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REACTION OF BUTYLMERCURY NITRATE WITH LEWIS BASES

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Summary

The reaction of butylmercury nitrate with organic bases has been studied in four solvents. $BuHgNO_3$ is molecular in benzene and acetone but ionic in water; in acetonitrile there is an equilibrium between molecular and ionic species. In benzene solution bases form 1 : 1 adducts, 3-coordinate with pyridine, 4-methylpyridine, bipyridine, Et_3N, Bu_3N, PBu_3, PPh_3 or diphos, 4-coordinate with tetramethyldiaminoethane. Adduct stabilities and enthalpies of formation are reported. In acetone solution bases displace nitrate, in water bases displace coordinated water and in acetonitrile they displace nitrate or coordinated solvent; in all three solvents the end products are $BuHg \cdot base^+$ and NO_3^-. Enthalpies are reported for these reactions.

Distribution of $BuHgNO_3$ between benzene and water is concentration dependent. Addition of phosphines increases the proportion of the mercury in the benzene phase; addition of heterocyclic bases increases the proportion in the aqueous phase; addition of tertiary amines first increases the proportion in the benzene phase, then, with higher base concentrations, that in the aqueous phase.

Introduction

There has been considerable interest in the toxicity of organomercury compounds, which become serious environmental pollutants when generated from mercurial wastes by processes such as bacterial methylation. There is some reduction in toxicity when complexes are formed between the methylmercury cation and S-ligands, such as cysteine [1] or penicillamine [2,3] and particularly effective protection may be given by some Se-donors [4].

Most compounds of the type RHgX ionise in aqueous solution and equilibrium constants have been determined for the association of $MeHg^+$ with a wide range of donor ions and molecules. The range of association constants extends from $\log K = 1.5$ for F^- through 5.25 for Cl^- and 9.37 for OH^- to 15 for PEt_3 and 21.2 for S^{2-} [5]. Detailed studies have also been made for association of $MeHg^+$

with amines and amino acids, log $K = 5.05$ for NMe_3 being typical [6], though smaller association constants are observed for heterocyclic bases [7]. The association constants of RHg^+ with I^- increase in the order R = Me < Et < Pr, thou the reverse order is observed with Br^-, Cl^- and OH^- [8] and also with SCN and thiourea for which an extended series shows decreasing association constants in the order R = Me > Et > Pr > iPr > Bu > iBu [9]. Kinetic studies have also been made recently of the reaction of the hydroxide EtHgOH with bromide [10].

The toxicity of organomercurials also depends upon their transfer from aqueous to lipid phase, but there have been few studies of these compounds made in non-aqueous solutions. The effect of S-ligands on the distribution of $MeHg^+$ between water and toluene has been examined [11] and studies have been made of the reactions of the halides RHgX with Lewis bases in various solvents. These compounds, though ionised in water, dissolve undissociated in benzene and are non-conductors in acetone [12]; they react with excess halide ions in acetonitrile solution, giving the complex anions $RHgX_2^-$ [13]. In benzene solution they react with amines, heterocyclic bases, phosphines etc., givin addition compounds in which the mercury atom is usually 3-coordinate [14,1

In contrast to the halides, adducts of $RHgNO_3$ with bidentate bases have been shown by infrared spectra to have ionised nitrate [16] and this is confirmed by the crystal structure of $[MeHg \cdot bipy]^+NO_3^-$ (bipy = 2,2′-bipyridine) which contains 3-coordinate mercury and discrete nitrate ions [17]. By makin use of the Raman spectra it has been shown [18] that $MeHgNO_3$ dissolves in benzene without dissociation, but when it dissolves in water ionisation takes place, the coordinated NO_3^- ion being displaced by water molecules:

$$MeHgNO_3 + H_2O = MeHgOH_2^+ + NO_3^-$$

addition of the "soft" base SMe_2 displaces the water forming a complex cation

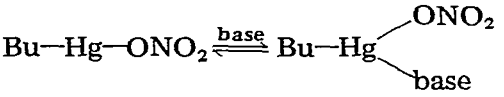
$$MeHgOH_2^+ + SMe_2 = MeHgSMe_2^+ + H_2O$$

The present paper reports reactions of $BuHgNO_3$ with a variety of bases in four different solvents: benzene, acetone, water and acetonitrile. Thermodyna data have been obtained for many of the reactions and the effect of the base o the distribution of mercury between benzene and water has been studied.

