SOLVENT EXTRACTION OF MERCURY COMPLEXES WITH DIISOPROPYLAMINOETHANETHIOL AND OTHER SUBSTANCES ACCOMPANYING AGENT VX

Oldrich NAVRATIL, Zbynek KOBLIHA and Emil HALAMEK

Department of Chemistry,
The Military College of Ground Forces, 682 03 Vyskov, The Czech Republic

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The distribution of 2-diisopropylaminoethanethiol (RSH) between aqueous phase containing picric acid at various pH values (ionic strength 0.1) and toluene as the organic phase was investigated. The protonation constant of the reagent is $K_a = 10^{6.27}$. The constants characterizing the formation of the ion-associate with the picrate anion were also determined. The distribution of mercury was also examined between solutions of RSH and its derivatives in low-polar organic solvents and aqueous phases containing mineral acids and/or their sodium salts. The composition of the extractable chelating complexes formed in neutral and alkaline aqueous phases is Hg : reagent = 1 : 3.

The synthesis of the nerve paralyzing agent VX, which is *O*-ethyl-*S*-(2-diisopropylaminoethyl)methylthiophosphonate, usually starts from two compounds[1], viz. 2-diisopropylaminoethanethiol, $(iPr)_2NCH_2CH_2SH$ (henceforth RSH), and *O*-ethylmethylphosphonic acid chloride. The two components are reacted in the presence of tertiary bases which bind the forming hydrogen chloride, and a high purity product is obtained. When stored, however, agent VX decomposes giving methylphosphonic acid derivatives, free thiols, and disulfides[2]. Agent VX and all accompanying substances are extremely toxic so that their detailed analysis is very difficult and only few publications dealing with this topic exist[3–5]. As far as complex compounds of agent VX and its decomposition products with metals are concerned, these have been studied only sparsely, mainly in relation to the mercurimetric determination of thiols formed by reduction of dialkyl disulfides[4].

This work examined the possibility of freeing agent VX from contaminants including the starting components, with special emphasis on RSH, whose acid-base properties have not been so far studied in sufficient detail. Since the reactivity of mercury(II) ions with thiols has been examined previously[4], this work focussed on complexes of mercury with RSH and also with VX and potential contaminants, viz. bis(2-diisopropylaminoethane) sulfide (RSR), bis(2-diisopropylaminoethane) disulfide (RSSR), methyl

2-diisopropylaminoethane sulfide (MeSR), and *O*-ethyl-*S*-hydrogen methylthiophosphonate (PSH). Solvent extraction was used employing the radionuclide ^{203}Hg.

EXPERIMENTAL

Chemicals and Apparatus

The reagents examined were synthesized in Army Factory 072 in Zemianske Kostolany (The Slovak Republic) following procedures[1,6]. Their purity was checked by ^{31}P NMR spectrometry and by paper chromatography. 2-Diisopropylaminoethanethiol was used in the form of RSH . HCl, in which it is most stable. Chloroform was freed from ethanol by extraction with water; the component boiling at 59 °C at normal pressure was then distilled. The other chemicals were preparations of reagent grade purity supplied by Lachema, Brno (The Czech Republic).

The radionuclide ^{203}Hg (Poland) was added to the aqueous phase in the form of mercury(II) nitrate. Its concentration in the working solutions was 0.5 – 5 μmol l^{-1}, activity 20 – 50 kBq cm^{-3}.

Gamma radioactivity of the solutions was measured with a Gamaautomat NA 3601 (Tesla Liberec, The Czech Republic) interfaced to an NaI(Tl) well-type detector; an NP 424L four-channel gamma spectrometer (MEV, Hungary), also equipped with an NaI(Tl) well-type detector, was used as well.

The pH of the aqueous phase was measured with an OP-208/1 instrument (Radelkis, Hungary) fitted with an OP-080SP combined glass electrode. Phthalate and citrate buffers were used for calibration. The ^{31}P NMR spectra of 50 wt.% solutions in $CDCl_3$ were scanned on a WP 80 SY instrument (Bruker, Germany) using H_3PO_4 as the external standard.

The absorbances of the two phases, measured in relation to the distribution of RSH in the presence of picric acid, were determined on a Spekol 11 instrument (Zeiss, Germany) at 345 nm (refs[7,8]) using glass cells 0.5 and 1 cm optical pathlength.

