Studies on some organometallic compounds of mercury and cadmium and their disproportionation

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STUDIES ON SOME ORGANOMETALLIC COMPOUNDS OF MERCURY AND CADMIUM AND THEIR DISPROPORTIONATION

- by -

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The author wishes to express his sincere thanks to Professor G.E. Coates, under whose direction this research was carried out, for his encouragement and valuable advice given throughout the course.

The author is also indebted to Ethyl Corporation for a Research Studentship.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1962 and June 1965. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of this work has been the subject of a publication with Professor Coates in the Journal of the Chemical Society (J., 1965, 1857).

SUMMARY

This thesis can be divided conveniently into two sections. The first deals with some complex salts containing the organomercury group, RHg- , and the second is concerned with the co-ordination complexes formed by the reactions of dimethylcadmium with alcohols and thiols.

Complex salts, $[RHgPR'_3]X$, are formed from alkylmercuric halides and tertiary alkyl phosphines. These complexes slowly disproportionate to give dialkylmercury and $(R'_3P)_2HgX_2$. Although triphenylphosphine derivatives, $[RHgPPh_3]X$, could not be isolated with halide anions the use of other anions enabled a range of salts containing the methylmercury cation complexed with a variety of ligands, including triphenylphosphine, to be isolated. Reaction between arylmercuric halides and tertiary phosphines results in rapid disproportionation:

$$RHgX + PR'_3 \longrightarrow R_2Hg + (R'_3P)_2HgX_2$$

and the relatively fast reaction of $[PhHgPEt_3]NO_3$ with sodium iodide in which Ph_2Hg and $(Et_3)_2HgI_2$ are formed was followed photometrically. Comparative conductometric and gravimetric studies on the disproportionation reactions of several organomercuric halides with triphenylphosphine indicate the influence of solvent, temperature, anion, phosphine and the organic group attached to mercury, on the reaction. Analytical difficulties encountered in the work are also discussed.

Alcohols and thiols react with dimethylcadmium in equimolar proportions with liberation of methane and formation of associated products, $(MeCdOR)_x$, $(MeCdSR)_x$. Those reactions with alcohols that were studied yielded products which were tetrameric in benzene solution, e.g. $(MeCdOPr^i)_4$, with the exception of t-butanol which gave a dimer, $(MeCdOBu^t)_2$. Disproportionation occurs on heating the complexes and dimethylcadmium is evolved. Thiols differ from alcohols in the degree of association of the complexes and give polymers $(MeCdSMe)_x$, $(MeCdSPh)_x$, a tetramer, $(MeCdSBu^t)_4$, and a hexamer, $(MeCdSPr^i)_6$. Some typical infra-red absorptions for the Cd - Me group in those compounds prepared are also reported.

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Experimental

COMPLEX SALTS DERIVED FROM ORGANOMERCURY COMPOUNDS AND THEIR DISPROPORTIONATION

INTRODUCTION

INTRODUCTION

The work described in this thesis consists of studies on the organic derivatives of mercury and cadmium. The first section is concerned with the preparation of complex salts derived from organomercuric halides and other anions by their reaction with ligands containing tertiary nitrogen, phosphorus, or arsenic e.g. $[RHgPR'_3]X$. The factors influencing the disproportionation of the halide complexes have been studied and some comparative and qualitative observations have been made on the rates of these reactions. In the second section investigations of the co-ordination complexes formed by dimethylcadmium on reaction with compounds containing acidic hydrogen, such as alcohols and thiols, are reported.

This introduction begins with a brief description of the inorganic complexes of zinc, cadmium and mercury which is followed by a discussion of the more important and relevant fields of organomercury chemistry. Preparative methods and physical properties are included as these are frequently informative as to the reactivity and nature of the organomercury compounds. For convenience in the nomenclature of mercury compounds the oxidation state of the metal has been replaced by the suffixes

-*ous* and -*ic* denoting oxidation states (I) and (II) respectively. Methylmercury (II) chloride is thus written methylmercuric chloride.

Zinc, cadmium and mercury.

Neutral zinc, cadmium and mercury atoms have two *s* electrons outside filled *d* shells giving them the general configuration, $(n-1)d^{10}ns^2$. As shown in Table I the third ionization potentials of these elements are extremely high which accounts for the absence of M^{3+} since energies of solvation or lattice formation are not great enough to stabilize the metals in the oxidation state (III). The usual oxidation state of the Group IIB metals is (II), although Hg(I) is found in many compounds as the mercurous ion, Hg_2^{2+}. The Hg(I) compounds are stable to disproportionation to Hg(II) and Hg(0) in the absence of reagents which give Hg(II) derivatives more insoluble or more complexed than their Hg(I) analogues, e.g. S^{2-}, OH^-, CN^-, amines and alkyl sulphides. There is no evidence to support the existence of Zn(I) or Cd(I) in aqueous solution although Cd(I) does appear to be formed in melts.[1]

TABLE I

Some properties of zinc, cadmium and mercury.

Elements	Outer electronic configuration	Ionization potentials (e.v.)			E^o(v.) for $M = M^{2+}+2e$
		1st	2nd	3rd	
Zn	$3d^{10}4s^2$	9.39	17.89	40.0	0.762
Cd	$4d^{10}5s^2$	8.99	16.84	38.0	0.402
Hg	$5d^{10}6s^2$	10.43	18.65	34.3	-0.854

Similarities between the elements of Group IIB are most apparent in the pair, zinc and cadmium. Standard electrode potentials, E^o, for the reaction $M \rightarrow M^{2+}+2e$, show that zinc and cadmium are rather electropositive, 0.762v. and 0.402v., respectively compared to mercury, -0.854v., which is electronegative and will not replace hydrogen from non-oxidising acids.

The first ionization potential, Table I, of 10.43e.v. for mercury is also considerably higher than those of zinc and cadmium and is in fact higher than any cation-forming element except hydrogen (13.53e.v.).

In the co-ordination complexes of Group IIB metals the usual co-ordination number is <u>four</u>, due to $\underline{sp^3}$ hybridization, and occasionally <u>six</u>, attributable to $\underline{sp^3d^2}$ hybridization or possibly to the formation of ion-dipole complexes. Mercury again differs from zinc and cadmium as it forms many compounds which exhibit linear co-ordination. This has been considered as indicating *sp* hybridization. An alternative interpretation suggested by Orgel[2] is that although a large energy difference between *ns* and *np* orbitals would encourage *sp* hybridization, the *s - p* separations in the metal ions with a d^{10} core, Cu^+, Ag^+, Au^+, Hg^{2+} which exhibit linear co-ordination are not so much greater than related ions Zn^{2+}, Cd^{2+}, to represent the complete reason for such a great difference in configuration. He proposes[3] that as the *d - s* energy separations for those ions which are known to form linear compounds are small, this is a significant factor in the formation of linear bonds. The *d - s* separations for the common d^{10} ions are shown in Table II. By promoting electrons from the *nd* to the *(n+1)s* orbitals, hybridization of the nd_{z^2} and *(n+1)s* orbitals can be obtained. The result of such hybridization is to transfer the

TABLE II

Energies (e.v.) of lowest d^9s states above the d^{10} ground state.

	Cu^+	Zn^{2+}	Ag^+	Cd^{2+}	Au^+	Hg^{2+}	Tl^{3+}
d^9s	2.7	9.7	4.8	10.0	1.9	5.3	9.3

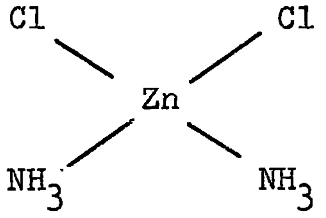
charge to the *xy* plane allowing strong two-covalent bonding along the *z* axis. The stability of this configuration is thus dependant on a small *d - s* energy separation. Nyholm has proposed[4] that the residual charge on the metal determines which is the better explanation of two co-ordination. If the charge is small then the larger *s - p* separation is the determining factor giving *sp* hybridization, if the charge is appreciable the smaller *d - s* separation and Orgel's picture is more likely.

Inorganic co-ordination complexes.

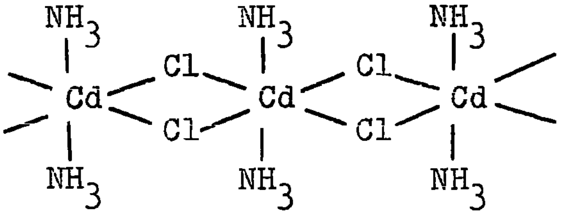
Where there is no possibility of partial double bond formation involving *d* orbitals, co-ordinate bonds are very dependant upon electronegativity effects. In the heavier metals, which have *d* orbitals available for back-coordination with suitable orbitals on the co-ordinating ligand, the effects of such interactions become significant factors in the strength of the resulting bond. As nitrogen and oxygen cannot function as electron acceptors, phosphorus and sulphur form stronger bonds with the heavier metals in low valency states. This is exemplified by the stabilization of Au(I) by phosphines in $RAuPR'_3$ but not by tertiary amines.[5] Complexes are readily formed by all of the ions Zn^{2+}, Cd^{2+} and Hg^{2+}, but the tendency to co-ordinate to nitrogen and oxygen *diminishes* markedly from zinc to mercury while the tendency to co-ordinate to phosphorus and sulphur containing donors increases in the same series.

Nitrogen containing ligands

Zinc, cadmium, and mercury halides all form complexes with ammonia of the form $(NH_3)_2MX_2$. Similar complexes are also formed with organic amines, e.g. $(PhNH_2)_2ZnCl_2$[6], $(MeNH_2)_2CdCl_2$[7], $(EtNH_2)_2HgCl_2$[8]. The zinc, cadmium, and mercury bisaminodichlorides are not however isostructural. The zinc compound is of tetrahedral structure[9] (i), the cadmium analogue forms an octahedral complex with bridging chlorine atoms[10] (ii), while the mercury compound exists as discreet $[H_3N\text{-}Hg\text{-}NH_3]^{2+}$ units randomly arranged in the crystal.[11] Reaction of gaseous ammonia with dry salts of zinc, cadmium, and mercury other than halides usually yields tetrammines in which there is a tetrahedral arrangement of ammonia molecules around the metal analogous to the arrangement in $(NH_3)_2ZnCl_2$.

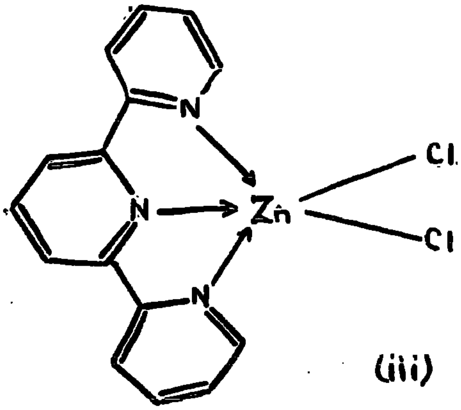


(i)



(ii)

Terpyridyl derivatives of all three metal halides are known[12] and it was suggested that the metal was in a tetrahedral environment as [terpyMX]$^+$. Crystal structure determinations[13] however have shown that terpyridyl dichlorozinc (11) has a distorted bipyramid structure (iii) in which the zinc is five co-ordinate and presumably in a state of sp^3d hybridization. The cadmium complex is isomorphous to



(iii)

that of zinc and is assumed to have the same structure. Although five co-ordination is not common the filled 3d shell in Zn(11) has spherical symmetry and is therefore not energetically favourable to any particular stereochemical arrangement. More recently other five co-ordinate zinc complexes have been prepared. Bisacetylacetonatozinc (11) monohydrate and the 4-methylpyridine derivative of $(acac)_2Zn$ are other examples. It is interesting that the bis 4-methylpyridine complex which is octahedral dissociates in benzene solution l~~o~~osing one molecule of 4-methylpyridine.[14] The methanol adduct of bisbenzoylacetonatozinc (11), NN'-

disalicylidene-ethylenediaminezinc (11)monohydrate[16] and bis(N-methylsalicylaldiminato)zinc(11)[17] also contain five-coordinate zinc.

Octahedral co-ordination of zinc and cadmium is obtained with small ligands such as ammonia and methylamine. The hexammines are only weakly co-ordinated[18,19] as is shown by the temperature at which the dissociation tension of ammonia is 10cm.

	MCl_2	MBr_2	MI_2
$ZnX_2.6NH_3$	23°	31°	28°
$CdX_2.6NH_3$	24°	45°	65°

Additional stability of the octahedral state is obtained in complexes formed with chelating ligands and all three metals form stable complexes with ethylenediamine, e.g. $(en)_3HgX_2$.[20]

Tertiary phosphines and arsines

Zinc forms the least stable tertiary phosphine and arsine complexes of the three metals. Complex formation does not appear to occur when the reagents are mixed in aqueous solution[21] but reaction in alcohol or acetone yields in some cases the 2:1 adduct,[22,23] $[R_3P(As)]_2ZnX_2$. The effects of electronically active substituents upon the stability of these complexes is considerable.[22] Thus $(\underline{p}\text{-}Me_2NC_6H_4PMe_2)ZnI_2$ is stable, $(Ph\,PMe_2)_2\,ZnI_2$ and $(PhPEt_2)_2\,ZnI_2$ smell of phosphine and readily dissociate, and $(\underline{p}\text{-}CF_3C_6H_4PEt_2)_2\,ZnI_2$ could not be prepared. Free phosphine or arsine is liberated from all of the zinc complexes on reaction with 2:2' bipyridyl and formation of the sparingly soluble bipyridyl complex, bipy ZnX_2, occurs.

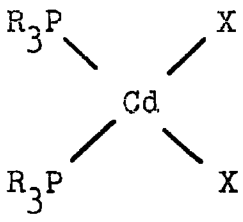
Stronger complexes are formed by cadmium than those of zinc. They can be divided into three types:

a) $[R_3P(As)]_2CdX_2$

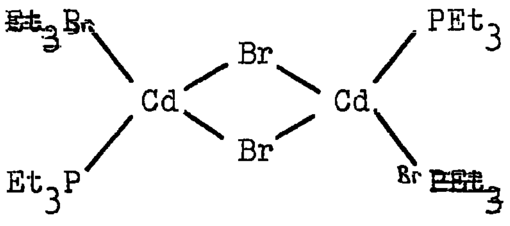
b) $[R_3P(As).CdX_2]_2$

c) $[R_3P(As)]_3[CdX_2]_2$

Complexes of type (a) are monomeric and appear to be derived from the stronger donors.[22] They presumably have the simple tetrahedral arrangement shown in fig.(iv).



(iv)



(v)

Type (b) complexes have been shown by crystallographic studies to be dimeric in the solid state with a tetrahedral trans-symmetric structure, fig.(v). Molecular weight determinations in benzene show that the complexes are dimeric,[21] but measurements in acetone indicate a monomeric species possibly due to co-ordination by solvent as association to the dimer is favoured by non-polar solvents.[22]

Although complexes of type (c) have been prepared, their structure has not been investigated.

Mercury co-ordinates very strongly with phosphine and arsine donors capable of $\underline{d_{\pi}-d_{\pi}}$ bonding. The complexes are odourless and can be recrystallised without decomposition. Five classes of compounds are known:[21]

(a) $[R_3P(As)]_2HgX_2$

(b) $[R_3P(As).HgX_2]_2$

(c) $[R_3P(As)]_2[HgX_2]_3$

(d) $[R_3P(As)]_2[HgX_2]_4$

(e) $[R_3P(As)]_3[HgX_2]_2$

Classes (a) and (b) have the same structure as their cadmium analogues. Crystallographic observations have shown that class (c) compounds occur in more than one form. Only one compound, $(Bu_3^nAs)_2(HgBr_2)_3$, has however been fully analysed in this way. The results show that it is a molecular complex of mercuric bromide and the bridged dimer structure of type (b). Compounds of class (d) have not been studied crystallographically but they are probably an extended halogen bridged version of type (b) or a molecular complex of type (b) with two molecules of mercuric bromide. Only the iodo-derivatives of class (e) have been isolated and they are remarkable in being stable to 2:2'- bipyridyl.

Complexes of cadmium and mercury of the types $(R_3P)_2MX_2$ and $(R_3P.MX_2)_2$ differ in their reactions with iodomethane. No reaction was observed with the cadmium compounds, whereas the mercury derivatives readily form phosphonium salts:[22,24]

$$(Ph_3P)_2HgI_2 + 2MeI \longrightarrow (Ph_3PMe)_2HgI_4$$

$$(Ph_3P.HgI_2)_2 + 2MeI \longrightarrow 2(Ph_3PMe)HgI_3$$

Oxygen donors

Towards oxygen ligands in particular there is a marked decrease in affinity from zinc to mercury. Zinc forms many oxygen complexes, only a few are reported for cadmium and mercury exhibits a considerable reluctance to form bonds to oxygen. Thus zinc readily forms oxyanions, the zincates, and solid co-ordination complexes with oxygen containing organic molecules[25] e.g. $2Et_2O.ZnBr_2, Et_2O.ZnBr_2$. Similar compounds of cadmium are rare although cadmium iodide forms an etherate[26] with cineol, $(C_{10}H_{18}O)_2CdI_2$. The formation of weak complexes between Hg^{2+} and oxygen containing solvents have been observed by Raman spectroscopic studies[27,28,29] and solid complexes of triphenylphosphine oxide with mercuric halides $(Ph_3PO)_2HgX_2$, where X = Cl,Br,I, are known.[30] The complex formed from mercuric chloride and triphenylarsine oxide, $(Ph_3AsO.HgCl_2)_2$ is of interest in being a dimer which is oxygen, rather than halogen, bridged.[31a] Other complexes of mercury(11) with oxygen donors have recently been prepared and they are unusual in the respect that the metal is six co-ordinate. White crystals, $(HgL_6)(ClO_4)_2$, are formed when L =pyridine N-oxide, dimethyl sulphoxide, tetrahydrothiophen oxide, and thioxan oxide.[31b]

Chelating ligands stabilize the oxygen complexes and all three metals form complex acetylacetonates.[32] The anhydrous compounds, M $(acac.)_2$, are four co-ordinate and tetrahedral. The hydrates and other adducts have been described earlier in connection with the five co-ordinate complexes they form with zinc.[14,15] Similarly the oxalate ion is strongly enough co-ordinating to overcome the weakness of the mercury-to-oxygen bond and this is confirmed by freezing point measurements and lack of reaction of oxalate and mercuric ions in a solution of the complex.[33]

Sulphur donors

Little work on sulphur-donor complexes of Group IIB metals has been reported. Zinc halides appear to form 1:1 and 1:2 complexes, $Me_2S.ZnX_2$, 2thiourea.$ZnCl_2$ [34] and an ethylenethiocarbamide (etu) complex of cadmium, $[Cd(etu)_4](NO_3)_2$, is described. Mercury co-ordinates much more strongly to sulphur than to oxygen and the complexes reported by earlier workers[35,36] obtained from dimethylsulphide and mercuric halides in 2:1, 1:1 and 1:2 molar ratios are probably salts. Crystal studies of the complexes derived from mercuric chloride and diethylsulphide and tetrahydrothiophen respectively indicate that the affinity of mercury for sulphur is so great that sulphur ligands will displace halogen forming covalent Hg-S bonds, and discreet $[Cl\text{-}Hg\text{-}SEt_2]^+$ and $[Cl\text{-}Hg\text{-}SC_4H_8]^+$ and Cl^- units occur in the crystalline states.[37,38]

Halide complexes

Abnormalities in conductance values and transference numbers are observed in aqueous solutions of zinc, cadmium and mercury halides other than the fluorides which behave as normal electrolytes. Zinc halides act in this manner only in concentrated solution,[39] cadmium halides show peculiarities at much lower concentrations and solutions of mercuric halides are abnormal regardless of dilution. E.m.f.[40-42]

and conductance studies[43] on solutions of cadmium halides indicate autocomplex formation giving species CdX^+, Cd^{2+}, CdX_2, $[CdX_3]^-$, $[CdX_4]^{2-}$, (hydration being omitted from these formulae).

Similar equilibria explain the peculiar values obtained in concentrated zinc halide solutions, but the very low conductance of mercuric halide solutions is caused by the molecules remaining in the covalent state. A slight dissociation (~1%) does take place : $HgX_2 \rightleftharpoons HgX^+ + X^-$ but concentrations of HgX_3^- and HgX_4^{2-} are negligible. Addition of alkali halide to a solution of metal halide increases the concentration of the $MX_4^{\ 2-}$ species, the stability of which increases with the increasing size of both cation and anion giving maximum stability in $[HgI_4]^{2-}$. The increasing stabilization effect of $Cl^- < Br^- < I^-$ is shown by the marked increase of pH required to precipitate mercuric oxide as the halogen is changed.[44] Table III shows the equilibrium constants for the $[MX_4]^{2-}$ complexes of zinc, cadmium and mercury. The $[ZnX_4]^{2-}$ complexes are the least stable but can be isolated as the salts of large cations.

TABLE III

Log equilibrium constants for some halide complexes of zinc, cadmium and mercury.

$$M^{2+}_{aq.} + 4X^- = MX_4^{\ 2-} ; \quad K = \frac{[MX_4^{2-}]}{[M^{2+}_{aq.}][X^-]^4}$$

Halide	Log K		
	Zn	Cd	Hg
Cl^-	0	3	16
Br^-	-1	4	22
I^-	-2	6	30

Organomercury compounds

The study of organomercury compounds has been greatly facilitated by their lack of reactivity to air and water and a large number of compounds have been prepared out of an interest in their toxic or pharmacological properties. The ability of mercury to replace hydrogen in many organic compounds, e.g. ethane hexamercarbide, $C_2Hg_6O_2(OH)_2$, from the prolonged action of yellow mercuric oxide and boiling aqueous alkali on ethanol, has led to the description of a considerable number and variety of compounds in the chemical literature.[45] Two classes of organomercury compounds are of particular relevance to this work.

i) R_2Hg compounds in which mercury is bound to two organic groups,

ii) RHgX compounds, where one organic group has been replaced by an electronegative radical.

Dialkyl and diaryl mercurials, R_2Hg.

The most general method of preparation, suitable for both dialkyl and diaryl mercurials is the reaction of the appropriate Grignard or lithium reagent with mercuric halide. A slight excess of the Grignard is used, usually in diethylether or T.H.F. (tetrahydrofuran) solution and the reaction takes place in two stages :

i) $RMgX + HgCl_2 \longrightarrow RHgCl + MgXCl$

ii) $RMgX + RHgCl \longrightarrow R_2Hg + MgXCl$

The first stage is considerably faster than the second but on refluxing the solution for several hours good yields of diorganomercury compounds can be obtained.[46]

The only other method of general synthetic value is the reaction of the requisite organic halide with sodium amalgam :

$$2PhBr + 2Na/Hg \longrightarrow Ph_2Hg + 2NaBr$$

The organic halide is diluted with xylene and ethyl acetate is added as catalyst. After several hours reflux the mercurial is formed in about 50% yield.[47]

An interesting method of preparing dimethylmercury in high yield, 92%, is by the electrolysis of an aqueous solution of methylmercuric acetate containing pyridine.[48]

$$CH_3\text{-}Hg^+ + e^- \longrightarrow CH_3\text{-}Hg^{\bullet} \longrightarrow \tfrac{1}{2}Hg + \tfrac{1}{2}(CH_3)_2Hg$$

The preparation of higher homologues and some diarylmercury compounds by the electrolysis of the alkyl- and aryl-mercuric chlorides in liquid ammonia solution at -78° has been carried out.[49] Black solids, possibly organic metals,[50] are initially deposited on the platinum electrodes but decomposition occurs at slightly higher temperatures giving metallic mercury and the respective diorganomercury compound as decomposition products.

Organomercuric halides and other salts can be converted to the diorganomercury derivatives by the action of reducing agents. Thus methylmercuric iodide is reduced by granulated zinc[51] giving dimethylmercury and alkyl and aryl mercuric halides are reduced by copper powder[52,53] forming cuprous chloride and the mercurial.

$$2RHgCl + 2Cu \longrightarrow R_2Hg + 2CuCl$$

Diphenylmercury can also be obtained in good yield by stirring phenylmercuric acetate with alkaline sodium stannite.[54]

$$2PhHgX + Na_2SnO_2 + 2NaOH \longrightarrow Ph_2Hg + Hg + 2NaX + Na_2SnO_3$$

Disproportionation of organomercuric salts occurs on treatment with anions which form very stable complexes with mercury[55,56] e.g. CN^-, SCN^-, I^-. The equilibrium is displaced so much in favour of the anionic complex as to make the reaction a useful synthesis for diorganomercurials.

$$2RHgX + 4KCN \longrightarrow R_2Hg + 2KX + K_2Hg(CN)_4$$

Mercury can also be removed from the system by forming a highly insoluble derivative. In this way dialkylmercury compounds can be obtained by warming the corresponding sulphide.

$$(RHg)_2S \longrightarrow R_2Hg + HgS$$

Mixed dialkyls, diaryls and alkyl aryls of mercury can be prepared from the respective Grignard reagent and organomercuric halide.[57,58]

$$RHgX + R'MgX \longrightarrow RHgR' + MgX_2$$

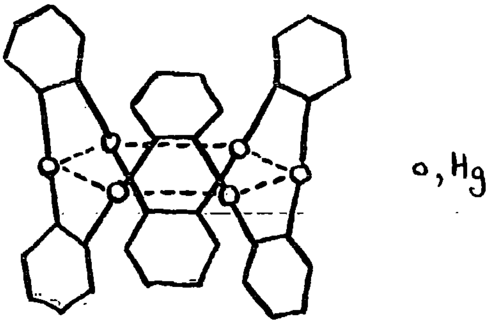
Mixed organic derivatives of this type are initially quite stable but tend to disproportionate on standing, forming the symmetrical products. Rearrangement takes place rapidly in the presence of catalysts such as halogen or organomercuric halides.

Dialkylmercurials are mostly colourless volatile monomeric liquids[59] of high density, e.g. Me_2Hg, b.p.92°; Et_2Hg, b.p.159°; n-Pr_2Hg, b.p.189°; i-Bu_2Hg, b.p.206°.
Like all other organomercury compounds they are extremely toxic,

dimethylmercury being particularly dangerous in having a vapour pressure of about 10cm. at room temperature. All dialkylmercurials except the dimethyl derivative are thermally unstable at room temperature and decompose slowly with formation of hydrocarbon and metallic mercury. Dimethylmercury does decompose to ethane and mercury at 300° [60] or at room temperature on exposure to mercury radiation[61] of 2537Å.

The diaryls are usually solids, Ph_2Hg,m.p.125°; di-m-tolylmercury, m.p.102°; bis-diphenylmercury, m.p.216°. They are more thermally stable than the dialkyls and some can be sublimed under reduced pressure without decomposition. Decomposition does, however, occur on excessive heating and diphenylmercury slowly breaks up at 200°. Dibenzylmercury, which is one of the least stable,[62] begins to decompose at 75° and decomposition is complete by 160°. Many diaryls are light-sensitive and on exposure to diffuse light become discoloured, for example diphenylmercury turns yellow.

The dipole moments[63] of bisarylmercurials are generally small and consistent with co-linear C-Hg-C bonds; Ph_2Hg, d.m.0.44D. The moments of di-para substituted diphenyls measured in decalin at 140° are somewhat higher; p-tolyl,0.74; p-chlorophenyl, 1.15; p-bromo, 0.92; p-fluoro, 0.87D. Many structures assigned to diarylmercurials have involved bent C-Hg-C bonds and it has been claimed[64] that the apparent dipole moments of these compounds are due to the effective non-linearity of the C-Hg-C bonds as measured distortion polarizations indicate that they do not exhibit exalted atom polarizations. A recent determination of the crystal structure of di-p-tolylmercury,[65] however, proves that the C-Hg-C bond angle is 180°. Association of the compounds in which two mercury atoms are bound to one benzene ring can allow the formation of a structure in which the C-Hg-C bond is co-linear. Accordingly o-phenylenemercury has been shown to be hexameric[66] and have the structure depicted in fig. (vi).



(vi)

Bis-organomercurials are chemically rather inert. They are uneffected by air, water and dilute acids making them unique in Group II and differ further in not forming co-ordination complexes with ethers and amines.

Dialkyl and diaryl mercury compounds react with concentrated acids evolving hydrocarbon and giving the corresponding organomercuric salt :

$$Et_2Hg \quad + \quad HOAc \xrightarrow[16\ hours]{220^{\circ}} EtHgOAc \quad + \quad C_2H_6$$

Dilute solutions of hydrogen chloride in non-aqueous solvents readily attack bismercurials :

$$R\text{-}Hg\text{-}R \quad + \quad HCl \longrightarrow RH \quad + \quad RHgCl$$

The carbon-mercury bond is rapidly cleaved by halogen and the mercurial is converted to mercuric halide by an exothermic reaction.

$$R_2Hg \quad + \quad X_2 \longrightarrow RHgX \quad + \quad RX$$

$$RHgX \quad + \quad X_2 \longrightarrow HgX_2 \quad + \quad RX$$

Metal halides react with dialkylmercury compounds and an alkyl halogen exchange takes place. Only one alkyl group is transferred unless relatively high temperatures are used :

$$Me_2Hg \quad + \quad SbCl_3 \longrightarrow MeHgCl \quad + \quad MeSbCl_2$$

This method is particularly applicable to mercuric halides and provides a rapid route for preparing organomercuric halides in high yield :

$$R_2Hg \quad + \quad HgX_2 \longrightarrow 2RHgX$$

Alkyl and aryl exchange reactions of bis-mercurials with other metals are of great synthetic value. Many such reactions were superseded as preparative methods with the discovery of Grignard reagents, but several of these reactions still provide a clean and rapid method of obtaining other organometallic compounds. Dialkyl and diaryl exchange takes place with the alkali metals, alkaline earths, zinc, aluminium, gallium, tin, lead, antimony, bismuth, selenium and tellurium, but reversible equilibria are obtained with cadmium, indium and thallium. The mechanism of such transfer reactions has been the basis of several studies.[67,68]

Organomercuric salts.

Preparation of organomercuric halides by the direct reaction of alkyl halide with mercury, which is so useful in the cases of magnesium and zinc, is of limited application. This was the original method of obtaining organomercury compounds but only with methyl, benzyl and some unsaturated iodides, particularly allyl, does it give good yields.[69] The best method of preparing alkyl- and arylmercuric halides is the cleavage of the bis-mercurial with the respective mercuric halide. Arylmercuric halides can be obtained by several methods not applicable to the alkyls. One of the most useful is from a diagonium compound on stirring with mercury :[70]

$$ArN_2Cl + Hg \longrightarrow ArHgCl + N_2$$

or by reduction of mercuric chloride :

$$ArN_2Cl + HgCl_2 + 2Cu \longrightarrow ArHgCl + 2CuCl + N_2$$

Diazomethane reacts with mercuric chloride to give chloromethylmercuric chloride :[71]

$$HgCl_2 + CH_2N_2 \longrightarrow ClCH_2HgCl + N_2$$

and the product will react with a further mole of diazomethane.

$$ClCH_2HgCl + CH_2N_2 \longrightarrow (ClCH_2)_2Hg + N_2$$

Similar substituted alkylmercuric halides are obtained from mercuric salts and olefins and these compounds are discussed more fully later in this introduction.

Treatment of the organomercuric halide with silver oxide or alcoholic potash yields the corresponding hydroxide from which many salts can be obtained by neutralization with the appropriate acid. The properties of organomercuric salts are very dependant upon the nature of the anion and those compounds which show a high degree of covalency, e.g. Cl^-, Br^-, I^-, CN^- are crystalline solids soluble in organic solvents but not very soluble in water. The partition coefficients for methylmercuric halides between toluene and water increase with the increasing affinity of the $MeHg^+$ cation for the halide, Cl^-,11; Br^-,45; I^-,300-500; corresponding also to the increasing covalent character of the mercury-halogen bond.[72] Alkylmercury cations, RHg^+, are always complexed in solution and show typical B-cation character in preferring ligands derived from elements of low electronegativity. In a benzene solution of methylmercuric nitrate the Raman spectrum observed is that due to $Me\text{-}Hg\text{-}O\text{-}NO_2$ only. In aqueous solution there is competition for co-ordination with the $MeHg^+$ cation between the solvent and the nitrate group and the spectrum is more complex. An equilibrium is established in which $[MeHg\text{-}O\text{-}NO_2]$, $[MeHg\text{-}OH_2]^+$ and $[NO_3]^-$ ions can be observed. The addition of dimethylsulphide to the equilibrium mixture in equivalent molar proportions causes the complete displacement of oxygen donors and the corresponding exclusive formation of the $[MeHgSMe_2]^+$ complex.[29]

Anionic complexes of alkylmercury compounds are very weak. Evidence from anion exchange studies indicates the presence of anionic complexes of $MeHg^+$ with chloride and thiocyanate groups. Ethylmercuric chloride also shows absorption onto anion exchange resins in aqueous lithium chloride solution.[73]

The methylmercury cation forms polynuclear complexes more readily than H^+ and a weak binuclear complex is formed with cyanide :

$$MeHg^+ + CN^- \rightleftharpoons MeHgCN \qquad \log K_1 = 14$$

$$MeHg^+ + MeHgCN \rightleftharpoons (MeHg)_2CN^+ \qquad \log K_2 = 0$$

Stronger complexes are formed with oxygen and sulphur and a tetramethylmercury sulphide, $[(MeHg)_4S]^{2+}$ can be detected.[74]

Methylmercuric hydroxide, obtained by the action of silver oxide on a solution of methylmercuric halide followed by evaporation to dryness, has several different reported melting points. It has a low equivalent conductance, $0.71\,\Omega^{-1}cm.^2$

(c.f. methylmercuric nitrate 101.0 Ω^{-1}cm.^{2}), showing it to be a weak base and only slightly ionized in solution.[75] Subsequent attampts to isolate the compound yielded only a mixture of methylmercuric oxide, $(MeHg)_2O$, m.p. 137.5°, and trismethylmercury oxonium hydroxide, $[(MeHg)_3O]^+OH^-$ m.p. 88°. Prolonged drying in a vacuum desiccator converts the latter to methylmercuric oxide. Methylmercuric oxide acts as a hydroxide and can be neutralised in dilute solution to give methylmercuric salts. Neutralization of a concentrated aqueous solution causes the precipitation of trismethylmercury oxonium salts, e.g. $[(MeHg)_3O]NO_3$, m.p. 188°. Titration of a dilute methanolic solution of methylmercuric oxide with nitric acid gives inflections corresponding to $[(MeHg)_3O]NO_3$, $[(MeHg)_2OH]NO_3$ and $MeHgNO_3$ respectively.[76] The binuclear intermediate complex $[(MeHg)_2OH]^+$ is much more stable than its proton complex analogue, H_3O^+.

$$\begin{array}{rcll} MeHg^+ + OH^- & \rightleftharpoons & MeHgOH & \log K_1 = 9.4 \\ MeHg^+ + MeHgOH & \rightleftharpoons & (Me_2Hg)_2OH^+ & \log K_2 = 2.4 \\ H^+ + OH^- & \rightleftharpoons & H_2O & \log K_1 = 15.6 \\ H^+ + H_2O & \rightleftharpoons & H_3O^+ & \log K_2 = -1.7 \end{array}$$

The trismethylmercury oxonium salts can be prepared by partial neutralization of methylmercuric oxide. Alternatively addition of methylmercuric salts can take place and trismethylmercury oxonium bromide is formed from methylmercuric bromide and methylmercuric oxide in boiling benzene.

$$(MeHg)_2O \quad + \quad MeHgBr \longrightarrow [(MeHg)_3O]Br \qquad m.p.\ 116^\circ$$

Aqueous solutions of oxonium salts are stable if the methylmercuric salt is water-soluble and ionic compounds, e.g. those containing the anions NO_3^-, ClO_4^-, PF_6^- are therefore not decomposed. Where the methylmercuric salt is insoluble in water, e.g. Cl^-, Br^-, I^-, CN^-, it is precipitated on addition of the oxonium salt to water.

$$[(MeHg)_3O]Br \quad \xrightarrow{\text{water}} \quad (MeHg)_2O \quad + \downarrow MeHgBr$$

Polynuclear complexes are formed with sulphur even more readily than with oxygen giving compounds with similar reactions to the oxygen complexes. Trismethylmercury sulphonium salts can be prepared in an analogous manner to the oxonium salts. When methylmercuric sulphide in warm benzene is added to aqueous potassium dichromate an immediate precipitate of trismethylmercury sulphonium dichromate is produced. The salt is soluble in water but insoluble in organic solvents. Double decomposition with lead nitrate in ethanol gives the sulphonium nitrate which crystallises as colourless needles.[77]

The association constants for the reaction

$$MeHg^+ \quad + \quad L^{\lambda -} \rightleftharpoons \quad MeHg\,L^{\ (1-\lambda)}$$

have been measured for several ions and neutral ligands (L).[72,74] The order of affinity for the $MeHg^+$ cation of the more common groups are as follows : $RS^- > CN^- > OH^- > I^- >$ ethylenediamine $> NH_3 > Br^- > SCN^- > Cl^- >$ pyridine $>$ acetate $> F^-$. The B - character of the methylmercury cation is demonstrated in this sequence and sulphides are shown to complex most strongly.

Perfluoro -alkyl and -aryl mercurials

Perfluoroalkylmercuric iodides can be prepared from the corresponding perfluoroalkyl iodides and mercury.[78-80] Cadmium amalgam reduces the iodides to the bisperfluoroalkylmercurial :[78,79]

$$R_fI + Hg \xrightarrow[\text{or u.v.}]{\text{heat}} R_fHgI \xrightarrow[\text{amalgam}]{\text{Cd}} (R_f)_2Hg$$

The method is not completely general as a mixture of decomposition products only was obtained in an attempted preparation of bisheptafluoro-n-propylmercury.[81]

Partially or fully fluorinated olefins react with HgF_2 at 50 - 150°C to give fluoroalkyl- or perfluoroalkyl- mercury derivatives.[82] Bispentafluoroethylmercury, m.p. 96 - 98°, has been obtained from tetrafluoroethylene in good yield by this method :[83]

$$2\ CF_2 = CF_2 + HgF_2 \longrightarrow (C_2F_5)_2Hg$$

Bistrifluoromethylmercury is extremely soluble in water (473 gm./l., 1.3M) in which it is weakly conducting.[81] The general behaviour of $(CF_3)_2Hg$ suggests that the CF_3 group functions as a pseudo-halogen, intermediate in electronegativity between F and Cl. The aqueous solution of

$(CF_3)_2Hg$ however shows no indication of the presence of Hg^{2+} ions, unlike $HgCl_2$ which is slightly dissociated in solution. It is generally considered that the conductance of $(CF_3)_2Hg$ is due to ~~hydrolysis~~ hydration, without the displacement of a trifluoromethyl group, and ionization of the hydrate.

$$(CF_3)_2Hg \rightleftharpoons (CF_3)_2HgOH_2 \rightleftharpoons (CF_3)_2HgOH^- + H_3O^+$$

Electrolysis of this aqueous solution yields fluoroform at both anode and cathode. CF_3Hg^+ ions would give CF_3H at the cathode and it would also be formed together with oxygen by the discharge of $(CF_3)_2HgOH^-$ at the anode.[82]

Bistrifluoromethylmercury forms addition compounds with halide ions[80,84] analogous to mercuric halides. Conductometric titrations of aqueous $(CF_3)_2Hg$ and CF_3HgI with KX indicated the formation of complexes corresponding to $[Hg(CF_3)_2X]^-$, $[Hg(CF_3)_2X_2]^{2-}$ and $[Hg(CF_3)IX]^-$, $[Hg(CF_3)IX_2]^{2-}$ respectively. The stability of the complexes decreases from X = I to X = Cl. Complex anions $[CF_3HgI_3]^{2-}$, $[(CF_3)_2HgI_2]^{2-}$ and $[C_3F_7HgI_3]^{2-}$ are precipitated from aqueous solution using salts of ethylenediamine metal complexes[80] e.g. $Cu(en)_2^{2+}$, $Ni(en)_3^{2+}$, $Cd(en)_2^{2+}$ and $Zn(en)_3^{2+}$. Cryoscopic measurements on aqueous solutions of $(CF_3)_2Hg$ and Cl^-, Br^- and I^- respectively also indicate the formation of labile 1:1 adducts.[85]

Complexes of $(R_f)_2Hg$ with neutral ligands (L) have been shown to exist in benzene solution by oscillometric titration.[86] The results indicated that both $(CF_3)_2Hg.L$ and $(CF_3)_2HgL_2$

complexes are formed with ligands such as pyridine, triphenylphosphine, dimethyl sulphide and ethanol. Further titration gave no indication of higher complexes.

Pentafluorophenylmagnesium bromide reacts with mercuric chloride to give bispentafluorophenylmercury,[87] m.p. 142°. This compound is of high thermal stability, being unchanged after five hours at 250°, and extremely resistant to protonic acids. It can be recrystallized without reaction from concentrated sulphuric acid. Reaction with halogen is slow,

$$(C_6F_5)_2Hg \quad + \quad Br_2 \quad \xrightarrow[60^\circ]{5\text{ days}} \quad C_6F_5HgBr$$

but cleavage by mercuric bromide is rapid in methanol.

$$(C_6F_5)_2Hg \quad + \quad HgBr_2 \quad \longrightarrow \quad 2C_6F_5HgBr$$

Rearrangement of pure bispentafluorophenylmercury and dimethylmercury was found to be very slow but the addition of catalytic amounts of pentafluorophenylmercuric bromide increased the rate considerably, indicating that the exchange reaction

$$(C_6F_5)_2Hg \quad + \quad Me_2Hg \quad \longrightarrow \quad 2C_6F_5HgMe$$

is readily brought about but dependant upon halide impurities as promoters.

Bispentafluorophenylmercury forms a stable 1:1 complex with 2,2' - bipyridyl of m.p. 122-3°. Similarly, bispentafluorophenyl (bis 1,2 diphenylphosphino-ethane) mercury, m.p. 158-9°, can be prepared. Analogous compounds could not be isolated from pentafluorophenyl(phenyl)mercury or methyl(pentafluorophenyl)mercury respectively with either ligand.

Olefin Addition Compounds

Addition of an olefin to a solution of a mercuric salt may result in the production of various addition compounds depending upon the conditions of the reaction. The mechanism of formation, and the configuration and nature of these compounds as indicated by their reactions has aroused much interest since their original preparation.

When the conditions for the formation of addition products of olefins with basic mercuric salts were first elucidated,[88,89] compounds of the type $HOCH_2CH_2HgCl$ and $O(CH_2CH_2HgCl)_2$ were obtained and recognised as having been formed by addition of ^+HgCl and ^-OH across the double bond of the olefin. Experimental conditions are of extreme importance and the reaction products formed in aqueous solution were found to be dependant upon the following factors :

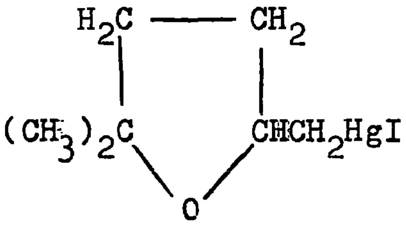
i) the structure of the olefin,
ii) the acidity of the solution,
iii) the acid of the mercuric salt,
iv) temperature,
v) the concentration of the solution.