Results and discussion

Benzene solution

Though some organomercury compounds are not very soluble in non-donor solvents, $BuHgNO_3$ is freely soluble in benzene. The solution shows two very strong infrared bands at 980 and 1280 cm^{-1}, characteristic of covalently bound nitrate [19] (the third band expected in the region 1500—1600 cm^{-1} is obscured by solvent absorption). On addition of a typical Lewis base, 4-methyl pyridine, these two bands are progressively replaced by bands at 1075 and 131 cm^{-1}, though excess base is required for complete replacement. These new bands are still in the region expected for covalently bound nitrate and there is no evidence of new bands at 830 or 720 cm^{-1}, which would be expected for ionic nitrate. It is thus clear that an addition compound is formed without nitrate displacement and the small shifts in the covalent nitrate bands are due to the changed nitrate environment when the base becomes coordinated to the mercury atom:



$$\mathrm{Bu{-}Hg{-}ONO_2} \underset{}{\overset{\text{base}}{\rightleftharpoons}} \mathrm{Bu{-}Hg}\begin{smallmatrix}\nearrow \mathrm{ONO_2} \\ \searrow \text{base}\end{smallmatrix}$$

Calorimetric titration of bases into benzene solutions of $BuHgNO_3$ confirmed the formation of 1 : 1 adducts. With phosphines these were of very high stability and the titrations were virtually quantitative, but adducts with unidentate N-bases were of only moderate stability (Table 1) and the form of the equilibrium constant:

$$K = \frac{[\mathrm{BuHgNO_3 \cdot base}]}{[\mathrm{BuHgNO_3}][\mathrm{base}]}$$

confirms the formulation of the reaction product as a 1 : 1 adduct without nitrate displacement. Thermodynamic data for these equilibria are summarised in Table 1.

Comparison of these results with data for the addition of bases to other mercury compounds shows that, in general, both K and $-\Delta H^0$ are larger than for the organomercury halides [15] but smaller than for $HgCl_2$ [20,21]; stabilities of the heterocyclic base adducts of $BuHgNO_3$ are comparable to those of Cl_3CHgCl [15]. These results place $BuHgNO_3$ in the middle of the range of mercury compounds as a Lewis acid and show that the nitrate group has a larger electrophilic inductive effect than chloride when attached to the mercury atom.

Substitution of a methyl group in the 4-position on pyridine has the usual effect of increasing slightly both the enthalpy of adduct formation and adduct

TABLE 1

THERMODYNAMIC DATA FOR FORMATION OF 1 : 1 ADDUCTS OF $BuHgNO_3$ WITH BASES IN BENZENE SOLUTION AT 30°C

Base	[Hg] (mmol l^{-1})	K (l mol^{-1})	$-\Delta H^0$ (kJ mol^{-1})	$-\Delta G^0$ (kJ mol^{-1})	$-\Delta S^0$ (J K^{-1} mol^{-1})
Pyridine	3.2—4.8	30 ± 2	39.0 ± 1.0	8.7 ± 0.2	100 ± 4
4-mepy	1.7—2.8	88 ± 10	44.0 ± 1.7	11.3 ± 0.4	108 ± 7
bipy	3.2—4.6	69 ± 4	39.5 ± 1.3	10.7 ± 0.2	98 ± 5
Et_3N	3.2—4.7	533 ± 35	40.8 ± 1.0	15.9 ± 0.2	82 ± 4
Bu_3N	2.2—3.1	244 ± 10	39.9 ± 1.2	13.9 ± 0.2	86 ± 5
tmed	2.3—3.6	1.8×10^4	61.6 ± 0.6	24.7 ± 0.6	122 ± 4
PBu_3	2.8—4.0	$>10^5$	85.8 ± 1.0	>29	<187
PPh_3	1.7—3.7	6.9×10^3	47.2 ± 0.3	22.3 ± 0.6	82 ± 3
diphos [a]	2.8—4.3	$>10^5$	58.1 ± 0.4	>29	<96

[a] Product is diphos$(BuHgNO_3)_2$; data per g-atom Hg.

stability. As in many other mercury compounds, bipy is little more effective as a ligand than pyridine and may be only unidentate in solution, though shown by X-ray analysis to be bidentate in crystalline $MeHgNO_3 \cdot$ bipy [17]. However, even in this compound there are unequal Hg—N bonds and the shorter one forms a very large bond angle of 164° with the Hg—C bond. It thus seems likely that the second, weaker, Hg—N bond may be formed by displacement of the nitrate during crystallisation.

