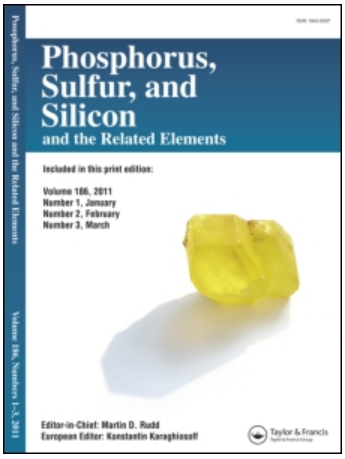

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MERCURIMETRY OF PHOSPHOROUS TRIESTERS AND OF SOME OTHER ORGANIC P(III) COMPOUNDS

M. C. Demarcq[a]
[a] P. C. Ugine Kuhlmann, Centre de Recherches de Lyon, Pierre, Bénite

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MERCURIMETRY OF PHOSPHOROUS TRIESTERS AND OF SOME OTHER ORGANIC P(III) COMPOUNDS

M. C. DEMARCQ

P. C. Ugine Kuhlmann, Centre de Recherches de Lyon, F 69310 Pierre-Bénite

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Non-hindered trialkyl(aryl)phosphites reduce mercuric acetate to metallic mercury in methanolic solution. The reaction is fast enough to allow direct titration by potentiometry, using a Pt electrode; adding a little Et_3N is beneficial. Phosphorous diesters do not interfere, but halide ions disturb the titration. Alkylphosphonous dialkylesters behave like phosphorous triesters but dialkylphosphinous esters and trialkyl- or triarylphosphines give rise only to complexes. The reaction products of the titration of $(EtO)_3P$ are mixed phosphates $(MeO)_n(EtO)_{3-n}PO$ (n = 0,1,2), AcOH, AcOMe, AcOEt, Me_2O, MeOEt and Hg. The mechanism is discussed.

INTRODUCTION

Despite the tremendous development of the nmr and other physical methods in the analysis of organophosphorus, there is still a need, especially for routine work, for reliable titrimetric methods. The chemical literature is scarce as regards the chemical analysis of P(III) esters. The reference book by Halmann[1] devotes one page only—out of 850—to this topic. Known methods are by hydrolysis[2] or oxidation with ozone, nitrogen dioxide,[1] cumene hydroperoxide[3] or iodine.[4] The latter is probably the most widely used; according to a classical procedure,[4] trialkylphosphites are directly titrated by an iodine liquor in a methanolic solution containing pyridine:

$$(RO)_3P + I_2 + MeOH + Py \longrightarrow (RO)_2PO(OMe) + MeI + [Py,HI] \quad (1)$$

Drawbacks are lack of selectivity towards dialkylphosphites (otherwise known as dialkylphosphonates) $HPO(OR)_2$—common impurities in trialkylphosphites—and unsuitability for determination of triarylphosphites.

The oxidation of triesters of phosphorous acid with mercuric carboxylates has been studied by several authors,[5,6,7] using aprotic solvents or neat reactants. Characterized products of the redox process were metallic mercury, trialkylphosphates, carboxylic esters and, in one case, carboxylic anhydride.[7] No mercurous salt was formed and, actually, it was found that Hg(I) propionate was likewise reduced to Hg.[7] Under mild conditions, an Arbuzov-like reaction may take place with the production of a dialkoxyphosphinylmercuric carboxylate:[6]

$$(AcO)_2Hg + P(OEt)_3 \longrightarrow AcOHg\text{-}PO(OEt)_2 + AcOEt \quad (2)$$

Ia

Heating at ≥70°C or adding a trace of alkali causes **Ia** to decompose with deposition of free mercury[8,9]

Oxidation of trialkylphosphites has also been made by mercurated amides $(RCONH)_2Hg$[10] and by HgO.[11]

Trialkyl(aryl)phosphines may react with mercuric salts in the same way as trialkylphosphites[7,12,13] but complexation of Hg(II) often prevails in that case over its reduction.[13-18]