Procedure

Extraction of the systems in ground-in test tubes was performed on a homemade rotary shaking machine. The two phases (5/5 ml) were agitated at 20 ± 1 °C for 60 min, which was sufficient for the extraction equilibrium to establish. The two phases were then allowed to separate, the pH of the aqueous phase was determined, 2 ml aliquots of either phase were taken and measured for gamma activity, or their absorbance was determined. Safety precautions had to be made when working with agent VX. The pulse frequency of the well detector was adjusted so that the relative mean square error of the individual measurements did not exceed 2%.

The pH and ionic strength (0.1) of the aqueous phase was adjusted with solutions of HCl, NaCl and NaOH, or $HClO_4$, $NaClO_4$ and NaOH.

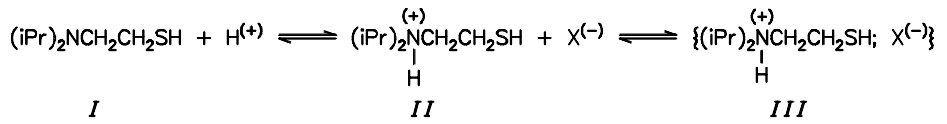
The distribution ratios of picric acid were calculated from the absorbances of the organic and aqueous phases after extraction at 345 nm.

RESULTS AND DISCUSSION

Characterizing the Reagent RSH

Existing data[2–4] indicated that RSH in the aqueous phase would behave as a weak base (*I*); acid solutions would contain the protonated species RSH_2^+ (*II*), which would react

with suitable univalent anions X^- such as the picrate anion Pi^- giving the extractable ion-associate (*III*) (see Scheme 1).



SCHEME 1

This fact was confirmed by examining the distribution of picric acid (starting concentration $2 \cdot 10^{-4}$ mol l^{-1}) between the aqueous phase at an ionic strength of 0.1 (NaCl, HCl, NaOH) in the presence of RSH, and toluene as the organic phase. This distribution is shown in Fig. 1 in dependence on the pH of the aqueous phase, and in Fig. 2 in dependence on the starting concentration of RSH at pH 3.0 – 4.0.

The process can be described as follows:

$$RSH + H^+ \rightleftharpoons RSH_2^+ \qquad (A)$$

$$RSH_2^+ + Pi^- \rightleftharpoons \{RSH_2^+;Pi^-\} \qquad (B)$$

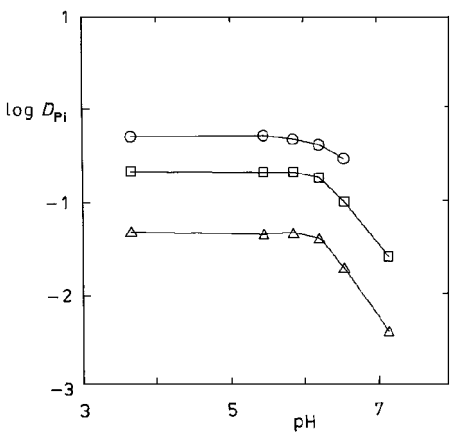


FIG. 1
Effect of pH of the aqueous phase on the distribution of the $\{RSH_2^+;Pi^-\}$ ion-associate between aqueous phase (ionic strength 0.1 adjusted with NaCl, HCl, NaOH) and toluene. Concentration of picric acid 0.2 mmol l^{-1}, concentration of RSH (mmol l^{-1}): ❍ 5, ❒ 2, Δ 0.5