Much of the work carried out on the preparation and reactions of these compounds has been reviewed.[90] During the preparation of the addition compound it is often proved necessary to add alkali in order to neutralize the acid as it is formed as the products are unstable in acid solution and readily liberate the original olefin. Care must be taken in such neutralization as the addition compounds are not formed in alkaline solution:

$$C_2H_4 + Hg(NO_3)_2 + NaOH \longrightarrow C_2H_2Hg(OH)NO_3 + NaNO_3$$

Several reactions indicate that these compounds can be classified as either:

i) simple addition compounds, $HOCH_2CH_2HgCl$, $CH_3OCH_2CH_2HgBr$,
ii) ether compounds, $O(CH_2CH_2HgCl)_2$,
iii) ring compounds,



The olefin is regenerated on acidification, in some cases in very mild conditions, of the complex:

$$HOC_2H_4HgCl + HCl(5\%) \longrightarrow C_2H_4 + HgCl_2 + H_2O$$

Decomposition with liberation of olefin also occurs on treating the organomercuric halide with aqueous alkali cyanide or thiocyanate:

$$HOC_2H_4HgBr + 4KCN \longrightarrow C_2H_4 + K_2Hg(CN)_4 + KOH + KBr$$

Iodine, either in aqueous KI solution or organic solvent, reacts as if the olefin~~e~~ complex were simply a substituted alkylmercuric iodide giving the corresponding iodo-alcohol and mercuric iodide in almost quantitative yield:[91]

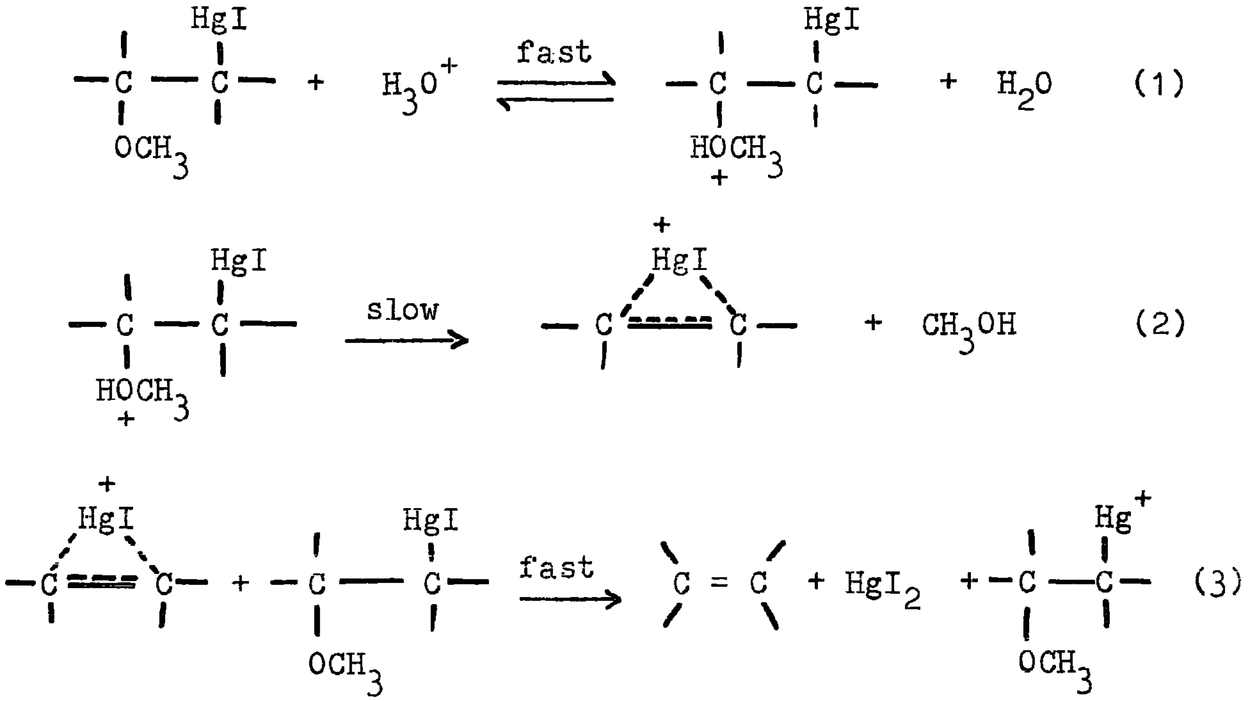
$$HOCH_2CH_2HgI + I_2 \longrightarrow HOCH_2CH_2I + HgI_2$$

Reduction with sodium amalgam also proceeds as would be expected for the alkylmercury halide:

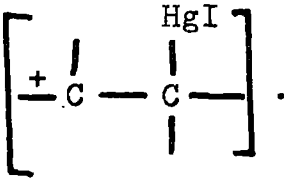
$$HOCH_2CH_2HgI + 2H \longrightarrow CH_3CH_2OH + Hg + HI$$

Examination of the proton magnetic resonance spectra of 2-methoxyethylmercuric acetate, $MeOCH_2CH_2HgOAc$, and

2-hydroxyethylmercuric hydroxide, $HOCH_2CH_2HgOH$, confirmed the structure of the normal σ-bonded compounds rather than π-complexes. The spectrum of the methylene group adjacent to mercury can readily be distinguished from that of the methylene group adjacent to methoxy or hydroxy groups.[92] Several mechanisms for the formation of olefin addition compounds have been postulated.[90,93] More recently kinetic studies of deoxymercuration reactions have indicated the mechanism shown below.[94]



Equation (2) is the rate determining step and equation (3) comprises a series of fast steps. The presence of a proton in the transition state is implied by the observed first-order dependance on the rate on perchloric acid concentration. Although the electron distribution in the transition state cannot be stated with certainty it can probably be represented by a resonance hybrid involving the protonated starting state, the olefin - mercuric iodide complex and the carbonium ion,



$$\left[\overset{+}{\text{—}}\overset{|}{\text{C}}\text{—}\overset{\text{HgI}}{\underset{|}{\overset{|}{\text{C}}}}\text{—}\right].$$

Acetylene compounds of mercury

The acid hydrolysis of acetylene to acetaldehyde,[95] which was once of industrial importance, was first observed in 1881. In the presence of mercuric salts, acetylene and methylacetylene form acetaldehyde and acetone respectively on hydrolysis and it is conceivable that these reactions could well involve an organomercury intermediate. If acetylene is passed into an aqueous solution of mercuric chloride strongly acidified with hydrochloric acid, hydrolysis does not take place but an addition reaction occurs similar to that observed between olefins and mercuric salts.[96]

$$C_2H_2 \quad + \quad \text{acidic } HgCl_2 \quad \longrightarrow \quad ClCH{=}CHHgCl$$

On bubbling dry ammonia through a solution of 2-chlorovinylmercuric chloride in chloroform bis~~(~~aminodichloromercury, $(NH_3)_2HgCl_2$, slowly precipitates with the corresponding formation of the soluble bis(2-chlorovinyl)mercury.

$$2\ (ClCH{:}CH)HgCl \quad + \quad 2\ NH_3 \longrightarrow (NH_3)_2HgCl_2 + (ClCH{:}CH)_2Hg$$

When a solution of bis(2-chlorovinyl)mercury is heated acetylene is evolved and 2 -chlorovinylmercuric chloride reformed. The chlorovinylmercuric chloride, m.p. 124°, obtained from the reaction of acetylene and mercuric chloride in hydrochloric acid solution is a pure trans isomer and the configuration is retained on disproportionation to bis(2-chlorovinyl)mercury m.p. 70°. The *cis*-chlorovinylmercuric chloride, m.p. 79°, can be obtained by mixing acetylene and mercuric chloride vapour at 120° and disproportionation with ammonia gives a pure liquid stereoisomer of the bis mercurial.[97] The solid bis(2-chlorovinyl)mercury is readily converted to the liquid isomer by ultra violet irradiation but chemical reactions do not cause isomerisation.[98] 2-Chlorovinylmercuric salts can be prepared from the chloride in aqueous solution by treatment with silver oxide followed by reaction with the appropriate acid.

$$\mathrm{ClCH{:}CHHgCl} \xrightarrow{\text{'AgOH'}} \mathrm{ClCH{:}CHHgOH} \xrightarrow{\mathrm{HX}} \mathrm{ClCH{:}CHHgX}$$

The corresponding iodide can be prepared from the chloride by reaction of one molar equivalent of sodium iodide in absolute alcohol :

$$\mathrm{ClCH{:}CHHgCl} + \mathrm{NaI} \longrightarrow \mathrm{ClCH{:}CHHgI} + \mathrm{NaCl}$$

but if an excess of sodium iodide is used acetylene is extensively evolved.

Reagents which cause disproportionation in alkyl- and aryl- mercuric salts such as sodium iodide, potassium cyanide and triphenylphosphine react in a similar manner with the organomercuric halides derived from acetylene.[99]

$$ClCH{:}CHHgCl + 4KI \longrightarrow C_2H_2 + K_2HgI_4 + 2KCl$$

$$ClCH{:}CHHgCl + 4KCN \longrightarrow C_2H_2 + K_2Hg(CN)_4 + 2KCl$$

$$ClCH{:}CHHgCl + 2Na_2S_2O_3 \longrightarrow C_2H_2 + Na_2[Hg(S_2O_3)_2] + 2NaCl$$

$$ClCH{:}CHHgCl + 2\ PPh_3 \longrightarrow C_2H_2 + (PPh_3)_2\ HgCl_2$$

In the above cases acetylene is evolved and the mercury is bound as the stable anionic or neutral complex. Pyridine however forms a complex salt differing in this respect from ammonia which causes disproportionation.

$$ClCH{:}CHHgCl + py \longrightarrow [ClCH{:}CHHgpy]Cl \quad \text{m.p. } 76^{\circ}\text{(dec.)}$$

Mercuric salts do not always add across the carbon-carbon acetylenic linkage and many compounds have been prepared by passing various acetylenes into solutions of mercuric salts.[100] Brightly coloured solids can be obtained such as the yellow product from the addition of phenylacetylene to mercuric perchlorate solution.[101] These compounds are of unknown structure and constitution. Mercuric oxide reacts with acetylenes to give crystalline compounds corresponding to the formula R-C⋮C-Hg-C⋮C-R. Reactions of acetylenes with organomercuric salts in alkaline solution also yield similar compounds which are hydrolysed to aldehydes by atmospheric moisture when R is an alkyl group.[102]

Alkyl- and arylmercuric acetylides, RHgC⋮CR', and mercuric acetylides, $(RC{⋮}C)_2Hg$, are reported in the literature. Ethyl(phenylethynyl)mercury results in good yield from ethylmercuric chloride and sodium phenylacetylide on refluxing in ether.[103]

$$\mathrm{EtHgCl + NaC{\vdots}CPh \xrightarrow{8\ hours} NaCl + EtHgC{\vdots}CPh\quad (70\%)}$$

Phenylmercuric acetylides can be prepared in a similar manner.[104]

$$\mathrm{PhHgCl + KC{\vdots}CR' \longrightarrow KCl + PhHgC{\vdots}CR'}$$

Acetylenic Grignard reagents also react with alkylmercuric halides to give alkylmercuric acetylides.

$$\mathrm{MeHgX + CH{\vdots}CMgBr \longrightarrow MgXBr + MeHgC{\vdots}CH}$$

Methylethynylmercury and ethylethynylmercury are solids while higher homologues are liquids of low volatility.[105] The reactions of acetylenes with mercuric halides result in the replacement of both halide atoms by acetylenic groups with formation of bis(alkynyl)mercury compounds.[103]

$$\mathrm{{}^{i}BuC{\vdots}CH + HgI_2 \longrightarrow ({}^{i}BuC{\vdots}C)_2Hg}$$

The above compound is also somewhat surprisingly formed from the stable tetraiodomercury anion.

$$\mathrm{RC{\vdots}CH + K_2HgI_4 \longrightarrow (RC{\vdots}C)_2Hg}$$

In a similar manner to other bisorganomercurials the bis alkylethynyl and arylethynyl derivatives are readily cleaved by mercuric chloride to give the corresponding organomercuric chloride.

$$\mathrm{(PhC{\vdots}C)_2Hg + HgCl_2 \longrightarrow 2PhC{\vdots}CHgCl\quad m.p.\ 320^{\circ}\ (dec.)}$$

Disproportionation of organomercury compounds

Cleavage reactions of the type

$$\mathrm{R_2Hg + HgX_2 \longrightarrow 2RHgX}$$

are rapid and the organomercuric halide is readily formed. Under certain conditions however this reaction can be reversed and alkyl and aryl mercuric halides converted to the corresponding bis mercurial. The reaction is an equilibrium and is displaced to give the di-organomercury compound by ligands, such as cyanide, iodide, ammonia and triphenylphosphine, which can complex with the mercuric halide. Ammonia and triphenylphosphine cause precipitation of the mercuric halide complex, thus removing it from the reaction, whereas cyanide and iodide form anionic complexes, $Hg(CN)_4{}^{2-}$, $HgI_4{}^{2-}$, with very large stability constants. Since the formation of bis arylmercurials from arylmercuric chlorides and sodium iodide was first observed many such disproportionations have been reported and a detailed study of the effect of inorganic iodides on the reaction

$$Ar_2Hg + HgX_2 \rightleftharpoons 2ArHgX$$

has been made.[55] When arylmercuric iodides are refluxed with excess alcoholic sodium iodide diarylmercurials are usually formed according to the equation :

$$2ArHgI + 2NaI \rightleftharpoons Na_2HgI_4 + Ar_2Hg$$

When the organic group is o-, m-, or p- tolyl, m- xylyl, mesityl, α- or β-naphthyl, the organomercuric iodide gives solely the bis organomercury compound on refluxing with sodium iodide. Para-ethylphenylmercuric iodide gives a mixture of starting material and disproportionation products and phenylmercuric iodide can be recovered unchanged. Solubility considerations show that in the above compounds there is never more than a 5 fold difference in solubility between the organomercuric iodide and the mercurial except in the case of the phenyl derivative where the mercurial is 40 times more soluble than phenylmercuric iodide. In this particular case the unfavourable solubility effect cannot be overcome by complex formation. Usually the percentage of bisorganomercury compound formed in the reaction increases with increasing molar ratio of sodium iodide to organomercuric iodide but even with a molar ratio of sodium iodide to phenylmercuric iodide of 16:1 no diphenylmercury could be isolated from the reaction mixture. This is consistent with a subsequent observation of an increase in conductance of a dilute aqueous dioxan solution of phenylmercuric chloride on addition of triphenylphosphine, indicative of a 1:1 salt. Attempts to isolate the complex salt led to the recovery of phenylmercuric chloride only and no trace of complex salt or disproportionation products were detected.[106] On the other hand p-tolylmercuric iodide which is 5 times more soluble than di-p-tolylmercury yields only the disproportionation products on treatment with sodium iodide.

The preferential formation and precipitation of diorganomercury compounds on cooling the reaction mixture does not reflect the position of equilibrium of the reaction as hot solutions of the reactants poured onto ice-water consist almost entirely of organomercuric iodide. For example on cooling the reaction of p-cymylmercuric iodide with excess sodium iodide only di-p-cymylmercury was obtained.

$$2\ C_{10}H_{13}HgI + 2\ NaI \rightleftharpoons Na_2HgI_4 + (C_{10}H_{13})_2Hg$$

However on quenching the hot equilibrium mixture by pouring it onto ice-water only 1% of the disproportionation product was found, the product obtained was almost completely p-cymylmercuric iodide.

Iodides are not the only reagents to bring about disproportionation. Alkali cyanides react in a similar manner. Strong potassium cyanide solution reacts rapidly with allylmercuric iodide forming diallylmercury.[107]

$$2CH_2{:}CHCH_2HgI + 2KCN \longrightarrow (CH_2{:}CHCH_2)_2Hg + \tfrac{1}{2}K_2HgI_4 + \tfrac{1}{2}K_2Hg(CN)_4$$

Small amounts of diallylmercury can be obtained with aqueous or alcoholic potassium iodide but potassium cyanide is the only reagent to react in the cold.

Equivalent quantities of alkali cyanides convert arylmercuric halides to arylmercuric cyanides but an excess of alkali cyanide causes disproportionation of the organomercury compound. The yields of di-organomercurials obtained in this way are generally lower than those obtained on reaction with sodium iodide. Sodium alkoxides and alcoholic potassium hydroxide also cause disproportionation but again yields of the mercurial are even lower than with potassium cyanide.[56]

In contrast to the reaction of sodium iodide and phenylmercuric iodide, from which only starting material can be recovered, are the reactions shown below :

$$PhHgCN + 2KCN \xrightarrow[\text{reflux 1 hr.}]{\text{alcohol}} Ph_2Hg\ (38\%)$$

$$\text{PhHgCl} + \text{NaOMe} \xrightarrow[\text{reflux 3 hours}]{\text{MeOH}} \text{Ph}_2\text{Hg} \quad (34\%)$$

Alteration of the adverse solubility relationship or the position of equilibrium enables the isolation of diphenylmercury.

The reactions of bis(perchlorovinyl)mercury and perchlorovinylmercuric halides are of interest as the latter is unstable and readily disproportionates.[108] In general, the greater the difference in electronegativity between the two different substituents in an unsymmetrical organomercury compound, the more stable is that compound towards disproportionation. In the cases of the perchloro- and perfluoro-vinylmercuric halides the unsymmetrical groups are of similar electronegativity. The reaction of bis(perchlorovinyl)mercury and bromine in 1:1 ratio does not yield the organomercuric bromide as might be expected but the actual products isolated are mercuric bromide and half of the starting material. This is presumably due to disproportionation of perchlorovinylmercuric bromide which can however be isolated from the reaction between the bis-mercurial and hydrogen bromide :

$$(\text{CCl}_2\text{:CCl})_2\text{Hg} + \text{HBr} \longrightarrow (\text{CCl}_2\text{:CCl})\text{HgBr}$$

The corresponding chloride is more stable but the iodide cannot be isolated. Addition of sodium iodide to the chloride causes disproportionation :

$$2(\text{CCl}_2\text{:CCl})\text{HgCl} + 2\text{NaI} \longrightarrow \text{HgI}_2 + (\text{CCl}_2\text{:CCl})_2\text{Hg} + 2\text{NaCl}$$

Potassium thiocyanate reacts in a similar manner to sodium iodide and presumably any anion which gives an unstable intermediate such as $(CCl_2{:}CCl)HgI$ or $(CCl_2{:}CCl)HgSCN$ will cause disproportionation. Similar disproportionation reactions of arylmercuric compounds described previously required an excess of potassium iodide or other reactive anion but in the perchlorovinyl and perfluorovinyl cases equimolar quantities only are required.

Neutral ligands also bring about disproportionation and the use of ammonia in this way in the preparation of bis(2-chlorovinyl)mercury[97] has already been mentioned. Tertiary phosphines act in a similar manner with many organomercuric salts,[109, 110] and the reaction has been utilized as a preparative method in such cases as bis(perchlorovinyl)mercury[108] and bis-carbomethoxymercury. The former is prepared in good yield on addition of triphenylphosphine to perchlorovinylmercuric chloride :

$$2CCl_2{:}CClHgCl + 2PPh_3 \longrightarrow (Ph_3P)_2HgCl_2 + (CCl_2{:}CCl)2Hg$$

The latter can be obtained from carbomethoxymercuric chloride and triphenylphosphine.[115]

$$2ClHgCOOMe + 2PPh_3 \longrightarrow (Ph_3P)_2HgCl_2 + Hg(COOMe)_2$$

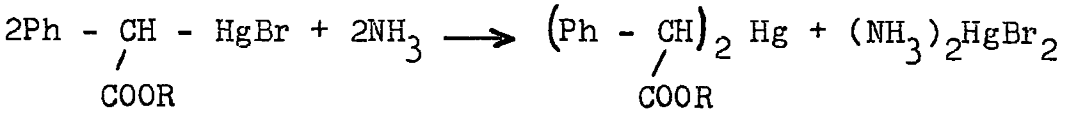
The carbomethoxymercuric chloride is formed from mercuric acetate according to the reactions :

$$Hg(OOCMe)_2 + MeOH + CO \longrightarrow MeOOCHgOOCMe + MeCOOH$$

$$MeOOCHgOOCMe + NaCl \longrightarrow NaOOCMe + MeOOCHgCl$$

and the disproportionation reaction with triphenylphosphine is thus a useful method of obtaining the bis-mercurial.

An extensive kinetic study of the disproportionation of esters of α-bromomercuriphenylacetic acid on reaction with ammonia has been carried out by Reutov and co-workers. Insoluble bisammino-dibromomercury is precipitated from chloro-



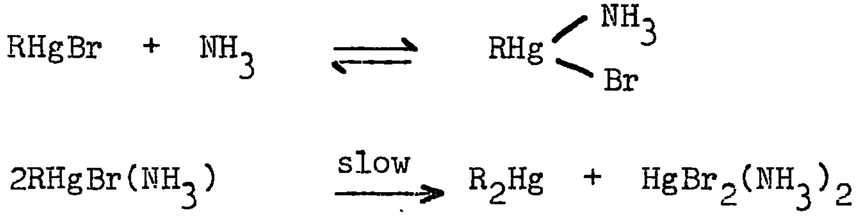
$$2Ph-\underset{COOR}{CH}-HgBr + 2NH_3 \longrightarrow (Ph-\underset{COOR}{CH})_2Hg + (NH_3)_2HgBr_2$$

form solution as the disproportionation proceeds according to the equation shown. The kinetic results show that the reaction is of second order with respect to both the organomercuric salt[111] and ammonia.[112] It was further found that the inductive effect of a substituent X (X = Cl, Br, H, Me) on esters of the type *p*-$XC_6H_4CH(HgBr)COOEt$ had a very pronounced effect on the rate of disproportionation which decreased on changing from chloride to methyl substituents, Cl > Br > H ≫ Me.[113] In the case of *p*-$MeC_6H_4CH(HgBr)COOEt$ the reaction practically did not take place. Steric factors also had a pronounced influence on the rate of disproportionation of PhCH(HgBr)COOR (where R = Me, Et, *i*-Pr, *t*-Bu, *n*-nonyl and *l*-menthyl).[114] The magnitude of the effect upon the rate was found to be in the order Me > Et > *i*Pr > *n*-nonyl > *l*-menthyl ≫ *t*-Bu .
A critical examination of the results of Reutov's disproportionation studies has been made by Jenson and Rickborn.[116] They criticize the mechanism postulated by Reutov :

$$2\ RHgBr \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2Hg + HgBr_2$$

$$HgBr_2 + 2NH_3 \overset{k_2}{\rightleftharpoons} \downarrow(NH_3)_2HgBr_2$$

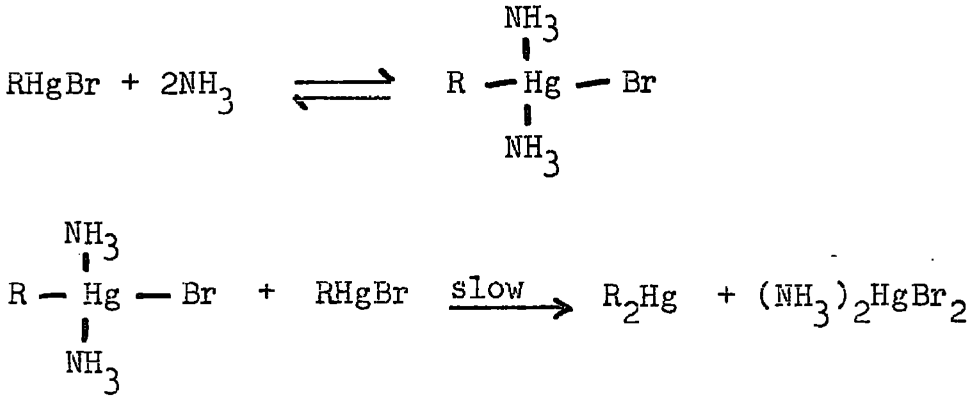
as being inconsistent with the observed kinetics. They propose two possible mechanisms, both of which fit the reported kinetics, and both involve the formation of a complex between ammonia and the organomercuric bromide. Firstly the formation of a 1:1 complex which disproportionates according to a bimolecular reaction :



$$RHgBr + NH_3 \rightleftharpoons RHg\begin{matrix} NH_3 \\ Br \end{matrix}$$

$$2RHgBr(NH_3) \xrightarrow{\text{slow}} R_2Hg + HgBr_2(NH_3)_2$$

Or alternatively a 2:1 complex is formed which further reacts with one molecule of alkylmercuric bromide to give the disproportionation products :



$$RHgBr + 2NH_3 \rightleftharpoons R-\overset{NH_3}{\underset{NH_3}{Hg}}-Br$$

$$R-\overset{NH_3}{\underset{NH_3}{Hg}}-Br + RHgBr \xrightarrow{\text{slow}} R_2Hg + (NH_3)_2HgBr_2$$

Without detailed kinetic evidence it is impossible to assign a mechanism and Jenson and Rickborn conclude that a reinvestigation of the kinetics is necessary.

EXPERIMENTAL

EXPERIMENTAL

Preparation of starting materials

Dimethylmercury

Dimethylmercury was prepared by the reaction of methylmagnesium bromide and mercuric chloride according to the method described by Gilman.[46] The Grignard reagent (a slight excess over 2 moles) in dry ether (1 l.) was prepared from bromomethane and magnesium, using a sold carbon dioxide condenser to prevent loss of alkyl halide, in a nitrogen atmosphere. Excess magnesium was removed by filtering the resulting solution through a glass-wool plug against a counter current of nitrogen into a 3-litre flask fitted with a mercury-sealed stirrer and a Soxhlet extractor containging mercuric chloride (1 mole) in the thimble. The solution was made up to 1500 mls. with dry ether and refluxed until the extraction of the mercuric chloride was complete. This took about six hours. The Soxhlet extractor was then replaced by a distillation apparatus and almost all of the ether was removed. The reaction was stirred throughout and carried out under an atmosphere of nitrogen up to this point. When the ether distillate had cooled to room temperature it was returned to the reaction flask and the excess Grignard reagent carefully hydrolysed with water and dilute sulphuric acid. The two layers were separated, the aqueous layer washed with ether (2 x 50 ml.) and the total ether solution was dried with anhydrous calcium chloride overnight. The dimethylmercury ether solution was added from a dropping funnel to a small flask from which the ether was distilled. When the ether had been removed completely the dimethylmercury distilled at 92° (140 gm. 61%)

Methylmercuric chloride

This compound was prepared by utilizing the general reaction of dialkylmercurials with mercuric halides.

$$Me_2Hg + HgCl_2 \longrightarrow 2MeHgCl$$

Dimethylmercury (34.3 gm., 1% excess) in ether (100 ml.) was added slowly from a dropping funnel to mercuric chloride (39.8 gm.) in ether (400 ml.). The solution was stirred continuously and methylmercuric chloride crystallised from solution as large plates as the addition continued. After addition of dimethylmercury the solution was refluxed for 30 minutes to ensure complete reaction of mercuric chloride which was initially only partly dissolved. On cooling methylmercuric chloride was obtained as lustrous leaflets m.p. 172° (68 gm. 92%). Similarly prepared from dimethylmercury and corresponding mercuric halides were methylmercuric bromide (80%), m.p. 162.5°; methylmercuric iodide (71%) m.p. 143°; both in the form of colourless lustrous leaflets. The iodide slowly turned yellow on storing for several months in the dark or more rapidly in diffuse daylight.

As organomercury compounds are extremely toxic and dialkylmercurials in particular have a high vapour pressure all preparations were carried out in a fumes cupboard and rubber gloves were worn whenever solutions of mercurials were handled. Waste solutions such as mother liquors from crystallisations and washings were treated with a solution of bromine in carbon tetrachloride until the colour of the bromine no longer faded on standing. This converted all toxic organomercury compounds to mercuric bromide and rendered them in a water soluble state suitable for disposal.

Di-m-tolylmercury.

Di-m-tolylmercury was prepared from excess sodium amalgam and m-bromotoluene.[47] The sodium amalgam was obtained by adding mercury (3,200gm.) from a dropping funnel to sodium (86 gm.) in a stainless steel beaker with vigorous stirring. When all of the mercury was added the amalgam was heated and stirred to ensure complete amalgamation. Vigorous stirring was continued as the solution cooled and a granular solid was obtained. Large granules were ground to a convenient size and the 2.8% sodium amalgam was ready for use. m-Bromotoluene (160 gm.) mixed with m-xylene (170 ml.) as solvent and ethyl acetate (10 ml.) as catalyst were added to the amalgam and the solution was heated under reflux for nine hours. The solution was then cooled and benzene (200 ml.) was added to dissolve any solid product which may have separated. The resulting solution was filtered free of sodium bromide and unreacted amalgam, and distilled to dryness. The pale-brown solid residue was recrystallised from ethyl acetate to yield di-m-tolylmercury (54gm., 30%), m.p. 101°.

m-Tolylmercuric chloride.

Di-m-tolylmercury (23.6gm.) was dissolved in meths and the solution refluxed to extract mercuric chloride (22.4gm.1 mol.) from a thimble of the attached Soxhlet extractor. After complete extraction of the mercuric chloride the m-tolylmercuric chloride (41gm., 89%) so formed was filtered from the solution and recrystallised from a large volume of alcohol which yielded the compound as colourless needles, m.p. 159-160°.

m-Tolylmercuric bromide.

Mercuric bromide (15.3 gm.) in hot acetone (100 ml.) was added to di-m-tolylmercury (16.3gm.,1 mol.) in acetone (200 ml.). The volume of the solution was made up to 400 ml. to dissolve the product completely and m-tolylmercuric bromide, m.p. 184° crystallised from hot acetone solution.

Phenylmercuric chloride.

This reagent was purified by Soxhlet extraction from the crude purchased compound using alcohol as solvent. Recrystallisation from methanol yielded phenylmercuric chloride as lustrous plates, m.p. 251°.

Phenylmercuric cyanide.

Phenylmercuric chloride (65.6 gm.) in alcohol (1 l.) was added to potassium cyanide (13.7 gm.,1 mol.) in alcohol (1 l.).

The solution was made up to 800 ml. with alcohol and water (10 ml.) was added to retain any remaining potassium chloride in solution. Crystallisation occurred as the solution cooled yielding colourless needles of phenylmercuric cyanide(60 gm., 94%), m.p. 203°.

<u>p-Tolylmercuric chloride</u> was recrystallised from boiling xylene, m.p. 233°.

<u>Trimethylphosphine</u>

Trimethylphosphine was available in the form of a solution in 2N sulphuric acid containing trimethylphosphine (0.071 gm. $ml.^{-1}$). The phosphine was liberated by adding a concentrated solution of sodium hydroxide to the acid (100 ml.) in an apparatus purged with nitrogen under reduced pressure (1cm.Hg). The trimethylphosphine so generated was condensed onto sodium hydroxide pellets in a two neck flask cooled in liquid air. This flask was then connected to another containing sodium dried ether (35 ml.). The ether was cooled to liquid air temperature, the system evacuated, and the dry trimethylphosphine allowed to condense onto the ether. The solution containing trimethylphosphine (7 gm.) in ether (35ml.) was stored under dry nitrogen. The strength of the phosphine solution was checked by addition of an aliquot to excess methyl iodide. The weight of tetramethylphosphonium iodide formed was in agreement with the estimated concentration of the solution.

<u>Solvents</u>

<u>Benzene</u> and <u>diethyl ether</u> were dried by allowing them to

stand over fresh sodium wire for at least one week before use.

Purification of reagents for conductance measurements

Methylmercuric chloride was recrystallised from methanol as colourless leaflets, m.p. 171°.

Methylmercuric bromide was recrystallised from ether as colourless leaflets, m.p. 162°.

Methylmercuric iodide was recrystallised from acetone as colourless leaflets, m.p. 143°, and stored in the dark.

Di-*m*-tolylmercury was recrystallised from acetone as colourless needles m.p. 101°.

m-Tolylmercuric chloride was recrystallised from acetone m.p. 160°.

m-Tolylmercuric bromide was recrystallised from a large volume of methanol, m.p. 184°.

Triphenylphosphine was recrystallised twice from methanol followed by recrystallisation from acetone. The small colourless crystals, m.p. 80°, were stored under nitrogen in the dark.

The dichlorobistriphenylphosphinemercury used was that which crystallised slowly from the disproportionation reaction between methylmercuric chloride and triphenylphosphine in benzene solution.

Acetone used as solvent in conductance reactions was purified by distillation from potassium permanganate and sodium hydroxide followed by fractional distillation, a large 'head' and 'tail' being rejected.

Methanol was used in most conductimetric titrations as solvent.

It was dried by reaction with magnesium. A solution containing magnesium methoxide (10%) was placed in a still fitted with a fractionating column 12" long packed with glass helixes. Methanol was removed from the top of the column by an electronically controlled take-off head. A glass plunger containing a metal core controlled the flow of methanol from the fractionation column into the receiving flask. The frequency with which the plunger was raised by an external electromagnetic was adjusted to give a 10% take-off. The apparatus was fitted with a calcium chloride soda lime guard tube to dry and remove carbon dioxide from the air drawn in as the methanol cooled. When solvent was required the heater was switched on and the solution refluxed for about one hour before any methanol was collected. The methanol was used soon after distillation.

Apparatus and technique

Nitrogen was used as an inert atmosphere in many of the reactions studied. It was purified by passing it through a furnace containing copper heated to 400° to remove traces of oxygen and then through a tower packed with molecular sieve to remove water vapour. The copper was regenerated whenever necessary by passing hydrogen through the heated furnace until the black oxide was reconverted to copper. The molecular sieve was dried periodically by heating the tower to about 100° and pumping off the water.

Reactions involving air-sensitive material were carried out in a double Schlenk tube in which the two limbs were separated by a porosity 3 sintered disc. The tube was evacuated to a high vacuum and then let down to atmospheric pressure slowly with dry nitrogen. Solutions of compounds of low volatility such as organomercuric salts could also be degassed in the Schlenk tube by pumping to a low vacuum and letting down to nitrogen two or three times before the air-sensitive material was added. Either method was considerably more rapid than purging the apparatus with nitrogen.

All conductance experiments were carried out in a thermostat maintained at 25 ± 0.1°C. A simple cell shown in figure (vii) was used. Platinum electrodes, which were replatinised as proved necessary, were held in position by glass spacers. Electrical contact was achieved by placing mercury in the tubes to which the electrodes were fused. The cell was fitted with a tap through which nitrogen could be passed and a small neck for the addition of reagents. If air-sensitive material was to be used, the cell was purged with dry nitrogen for an hour before the titration and a purged nitrogen-equilibrated burette was attached by a short length of rubber tubing. In this way triethylphosphine could be titrated without any oxidation. If the reagents were air-stable the cell was purged with nitrogen to remove water vapour and carbon dioxide and the burette was fitted with a calcium chloride/soda lime guard tube. The cell was shaken to obtain a homogenous solution before readings were taken, and

Conductance cell

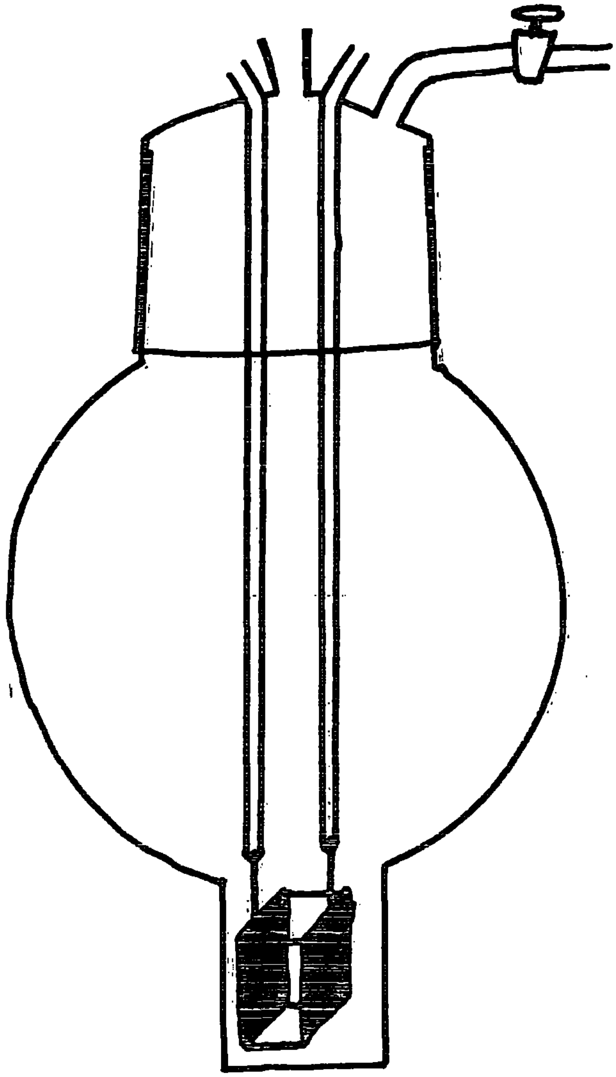


fig. (vii)

measurements of resistance were made using a Mullard bridge, type GM.4140/1. When not in use the electrodes were immersed in distilled water or acetone.

Molecular weights

These were determined cryoscopically in water or benzene solution. The benzene used was dried with sodium wire and standardized with triphenylphosphine. In either case an ice-salt cooling bath was used. If the compound was air-stable known weights were added to a known weight of solvent in the apparatus. Air-sensitive compounds were dissolved in a known volume of benzene and further aliquots of benzene were subsequently added. The solution was allowed to supercool by 0.2°C and was then stirred vigorously until it showed a constant maximum reading. The Beckmann thermometer was tapped sharply at this point to prevent 'sticking' of the mercury thread. Determinations of molecular weight were normally carried out at three concentrations. In all cases a current of dry nitrogen was blown continuously through the top of the apparatus to prevent water vapour condensing into the cool solution.

Preparation of complex salts

Synthesis involving air-sensitive materials, tertiary phosphines and arsines with the exceptions of the triphenyl derivatives, were carried out in a Schlenk tube under a nitrogen atmosphere. The phosphine or arsine was added to a solution of the mercurial in the Schlenk tube, by means of an automatic pipette previously purged with nitrogen, against a counter current of nitrogen. Usually a good yield of the product was sacrificed to obtain a pure crystalline sample. Melting points and analyses on these complex salts were determined soon after their initial preparation. Melting points were determined in sealed tubes in the normal manner for organic compounds. The time taken to heat the compound to its melting point was kept to the minimum consistent with reasonable accuracy.

<u>Methyl(trimethylphosphine)mercury chloride</u>, $[MeHgPMe_3]Cl$.

Addition of trimethylphosphine (0.9 gm., excess over 1 mol) in ether (15ml.) to methylmercuric chloride (2.5gm.) in acetone (100 ml.) resulted in an immediate precipitation of the complex. The filtrate from the reaction was cooled to -76° when crystallisation slowly occurred. The colourless crystalline solid melted with decomposition from 86°. (Found: C, 14.7; H, 3.7; Cl^-, by ion exchange, 10.95. $C_4H_{12}ClHgP$ requires C, 14.5; H, 3.7; Cl^-, 10.83%).

<u>Methyl(triethylphosphine)mercury chloride</u>, $[MeHgPEt_3]Cl$.

The complex was precipitated on mixing ether solutions of methylmercuric chloride and triethylphosphine (slight excess over 1 mol.) and crystallised from a chloroform-ether mixture as colourless needles.

The crystalline complex was also obtained by adding triethylphosphine (slight excess over 1 mol.) to methylmercuric chloride in acetone and concentrating the resulting solution, m.p. 84-85$_0$ with decomposition. (Found: C, 22.8; H, 5.0; Hg, 53.0 $C_7H_{18}ClHgP$ requires C, 22.8; H, 4.91; Hg, 54.3%)

Methyl(phenyldimethylphosphine)mercury chloride, $[MeHgPMe_2Ph]Cl$

Addition of phenyldimethylphosphine (2 ml., excess over 1 mol.) to methylmercuric chloride (3.3gm.) in acetone (30 ml.) slowly yielded colourless crystals of the salt on cooling in an acetone -CO_2 bath. M.p. 95-97° with decomposition (Found: C, 27.5; H, 3.7; Cl^-, by ion exchange, 9.19. $C_9H_{14}ClHgP$ requires C, 27.8; H, 3.6; Cl, 9.19%). The complex was found to be light sensitive, turning grey on exposure to diffuse daylight for a few hours. This compound and those subsequently prepared and found to be light sensitive were handled in flasks wrapped in black paper to prevent decomposition.

Methyl(triethylphosphine)mercury bromide, $[MeHgPEt_3]Br$

This compound has been reported in a preliminary communication and was prepared from ether solution in a similar manner to the corresponding chloride.[110] Addition of triethylphosphine to methylmercuric bromide in acetone followed by concentration of the solution also yielded colourless crystals, m.p. 92-93° with decomposition. (Found: C, 20.5; H, 4.5 Calc. for $C_7H_{18}BrHgP$: C, 20.3; H, 4.39%)

Methyl(phenyldimethylphosphine)mercury iodide, $[MeHgPMe_2Ph]I$.

Addition of phenyldimethylphosphine (excess over 1 mol.)

to methylmercuric iodide (3.2gm.) in acetone (40 ml.) gave an initially clear solution from which the complex was slowly deposited as colourless needles, m.p. 107° with decomposition. (Found: C, 22.5; H, 2.92. $C_9H_{14}HgIP$ requires C, 22.5; H, 2.94%). The complex was also precipitated on addition of ether solutions of the phosphine and methylmercuric iodide and crystallised as colourless needles from isopropanol.

Ethyl(trimethylphosphine)mercury chloride,

$[EtHgPMe_3]Cl$.

Trimethylphosphine (0.6 gm., slight excess over 1 mol.) in ether (10ml.) was added to ethylmercuric chloride (2.0 gm.) in warm acetone (20 ml.). An immediate white precipitate of the sparingly soluble salt was formed. On cooling the filtrate to -78° the complex crystallised from the solution as fine colourless needles. Decomposition from 86°. (Found: C, 17.4; H 4.2; Cl, by ion exchange, 10.8. $C_5H_{14}ClHgP$ requires C, 17.6; H, 4.1; Cl, 10.4%).

Ethyl(triethylphosphine)mercury bromide,

$[EtHgPEt_3]Br$.

