# Durham E-Theses

*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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## <u>MEMORANDUM</u>

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 alkyl-mercuric halides and tertiary alkyl phosphines. These complexes slowly disproportionate to give dialkylmercury and $(R_3'P)_2HgX_2$. 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 :

$$RHgX + PR_3' \longrightarrow R_2Hg + (R_3'P)_2HgX_2$$
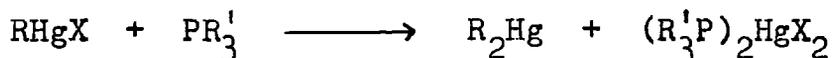
and the relatively fast reaction of $[PhHgPEt_3]NO_3$ with sodium iodide in which $Ph_2Hg$ and $(Et_3)_2HgI_2$ are formed was followed photometrically. Comparative conductometric

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 $\underline{t}$-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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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(O) 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 electro-negative 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 four, due to $sp^3$ hybridization, and occasionally six, attributable to $sp^3d^2$ 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 $nd_{g}2$ 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 $\underline{xy}$ plane allowing strong two-covalent bonding along the $\underline{z}$ axis. The stability of this configuration is thus dependant on a small $\underline{d - s}$ 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 $\underline{s - p}$ separation is the determining factor giving $\underline{sp}$ hybridization, if the charge is appreciable the smaller $\underline{d - s}$ separation and Orgel's picture is more likely.

### Inorganic co-ordination complexes.

Where there is no possibility of partial double bond formation involving $\underline{d}$ orbitals, co-ordinate bonds are very dependant upon electronegativity effects. In the heavier metals, which have $\underline{d}$ 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(1) 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 $\underline{diminishes}$ markedly from zinc

to mercury while the tendency to co-ordinate to phosphorus
and sulphur containing donors <u>increases</u> in the same series.

<u>Nitrogen containing ligands</u>

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



(i)                              (ii)
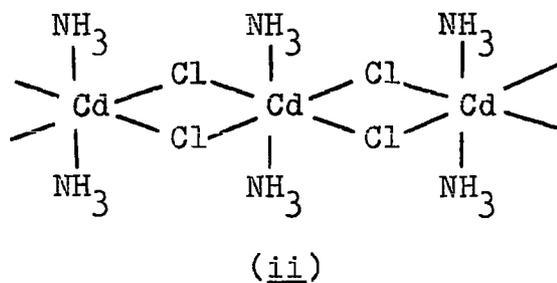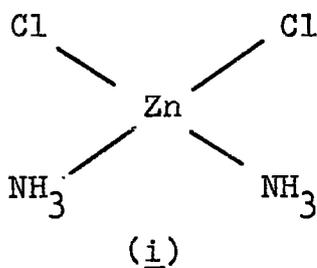
cadmium analogue forms an octahedral complex with bridging
chlorine atoms[10] (ii), while the mercury compound exists as
discreet $[H_3N-Hg-NH_3]^{2+}$ units randomly arranged in the crystal.[11]
Reaction of gaseous ammonia with dry salts of zinc, cadmium,
and mercury other than halides usually yields tetrammines in
which there is a tetrahedral arrangement of ammonia molecules
around the metal analogous to the arrangement in $(NH_3)_2ZnCl_2$.

Terpyridyl derivatives of all three metal halides are

known[12] and it was suggested that the metal was in a tetra-
hedral environment as $[\text{terpyMX}]^+$. Crystal structure
determinations[13] however have shown that terpyridyl dichloro-
zinc (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)
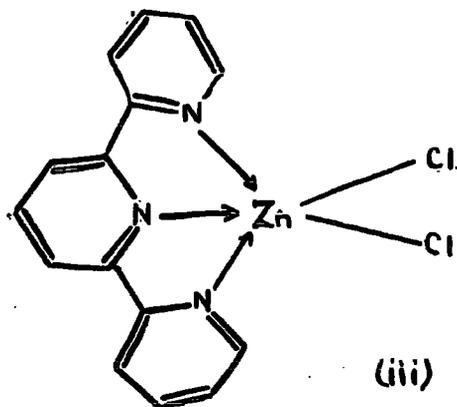
that of zinc and is assumed to have the same structure.
Although _five_ co-ordination is not common the filled _3d_
shell in Zn(11) has spherical symmetry and is therefore not
energetically favourable to any particular stereochemical
arrangement.    More recently other _five_ co-ordinate zinc
complexes have been prepared.    Bisacetylacetonatozinc (11)
monohydrate and the 4-methylpyridine derivative of $(\text{acac})_2\text{Zn}$
are other examples.    It is interesting that the bis 4-methyl-
pyridine complex which is octahedral dissociates in benzene
solution løosing 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.