The tertiary amines, Et_3N and Bu_3N, form much more stable adducts than heterocyclic bases, though with unchanged enthalpies of formation; they are thus stabilised relative to the heterocyclic base adducts by entropy factors, of which the most likely seems to be increased solvent displacement by the bulkier ligands. Unlike bipy, *N,N,N',N'*-tetramethyl-1,2-diaminoethane (tmed) is clearly bidentate and chelate, though even in this instance the enthalpy of adduct formation is much less than twice that with unidentate amines.

As is commonly observed with mercury compounds the phosphine adducts are much more stable than those with N-bases and PBu_3 gives a more stable adduct than PPh_3. The behaviour of 1,2-bis(diphenylphosphino)ethane (diphos) in this system is unusual, as it appears to behave as a unidentate base whereas it is usually chelate. It may be noted in this context that the halides, RHgBr, fail completely to react with either diphos or PPh_3 in benzene solution, though forming stable 1 : 1 adducts with PBu_3 [15].

Acetone solution

Solutions of $BuHgNO_3$ in acetone at concentrations of $1—4 \times 10^{-3}$ *M* are non-conducting, but become conducting on addition of bases with Λ_M approaching a terminal value of about 150 $ohm^{-1}\ cm^2\ mol^{-1}$, which is that expected for a 1 : 1 electrolyte [22]. This implies that the reaction observed on addition of base is not adduct formation but nitrate displacement:

$$BuHgNO_3 + base \rightleftharpoons BuHg \cdot base^+ + NO_3^-$$

This was confirmed by infrared studies in acetone solution: in the range 600—1200 cm^{-1} acetone solutions of $BuHgNO_3$ show two absorption bands at 750(m) and 980(s) cm^{-1}, indicating covalently bound nitrate; on addition of 4-methylpyridine these are replaced by bands at 820(s) and 720(w) cm^{-1}, characteristic of ionic nitrate [19]. At the same time the two bands of 4-methylpyridine at 1040 and 1075 cm^{-1} are considerably enhanced in intensity, showing that the 4-methylpyridine has an environment of different symmetry from that in $BuHgNO_3 \cdot$ 4-mepy. Since the mercury is 3-coordinate in the latter compound and 2-coordinate in $BuHg \cdot base^+$ this is expected.

The conclusion from conductance and infrared studies that the reaction of $BuHgNO_3$ with bases in acetone involves nitrate displacement was confirmed by calorimetric titrations, which showed stoichiometric 1 : 1 reactions but with equilibrium constants too large to measure. Enthalpy data for these reactions are given in Table 2. The most remarkable feature of these results is the very close similarity to those obtained in benzene solution in spite of the quite different reactions taking place. Combination of the data obtained in both solvents leads to the conclusion that the enthalpy of ionisation of $BuHgNO_3$ is

TABLE 2

ENTHALPIES OF REACTION, $-\Delta H^0$ in kJ mol^{-1}, OF $BuHgNO_3$ WITH BASES IN VARIOUS SOLVENTS

Base	Benzene	Acetone	Water	MeCN [a]
Pyridine	39.0 ± 1.0	39.4 ± 1.9	30.5 ± 0.4	29.7
4-mepy	44.0 ± 1.7	40.5 ± 1.0	30.2 ± 0.3	31.5
bipy	39.5 ± 1.3	40.7 ± 0.7	33.8 ± 1.6	30.6
Et_3N	40.8 ± 1.0	37.6 ± 0.6	25.4 ± 0.3	35.5
Bu_3N	39.9 ± 1.2	38.4 ± 0.7		33.3
tmed	61.6 ± 0.6	66.7 ± 0.3		56.2
PBu_3	85.8 ± 1.0	93.0 ± 0.6		
PPh_3	47.2 ± 0.3	53.9 ± 0.5		47.0
diphos	58.1 ± 0.4			