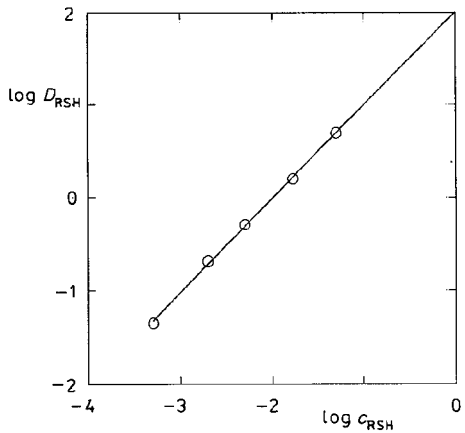


FIG. 2
Effect of the starting concentration of RSH on the distribution of the $\{RSH_2^+;Pi^-\}$ ion-associate between aqueous phase (ionic strength 0.1) and toluene. Aqueous phase pH 3 – 4, concentration of picric acid 0.2 mmol l^{-1}

$$\{RSH_2^+;Pi^-\} \rightleftharpoons \{RSH_2^+;Pi^-\}_o \qquad (C)$$

with the respective constants

$$K_a = [RSH_2^+]/[RSH][H^+] \qquad (1)$$

$$K_{IA} = [\{RSH_2^+;Pi^-\}]/[RSH_2^+][Pi^-] \qquad (2)$$

$$K_{D,IA} = [\{RSH_2^+;Pi^-\}]_o/[\{RSH_2^+;Pi^-\}] \,. \qquad (3)$$

The analytical (total) concentration of RSH can be written in the form

$$c_{RSH} = [\{RSH_2^+;Pi^-\}]_o + [[RSH_2^+]] + [RSH] = K_{D,IA}\,K_{IA}[RSH_2^+][Pi^-] +$$

$$+ [RSH_2^+] + [RSH_2^+]/K_a[H^+] = [RSH_2^+](K_{D,IA}\,K_{IA}[Pi^-] + 1 + 1/K_a[H^+]) \,. \qquad (4)$$

In these equations, brackets denote equilibrium concentrations, subscript o refers to the organic phase, whereas concentrations without any subscript refer to the aqueous phase.

The pK of picric acid is 0.38 (ref.[9]), and so the distribution ratio of the Pi^- anion at a pH of the aqueous phase not lower than 3 can be defined as

$$D_{Pi} = [\{RSH_2^+;Pi^-\}]_o/[Pi^-] = K_{D,IA}\,K_{IA}[RSH_2^+] \,. \qquad (5)$$

Based on Eqs (*4*) and (*5*), two limiting states can be identified, viz. $\log D_{Pi} = \log c_{RSH}$ const at $K_a[H^+] >> 1$, and $\log D_{Pi} = \log \text{const} - \text{pH}$ at $K_a[H^+] << 1$. The point of intersection of their asymptotes gives the pK_a value. This is demonstrated in Fig. 1, showing the dependence of $\log D_{Pi}$ on pH for various starting concentrations of RSH. A value of pK_a = 6.27 is obtained from the point of intersection of the asymptotes.

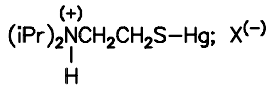
The $\log D_{Pi}$ value at $\log c_{RSH} = 0$ (Eq. (*5*)) and pH 3 – 4 (Fig. 2) is $\log K_{D,IA}\,K_{IA}$ = 2.00, hence $K_{D,IA}\,K_{IA} = 100$. The molar absorptivity of the picrate anion at 345 nm is $1.40 \cdot 10^4$ l mol^{-1} cm^{-1} in the aqueous phase at pH > 3, and $1.37 \cdot 10^4$ l mol^{-1} cm^{-1} in the toluene phase. The former value was directly obtained from the absorbance of the aqueous phase, the latter, from the absorbance of the extract of the ion-associate $\{RSH_2^+;Pi^-\}$ in toluene.

Mercury Complexes

Figure 3 shows the distribution of mercury between the organic phase, consisting of a solution of RSH ($1 \cdot 10^{-2}$ mol l^{-1}) in chloroform or toluene, and the aqueous phase,

containing 0.1 mol l^{-1} (H,Na)Cl or (H,Na)ClO_4, in dependence on pH of the latter phase. Each extraction curve exhibits two saddles, separated by the region of pH 5.5 – 7.0. This suggests that within this pH region the mercury extraction mechanism changes due to the acid-base change of the reagent. The mercury distribution ratio is higher if chloroform is used, whereas the difference between the chloride and perchlorate medium is less pronounced. In a medium of 0.1 mol l^{-1} (H,Na)Cl, mercury chloro complexes predominate over Hg^{2+} ions (tabulated values[10] indicate that $c_{Hg} = 10^{11.2}\,[Hg^{2+}]$), this, however, is not very important because neither the stability constant nor the extraction constant is calculated in this work. The situation with the hydrolysis of Hg^{2+} ions in the aqueous phase is similar[10] ($K_{1,hydrol} = 10^{-3.68}$, $K_{2,hydrol} = 10^{-2.57}$).