When triethylphosphine (2.2 ml., slight excess over 1 mol.) was added to incompletely dissolved ethylmercuric bromide (4.0 gm.) in acetone (40 ml.) the solid quickly went into solution which was then concentrated to half volume, by evaporation under reduced pressure, at which concentration colourless needles of the complex began to crystallise, m.p. 87° with decomposition. (Found: C, 22.5; H, 4.8.

$C_8H_{20}BrHgP$ requires C, 22.5; H, 4.7%).

Conductance of $[EtHgPEt_3]Br$ in water

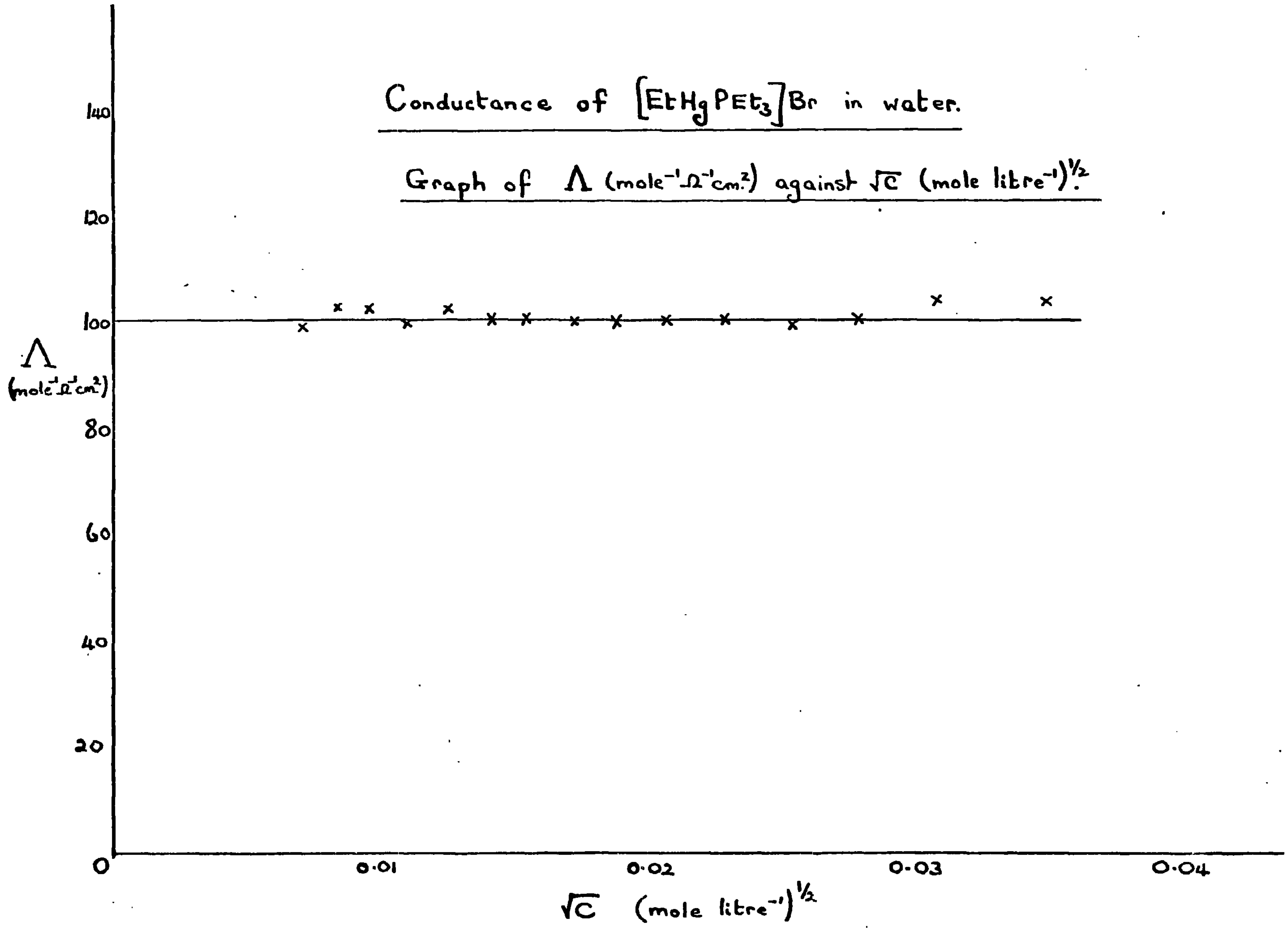
Ethyl(triethylphosphine)mercury bromide (0.0578 gm.) was accurately weighed under nitrogen in a 50 ml. two-necked flask and distilled water (20 ml.) was added by pipette against a counter current of nitrogen. Half of the solution was transferred under nitrogen to a 'grade A' 10 ml. burette which was then fitted with a pressure-equilibrated nitrogen inlet. The conductance cell, which was purged with nitrogen and contained distilled water (20ml.), was placed in the thermostat at 25° for two hours prior to titration. The apparatus used was identical to that described earlier. Aliquots of the solution from the burette were run into the cell against a counter-current of nitrogen, the cell shaken to obtain a homogenous solution, and the resistance of the solution measured. After 10 minutes the resistance was re-determined and in all cases was found to be unchanged. Measurements were taken until almost all the solution had been added from the burette and the results obtained are tabulated below. A graph of Λ (mole^{-1} ohm^{-1} cm^2) against $\sqrt{C}$ (mole lit^{-1})$^{\frac{1}{2}}$ is shown. 'Conductance water' has a specific conductance, K, of about 0.05 x 10^{-6} ohm^{-1} cm^{-1} at 25° and all observed values of specific conductance were corrected for this.

TABLE IV

Cell constant = 0.143 Thermostat temperature = 25°C

Conductance of $[EtHgPEt_3]Br$ in water

Vol. $[EtHgPEt_3]Br$ solution added (ml.)	$C \times 10^{-3}$ (mole lit^{-1})	$\sqrt{C}$ (mole $lit^{-1})^{\frac{1}{2}}$	$R \times 10^{4}$ (ohm)	$K \times 10^{-6}$ obs. (ohm^{-1} $cm.^{-1}$)	$K \times 10^{-6}$ corr. (ohm^{-1} $cm.^{-1}$)	Λ (ohm^{-1} $cm.^{2}$)
0.00	0.00	0.00	3.38	4.23	0.05	-
0.05	0.0169	0.00411	2.62	5.46	1.28	75.7
0.10	0.0336	0.00580	1.97	7.26	3.08	91.5
0.15	0.0503	0.00709	1.56	9.17	4.99	99.1
0.21	0.0702	0.00838	1.25	11.44	7.26	103.4
0.27	0.0900	0.00949	1.07	13.37	9.19	102.1
0.37	0.1228	0.01108	0.870	16.44	12.26	99.8
0.48	0.1583	0.01258	0.697	20.51	16.33	103.1
0.62	0.2032	0.01425	0.580	24.65	20.47	100.7
0.74	0.2411	0.01552	0.501	28.54	24.36	101.0
0.92	0.2972	0.01724	0.421	33.96	29.78	100.2
1.11	0.3542	0.01885	0.361	39.61	35.43	100.0
1.35	0.4272	0.02066	0.303	47.20	43.02	100.7
1.70	0.5291	0.02300	0.250	57.20	53.02	100.2
2.13	0.6503	0.02551	0.209	68.42	64.24	98.8
2.61	0.7798	0.02793	0.173	82.66	78.48	100.7
3.30	0.9568	0.03093	0.142	100.7	96.5	100.8
4.45	1.229	0.03506	0.111	128.8	124.6	101.4
5.56	1.470	0.03834	0.086	166.3	162.1	110.3
6.71	1.697	0.04120	0.076	188.1	183.9	108.4
7.92	1.916	0.04378	0.068	210.3	206.1	107.6
9.95	2.245	0.04739	0.060	238.3	234.1	104.0



Conductance of $[EtHgPEt_3]Br$ in water.

Graph of Λ $(mole^{-1}\Omega^{-1}cm^2)$ against $\sqrt{C}$ $(mole\ litre^{-1})^{1/2}$.

The latter values of equivalent conductance, Λ, are high due to increased experimental error in the determination of the resistance in this region. Extrapolation of the plot of Λ against $\sqrt{C}$ gives the value of equivalent conductance at 'infinite dilution' Λ_0.

$$\underline{\Lambda_0 = 100.5 \text{ ohm.}^{-1} \text{ cm.}^2}$$

As $\Lambda_0 = \lambda_+ + \lambda_-$ where λ_+ and λ_- are the ion conductances at infinite dilution of the anion and cation respectively, and for Br^- $\lambda_- = 78.4 \text{ ohm.}^{-1}\text{cm.}^2$

Then for $[EtHgPEt_3]^+$, $\lambda_+ = 22.1 \text{ ohm.}^{-1}\text{cm.}^2$

n-Propyl(trimethylphosphine)mercury chloride, $[Pr^nHgPMe_3]Cl$.

Addition of trimethylphosphine (0.9 gm., slight excess over 1 mol.) in ether (15 ml.) to n-propylmercuric chloride (3.0 gm.) in acetone (40 ml.) at room temperature resulted in an immediate white gelatinous precipitate of crude $[Pr^nHgPMe_3]Cl$. A further quantity of acetone (50 ml.) was added and the solution was warmed to about 40°, at which temperature the precipitate was partially dissolved. The crude product was removed by filtering the solution through the Schlenk disc and the filtrate was cooled to 0°C, at which temperature the complex slowly crystallised as fine colourless needles, m.p. 121-124° with decomposition. (Found: C, 20.2; H, 4.6; Cl^-, by cation exchange, 9.98.

$C_6H_{16}ClHgP$ requires C, 20.3; H, 4.5; Cl, 9.98%)

n-Propyl(phenyldimethylphosphine)mercury chloride, $[Pr^nHgPMe_2Ph]Cl$

Phenyldimethylphosphine (1.5 ml., slight excess over 1 mol.) in ether (20ml.) was added to n-propylmercuric chloride (2.2 gm.) in ether (100ml.). The solution was concentrated to a volume of about 80 ml. when an oil began to separate. Further concentration to about 60 ml. by rapidly pumping off the ether solvent caused the solution to become quite cold and on vigorous shaking a white solid was formed. The $[Pr^nHgPMe_2Ph]Cl$ so formed was immediately filtered from the ether solution on the sintered disc of the Schlenk tube, transferred to a two-neck flask under nitrogen and pumped until dry. m.p. 76-77° with decomposition. (Found: C, 31.5; H, 4.3; Cl^-, by cation exchange, 8.39. $C_{11}H_{18}ClHgP$ requires C, 31.7; H, 4.35; Cl, 8.50%). Attempts to recrystallise the complex from benzene, ether, hexane, acetone, methanol, iso-propanol and mixtures of these solvents were not successful. The compound was readily soluble in polar solvents and sparingly soluble in non-polar solvents but always separated as an oil on attempted isolation from solution in all solvents and solvent mixtures tried. The solid $[Pr^nHgPMe_2Ph]Cl$ was found to be light sensitive, darkening on exposure to light for several days, and was therefore handled in flasks wrapped in black paper to prevent its decomposition.

n-Butyl(trimethylphosphine)mercury chloride, $[Bu^{n}HgPMe_3]Cl$.

Trimethylphosphine (0.9 gm., slight excess over 1 mol.) in ether (15 ml.) was added to n-butylmercuric chloride (3.0 gm.) in acetone (70 ml.) at room temperature. The immediate flocculent white precipitate was removed by filtration through the sintered disc and on cooling the filtrate in ice-water $[Bu^{n}HgPMe_3]Cl$ slowly crystallised as colourless needles, m.p. 107-8° with decomposition. (Found: C, 22.75; H, 4.8; Cl^-, by cation exchange, 9.60. $C_7H_{18}ClHgP$ requires C, 22.8; H, 4.9; Cl, 9.61%).

n-Butyl(phenyldimethylphosphine)mercury chloride, $[Bu^{n}HgPMe_2Ph]Cl$.

This complex was prepared by adding phenyldimethylphosphine (1.1 ml., slight excess over 1 mol.) to n-butylmercuric chloride in ether (100 ml.). On cooling the solution well below room temperature a colourless crystalline solid formed (about o.5 gm.) from which the ether solution was decanted. The $[Bu^{n}HgPMe_2Ph]Cl$ so obtained was light sensitive. It was transferred under nitrogen to a two-neck flask wrapped in black paper, and pumped dry, m.p. 86-88° with decomposition. (Found: C, 33.4; H, 4.7; Cl^-, by cation exchange, 8.17. $C_{12}H_{20}ClHgP$ requires C, 33.4; H, 4.7; Cl, 8.22%). The complex resembled $[Pr^{n}HgPMe_2Ph]Cl$ in its solubility, being soluble in polar solvents and sparingly soluble in non-polar solvents.

On concentration it similarly formed an oil and attempts to recrystallise the compound failed.

n-Butyl(trimethylphosphine)mercury iodide, $[Bu^nHgPMe_3]I$.

Trimethylphosphine (0.6gm., slight excess over 1 mol.) in ether (10 ml.) was added to n-butylmercuric iodide (1.9 gm,) in acetone (70 ml.). The resulting clear solution was shaken to make it homogenous and then cooled to -20° in an acetone -CO_2 bath. The complex slowly crystallised as fine colourless needles, m.p. 87-88° with decomposition. (Found: C, 18.1; H, 3.9. $C_7H_{18}HgIP$ requires C, 18.25; H, 3.9%).

Reactions of tertiary phosphines and arsines with methylmercuric perchlorate

Reactions involving air-sensitive tertiary phosphines and arsines were carried out in a Schlenk tube under nitrogen similar to the preparations of $[RHgPR'_3]X$ already described. Triphenyl-phosphine and -arsine respectively could be added to the methylmercuric perchlorate solution in air in ordinary flasks and the use of a Schlenk tube was unnecessary. The reactions were exothermic, this having been particularly noticeable with trimethyl- amd triethylphosphine, and the products were light sensitive and therefore handled in flasks wrapped in black paper, with the exception of $[MeHgAsPh_3]ClO_4$ which was stable to light. No sign of any disproportionation to dimethylmercury on storage was observed over several months, unlike the behaviour of the corresponding halides, and the complexes were air stable.

Preparation of methylmercuric perchlorate solution

A solution of methylmercuric perchlorate was obtained by adding aqueous silver perchlorate to methylmercuric chloride dissolved in the minimum of methanol. Aqueous sodium hydroxide (12 gm.) was added slowly with stirring to silver nitrate (42.5 gm., 0.25 mole) solution and the resulting precipitate of silver oxide was washed by decantation with distilled water twelve times. Perchloric acid, 80% solution, was added to the wet silver oxide until only a trace of oxide remained after standing for two hours. The silver perchlorate solution was filtered free of the slight excess oxide. Silver perchlorate (11.5 gm., 40 ml. of stock solution) was added slowly with shaking to methylmercuric chloride (14 gm.) in methanol (100 ml.) and the solution allowed to stand in the dark for two hours. The solution of methylmercuric perchlorate (17.5 gm.) in 1:2.5 water-methanol mixture (140 ml.) was filtered free of silver chloride and stored in a stoppered flask. This solution was handled with great care because of its dangerous vesicant action on the skin.

Methyl(trimethylphosphine)mercury perchlorate, $[MeHgPMe_3]ClO_4$

Trimethylphosphine (1 gm.) in ether (5 ml.) was added by syringe to de-aerated acetone (15 ml.) in one limb of a Schlenk tube. Methylmercuric perchlorate (2.5 gm., slightly less than 1 mol.) in the stock solution (20 ml.) was placed in the other limb and the trimethylphosphine solution was filtered through the disc and shaken to give a homogenous solution. The reaction was exothermic and the solution became warm, depositing at the same time a sparse grey precipitate of metallic mercury. After pumping to remove the slight excess of trimethylphosphine the solution was filtered through a sintered disc under suction into a two-neck flask and further isolation was carried out in air. The volume was reduced to about 30 ml. when crystallisation began. The product, $[MeHgPMe_3]ClO_4$, was obtained as white needles which quickly turned grey on exposure to light. Decomposition from 215°. (Found: Hg, 50.0, ClO_4, by ion exchange, 25.1. $C_4H_{12}ClHgO_4P$ requires Hg, 51.3; ClO_4, 25.4%).

<u>Methyl(triethylphosphine)mercury perchlorate</u>, $[MeHgPEt_3]ClO_4$

Addition of triethylphosphine (1.6 gm.) in acetone (40 ml.) to some of the stock solution (30 ml.) containing methylmercuric perchlorate (3.6 gm., slightly less than 1 mol.) caused a slight grey precipitate of metallic mercury and a small increase in the temperature of the solution due to the exothermic reaction. After filtration and concentration of the solution to 60 ml. by evaporation of solvent at reduced pressure the complex was obtained as white needles. Decomposition from 137°. (Found: Hg, 46.2; ClO_4, by ion exchange, 22.8. $C_7H_{18}ClHgO_4P$ requires Hg, 46.3; ClO_4, 23.0%). The complex was stable to air but turned grey after several hours exposure to diffuse light.

<u>Methyl(triphenylphosphine)mercury perchlorate</u>, $[MeHgPPH_3]ClO_4$

A solution (30 ml.) of methylmercuric perchlorate (3.6 gm.) was slowly added to triphenylphosphine (2.8 gm. 1 mol.) in acetone (80 Ml.). A sparse white precipitate, presumably triphenylphosphine, was formed but quickly redissolved after 80% of the methylmercuric perchlorate solution had been added. The solution was filtered and concentrated to a volume of about 90 ml., by evaporation of solvent under reduced pressure, when the crystalline $[MeHgPPh_3]ClO_4$ separated from solution, m.p. 213-218° with decomposition. (Found: Hg, 34.4. $C_{19}H_{18}ClHgO_4P$ requires Hg, 34.7%). On exposure to light for several hours the complex turned bright yellow.

Methyl(triethylarsine)mercury perchlorate, $[MeHgAsEt_3]ClO_4$

As triethylarsine is readily oxidised by air this preparation was carried out under nitrogen in a Schlenk tube similar to reactions involving air-sensitive phosphines. Triethylarsine (1.1 gm., slightly more than 1 mol.) in ether (20 ml.) was added to a solution (20 ml.) of methylmercuric perchlorate (2.4 gm.) and an equal volume of acetone. No precipitate was formed so the solution was concentrated by pumping to about 30 ml., when white solid was precipitated. The solution was warmed to dissolve the complex, filtered through the sintered disc, and allowed to crystallise. Decomposition from 120°. (Found: Hg, 41.5. $C_7H_{18}ClAsHgO_4$ requires Hg, 42.0%). The $[MeHgAsEt_3]ClO_4$ so obtained was light-sensitive, turning grey after several hours exposure to daylight.

Methyl(triphenylarsine)mercury perchlorate, $[MeHgAsPh_3]ClO_4$

Slow addition of triphenylarsine (2.1 gm., 1 mol.) in acetone (30 ml.), with continuous stirring, to methylmercuric perchlorate solution resulted in an immediate white precipitate of the complex. The solid so obtained appeared to be insoluble in benzene, ether, water and alcohol, and only slightly soluble in acetone. A saturated acetone solution (200 ml.) yielded the complex as colourless needles on cooling, m.p. 224-225° with decomposition. (Found: C, 36.95; H, 2.9. $C_{19}H_{18}AsClHgO_4$ requires C, 36.73; H, 2.9%). Unlike the other perchlorate complexes prepared, $[MeHgAsPh_3]ClO_4$ was stable to light. Difficulty in analysing this compound is mentioned in the section dealing with mercury analysis.

<u>Preparation of methylmercuric tetrafluoroborate solution</u>

Silver oxide (13.6 gm.) was precipitated from silver nitrate (20 gm.) and sodium hydroxide (6 gm.) in aqueous solution. After washing by decantation 15-20 times in a polythene beaker 80% hydrofluoric acid was added until only a trace of silver oxide remained. The aqueous solution of silver fluoride (15.5 gm.) was filtered free of oxide and borontrifluoride etherate, $BF_3.OEt_2$, (16.7 gm.) was added dropwise with stirring. On complete addition the solution was filtered and concentrated by pumping to give a solution of silver tetrafluoroborate (21 gm.) in water (36 ml.). Part of this solution (12 ml., containing 7 gm. $AgBF_4$) was added slowly and with stirring to methylmercuric bromide (11 gm., 1 mol.) in methanol (300 ml.) and filtered free of the precipitated silver bromide. Concentration by evaporation of solvent under reduced pressure gave a solution containing methylmercuric tetrafluoroborate (11 gm.) in aqueous methanol (57 ml.)

Methyl(triethylphosphine)mercury tetrafluoroborate, $[MeHgPEt_3]BF_4$

Addition of triethylphosphine (slight excess over 1 mol.) by means of a syringe against a counter current of nitrogen to an aqueous-methanolic solution of methylmercuric tetrafluoroborate in a two-neck 50 ml. flask purged with nitrogen resulted in heat evolution and the precipitation of a little metallic mercury. The complex was found to be extremely soluble in water, so that after filtration the solution was pumped to dryness. The residue was dissolved in warm isopropanol and crystalline $[MeHgPEt_3]BF_4$, m.p. 120-125° (decomposition) obtained on cooling the solution well below room temperature. (Found: C, 20.5; Hg, 47.4; BF_4, by ion exchange, 21.2; M, cryoscopically in water, 215 and 212 at 3.2 and 2.9 wt.% respectively. $C_7H_{18}F_4BHgP$ requires C, 20.0; Hg, 47.7; BF_4, 20.65%. M, 421). The cryoscopic result is consistent with the complete dissociation of a 1:1 electrolyte.

Methyl(triphenylphosphine)mercury tetrafluoroborate $[MeHgPPh_3]BF_4$

An aqueous methanolic solution of methylmercuric tetrafluoroborate was added to triphenylphosphine (1 mol.) in acetone in a two-neck flask. On concentrating to a very small volume the complex salt, m.p. 215-220°, slowly crystallised. (Found: C, 40.7; H, 3.2. $C_{19}H_{18}BF_4HgP$ requires C, 40.4; H, 3.2%). The product was readily soluble in water, acetone, and methanol, less soluble in the higher alcohols and insoluble in ether.

Reaction of methyl(triethylphosphine)mercury chloride and sodium tetraphenylborate

The reagents were added in methanol solution and, on concentration, colourless crystals, m.p. 100-120° (dec.), soluble in acetone but insoluble in water, were obtained. This was most likely $[MeHgPEt_3]BPh_4$ but combustion analysis gave unsatisfactory results possibly due to the difficulty of obtaining complete combustion of compounds containing both boron and carbon.

Methylmercury tetrathiocyanatodiamminechromate (III), $MeHgCr(NH_3)_2(SCN)_4$

Reinecke salt, $NH_4[Cr(NH_3)_2(SCN)_4]$, (40 gm.) was recrystallised by dissolving it in distilled water (450 ml.) at 70°C, stirring briskly and filtering at once through a pleated filter paper. The filtrate deposited crystals copiously on cooling in ice-water. The salt was recrystallised a second time and pumped dry giving 18 gm. of pure ammonium reineckate.

Ammonium reineckate (14.8 gm.) in 1:1 acetone water mixture (400 ml.) was allowed to drip slowly into a vigorously stirred solution of methylmercuric chloride (10.2 gm., 1 mol.) in acetone (300 ml.). A deep purple solution was obtained but no solid was precipitated. On concentration by evaporation under reduced pressure methylmercuric reineckate began to separate as a finely divided pale pink powder, sparingly soluble in acetone and insoluble in water, alcohol and ether. Attempts to crystallise the compound were unsuccessful and analysis was carried out on the powder obtained from dilute aqueous acetone solution, decomposition from 190°. (Found: C, 11.2; H, 1.74; Hg, 36.1. $C_5H_9CrHgN_6S_4$ requires C, 11.25; H, 1.70; Hg, 36.4%).

Methyl(triethylphosphine)mercury tetrathiocyanatodiamminechromate(III)

$[MeHgPEt_3][Cr(NH_3)_2(SCN)_4]$

A red precipitate was obtained when ammonium reineckate (0.45 gm.) in water (15 ml.) was added to methyl(triethylphosphine)mercury chloride (0.5 gm., 1 mol.) in methanol (15ml.). The product was insoluble in water and ether, sparingly soluble in methanol, and was crystallised from aqueous acetone as red needles, decomposition from 135°. (Found: Cr, 7.86; Hg, 28.9. $C_{11}H_{24}CrHgN_6PS_4$ requires Cr, 7.98; Hg, 30.8%).

Methyl(triphenylphosphine)mercury tetrathiocyanatodiamminechromate(III),

$[MeHgPPh_3][Cr(NH_3)_2(SCN)_4]$

Triphenylphosphine (1.1 gm,, 1 mol.) was added to a suspension of methylmercuric reineckate (2.2 gm.) in acetone (40 ml.) and the solution was vigorously stirred. The pink suspension dissolved within five minutes at room temperature to give a purple solution which yielded the phosphine complex on concentration. Recrystallisation from aqueous acetone gave methyl(triphenylphosphine)mercury reineckate as deep pink needles containing one mol. of acetone of crystallisation, $[MeHgPPh_3][Cr(NH_3)_2(SCN)_4]Me_2CO$. (Found: C, 36.3; H, 3.7. $C_{26}H_{30}CrHgN_6OPS_4$ requires C, 36.55; H, 3.5%). The presence of acetone resulted in an infra-red absorption at 1701 $cm.^{-1}$, which disappeared after the salt had been kept at 60^o in vacuo for 24 hours. The deep pink needles collapsed to a pink powder of the anhydrous phosphine complex, $[MeHgPPh_3][Cr(NH_3)_2(SCN)_4]$. (Found: C, 34.9; H, 3.1. $C_{23}H_{24}CrHgN_6PS_4$ requires C, 34.8; H, 3.05%). Decomposition from 145^o.

Preparation of phenylmercuric nitrate solution

This was prepared by filtering the solution free from precipitated silver chloride after silver nitrate (4.9 gm.) in 1:5 water-acetone mixture (30 ml.) had been added with stirring to phenylmercuric chloride (9.1 gm., 1 mol.) in hot acetone (400 ml.). After slight concentration a stock solution containing phenylmercuric nitrate (9.9 gm.) in acetone (365 ml.) was obtained.

Phenyl(triethylphosphine)mercury nitrate,
$[PhHgPEt_3]NO_3$

Triethylphosphine (1.2 ml.) was added to phenylmercuric nitrate (2.7 gm.) in acetone (100 ml.). After concentration, by evaporation of acetone under reduced pressure, to 20 ml. the complex crystallised as long colourless needles, m.p. $120-121^o$ with decomposition, when the solution cooled. (Found: C, 31.5; H, 4.7; NO_3, by ion exchange, 13.5.

$C_{12}H_{20}HgNO_3P$ requires C, 31.5; H, 4.4; NO_3, 13.5%). The complex was stored under an atmosphere of nitrogen in a flask wrapped in black paper as exposure to daylight caused the crystals to darken within a few hours.

Conductance of $[PhHgPEt_3]NO_3$ in methanol

The apparatus was the same as that previously described. The conductance cell was purged with nitrogen, methanol (20 ml.) was added, the flask stoppered and placed in the thermostat at 25° for three hours. $[PhHgPEt_3]NO_3$ (0.0711 gm.) was dissolved in methanol (20 ml.) and some of this solution was transferred to a burette fitted with a soda lime/$CaCl_2$ tube to prevent water and carbon dioxide dissolving in the solution. Aliquots of the complex solution were added and the resistance measured in the usual way. The results obtained are tabulated on the following page.

TABLE V

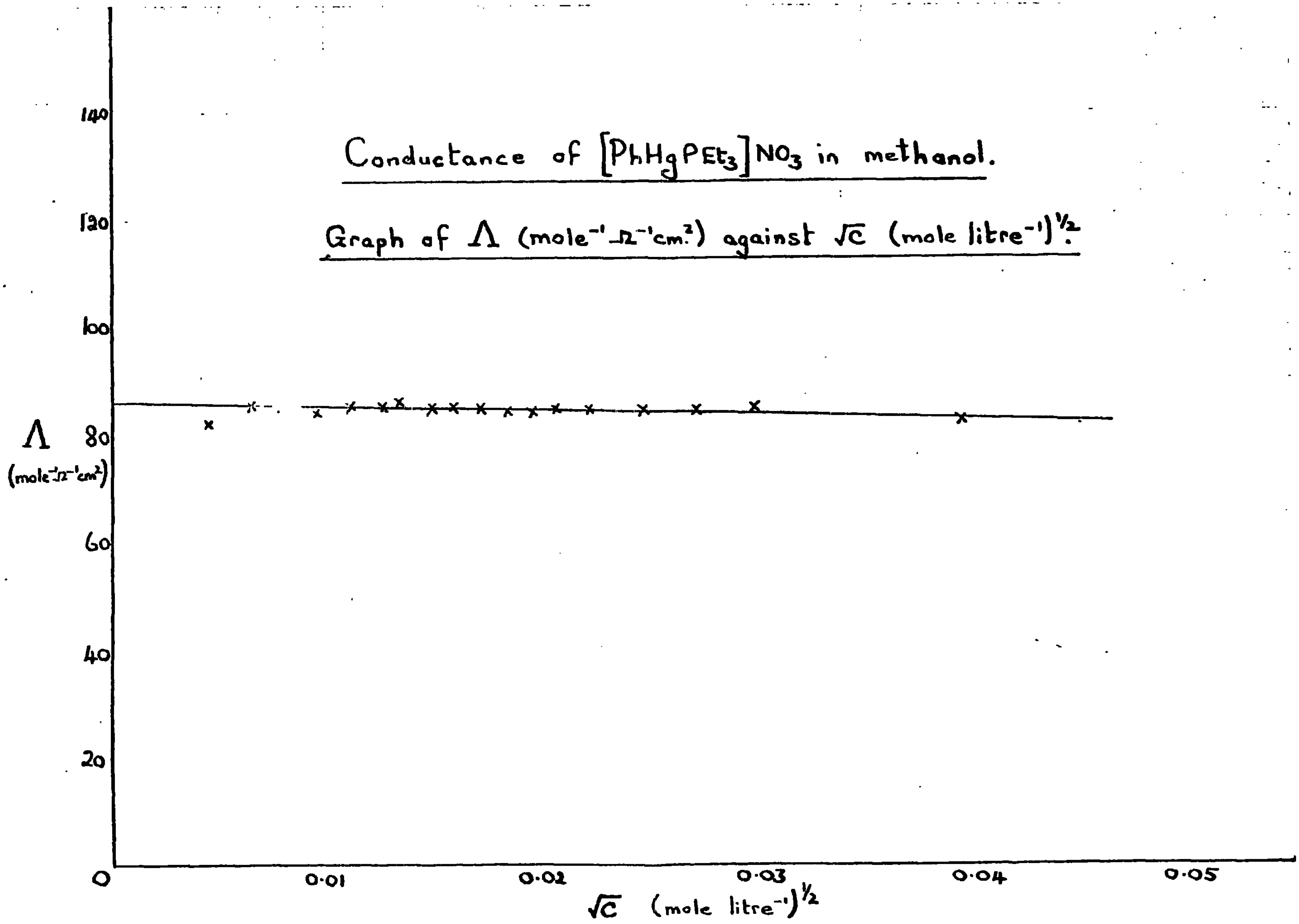
Conductance of $[PhHgPEt_3]NO_3$ in methanol

Volume $[PhHgPEt_3]NO_3$ added (ml.)	C x 10^{-3} (mole lit.$^{-1}$)	$\sqrt{C}$ (mole lit.$^{-1}$)$^{\frac{1}{2}}$	R x 10^{4} (ohm)	K x 10^{-6} obs. (ohm^{-1}cm^{-1})	K x 10^{-6} corr. (ohm^{-1}cm^{-1})	Λ (ohm^{-1} cm^{2}
-	-	-	6.90	2.072	0.001	-
0.05	0.0194	0.00440	3.91	3.657	1.586	81.9
0.11	0.0425	0.00652	2.51	5.697	3.626	85.4
0.17	0.0654	0.00809	1.86	7.692	5.621	85.9
0.24	0.0920	0.00959	1.46	9.792	7.721	83.9
0.33	0.1260	0.01123	1.11	12.88	10.81	85.8
0.42	0.1596	0.01264	0.913	15.66	13.59	85.2
0.50	0.1893	0.01376	0.777	18.41	16.34	86.3
0.60	0.2261	0.01504	0.668	21.40	19.33	85.5
0.70	0.2625	0.01620	0.585	24.44	22.37	85.2
0.80	0.2985	0.01728	0.521	27.45	25.38	85.0
0.93	0.3449	0.01858	0.458	31.22	29.15	84.5
1.05	0.3872	0.01968	0.411	34.79	32.75	84.5
1.18	0.4324	0.02080	0.369	38.76	36.69	84.9
1.37	0.4976	0.02231	0.324	44.14	42.07	84.5
1.73	0.6180	0.02486	0.264	54.17	52.10	84.3
2.10	0.7376	0.02716	0.221	64.71	62.64	84.9
2.60	0.8930	0.02992	0.183	78.12	76.05	85.2
3.20	1.071	0.03273	0.147	97.27	95.20	88.9
3.80	1.239	0.03521	0.136	105.2	103.1	83.2
5.00	1.552	0.03945	0.110	130.0	127.9	82.4

From the graph of equivalent conductance, Λ, against $\sqrt{C}$ the equivalent conductance for the salt at infinite dilution, Λ_o, is 86.6 ohm^{-1}cm.^{2}

Conductance of $[PhHgPEt_3]NO_3$ in methanol.

Graph of Λ (mole^{-1} Ω^{-1} cm^2) against $\sqrt{c}$ (mole litre^{-1})$^{1/2}$.



Complexes of methylmercuric salts with nitrogen ligands

As complexes from methylmercuric salts and tertiary phosphines could be isolated, attempts were made to prepare similar complexes with nitrogen compounds but with only limited success. The amines were markedly more weakly held in their complexes than the corresponding phosphines and the only stable complexes obtained were those from pyridine or bipyridyl and containing anions of low co-ordination affinity for mercury, e.g. ClO_4^- and NO_3^-. Evidence for the formation of complexes of tertiary aliphatic amines with methylmercury salts was obtained but characterization in stoichiometric ratios was not possible due to the ease with which the amine was lost. Unlike the phosphine reactions, there was no danger of oxidation so reactions were carried out in air.

Reaction of methylmercury chloride and ammonia

A dilute solution of methylmercuric chloride (2.5 gm.) in ether (200 ml.) was added dropwise with stirring to an excess of aqueous ammonia (2 ml., density 0.88 gm/ml.) in ether (110 ml.). An immediate white precipitate occurred on mixing the solutions and a solid was obtained by filtration under suction, m.p. 171°, (m.p. MeHgCl 171°). The solid so obtained had a strong smell of ammonia and, unlike methylmercuric chloride, was readily soluble in water. (Found: Hg, 74.2. CH_6ClHgN requires Hg, 74.8%. CH_3ClHg requires Hg, 79.9%). Analysis for carbon and hydrogen could not be obtained due to a continuous decrease in weight of the sample, presumably due to loss of ammonia. The infrared spectrum of the complex was identical to that of methylmercuric chloride and showed no absorption due to ν(N-H), again presumably due to loss of ammonia from the complex before the recording of the spectrum.

Reaction of methylmercuric chloride and triethylamine

Addition of excess triethylamine to methylmercuric chloride in ether solution followed by concentration of the solution by evaporation under reduced pressure and filtration yielded a white solid smelling strongly of triethylamine. Melting point and infra-red spectrum were identical to those of methylmercuric chloride. Analysis showed the presence of additional carbon and hydrogen but very much less than required for a 1:1 complex. (Found: C, 9.1; H, 2.2. $C_7H_{18}ClHgN$ requires C, 23.85; H, 5.1%).

Reaction of methylmercuric chloride and pyridine

On addition of excess pyridine to a solution of methylmercuric chloride in ether followed by concentration under reduced pressure, large leaf-like crystals of methylmercuric chloride, identified by melting point and infra-red spectrum, were formed. No evidence for the formation of a complex was obtained.

Reaction of methylmercuric perchlorate and pyridine

When excess pyridine (1 ml.) was added to methylmercuric perchlorate (3 gm.) in acetone-water (9:1, 30 ml.), methyl(pyridine)mercury perchlorate, [MeHgpy] ClO_4 crystallised. Decomposition from 210°. (Found: C, 18.6; H, 2.09; ClO_4, by ion exchange 25.7. $C_7H_8ClHgNO_4$ requires C, 18.3; H, 2.05; ClO_4, 25.2%). The infra-red spectrum (Nujol mull) included a strong sharp absorption band at 423 $cm.^{-1}$ characteristic of co-ordinated pyridine.

Preparation of methylmercuric nitrate solution

Silver nitrate (10.7 gm.) in aqueous acetone (1:1, 20 ml.) was added to methylmercuric chloride (15.8 gm., 1 mol.) in hot acetone (230 ml.). After filtration from the precipitated silver chloride a solution containing methylmercuric nitrate (17.5 gm.) in aqueous acetone (250 ml.) was obtained.

Reaction of methylmercuric nitrate and bipyridyl

A white precipitate was obtained when 2,2'-bipyridyl (0.9 gm., 1 mol.) in acetone (10 ml.) was added to methylmercuric nitrate in aqueous acetone. Crystallisation of the crude complex from methanol or ethanol yielded long fine colourless needles of methyl(bipyridyl)mercury nitrate, [MeHgbipy]NO_3. m.p. 200-201° with decomposition. (Found: C, 30.4; H, 2.55; NO_3, by ion exchange, 14.5. $C_{11}H_{11}HgN_3O_3$ requires C, 30.45; H, 2.55; NO_3, 14.3%).

Reaction of methylmercuric nitrate and triethylamine

Addition of excess triethylamine (1 ml.) to methylmercuric nitrate in aqueous acetone (20 ml.) caused an immediate white precipitate. After washing the solid with acetone and filtering under suction analysis showed the complex to be very low in carbon and hydrogen content for a 1:1 adduct. The complex smelled strongly of amine.

Reaction of methylmercuric nitrate and trimethylamine

Excess trimethylamine was condensed into an acetone solution (20 ml.) containing methylmercuric nitrate (1.6 gm.) The white precipitate obtained was soluble in water and alcohols and was recrystallised from ethanol. Decomposition from 140°. (Found: C, 12.1; H, 2.7. Found after 30 mins. 'in vacuo': C, 10.4; H, 2.5. $C_4H_{12}HgN_2O_3$ requires C, 14.3; H, 3.6%). The trimethylamine was apparently readily lost on evacuation of the sample during the removal of solvent alcohol resulting in low analysis figures.

Reaction of methylmercuric perchlorate and trimethylamine

Excess trimethylamine was condensed into a solution of methylmercuric perchlorate (2.2 gm.) in acetone (20 ml.). The white precipitate obtained was filtered under slight suction and then washed with much benzene containing trimethylamine. The complex was dried by placing the benzene-moist solid in a desicator containing paraffin wax, under an atmosphere saturated with trimethylamine. On attempted analysis after two days the complex lost trimethylamine so rapidly that an accurately weighed sample could not be obtained.

DISPROPORTIONATION REACTIONS

Reaction of methylmercuric chloride and triethylphosphine

Methylmercuric chloride (7.1 gm.) in acetone (75 ml.) was placed in one limb of a Schlenk tube under nitrogen. Triethylphosphine (3.6 gm., 4.5 ml., slight excess over 1 mol.) was added by pipette and the solution shaken to make it homogenous. The reaction was exothermic and the solution became warm. On standing for three days large prismatic crystals began to crystallise slowly from the solution. After several days the solution was filtered and colourless crystalline dichlorobistriethylphosphinemercury, m.p. 161° (decomposition) was obtained. (Found: C, 28.45; H, 6.0; Hg, 38.7; Cl, 13.85; M, cryoscopically in 1.8, 2.7, 4.7, 6.0 weight % aqueous solution, 296, 315, 352, 399. $C_{12}H_{30}Cl_2HgP_2$ requires C, 28.4; H, 5.95; Hg, 39.5; Cl 14.0%; M, 508). The infra-red spectrum corresponded to that of co-ordinated triethylphosphine, but contained two weak bands at 3413 and 1649 cm^{-1} suggesting the presence of a trace of water which was not revealed by elemental analysis. Dichlorobistriethylphosphinemercury was also formed by slow crystallisation from acetone solutions of triethylphosphine and ethyl-, n-propyl- and n-butylmercuric chloride. (Found: C, 28.3; H, 5.9; C, 28.0; H, 5.9; Hg, 39.2; C, 29.0; H, 6.4; Hg, 39.0 respectively. $C_{12}H_{30}Cl_2HgP_2$ requires C, 28.4; H, 5.95; Hg, 39.5%).

Reaction of methylmercuric bromide and triethylphosphine

An acetone solution containing equimolar quantities of triethylphosphine and methylmercuric bromide slowly deposited large colourless crystals of dibromobistriethylphosphinemercury, m.p. 155° (decomposition) on standing for several days. The dibromo-complex was also formed from solutions of triethylphosphine and ethyl-, n-propyl, and n-butyl-mercuric bromide in acetone.(Found: C, 24.0; H, 5.1; C, 24.2; H, 5.2; C, 24.2; H, 5.0; Hg, 33.3; C, 24.0; H, 5.3; respectively. $C_{12}H_{30}Br_2HgP_2$ requires C, 24.15; H, 5.1; Hg, 33.6%).

Reaction of n-butylmercuric iodide and triethylphosphine

When n-butylmercuric iodide and triethylphosphine in equimolar ratio were allowed to stand in acetone solution large colourless needles of di-iodobistriethylphosphinemercury, m.p. 161°, lit.[22] m.p. 157-158°, crystallised slowly over several days. (Found: C, 20.8; H, 4.5. Calc. for $C_{12}H_{30}HgI_2P_2$: C, 20.9; H, 4.4%).

Solubilities of dihalogenobistriethylphosphinemercury compounds

The solubilities of these complexes show a regular decrease from chloride to iodide in polar solvents and a similar increase in non-polar solvents. The dichloride is soluble in cold water, acetone, and methanol but insoluble in hot or cold ether and benzene. The dibromo compound is soluble in cold methanol and acetone and in hot water. Although insoluble in ether, hot or cold, it will dissolve in hot benzene. The di-iodo derivative is insoluble in water but dissolves in warm methanol. It is slightly soluble in cold benzene but insoluble in ether. All three derivatives are soluble in nitrobenzene.