|  | $MCl_2$ | $MBr_2$ | $MI_2$ |
|---|---|---|---|
| $ZnX_2 \cdot 6NH_3$ | 23° | 31° | 28° |
| $CdX_2 \cdot 6NH_3$ | 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] $\left[R_3P(As)\right]_2ZnX_2$.   The
effects of electronically active substituents upon the

stability of these complexes is considerable.[22]   Thus
$(p\text{-}Me_2NC_6H_4PMe_2)\,ZnI_2$  is stable, $(Ph.PMe_2)_2\,ZnI_2$ and
$(PhPEt_2)_2\,ZnI_2$  smell of phosphine and readily dissociate,
and $(p\text{-}CF_3C_6H_4PEt_2)_2\,ZnI_2$ 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)   $\left[R_3P(As)\right]_2 CdX_2$

b)   $\left[R_3P(As).CdX_2\right]_2$

c)   $\left[R_3P(As)\right]_3 \left[CdX_2\right]_2$

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).
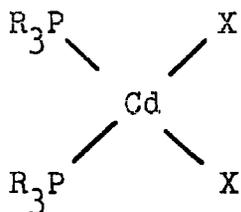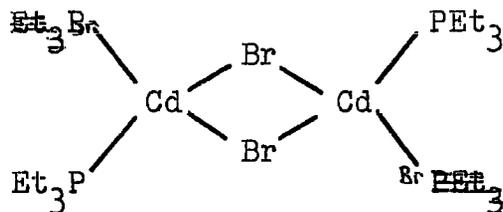


$\underline{(iv)}$                              $\underline{(v)}$

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 $d_\pi - d_\pi$ bonding.   The complexes

are odourless and can be recrystallised without decomposition.

Five classes of compounds are known:[21]

(a)   $[R_3P(As)]_2 HgX_2$

(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 crystallo-
graphically 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]

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

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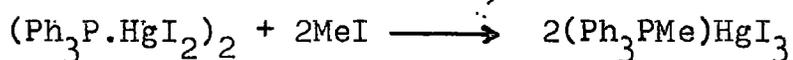
## Oxygen donors

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, tetrahydro-thiophen 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 tetrahydro-
thiophen 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 $[Cl-Hg-SEt_2]^+$
and $[Cl-Hg-SC_4H_8]^+$ 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.

$$M_{aq.}^{2+} + 4X^- = MX_4^{2-} \quad ; \quad K = \frac{[MX_4^{2-}]}{[M_{aq.}^{2+}][X^-]^4}$$
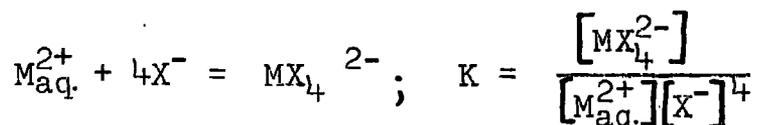
| Halide | Log K | | |
|---|---|---|---|
| | Zn | Cd | Hg |
| Cl$^-$ | 0 | 3 | 16 |
| Br$^-$ | -1 | 4 | 22 |
| I$^-$ | -2 | 6 | 30 |