At r.t. dialkylphosphites only react slowly with Hg(II) acetate, giving dialkoxyphosphinyl-mercuric acetate (**I**):[8,19]

$$(AcO)_2Hg + HPO(OR)_2 \longrightarrow AcOHgPO(OR)_2 + AcOH \qquad (3)$$

I

A true oxido-reduction takes place only upon prolonged heating in the presence of an alcohol:[20]

$$(AcO)_2Hg + HPO(OBu)_2 + BuOH \xrightarrow[4\ h]{50 \rightarrow 200^\circ} OP(OBu)_3 + Hg + 2\ AcOH \qquad (4)$$

RESULTS

Selected method

We have found that most tertiary phosphites reduce mercuric acetate to elemental mercury in methanolic solution; the reaction is fast enough to allow direct titration of the phosphite by the Hg(II) salt. The equivalence point may be determined by means of a redox indicator, such as Variamine Blue, but, owing to the blackening of the solution by dispersed mercury, a potentiometric titration, using a Pt electrode, proved to be much more appropriate.

Addition of trace amounts of triethylamine was found to be beneficial in certain cases: it stabilizes the potential and renders the equivalence point more accurate; pyridine and potassium acetate act in the same way but less efficiently; urea and DMF are inoperative.

The method was successfully used for the titration of a variety of phosphorous triesters (Table I); failures were encountered only with sterically hindered phosphites. Dialkyl alkylphosphonites behave just as the phosphites but alkyl dialkylphosphinites and trialkyl—or triarylphosphines give rise only to complexes (Table I). Examples of titration curves are shown in Figure 1.

A detailed procedure is described in the Experimental part. Simple observation of the mercury deposit may also be used for qualitative purposes.

The products of the reaction of $P(OEt)_3$ were found to be mixed methyl/ethyl phosphates, acetic acid, methyl and ethyl acetates, dimethyl and methyl-ethyl ethers, together with mercury; no strong acid (phosphoric acid partial ester) was generated.

Quantitative data obtained in one case (Et_3N added, see exptl. part) are summarized as follows:

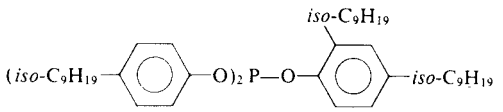
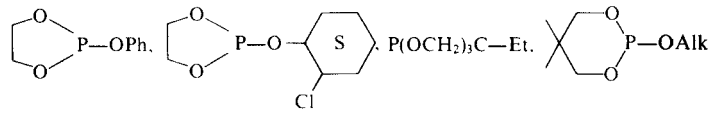
$$P(OEt)_3 + Hg(OAc)_2 + 1.62\ MeOH \xrightarrow{Et_3N} \begin{cases} Hg + 0.51\ OP(OEt)_3 + 0.36\ OP(OMe)(OEt)_2 \\ + 0.13\ OP(OMe)_2(OEt) + 0.82\ AcOMe + \\ 0.08\ AcOEt + 0.08\ Me_2O + 0.02\ MeOEt \\ + 0.52\ EtOH + 1.1\ AcOH \end{cases} \qquad (5)$$

In the absence of Et_3N the acetic esters/phosphoric esters molar ratio decreases from *ca* 90% to *ca* 30%, without substantial change of the AcOMe/AcOEt ratio.

The new method proved to be entirely selective towards dialkyl phosphites, whether Et_3N was added or not.