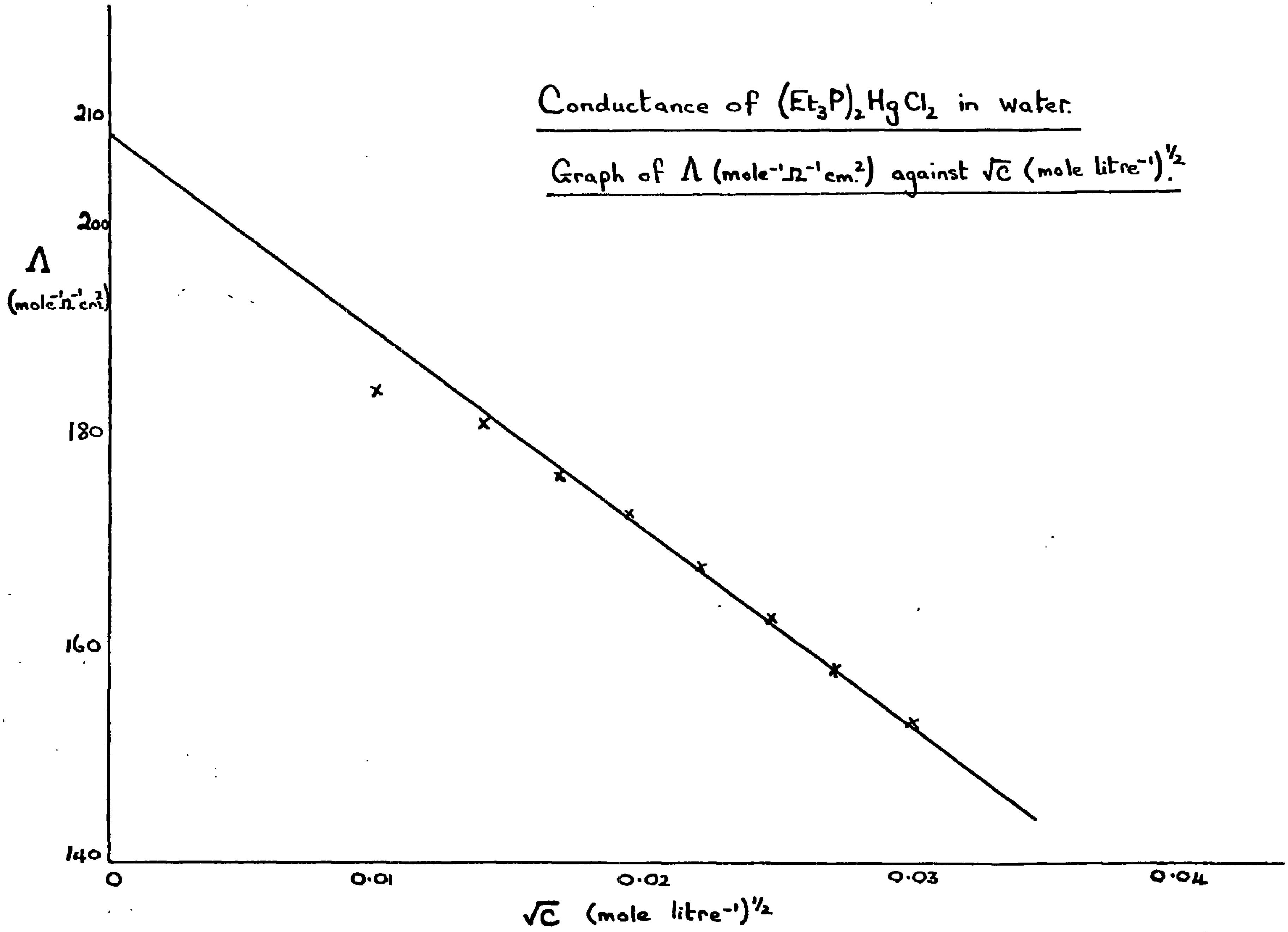
Conductance of dichlorobistriethylphosphinemercury in water

A solution of the dichloro complex (0.0456 gm. in 20 ml. water) was added from a burette to water (20 ml.) in the cell. Values of specific conductance are corrected and a graph of molar conductance, Λ , against $\sqrt{C}$ is shown.

TABLE VI

Conductance of $(Et_3P)_2HgCl_2$ in water

Vol. added (ml.)	C x 10^{-5} (mole $lit.^{-1}$)	C x 10^{-3} (mole $lit.^{-1})^{\frac{1}{2}}$	R x 10^{4} (ohm)	$\underline{K}$ x 10^{-5} obs. ($\Omega^{-1}cm.^{-1}$)	K x 10^{-5} ($\Omega^{-1}cm.^{-1}$)	Λ ($\Omega^{-1}cm.^{2}$)
-	-	-	2.50	0.676	0.004	-
0.2	4.441	6.66	1.16	1.455	0.780	176.3
0.5	10.94	10.46	0.630	2.683	2.011	184.3
0.9	19.32	13.90	0.405	4.173	3.501	181.2
1.3	27.38	16.68	0.308	5.487	4.815	175.9
1.8	37.05	19.25	0.239	7.071	6.399	172.7
2.4	48.08	21.92	0.194	8.712	8.040	167.3
3.0	58.53	24.20	0.165	10.24	9.570	163.5
4.0	74.80	27.35	0.135	12.52	11.85	158.2
5.0	89.76	29.96	0.117	14.44	13.77	153.4



Conductance of $(Et_3P)_2HgCl_2$ in water.

Graph of Λ $(mole^{-1}\Omega^{-1}cm.^2)$ against $\sqrt{C}$ $(mole\ litre^{-1})^{1/2}$.

Extrapolation of the graph to infinite dilution gives a value of Λ_o for the complex = 208 $ohm^{-1}cm.^2$

$$\text{As } \Lambda_o = \lambda_+ + \lambda_-$$

$$\text{and for } Cl^- \quad \lambda_- = 76.3\ ohm^{-1}cm.^2$$

$$\text{then } \tfrac{1}{2}(Et_3P)_2Hg^{2+} = 27.7\ ohm^{-1}cm.^2$$

Reaction of methylmercuric chloride and triphenylphosphine

Methylmercuric chloride (2.5 gm) in acetone (60 ml.) was added to triphenylphosphine (2.6 gm., 1 mol.) in acetone (40 ml.). The solution was shaken and then pumped to concentrate it. On reducing the volume almost to dryness the white solid obtained was filtered and dried. The product was readily soluble in acetone and the infra-red spectrum indicated a mixture of initial reactants, m.p. 60-278°. Similar mixtures were obtained on concentrating ether and benzene solutions of the reactants soon after mixing. On allowing the acetone solution to stand colourless crystals of dichlorobistriphenylphosphinemercury, m.p. 274-276° (decomposition), lit.[21] m.p. 273° (decomposition), were obtained after 5 days. (Found: C, 54.0; H, 4.0. Calc. for $C_{36}H_{30}Cl_2HgP_2$ C, 54.3; H, 3.9%). In another reaction methylmercuric chloride (6.9 gm.) and triphenylphosphine (7.2 gm.) in acetone (250 ml.) were allowed to stand for 150 days at room temperature. After this period dichlorobistriphenylphosphinemercury 6.2 gm., 56.8%) had crystallised.

Reaction of methylmercuric bromide and triphenylphosphine

An acetone solution (100 ml.) containing methylmercuric bromide (2.2 gm.) and triphenylphosphine (1.98 gm. 1 mol.) deposited colourless crystals of dibromobistriphenylphosphinemercury, m.p. 259-263° (decomposition), lit.[21] m.p. 258-259° (dec.), after several days. (Found: C, 48.9; H, 3.3. Calc. for $C_{36}H_{30}Br_2HgP_2$: C, 48.8; H, 3.4%).

Reaction of methylmercuric iodide and triphenylphosphine

On mixing solutions of triphenylphosphine (2.01 gm.) and methylmercuric iodide (2.69 gm., 1 mol.) in a total volume of acetone of 100 ml and allowing the mixture to stand for 5 days colourless crystals of di-iodobistriphenylphosphinemercury (1.3 gm., 34%), m.p. 249-253°, lit.[21], m.p. ca.250° (Found: C, 44.2; H, 3.1. Calc. for $C_{36}H_{30}HgI_2P_2$ C, 44.1; H, 3.1%). After a further 40 days 0.8 gm. of the complex was deposited giving a total of 52.2% of the theoretical amount of complex precipitated in this time.

Disproportionation of methylmercuric halides in boiling benzene

Methylmercuric chloride

Triphenylphosphine (2.50 gm.) in benzene (10 ml.) was added to methylmercuric chloride (2.39 gm., 1 mol.) in benzene (20 ml.) and the resulting solution was boiled for twenty hours in a flask fitted with a reflux water condenser, on an oil bath at 125°. As the refluxing proceeded a solid was gradually deposited from the solution. After this time the solution was cooled to 6° and filtered through a sintered glass filtering crucible to remove the insoluble dichlorobistriphenylphosphinemercury (1.52 gm., 40.1%), m.p. 276-280° (decomposition), lit.[22] 273° (dec.). (Found: C, 54.5; H, 4.25. Calc. for $C_{36}H_{30}Cl_2P_2Hg$: C, 54.3; H, 3.9%). The filtrate from the reaction was distilled to dryness. Benzene (10 ml.) was added to the residual solid and the solution again distilled to dryness leaving more of the dichloro complex (2.205 gm., 58.1%), m.p. 274-279°, as an off white solid. The benzene distillate which contained dimethylmercury was made up to 100 ml. with benzene and a 10 ml. aliquot taken by automatic pipette and refluxed gently for thirty minutes with standard iodine solution (20 ml.), chloroform (2 ml.) and potassium iodide (1 gm.). Titration of excess iodine with standard thiosulphate solution showed that the distillate contained dimethylmercury (0.9378 gm., 85.3%).

Methylmercuric bromide

Triphenylphosphine (2.50 gm.) in benzene (10 ml.) and methylmercuric bromide (2.82 gm.,1 mol.) reacted under the same conditions as described above. After refluxing, the solution was cooled and filtered free of crystalline dibromobistriphenylphosphinemercury (2.54 gm., 60.2%), m.p. 259-263° (decomposition), lit.[24] m.p. 258-259° (dec). (Found:

C, 48.9; H, 3.9. Calc. for $C_{36}H_{30}Br_2HgP_2$: C, 48.8; H, 3.4%). On distillation of the filtrate more of the dibromo complex (1.675 gm., 39.7%), m.p. 250-259° (decomposition) was obtained as a pale brown residue. The total recovery of the complex was 99.9%. Estimation by iodine and thiosulphate showed that the distillate contained dimethylmercury (0.9972 gm., 90.7%).

Methylmercuric iodide.

Triphenylphosphine (2.50 gm.) in benzene (10 ml.) and methylmercuric iodide (3.27 gm., 1 mol.) reacted under analogous conditions. On filtration, di-iodobistriphenylphosphinemercury (3.96 gm., 84.9%), m.p. 249-253° (decomp.) lit.[22] ca. 250° (dec.). (Found: C, 44.2; H, 3.2. Calc. for $C_{36}H_{30}HgI_2P_2$: C, 44.1; H, 3.1%). The filtrate yielded more complex (0.689 gm., 14.8%), m.p. 247-252° (dec.), on distillation giving a total recovery of 99.7%. Analysis of the distillate showed dimethylmercury (0.9675 gm., 88%) was present.

Solvent effect on rate of disproportionation

The reaction between triphenylphosphine (2.5 gm.) and methylmercuric bromide (2.82 gm., 1 mol.) in a total volume of 30 ml. solvent was studied in methanol, acetone and tetrahydrofuran under identical conditions to those used in benzene solution.

Acetone

After reaction dibromobistriphenylphosphinemercury (3.956 gm., 93.8%), m.p. 259-263° (decomposition) was obtained on filtering the solution. (Found: C, 48.7; H, 3.7. Calc. for $C_{36}H_{30}Br_2HgP_2$: C, 48.8; H, 3.4%). The filtrate was distilled and more complex (0.15 gm., 1.6%) recovered.

Methanol

On cooling the reaction solution, and filtering, the crystalline dibromo complex was obtained (3.98 gm., 94.4%) m.p. 258-263° (decomposition). (Found: C, 48.9; H, 3.3. Calc. for $C_{36}H_{30}Br_2HgP_2$: C, 48.8; H, 3.4%). After distillation of the filtrate more complex (0.15 gm., 1.6%) was recovered.

Tetrahydrofuran

When the solution was filtered after twenty hours reflux dibromobistriphenylphosphinemercury (2.72 gm., 64.6%), m.p. 259-263° (decomposition), was obtained. A recovery of a further 31.2% of the complex was made on distillation of the filtrate.

Ethylmercuric bromide and triphenylphosphine

Triphenylphosphine (2.5 gm.) and ethylmercuric bromide (2.95 gm., 1 mol.) in benzene (30 ml.) were treated in the same way as the methyl derivative. In this way a precipitate of dibromobistriphenylphosphinemercury (0.695 gm., 16.5%), m.p. 259-263° (decomposition), was obtained.

n-Propylmercuric bromide and triphenylphosphine

The organomercury compound (3.08 gm.) quickly dissolved in the hot benzene solution (30ml.) containing triphenylphosphine (2.5 gm., 1 mol.). Filtration after twenty hours gave the dibromo compound (0.133 gm, 3.15%) m.p. 259-264° (decomposition).

n-Butylmercuric bromide and triphenylphosphine

Reaction of n-butylmercuric bromide (3.22 gm., 1 mol.) under identical conditions gave the dibromo compound (0.165 gm., 3.9%), m.p. 258-263° (decomposition) on filtration.

Reaction of trichloromethylmercuric chloride and triphenylphosphine

Triphenylphosphine (2.2 gm.) in acetone (20 ml.) was added to trichloromethylmercuric chloride (1.6 gm., 1 mol.) in acetone (20 ml.) and the solution allowed to stand for several hours before concentration. When the volume was reduced to about half a white solid slowly crystallised from solution. Dichlorobistriphenylphosphinemercury, m.p. 273-276° (decomposition), lit.[21] m.p. 273° (dec.), was obtained. (Found: Hg, 24.9. Calc. for $C_{36}H_{30}Cl_2HgP_2$: Hg, 25.2%).

Reaction of p-tolylmercuric chloride and triphenylphosphine

Triphenylphosphine (1.6 gm.) and p-tolylmercuric chloride (2.0 gm., 1 mol.) in acetone solution (200 ml.) were shaken and allowed to stand. Colourless crystals began to form within an hour and an appreciable quantity was precipitated overnight. After 10 days the solution was filtered free of dichlorobistriphenylphosphinemercury, (2.4 gm., 99%), m.p. 271-279° (dec.) lit.[21] m.p. 273° (dec.). (Found: C, 54.3; H, 3.8. Calc. for $C_{36}H_{30}Cl_2HgP_2$: C, 54.3; H, 3.9%).

Reaction of m-tolylmercuric chloride and triethylphosphine

This reaction was carried out in a Schlenk tube under a nitrogen atmosphere. Triethylphosphine (2.15 ml., a slight excess over 1 mol.) in acetone (10 ml.) was added to m-tolylmercuric chloride (4.18 gm.) in acetone (160 ml.). Slight heat evolution was observed and a clear solution resulted. The solution was concentrated by evaporation under reduced pressure to 20 ml., and the dichlorobistriethylphosphinemercury (1.1 gm., 33.9%), m.p. 161-8° (dec.), which had formed as colourless crystals was separated by filtration. (Found: C, 28.9; H, 5.9; Hg, 39.0. $C_{12}H_{30}Cl_2HgP_2$ requires C, 28.4; H, 5.95; Hg, 39.5%). The infra-red spectrum was identical to the dichloro complex otherwise prepared. Water (20 ml.) was added to dissolve traces of the phosphine compound and to precipitate di-m-tolylmercury from solution. The solution was further concentrated and the precipitate obtained crystallised from ether, yielding di-m-tolylmercury (2.22 gm., 90.2%), m.p. 98-100°, mixed m.p. 98-101°. No attempt was made to isolate the remaining phosphine complex in the aqueous acetone solution.

Reaction of m-tolylmercuric chloride and triphenylphosphine

The phosphine (2.36 gm.) in acetone (20 ml.) was added to a solution of m-tolylmercuric chloride (2.94 gm., 1 mol.) in hot acetone. Crystallisation began after about ½ minute and ceased after 7 minutes. After 30 minutes at room temperature dichlorobistriphenylphosphinemercury, 2.14 gm., 59.8%, m.p. 274-276° (decomposition), lit.[21] m.p. 273° (decomp.), was separated. Solvent was distilled from the filtrate and the di-m-tolylmercury, 1.57 gm., 91.3%, m.p. 99-101°, mixed m.p. 99-101°, was separated by ether extraction leaving a residue of more of the dichloro complex, m.p. 274-278°, 1.20 gm. In all 3.34 gm., 93.4%, dichloro complex was recovered.

Reaction of phenylmercuric nitrate and triphenylphosphine

Triphenylphosphine (1.4 gm.) in acetone (20 ml.) was added to a solution of phenylmercuric nitrate (1.8 gm., 1 mol.) in acetone (65 ml.) and the mixture allowed to remain at room temperature for a week. The colourless prisms which slowly formed were collected and found to be dinitratobistriphenylphosphinemercury, $(Ph_3P)_2Hg(NO_3)_2$, (0.70 gm., 22%), m.p. 190° (Found: C, 50.5; H, 3.6. $C_{36}H_{30}HgN_2O_6P_2$ requires C, 50.9; H, 3.6%). In another experiment the phosphine (1.4 gm. 1 mol.) in acetone (10 ml.) was added to phenylmercuric nitrate (1.8gm.) in acetone (65 ml.). The solution was immediately concentrated to a volume of about 50 ml. by evaporation under reduced pressure, when the dinitrato complex (0.6 gm. 20%) crystallised. (Found: C, 50.6; H, 3.7%. The infra-red spectrum was identical with that of the earlier preparation and to an authentic specimen).

Dinitratobistriphenylphosphinemercury

Triphenylphosphine (3.9 gm., 1 mol.) was added to basic mercuric nitrate (4.3 gm.) in dilute (2N) nitric acid (20 ml.) and acetone (200 ml.) and the solution was shaken. On standing overnight small colourless crystals of the dinitrato complex, m.p. 188-189° were deposited. (Found: C, 50.8; H, 3.6. $C_{36}H_{30}HgN_2O_6P_2$ requires C, 50.9; H, 3.6%).

Thermal decomposition of methyl(phenyldimethylphosphine)mercury iodide

The salt (1.1322 gm.) was weighed under nitrogen into a 25 ml. two-neck flask, fitted with a porosity 3 sintered-disc to prevent subsequent loss by sublimation, and attached to a vacuum line suitable for the quantitative manipulation of volatile substances. The flask was then evacuated and heated to 80° by an oil bath. After 30 minutes the crystalline salt had liquified to a viscous melt (i.e. below its melting point of 107°) which bubbled gently as dimethylmercury was slowly evolved. When, after a further 30 minutes, the evolution of dimethylmercury had apparently ceased, the volatile material (0.2478 gm.) was condensed into a V-tube and the residue (0.8856 gm.) was also weighed. The compounds were returned to the vacuum line and heating at 80° was continued for a further 4 hours resulting in a small loss in weight of the residue. The pale yellow viscous residue (0.8809 gm.), which solidified on standing overnight at room temperature, was dissolved in hot methanol (30 ml.) and on cooling yielded colourless needles of di-iodobisphenyldimethylphosphinemercury m.p. 120-121°, mixed m.p. 120-121°. (Found: C, 26.4; H, 2.9. Calc. for $C_{16}H_{22}HgI_2P_2$: C, 26.3; H, 3.0%). The volatile material from the pyrolysis was condensed on an excess of methyliodide which on warming to room temperature, and standing for 30 minutes yielded trimethylphenylphosphonium iodide (0.0436 gm.) derived from the correspondingly small amount of phenyldimethylphosphine (0.0215 gm.) present. The remaining dimethylmercury, together with the excess methyl iodide, was condensed into 0.IN iodine solution (50 ml.) and allowed to remain overnight at room temperature. The solution was then gently boiled with reflux for 3 hours and on cooling the excess iodine was determined by titration with standard thiosulphate solution. The weight of dimethylmercury amounted to 0.2303 gm. (85% of the theoretical for complete disproportionation).

Di-iodobisphenyldimethylphosphinemercury

Addition of phosphine (2 ml., excess over 2 mol.) in methanol (25 ml.) to mercuric iodide (2 gm.) in methanol (45 ml.) caused an immediate yellow precipitate which redissolved on complete addition of the phosphine solution on warming. On cooling the di-iodo complex crystallised as colourless needles. m.p. 121-122°C lit.[22] m.p. 115-7C° (Found: C, 26.3; H, 3.2. Calc. for $C_{16}H_{22}HgI_2P_2$: C, 26.2; H, 3.0%).

Reaction of diphenylmercury and dichlorobistriphenylphosphinemercury

The dichloro complex (1.16 gm.) was added to a solution of diphenylmercury (0.5188 gm., 1 mol.) in a 4:1 acetone/water solution (150 ml.). The dichloro complex did not dissolve appreciably and the solution was vigorously stirred for 4 hours. After this time the white insoluble material (0.96 gm.) was filtered from the solution and washed with acetone. m.p.275° mixed m.p. with starting material 275°.

The above reaction was repeated in aqueous dioxan. Diphenylmercury (0.544 gm.) was added to the dichloro complex (1.131 gm., 1 mol.) in 4:1 dioxan/water solution (144 ml.). The solution was stirred vigorously for 30 minutes after which time all the solid had dissolved. Stirring was continued for an hour and the clear solution allowed to stand overnight. The solution was then distilled to a volume of 40 ml., and on cooling deposited phenylmercuric chloride (0.571 gm., 59.5%) m.p. 254° as pearly plates. After removing the crystalline material the solution was concentrated to about 5 ml. and the phenylmercuric chloride (0.345 gm., 35.9%), m.p. 246-253°, was removed. On further concentration a syrup was obtained which crystallised overnight yielding large colourless needles of triphenylphosphine oxide (0.05 gm.) m.p. 153-154°, lit. m.p. 153°. The infra-red spectrum was identical to that of an authentic sample.

As commercial dioxan had been used without purification as solvent it was possible that impurities in it were reacting with the starting material causing it to dissolve. The dichloro complex (0.518 gm.) was added to a 4:1 dioxan/water solution (66 ml.) and after vigorous stirring for 2 hours it had completely dissolved.

CONDUCTIMETRIC EXPERIMENTS

Determination of the cell constant

This was evaluated by conductance measurements on a solution of 0.01N potassium chloride solution made up by weight to contain 0.37275 gm. salt in distilled water (500 ml.) The solution (20 ml.) was placed in the cell which had previously been purged with nitrogen and allowed to stand in the thermostat for two hours. After this period the resistance of the solution was measured and this value showed no change over a further hour. The determination was repeated with 0.005 N potassium chloride, from dilution of the stock solution, and the resistance of the solution again measured.

Resistance, R, of 0.01NKCl = 1.011×10^2 ohm

Resistance, R, of 0.005NKCl = 1.99×10^2 ohm

At 25° Λ, equivalent conductance, of 0.01NKCl[117] = 141.27 $\text{ohm}^{-1}\ \text{cm.}^2$

and Λ for 0.005NKCl[117] = 143.55 $\text{ohm}^{-1}\ \text{cm.}^2$

As K, specific conductance, = $\frac{l}{a} \cdot \frac{1}{R}$ $\text{ohm}^{-1}\ \text{cm.}^{-1}$

where $\frac{l}{a}$ is the cell constant

then $\frac{l}{a} = K_oR_o$ Where K_o is the specific conductance of the solution and R_o is the measured resistance.

In 0.01NKCl $\frac{l}{a} = 141.27 \times 1.011 \times 10^2 \times 10^{-5} = 0.143\ \text{cm.}^{-1}$

In 0.005NKCl $\frac{l}{a} = 143.55 \times 1.99 \times 10^2 \times 10^{-5} = 0.143\ \text{cm.}^{-1}$

The cell constant, $\frac{l}{a} = 0.143\ \text{cm.}^{-1}$

During this work two conductance cells were used and the cell constant given above pertains to the one used in the later experiments. The cell constant of the cell used in the earlier experiments was determined in an analogous way and was found to be 0.169 cm^{-1}

Conductance of methylmercuric chloride in methanol

Methylmercuric chloride (0.2316 gm.) was dissolved in methanol (100 ml.) to give a 0.00920 M solution. Methanol (20 ml.) was placed in the purged cell and after one hour in the thermostat the resistance of the pure solvent was measured. Methylmercuric chloride solution was run in from a grade 'A' burette and after addition of each aliquot the cell was shaken and allowed to stand 20 minutes to equilibrate to 25° before the resistance was measured. It was subsequently found that the variation in resistance on standing this length of time was insignificant and measurements could be taken immediately after mixing the solution. The change of specific conductance with concentration was calculated from the results tabulated on the following page.

TABLE VII

Conductance of MeHgCl in methanol

Volume MeHgCl solution added (ml.)	Resistance (ohm)	K x 10^{-5}ohm^{-1}cm.$^{-1}$
0.00	7,320	2.309
1.00	7,250	2.331
2.00	7,200	2.348
3.00	7,200	2.348
4.00	7,240	2.334
5.00	7,200	2.348
18.50	7,200	2.348

The specific conductance of methylmercuric chloride of 2.34×10^{-5}ohm^{-1}cm^{-1} did not vary with dilution over the range observed and was not likely to be a significant contribution to the specific conductance of any salt formed in subsequent reactions.

The specific conductance of a 0.0209 M methanolic solution of triphenylphosphine was similarly found to be 2.028×10^{-5}ohm^{-1}cm.$^{-1}$

Conductimetric titration of methylmercuric chloride against triphenylphosphine in methanol

Methanolic methylmercuric chloride solution (20 ml., 0.0092M) was placed in the cell and methanolic triphenylphosphine solution (0.0209M) put in the burette. The phosphine solution was run in from the burette in approximately

1 ml. aliquots. After each addition the cell was shaken to give a homogenous solution and the resulting resistance of the solution was measured. The reading was checked and then a further aliquot of triphenylphosphine solution was added. In this way complete titrations were carried out in a reasonably short period of time minimising any change in conductance resulting from a slow disproportionation reaction. The titration was continued until the conductance of the solution passed through a maximum. The concentration of triphenylphosphine in solution and the corresponding specific conductance values were calculated and plotted against each other. The results obtained are tabulated on the following page.

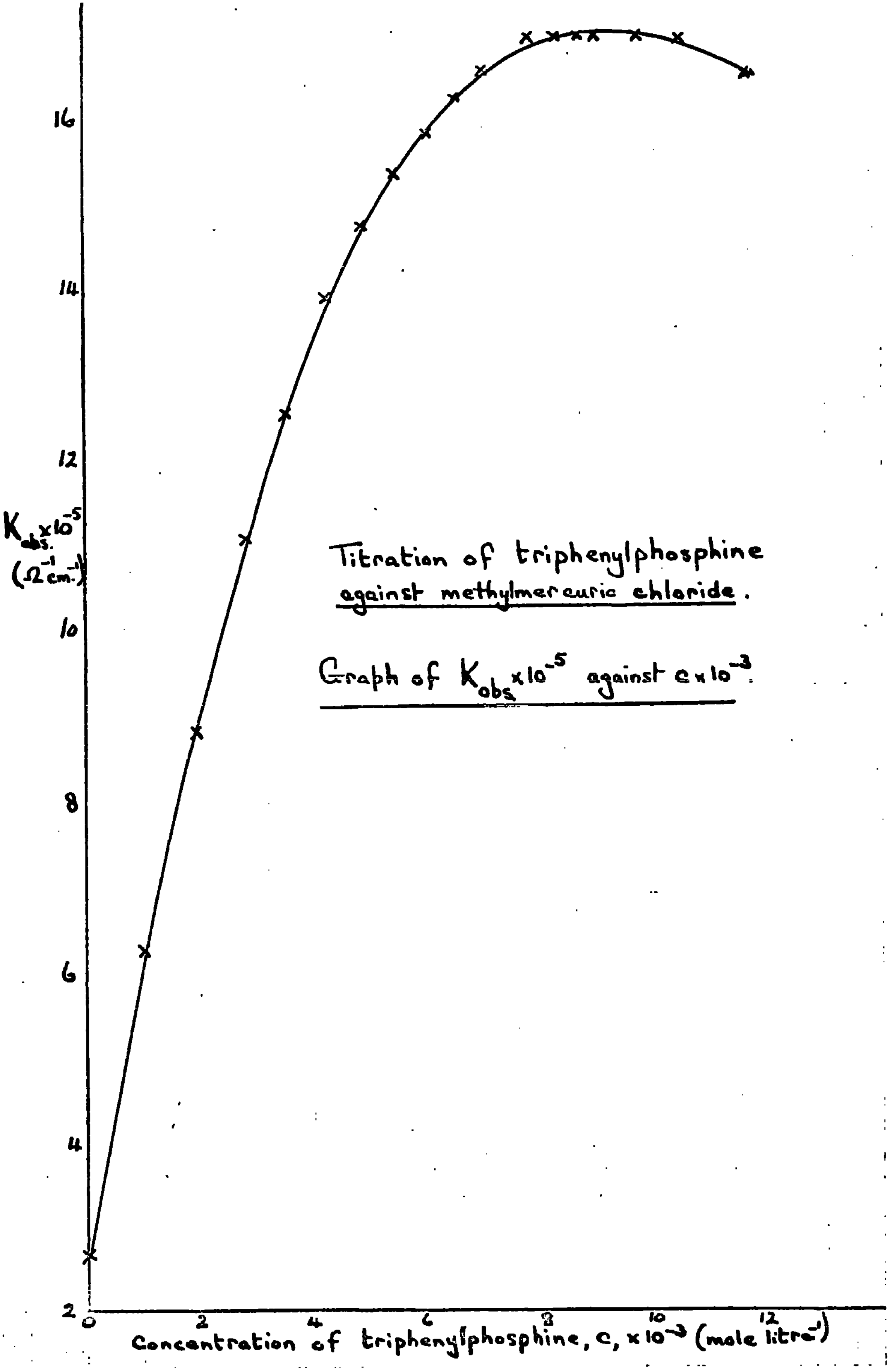
TABLE VIII

20 ml. of 0.0092M MeHgCl solution in cell. Cell constant = 0.169

Conductimetric titration of PPh_3 with MeHgCl in methanol

Vol.PPh_3 solution added (ml.)	conc.C x 10^{-3} (mole.lit^{-1})	R $\pm$ 10(ohm)	K x 10^{-5}ohm^{-1}cm^{-1}
0.00	0.00	6,300	2.68
1.00	0.995	2,710	6.24
2.00	1.900	1,920	8.80
3.00	2.726	1,530	11.05
4.00	3.483	1,350	12.52
5.00	4.180	1,220	13.86
6.00	4.823	1,150	14.70
7.00	5.419	1,100	15.37
8.00	5.971	1,070	15.80
9.00	6.486	1,040	16.25
10.00	6.967	1,020	16.57
11.00	7,416	1,000	16.90
12.00	7.838	1,000	16.90
13.00	8.233	1,000	16.90
14.00	8.606	1,000	16.90
15.00	8.957	1,000	16.90
17.00	9.603	1,000	16.90
20.00	10.450	1,000	16.90
25.00	11.611	1,025	16.49

The maximum specific conductance, K, of the solution of 16.9 x 10^{-5}ohm^{-1}cm^{-1} was attained in a solution 0.007416M in triphenylphosphine and 0.00593M in methylmercuric chloride. The molar equivalence point was after addition of 8.80 ml. of



Titration of triphenylphosphine against methylmercuric chloride.

Graph of $K_{obs} \times 10^{-5}$ against $c \times 10^{-3}$.

phosphine solution. Maximum conductance occurred at a molar ratio of phosphine to mercurial of 1:1.25.

Conductimetric titration of methylmercuric bromide against triphenylphosphine in methanol

Methanolic triphenylphosphine(0.02278M) was titrated from a burette against methanolic methylmercuric bromide (20 ml., 0.00987M) in the cell in a similar manner to that described for the chloride. The concentration of triphenylphosphine was plotted against the specific conductance of the solution and the concentration of mercury at the point of maximum conductance was calculated.

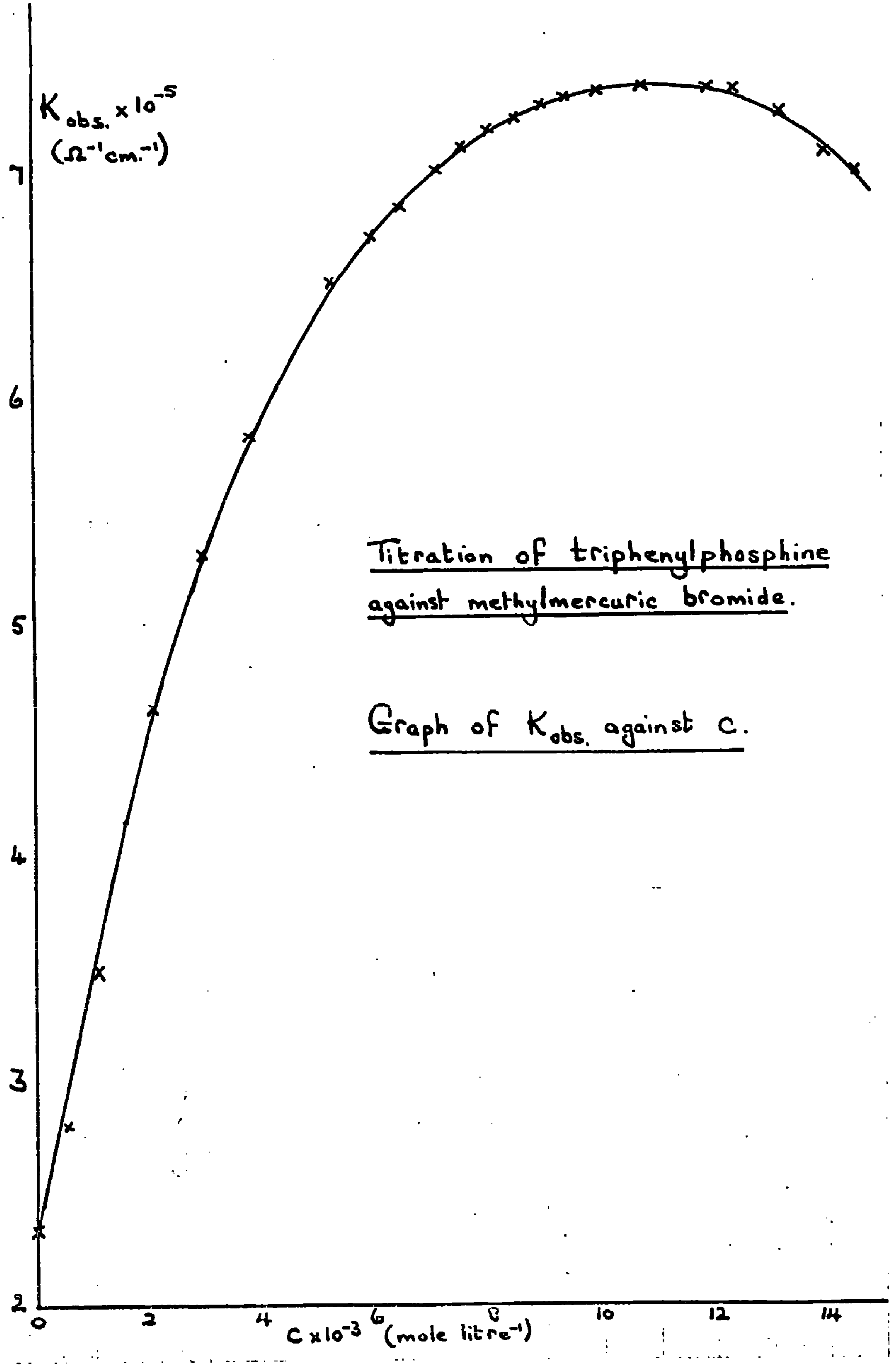
The maximum specific conductance of the solution of $7.35 \times 10^{-5} \text{ohm}^{-1} \text{cm.}^{-1}$ was attained in a solution 0.009763M in triphenylphosphine and 0.00564M in methylmercuric bromide giving a molar ratio of phosphine to mercurial of 1:1.73. The theoretical equivalence point was on addition of 8.66 ml. phosphine solution.

TABLE IX

In cell 20 ml. MeHgBr solution (0.00987M). Cell constant =0.169

Conductimetric titreation of PPh_3 against MeHgBr in methanol

Vol. PPh_3 solution added (ml.)	$C \times 10^{-3}$ (mole lit.$^{-1}$)	$R \pm 10$ (ohm)	$K \times 10^{-5}$ (ohm^{-1} cm.$^{-1}$)
0.00	0.00	7,270	2.330
0.50	0.556	6,050	2.793
1.00	1.085	4,870	3.471
2.00	2.071	3,700	4.568
3.00	2.971	3,180	5.315
4.00	3.797	2,900	5.828
5.00	4.556	2,730	6.190
6.00	5.257	2,600	6.500
7.00	5.906	2,520	6.706
8.00	6.509	2,470	6.839
9.00	7.069	2,410	7.003
10.00	7.593	2,380	7.101
11.00	8.083	2,350	7.191
12.00	8.543	2,340	7.223
13.00	8.974	2,320	7.284
14.00	9.380	2,310	7.317
15.00	9.763	2,300	7.349
16.00	10.124	2,300	7.349
18.00	10.791	2,300	7.349
21.00	11.668	2,300	7.349
24.00	12.426	2,300	7.349
28.00	13.288	2,340	7.223
32.00	14.019	2,380	7.101
36.00	14.644	2,410	7.003



Titration of triphenylphosphine against methylmercuric bromide.

Graph of $K_{obs.}$ against c.

Conductimetric titration of methylmercuric iodide against triphenylphosphine in methanol

Methanolic triphenylphosphine (0.02278M) was titrated against methanolic methylmercuric iodide (20 ml., 0.00991M) placed in the cell. A plot of concentration of phosphine against specific conductance was made and the concentration of mercurial at the point of maximum conductance evaluated.

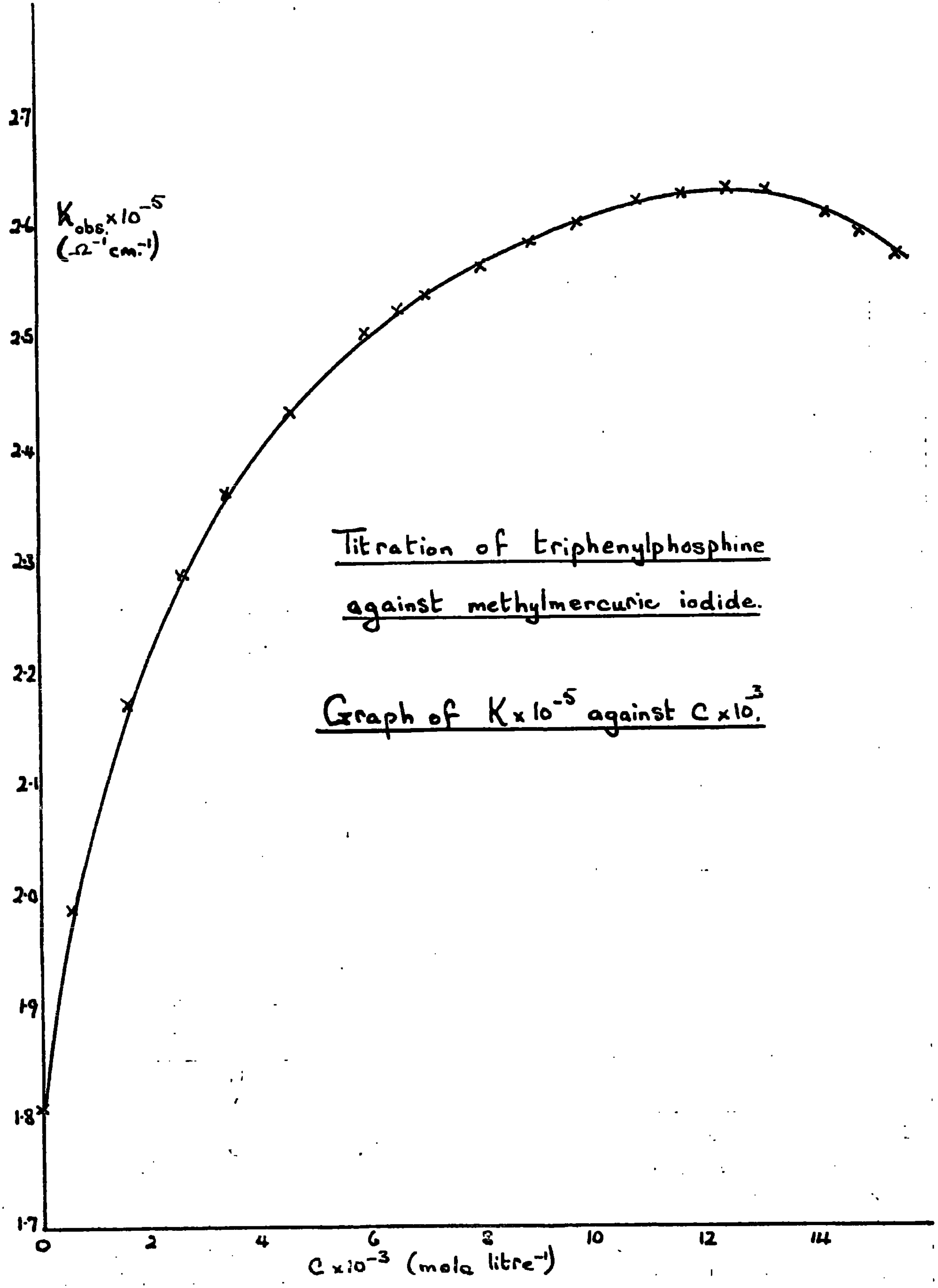
The maximum specific conductance of the solution of 2.63×10^{-5} ohm^{-1}cm.$^{-1}$ was shown in a solution 0.01264M in triphenylphosphine and 0.00435M in methylmercuric iodide giving a molar ratio of phosphine to mercurial of 1:2.87 at the point of maximum conductance. The molar equivalence point was attained after addition of 8.7 ml. of phosphine solution.

TABLE X

Cell constant = 0.169

Conductimetric titration of PPh_3 against MeHgI in methanol

Vol. PPh_3 solution added (ml.)	C x 10^{-3} (mole $lit.^{-1}$)	R ± 10(ohm)	K x 10^{-5}($ohm^{-1}cm^{-1}$)
0.00	0.000	9,350	1.807
0.50	0.556	8,500	1.988
1.50	1.589	7,800	2.167
2.50	2.531	7,400	2.284
3.50	3.393	7,150	2.363
5.00	4.556	6,940	2.435
6.00	5.257	6,840	2.473
7.00	5.906	6,750	2.503
8.00	6.509	6,700	2.523
9.00	7.070	6,660	2.537
10.00	7.593	6,610	2.558
11.00	8.083	6,600	2.561
13.00	8.974	6,560	2.576
15.00	9.763	6,500	2.600
18.00	10.791	6,450	2.620
21.00	11.668	6,440	2.624
24.00	12.426	6,420	2.632
28.00	13.288	6,430	2.628
33.00	14.184	6,480	2.607
38.00	14.925	6,520	2.592
43.00	15.548	6,580	2.568



Titration of triphenylphosphine against methylmercuric iodide.