## 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]

$$CH_3-Hg^+ + e^- \longrightarrow CH_3-\overset{\bullet}{Hg} \longrightarrow \tfrac{1}{2}Hg + \tfrac{1}{2}(CH_3)_2Hg$$
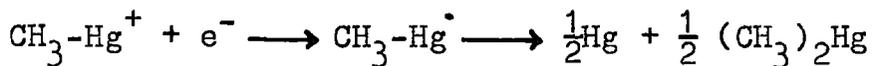
The preparation of higher homologues and some diarylmercury compounds by the electrolysis of the alkyl- and aryl-mercuric chlorides in liquid ammonia solution at $-78°$ has been carried out.[49]  Black solids, possibly organic metals,[50] are initially deposited on the platinum electrodes but decomposition 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]

$$2PhHgX + Na_2SnO_2 + 2NaOH \longrightarrow Ph_2Hg + Hg + 2NaX + Na_2SnO_3$$
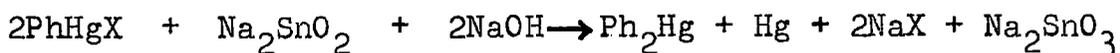
Disproportionation of organomercuric salts occurs on treatment with anions which form very stable complexes with mercury[55,56] e.g. $CN^-$, $SCN^-$, $I^-$.  The equilibrium is displaced so much in favour of the anionic complex as to make the reaction a useful synthesis for diorganomercurials.

$$2RHgX + 4KCN \longrightarrow R_2Hg + 2KX + K_2Hg(CN)_4$$
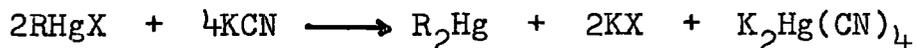
Mercury can also be removed from the system by forming a highly insoluble derivative.  In this way dialkylmercury compounds can be obtained by warming the corresponding sulphide.

$$(RHg)_2S \longrightarrow R_2Hg + HgS$$
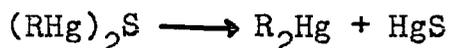
Mixed dialkyls, diaryls and alkyl aryls of mercury can be prepared from the respective Grignard reagent and organomercuric halide.[57,58]

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

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 $300^O$ [60] or at room
temperature on exposure to mercury radiation[61] of $2537Å$.

The diaryls are usually solids, $Ph_2Hg$,m.p.$125^O$;
di-m-tolylmercury, m.p.$102^O$;. bis-diphenylmercury, m.p.$216^O$.
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 $200^O$.  Dibenzylmercury,
which is one of the least stable,[62] begins to decompose at
$75^O$ and decomposition is complete by $160^O$.  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 $140^O$ 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

- 20 -

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).



o,Hg

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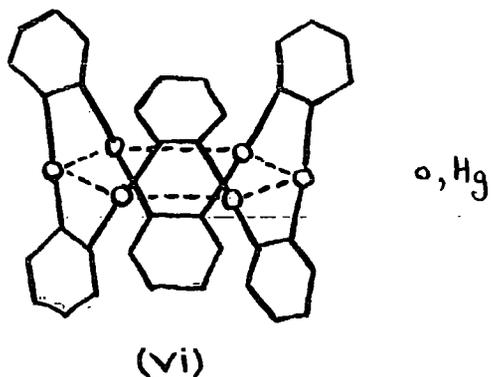
Bis-organomercurials are chemically rather inert.  They are uneffected by air, water and dilute acids making them unique in Group II and differ further in not forming co-ordination complexes with ethers and amines.

Dialkyl and diaryl mercury compounds react with concentrated acids evolving hydrocarbon and giving the

corresponding organomercuric salt :

$$Et_2Hg + HOAc \xrightarrow[\text{16 hours}]{220^o} EtHgOAc + C_2H_6$$
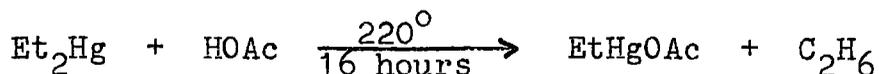
Dilute solutions of hydrogen chloride in non-aqueous solvents readily attack bismercurials :

$$R-Hg-R + HCl \longrightarrow RH + RHgCl$$

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

$$R_2Hg + X_2 \longrightarrow RHgX + RX$$
$$RHgX + X_2 \longrightarrow HgX_2 + RX$$

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 :

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

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

$$R_2Hg + HgX_2 \longrightarrow 2RHgX$$
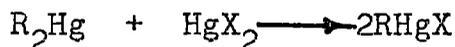
Alkyl and aryl exchange reactions of bis-mercurials with other metals are of great synthetic value.   Many such reactions were superseded as preparative methods with the discovery of Grignard reagents, but several of these reactions still provide a clean and rapid method of obtaining other organometallic

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]

$$ArN_2Cl + Hg \longrightarrow ArHgCl + N_2$$
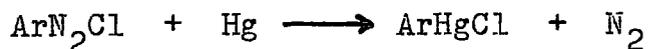
or by reduction of mercuric chloride :

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

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.

$$ClCH_2HgCl + CH_2N_2 \longrightarrow (ClCH_2)_2Hg + N_2$$
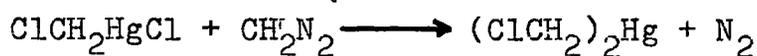
Similar substituted alkylmercuric halides are obtained from mercuric salts and olefins and these compounds are discussed more fully later in this introduction.