The formation of the ion-associate $\{RSH_2^+;HgX_3^-\}$ may occur in the acid region, although the formation of the complex cation $RSHHg^+$ with the protonated nitrogen (ammonium system), forming an extractable ion-associate with the mineral acid anion (*IV*), is not impossible. This means that reduction of mercury(II) to mercury(I) is feasible.



IV

In the alkaline region of the aqueous phase, the reagent RSH loses its proton coordinated to nitrogen (*II*) and can react with mercury as a weak acid by exchanging the proton in the –SH group, giving rise to the electroneutral chelate (*V*) (see Scheme 2). In the absence of the reagent, mercury nearly completely remains in the aqueous phase. Figure 4 shows the dependence of the mercury distribution ratio D_{Hg} on the starting

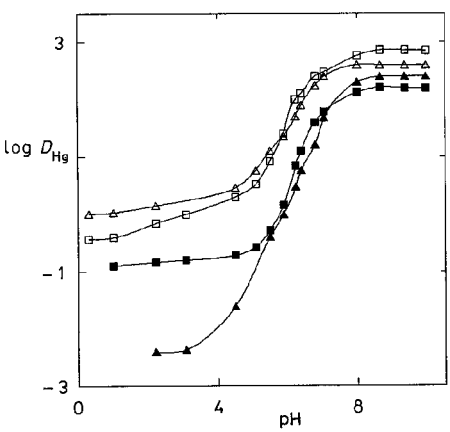
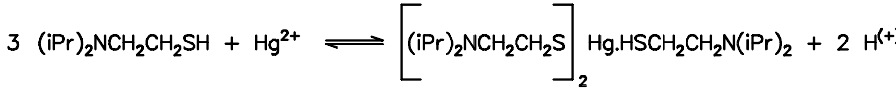


FIG. 3
Effect of the aqueous phase pH on the distribution of mercury between the aqueous phase (ionic strength 0.1) and chloroform (❒,Δ) or toluene (▲, ■). Medium: Δ, ■ perchlorate, ❒, ▲ chloride. Concentration of RSH: 1 . 10^{-2} mol l^{-1}, concentration of mercury: 9 . 10^{-8} mol l^{-1}

concentrations of all reagents used in the organic (toluene) phase and in the aqueous phase, for aqueous phase pH 8 – 9.5. Invariably, the extraction curves exhibited maximum slopes of 3. The extractability of mercury increased in order PSH < RSR < VX < RSSR << RSH. Of importance is the stability of mercury complexes with RSH, a five-fold excess being sufficient for its quantitative transfer into the organic phase. This fact



V

SCHEME 2

might be made use of for separation of RSH from the other compounds under study, which problem, however, was not pursued by us in more detail. The above slope of the log D_{Hg} vs log $c_{reagent}$ plot suggests that complexes of the composition HgR_2 . NaR (reagents with acid hydrogen) or HgR_3 (other reagents) pass into the organic phase.

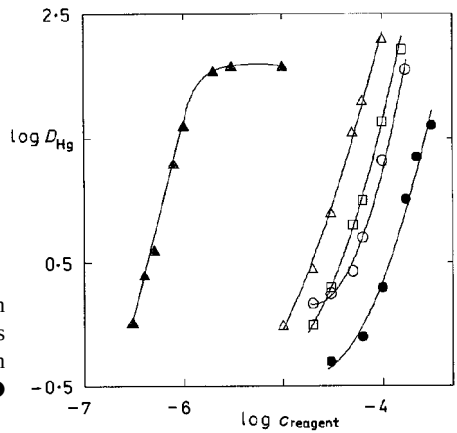


FIG. 4
Effect of the starting concentration of reagent on the distribution of mercury between aqueous phase (pH 8 – 10, ionic strength 0.1 adjusted with $NaClO_4$ and NaOH) and toluene. Reagent: ● PSH, ❍ RSR, ❒ VX, Δ RSSR, ▲ RSH

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