Graph of $K \times 10^{-5}$ against $c \times 10^{-3}$.

Variation of conductance with time

Solutions of organomercuric halides and triphenylphosphine in methanol and acetone solution were observed. The formation of $(PPh_3)_2HgX_2$ compounds, which crystallised from solutions containing organomercuric halides and triphenylphosphine was accompanied by a decrease in conductance. This was observed for several systems.

Methylmercuric chloride and triphenylphosphine in methanol

Methanolic methylmercuric chloride (20 ml., 0.0092M) and methanolic triphenylphosphine (20.5 ml., 0.01113M) were mixed in the ratio previously found to give the maximum specific conductance. The solution was placed in the cell and values of the resistance were measured over a period of 44 hours. The conductance of the mixture decreased slightly in the first hour and subsequently remained constant. At the conclusion of the experiment a very small colourless crystal presumably $(PPh_3)_2HgCl_2$, had formed in the solution.

TABLE XI

MeHgCl - PPh_3 system. Variation of conductance with time.

Time (hours)	Resistance (ohm)	K x 10^{-5} (ohm^{-1}cm^{-1})
0	980	17.25
½	990	17.07
1	1000	16.90
1½	1000	16.90
18	1000	16.90
19	1000	16.90
24	1000	16.90
42	1000	16.90
44	1000	16.90

It is possible that the two readings in the first 30 minutes are of no significance as the differences from 16.90 are almost within the experimental error.

Methylmercuric bromide and triphenylphosphine in methanol

This system was made up to contain methylmercuric bromide (10 ml., 0.00987M) and triphenylphosphine (15 ml., 0.01113M) in methanol, the ratio previously found to give maximum conductance. The solution was placed in the cell and the change of resistance with time measured. The specific conductance of the solution slowly decreased to a constant value of 4.76 x 10^{-5} after 198 hours. Colourless crystals of dibromobistriphenylphosphinemercury gradually formed in the cell and could be observed after 49 hours.

TABLE XII

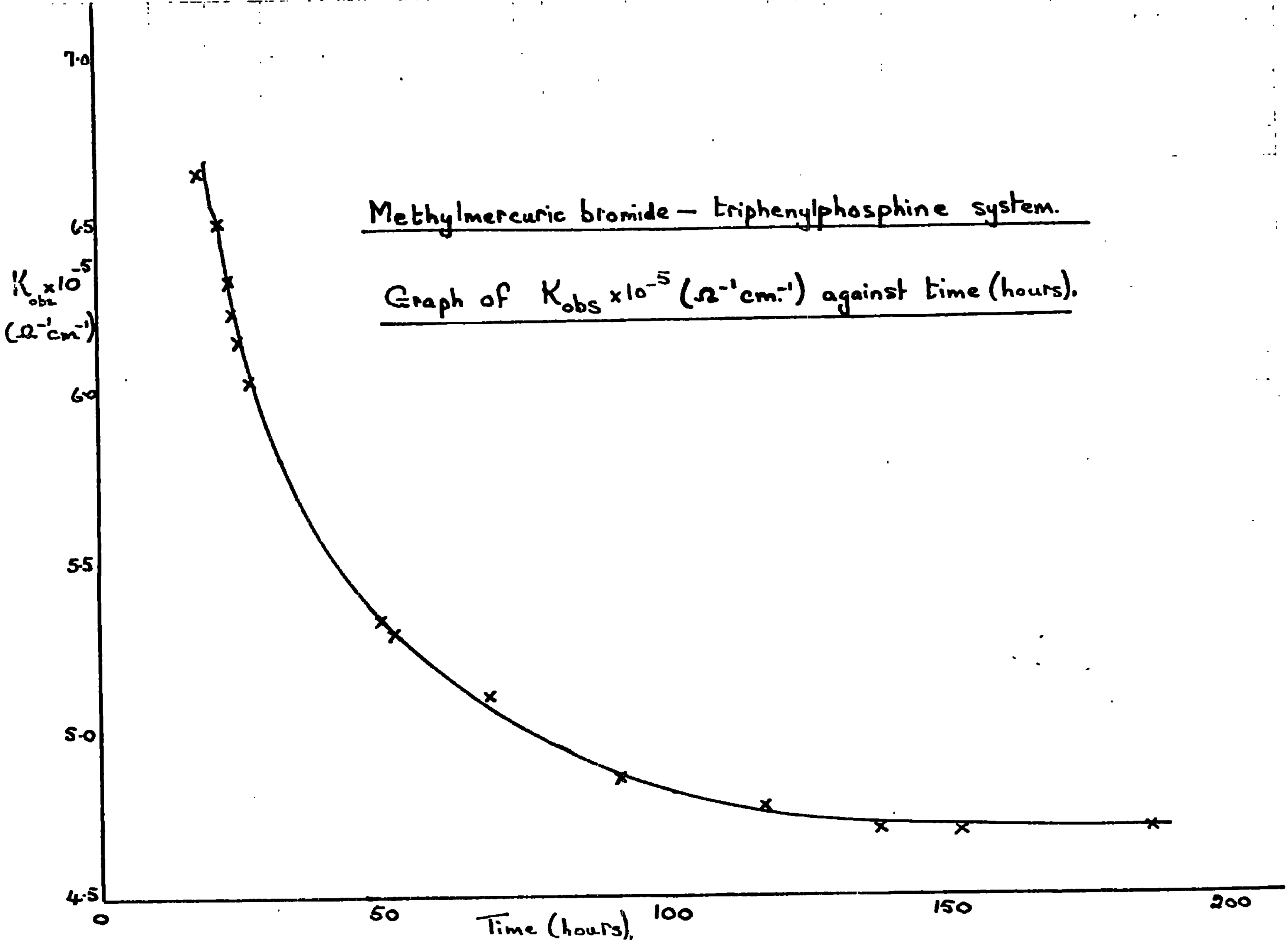
MeHgBr - PPh_3 system. Variation of conductance with time.

Time (hours)	R (ohm)	$K \times 10^{-5}$ $ohm^{-1} cm^{-1}$	Time (hours)	R (ohm)	$K \times 10^{-5}$ $ohm^{-1} cm^{-1}$
0	2490	6.787	69	3320	5.091
18	2540	6.655	92	3480	4.856
22	2600	6.500	117	3540	4.774
23	2670	6.330	162	3600	4.695
24	2710	6.236	186	3590	4.708
25	2750	6.146	198	3550	4.761
27	2800	6.036	210	3550	4.761
49	3140	5.383	219	3550	4.761
50	3180	5.315	282	3550	4.761
52	3200	5.282	292	3550	4.761

A graph of specific conductance against time was plotted.

m-Tolylmercuric chloride and triphenylphosphine in acetone

Triphenylphosphine (2.00 gm.) was dissolved in acetone (30ml.) to give an 0.254M solution. An acetone solution of m-tolylmercuric chloride (0.127M) was made up and 20 ml. placed in the cell. The resistance of the solution was measured and triphenylphosphine solution (10 ml., 1 mol.) was added quickly by pipette. The cell was shaken to give a homogenous solution and readings of resistance with time were noted. The addition of phosphine solution resulted in a rapid large increase in conductance followed after about ½ minute by a steady fall as dichlorobistriphenylphosphinemercury crystallised over a period of about six minutes.


Methylmercuric bromide – triphenylphosphine system.

Graph of $K_{obs} \times 10^{-5}$ ($\Omega^{-1}cm^{-1}$) against time (hours).

TABLE XIII

Specific conductance, K, of the purified acetone = 4.30×10^{-6} ohm^{-1}cm.$^{-1}$

Cell constant = 0.169

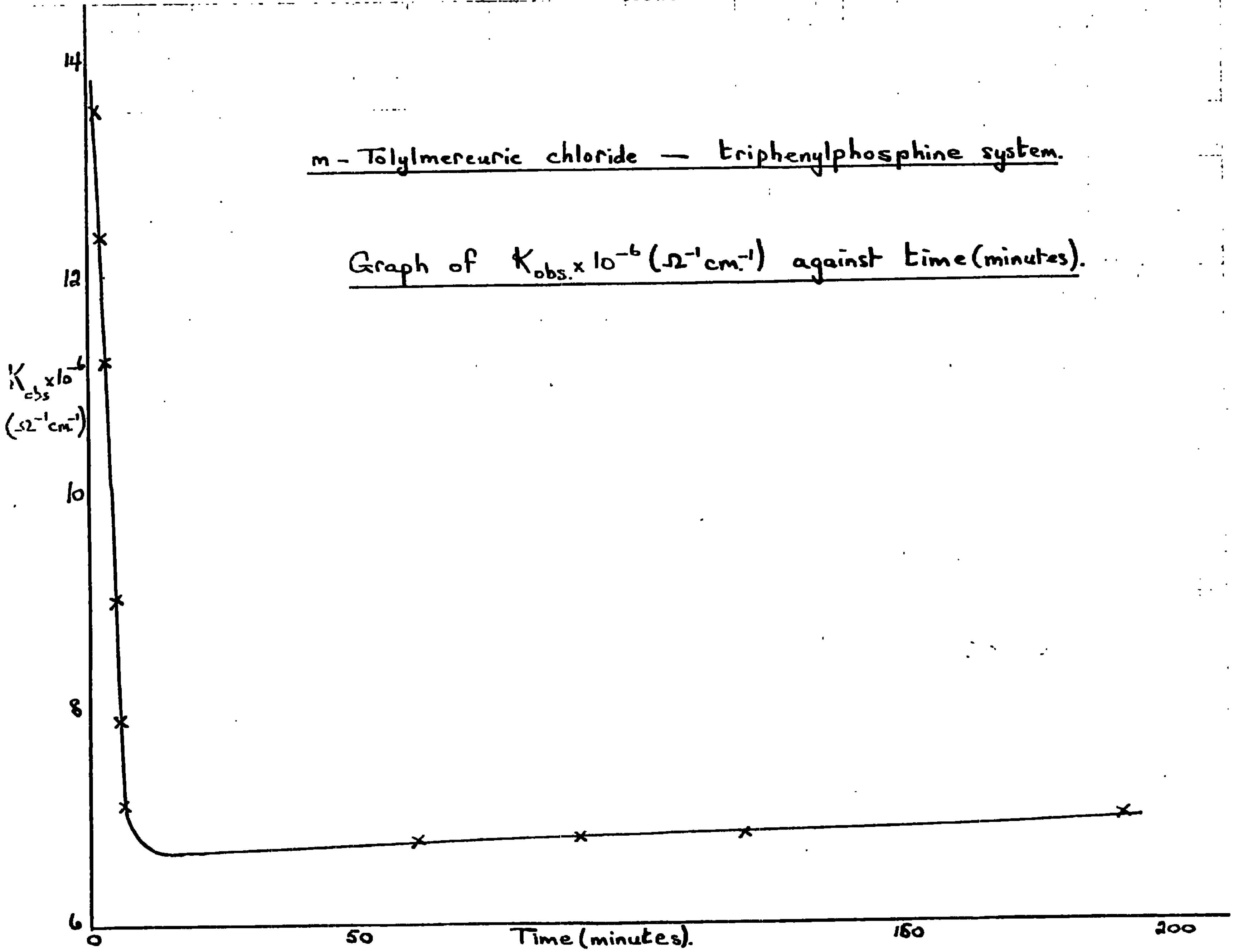
Variation of conductance with time of m-MeC_6H_5HgCl-PPh_3 system.

Time (mins.)	Resistance, R, (ohm.)	K x 10^{-6} (ohm^{-1}cm.$^{-1}$)
0	39000	4.33
0.25	12900	13.10
1.00	12500	13.52
1.50	13500	12.52
2.00	13700	12.34
3.00	15100	11.19
3.50	16800	10.06
4.00	18700	9.04
4.50	20200	8.37
5.00	21500	7.86
5.50	23300	7.25
6.00	23800	7.10
7.00	23800	7.10
9.00	23800	7.10
11.00	23800	7.10
60.00	25000	6.76
90.00	24800	6.81
120.00	24600	6.87

A graph of specific conductance against time was plotted.

A similar reaction was studied in methanol using solutions which were considerably more dilute. To triphenylphosphine solution (20 ml., 0.0113M, K = 2.633×10^{-5}ohm^{-1}cm.$^{-1}$) was added a methanolic solution of m-tolylmercuric chloride m - Tolylmercuric chloride — triphenylphosphine system.

Graph of $K_{obs.} \times 10^{-6}$ ($\Omega^{-1} cm.^{-1}$) against time (minutes).



(7.75 ml., 0.02913M, 1 mol.). The conductance increased immediately on mixing the solutions, and the value of specific conductance ($K = 17.16 \times 10^{-5} ohm^{-1} cm^{-1}$) measured within about ten seconds of mixing the reagents remained unchanged for 19 hours. No disproportionation product was observed to crystallise from solution during this period.

m-Tolylmercuric chloride and triphenylphosphine in acetone

Using the solutions prepared for the conductimetric study of this reaction a quantitative experiment was carried out under similar conditions. Triphenylphosphine (0.65 gm.) in acetone (10 ml.) was added to m-tolylmercuric chloride (0.83 gm., 1 mol.) in acetone (20 ml.) and the resulting solution shaken. Solid material formed in the solution within 5-10 seconds and precipitation ceased after about six minutes. The solution was filtered free of dichlorobistriphenylphosphinemercury (0.59 gm., 59.8%) and evaporated to dryness under reduced pressure. The residue was dissolved in ether and more insoluble phosphine complex was isolated (0.32 gm., 32.4%). On evaporation of ether di-m-tolylmercury (0.51 gm., 103.5%), m.p. 89-100°, contaminated with a trace of the dichloro complex was obtained

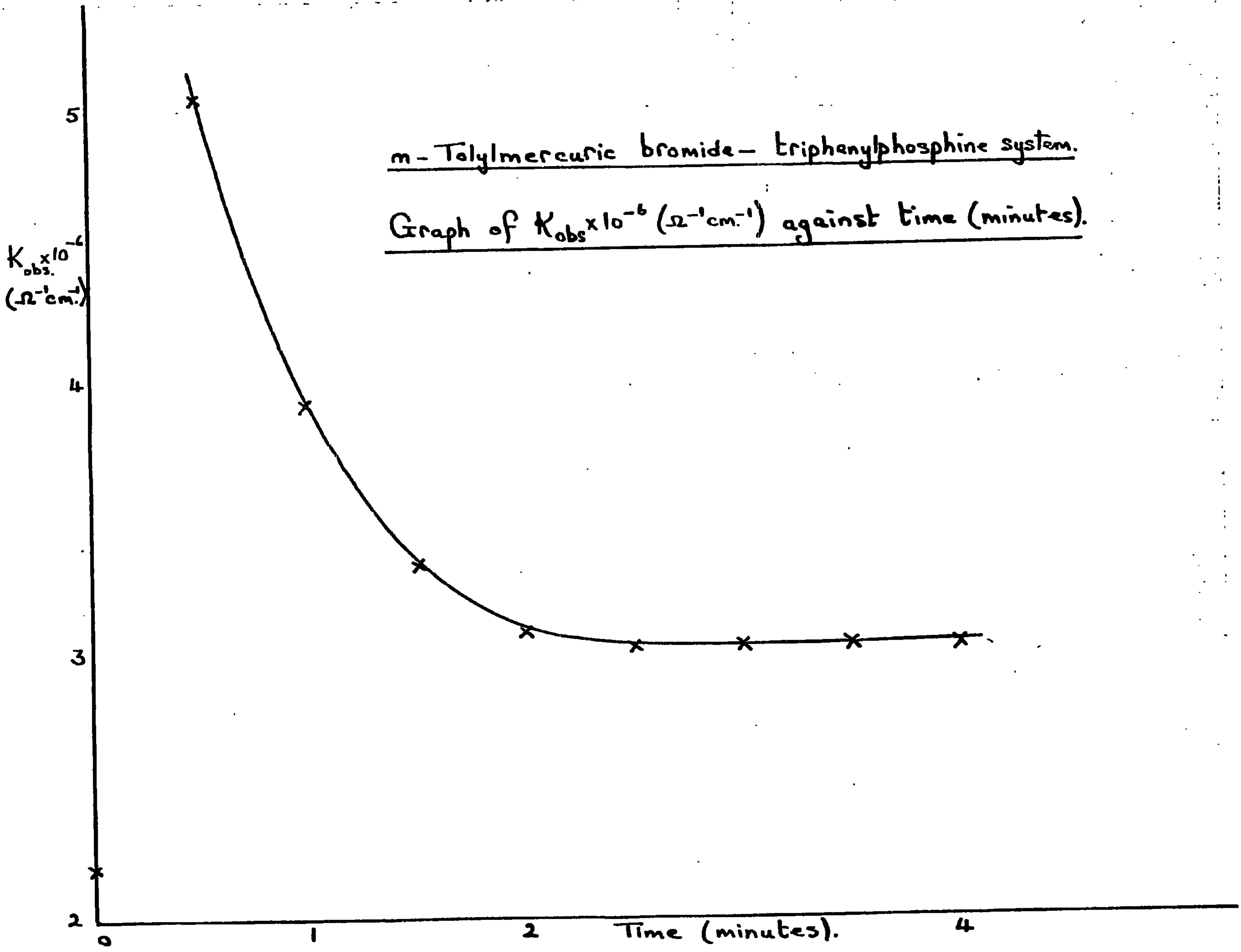
m-Tolylmercuric bromide and triphenylphosphine in acetone

Triphenylphosphine solution (10 ml., 0.254M) was added to an acetone solution of m-tolylmercuric bromide (20 ml., 0.127M, 1 mol.) placed in the conductance cell and the resulting solution shaken. The conductance increased immediately and precipitation of the dibromo complex commenced after about 20 seconds. The conductance was decreasing by the time of the first reading and fell to a steady value after 2½ minutes when the crystallisation of complex also ceased. The results obtained are tabulated below and a graph of specific conductance against time is plotted.

TABLE XIV

Variation of conductance with time of m-$MeC_6H_4HgBr-PPh_3$ system

Time (mins.)	Resistance (ohm)	$K \times 10^{-6} (ohm^{-1} cm^{-1})$
0	77000	2.195
½	33500	5.046
1	43000	3.930
1½	51000	3.313
2	55000	3.073
2½	56000	3.018
3	56000	3.018
3½	56000	3.018



m-Tolylmercuric bromide–triphenylphosphine system.

Graph of $K_{obs} \times 10^{-6}$ ($\Omega^{-1}cm^{-1}$) against time (minutes).

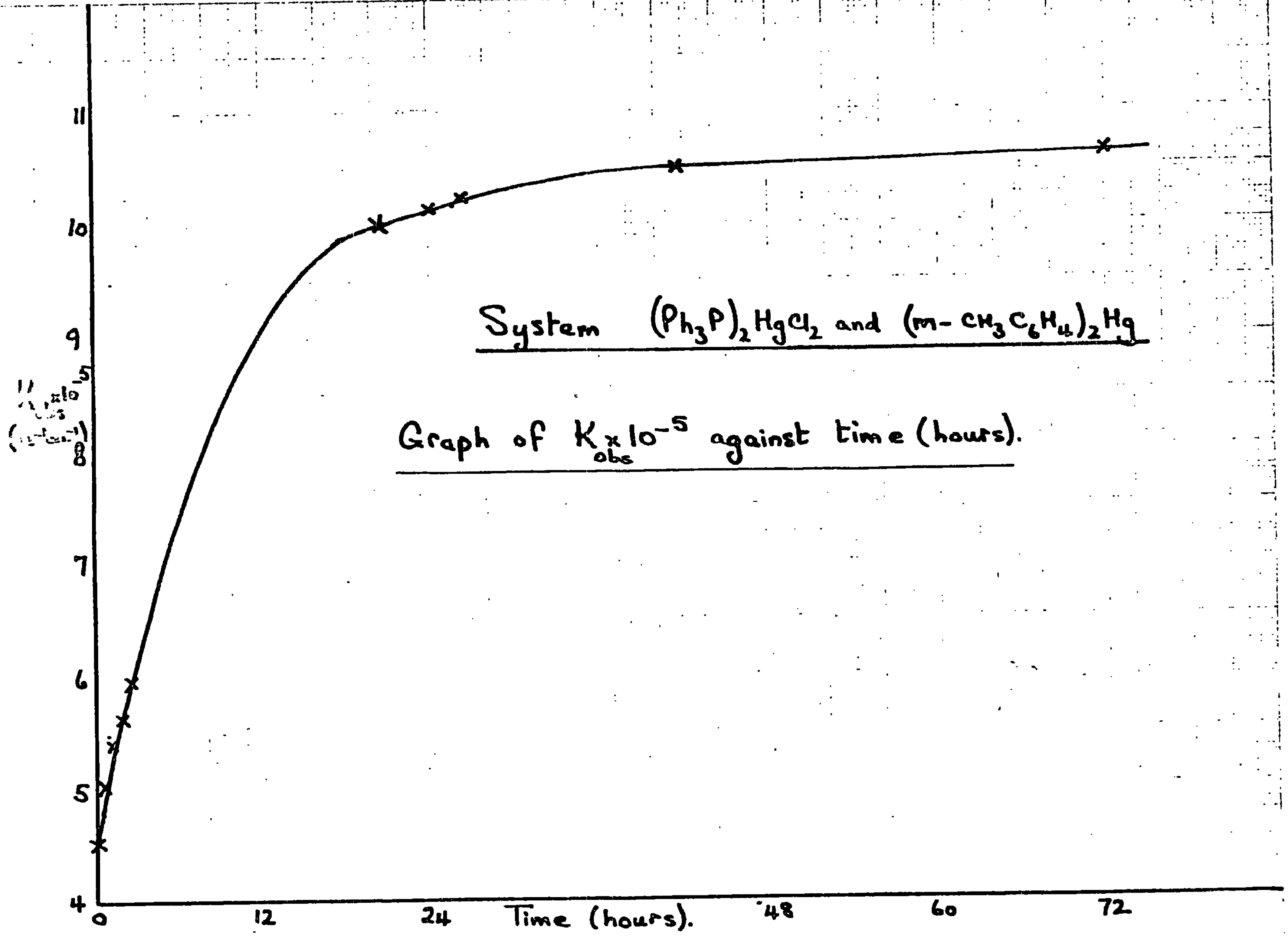
Dichlorobistriphenylphosphinemercury and di-m-tolylmercury in methanol

A saturated methanolic solution of the dichloro complex together with some solid material was placed in the conductance cell and allowed to stand overnight. The resistance of the solution was constant for 3 hours before the addition of di-m-tolylmercury (0.017 gm., in 5 ml. methanol). The specific conductance, K, of the mercurial solution was 2.34 x 10^{-5}ohm^{-1}cm^{-1}. After the addition of di-m-tolylmercury the conductance increased rapidly for several hours but after one day the rate of increase in conductance was very slow.

TABLE XV

Conductance of $(Ph_3P)_2HgCl_2$ - $(m\text{-}MeC_6H_4)_2Hg$ system

Time (hours)	Resistance, R x 10^4(ohm)	K x 10^{-5}ohm^{-1}cm.$^{-1}$ ob.
0	0.307	4.66
½	0.282	5.07
1	0.264	5.42
1½	0.251	5.70
2	0.240	5.96
2½	0.232	6.17
3	0.224	6.38
18½	0.145	9.86
20	0.143	10.00
24	0.141	10.14
43	0.136	10.52
90	0.131	11.91



System $(Ph_3P)_2HgCl_2$ and $(m\text{-}CH_3C_6H_4)_2Hg$

Graph of $K_{obs} \times 10^{-5}$ against time (hours).

Reaction of phenyl(triethylphosphine)mercury nitrate, $[PhHgPEt_3]NO_3$, and sodium bromide

Sodium bromide (0.1 gm., slight excess over 1 mol.) in water (10 ml.) was added to a solution of the nitrate (0.43 gm.) in acetone (30 ml.) and the resulting solution was allowed to stand overnight. The solution was concentrated to 20 ml. and on cooling deposited crystalline diphenylmercury (0.13 gm., 78%) identified by mixed m.p. 122°C and infra-red spectrum. The aqueous-acetone filtrate was evaporated to dryness under reduced pressure and acetone (15 ml.) added to the residue. Sodium nitrate (0.06 gm.) m.p. 305°C was separated by filtration, and evaporation of the filtrate yielded dibromobistriethylphosphinemercury (0.19 gm., 68%), m.p. 158°C, infra-red spectrum identical with an authentic specimen.

Reaction of phenyl(triethylphosphine)mercury nitrate and sodium iodide in methanol

The ultra-violet spectrum of the disproportionation product $(Et_3P)_2HgI_2$ in methanol solution has an absorption maximum centred on 2700Å. The region 2,000- 3400Å was scanned for methanolic solutions of other compounds that could possibly result from the addition of sodium to $[PhHgPEt_3]NO_3$, viz. $NaNO_3$, NaI, PEt_3, Ph_2Hg and PhHgI. Only phenylmercuric iodide had a slight absorption at 2700Å, approximately 5% of that obtained in $(Et_3P)_2HgI_2$ at similar concentration. Measurement of optical density of the di-iodo complex at 2800Å, however, was completely free from any interference.

Methanolic solutions of this complex obey Beer's law at the concentrations studied.

TABLE XVI

Optical density and extinction co-efficients of $(Et_3P)_2HgI_2$

$(PEt_3)HgI_2$ (mole lit^{-1})	2700Å		2800Å	
	Opt.Den.	E	Opt.Den.	E
3.481×10^{-5}	0.373	10,720	0.326	9,365
2.321×10^{-5}	0.248	10,690	0.219	9,434
1.161×10^{-5}	0.124	10,690	0.110	9,470

Spectra were recorded on an Optica C.F.4.D.R. double-beam recording spectrophotometer using spectral grade methanol as solvent in 1 cm. silica cells. Sodium iodide (5.40×10^{-7}mole) in methanol (0.10 ml.), $[PhHgPEt_3]NO_3$ (4.72×10^{-7}mole) in methanol (0.10 ml.) and methanol (4.80 ml.) were mixed and the resulting solution quickly transferred to the spectrometer. The optical density at 2800Å rose rapidly at first and then became constant after 30 minutes at room temperature (ca. 25°) at a value corresponding to 84.5% towards completion of the reaction: $[PhHgPEt_3]NO_3 + NaI \longrightarrow \frac{1}{2} Ph_2Hg + \frac{1}{2}(Et_3P)_2HgI_2 + NaNO_3$. Within 4 minutes of mixing the reactants the concentration of di-iodide had reached 74.5% of its equilibrium value. The reversibility of the reaction was shown by adding diphenylmercury to a methanol solution (originally containing 10.81×10^{-5} mole $litre^{-1}$ NaI and 9.42×10^{-5} mole $litre^{-1}$

[$PhHgPEt_3$] NO_3) and measuring the concentration of $(Et_3P)_2HgI_2$ optically after the elapse of one hour. As the concentration of diphenylmercury was raised to 3.8, 7.5, 11.0, 18.6 and 368 x 10^{-5} mole litre^{-1}, that of $(PEt_3)_2HgI_2$ fell to 3.83, 3.72, 3.39, 3.33 and 1.83 x 10^{-5} mole litre^{-1}.

ANALYTICAL METHODS

The methods of analysis used to determine the content of mercury, carbon and hydrogen, chromium and anions such as halides, perchlorate and tetrafluoroborate are described. The difficulties of obtaining a satisfactory method for mercury determination and the interference of this element in combustion analyses are discussed.

Mercury

Mercury is completely volatilized when its compounds are burnt and partially volatilized when solutions containing mercury salts, particularly the chloride and organic derivatives, are evaporated or boiled. The loss of mercury on evaporating to dryness a solution of mercuric chloride can amount to 40% in a large dish. The extent of loss is less on boiling and amounted to 2.2 mg. of the chloride from a solution containing 1% of mercuric chloride on distilling 150 ml. of water from 300 ml. of solution in 40 minutes.[118] Prevention of mercury-loss by volatilization is thus very important in the decomposition of mercury compounds as several methods involve heating the mercury-containing solution.

Methods of decomposition

There are four important methods by which mercury-containing compounds can be decomposed. Distillation with lime liberates mercury directly and it can be weighed by absorption onto gold foil or dissolved in nitric acid and determined by thiocyanate titration. Although a useful method for micro-determinations[119] it does not appear to be satisfactory on a larger scale.[120] Wet decomposition of the mercury-containing compound with strong acids or liquid bromine and reduction with zinc are of more general application. The difficulty with these methods lies in the limitations they impose on the final method of determination used. Combustion of the sample in oxygen followed by digestion with nitric acid is also limited by the same considerations. The four methods are shown schematically in Table XVII.

Wet Decomposition

Decomposition of methylmercuric chloride by boiling under reflux with concentrated nitric and sulphuric acids respectively or a mixture of these reagents followed by determination of mercury content by thiocyanate titration resulted in low results which were not reproducible. The solutions were refluxed for up to three hours but it is possible that decomposition was not complete. Loss of mercurial from the top of the condenser could not be detected by addition of a drop of dilute bromine solution (the bromine colouration was

TABLE XVII

Methods of decomposing organomercury compounds.

Method of treatment	Form in which Hg is liberated	Comments
Distillation with lime	Metallic Hg	
Wet decomposition		
a) H_2SO_4/HNO_3	Hg^{2+}	Acid digestion
b) H_2SO_4/KNO_3	Hg^{2+}	can be very
c) HNO_3	Hg^{2+}	slow depending
d) $3M-H_2SO_4/KMnO_4$	Hg^{2+}	upon the
e) HCl	Hg^{2+}	mercurial.
f) Liquid Br_2	Hg^{2+}	Bromine decomposition
Br_2/water	Hg^{2+}	is rapid and of
Br_2/acetic acid	Hg^{2+}	general application.
Reduction		
a) Zn/water	Zn/Hg	Zn wool is
b) Zn/H_2SO_4	Zn/Hg	superior to Zn
c) Zn/CHOOH	Zn/Hg	powder.
Oxygen combustion		
O_2/HNO_3 digestion	Hg^{2+}	Gives product free of halogen.

not destroyed) to an exit bubbler fitted to the top of the condenser throughout reflux but a smell of "methylmercury" was discernable. Incomplete removal of halide could also account for the observed results but as other methods of decomposition were found to be superior the problem was not pursued.

Bromine decomposition

Decomposition by bromine, bromine-water, or bromine dissolved in acetic acid was found to be rapid and generally applicable to all mercurials used. The sample was weighed in a small glass boat and transferred in the boat to a beaker covered with an evaporating basin containing ice to prevent loss of mercury by volatilization. Bromine (ca. 5 ml.) was carefully poured over the sample and allowed to react for 10 minutes. Water (ca. 20 ml.) was added and the bromine removed by boiling the solution until it was colourless. Complete decomposition of the organomercury compound was achieved in this way and an aqueous solution of mercuric bromide obtained.

Reduction

Amalgamation with zinc has the advantage of rendering the mercury free from halogen and in a satisfactory state for determination by thiocyanate titration. Analyses using zinc dust for the determination of mercury in dry mercuric chloride (Anala R standard) produced low results. (Found: Hg, 70.7, 71.5, 69.3, 72.2, 72.1. Calc. for $HgCl_2$: Hg, 73.9%).

Variations of the basic method were employed but the theoretical content could not be achieved. Zinc dust was added to the sample in water, acetic or dilute hydrochloric acid respectively until a considerable excess of zinc was present. The solution was allowed to stand several hours, or in some cases was refluxed for 30 minutes, finely ground silica gel was added to precipitate any colloidal mercury and the amalgam washed by decantation through a Gooch crucible prepared by lining with a thick pad of asbestos covered with a layer of silica gel. When the filtrate was no longer acid to litmus the asbestos pad was added to the amalgam in a beaker and dilute (IN) nitric acid added. When action ceased, concentrated nitric acid was added and the solution warmed until all the mercury had dissolved. Permanganate solution was added until a permanent pink colour was obtained and excess removed with aqueous hydrogen peroxide. The solution was then titrated with thiocyanate solution. In many cases the solid material made detection of the end point difficult but in those determinations which gave a sharp end point low values were recorded.

A more satisfactory method was to use zinc wool in place of powder, which led to a simpler procedure. The zinc wool and mercury-containing sample were refluxed in water for an hour. (The mercurial did not have to be in solution). Filtration by Buchner funnel through two Whatman No. 40 filter papers followed by washing with water yielded the amalgam.

With zinc wool the danger of loss of amalgam was considerably smaller than in the case of zinc powder. The amalgam and filter papers were dissolved in nitric acid in a small flask fitted with a reflux water condenser and the resulting solution filtered through a sintered glass disc. Treatment with permanganate and hydrogen peroxide followed by titration with thiocyanate gave acceptable results.

Oxygen combustion

The apparatus used is shown in fig. (viii). The flask was purged with oxygen and concentrated nitric acid (ca. 10 ml.) introduced. Samples were weighed in gelatin capsules and placed in the platinum-wire basket. A fuse of filter paper was attached to the capsule and the fuse ignited. The stopper carrying the basket was quickly put in the flask and the apparatus tightly held. The capsule and mercurial were burnt in this way and after refluxing the nitric acid solution for 30 minutes the sample was ready for determination by one of the finishing methods. This rapid method of determination was accurate in most cases but failed when iodide was present. Attempts to analyse $(Et_3P)_2HgI_2$ and $(Ph_3P)_2HgI_2$ by combustion were unsuccessful as an insoluble solid was obtained at the stage of digestion with nitric acid.

Methods of determination of mercury content

Many methods are described in the chemical literature for the determination of mercury but a volumetric method, particularly thiocyanate titration, is preferable as

Combustion flask

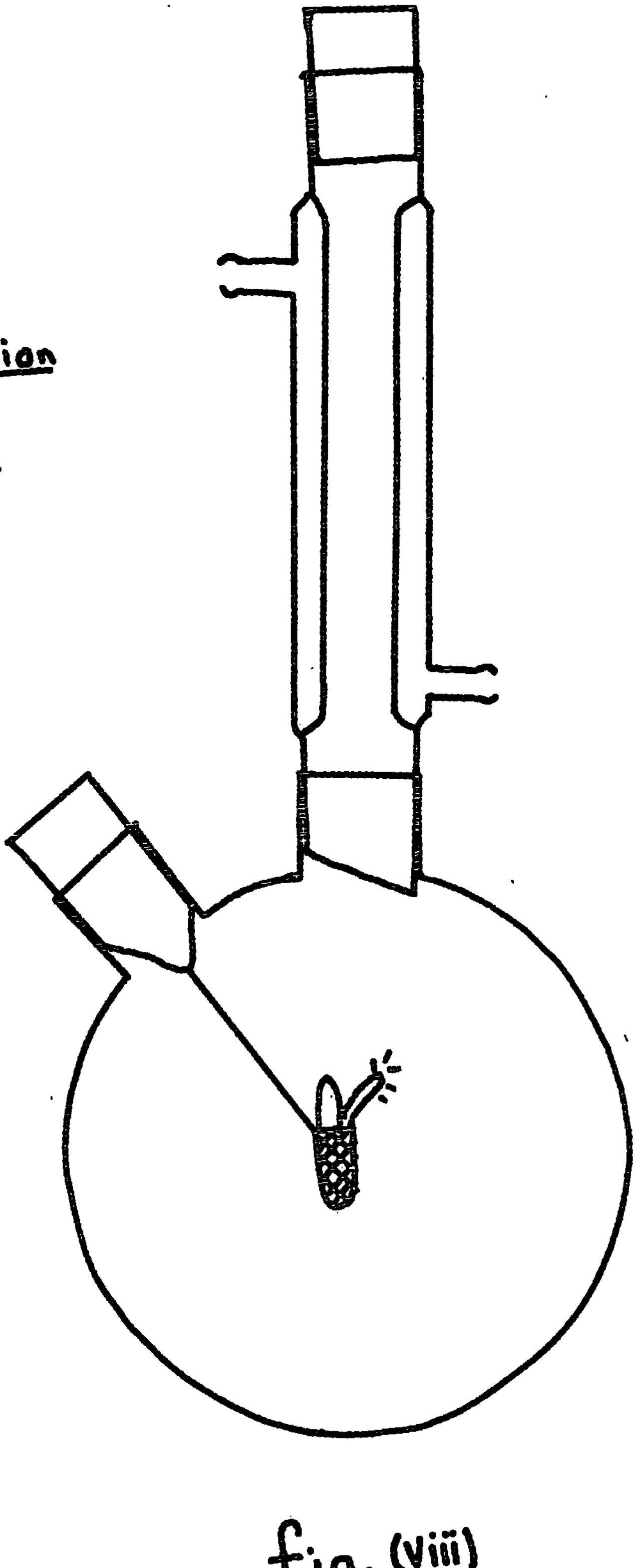


fig. (Viii)

gravimetric methods tend to be lengthy. The method of decomposition of the mercurial is, however, a very important factor and sometimes excludes certain methods of determination. Thus, compounds decomposed by wet decomposition or oxygen-flask combustion methods are unsuitable for determination by thiocyanate titration, as if the sample contains iodine or to a lesser degree bromine these halogens are difficult to remove without volatilization of mercury and they interfere with the volumetric analysis method. For this reason one of the 'finishing' methods used in mercury analysis was a gravimetric determination which could be carried out in the presence of halide as it involved the precipitation of mercuric reineckate from aqueous solution. The other two methods of analysis used were volumetric and involved thiocyanate and E.D.T.A. titrations.

Gravimetrically as reineckate

Ammonium tetrathiocyanatodiamine chromate, Reinecke's salt, was recrystallised as described earlier in this section. A quantity of material to be analysed with a mercury content of less than 50 mg. was weighed in a small glass boat and decomposed by the bromine method. When the bromine had been boiled from solution sodium metabisulphite was added until the colour of bromine disappeared completely and the solution became colourless. The volume was made up to about 300 ml. with distilled water and hydrochloric acid was added until the solution was approximately 0.5N in HCl. The solution was warmed to 60°, removed from the source of heat and a cold aqueous solution (25ml.) of ammonium reineckate (ca.0.5 gm.) was slowly added from a dropping funnel with continuous stirring of the mercury solution. A pale pink flocculent precipitate of mercuric reineckate was formed and when all of the Reinecke salt had been added the solution was allowed to cool for 10 minutes. A Gooch crucible with a porosity 4 sintered glass disc was used to collect the precipitate. The crucible was washed with hot water and methanol, dried in an oven at 110° for 45 minutes, cooled for 30 minutes in a desiccator and weighed after 5 mimutes on the balance pan. The mercuric reineckate was collected on the crucible by filtration under suction, washed with hot water and methanol and weighed after drying in the same manner as that described for the empty crucible. The percentage of mercury in the compound was calculated and determinations were done in duplicate and triplicate. In all a determination took 2 hours.

Occasionally only a very sparse precipitate was obtained due to the solution being too hot on addition of the ammonium salt. The method gave erratic results in the presence of iodide and could not be used for iodine-containing compounds A further drawback of the method was the formation of oily bromination products from compounds containing aromatic groups such as triphenylphosphine and -arsine on initial decomposition. Decomposition of $[MeHgAsPh_3]ClO_4$ with bromine and subsequent treatment of the solution with ammonium reineckate gave only a trace of mercuric reineckate along with a colourless precipitate which was soluble in methanol. The original complex had not apparently been destroyed completely by treatment with bromine.

TABLE XVIII

Determination of Mercury by the reineckate method

Compound	Required Hg%	Found Hg%
$HgCl_2$	73.9	73.4, 72.9, 74.6, 74.4
MeHgBr	67.9	66.7, 68.3, 67.1, 68.7
$[MeHgPEt_3]Cl$	54.3	53.2, 54.4
$[MeHgPEt_3]ClO_4$	46.3	46.4, 46.5
$[MeHgPPh_3]ClO_4$	34.7	34.6, 34.6
$[MeHgPMe_3]ClO_4$	51.3	49.9, 50.0
$[MeHgAsEt_3]ClO_4$	42.0	41.3, 41.5

E.D.T.A. titration

Titration with E.D.T.A. is a satisfactory method for the determination of mercury in the absence of interfering material such as zinc. It is obviously not suitable if the mercurial has been decomposed by reduction with zinc but can be used to finish wet decomposition or preferably oxygen combustion methods.

In a determination the mercury-containing solution was made up to a known volume and an aliquot titrated with sodium hydroxide solution to pH 4.5 using B.D.H. 4.5 as indicator.

Further aliquots of the solution were similarly treated and brought to pH 4.5 omitting the indicator. At this point hexamine (0.5 gm.) was added as a buffer and four drops of xylenol orange as indicator. The solution was titrated with standard E.D.T.A. to the end point shown by a colour change from red to yellow. The mercury content was then calculated.

The pH of the solution was critical and slight errors in the titration with sodium hydroxide caused considerable variation in the E.D.T.A. titre. The xylenol orange could be screened with B.D. H. 4.5, enabling accurate adjustment of pH for each titration. This, however, detracted slightly from the end point giving a colour change from mauve to grey. The presence of bromide in the solution made the end point less distinct thus limiting the application of the method. Organomercury complex salts other than bromide and iodide gave satisfactory results and coupled with an oxygen combustion decomposition this is a rapid method for the determination of mercury.

Thiocyanate titration

This was carried out as described in the literature using ferric alum as indicator. It is an accurate method but fails in the presence of halide which constitutes the chief drawback. It was not suitable therefore as a finishing method following bromine decomposition nor after an oxygen combustion when the compound contained bromide or iodide. The only general decomposition method, by amalgamation with zinc, was however, readily completed by a thiocyanate titration. E.D.T.A. of course was not applicable to determination of zinc amalgams. A complete determination of mercury content in an organomercury sample by amalgamation with zinc and thiocyanate titration took in all about two hours.

Summary of methods of mercury analysis

Several methods are available for the decomposition and subsequent determination of mercury in organomercury compounds. The 'finishing' method used is frequently dependent upon the way in which the mercurial was decomposed. Only combustion, reduction by amalgamation with zinc, and reaction with bromine were found to decompose the organomercury compounds satisfactorily and these methods, among others, are set out in Table XVII.

Interference in the actual determination of mercury arose from the presence of organic material in the case of E.D.T.A. titrations but this could be overcome by fuming the solution containing added concentrated nitric acid almost to dryness. The most general interfering species was halide ion and this resulted in poor end points. In this respect the gravimetric determination of mercury by reineckate precipitate was advantageous as it was uneffected by chloride or bromide and the rapid bromine decomposition method was used to render the mercury in a suitable form. The drawbacks to this particular method were the occasional failure of the precipitate to form and the time involved in drying the crucible and precipitate. Decomposition with bromine was also of restricted application and excluded determinations involving thiocyanate or E.D.T.A. due to the interfering bromide introduced.