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 electro-negativity. In a benzene solution of methylmercuric nitrate the Raman spectrum observed is that due to $Me-Hg-O-NO_2$ 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 $[MeHg-O-NO_2]$, $[MeHg-OH_2]^+$ 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 :

$$MeHg^+ + CN^- \rightleftharpoons MeHgCN \qquad \log K_1 = 14$$
$$MeHg^+ + MeHgCN \rightleftharpoons (MeHg)_2CN^+ \qquad \log K_2 = 0$$
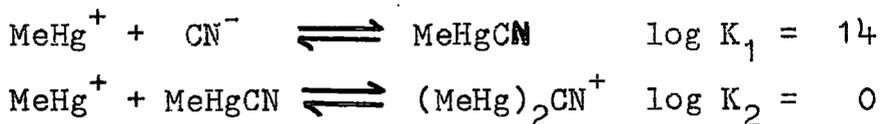
Stronger complexes are formed with oxygen and sulphur and a tetramethylmercury sulphide, $[(MeHg)_4S]^{2+}$ can be detected.[74]

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 $\Omega^{-1}$ 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, $H_3O^+$.

$$MeHg^+ + OH^- \rightleftharpoons MeHgOH \qquad \log K_1 = 9.4$$
$$MeHg^+ + MeHgOH \rightleftharpoons (Me_2Hg)_2OH^+ \qquad \log K_2 = 2.4$$
$$H^+ + OH^- \rightleftharpoons H_2O \qquad \log K_1 = 15.6$$
$$H^+ + H_2O \rightleftharpoons H_3O^+ \qquad \log K_2 = -1.7$$
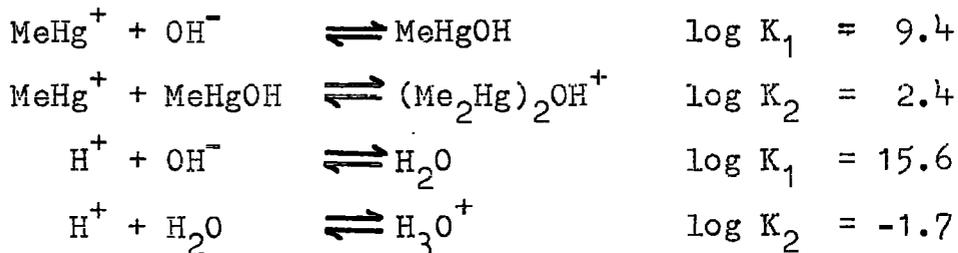
The trismethylmercury oxonium salts can be prepared by partial neutralization of methylmercuric oxide. Alternatively addition of methylmercuric salts can take place and trismethyl-mercury oxonium bromide is formed from methylmercuric bromide

and methylmercuric oxide in boiling benzene.

$$(MeHg)_2O + MeHgBr \longrightarrow \left[(MeHg)_3O\right]Br \quad \text{m.p. } 116^{\circ}$$
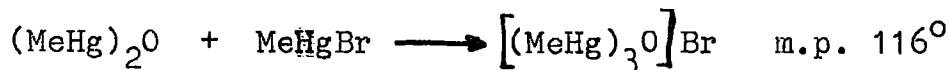
Aqueous solutions of oxonium salts are stable if the methyl-mercuric salt is water-soluble and ionic compounds, e.g. those containing the anions $NO_3^-$, $ClO_4^-$, $PF_6^-$ are therefore not decomposed.   Where the methylmercuric salt is insoluble in water, e.g.  $Cl^-$, $Br^-$, $I^-$, $CN^-$, it is precipitated on addition of the oxonium salt to water.