TABLE I

Examples of attempted titrations of organic P(III) compounds

(1) *Fast and quantitative reduction of $Hg(OAc)_2$ to Hg*	
$P(OAlk)_3$	Alk = {Me, Et[a], 2-Pr[a,b], *n*-Bu, *iso*-$C_{10}H_{21}$, *n*-$C_{12}H_{25}$; $ClCH_2CH_2$—, ClCHMe—CH_2—, $(ClCH_2)_2CH$—
$P(OAr)_3$	Ar = Ph[a], Xylenyl, 4-*iso*-Nonylphenyl
	
$P(OAlk)_n(OAr)_{3-n}$	$(PhO)_2$ PO-*iso*-$C_{10}H_{21}$ $PhOP(O\text{-}iso\text{-}C_{10}H_{21})_2$
Cyclic Phosphites	
$R'P(OR)_2$	$PhP(OPh)_2$, $BuP(OEt)_2$[a,c], $PhP(OCH_2CH_2Cl)_2$
$P(NR_2)_3$	R = 
(2) *Reduction of $Hg(OAc)_2$ too slow to allow direct titration*	
$P(OAr)_3$	Ar = phenyl group, ortho-substituted by at least one bulky group, such as 2-Pr, *tert*-Bu, Ph
$P(SR)_3$	R = *n*-$C_{12}H_{21}$
(3) *Formation of Hg(II) complexes*	
R'_2POR	Bu_2POEt } 2:1 complexes
Alk_3P	Alk = 2-Pr[d], *n*-Bu[a,d] } 2:1 complexes
Ar_3P	Ar = Ph[a] 2:1 and 1:1 complexes

[a] see Figure 1.

[b] a faint intermediate wave at $P(OAlk)_3$:$Hg(OAc)_2$ = ca 2:1 is visible on the potentiometric curve; adding a little Et_3N smoothes out the latter (Figure 1).

[c] a variable faint intermediate wave is observed at $R'P(OR)_2$:$Hg(OAc)_2$ = 1.1 to 1.2, even in the presence of Et_3N.

[d] $(EtO)_3P$ fails to reduce $Hg(OAc)_2$ when $(2\text{-}Pr)_3P$ or $(n\text{-}Bu)_3P$ are present.

Its main drawback is sensitivity to halide ions, due to their forming stable Hg(I) complexes, which badly disturb the titration. For this reason, use of Et_3N is not advisable whenever "labile" halogen atoms are present.

Attempted alternative methods

At the onset of our work we were using Hg(II) pivalate instead of Hg(II) acetate, because we thought a substituted acid was less likely to be involved in secondary