Oxygen combustion was a rapid decomposition method very well suited to mercurials that did not contain bromine or iodine. Subsequent titration with thiocyanate provided a method of analysis for mercury which could be carried out in 30 minutes. In general thiocyanate was preferred to E.D.T.A. titrations because of the stringent pH requirements of the latter.

The great advantage of decomposition by amalgamation with zinc lay in the analysis of iodides or otherwise difficult compounds such as $[MeHgAsPh_3]ClO_4$. The mercury was obtained in a state free from halide. Due to the presence of excess zinc E.D.T.A. determination was unsuitable and thiocyanate was used to finish the method.

TABLE XIX

Analysis scheme for mercury

Method of decomposition	Method of determination
Bromine	Reineckate precipitate
Zinc amalgam	Thiocyanate
Oxygen combustion	Thiocyanate or E.D T.A.

The methods of decomposition and determination fall naturally into pairs and are shown in Table XIX

Carbon and hydrogen

Combustion analyses were carried out by Mr. T.F. Holmes of this department. Difficulty was experienced in the course of determining the carbon and hydrogen content of mercury-containing compounds due to volatilization of the metal and its transport in the oxygen flow to the absorption train. In this way high values of hydrogen were always obtained and frequently the determined percentage of carbon was also unacceptable. This difficulty has been overcome in slow combustion methods by packing gold wire into the end of the combustion tube. However, in the rapid empty tube method used in these laboratories, attempts to remove the mercury by a baffle of gold foil failed, no doubt due to the high flow rate and correspondingly short contact time. The mercury was finally removed by depositing gold on asbestos wool and packing this loosely in a 'Flaschentrager' tube which was placed between the combustion tube and the absorption train. In this way numerous determinations were carried out without it being necessary to regenerate the gold-asbestos which was easily done by heating the tube containing it in a fumes cupboard. Although there was a risk of absorption of water in the gold tube, as this was not heated, such a discrepancy did not occur in any of the determinations carried out.

Gold— asbestos was prepared by first heating "Gooch" asbestos to 800-1000°C for several hours to remove any organic material. After cooling, the asbestos was soaked in an ether solution of gold (III) bromide and the asbestos so saturated was pumped dry. On heating, bromine was readily lost and the gold asbestos was heated at about 800°C for three hours. It was then ready for use.

Determinations of carbon and hydrogen using the gold tube to amalgamate with mercury volatilized on combustion are shown in Table XX.

The combustion method for carbon and hydrogen analysis could not be applied to obtain a simultaneous determination of mercury content by weighing the metal amalgamated on the gold asbestos. Attempts to do this showed that only a variable percentage of total mercury in the sample was collected in the tube containing the asbestos. Examination of the boat, which originally contained the sample, at the termination of the combustion revealed that some solid material still remained. Apart from this possible source of loss, mercury vapour also condensed on emerging from the furnace before entering the absorption train thus rendering a quantitative recovery impossible.

Chromium

Approximately 0.4 gm. complex was weighed accurately, concentrated sulphuric (20 ml.) and nitric (4 ml.) acids were added, and the solution boiled for several minutes. After cooling the solution was diluted to about 300 mls. and again brought to the boil. A 2.5% silver nitrate solution (containing about 0.01 gm. $AgNO_3$ per 0.01 gm. Cr) was added

TABLE XX

Determination of carbon and hydrogen in mercury-containing compounds

Compound	Molecular formula	Required		Found	
		C%	H%	C%	H%
$[\mathrm{MeHgPMe_3}]\mathrm{Cl}$	$C_4H_{12}ClHgP$	14.5	3.70	14.7	3.73
$[\mathrm{MeHgPMe_2Ph}]\mathrm{Cl}$	$C_9H_{14}ClHgP$	27.8	3.60	27.5	3.66
$[\mathrm{MeHgPEt_3}]\mathrm{Br}$	$C_7H_{18}BrHgP$	20.3	4.35	20.5	4.50
$[\mathrm{MeHgPMe_2Ph}]\mathrm{I}$	$C_9H_{14}HgIP$	22.5	2.94	22.5	2.92
$[\mathrm{EtHgPMe_3}]\mathrm{Cl}$	$C_5H_{14}ClHgP$	17.6	4.13	17.4	4.23
$[\mathrm{EtHgPEt_3}]\mathrm{Br}$	$C_5H_{14}BrHgP$	22.5	4.71	22.5	4.75
$[\mathrm{Pr^nHgPMe_3}]\mathrm{Cl}$	$C_6H_{16}ClHgP$	20.3	4.54	20.2	4.60
$[\mathrm{Pr^nHgPMe_2Ph}]\mathrm{Cl}$	$C_{11}H_{18}ClHgP$	31.7	4.35	31.5	4.30
$[\mathrm{Bu^nHgPMe_3}]\mathrm{Cl}$	$C_7H_{18}ClHgP$	22.8	4.91	22.7	4.81
$[\mathrm{Bu^nHgPMe_2Ph}]\mathrm{Cl}$	$C_{12}H_{20}ClHgP$	33.4	4.67	33.4	4.74
$[\mathrm{Bu^nHgPMe_3}]\mathrm{I}$	$C_7H_{18}HgIP$	18.25	3.91	18.1	3.86
$[\mathrm{MeHgbipy}]\mathrm{NO_3}$	$C_{11}H_{11}HgN_3O_3$	30.45	2.55	30.4	2.55
$[\mathrm{MeHgAsPh_3}]\mathrm{ClO_4}$	$C_{19}H_{18}AsClHgO_4$	36.7	2.90	36.95	2.90
$[\mathrm{MeHgPPh_3}]$ $[\mathrm{Cr(NH_3)_2(SCN)_4}]$	$C_{23}H_{24}CrHgN_6PS_4$	34.8	3.05	34.9	3.15
*$(\mathrm{Et_3P})_2\mathrm{HgBr_2}$	$C_{12}H_{30}Br_2HgP_2$	24.15	5.07	24.2±0.1	5.13±0.14

* This compound was used as a standard. The analytical values and the errors quoted are from 12 separate determinations.

followed by ammonium persulphate (ca. 0.5 gm.) and the solution was further boiled for 10 minutes. When the solution had cooled, a known excess of standard ferrous ammonium sulphate solution was added and the excess titrated with standard permanganate. The solution was again boiled to destroy the slight excess permanganate and titrated again to obtain a blank which was subtracted from the original titre.

Chromium was determined in the reineckate complexes in this way. $[MeHgPEt_3][Cr(NH_3)_2(SCN)_4]$ was so analysed. (Found: Cr, 7.9. $C_{11}H_{24}CrHgN_6PS_4$ requires Cr, 8.0%). The triphenylphosphine complex was also analysed, (Found: Cr, 6.4. $C_{23}H_{24}CrHgN_6PS_4$ requires Cr, 6.5%).

Anion determination

Complexes derived from anions of strong acids, BF_4^-, ClO_4^-, NO_3^-, were suitable for anion exchange analytical methods. A 10 cm. column was packed with Amberlite I.R.A. 400 resin in the Cl^- form. This was converted to the OH^- form by treating with 4% NaOH (250 ml.) at a flow rate of 10 ml./minute. The column was washed with 1 litre of demineralised water at a flow rate of 1 ml. per minute and protection with a soda-lime tube against atmospheric carbon dioxide was included. The complex (ca.2 m.equiv.) in water or water-acetone solution (5-10ml.) was allowed to percolate through the column and drip into standard $HClO_4$ (25 ml.) at a rate of about one drop every five seconds. The column was washed with demineralised water until the washings were no more alkaline than pH 8-9.

The perchloric acid excess was then back titrated with standard NaOH using bromocresol green as indicator. This method was satisfactory for anions of strong acids except when the cation was methyl(triphenylphosphine)mercury. In this case the salt was sparingly soluble in water and attempts to carry out exchange in acetone solution caused deposition of the insoluble complex on the column while washing the hydroxide out.

Cation exchange on a column of Amberlite IR - 120 resin in the hydrogen form followed by titration of the acid produced with standard NaOH solution was also successful.

DISCUSSION

DISCUSSION

Mercuric halides readily form complexes and those derived from tertiary phosphines and arsines are particularly numerous. On the other hand complexes of dialkyl- or diaryl- mercurials have never been reported (with the exception of compounds such as $(C\,Cl_3)_2Hg$ and $(C_6F_5)_2Hg$ containing strongly electron-attracting organic groups), presumably due to the high electron density on the mercury atom in this environment and its corresponding inability to accept a further partial negative charge. The complex-forming strength of organomercury salts has been relatively little studied. Raman spectra studies have demonstrated the formation of the salt $[MeHgSMe_2]NO_3$ in aqueous solution when dimethylsulphide is added to methylmercuric nitrate in water.[29] Pyridine forms a 1:1 complex with p-tolylmercuric nitrate,[121] $[\underline{p}\text{-}MeC_6H_4Hgpy]NO_3$, m.p. 210°C, and also with 2-chlorovinylmercuric chloride, $[ClCH{:}CHHgpy]Cl$, m.p. 76°C with decomposition.[99] The triethylphosphine complex of methylmercuric chloride, $[MeHgPEt_3]Cl$, which behaves as a 1:1 electrolyte in solution, has been isolated and conductometric titrations of triethylphosphine and phenyldimethylphosphine against ethylmercuric chloride in methanol confirm that similar 1:1 salts are formed in these cases.110 Conductometric evidence indicating the presence of the salt

$[PhHgPPh_3]Cl$ in dilute aqueous dioxan is reported but only phenylmercuric chloride was recovered from the solution.[106] In contrast to these results is the statement that tertiary phosphines cause disproportionation of alkyl- and aryl-mercuric halides.[109] This reaction has subsequently been applied to prepare bis-carbomethoxymercury from the organo-mercuric chloride and triphenylphosphine:[115]

$$2\ ClHgCOOMe + 2\ PPh_3 \longrightarrow (Ph_3P)_2HgCl_2 + Hg(COOMe)_2$$

In a similar manner perchlorovinylmercuric chloride can be converted to the bis-mercurial.[108] By a presumably analogous reaction ammonia has been used to obtain bis-2-chlorovinyl-mercury from 2-chlorovinylmercuric chloride,[97] in contrast to pyridine which forms a salt, and a detailed kinetic study of the disproportionation reaction that occurs on addition of ammonia to a solution of an ester of α-bromomercuriphenylacetic acid, PhCH(HgBr)COOR, has been made.[111-4] The aim of this work was to prepare a representative series of organomercury complexes, mainly with tertiary phosphines, and to gather some information on factors affecting their disproportionation.

Alkyl(tertiary phosphine)mercury halides

Organomercury tertiary phosphine halides were isolated only with alkylmercuric halides. Attempts to prepare similar complexes of aryl derivatives resulted in rapid disproportionation and isolation of the dihalo complex, $(R'_3P)_2HgX_2$, and the mercurial, R_2Hg. Disproportionation slowly occurred if a solution of an alkyl complex was allowed to stand for a prolonged period of time. For instance, on addition of triethylphosphine to methylmercuric chloride in acetone a clear solution was obtained which yielded the complex salt, $[MeHgPEt_3]Cl$, m.p. 84-85°C, on concentration. If, however, the solution was allowed to stand at room temperature, large prismatic crystals of the disproportionation product, $(Et_3P)_2HgCl_2$, m.p. 161°C, appeared after three days. Decomposition even occurred in the solid phase and compounds stored at room temperature under a nitrogen atmosphere for several weeks began to cake and lose their crystalline appearance, due presumably to disproportionation. Storage at -15°C did not prevent this decomposition although it appeared to prolong the time that the product could usefully be stored.

The complex salts derived from alkylmercuric halides and various tertiary phosphines are shown in Table XXI. They were prepared by addition of the phosphine to a solution of alkylmercuric halide. If the preparation was carried out in ether an immediate precipitate of the complex salt was usually obtained and this was quickly recrystallised from another solvent, frequently acetone or alcohol. Alternatively the complex could be prepared in acetone, in which case the solution had often to be concentrated to small volume before crystallisation occurred. In either case isolation and characterization by melting point and analysis were carried out quickly to prevent any contamination of the complex by products of the disproportionation reaction.

TABLE XXI

Alkyl(tertiary phosphine)mercury halides

Salt	M.p.[a]	(Hg - C)[b] cm.$^{-1}$
$[MeHgPMe_3]Cl$	86°	528 s
$[MeHgPEt_3]Cl$	84-85°	
$[MeHgPMe_2Ph]Cl$[d]	95-97°	515.5 s
$[MeHgPEt_3]Br$	92-93° [e]	516 s[c]
$[MeHgPMe_2Ph]I$[d]	107°	524 s
$[EtHgPMe_3]Cl$	86°	504 s
$[EtHgPEt_3]Br$	87°	508 m[c]
$[Pr^nHgPMe_3]Cl$	121-124°	504 m
$[Pr^nHgPMe_2Ph]Cl$[d]	76-77°	absent
$[Bu^nHgPMe_3]Cl$	107-108°	504 w
$[Bu^nHgPMe_2Ph]Cl$[d]	86-88°	
$[Bu^nHgPMe_3]I$	87-88°	517 s

Notes: [a] with decomposition; [b] Nujol mull; [c] potassium bromide disc; [d] darkens on exposure to light; [e] lit.[110] m.p. 90-91°; s, strong; m, medium, w, weak.

Trimethylphosphine complexes were the least soluble and were normally thrown out of solution on mixing the reagents but crystallised as colourless needles from acetone-ether solution on cooling to 0°C. The phenyldimethylphosphine complexes of n-propyl- and n-butyl- mercuric chlorides presented difficulties in isolation. They were fairly soluble in all solvents tried including such non-polar solvents as ether and benzene and on concentration separated as an oil. They were eventually crystallised by cooling ether solutions well below room temperature and shaking vigorously until solid formed. This was rapidly filtered and pumped dry as the presence of ether at room temperature caused the reformation of an oil. Several of the complex salts were light sensitive and turned grey, presumably due to deposition of metallic mercury, on exposure to diffuse light and such decomposition took place more rapidly in sunlight. These compounds which are indicated in Table XXI and Table XXIV were handled in flasks wrapped in black paper to prevent decomposition. Infra-red spectra, which were recorded in the form of Nujol mulls or potassium bromide discs, were used for identification purposes. The (C-Hg) stretching frequencies are reported in Table XXI. Halogen exchange takes place if KBr discs are used for salts other than bromides and an extra absorption can be observed in the ν(C-Hg) region corresponding to that observed in the spectrum of the bromide. Thus, $[\mathrm{MeHgPEt_3}]\mathrm{BF_4}$ shows two absorptions at 532 cm.$^{-1}$ and 518 cm.$^{-1}$, the former being due to the ν(C-Hg) band in the tetrafluoroborate and the latter is identical to that found in the bromide.

The method of determining the melting points of freshly prepared complexes was similar to that for any organic compound. As the compounds disproportionate slowly at room temperature but more rapidly as the temperature is increased the melting points are dependant upon the rate of heating and the time that has elapsed since their preparation. Consequently they should be regarded as decomposition temperatures. At low pressure alkyl(tertiary phosphine)mercury halides sublime at temperatures below 100°C, no doubt due to dissociation to mercurial and phosphine followed by recombination. Although the salts could be pumped for a considerable time at room temperature, as they were on drying, without loss of phosphine, when $[\mathrm{MeHgPMe_3}]\mathrm{Cl}$ was sublimed under vacuum at 70°C a slight pressure due to trimethylphosphine developed and the sublimate was impure and contained methylmercuric chloride. Sublimation therefore did not prove an effective method of purification as it caused some dissociation and as it entailed heating the complex it also encouraged disproportionation.

In the quantitative investigation of the decomposition of $[\mathrm{MeHgPPhMe_2}]\mathrm{I}$ on pyrolysis the compound was heated under vacuum in a flask fitted with a sintered disc which effectively contained any sublimation product to the reaction vessel. Disproportionation occurred on heating to 80°C (below its melting point of 107°C) and the compound liquified to a viscous melt after thirty minutes. Dimethylmercury (85% of the theoretical for complete disproportionation) was recovered along with $(\mathrm{PPhMe_2})_2\mathrm{HgI_2}$ as the other major product. Tertiary phosphine (2.4% total) was also recovered. This was produced either by dissociation of the original salt or from the pyrolysis of the di-iodo complex, and it may be noted that $(PEt_3)_2HgCl_2$ liberates triethylphosphine when it is heated, although not in any stoichiometric quantity, and forms a sticky glass.

Relative affinities for the alkylmercury cation of halides and tertiary phosphines

The rate of cleavage of the mercury-~~carbon~~ halogen bond by tertiary phosphine is rapid and complete in all cases involving trimethyl-, triethyl- and phenyldimethylphosphines and alkylmercuric halides. This is reflected in the immediate precipitation of, for instance, $[MeHgPEt_3]Cl$ from ether, and $[Bu^nHgPMe_3]Cl$ from acetone-ether as soon as the reagents were added. The rapid formation of an ionic species on addition of equimolar quantities of triphenylphosphine and methylmercuric chloride and bromide respectively in methanol solution is demonstrated by the immediate increase in conductance. Conductimetric titrations of triethylphosphine and phenyldimethylphosphine against methylmercuric bromide, which show a maximum conductance at 1:1 molar ratios, demonstrate the complete displacement of halide by phosphine in these cases. The normal molar conductance in water of $[EtHgPEt_3]Br$ (Λ_o = 100.5 ohm^{-1} cm.^{2}) expected for such an electrolyte is additional confirmation. This is in good agreement with the equivalent conductance previously reported[110] for $[MeHgPEt_3]Br$ (Λ_o = 100.7 ohm^{-1} cm.^{2}). As the ionic conductance of the bromide ion, λ^-_o, is 78.4 ohm^{-1}cm.^{2} this gives values of ionic conductance, λ_o^+, for $[\mathrm{MeHgPEt_3}]^+$ and $[\mathrm{EtHgPEt_3}]^+$ of 22.3 and 22.1 $\mathrm{ohm^{-1}cm.^2}$ respectively which is similar to those values of tetra-alkylammonium and other large ions in water at 25°C. Futhermore, alkylmercury tertiary phosphine halide complexes can be recrystallised without the addition of free phosphine indicating that any displacement of phosphine by halide to regenerate alkylmercuric halide is insignificantly small. Although this is the case with trimethyl—, triethyl-, and phenyldimethyl- phosphines it does not apply to triphenylphosphine. Here addition of one molar equivalent of triphenylphosphine to methylmercuric halide results in a competition between phosphine and halide for co-ordination to the methylmercury cation. Conductimetric titrations of these reagents in methanol solution are shown graphically in figure (ix). In a methanol solution 0.0060 molar in methylmercuric chloride the conductance maximum of 17×10^{-5} $\mathrm{ohm^{-1}cm.^{-1}}$ was not reached until the molar ratio of $\mathrm{PPh_3}$:Hg was 1.25:1. Under similar conditions titration of triphenylphosphine against methylmercuric bromide gave a conductance maximum of 7.3×10^{-5} $\mathrm{ohm^{-1}cm.^{-1}}$ at a molar ratio of 1.73:1 in a solution 0.0056 molar in mercury and the triphenylphosphine-methylmercuric iodide system had the still lower maximum conductance of $2.6 \times 10^{-5}\mathrm{ohm^{-1}cm.^{-1}}$ in a solution 0.0044 molar in mercury when the molar ratio of $\mathrm{Ph_3P}$:Hg was 2.87:1. The relative affinities of halide ions for the methylmercury cation would therefore appear to be $\mathrm{I} > \mathrm{Br} > \mathrm{Cl}$ and this is

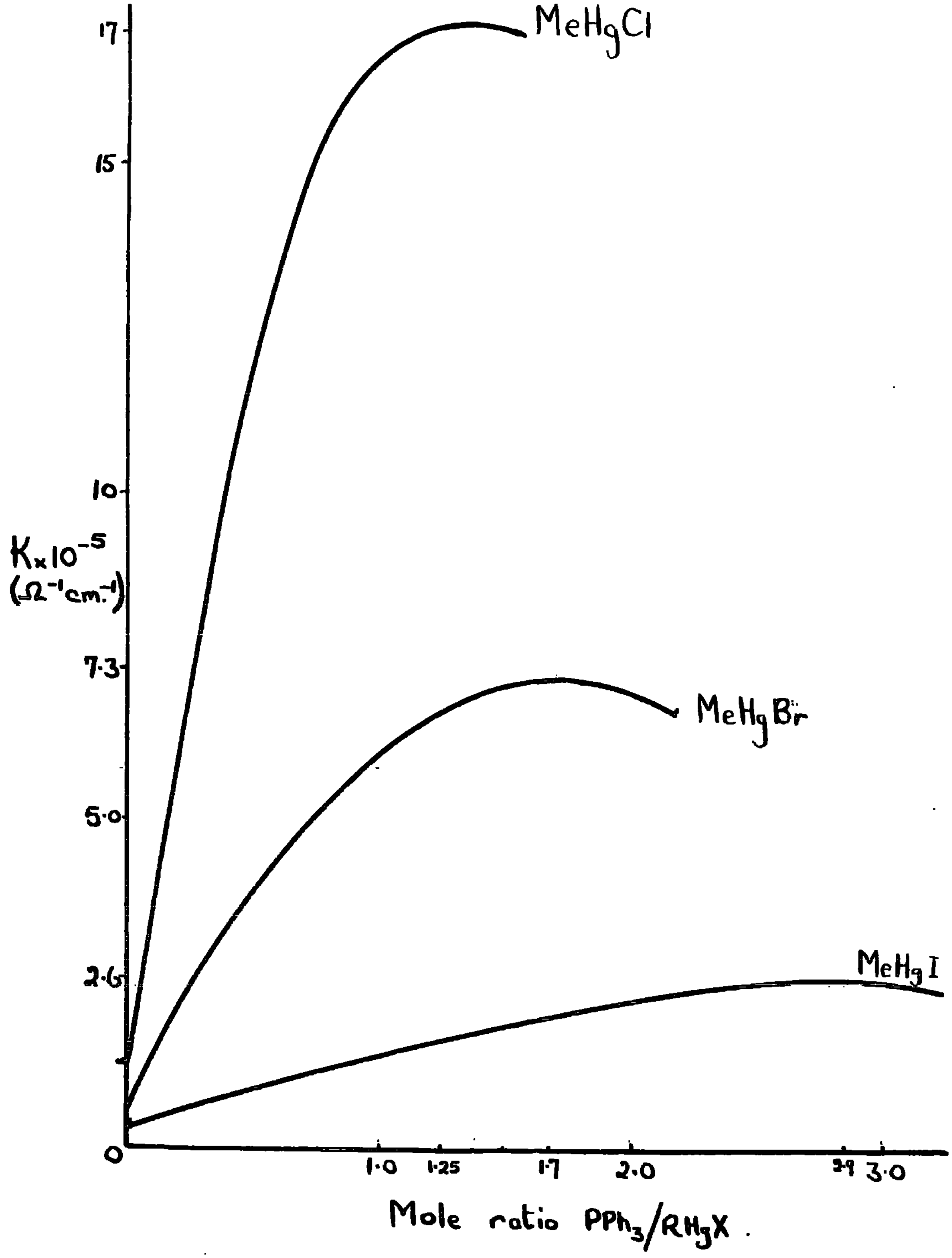

MeHgCl
MeHgBr
MeHgI
17
15
10
7·3
5·0
2·6
0
K×10⁻⁵
(Ω⁻¹cm.⁻¹)
1·0
1·25
1·7
2·0
2·9
3·0
Mole ratio PPh₃/RHgX .

fig. (ix).

consistent with values already obtained by partition measurements.[72] Neglecting for the moment the disproportionation reaction, the rate of which, at least in the alkylmercury complexes, is slow enough to allow isolation of the complex salts, then the salient factors which govern the formation of the compounds $[RHgPR'_3]X$ are the position of equilibrium in the reaction:

$$RHgX + PR'_3 \rightleftharpoons [RHgPR'_3]X$$

and the relative solubilities of reactants and products. If the equilibrium lies exclusively or very largely in favour of the complex salt in any particular solvent then its isolation presents no difficulty as it can be precipitated from solution by concentration. This is the case with the complexes derived from methylmercuric halides and trimethyl=, triethyl= and phenyldimethylphosphines respectively as is borne out by their isolation, conductance titrations and absence of smell of phosphine in the freshly prepared salts. The inability to isolate salts of organomercuric halides and triphenylphosphine must have a direct bearing on the position of equilibrium of the system. The undoubted formation of salts $[RHgPPh_3]X$ is shown by the conductance titrations previously described, the increase in conductance on adding the phosphine to acetone solutions of m-tolylmercuric chloride and bromide respectively, similar observations by Dessy involving phenylmercuric chloride in aqueous dioxan,[106] and the actual isolation of $[MeHgPPh_3]^+$ salts with weakly co-ordinating anions such as ClO_4^-, BF_4^-.

In the case of triphenylphosphine the equilibrium

$$\mathrm{MeHgX} + \mathrm{PPh_3} \rightleftharpoons [\mathrm{MeHgPPh_3}]\mathrm{X}$$

appears to favour the initial reactants to such an extent that the solubility of the complex salt is not exceeded. Furthermore, as the salt must have considerable ionic character, as is shown by the substantial increase in conductance in methanol, it should be most likely to precipitate from a non-polar solvent such as benzene or ether. This does not occur and concentration of such a solution yields methylmercuric chloride and triphenylphosphine along with a small amount of disproportionation product, $(\mathrm{Ph_3P})_2\mathrm{HgCl_2}$. This would suggest a displacement of equilibrium in non-polar solvents favouring dissociation although the possibility of substantial ion-pairing of the salt should not be neglected. Whichever explanation, or a combination of both, is applicable the result is to render the organomercuric halide the least soluble component of the system and on concentration this separates preferentially from solution. The solubility of $[\mathrm{Pr^nHgPPhMe_2}]\mathrm{Cl}$ and $[\mathrm{Bu^nHgPPhMe_2}]\mathrm{Cl}$ in ether and accompanying difficulty of isolation could be due to a similar effect although the methyl complex of phenyldimethylphosphine was isolated without difficulty. As the trimethylphosphine complexes of n-propyl- and n-butyl- mercuric chlorides and $[\mathrm{Bu^nHgPMe_3}]\mathrm{I}$ were readily crystallised the increasing aryl nature of the substituents of the tertiary phosphine appears to have a destabilising effect upon the formation of salts

$[RHgPR'_3]X$ and the tertiary alkyl phosphines thus have a greater affinity for organomercury cations than their aryl counterparts.

Disproportionation reactions of alkylmercuric halides

Reactions which involved refluxing methylmercuric halides and triphenylphosphine in equimolar quantities in concentrated solution for 20 hours indicated that the rate of disproportionation increased with increasing molecular weight of halogen $Cl < Br < I$. After reflux the solution was cooled to 6°C and the precipitated $(Ph_3P)_2HgX_2$ was filtered and weighed. As the MeHgX - PPh_3 system is complicated and apparently involves at least two reversible equilibria and the weights of $(Ph_3P)_2HgX_2$ were not corrected for the fraction still in solution the absolute values may not be of much significance. However, as the dihalo complexes are at best very slightly soluble in the solvents used and the conditions of the reactions were controlled so as to be as similar as possible the relative values obtained are of interest. The greater tendency of bromide to produce disproportionation than chloride is also shown by the decrease in conductance with time of the MeHgBr - PPh_3 system in dilute methanolic solution and the corresponding formation of $(Ph_3P)_2HgBr_2$ as the reaction proceeds. At a similar molarity the conductance of a MeHgCl - PPh_3 system remained unchanged over a period of 44 hours - a time which produced a considerable change in the former case. On the basis of mol. % $(Ph_3P)_2HgBr_2$ formed from methylmercuric bromide and triphenylphosphine after 20 hours reflux it was shown that disproportionation is increased by a solvent of high dielectric constant, benzene $<$ tetrahydrofuran $<$ acetone $<$ methanol. The relative rates of disproportionation obtained in various solvents and with chloride, bromide and iodide as indicated by the mol.% of $(Ph_3P)_2HgX_2$ formed in 20 hours are dependent upon the equilibrium:

$$2[MeHgPPh_3]X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Me_2Hg + (Ph_3P)_2HgX_2$$

not being achieved rapidly (which appeared to be valid as the precipitate did not form immediately but after some hours and it was gradually deposited as refluxing continued) and that the rate of disproportionation and formation of $(Ph_3P)_2HgX_2$, k_1, is slow and rate determining.

TABLE XXII

Disproportionation of MeHgBr and PPh_3 in various solvents

Solvent	Dielectric constant	$(Ph_3P)_2HgBr_2$ formed after 20 hours reflux	m.p.
Benzene	2.2	60.2%	259-263°C
T.H.F.	7.3	64.6%	259-263°C
Acetone	20.7	93.8%	259-263°C
Methanol	35.4	94.4%	258-263°

This is also a reasonable assumption as the initial cleavage of mercury-halogen bonds by phosphine is rapid,

$$RHgX + PR'_3 \rightleftharpoons [RHgPPh_3]X \rightleftharpoons \tfrac{1}{2}R_2Hg + \tfrac{1}{2}(Ph_3P)_2HgX_2$$

and the rate of formation of disproportionation products is claimed to be the rate controlling step in the disproportionation of esters of α-bromomercuriphenylacetic acid by ammonia[116] which could well proceed by a similar mechanism to the above reaction.

The considerably reduced formation of $(Ph_3P)_2HgX_2$ from ethyl-, n-propyl- and n-butyl- mercuric bromides respectively on reaction with triphenylphosphine in refluxing benzene for 20 hours compared to the reactions with methylmercuric bromide calls for comment. Three factors could contribute to the decrease in amount of disproportionation product formed from alkyl groups of increasing chain length. Dissociation into initial reactants could become more significant thus reducing the concentration of $[RHgPPh_3]Br$ in solution. Secondly, an

TABLE XXIII

Disproportionation of alkylmercuric bromides

Mercurial	$(Ph_3P)_2HgBr_2$ formed after 20 hours	m.p.
MeHgBr	60.2%	259-263°C
EtHgBr	16.5%	259-263°C
Pr^nHgBr	3.2%	259-264°C
Bu^nHgBr	3.9%	258-263°C

electronic effect found in alkyl compounds of the increased ability of the longer chain alkyls to transmit electrons to the bonded atom or group. This would oppose the general tendency that the more electron withdrawing the group attached to the mercury atom is, the more readily does disproportion take place. Thirdly, a steric effect of the longer alkyl chain in the transition complex analogous to that found in the disproportionation reaction of ammonia and PhCH(HgBr)COOR where the rate decreases as the size of the R substituent increases.[114]

Complex salts derived from nitrogen donor ligands

Nitrogen-containing donor molecules did not complex as strongly with the methylmercury cation as did tertiary phosphines and no stoichiometric complexes could be isolated. Disproportionation reactions were not observed with nitrogen ligands but dissociation of the weak complexes formed with methylmercuric halides readily occurred. Concentrated aqueous ammonia solution gave an immediate precipitate on addition to an ether solution of methylmercuric chloride. The solid rapidly lost ammonia and its melting point and infra-red spectrum were identical to that of methylmercuric chloride. A sample for combustion analysis could not be weighed due to a rapid decrease in weight of the sample. The formation of a complex salt analogous to those formed with tertiary phosphines is strongly indicated by the ready solubility of the ammonia compound in water in contrast to the insoluble methylmercuric chloride. Similar complexes with ammonia and methylmercuric chloride[106] and sec-butylmercuric chloride[116] respectively are reported but in neither case could the complex be analysed due to loss of ammonia. An even weaker complex appears to be formed between methylmercuric chloride and triethylamine. Analysis of the solid which was appreciably soluble in ether and smelled strongly of amine showed a carbon and hydrogen content much less than that required for a 1:1 adduct. Concentration of an ether solution of methylmercuric chloride containing pyridine caused the crystallisation of mercurial and no indication of a pyridine complex was observed. The greater stability of tertiary phosphine complexes compared to those derived from amines is consistent with the increased stabilisation they impart to the heavier B-type metals in their lower valency states and $[MeHgPEt_3]^+$ and $[MeHgNEt_3]^+$ are analogous to the stable $MeAuPEt_3$[122], m.p. 62°C, and the apparently unstable $MeAuNEt_3$ which has not been reported.

Other complex salts

Salts of the methylmercury cation complexed with various nitrogen, phosphorus and arsenic donor ligands and anions other than halides are listed in Table XXIV.

Methylmercuric perchlorate and tetrafluoroborate were prepared in aqueous methanol by addition of the respective silver salt to methylmercuric chloride or bromide and filtering the precipitated silver halide. The solutions of

TABLE XXIV

Methylmercury salts of anions other than halide

Salt	M.p.[a]
$[MeHgPMe_3]ClO_4$[b]	215°C
$[MeHgPEt_3]ClO_4$[b]	137°C
$[MeHgPPh_3]ClO_4$[b]	213-218°C
$[MeHgAsEt_3]ClO_4$[b]	120°C
$[MeHgAsPh_3]ClO_4$	224-225°C
$[MeHgPEt_3]BF_4$	120-125°C
$[MeHgPPh_3]BF_4$	215-220°C
$MeHg[Cr(NH_3)_2(SCN)_4]$	decomp. from 190°C
$[MeHgPEt_3][Cr(NH_3)_2(SCN)_4]$	dec. from 135°C
$[MeHgPPh_3][Cr(NH_3)_2(SCN)_4]$	dec. from 145°C
$[MeHgpy]ClO_4$	210-260°C
$[MeHgbipy]NO_3$	200-201°C

Notes: [a] with decomposition; [b] darkens on exposure to light.

methylmercuric salts did not deposit any oxonium salts,[76] $(MeHg)_3O^+$, although they were in fairly concentrated solution (17.5 gm. $MeHgClO_4$ in 140 ml. aqueous methanol). Complexes were prepared by adding the required ligand to the solution containing the methylmercury cation, presumably hydrated, $[MeHgOH_2]^+$, in solution as Raman spectra studies have shown in the case of methylmercuric perchlorate.[29] The salts $[MeHgL]X$, where X = ClO_4^-, BF_4^-, $Cr(NH_3)_2(SCN)_4^-$, so obtained were readily soluble except the triphenylarsine derivative of the perchlorate. The salt $[MeHgPEt_3]BF_4$ was so extremely soluble in water that it had to be evaporated to dryness under reduced pressure and recrystallised from iso-propanol at low temperature. A molecular weight determination on this salt in aqueous solution was consistent with it being a 1:1 electrolyte. All of the complex phosphine salts derived from methylmercuric perchlorate were light sensitive, particularly the trimethylphosphine compound. In an attempt to obtain less soluble complexes the reineckate anion was used. Methylmercuric reineckate was obtained from aqueous acetone solution as a very sparingly soluble pink solid on addition of ammonium reineckate to methylmercuric chloride. It had the composition, $MeHgCr(NH_3)_2(SCN)_4$, but it was necessary to consider the possibility that water might be co-ordinated as in the ionized structure: $[MeHgOH_2][Cr(NH_3)_2(SCN)_4]$, Elemental analysis indicated the absence of water and this was supported by infrared spectroscopic evidence. Further, salts containing the reineckate <u>anion</u> normally show a strong broad absorption in the region 2060-2120 cm.$^{-1}$. In mercuric reineckate this band is split into three distinct absorptions which have been attributed to mercury-sulphur interaction.[123] The spectrum of methylmercuric reineckate is rather similar, again suggesting some degree of bonding between mercury and sulphur. Several spectra of reineckate compounds are shown in Table XXV.

TABLE XXV

Infra-red spectra of reineckate compounds in the region 2060-2180 cm.$^{-1}$

Compound [a]	Absorption, cm.$^{-1}$
NH_4R	2117 — 2063 bs
HgR_2	2151, 2088, 2062 ds
MeHgR	2174, 2117, 2092 ds
$[MeHgPEt_3]R$	2105 —2073 bs
$[MeHgPPh_3]R$	2119—2075 bs

Notes: [a] R = reineckate, $Cr(NH_3)_2(SCN)_4$,
b, broad; d, discrete; s, strong.

The complex $[MeHgPPh_3][Cr(NH_3)_2(SCN)_4]$, was the only compound prepared which was isolated with solvent of crystallisation, and it contained 1 mol. of acetone per mercury atom. The acetone was lost at 60°C in vacuo to give the anhydrous salt. The complex salts obtained with the anions described other than halides showed no tendency to disproportionate and were air-stable. The co-ordinating ligand was more strongly held in these salts than in the halides probably as there was no competition for co-ordination to mercury. Hence triphenylphosphine formed stable complexes even with methylmercuric reineckate where some degree of competition from the anion could be envisaged.

The only nitrogen ligands to give stable stoichiometric complexes were pyridine and bipyridyl. The salts $[MeHgpy]ClO_4$ and $[MeHgbipy]NO_3$ were isolated and in the latter case it is not known whether the bipyridyl is chelating or attached by one nitrogen only. Attempts to prepare a complex containing a trialkylamine were unsuccessful as $[MeHgNMe_3]ClO_4$, which apparently crystallised from trimethylamine and methylmercuric perchlorate in aqueous acetone, lost amine so rapidly that it could not be analysed.

Disproportionation reactions of arylmercuric halides

As has been mentioned, arylmercuric halides differed from alkyl derivatives in that no complex salts could be isolated. Attempts to prepare such complexes resulted in disproportionation and the isolation of the dihalo complex, $(R'_3P)_2HgX_2$ and the mercurial, R_2Hg. For instance heat was evolved on adding triethylphosphine to m-tolylmercuric chloride in acetone, no doubt due to the formation of $(m\text{-}CH_3C_6H_4HgPEt_3)Cl$, but on concentration $(Et_3P)_2HgCl_2$ crystallised. Dessy's observation[106] of an increase in conductance due to the formation of $[PhHgPPh_3]Cl$ in aqueous dioxan and his subsequent isolation of phenylmercuric chloride is compatible with the very low solubility of phenylmercuric chloride and is comparable to the reaction of the corresponding iodide with excess sodium iodide carried out by Whitmore.[55]

In this case the initial reactants were recovered and no diphenylmercury obtained due to the adverse solubility relationship pertaining. However, reaction of the much more soluble m-tolylmercuric chloride and bromide respectively with triphenylphosphine resulted in rapid disproportionation and formation of the dihalo complex $(Ph_3P)_2HgX_2$ and mercurial, $(\underline{m}\text{-}MeC_6H_4)_2Hg$. Conductance studies of these reagents show that on addition of concentrated (ca. 0.1 molar) acetone solutions of phosphine and organomercuric halide the conductance immediately increases followed after about 15 seconds by a steady fall as $(Ph_3P)_2HgX_2$ is precipitated. The conductance values become constant after 6 minutes in the case of the chloride and 2½ minutes for the bromide, after which time crystallisation of the disproportionation product also ceases. Although the initial increase in conductance is most likely due to $[\underline{m}\text{-}MeC_6H_4HgPPh_3]X$ there could be some contribution to the conductance due to $(Ph_3P)_2HgX_2$ compounds, which are themselves slightly conducting and could be present in supersaturated solution in ionised form. Likewise the final conductance ($K = 7.1 \times 10^{-6}$ ohm^{-1}cm.$^{-1}$ for chloride, 3.0×10^{-6} ohm^{-1}cm.$^{-1}$ for bromide) was higher than the initial value of the organomercuric halide ($K = 4.3 \times 10^{-6}$ ohm^{-1}cm.$^{-1}$ for chloride, 2.2×10^{-6} ohm^{-1} cm.$^{-1}$ for bromide) due to the small amount of $(Ph_3P)_2HgX_2$ in solution as well as the salt $[MeC_6H_4HgPPh_3]X$. A quantitative reaction using the same solutions of phosphine and chloride used in the conductance reaction showed that 60% of $(Ph_3P)_2HgCl_2$ was precipitated after six minutes.

The reversal of the second stage of the reaction:

$$RHgX + PPh_3 \rightleftharpoons [RHgPPh_3]X \rightleftharpoons \tfrac{1}{2}R_2Hg + \tfrac{1}{2}(Ph_3P)_2HgX_2$$

is indicated by the increase in conductance of a saturated methanol solution of $(Ph_3P)_2HgCl_2$ ($K = 3.8 \times 10^{-5}$ ohm^{-1}cm.$^{-1}$), on addition of a concentrated solution of di-m-tolylmercury (1 mol), to a value of $K = 10.0 \times 10^{-5}$ over a period of hours. The increase was initially fairly rapid but decreased over several hours to a value which rose very slowly.

The only phosphine complex of an arylmercury compound was prepared by adding triethylphosphine to phenylmercuric nitrate in aqueous acetone followed by concentration and crystallisation of $(PhHgPEt_3)NO_3$. This complex is a strong 1:1 electrolyte in methanol as indicated by its equivalent conductance. ($\Lambda_o = 86.6$ ohm^{-1}cm.^{2}). This compares with similar values of 87.0 and 87.5 ohm^{-1}cm.^{2} found in methanol for $[EtHgPEt_3]Br$ and $[EtHgPMe_2Ph]Br$ respectively. Attempted preparation of the triphenylphosphine analogue yielded instead the dinitrato complex, $(Ph_3P)_2Hg(NO_3)_2$, which demonstrates that halide is not essential for disproportionation to take place. Although $[PhHgPEt_3]NO_3$ is stable to disproportionation in acetone solution, addition of sodium bromide (slight excess over 1 mol.) results in crystallisation of diphenylmercury and recovery of sodium nitrate and $(PEt_3)_2HgBr_2$.

$$[PhHgPEt_3]NO_3 + NaBr \longrightarrow \tfrac{1}{2}Ph_2Hg + \tfrac{1}{2}(PEt_3)_2HgBr_2 + NaNO_3$$

A similar reaction occurs with sodium iodide and this was followed spectrophotometrically. Solutions of $[PhHgPEt_3]NO_3$ and NaI in equimolar ratios were mixed and the reaction followed by tracing the increasing absorption at 2800Å due to the formation of the disproportionation product, $(Ph_3P)_2HgI_2$.

$$2[PhHgPEt_3]I \underset{-k_1}{\overset{k_1}{\rightleftharpoons}} Ph_2Hg + (PEt_3)_2HgI_2$$

The optical density increased rapidly and became constant after 30 minutes at room temperature corresponding to 84.5% completion of the reaction. Within 4 minutes of the addition the concentration of di-iodide had reached 74.5% of the equilibrium value. Constant values of the rate constant, k_1, for the disproportionation reaction could not be obtained. Calculations based on the assumption that the reaction was of second order and reversible were dependent upon a knowledge of the reactive species and even if this were $[PhHgPEt_3]I$ significant dissociation would make evaluation of k_1 extremely difficult. The reversibility of the reaction was shown by adding diphenylmercury to solution of NaI and $[PhHgPEt_3]NO_3$ in methanol and measuring the optical density after one hour. As the concentration of mercurial was raised so did the concentration of $(PEt_3)_2HgI_2$ fall. This is in agreement with similar observations[116] made by Jensen on the effect of added dialkylmercurial on the ammonia disproportionation of esters of $C_6H_5CH(HgBr)COOR$.

