglected. The dependence of $\log D_{\text{Hg}}$ on c_{H^+} at $c_{\text{HA}} = 2.5 \text{ mmol} \cdot \text{l}^{-1}$ was linear with a slope of -2.0 ± 0.1 , the dependence of $\log D_{\text{Ag}}$ on c_{HA} at $c_{\text{HCl}} = 0.5 \text{ mol l}^{-1}$, examined over the region of $c_{\text{HA}} = 0.1 - 5 \text{ mmol l}^{-1}$, was also

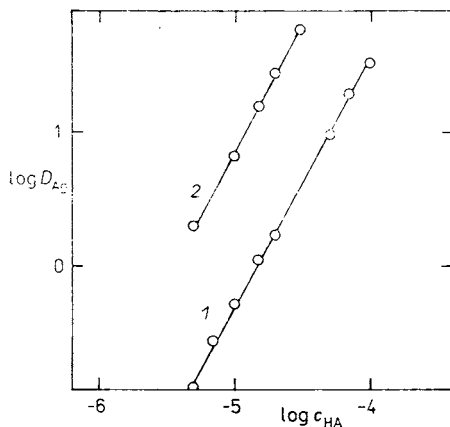


FIG. 1

Dependence of distribution of silver between aqueous solution of HNO_3 and benzene solution of HA on the initial concentration of HA. c_{HNO_3} , mol l^{-1} : 1 1.0, 2 0.1

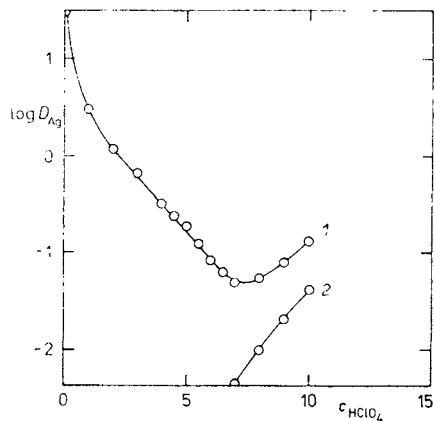


FIG. 2

Dependence of distribution of silver between aqueous solution of HClO_4 and benzene solution of HA ($25 \mu\text{mol l}^{-1}$) 1 or pure benzene 2 on the concentration of HClO_4

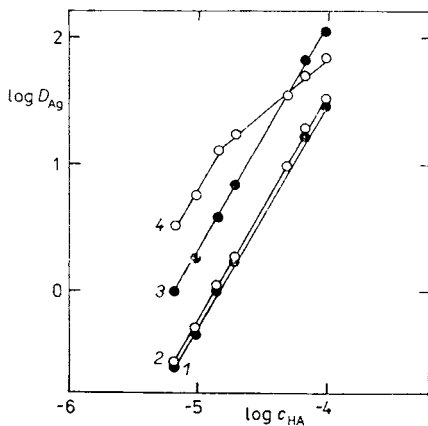


FIG. 3

Dependence of distribution of silver between aqueous solution of 1M-HNO_3 and solution of HA in organic solvent on the initial concentration of HA. Organic solvent: 1 methylbenzene, 2 benzene, 3 tetrachloromethane, 4 cyclohexane

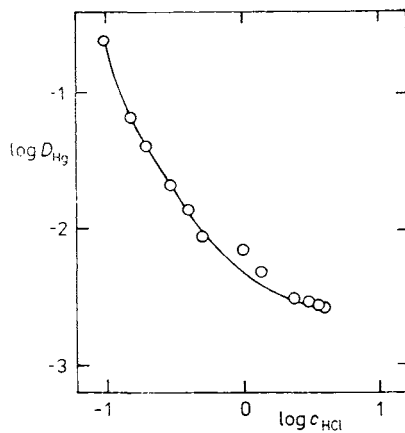
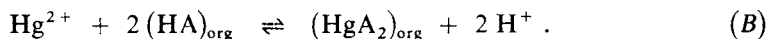


FIG. 4

Dependence of distribution of mercury(II) between aqueous solution of HCl and benzene on the concentration of HCl

linear with a slope of 2.0 ± 0.1 . This suggests that at $c_{\text{Hg}} = 0.6 \mu\text{mol l}^{-1}$ and $c_{\text{HCl}} = 0.5 \text{ mol l}^{-1}$, extraction of mercury(II) with HA into benzene corresponds to the equilibrium