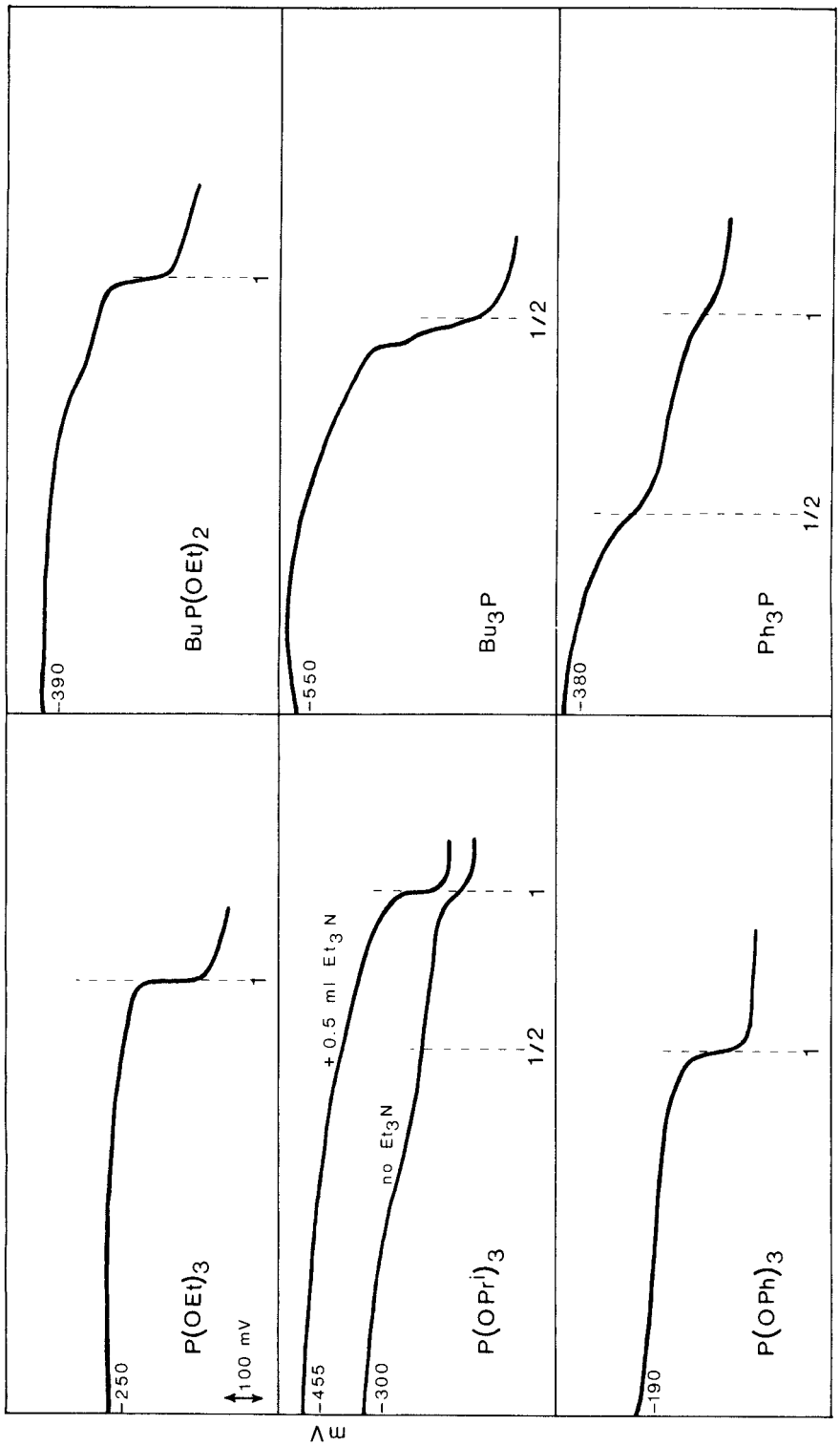


FIGURE 1 Examples of titration curves of organic P(III) compounds in methanol (for Ph_3P, a 80/20 v/v MeOH—toluene mixture was used)

reactions with trialkylphosphites such as (6)[21-23] or (7):[24]

$$P(OR)_3 + AcOH \longrightarrow HPO(OR)_2 + AcOR \quad (R = \text{alkyl or aryl}) \qquad (6)$$

$$P(OR)_3 + AcOH \longrightarrow Ac\text{-}PO(OR)_2 + ROH \quad (R = \text{alkyl}) \qquad (7)$$

This was used until we found evidence that, in our experimental conditions (r.t., highly diluted AcOH, brief contact time), the feared secondary reactions did not in fact appear to take place to a significant extent, even with acetic acid.

Highly dissociated Hg(II) salts, such as nitrate or perchlorate[25] behave quite differently from the (moderately dissociated) Hg(II) acetate: a stable $[(EtO)_3PHgP(OEt)_3]^{2+}$ complex† appears to form, as evinced by a break in the titration curves; metallic mercury becomes apparent only on standing.

No systematic investigation was made of the titration solvents. The oxido-reduction was found to take place also in acetonitrile, but the end point was less clear cut in this solvent than in methanol.

If the normal order of adding the reactants is reversed, *e.g.* if $Hg(OAc)_2$ is titrated by $(EtO)_3P$ in methanolic solution, a nacreous precipitate of mercurous acetate $(HgOAc)_2$ appears first; this converts further to black mercury, when more phosphite is added. Conversely, Hg(I) acetate may form at the expense of the mercury if, in the normal way (Hg^{2+} as a titrant), the equivalence point is exceeded; this Hg + Hg(II) → 2 Hg(I) comproportionation is faster if Et_3N or DMF are present.