[a] Concentration dependent; mean value with $[Hg] = 3 \times 10^{-3}$ *M*.

close to zero; thus for pyridine:

$$BuHgNO_3 \cdot py = BuHgNO_3 + py; \quad \Delta H^0 = +39.0 \quad \text{in benzene}$$

$$BuHgNO_3 + py = BuHgpy^+ + NO_3^-; \quad \Delta H^0 = -39.4 \quad \text{in acetone}$$

$$BuHgNO_3 \cdot py = BuHgpy^+ + NO_3^-; \quad \Delta H^0 = -0.4$$

While this simple calculation takes no account of any differences in solvation energies, it does suggest that the enthalpy of ionisation is small and this may be an important factor in determining distribution between solvents.

Aqueous solution

Aqueous solutions of $BuHgNO_3$ in the concentration range 1—4×10^{-3} *M* gave molar conductances of 240 ohm^{-1} cm^2 mol^{-1}. This rather high value suggests secondary ionisation of the aquo-ion first produced [18] by nitrate displacement:

$$BuHgNO_3 + H_2O \rightleftharpoons BuHgOH_2^+ + NO_3^-$$

$$BuHgOH_2^+ \rightleftharpoons BuHgOH + H^+$$

The known data for the behaviour of $MeHg^+$ as an acid, $K_a = 2.5 \times 10^{-5}$ [5], would lead to 10—15% secondary ionisation in this concentration range and $BuHg^+$ is likely to be similar.

On addition of a base to the aqueous solution a stoichiometric 1 : 1 reaction is observed and Λ_M falls to about 180 ohm^{-1} cm^2 mol^{-1}. Such a change could be expected since the replacement of either $-OH_2$ or $-OH$ in the complex ion by —base would eliminate ionisation of H^+, which is responsible for the unusually high conductance. Comparable results were obtained with the bases: pyridine, 4-methylpyridine, bipyridine and Et_3N. Phosphines could not be studied because of their low solubilities in water.

Calorimetric titration of water-soluble bases into aqueous solutions of $BuHgNO_3$ confirmed the 1 : 1 stoichiometry, with equilibrium constants too large to measure. Enthalpies of reaction are included in Table 2. These are significantly different from those observed in benzene or acetone solutions. This could be expected since they represent a quite different reaction, the displacement of coordinated water by base in the complex organomercury cation:

$BuHgOH_2^+ + \text{base} \rightleftharpoons BuHg \cdot \text{base}^+ + H_2O$

$BuHgOH + \text{base} \rightleftharpoons BuHg \cdot \text{base}^+ + OH^-$

Acetonitrile solution

Solutions of $BuHgNO_3$ in acetonitrile resemble those in water rather than in benzene or acetone, in that they are conducting. However, the conductance is concentration dependent, Λ_M falling from about 150 ohm^{-1} cm^2 mol^{-1} in 10^{-3} M solution to about 80 in 4×10^{-3} M (Fig. 1). Since the molar conductance expected for a 1 : 1 electrolyte in acetonitrile is about 140 ohm^{-1} cm^2 mol^{-1} [22], this indicates that ionisation approaches completeness in 10^{-3} M solution but molecular species are in equilibrium at higher concentrations. It can be concluded that in acetonitrile solution there is partial displacement of nitrate by the solvent:

$BuHgNO_3 + MeCN \rightleftharpoons BuHg \cdot NCMe^+ + NO_3^-$

On addition of a base Λ_M increases to about 200 ohm^{-1} cm^2 mol^{-1}, the exact figure varying from one base to another in the range 180—260; the reaction is stoichiometric 1 : 1 and must represent displacement of either nitrate or solvent by the base, depending upon the proportion of molecular or ionic species in equilibrium.