Conclusions

A summary of the findings indicate that complex salts $[RHgPR'_3]X$ can be isolated only in certain cases. Those derived from the more ionic anions and cationic methylmercury complexes are stable but halide salts slowly disproportionate. Triphenylphosphine complexes could not be isolated with organomercuric halides although their formation was indicated by conductometric titrations. Although arylmercuric halides disproportionated on reaction with tertiary phosphines one stable salt, $[PhHgPEt_3]NO_3$, was isolated. Its triphenylphosphine analogue rapidly disproportionated showing that halide was not necessary for such a reaction to occur. Phosphorus and arsenic ligands formed much more stable complexes than those of nitrogen. The only stable representatives of the latter type of compound isolated were $[MeHgpy]ClO_4$ and $[MeHgbipy]NO_3$.

The rate of the disproportionation reaction was dependent upon the organic group attached to the mercury atom, anion, phosphine, solvent and temperature. The rate increased with increasing temperature and also with increasing dielectric constant of the solution, methanol $>$ acetone $>$ tetrahydrofuran $>$ benzene. Although in most cases changes in the nature of the tertiary phosphine had little effect on the rate of disproportionation, the formation of a stable salt between triethylphosphine and phenylmercuric nitrate is in sharp contrast to the rapid disproportionation brought about by triphenylphosphine. The important role played by the anion is shown in that the only arylmercury tertiary phosphine complex that could be isolated was $[PhHgPEt_3]NO_3$ in which the anion had little co-ordinative affinity for mercury. Similarly, complex salts derived from the more ionic anions, such as ClO_4^-, BF_4^-, $Cr(NH_3)_2(SCN)_4^-$, showed no tendency to disproportionate and these anions formed stable compounds with the methyl(triphenylphosphine)mercury cation. Disproportionation always occurred with halide anions and triphenylphosphine salts could not be isolated. The rate of disproportionation was shown to decrease with decreasing affinity of the halogen for the methylmercury cation $I > Br > Cl$.

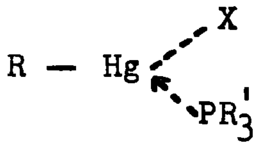
The remaining factor of major importance is the influence of the organic group attached to the mercury atom. The overall indication is that electron withdrawing groups facilitate disproportionation and thus perchlorovinyl-, trichloromethyl, carbomethoxy- and aryl- mercuric halides disproportionate rapidly with tertiary phosphines whereas methyl derivatives form isolable complexes which only disproportionate slowly. The rate of disproportionation of alkylmercuric halides on reaction with triphenylphosphine appears to be in the order Me > Et > n-Pr ≃ n-Bu.

The mechanism of the disproportionation reaction cannot be elucidated without detailed kinetic data. However, it does not seem unreasonable to assume that the reaction is second order with respect to both tertiary phosphine and organomercuric halide by analogy to the similar reaction between ammonia and esters of α-bromomercuriphenylacetic acid. 111-4,116

The reversibility of the reactions:

$$\mathrm{RHgX} + \mathrm{PR'_3} \rightleftharpoons [\mathrm{RHgPR'_3}]\mathrm{X} \rightleftharpoons \tfrac{1}{2}\mathrm{R_2Hg} + \tfrac{1}{2}(\mathrm{PR'_3})_2\mathrm{HgX_2}$$

has been established and again it seems a fair assumption that the intermediate salt plays some role, possibly in the less ionic form,



in the disproportionation transition complex. The idea of a 4-centre transition complex as postulated in the ammonia disproportionation, the reaction of R_2Hg and $HgCl_2$,[124-5] and the cleavage of di-organomercurials with HCl[126] is also acceptable, but the actual structure of this complex is a matter of speculation.

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Reactions of dimethylcadmium with compounds containing acidic hydrogen.

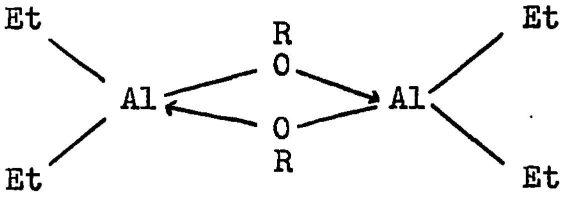
INTRODUCTION

INTRODUCTION

The work described in this section is concerned with the reactions of dimethylcadmium and compounds such as alcohols, thiols and secondary amines which contain acidic hydrogen. The interest lies in the co-ordincation complexes resulting from such reactions when only one methyl group is displaced. For example dimethylcadmium reacts with ethanol evolving methane:

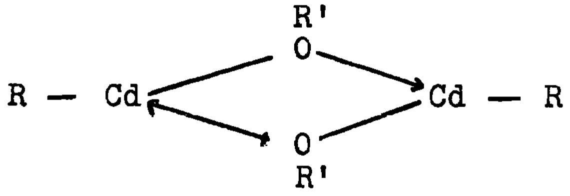
$$Me_2Cd \quad + \quad EtOH \longrightarrow MeCdOEt \quad + \quad MeH$$

In the product, methylcadmium ethoxide, the acceptor character of the metal is enhanced by the replacement of one of the carbon atoms by a more electronegative element, in this case oxygen, and the donor character of oxygen is similarly enhanced by attachment to a more electropositive element, cadmium. These factors lead to association and an increase in the co-ordination number of the metal. Similar effects have been observed with Group III metals where association of similar derivatives can occur to give dimeric species shown in figure (i)



(i)

However the formation of dimers, figure (ii) of organocadmium derivatives would yield complexes



(ii)

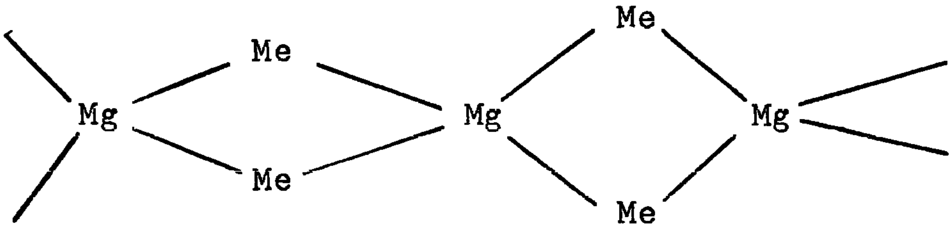
containing the metal in a state of <u>three</u> co-ordination, which is still co-ordinately unsaturated and capable of further association. The formation of tetramers and more highly associated species would be opposed on entropy and in some cases steric grounds. Co-ordination complexes derived from the reactions of dimethylcadmium with some alcohols and thiols respectively in equimolar ratios were therefore prepared.

General

The organic derivatives of the elements of Group II show a gradation of reactivity which parallels the decreasing electropositive nature of the metals.

Organic compounds of calcium, strontium and barium have been little studied. Solid dimethyl derivatives of all three metals have been obtained and they are highly reactive and resemble methyl lithium in many of their reactions.

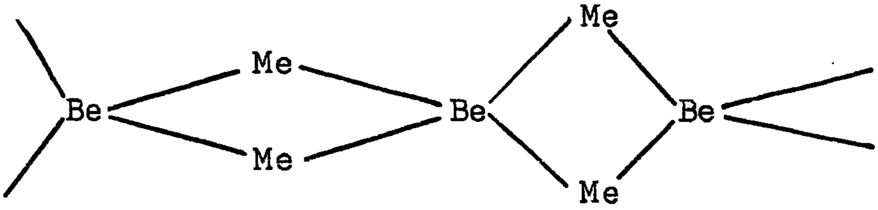
Apart from the extremely useful Grignard reagents, magnesium forms organic derivatives of the type, R_2Mg. These can be obtained from the dialkyl- or diaryl- mercurial on reaction with magnesium[2] or by precipitating the sparingly soluble dioxan-magnesium halide complex on addition of dioxan; the dialkylmagnesium compound left in solution can be obtained by concentration[3]. Dimethylmagnesium can be sublimed only with difficulty in a good vacuum[4] although it sublimes a little more readily in a stream of ether vapour - possibly as a co-ordination complex. Powder photograph studies show that dimethylmagnesium exists in the solid phase as polymeric chains.[5] The magnesium atoms are connected by methyl bridges with an almost tetrahedral arrangement of methyl groups about each magnesium atom as shown in figure (iii). The bond distances indicate a more strongly bound polymer than dimethylberyllium which explains the lower volatility of the magnesium compound.



(iii)

The organic compounds of beryllium resemble those of magnesium and some Group III metal derivatives in exhibiting a tendency of the metal to utilize all of its low energy orbitals in bonding, thus leading to the formation of electron deficient structures. Although beryllium is most frequently <u>four</u> co-ordinate in its compounds it is occasionally found in a state of <u>sp</u> hybridisation in <u>two</u> covalent compounds such as the monomeric di-t-butyl derivative and sp^2 hybridised in three covalent compounds such as $Me_2Be \leftarrow NMe_3$

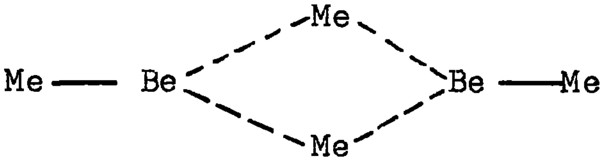
Solid dimethylberyllium has a covalent long chain polymeric structure[6] with bridging methyl groups approximately tetrahedrally arranged about the beryllium atoms, figure (iv), similar to dimethylmagnesium.



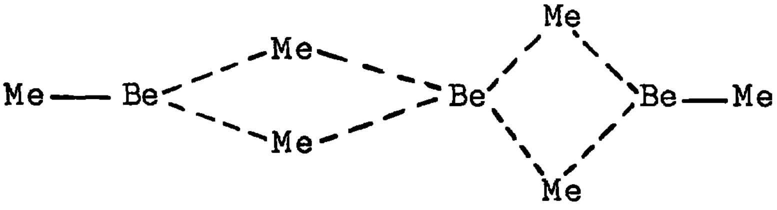
(iv)

Three centre molecular orbitals $Be(sp^3) + C(sp^3) + Be(sp^3)$ are most likely formed giving bent Be - C - Be bonds each containing two electrons. In the formulae shown dotted lines represent half bonds.

monomer



dimer



trimer

(v)

The polymer is broken into smaller units on heating and studies of the vapour phase between 160-200° indicate that dimethylberyllium is composed of monomer, dimer and trimer, figure (v), at this temperature. Higher polymers become significant at near saturation conditions.[7]

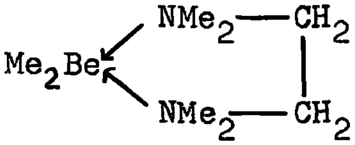
The organic derivatives of zinc, cadmium and mercury do not show a sufficient tendency to increase their covalency above the group valency of two to give rise to electron deficient structures. The dialkyl derivatives of zinc, cadmium and mercury are thus covalent monomeric compounds which have a co-linear structure and hence are non-polar. Studies of the infra-red spectra of the dimethyl derivatives indicate that the methyl groups are freely rotating.[8] The boiling points of these compounds show a surprising anomalous order, Me_2Zn, 44°; Me_2Cd, 105.5°; Me_2Hg, 92°. Dimethylcadmium must be distilled at reduced pressure to avoid thermal decomposition and the higher dialkyl homologues of all three metals are thermally unstable at room temperature and slowly decompose with deposition of metal and liberation of hydrocarbon.

Co-ordination complexes of Group II metal dialkyls and diaryls

Many co-ordination complexes derived from dialkyl and diaryl derivatives of beryllium, magnesium, zinc and cadmium on reaction with ligands containing donor atoms of Groups V and VI respectively have been prepared. Only those mercurials, such as $(CF_3)_2Hg$, $(CCl_3)_2Hg$ and $(C_6F_5)_2Hg$, which contain alkyl or aryl groups highly substituted with electron withdrawing elements form similar complexes, probably due to the inability of the mercury atom to accept a further partial negative charge.

Beryllium

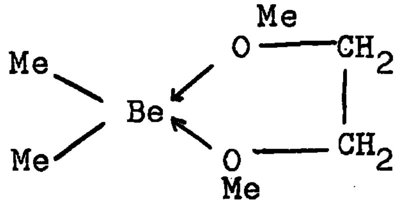
Dimethylberyllium has a long chain polymeric structure which gives co-ordinate saturation to the beryllium atoms. Due to the stability of this arrangement co-ordination complexes are formed only with those donor molecules where the heat of co-ordination is greater than the heat of polymerisation of dimethylberyllium. As would be expected on grounds of electronegativity trimethylamine forms a very stable 1:1 complex,[9] $Me_2Be \leftarrow NMe_3$ m.p. 36°. A slight degree of association is observed in benzene solution[10] (ca. 12%) and the complex is stable as a monomer[9] up to 180°.

The donor strength of trimethylphosphine towards beryllium is less than that of trimethylamine and is comparable to the strength of association between dimethylberyllium molecules. This leads to a range of stoichiometric complexes being formed. The formation of $(Me_3P)_2BeMe_2$ and absence of any report of the successful preparation of the trimethylamine analogue is surprising as the amine is a stronger donor than the phosphine. It has been proposed that the lack of formation of $(Me_3N)_2BeMe_2$ is unlikely to be steric as both $(Me_3P)_2BeMe_2$ and  are known and the formation is possibly opposed by entropy effects.

Dimethyl and diethyl ethers have a similar affinity for dimethylberyllium as trimethylphosphine and in an analogous manner a range of products is formed. The strength of co-ordination is less for ethers than trimethylphosphihe as indicated by the lower temperatures at which the compounds dissociate. Dimethyl sulphide and trimethylarsine complexes of dimethylberyllium could not be prepared. The order of donor strength of the ligands discussed towards dimethylberyllium is thus $Me_3N > Me_3P > OMe_2 > AsMe_3$, $SMe_2 = 0$.

Bidentate ligands form relatively stable complexes with beryllium. Those complexes derived from 2:2'- bipyridyl and organo-beryllium compounds are in several instances highly coloured and it was suggested that the colour is due to electron-transfer from one of the beryllium - alkyl or -aryl bonds to the lowest unoccupied orbital of the bipyridyl.[11] This proposal is supported by subsequent electron spin resonance studies[12] which indicate that the chelate complexes derived from such ligands as 2:2' bipyridyl and 1:10 -phenanthroline contain two unpaired electrons.

Chelating ether complexes can be obtained and are stable to dissociation in contrast to the dimethyl- and diethyl- ether derivatives. Thus, 1, 2 - dimethoxyethane forms a crystalline complex, figure (vi), which is monomeric in benzene and can be



(vi)

sublimed at 70°/0.06 mm., indicating that the dissociation pressure is low.[11]

Higher beryllium dialkyls also form complexes and 1:1 adducts with trimethylamine are reported for diethyl- and di-isopropyl- beryllium.[13] A 2:1 adduct between trimethylamine and diethylberyllium, $(Me_3N)_2BeEt_2$, which dissociates above -35° is also reported.[14] 2:2'-Bipyridyl forms a red monomeric complex, $bipy.BeEt_2$, and an orange-yellow adduct, also monomeric in benzene, is formed with two molecules of pyridine, $py_2.BeEt_2$.

Magnesium

Dioxan forms 1:1 adducts with magnesium dialkyls during the preparation of the latter from dioxan solution. Flash distillation 'in vacuo' gives the pure dialkyl as a polymeric solid.[15] Other complexes of magnesium dialkyls are the 1:1 adducts obtained from tetramethylethylenediamine, which are crystalline solids of high thermal stability[16] and are monomeric in benzene[17]. Diphenylmagnesium forms a solid 2:1 complex with tetrahydrofuran which is also monomeric in benzene.

Zinc

Organozinc compounds form co-ordination complexes of the types $L.ZnR_2$ and L_2ZnR_2 with ligands containing nitrogen, phosphorus, arsenic, oxygen and sulphur donor atoms. Many of these compounds are weakly co-ordinated and dissociate to the corresponding dialkylzinc and ligand in solution.

Nitrogen and phosphorus ligands

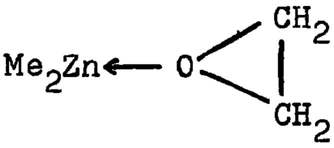
Trimethylamine forms a stable 1:1 adduct with dimethyzinc, $Me_3N.ZnMe_2$, which is monomeric in benzene. The 2:1 complex, which can be prepared, is fully dissociated in solution. Triethylamine and pyridine respectively form only 1:1 complexes with dimethylzinc and the latter is partially dissociated in solution even at low temperature and is difficult to isolate in stoichiometric composition.[18] Isoquinoline, however, forms a complex, $(C_9H_7N)_2ZnEt_2$, m.p. 25-28° with diethylzinc.[19] Tertiary phosphine complexes have been prepared using triphenylphosphine. Diphenylzinc and its fluorinated analogue both give 2:1 adducts, $Ph_2Zn(PPh_3)_2$, m.p. 142-3°; $(C_6F_5)_2Zn(PPh_3)_2$, m.p. 166-7°, but no such complex could be obtained with dibutylzinc. This is in keeping with an increase in donor-acceptor bond strength due to the increasing electronegative character of the organic group attached to zinc which enhances the polar character of the zinc-carbon bond. Thus dibutylzinc forms fewer and less stable complexes than diphenylzinc. Stabilisation of complexes of phosphorus and arsenic ligands by $d_\pi - d_\pi$ back-co-ördination between the filled *3d* orbitals of zinc and empty *d* orbitals on the ligands can not be of great importance and the strength of the ligand to zinc σ bond is the major factor. This is shown by the increased stability of organozinc complexes corresponding to the increased electronegativity of the group bonded to the zinc atom, which tends to increase the strength of the σ bond formed with the ligand but decrease the possibility of back-coordination.[20]

Chelating ligands

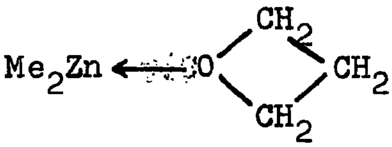
Bidentate nitrogen containing ligands form strongly bound complexes with organozinc derivatives. Thus, N,N,N',N'-tetramethylethylenediamine yields 1:1 adducts with dimethyl,[18] dibutyl,[20] diphenyl and dipentafluorophenyl-zinc in which the ligand is assumed to be chelating and the zinc is in a state of *sp^3* hybridisation with tetrahedral configuration. 2:2'-Bipyridyl gives complexes varying in colour from deep red to colourless depending upon the organic group attached to zinc.[11,18,21] A similar colour transition effect is observed in the complexes of 1, 10-phenanthr~~acene~~oline[18,21] due to an analogous effect to that postulated for the beryllium compounds.[11,12] Chelating phosphine and arsine complexes of bisorganozinc derivatives have been isolated with bisdiphenylphosphinoethane (Bu^n, m.p. 114°; Ph, m.p. 185-7°; C_6F_5, 211-3°) and *o*-phenylenebis(dimethylarsine) (Bu^n, liquid; Ph, m.p. 132-3°; C_6F_5, m.p. 136-7°) respectively. The decreasing affinity of zinc for the heavier donor atoms of Group V is indicated by the failure of attempts to prepare the $Ph_2AsCH_2CH_2AsPh_2$ and triphenylarsine complexes respectively, analogous to those of phosphorus which are reported.[20]

Oxygen and sulphur donors

Frankland[22] first indicated the formation of a complex between dimethylzinc and dimethylether in 1859. Subsequent work[23] showed that a 1:1 complex, $Me_2Zn.OMe_2$, which lost ether on fractional distillation, was formed between these two components. Dimethylzinc also yields liquid co-ordination complexes with ethylene-, trimethylene-, tetramethylene- and pentamethylene- oxide respectively which are dissociated in solution. The formation of 1:1 adducts

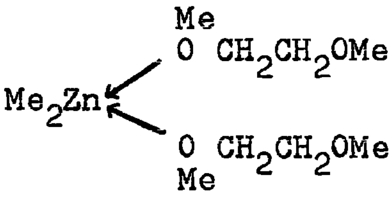


and

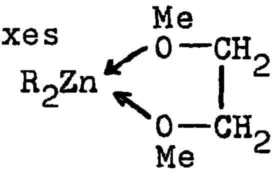


and 2:1 complexes $Me_2Zn[O(CH_2)_4]_2$ and $Me_2Zn[O(CH_2)_5]_2$ is surprising on steric grounds since it might be expected that the smaller ligands would form a 2:1 complex more readily. The experimental observations have been explained as being due to the p - character of the bonding orbitals of the oxygen, which is favoured by increasing ring size.

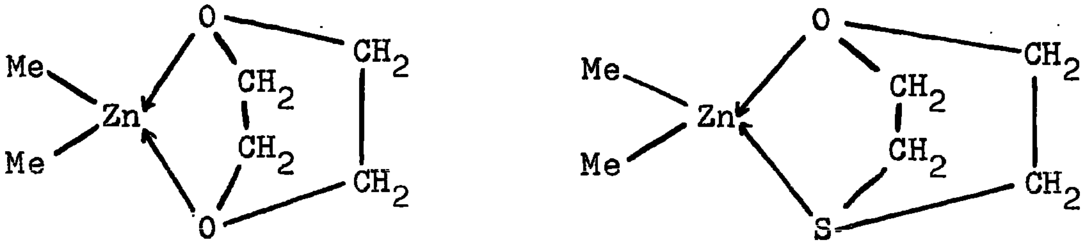
Bidentate oxygen ligands form both 1:1 and 2:1 adducts with organozinc derivatives. A colourless liquid, b.p. 91°, is obtained on mixing dimethylzinc and dimethoxyethane in 1:2 proportions. The 1:2 adduct



dissociates in solution to give a 1:1 compound, which is also dissociated in solution, but can be crystallised on cooling to give a low melting solid, m.p. 5.5°. Above 50° this 1:1 complex disproportionates to dimethylzinc (b.p. 46°) and the 2:1 complex (b.p. 92°). The 1:1 chelate complexes



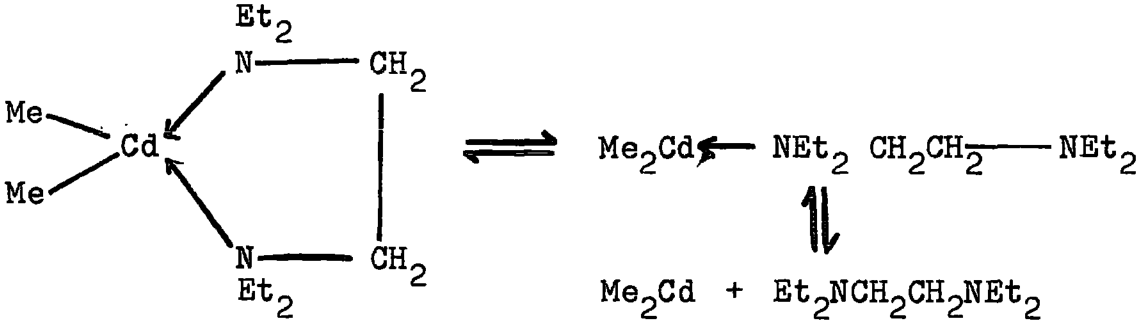
derived from bispentafluorophenyl- and diphenylzinc are much more stable towards dissociation and ether is not lost *in vacuo* at room temperature.[20] The chelate complexes formed between dimethylzinc and 1,4-dioxan and 1,4-thioxan, figure (vii), are also stable to dissociation and molecular weight determinations on the former indicate that it is monomeric in benzene.[24] Diarylzinc dioxanates such as $Ph_2Zn(O_2C_4H_8)$, m.p. 105° and $(\underline{o}\text{-}MeC_6H_4)_2Zn(O_2C_4H_8)$, m.p.69-71° are also reported.[25,26]



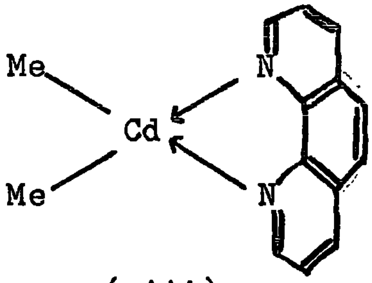
(vii)

Cadmium

Ligands containing only one donor atom yield liquid 1:1 complexes with dimethylcadmium which dissociate into their components at low temperature making it difficult to isolate these compounds in stoichiometric composition. Thus dimethylcadmium is lost from the pyridine complex and the $Me_2Cd.O(CH_2)_4$ complex slowly loses tetrahydrofuran on distillation. The tendency of complexes of cadmium dialkyls to dissociate in contrast to other similar complexes of Group II metals so far discussed is further exemplified in the chelate compounds. N,N,N',N'-tetraethylethylenediamine deposits a 1:1 crystalline complex from hexane solution which can be sublimed at 55° *in vacuo*. Cryoscopic determinations of molecular weight show that the complex is slightly dissociated in benzene. The complex has a smell of dimethylcadmium presumably due to dissociation, possibly by an opening of the chelate complex and subsequent dissociation of the adduct similar to that observed with the T.H.F. and pyridine compounds.[27]

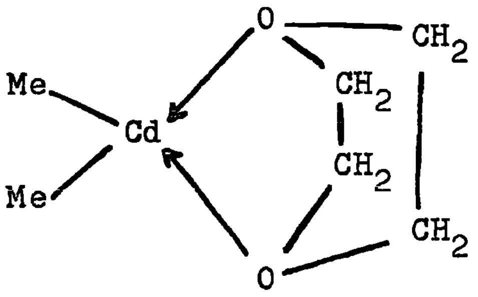


The bright yellow bipyridyldimethylcadmium complex, decomposition from 120°, which loses dimethylcadmium on pumping at room temperature[11] is also very much dissociated in benzene solution. In contrast the complex derived from dimethylcadmium and 1,10-phenanthroline, figure (viii) is



(viii)

monomeric in benzene.[27] Dimethylcadmium forms a 1:1 complex with 1,4-dioxan, figure (ix), m.p. 57°, which can be vacuum sublimed. In benzene solution, however, the complex is almost completely dissociated. This is in sharp contrast to



(ix)

the zinc analogue which is monomeric and undissociated in benzene. Diarylcadmium derivatives also form solid complexes with dioxan.

Mercury

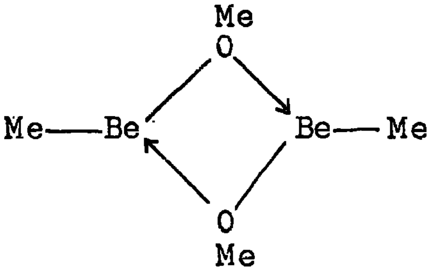
No co-ordination complexes of alkyl- or aryl- mercurials, with the exception of chlorinated and fluorinated derivatives, have been isolated. Indications of the formation of 1:1 and 2:1 compounds between such ligands as piperidine, triphenylphosphine and acetone respectively and diphenylmercury have been obtained by oscillimetric titration in benzene solution but the concentration of such complexes if formed must be small and they dissociate very readily.[28]

Reactions of Group II metal dialkyls with acidic hydrogen

The steady decrease in reactivity of dialkyls of Group II with ligands such as water and alcohol which contain acidic hydrogen bonded to an atom of donor character is most striking. This trend follows the decreasing electropositive nature of the metals in such a way that dimethylberyllium and dimethylzinc are hydrolysed by water with explosive violence, dimethylcadmium is less vigorous in its reaction but rapidly evolves methane on hydrolysis and dimethylmercury is without reaction even with dilute oxyacids.

Beryllium

Donor molecules containing reactive hydrogen also co-ordinate to dimethylberyllium.[29] Methane is readily eliminated from such complexes and the resulting compounds associate to give dimeric, trimeric or polymeric products. Methane is evelved so rapidly from methanol and dimethylberyllium that the adduct $Me_2Be.MeOH$ is not observed and only the dimeric product, figure (x) is isolated.

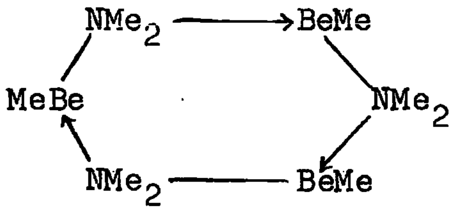


(x)

The compound is stable to 120° but above this temperature disproportionation to dimethylberyllium and beryllium methoxide occurs:

$$(MeBeOMe)_2 \longrightarrow Me_2Be + Be(OMe)_2$$

Methane thiol and dimethylphosphine both react with dimethylberyllium, the product of the latter reaction is apparently polymeric but neither of the products were characterised. Dimethylamine complexes with dimethylberyllium to give a solid adduct which melts as 44° with evolution of methane and formation of a complex trimer, $(MeBe.NMe_2)_3$, m.p. 55-56°, for which a cyclic structure has been postulated, figure (xi).



(xi)

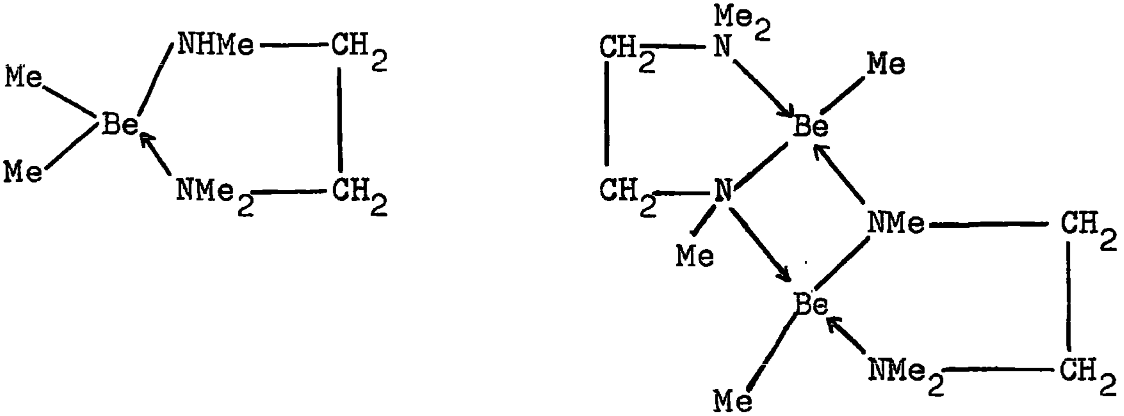
Phenol and dimethylberyllium in 2:1 proportions give beryllium phenoxide[30] even at -70° :

$$Me_2Be \quad + \quad 2PhOH \quad \xrightarrow[-70^{o}]{Et_2O} \quad MeOH \quad + \quad Be(OPh)_2$$

Dimethylberyllium reacts with both piperidine and morpholine to give the 1:1 adducts, $Me_2BeHNC_5H_{10}$ and $Me_2BeHNC_4H_8O$, respectively. Above 0°C these compounds evolve methane but no molecular weight information for the products is given.[31] Above 20° in the presence of excess amine a second molecule of methane is evolved giving the products $Be(NC_5H_{10})_2$ and $Be(NC_4H_8O)_2$ respectively.

N-Methyl substituted ethylenediamines also complex with dimethylberyllium[11], eliminate methane at their respective decomposition temperatures and form associated or polymeric compounds in which the beryllium atoms are tetrahedrally surrounded and co-ordinatively saturated.

NNN' - Trimethylethylenediamine forms a complex which loses methane at room temperature to give a dimeric product, m.p. 116-118°, figure (xii).



(xii)

Polymeric products were the final compounds isolated from ethylenediamines containing two or more acidic hydrogens.

Higher alkyls of beryllium also react vigorously with acidic hydrogen. Violent hydrolysis of diethylberyllium occurs even at low temperatures and methanol reacts violently at - 80°.[32] Diphenylamine reacts less vigorously in benzene solution liberating two moles of ethane and giving the insoluble complex, Be(NPh$_2$)$_2$, which is no doubt associated.[33] N - Methyl substituted hydrazines also evolve ethane with diethylberyllium forming such products as (EtBeNMeNMe$_2$)$_x$, for which a degree of association of about 1:4 in benzene solution has been reported. Other derivatives are highly associated or polymeric but even with excess hydrazine both ethyl groups are not quantitatively cleaved.

Di-*iso*propylberyllium reacts with one molar ratio of methanol to give *iso*propylberyllium methoxide, (i-PrBeOMe)n and propane. A similar reaction occurs with dimethylamine and dimethylamino*iso*propylberyllium,(i-PrBeNMe$_2$)$_n$, is formed. With excess dimethylamine di-*iso*propyl- and di-t-butylberyllium react in an analogous manner and yield trimeric bis-dimethylaminoberyllium, $[Be(NMe_2)_2]_3$.

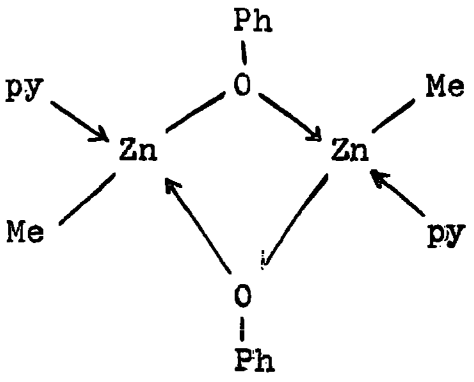
Magnesium

Relatively few observations of the reactions of magnesium dialkyls have been made by comparison to beryllium and zinc compounds. Trimethylethylenediamine does, however, react with dimethylmagnesium[17] in 1:1 proportions liberating methane and forming a product, $(MeMgNMeCH_2CH_2NMe_2)_2$, which is dimeric in benzene, analogous to the corresponding beryllium compound.[11]

Zinc

Reactions between zinc dialkyls and various alcohols[34,35] amines[36,37] and phosphines[38] have been observed but in these cases the complex resulting from the loss of only one alkyl group was either not isolated or if it was, no further investigation of its properties other than the fact that it was soluble in non-polar solvents was reported.

Recently the reactions of dimethyl- and diethyl- zinc with some alcohols, thiols and secondary amines have been reported.[39] The co-ordination complexes resulting from the displacement of one alkyl group were observed and found to have interesting constitutions. Reaction of dimethylzinc with alcohols in 1:1 proportions produced, in all cases studied, alkoxides which were tetrameric in benzene solution, $(MeZnOR)_4$. Observation of the proton magnetic resonance spectra of the methoxide and t-butoxide respectively suggested that the former could exist in isomeric forms which were denied to the latter on steric grounds. Only the phenoxide, of the methylzinc series, formed a pyridine derivative, figure (xiii), which suggests that the zinc atoms in these



(xiii)

complexes have a substantial degree of co-ordinative saturation.

Thiols, R'SH (R' = Me, Pr^n and Ph) reacted with dimethylzinc to give apparently polymeric solids, $(MeZnSR')_x$, from which pyridine complexes could not be isolated. On heating, disproportionation occurred as it did with the alkoxides (except the t-butoxide which evolved isobutene). Branched chain thiols reacted with dimethylzinc to give compounds soluble in benzene. The isopropylthiol derivative was hexameric in benzene, $(MeZnSPr^i)_6$, and that derived from t-butylthiol was pentameric, $(MeZnSBu^t)_5$. A pyridine derivative,

$(MepyZnSBu^t)_2$, of the latter was also prepared.

On reaction of dimethylzinc with dimethylamine only bisdimethylaminozinc, $[(Me_2N)_2Zn]_x$ was formed. Diphenylzinc however, gave a dimeric product, $(MeZnNPh_2)_2$, while NNN'-trimethylethylenediamine gave the product, $(MeZnNMeCH_2CH_2NMe_2)_2$, analogous to the beryllium derivative.

The reactions of the dialkyls of <u>cadmium</u> with molecules containing reactive hydrogen have been relatively little studied and dialkyl mercurials are stable even to water.

Reactions of sodium bis(trimethylsilyl)amide with zinc, cadmium and mercury halides respectively yield the volatile products, $(Me_3Si)_2N-M-N(SiMe_3)_2$, which are monomeric probably due to the steric effect of the large silylamide group.[44]

A series of observations of the reactions of hydrides of silicon, germanium and tin with dialkyls of zinc, cadmium and mercury respectively have been made.[45] Reactions of the type,

$$Et_3SiEt_2SiH + Et_2Hg \longrightarrow EtHgSiEt_2SiEt_3 \qquad (a)$$

$$Et_3SiH + Et_2Hg \longrightarrow EtHgSiEt_3 \qquad (b)$$

$$Et_3GeH + Et_2Cd \longrightarrow (Et_3Ge)_2Cd \qquad (c)$$

were carried out under conditions varying from 85°/6 hours in (c) to 140°/117 hours in (b). The products were distillable liquids which decomposed on exposure to air or ultra violet irradiation. Disproportionation of alkylmercury compounds occurred on heating:

$$Et_2Hg + Et_3SiEt_2SiH \xrightarrow[19\ hrs.]{160^\circ} EtHgSiEt_2SiEt_3$$

$$EtHgSiEt_2SiEt_3 \xrightarrow{170^\circ} Hg(SiEt_2SiEt_3)_2$$

Mercury dialkyls also evolve hydrocarbon with reactive hydrogen under such vigorous conditions as treatment with concentrated acid but dilute oxyacids are without effect.

EXPERIMENTAL

EXPERIMENTAL

Preparation of starting materials

Dimethylcadmium

This compound was prepared from anhydrous cadmium chloride and a methyl Grignard reagent under an atmosphere of dry nitrogen. Hydrated cadmium chloride was dried by refluxing with thionyl chloride until hydrogen chloride was no longer evolved. The anhydrous salt was washed several times with dry ether under a nitrogen atmosphere and then pumped dry. Methylmagnesium bromide (2 moles) in ether (2,500 ml.) was prepared from magnesium (very slight excess) and bromomethane using a solid - CO_2 reflux condenser to prevent loss of the alkyl halide. Anhydrous cadmium chloride (180 gm., 1 mol.) as a slurry in dry ether (200 ml.) was poured into a 5-litre flanged flask fitted with a large mercury-sealed paddle stirrer, nitrogen leads, and reflux condenser. The Grignard solution was filtered through a glass-wool plug, to remove the slight excess of magnesium, into the reaction vessel. The contents of the flask were vigorously stirred for three hours and then refluxed with stirring for a similar period. On cooling, the ether solution of dimethylcadmium was transferred to a large flask fitted with a porosity 3 sintered disc and was allowed to filter under gravity to remove precipitated magnesium halides. Aliquots of this solution were added from a large dropping funnel to a small flask from which the ether was fractionally distilled through a 12 inch column packed with glass helixes. The oil bath temperature was maintained below 65°C to prevent significant loss of dimethylcadmium by co-distillation with ether. The temperature of the distillate remained below 37°C and in this way the bulk of the ether was removed. The remaining solution was purified by fractional distillation at constant reduced pressure. The fractionation column described above was used and at an oil-bath temperature of 50°C solvent ether was distilled between 20° and 40°C at 20 cm. mercury pressure. The bath temperature was raised to 80°C and dimethylcadmium distilled at 63°, 61° and 57.5°C at pressures of 19, 17.4 and 14.7 cm. mercury respectively. The distillate was again fractionated and pure dimethylcadmium (70 gm., 50% with respect to $CdCl_2$) b.p. 63°/19.0 cm. mercury, was obtained.

Methanol and ethanol were dried by distillation from the magnesium alkoxides.

Iso-propanol and t-butanol were dried by distillation from the aluminium alkoxides.

Phenol was purified by vacuum distillation.

Trimethylethylenediamine was dried by distillation from lithium aluminium hydride.

Diphenylamine was purified by sublimation.

Hexane, benzene and toluene were dried over sodium wire. Other reagents, which were commercial products, were used without further purification in most cases.

Apparatus and technique

Storage of dimethylcadmium

If the reagent was to be retained for several months it was stored under vacuum in sealed glass vessels. These were tubes fitted with a side arm which was drawn out to a capillary at the end. Vessels could then be opened under vacuum or nitrogen simply by breaking open the capillary tube.

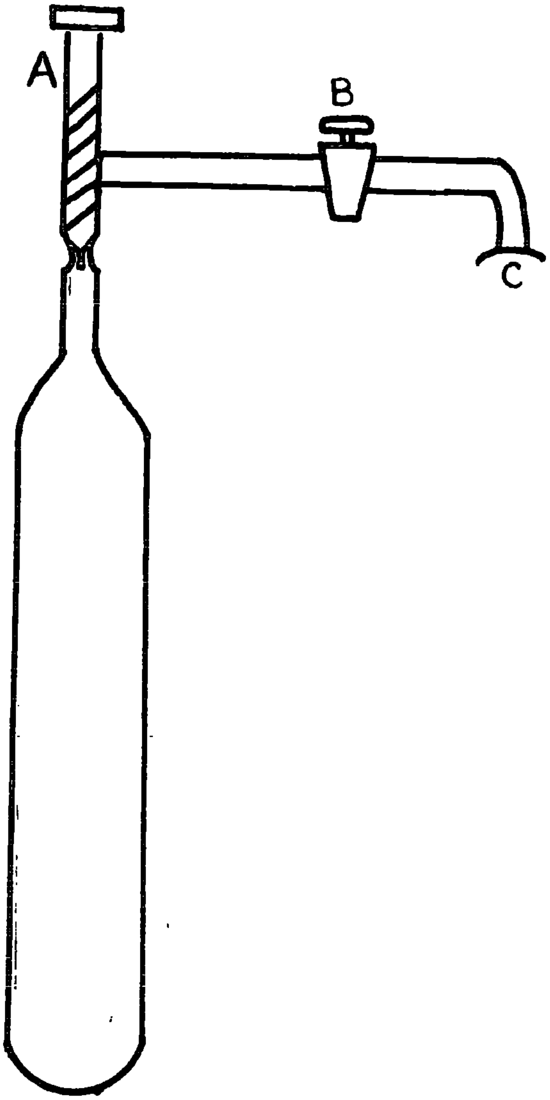
Difficulty in storage was experienced for that quantity of dimethylcadmium which was required for regular use. Storage on a vacuum line was obviously impossible due to the reversible equilibrium set up between cadmium alkyls and mercury:

$$R_2Cd + Hg \rightleftharpoons HgR_2 + Cd$$

This would lead to contamination of the sample with dimethylmercury and the mercury float valves of the apparatus would become fouled. If the reagent was stored in a flask, fitted with ungreased stoppers and taps under an atmosphere of nitrogen, oxidation due to slow diffusion of air into the flask occurred. This also happened when the ground glass joints were fitted with 'teflon' sleeves. When the joints were lightly greased dimethylcadmium either dissolved in the grease and became oxidised or reacted with the grease. In either case the reagent turned yellow after several days and solid material was slowly precipitated. The storage vessel finally adopted is shown in diagram I. Dimethylcadmium was originally condensed into the apparatus and the system brought to atmospheric pressure under nitrogen. The 'teflon' needle valve, A, was then closed sealing the reagent in the vessel. This valve was initially tested and found to hold a vacuum for several hours without detectable change in pressure. The greased tap, B, was then closed. The tap B was incorporated and the system retained at atmospheric pressure to provide additional protection against the possibility of a slow leak through the needle valve. In this manner dimethylcadmium was stored for several months. After this period of time a sparse yellow precipitate, possibly of metallic cadmium, had formed despite enclosing the vessel while not in use in a black paper sleeve to protect the contents from sunlight.