DISCUSSION

Composition of the Hg(II) acetate solution

The soft Hg^{2+} cation forms moderately stable complexes with the hard acetate ligand. Following values have been published[27-28] for the three stepwise formation constants in methanolic solution (temp. 20°C; ionic strength 2):

$$K_1 = \frac{[Hg(OAc)^+]}{[Hg^{2+}][AcO^-]} = 10^7;$$

$$K_2 = \frac{[Hg(OAc)_2]}{[Hg(OAc)^+][AcO^-]} = 4 - 5 \cdot 10^2$$

$$K_3 = \frac{[Hg(OAc)_3^-]}{[Hg(OAc)_2][AcO^-]} = 20 - 25$$

Assuming that in MeOH, as in H_2O,[29] the AcO^- ligands exchange very quickly,‡ and excluding complexation by other ligands, we estimated that, in our titration conditions (without Et_3N), the mercuric reactant was essentially made up of $HgOAc^+$ (*ca* 90%) and $Hg(OAc)_2$ (*ca* 10%). Existence in methanolic solution, of methoxide complexes, *e.g.* MeOHgOAc, need also be considered; such complexes have been suggested to account for the cis orientation in the methoxymercuration of alkenes.[30]

Of course, if Et_3N is added, amino complexes such as $Et_3NHgOAc^+$ are also likely to be present.[31]

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† Similar complexes $(R_3P)_2Hg(ClO_4)_2$ are known to form from triarylphosphines.[14,18]

‡ Consistent with this asumption, the ^1H nmr spectra of $Hg(OAc)_2$ in CD_3OD display one single line for CH_3 ($\delta = 1.98$ ppm).

Mechanism

It seems reasonable to assume, although difficult to establish, that the reduction of $Hg(OAc)_2$ to Hg goes directly and not through an intermediate mercurous salt; formation of AcOHgHgOAc would indeed require that two $Hg(OAc)_2$ molecules, instead of one, be involved in the primary reaction step. Formation of Hg(I) acetate, whenever occurring, is best explained by a secondary comproportionation Hg(II) + Hg.

Several mechanisms have been postulated for the reaction between trialkylphosphites and Hg(II) acetate in the absence of protic solvent. The first one (Eq. 8) was by Lutsenko *et al:*[5,10]

$$Hg(OAc)_2 + (RO)_3P \longrightarrow Hg + (RO)_3P(OAc)_2 \xrightarrow{-Hg} 2\ AcOR + (ROPO_2)_x \quad (8)$$

Should a metaphosphate $(ROPO_2)_x$ arise, this would, in our case, react at once with methanol to give the dialkyl hydrogen phosphate (RO)(MeO)PO(OH), a strong acid, contrary to our findings. Hence schema (8) will be rejected.

According to Levin and Kukhtin[6] and to Mukaiyama *et al,*[31] two distinct routes, (9a) and (9b), could be possible:

$$Hg(OAc)_2 + (EtO)_3P \longrightarrow \underset{\displaystyle OAc}{(EtO)_3P{-}HgOAc} \begin{cases} \xrightarrow{a} AcOHg{-}PO(OEt)_2 + AcOEt \\ \qquad\qquad \mathbf{Ia} \\ \xrightarrow{b} (EtO)_3PO + Hg + Ac_2O \end{cases} \quad (9)$$

None of these schemes is fully consistent with our results. Because we observed an immediate deposit of mercury in all cases (Et_3N added or not), path (9a) could at best contribute for a share to the whole process; we found indeed **Ia** to be fairly stable in methanol.† Moreover, **Ia** could not be detected in the decanted final solution. It follows that the participation of (9a), if any, should be altogether negligible.

On the other hand, primary formation of acetic anhydride as in path (9b) is not consistent with the observed relative amounts of AcOMe and AcOEt; in the case summarized by Eq. (5), competitive acetylation by Ac_2O of the solvent methanol and of the ethanol released by the methanolysis of triethylphosphite, should result in a AcOMe/AcOEt molar ratio of at least‡ 2000 instead of *ca* 10.