Calorimetric titration of base into acetonitrile solutions confirms the 1 : 1 stoichiometry with equilibrium constants too large to be measured. Enthalpies of reaction increase with increasing mercury concentration, approaching at high concentrations the values observed in benzene solution and at low concen-

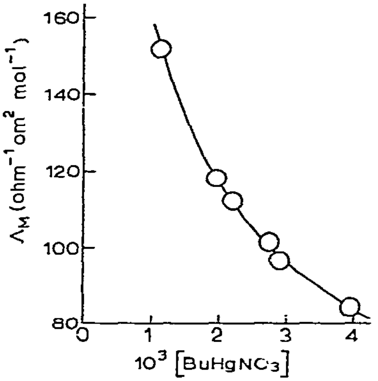


Fig. 1. Molar conductance of solutions of $BuHgNO_3$ in acetonitrile.

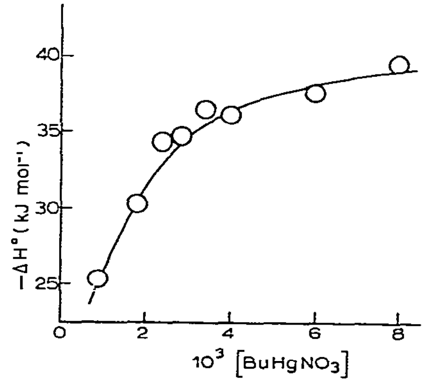
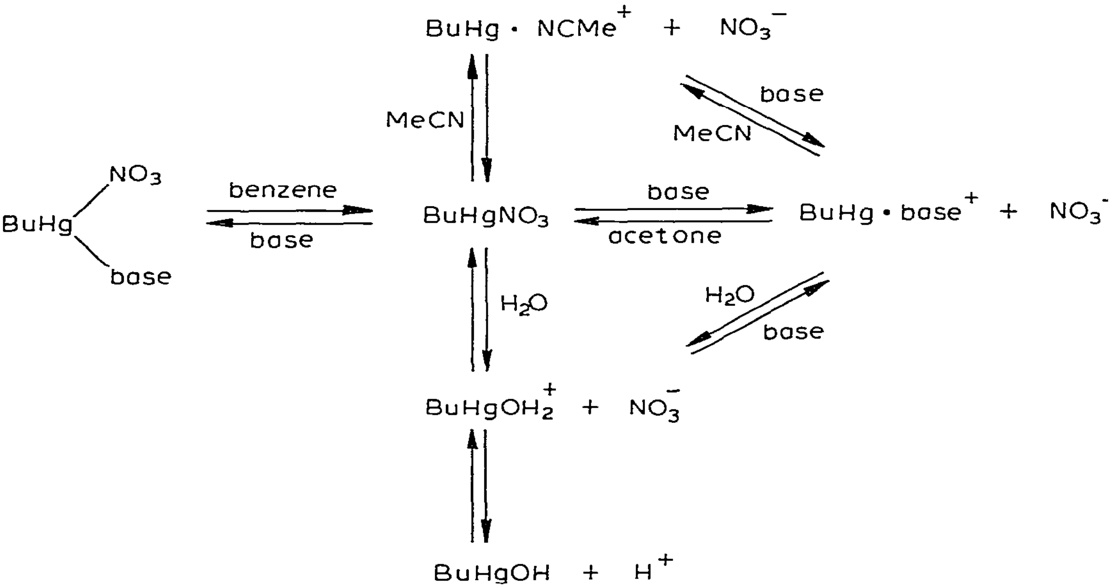


Fig. 2. Heat of reaction of $BuHgNO_3$ with Et_3N in acetonitrile.

trations those obtained in water (Fig. 2). Data included in Table 2 are for 3×10^{-3} M solutions, which are intermediate between the extremes and correspond to reaction of base with mixtures of roughly equal proportions of $BuHgNO_3$ and $BuHg \cdot NCMe^+$.

Comparison of the data obtained in four different solvents can be expressed in a set of related equilibria:



Distribution studies

In the absence of added base the distribution of $BuHgNO_3$ between water and benzene is concentration dependent, increasing proportions of the mercury being found in the benzene phase as the total mercury concentration increases. The results are shown in Fig. 3 and can be represented by a distribution function:

$$K_d = [Hg_{\text{aqueous}}]^a / [Hg_{\text{benzene}}]$$

where $1.5 < a < 1.8$. This is consistent with $BuHgNO_3$ dissolving undissociated in benzene but reacting with water to give a mixture of $BuHgOH_2^+$ and BuHgOH

Preliminary studies of the distribution of bases between the two solvents in the absence of mercury compound showed that they fell into three categories:

(1) tmed, 75% in the aqueous phase, 25% in benzene;

(2) Et_3N and 4-mepy, 10% in the aqueous phase, 90% in benzene;

(3) Bu_3N, $Hexyl_3N$ and bipy, more than 99% in the benzene phase.