When dimethylcadmium was required for a reaction the container was connected by the ball joint, C, through a tap to a Schlenk tube. The dimethylcadmium was cooled in liquid nitrogen and the complete system evacuated. One limb of the tube was then cooled and the reagent allowed to warm to room temperature when it slowly condensed into the cooled limb of the Schlenk. When enough dimethylcadmium had been removed, as indicated by a rough scale, the system was let down to atmospheric pressure with dry nitrogen and the needle valve and taps closed. As the storage vessel was small enough to be weighed accurately on a balance the amount of reagent

Diagram I



Dimethylcadmium container.

condensed into the Schlenk could be determined.

Schlenk-tube reactions

A double Schlenk tube was always used for reactions involving air-sensitive material. Reagents were either condensed into the tube under reduced pressure or introduced against a counter-current of nitrogen by syringe. The taps of the Schlenk had straight extensions to allow a syringe needle to be inserted through the bore of the tap to reduce diffusion of air into the tube.

Glove box

This was used frequently to transfer air-sensitive products from flask to flask. All discs for infra-red spectra of such compounds were prepared in the glove box as were samples for combustion analyses. The glove box was purged with dry, oxygen-free nitrogen and samples and apparatus were introduced *via* a transfer tube which could be purged separately from the main chamber.

Vacuum Apparatus

This was used for the manipulation of volatile substances and for gas analysis, usually by measurement of volumes of methane. Many of the methylcadmium compounds described in this section readily evolved methane on hydrolysis with water or dilute 2N- sulphuric acid. In a determination of hydrolyzable methyl content of a compound a weighed quantity of the solid was placed in a flask attached to the vacuum line and the system evacuated. Degassed water or acid was added and the methane liberated was collected and measured by means of a Töpler pump. When handling volumes of methane greater than about 100 N-cc. (a normal cc., written as N-cc, is one cc. at N.T.P.) the bulk of the gas was condensed into a large standard bulb attached to a manometer and the methane which did not condense at liquid nitrogen temperature was determined using the Töpler pump.

Methylcadmium methoxide

Dimethylcadmium (3.33 gm.) was condensed from the storage vessel onto frozen hexane (30 ml.) contained in one limb of a Schlenk tube and the mixture allowed to warm until a homogenous solution was obtained. The solution was again cooled to liquid air temperature and the apparatus was brought to atmospheric pressure with dry nitrogen. Methanol (1.0 ml., 1 mol.) was then added by syringe, against a counter current of nitrogen, to the other limb of the tube. The alcohol was also cooled in liquid air and the system evacuated to accommodate the methane which is liberated in the reaction. The liquid air trap was removed from the limb containing the methanol which then slowly condensed onto the dimethylcadmium solution. Methane was steadily evolved when the reaction mixture was brought to -78° using an acetone $-CO_2$ bath and the reaction was virtually complete after several minutes. As methane was evolved methylcadmium methoxide was precipitated. The solution was warmed to room temperature and allowed to stand for an hour to ensure complete reaction. The sparingly soluble product was filtered from solution and washed with a further 80 ml. of hexane and methylcadmium methoxide (2.7 gm., 73%), decomposition from 70°, was obtained. (Found: C, 15.0; H, 3.75; Cd, 70.6. C_2H_6CdO requires C, 15.2; H, 3.8; Cd, 71.0%). The infra-red spectrum of the compound recorded as a Nujol mull showed strong absorptions at 670 and 486 $cm.^{-1}$ corresponding to 'Me-rock' and ν(Me-Cd) respectively.

On exposure to air methylcadmium methoxide turns brown over a period of several hours indicating decomposition and this is confirmed by the disappearance of the characteristic infra-red spectrum of the original compound on such exposure.

The methoxide is sparingly soluble in hexane and benzene which rendered a reasonable cryoscopic determination of molecular weight in the latter solvent impossible. The compound was also only slightly soluble in nitrobenzene, apparently without reaction.

Addition of water or dilute (2N) sulphuric acid to the methoxide resulted in rapid and very vigorous hydrolysis.

Pyrolysis

Methylcadmium methoxide (ca. 0.2 gm.) was heated on an oil bath in a small evacuated flask connected to an evacuated infra-red cell for the determination of spectra of gases. The temperature was raised and decomposition, indicated by a yellow discolouration of the originally colourless complex, commenced at about 70°. The temperature was brought to 120° and maintained at this point for 30 minutes. On recording the spectrum of the gas after this period a weak spectrum corresponding to dimethylcadmium was obtained.

Reaction with pyridine

Addition of excess pyridine to the methoxide under a nitrogen atmosphere followed by filtration and evaporation of solvent under reduced pressure resulted in the recovery of methylcadmium methoxide. The infra-red spectra of the product and the starting material were super-imposable. The methoxide was only slightly soluble in pyridine.

Methylcadmium ethoxide

Dimethylcadmium (3.27 gm.) was condensed into hexane (20 ml.) in one limb of a Schlenk tube. Ethanol (1.34 ml., 1 mol.) was added by syringe against a counter-current of nitrogen to the other limb, the apparatus was evacuated and the alcohol condensed onto the dimethylcadmium solution cooled to liquid air temperature. The liquid air trap was replaced by an acetone -CO_2 bath at -78° at which temperature the reaction proceeded rapidly with evolution of methane. When methane was no longer evolved the solution was heated until the solvent refluxed gently for 30 minutes to ensure complete reaction. After this time the solvent was distilled into the other limb of the Schlenk tube leaving a white solid. The product was purified by sublimation under a high vacuum. The colourless sublimate was obtained on a cold finger cooled with powdered solid CO_2 when the ethoxide was heated on an oil bath at 100°. Decomposition and sublimation occurred concurrently and the residue slowly turned brown. The sublimation vessel was transferred to a glove box and the crystalline methylcadmium ethoxide collected in a flask. (Found: C, 21.2; H, 4.45; Cd, 65.4; hydrolyzable methyl, 8.71; M, cryoscopically in benzene, 744, 748, 746 at 2.33, 1.95, 1.67 weight % respectively. C_3H_8CdO requires C, 20.9; H, 4.7; Cd, 65.2; hydrolyzable methyl, 8.75%, M, 172.5).

The infra-red spectrum was recorded as a Nujol mull and the strong absorption at 667 cm.$^{-1}$ was assigned to the 'methyl rock'. The ν(Me–Cd) region was more complicated and two strong bands at 496 and 483 cm.$^{-1}$ were observed.

The ethoxide decomposed on exposure to the atmosphere overnight and was vigorously hydrolysed by water and dilute sulphuric acid.

Pyrolysis

Methylcadmium ethoxide (ca. 0.4 gm.) was heated on an oil bath in a small flask fitted with a sintered disc to prevent sublimation. The compound began to turn brown and gradually contract in volume from about 90°. After 30 minutes at an oil bath temperature of 110° the infra-red cell was detached from the pyrolysis flask and the spectrum recorded. The spectrum obtained was identified as that of dimethylcadmium.

Reaction with pyridine

Methylcadmium ethoxide (ca. 0.2 gm.) was dissolved in benzene (15 ml.) and excess pyridine (0.2 ml.) was added. The solution was shaken and allowed to stand for two hours. No precipitate was formed and the solution was concentrated by pumping and evaporated to dryness under reduced pressure. The infra-red spectrum of the resulting solid was identical to that of the starting material and no extra absorptions attributable to pyridine was observed.

Methylcadmium isopropoxide

Dimethylcadmium (3.465 gm.) was condensed onto hexane (20 ml.) in a Schlenk tube. Isopropanol was added by syringe to the other limb against a counter-current of nitrogen. An exit bubbler containing heavy white oil was attached to one of the Schlenk taps and the alcohol was passed through the disc of the tube into the solution of dimethylcadmium in hexane cooled to -78° in an acetone - CO_2 bath. The solution was shaken to make it homogenous but no gas evolution was observed. The solution was allowed to warm slowly with occasional shaking. At about 10° the reaction commenced and methane was gently evolved. The solution became warm due to the exothermic nature of the reaction. Evolution of methane ceased after several minutes and the solution was allowed to stand at room temperature for one hour. The solvent was evaporated under reduced pressure and crude methylcadmium isopropoxide obtained. The product was purified by vacuum sublimation on to a cold finger cooled with solid carbon dioxide. The oil bath temperature was about 105° and decomposition accompanied sublimation. The residue which did not sublime was a brown solid. Methylcadmium isopropoxide was obtained as colourless needles. (Found: C, 26.2; H, 5.6; Cd, 60.4; M, cryoscopically in benzene, 747, 738, 759 at 1.83, 1.57, 1.27 weight % respectively. $C_4H_{10}CdO$ requires C, 25.8; H, 5.4; Cd, 60.3%; M, 187). The infra-red spectrum of the complex contained an absorption at 668 $cm.^{-1}$ attributable to 'methyl rock.'

Freshly prepared colourless methylcadmium isopropoxide was readily soluble in hexane and benzene but on standing under nitrogen and even in the dark the complex turned yellow after several days and was much less soluble. Pyrolysis of the isopropoxide yielded dimethylcadmium, identified by infra-red spectrum but no initial decomposition temperature was observed as the reagent slowly turned from yellow to brown at about 180°.

The isopropoxide is decomposed on standing in air overnight, and hydrolysis with water is moderate but more vigorous with dilute sulphuric acid.

Reaction with pyridine

Excess pyridine was added to a solution of methylcadmium isopropoxide in hexane in a Schlenk tube under a nitrogen atmosphere. On evaporation to dryness under reduced pressure the white solid obtained was found to have an identical infra-red spectrum to that of the original reactant. No absorptions attributable to pyridine were observed.

Reaction with bipyridyl

2:2'-Bipyridyl (0.52 gm., 1 mol.) in benzene (5 ml.) was added to a solution of methylcadmium isopropoxide (0.62 gm.) in benzene (10 ml.). No apparent reaction occurred and the volume was reduced to about 4 ml. Dry ether (ca. 10 ml.) was added to the solution but did not cause precipitation. The volume was reduced further to about 1 ml. and the solid deposited was filtered. The infra-red spectrum of this material showed a composite spectrum of free bipyridyl and isopropoxide. A strong absorption was present at 392 $cm.^{-1}$, typical of free 2:2'-bipyridyl, but the region about 415 $cm.^{-1}$ where co-ordinated bipyridyl is sometimes observed was clear. The solid obtained from the filtrate by evaporating to dryness also possessed a similar infra-red spectrum.

Reaction with triethylphosphine

Addition of excess triethylphosphine (0.7 ml.) to the isopropoxide (0.6 gm.) in benzene (15 ml.) yielded a clear solution. After evaporation under reduced pressure to about 1 ml. all solid material remained in solution. Evaporation to dryness under reduced pressure left a white solid of identical infra-red spectrum to the original isopropoxide.

Methylcadmium t-butoxide

Tertiary butanol (0.8 ml., 1 mol.) was added by syringe against a counter current of nitrogen to a Schlenk tube. The alcohol was frozen at liquid air temperature and the system evacuated. t-Butanol was then allowed to condense into the other limb on to a solution of dimethylcadmium in hexane (20 ml.) The resulting mixture was warmed to -78° with an acetone -CO_2 bath when evolution of methane occurred. After 30 minutes the solution was heated to about 40° and the solution reduced to half volume. On cooling, the solution slowly deposited colourless plates of methylcadmium t-butoxide. (Found:

C, 29.5; H, 6.15; Cd, 55.3; M, cryoscopically in benzene, 387, 391, 405, 404 at 1.95, 1.74, 1.08, 0.74 weight % respectively. $C_5H_{12}CdO$ requires C, 29.95; H, 6.0; Cd, 56.1%; M, 200.5).

In another reaction dimethylcadmium (0.8 gm.) and t-butanol (1 ml. 2 mol.) reacted in hexane (10 ml.). The reaction mixture was boiled with reflux for 2 hours, and was then concentrated to about 4 mls. On cooling, colourless hexagonal plates of methylcadmium t-butoxide crystallised from solution. (Found: C, 29.3; H, 5.9; Cd, 56.2%). The infra-red spectrum of the butoxide recorded in the form of a Nujol mull showed an absorption at 669 cm.$^{-1}$ due to 'methyl rock'; the ν(Me - Cd) region was complex. On exposure to air overnight the complex lost its sharp infra-red spectrum. Hydrolysis of the butoxide with water was only just discernible and even strong (ca. 6 N) sulphuric acid reacted very slowly.

Pyrolysis

The butoxide was heated in an evacuated system connected to an infra-red cell. The compound slowly turned brown as the temperature was raised, and the solid was heated at 190° for 30 minutes. The infra-red spectra of the gas evolved showed the presence of isobutene.

Reaction with pyridine

Dry pyridine was added to methylcadmium t-butoxide and the solution warmed. The butoxide was not readily soluble.

Hexane (5 ml.) was added and the resulting solution was evaporated to dryness under reduced pressure. The resulting solid had an infra-red spectrum identical to that of the original butoxide and no absorptions attributable to pyridine were observed.

Methylcadmium phenoxide

Dimethylcadmium (2.7 gm.) was condensed into one limb of a Schlenk tube and the system let down to atmospheric pressure with dry nitrogen. A solution containing phenol (1.8 gm., 1 mol.) in hexane (20 ml.) and ether (10 ml.) was added to the other limb. The Schlenk tube was fitted with an exit bubbler to allow methane to escape and the phenol solution was passed through the sintered disc and mixed with the dimethylcadmium solution. The solution was shaken to make it homogenous and methane was gently evolved. The reaction was exothermic and the solution became warm. As the evolution of methane continued methylcadmium phenoxide crystallised from solution as fine colourless needles. The reaction was complete within 15 minutes and the crystalline product (2.1 gm. 50%) was filtered, dried, and transferred to a purged flask. (Found: 'hydrolyzable methyl', 6.87; Cd, 51.1; M, cryoscopically in benzene, 826, 746, 788, 887, 900 at 3.78, 2.87, 2.31, 1.93, 1.66 weight % respectively. C_7H_8CdO requires 'hydrolyzable methyl', 6.82; Cd, 51.0%; M, 220.5). On heating methylcadmium phenoxide in a sealed melting point tube decomposition, indicated by the sample turning yellow, slowly occurred from room temperature. The compound collapsed between 235-240° accompanied by reduction in volume and formed a brown-yellow solid residue.

Hydrolysis of the phenoxide with water caused vigorous evolution of methane. Exposure to air overnight resulted in decomposition indicated by the change in infra-red spectrum recorded as a Nujol mull.

Reaction with pyridine

Methylcadmium phenoxide (ca. 2 gm.) was dissolved in 1:1 hexane-benzene mixture (40 ml.) and pyridine (1 ml., excess) was added. On shaking the solution methyl(pyridine)-cadmium phenoxide was deposited as colourless crystals, m.p. 142°. (Found: 'hydrolyzable methyl', 5.0; Cd, 37.3; M, cryoscopically in benzene, 455, 520, at 4.3, 2.15 weight % respectively. $C_{12}H_{13}CdNO$ requires 'hydrolyzable methyl', 5.0; Cd, 37.5%; M, 299.6). The molecular weight values obtained in benzene correspond to degrees of association of 1.52 and 1.40 respectively.

Methylcadmium(methyl)sulphide

Dimethylcadmium (0.87 gm.) was condensed on to frozen toluene at liquid nitrogen temperature. Methane thiol (134 N-cc., slightly less than 1 mol.) was condensed from the vacuum line on to the frozen dimethylcadmium solution. The liquid nitrogen bath was replaced by one at - 78° and as the reactants warmed to this temperature reaction took place and methane was evolved. The evolution of methane was accompanied by the formation of a gelatinous white precipitate of methylcadmium(methyl)sulphide. The solution was allowed to warm to room temperature and hexane (10 ml.) was added. No further reaction occurred on heating the solvent to reflux and the product which was insoluble in toluene and hexane was filtered from solution. (Found: hydrolyzable methyl, 8.65; Cd, 64.3. C_2H_6CdS requires hydrolyzable methyl, 8.60; Cd, 64.6%). On heating, the complex turned brown above 150° but did not melt below 300°. Hydrolysis with water caused a moderate evolution of methane which became vigorous on addition of dilute sulphuric acid.

Reaction with pyridine

Methylcadmium(methyl)sulphide was dissolved in excess pyridine in which it was readily soluble. On concentration by distillation under reduced pressure all of the pyridine was removed and the solid residue was shown to be identical to the starting material by infra-red spectra examined as nujol mulls.

Reaction with triethylphosphine

Triethylphosphine also proved to be a good solvent for the complex but in a similar manner to pyridine the infra-red spectrum of the solid residue after evaporation of solvent under reduced pressure was identical to that of the starting material and did not show any absorptions characteristic of triethylphosphine.

Reaction with 2:2'- bipyridyl

A benzene solution of bipyridyl was added to methylcadmium(methyl)sulphide and the solvent warmed and shaken. The solid did not appear to dissolve and after 30 minutes the solution was filtered through the disc of the Schlenk tube and evaporated to dryness. The very readily soluble solid residue was shown by infra-red spectrum to be 2:2'-bipyridyl and no indication of any of the cadmium-containing compound could be observed.

Methylcadmium(isopropyl)sulphide

Dimethylcadmium (3.25 gm.) was condensed on frozen hexane (20 ml.) in one limb of a Schlenk tube. Isopropane thiol (2.15 ml., 1 mol.) was added by syringe against a counter-current of nitrogen to hexane (20 ml.) in the other limb. The thiol solution was passed through the sintered disc and mixed with the solution of dimethylcadmium which was cooled to -76° in an acetone-CO_2 bath. Methane was rapidly evolved and methylcadmium(isopropyl)sulphide was deposited. On completion of the reaction more hexane (30 ml.) was added and the solution boiled when all of the solid material dissolved. On cooling, the product crystallised as colourless prisms. On determination of the melting point in a sealed tube the compound turned brown over a long range, 30 - 300° but did not melt. (Found: C, 23.7; H, 5.0; Cd, 55.4; M, cryoscopically in benzene, 1221, 1210, 1233, 1235 at 6.24, 5.11, 4.33, 3.75 weight %. $C_4H_{10}CdS$ requires C, 23.7; H, 5.0; Cd, 55.5; M, 202.5).

The infra-red spectrum of the compound was recorded as a nujol mull and showed absorptions corresponding to 'methyl rock' at 658 $cm.^{-1}$ and ν(Me - Cd) at 467 $cm.^{-1}$

Hydrolysis of the compound with water was very slow and even with 2N sulphuric acid methane was evolved slowly at room temperature.

Reaction with pyridine.

Pyridine (excess) was added to methylcadmium(isopropyl)-sulphide in benzene and the solution concentrated to dryness under reduced pressure. The infra-red spectrum of the product was identical to that of the original cadmium containing material.

Methylcadmium(*t*-butyl)sulphide

Dimethylcadmium (4.8 gm.) was condensed on to frozen hexane (40 ml.) in one limb of a Schlenk tube. The solution was allowed to warm to 0°C and shaken to make it homogenous.

t-Butane thiol (1 mol.) was added to the solution by syringe and methane was evolved from the resulting very vigorous reaction. The solution was warmed and filtered through the Schlenk disc. On cooling the compound crystallised as colourless prisms. (Found: 'hydrolyzable methyl', 7.01; Cd, 51.8; M, cryoscopically in benzene, 881, 894, 880 at 2.92, 2.63, 2.23 weight % respectively. $C_5H_{12}CdS$ requires 'hydrolyzable methyl', 6.94; Cd, 51.95%; M, 213.5). The molecular weight values obtained in benzene solution corresponded to degrees of association of 4.06, 4.12 and 4.05 respectively.

The compound was hydrolysed by water and methane was evolved at a moderate rate. On addition of 2N sulphuric acid vigorous hydrolysis occurred. On heating, decomposition occurred above 100° indicated by reduction in volume of the compound, which turned brown.

Reaction with pyridine

Addition of pyridine in a small volume of hexane to the complex followed by filtration and concentration of the solution yielded a solid residue with an identical infra-red spectrum to that of methylcadmium(t-butyl)sulphide.

Methylcadmium(phenyl)sulphide

Dimethylcadmium (1.41 gm.) was condensed on to frozen hexane (20 ml.) in one limb of a Schlenk tube. Thiophenol (1.0 ml., 1 mol.) was added by syringe to hexane (20 ml.) in the other limb. The thiol solution was passed through the

Schlenk disc into the dimethylcadmium solution which was cooled in an acetone —CO_2 bath. On mixing a flocculent precipitate was produced and methane was evolved. A further aliquot of hexane (40 ml.) was added and the solution warmed but the solid product appeared to be insoluble. The solid was filtered free from the solution and benzene was added. The product which was only very sparingly soluble was again washed on a filter and pumped dry. (Found: hydrolyzable methyl, 6.34; Cd, 46.9. C_7H_8CdS requires hydrolyzable methyl, 6.35; Cd, 47.6%). On heating the compound it turned yellow and contracted in volume above 60° but did not melt.

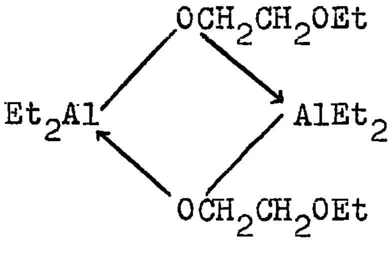
Reaction with pyridine

Methylcadmium(phenyl)sulphide was dissolved in pyridine and on concentration by evaporation of solvent at reduced pressure yielded a syrup. A crystalline compound could not be obtained. On further pumping pyridine was lost and the original cadmium compound recovered.

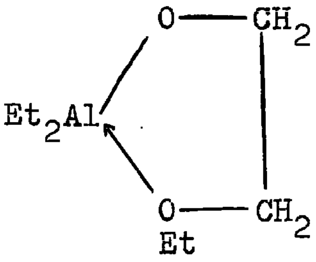
DISCUSSION

DISCUSSION

The effect of replacing one methyl group of dimethylcadmium by an atom of donor character such as oxygen or sulphur is to enhance the acceptor properties of the cadmium atom and also to increase the donor character of the oxygen or sulphur atom respectively. This effect is observed in alkylaluminium derivatives[42] and a difference in the donor strengths of the two oxygen atoms in $(Et_2AlOCH_2CH_2OEt)_2$ explains the observed association to give the structure (xiv) rather than formation of the monomer (xv).



(xiv)



(xv)

As cadmium dialkyls form co-ordination complexes with ethers,[27] which are considerably dissociated in the case of simple ethers and slightly dissociated in that of chelating ethers, then compounds such as MeCdOR and MeCdSR might be expected to be associated by relatively strong co-ordination.

A wide study of the reactions of trialkyl derivatives of Group III metals with molecules containing hydrogen bonded to an atom of donor ability has been made and many complexes characterised. Hydrocarbon is frequently eliminated immediately or on heating and the resulting compounds have been reviewed.[43] With the exception of boron which is anomolous in forming monomers e.g. $Me_2B.NME_2$,[44] $Me_2B.OMe$,[44] $Me_2B.SMe$,[45] the metals exhibit a tendency to increase their co-ordination number to <u>four</u> by the formation of trimers or dimers. Thus methane is liberated from trimethyl derivatives, Me_3M, (M = Al, Ga, In, Tl), with the formation of associated products, x = 2 or 3

$$Me_3M \quad + \quad MeOH \longrightarrow (Me_2MOMe)_x$$

The methoxides obtained are unaffected by trimethylamine.[46] Reaction with methane thiol yields dimeric products [46-48]

$$Me_3M \quad + \quad MeSH \longrightarrow (Me_2MSMe)_2$$

In contrast to the methoxide derivatives, $(Me_2InSMe)_2$ and $(Me_2TlSMe)_2$, the complexes $(Me_2AlSMe)_2$ and $(Me_2GaSMe)_2$ reversibly absorb trimethylamine to form addition complexes:[46]

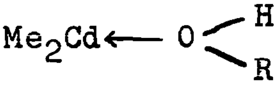
$$(Me_2AlSMe)_2 \quad + \quad 2NMe_3 \rightleftharpoons 2Me_2Al(SMe)N{:}Me_3$$

This indicates the comparable donor strength of the sulphur and nitrogen atoms in the latter cases. A similar effect involving pyridine is observed with tantalum <u>n</u>-alkoxides,[49] $Ta(OR)_5$, which are dimeric in benzene solution but monomeric in pyridine, probably due to co-ordination by solvent yielding $Ta(OR)_5py$. The tendency of donor molecules to add to metals with enhanced acceptor properties arising in this way, by bonding between the metal and an electron attracting group, is well known and accounts for the formation of such derivatives as $(CF_3)_2Hg.2PPh_3$[28], $Th(OCMe_2.CCl_3)_4 2py$ $Zr(OCH_2CCl_3)_4.2Me_2CO$.[49]

Reaction of dimethylcadmium with alcohols

Methylcadmium alkoxides were prepared from the reaction of dimethylcadmium with the respective alcohol in hexane solution at -76°.

$$Me_2Cd + ROH \longrightarrow MeCdOR + CH_4$$

In contrast to the other alkoxides evolution of methane and corresponding formation of methylcadmium phenoxide did not occur until the solution was warmed to about 30°. In no case was a co-ordination complex  $Me_2Cd \leftarrow O<^{H}_{R}$ isolated.

Only the methoxide was too sparingly soluble to allow the determination of molecular weight by cryoscopic means in benzene. The values obtained and the corresponding degrees of association for the other complexes are shown in Table I.

Methylcadmium ethoxide, -isopropoxide and -phenoxide were all found to be tetrameric and the t-butoxide was unique in being a dimer.

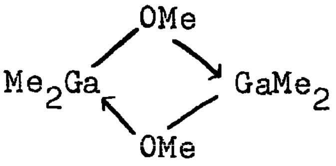
TABLE I

Reactions of dimethylcadmium with alcohols and thiols

Reagent	Product	Molecular Weight in benzene	Degree of Association
MeOH	$(MeCdOMe)_x^a$	-	-
EtOH	$(MeCdOEt)_4$	744, 748, 746	4.32, 4.35, 4.33
Pr^iOH	$(MeCdOPr^i)_4$	747, 738, 759	4.00, 3.96, 4.07
Bu^tOH	$(MeCdOBu^t)_2$	387,391,405,404	1.93,1.95,2.02,2.01
PhOH	$(MeCdOPh)_4$	826, 746, 788, 887, 900	3.75, 3.38, 3.58, 4.02, 4.08
MeSH	$(MeCdSMe)_x^a$	-	-
Pr^iSH	$(MeCdSPr^i)_6$	1221, 1210 1233, 1235	6.03, 5.97 6.09, 6.10
Bu^tSH	$(MeCdSBu^t)_4$	881, 894, 880	4.06, 4.12, 4.05
PhSH	$(MeCdSPh)_x^a$	-	-

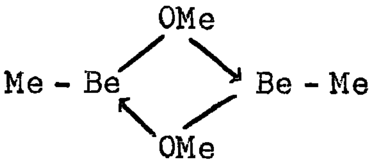
[a] Not soluble enough in benzene to allow a cryoscopic determination of molecular weight.

These results are interesting in comparison with alkoxides of other metals as they further indicate the factors which encourage and hinder the formation of associated complexes. The association of Group III metal alkoxides which brings the metal atoms to a commonly found co-ordination number of four such as $(Me_2GaOMe)_2$, figure (xvi) is



(xvi)

understandable and there is no tendency to increase the co-ordination of the metal atom further. In Group II metal derivatives, however, association to a dimeric species imparts a three co-ordinate state to the metal such as is found in methylberyllium methoxide,[29] figure (xvii). This



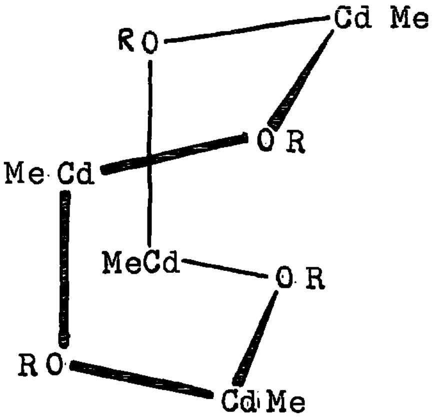
(xvii)

is not so surprising in this case as beryllium does in some cases exhibit stability in this state compared to that of sp^3 hybridisation and four co-ordination of the metal as exemplified by the stability of the trimethylamine derivative[9], $Me_2Be \leftarrow NMe_3$, in contrast to the failure to prepare $Me_2Be.2NMe_3$

and the instability of $Et_2Be.2NMe_3$. Metals of Group IIB, however, show a strong tendency towards a state of <u>four</u> co-ordination in their compounds, and methylzinc and methylcadmium alkoxides would not be expected to form dimers, particularly in view of the enhanced donor and acceptor properties arising from the oxygen -metal bond. This is supported experimentally and the methylzinc alkoxides reported[39] are all tetrameric as are the methylcadmium alkoxides (with the exception of $(MeCdOBu^t)_2$) discussed in this work.

Structure of the tetrameric alkoxides

The structure of $(MeCdOR)_4$ compounds can reasonably be assumed to be an eight membered ring. An open ring structure would lead to three co-ordinate and hence co-ordinatively unsaturated cadmium whereas a cubic arrangement, figure (xviii), such as has been proposed for thallium alkoxides[50,51], $(TlOR)_4$, $(PhAlNAr)_4$ [52,53] and $(RZnOR')_4$ [54,39], might allow an increase in co-ordination of both cadmium and oxygen by interaction



(xviii)

between adjacent cadmium and oxygen atoms shown as non-bonding in (xviii). Rapid interchange of the six isomeric forms in which the bond angles C-Cd-O and Cd-O-Cd are assumed to be about 120° and 108° respectively could take place resulting in a time average structure of a cube. Preliminary Xray crystallographic structure studies on $(PhAlNAr)_4$ indicate a cubic arrangement[53] and similar studies on $(TlOMe)_4$ and $(MeZnOMe)_4$ show that the metal atoms form a regular tetrahedron.[51,54] Alternatively, this arrangement can be considered as two interlocking tetrahedra of metal and oxygen atoms respectively. If the oxygen tetrahedron was smaller than that of the cadmium atoms thus giving a closer approach to tetrahedral co-ordination about oxygen, a distorted cubic structure would arise.

Additional evidence which supports the view that the metal atoms in $(MeCdOR)_4$ complexes have a substantial degree of co-ordinative saturation is their lack of reaction with pyridine (except $(MeCdOPh)_4$). If the metal atoms were only three - co-ordinate expansion of their co-ordination number to four by formation of a pyridine adduct would be expected in view of the enhanced acceptor properties of the metal due to bonding to an electron attracting group. The absence of such adducts therefore suggests a substantial degree of co-ordinative saturation in the tetramers. A similar lack of reaction of $(MeZnOR)_4$ with pyridine has been reported.[39]

In the cases of $(MeZnOPh)_4$[39] and $(MeCdOPh)_4$ however, a pyridine derivative is formed. This renders $(MeCdOPh)_4$ unique among the methylcadmium derivatives investigated in forming a crystalline pyridine complex, $(MeCd(py)OPh)_x$, (where x = 1.52, 1.40 at 4.3 and 2.15 weight % respectively in benzene). This is consistent with the donor character of oxygen attached to phenyl being weaker than when it is attached to an alkyl group. The zinc analogue is dimeric,[39] $(MeZn(py)OPh)_2$, but the dissociation of the cadmium compound is not surprising in the light of the ready dissociation of $Me_2Cd.py$.[27]

As cadmium exhibits more B-character than zinc, exemplified in the large number of tertiary phosphine and arsine complexes formed by metal halides of the former[55,56] and the few examples isolated of the latter,[56,57] an attempt was made to prepare a triethylphosphine complex of methylcadmium isopropoxide. No adduct was isolated in this case nor with 2:2'- bipyridyl in which case entropy effects should be relatively more favourable towards complex formation.

Methylcadmium *t*-butoxide

This complex is interesting in being the only dimeric alkoxide prepared. Although entropy grounds might be expected to support the formation of dimers rather than tetramers this cannot be a consideration of great importance in view of the many tetramers that have been observed among the methylzinc and methylcadmium alkoxides. Similarly, the angular strain involved in the formation of dimers cannot be of overwhelming importance in the light of the formation of such compounds as $(MeCdOBu^t)_2$, $(MeZnNPh_2)_2$.[39] The most important consideration in controlling the ring size appears to be steric. Interference of the large t-butyl groups apparently prevents the attainment of a tetrameric configuration in methylcadmium t-butoxide and results in the formation of a dimer. (However, the isolation of $(MeZnOPh)_4$ is apparently inconsistent with a substantial degree of steric hindrance and cannot be accounted for at the moment). The lack of isolation of a pyridine adduct with this complex, which necessarily contains three co-ordinate cadmium could be due to steric hindrance preventing the pyridine molecule approaching close enough to co-ordinate to cadmium, or to a ready dissociation of the adduct preventing its isolation. In the latter case it would resemble $Ta(OR)_5.py$ which is most likely formed in solution as the alkoxide is monomeric in pyridine but $[Ta(OR)_5]_2$ is recovered on removing the solvent.[49]

The influence of bulky alkyl groups has been observed in the alkoxides of other metals. In particular a study of the $M(OR)_4$ derivatives of Si, Ti and Zr showed that the volatility of the compounds increased with increased chain branching.[58] This was particularly marked in the derivatives of zirconium and ebullioscopic determinations of molecular weight in benzene showed a decrease in association on changing from primary to tertiary alcohol derivatives: $[Zr(OCH_2CH_2CH_2CH_2Me)_4]_3$, $[Zr(OCH(Me)Pr^i)_4]_2$, $[Zr(OCMe_2Et)_4]_1$. A similar decrease in association is observed in the series $[Zr(OCHMe_2)_4]_3$, $[Zr(OCHEt_2)_4]_2$, $[Zr(OCHPr^n)_4]_1$, $[Zr(OCHMeBu^t)_4]_1$, as the alkyl group becomes more bulky. These observations strongly indicate that association by the formation of co-ordinate bonds between oxygen and zirconium is restricted or excluded by the steric hindrance of the alkyl group R. The formation of monomeric species, $M(OCMe_2R)$, (M = Ti, Zr; R = Me, Et, n-Pr, i-Pr, n-Bu), in all derivatives of tertiary alcohols is as would be expected on steric grounds.

The reactions of methylcadmium alkoxides towards water and dilute sulphuric acid show a steady gradation, Table II. The vigour with which methane is liberated on hydrolysis decreases from a violent reaction with methylcadmium methoxide to an extremely slow evolution in the case of the butoxide, paralleling the increasing size of the alkyl group attached to the oxygen atom. This is consistent with an increasing degree of shielding of the cadmium atoms with increasing size of the respective alkyl groups.

Pyrolysis of methylcadmium alkoxides.

Pyrolysis of methylcadmium methoxide, ethoxide, and isopropoxide resulted in decomposition, presumably by disproportionation, at temperatures up to 180°.

TABLE II

Reactions of methylcadmium compounds

Compound	Reaction with :		
	water	$2N.H_2SO_4$	pyridine
	Evolve methane		
$(MeCdOMe)_x$	v.vig.	v.vig.	none
$(MeCdOEt)_4$	vig.	v.vig.	none
$(MeCdOPr^i)_4$	mod.	vig.	none
$(MeCdOBu^t)_2$	v.slow	slow	none
$(MeCdOPh)_4$	vig.	v.vig.	$(MepyCdOPh)_x$
$(MeCdSMe)_x$	mod.	vig.	dissolves [a]
$(MeCdSPr^i)_6$	v.slow	slow	none
$(MeCdSBu^t)_4$	mod.	vig.	none
$(MeCdSPh)_x$	mod.	vig.	dissolves [a]

vig., vigorous; mod., moderate; v., very.

[a] Pyridine lost on pumping.

$$2MeCdOR \xrightarrow{heat} Me_2Cd + Cd(OR)_2$$

Dimethylcadmium was identified by infra-red spectrum taken on the gas liberated but the residue was not characterised. Similar disproportionation reactions on pyrolysis are observed for $(MeBeOMe)_2$[29] and $(MeZnOR)_4$, but not for $(MeCdOBu^t)_4$. In the latter case zinc[39] and cadmium derivatives react in a similar manner and liberate isobutene.

Reactions of dimethylcadmium with thiols

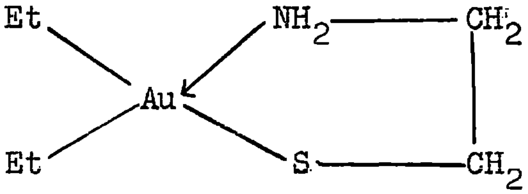
Dimethylcadmium reacts with methane thiol and thiophenol respectively at -78° to give products which are insoluble in benzene, toluene and hexane and are presumably polymeric. In this respect they resemble the mercaptides of mercury,[59,60] $[Hg(SMe)_2]_x$, $[Hg(SEt)_2]_x$ and $[Hg(SBu^t)_2]_x$ and the n-alkyl thiol derivatives of dimethylzinc,[39] $(MeZnSR)_x$, which are also polymers. Although insoluble in organic solvents $(MeCdSMe)_x$ is readily soluble in pyridine or triethylphosphine. Evaporation to dryness under reduced pressure leaves only the original cadmium compound (shown by infra-red spectrum) and in neither case could an adduct be prepared. The addition of a benzene solution of 2:2'-bipyridyl to $(MeCdSMe)_x$ does not cause the latter to dissolve and only bipyridyl was recovered from the solution. Similarly $(MeCdSPh)_x$ dissolves in pyridine but evacuation of the mixture causes the loss of the ligand. Evidently pyridine reacts reversibly, competing with sulphur atoms for co-ordination positions about the cadmium.

$(MeCdSPh)_x$ (insoluble) + py $\rightleftharpoons$ $(MepyCdSPh)_n$ (soluble)

Such a reaction is analogous to the equilibrium obtained between trimethylamine and the dimeric aluminium and gallium compounds.

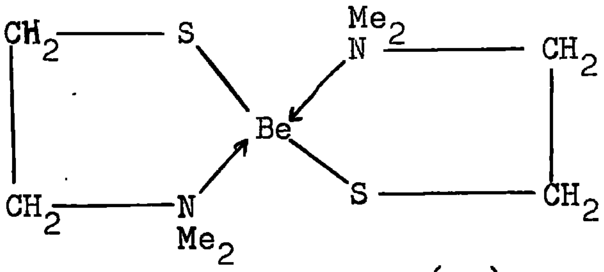
$$(Me_2AlSMe)_2 + 2NMe_3 \rightleftharpoons 2Me_2Al(NMe_3)SMe$$

Thiol derivatives of non-transition metals have been relatively little studied but monomeric compounds of beryllium and gold are known. The product derived from 2-amino-ethane thiol, $H_2NCH_2CH_2SH$, and $(Et_2AuBr)_2$ is monomeric,[61] figure (xix) in several solvents. This has



(<u>xix</u>)

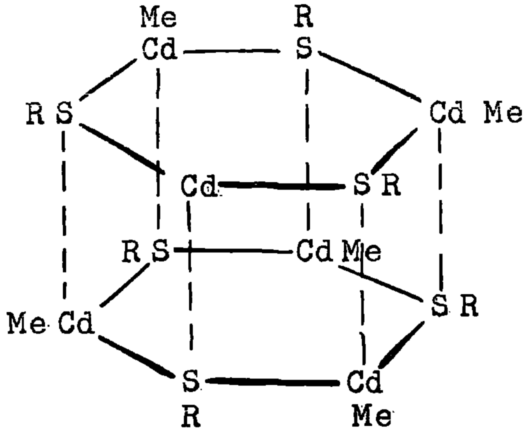
been attributed to co-ordination by the amine group which is surprising in that sulphur might have been expected to be a stronger donor than nitrogen towards gold and thus to produce a dimer. Dimethylamino-ethane thiol reacts with dimethylberyllium to give a monomer,[62] $(Me_2NCH_2CH_2S)_2Be$, possibly due to the formation of an internal co-ordination complex involving the nitrogen atoms, figure (xx).



(<u>xx</u>)

Branched chain thiols, i-PrSH and t-BuSH react with dimethylcadmium to give complexes which are soluble in organic solvents. Cryoscopic determinations of molecular weight in benzene solution, Table I, show that the complex derived from isopropane thiol is hexameric $(MeCdSPr^i)_6$ analogous to the corresponding zinc compound[39], while that derived from t-butane thiol is tetrameric. The zinc derivative is a pentamer, $(MeZnSBu^t)_5$.

Methylcadmium(t-butyl)sulphide could well have a structure similar to the cubic arrangement postulated for the alkoxides whereas methylcadmium(isopropyl)sulphide could conceivably have a similar structure involving two six-membered rings in which positive and negative centres are brought relatively close together, figure (xxi). Again the effect is to increase the effective co-ordination of the cadmium and sulphur atoms. This would oppose the formation of pyridine adducts and indeed such complexes could not be isolated.



(xxi)

TABLE III

Methylcadmium infra-red absorptions[a] (cm.$^{-1}$)

Compound	Cd-Me rock	ν(Cd-Me)
Me_2Cd	688 vs	522 vs
$(MeCdOMe)_x$	670 vs	486 vs
$(MeCdOEt)_4$	667 vs	483 vs
$(MeCdOPr^i)_4$	668 vs	482 s
$(MeCdOBu^t)_2$	669 vs	481 s
$(MeCdOPh)_4$	664 s	487 m
$(MepyCdOPh)_x$	656 m	471 m
$(MeCdSMe)_x$	649 s	468 s
$(MeCdSPr^i)_6$	658 s	465 s
$(MeCdSBu^t)_4$	665 s	469 m
$(MeCdSPh)_x$	659 s	472 s

s, strong; m, medium; v, very.

[a] As Nujol mulls except Me_2Cd (liquid film).

Infra-red absorptions of the Cd-Me group

The infra-red spectrum of dimethylcadmium has been studied,[63] but the spectra of other alkylcadmium compounds have not been reported.

The Cd-Me rocking and Cd-Me stretching frequencies observed for dimethylcadmium and the methylcadmium co-ordination complexes are shown in Table III. The Cd-Me rocking and stretching frequencies observed in the alkoxides show little variation between compounds and are generally at slightly higher frequencies than those observed for the sulphur derivatives. Both Cd-Me rock and ν(Cd-Me) are at considerably lower frequencies in the co-ordination complexes than those observed in dimethylcadmium in which the metal is two co-ordinate.

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