$$\left[(MeHg)_3O\right]Br \xrightarrow{\text{water}} (MeHg)_2O + \downarrow MeHgBr$$
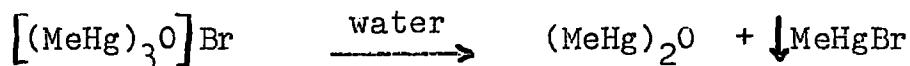
Polynuclear complexes are formed with sulphur even more readily than with oxygen giving compounds with similar reactions to the oxygen complexes.   Trismethylmercury sulphonium salts can be prepared in an analogous manner to the oxonium salts.   When methylmercuric sulphide in warm benzene is added to 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

$$MeHg^+ + L^{\lambda-} \rightleftharpoons MeHg\,L^{(1-\lambda)}$$
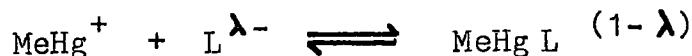
have been measured for several ions and neutral ligands (L).[72,74] The order of affinity for the $MeHg^+$ cation of the more common

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 bisperfluoroalkyl-mercurial :[78,79]

$$R_f I \ + \ Hg \ \xrightarrow[\text{or u.v.}]{\text{heat}} \ R_f HgI \ \xrightarrow[\text{amalgam}]{Cd} \ (R_f)_2 Hg$$
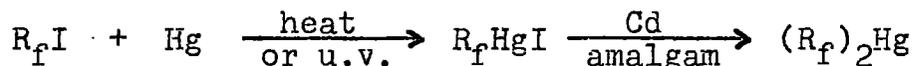
The method is not completely general as a mixture of decomposition products only was obtained in an attempted preparation of bisheptafluoro-n-propylmercury.[81]

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]

$$2 \ CF_2 = CF_2 + HgF_2 \ \longrightarrow \ (C_2F_5)_2 Hg$$

Bistrifluoromethylmercury is extremely soluble in water (473 gm./l., 1.3M) in which it is weakly conducting.[81]  The general behaviour of $(CF_3)_2 Hg$ suggests that the $CF_3$ group functions as a pseudo-halogen, intermediate in electro-negativity 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.

$$(CF_3)_2Hg \rightleftharpoons (CF_3)_2HgOH_2 \rightleftharpoons (CF_3)_2HgOH^- + H_3O^+$$
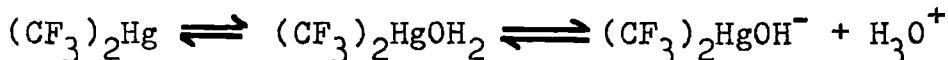
Electrolysis of this aqueous solution yields fluoroform at both anode and cathode.    $CF_3Hg^+$ ions would give $CF_3H$ at the cathode and it would also be formed together with oxygen by the discharge of $(CF_3)_2HgOH^-$ at the anode.[82]

Bistrifluoromethylmercury forms addition compounds with halide ions[80,84] analogous to mercuric halides.    Conducto-metric titrations of aqueous $(CF_3)_2Hg$ and $CF_3HgI$ with KX indicated the formation of complexes corresponding to $\left[Hg(CF_3)_2X\right]^-$, $\left[Hg(CF_3)_2X_2\right]^{2-}$ and $\left[Hg(CF_3)IX\right]^-$, $\left[Hg(CF_3)IX_2\right]^{2-}$ respectively.    The stability of the complexes decreases from X = I to X = Cl.    Complex anions $\left[CF_3HgI_3\right]^{2-}$, $\left[(CF_3)_2HgI_2\right]^{2-}$ and $\left[C_3F_7HgI_3\right]^{2-}$ 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, triphenyl-phosphine, 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,

$$(C_6F_5)_2Hg \ + \ Br_2 \ \xrightarrow[60°]{5 \text{ days}} \ : \ C_6F_5HgBr$$
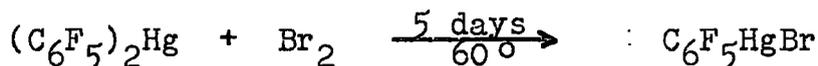
but cleavage by mercuric bromide is rapid in methanol.