Furthermore, schemes (8), (9a) and (9b) are all unable to explain the production of methyl ethers Me_2O and ROMe.

A complete rationalization of our results makes it necessary that methanol be involved in the very oxidation step of the phosphite, in addition to its entering into transesterification reactions with the latter. One possible pathway (omitting, for the sake of simplicity, to write the ionized forms of mercury and the transesterified forms of the phosphite) is displayed in scheme (10).

On the analogy of trialkylphosphines,[13] the 2 : 1 complex III is likely to be more stable than the 1 : 1 complex II in methanolic solution; the former is in fact well apparent on the potentiometric titration curves of $P(O^iPr)_3$, Bu_2POEt, Bu_3P and Ph_3P (Figure 1); complex II is visible, but less distinct, on the Ph_3P curve only.

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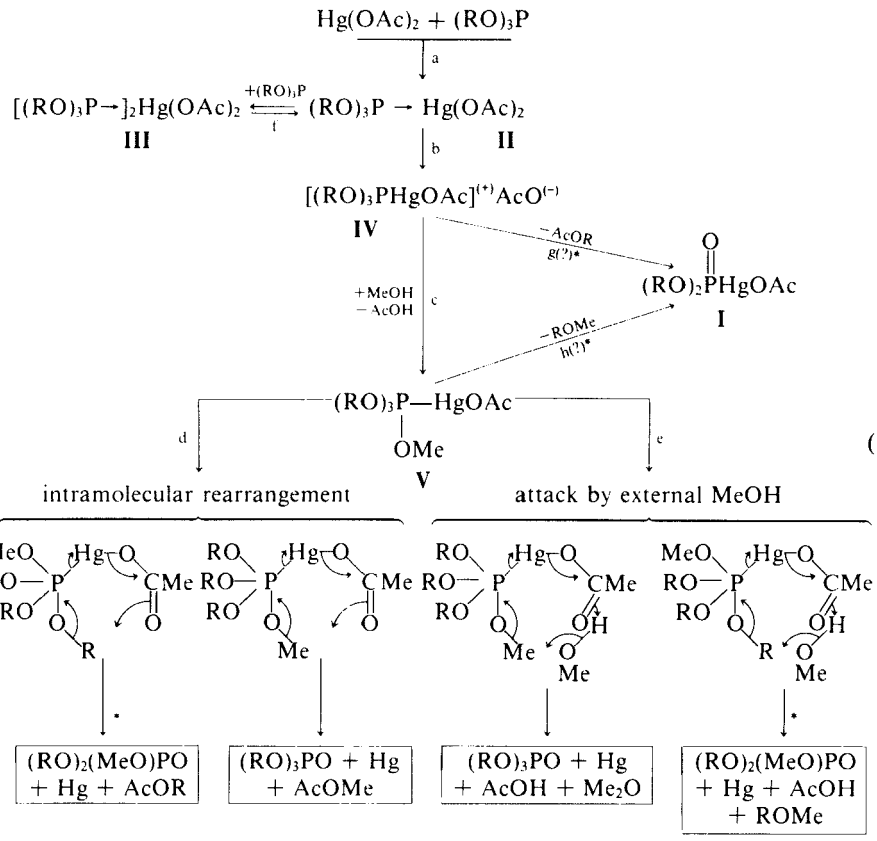
† Ia decomposes slowly in the presence of a little Et_3N or $(EtO)_3P$, more quickly if both Et_3N and $(EtO)_3P$ are added. Incidentally, the (so far unproved) direct Hg-P bonding in Ia was established by the nmr, with the considerable ^{31}P-^{199}Hg coupling constant of 13111 Hz (see exptl. part).

‡ MeOH reacts faster than EtOH with Ac_2O, when near or in water solution.[32]



(10)

* if R = Alkyl

Function of the added amine

Stabilization of the potential by Et_3N (or other trialkylamines) may be due to an acceleration of the redox process at the expense of the intermediate complexes **II** and **III**; this could result from the participation of amino complexes, *e.g.*:

$$(RO)_3P + Et_3N \longrightarrow HgOAc^+ \longrightarrow \underset{\textbf{(IV)}}{[(RO)_3P \longrightarrow HgOAc]^+} + Et_3N \qquad (11)$$

Adsorption on the Pt electrode is also to be considered;[33] titration curves were shifted towards negative potentials when Et_3N was added.