In contrast to silver, for mercury the extraction constant $K_{\text{ex}} = [\text{HgA}_2]_{\text{org}}[\text{H}^+]/[\text{Hg}^{2+}][\text{HA}]_{\text{org}}^2$ cannot be determined directly from distribution data because D_{Hg} includes all mercury species in the liquid phases. In the aqueous phase,

$$\begin{aligned} C_{\text{Hg,w}} &= [\text{Hg}^{2+}] + [\text{HgCl}^+] + [\text{HgCl}_2] + [\text{HgCl}_3^-] + [\text{HgCl}_4^{2-}] = \\ &= [\text{Hg}^{2+}] \left(1 + \sum_{i=1}^{i=4} \beta_i [\text{Cl}^-]^i \right), \end{aligned} \quad (4)$$

where β_i 's are the cumulative constants of the Hg chloro complexes, and this has to be taken into account in the relation for K_{ex} . From stability constant tables¹⁰, the value of $(1 + \sum \beta_i [\text{Cl}^-]^i)$ is $10^{13.6}$ at $I = 0.5$, and so

$$K_{\text{ex}} = [\text{HgA}_2]_{\text{org}} [\text{H}^+]^2 / \left\{ C_{\text{Hg,w}} / \left(1 + \sum_{i=1}^{i=4} \beta_i [\text{Cl}^-]^i \right) \right\} [\text{HA}]_{\text{org}}^2, \quad (5)$$

hence,

$$K_{\text{ex}} = 10^{13.6} D_{\text{Hg}} [\text{H}^+]^2 / [\text{HA}]_{\text{org}}^2, \quad (6)$$

which gives $\log K_{\text{ex}} = 19.6 \pm 0.5$ at $I = 0.5$.

In conclusion, tetraphenyl imidodithiophosphate, containing a sulphur atom, differs in properties appreciably from the oxygen analogue, tetraphenyl imidodiphosphate, owing to its enhanced reactivity with IB and IIB Group heavy metals and platinum metals and its very low reactivity with lanthanoids.

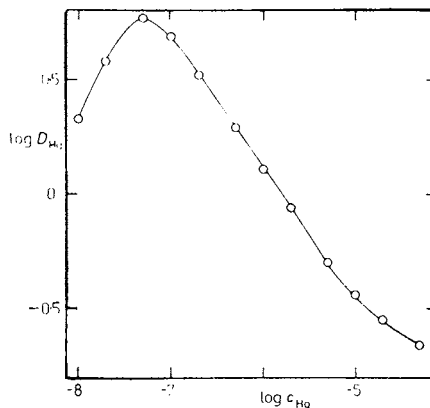


FIG. 5

Dependence of distribution of mercury between 0.5M-HCl and benzene solution of HA (0.5 mmol l^{-1}) on the initial concentration of mercury(II)

REFERENCES

1. Navrátil O., Fofana Momo, Smola J.: *Z. Chem.* 24, 30 (1984).
2. 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.
3. Mezník L., Mareček A.: *Z. Chem.* 21, 294 (1981).
4. Navrátil O.: *Collect. Czech. Chem. Commun.* 40, 1711 (1975).
5. Herrmann E., Hoang ba Nang, Dreyer R.: *Z. Chem.* 19, 187 (1979).
6. Šafařík L., Stránský Z.: *Odměrná analýza v organických rozpouštědlech*, p. 103. Published by SNTL — Nakladatelství technické literatury, Prague 1982.
7. Herrmann E., Navrátil O., Hoang ba Nang, Smola J., Friedrich J., Příhoda J., Dreyer R., Chalkin V. A.: *Collect. Czech. Chem. Commun.* 49, 201 (1984).
8. Marcus Y., Kertes A. S.: *Ion Exchange and Solvent Extraction of Metal Complexes*, p. 923. Wiley-Interscience, New York 1969.
9. Heslop R. B., Jones K.: *Anorganická chemie*, p. 758. Published by SNTL — Nakladatelství technické literatury, Prague 1982.
10. Bjerrum J., Schwarzenbach G., Sillén L. G.: *Stability Constants, Part II*, p. 105. The Chemical Society, London 1958.

Translated by P. Adámek.