Phosphines were too sparingly soluble in water for distribution studies to be made. All the distributions observed were independent of concentration over the range 10^{-3}—10^{-2} M.

The effect of added base on the distribution of $BuHgNO_3$ between water and benzene is shown in Fig. 4. Three distinct types of effect can be seen:

(1) Phosphines greatly increase the proportion of mercury in the benzene phase. These are all ligands which form highly stable adducts, $BuHgNO_3 \cdot PR_3$,

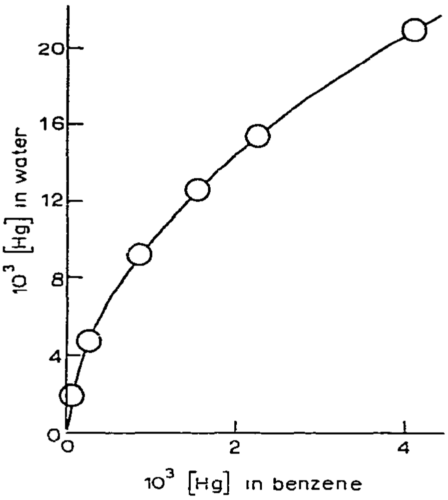


Fig. 3. Distribution of $BuHgNO_3$ between equal volumes of benzene and water.

in benzene solution and the very low solubility of the ligands themselves in water leads to excess ligand being almost wholly in the benzene phase.

(2) 4-Methylpyridine and bipyridine lower the proportion of mercury in the benzene phase. In benzene solution these bases form only moderately stable adducts with $BuHgNO_3$, but they form much more stable complex ions in aqueous solution, the stability of which evidently favours their transfer into the aqueous phase.

(3) The tertiary amines have the remarkable effect of first increasing the

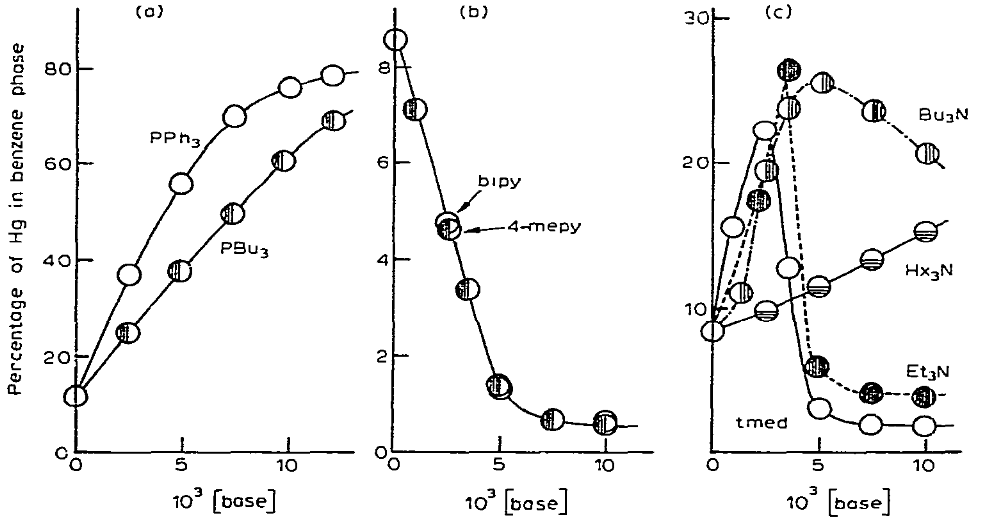


Fig. 4. Effect of bases on distribution of $BuHgNO_3$ between equal volumes of benzene and water. Total $[BuHgNO_3] = 8.7 \times 10^{-3}$ *M* (addition of PPh_3), 7.0×10^{-3} *M* (PBu_3) or 5.0×10^{-3} *M* (others).

proportion of the mercury in the benzene phase, then as the base concentration increases transferring the mercury to the aqueous phase. This appears to be the result of competition between the formation of relatively stable adducts in benzene solution and the transfer of mercury to the aqueous phase which occurs as the free $BuHgNO_3$ concentration is decreased. The results obtained in the absence of base show that as the total concentration of $BuHgNO_3$ decreases (whether by dilution or as a result of complex ion formation) all the mercury must eventually be transferred to the aqueous phase.