Neutralizing the solution is a further beneficial effect of Et_3N. Phosphorous triesters are much more prone to hydrolysis by moisture of the methanol, if the solution is acidic.[34] Mixed methyl tertiary phosphites, either added or generated *in situ* by transesterification, may also decompose, in the presence of acidity, to yield methylphosphonic diesters and dialkylphosphites;[35] according to our own results[26] a like degradation takes place with trimethylphosphite even at r.t. with minor amounts of acid.

CONCLUSIONS

Potentiometric titration by mercuric acetate in methanol, using a Pt electrode, provides a convenient means of determining a number of organic P(III) compounds, whether the latter become oxidized or complexed.

The specific scope of the new method makes it particularly valuable whenever iodometry is not suitable.

EXPERIMENTAL

Recommended procedure

Use *pro anal.* methanol containing less than 0.2% H_2O. Prepare a ~0.1 M Hg(II) acetate solution by dissolving 63.7 g $Hg(OAc)_2$ *pro anal.* in 1 l methanol containing 10 ml acetic acid; filtrate the solution if not clear. Standardize with KSCN or KCN and store in the dark.

Weight 1 to 2 meq. P(III) compound and dissolve in *ca* 50 ml MeOH (add some toluene if not fully miscible). Optionally add 0.5 ml Et_3N.

Titrate with the Hg(II) acetate liquor, using a Pt measuring electrode and a Hg/Hg_2SO_4 reference electrode. Use of an automatic titration device is advisable.

Diethoxyphosphinylmercuric acetate (Ia)

Ia was prepared according to 8; mp 104.5°C (*lit.* 106.8–107.6); ^{31}P nmr: one main singlet at 56.7 ppm and one doublet centered at 56.7 ppm, ^1J (^{31}P–^{199}Hg) 13111 Hz (+ shifts are downfield from H_3PO_4); the surface ratio of the doublet to the singlet is in agreement with the ^{199}Hg abundance in natural Hg (16.8%).

Quantitative determination of the reaction products of triethylphosphite

0.94 meq $(EtO)_3P$, dissolved in 50 ml MeOH and 0.5 ml Et_3N, was oxidized with the $Hg(OAc)_2$ solution without excess. The generated mercury was filtrated, washed with MeOH and dried in a dessiccator; it weighed 181 mg (calc. 188). The filtrate was analyzed by coupled glc/ms.

Composition of the Hg(II) acetate methanolic solution

Known K_1, K_2 and K_3 values[27-28] were corrected to zero ionic strength, using the classical Debye Hückel equation for the activity coefficients:

$$\log f = \frac{-Az^2 \sqrt{I}}{1 + Ba \sqrt{I}} + bI$$

with I = 2; A = 1.91; B = 0.51; a ~ 5.5 and b ~ 0.14 (estimated values; known data are a = 4.2 and b = 0.116 for 2 M $LiNO_3$ solns and a = 6.7 and b = 0.166 for $LiClO_4$ solutions). Thermodynamic values (i.e. for I = 0) were thus: $K_1 \sim 1.10^9$; $K_2 \sim 1.6 \cdot 10^3$; $K_3 \sim 22$.

The distribution of the Hg(II) acetate between the four considered species during the titration was calculated assuming: titrated P(III) compound = 1 mmole; total volume = 60 ml; temporary excess of titrant liquor = 10^{-4} M; pk_a of AcOH in methanol = 9.6. The excess Hg(II) acetate was thus found to distribute as ~12% $Hg(OAc)_2$, ~88% $Hg(OAc)^+$, ~0.001% Hg^{2+} and 0.023% $Hg(OAc)_3^-$.

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