Though there will be differences of detail in the behaviour of other mercury compounds RHgX, depending upon the nature of both R and X, it can be expected that $BuHgNO_3$ is broadly characteristic of all such compounds. In this case the present results provide a mechanism for the transport of organomercury compounds between aqueous and lipid phases. Such transport is an important factor in mercury poisoning, where the accumulation of organomercury compounds usually takes place in lipid phases, such as fish oils. It is now clear that their transport into such phases may be assisted by very small, even stoichiometric, concentrations of "soft" ligands such as phosphines. It seems probable that many sulphur compounds, which bind strongly to mercury, would be equally effective. This suggests that very great care is needed in any attempts to detoxify dilute solutions of mercury wastes by the use of sulphur or selenium compounds, as the end result might well be the reverse of that expected.

Experimental

Butylmercury nitrate was prepared according to the method of Johns [23]: butylmercury chloride was first prepared from mercury(II) chloride and butylchloride by the Grignard method [24]; this was then stirred with silver nitrate in ethanol for 3 h and the precipitated silver chloride filtered off; the filtrate was then evaporated under reduced pressure and the residual $BuHgNO_3$ recrystallised from dry diethyl ether. It was obtained as pure white crystals, stable for several weeks if kept in a sealed container in the dark but rapidly becoming discoloured when exposed. Purity was confirmed by C, H, N and Hg analyses.

Labelled $BuHgNO_3$ was prepared in the same way from mercury(II) chloride labelled with ^{203}Hg. This was obtained from The Radiochemical Centre Ltd., Amersham, Bucks., England in the form of a solution of $^{203}HgCl_2$ in hydrochloric acid, pH 1—2; this was added to an ethanolic solution of $HgCl_2$, which was then evaporated to dryness in a current of dry nitrogen, giving a residue of $HgCl_2$ labelled with ^{203}Hg.

Liquid bases were purified by distillation, under reduced pressure when necessary, and stored over anhydrous potassium carbonate. Solid bases were crystallised from ethanol. Solvents were purified by distillation and dried, benzene over calcium hydride, acetone and acetonitrile over molecular sieve.

Conductivity measurements were made using a Philips PW 9504 conductivity meter in cells specially modified for titration with protection from moist air; all measurements were made at 30°C. Infrared spectra were obtained on a Hitachi-Perkin Elmer model EPI-G2 spectrometer in rock-salt cells using 0.1 *M* solutions of $BuHgNO_3$.

Calorimetric measurements were made in a LKB 8700 titration calorimeter at 30°C using previously described techniques [25]. Briefly, a solution of base in the appropriate solvent was added incrementally to a solution of $BuHgNO_3$ in the concentration range 10^{-3}—10^{-2} M and the heat change measured after the addition of each increment. Control titrations were made to determine the heat of dilution of the titrant. Enthalpograms were obtained by plotting the cumulative heat of reaction, corrected for dilution, against the total base concentration. In systems with very large equilibrium constants the enthalpy of reaction was calculated from the total heat produced when reaction ceased. In reactions where addition of excess base does not lead to completion the enthalpy was obtained from the extrapolated, integrated heat of reaction and equilibrium constants then calculated at each point in the titration; the enthalpy was then refined iteratively until constant values of K were obtained throughout the titration. Values of ΔH^0 in the tables are the average of at least three determinations over a range of concentrations of $BuHgNO_3$ and uncertainties are mean deviations; values of K are the average of at least three determinations and uncertainties are the sum of the mean deviation and the average standard deviation in individual titrations.

Distribution studies were made by dissolving labelled $BuHgNO_3$ in benzene, shaking 10 ml of the solution with 10 ml of water and equilibrating overnight at 28—30°C. The layers were then separated and 1 ml of each layer taken for analysis. The activity of the ^{203}Hg was measured in a well crystal scintillation counter, taking an average of nine measurements on each phase; correction was made for background readings for solvent alone.

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