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

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

$$(C_6F_5)_2Hg \ + \ Me_2Hg \ \longrightarrow \ 2C_6F_5HgMe$$
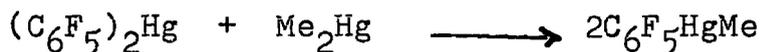
is readily brought about but dependant upon halide impurities as promoters.

Bispentafluorophenylmercury forms a stable 1:1 complex with 2,2' - bipyridyl of m.p. 122-3°. Similarly, bispenta-fluorophenyl (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(penta-fluorophenyl)mercury respectively with either ligand.

the addition compounds are not formed in alkaline solution:

$$C_2H_4 + Hg(NO_3)_2 + NaOH \longrightarrow C_2H_2Hg(OH)NO_3 + NaNO_3$$
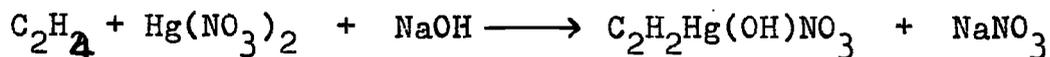
Several reactions indicate that these compounds can be classified as either:

i) simple addition compounds, $HOCH_2CH_2HgCl$, $CH_3OCH_2CH_2HgBr$,

ii) ether compounds, $O(CH_2CH_2HgCl)_2$,

iii) ring compounds,
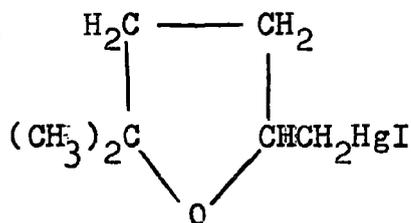


The olefin is regenerated on acidification, in some cases in very mild conditions, of the complex :

$$HOC_2H_4HgCl + HCl(5\%) \longrightarrow C_2H_4 + HgCl_2 + H_2O$$
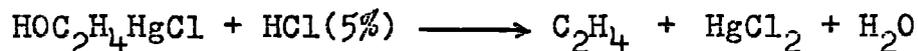
Decomposition with liberation of olefin also occurs on treating the organomercuric halide with aqueous alkali cyanide or thiocyanate :

$$HOC_2H_4HgBr + 4KCN \longrightarrow C_2H_4 + K_2Hg(CN)_4 + KOH + KBr$$
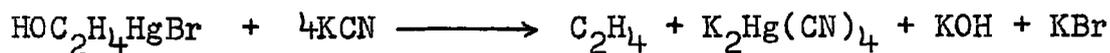
Iodine, either in aqueous KI solution or organic solvent, reacts as if the olefine complex were simply a substituted alkylmercuric iodide giving the corresponding iodo-alcohol and mercuric iodide in almost quantitative yield : [91]

$$HOCH_2CH_2HgI + I_2 \longrightarrow HOCH_2CH_2I + HgI_2$$
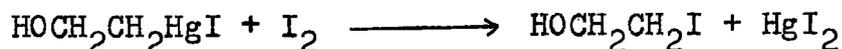
Reduction with sodium amalgam also proceeds as would be expected for the alkylmercury halide :

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

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 $\sigma$ -bonded compounds rather than $\pi$ -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]



$$\begin{array}{c}HgI\\|\\-C-C-\\|\quad\\OCH_3\end{array} + H_3O^+ \underset{}{\overset{fast}{\rightleftharpoons}} \begin{array}{c}HgI\\|\\-C-C-\\|\quad\\HOCH_3\\+\end{array} + H_2O \qquad (1)$$

$$\begin{array}{c}HgI\\|\\-C-C-\\|\quad\\HOCH_3\\+\end{array} \overset{slow}{\longrightarrow} \begin{array}{c}\overset{+}{HgI}\\/\quad\backslash\\-C\cdots C-\\|\quad\quad|\end{array} + CH_3OH \qquad (2)$$

$$\begin{array}{c}\overset{+}{HgI}\\/\quad\backslash\\-C\cdots C-\\|\quad\quad|\end{array} + \begin{array}{c}HgI\\|\\-C-C-\\|\quad\\OCH_3\end{array} \overset{fast}{\longrightarrow} \;\; C=C \;\; + HgI_2 + \begin{array}{c}Hg^+\\|\\-C-C-\\|\quad\\OCH_3\end{array} \qquad (3)$$
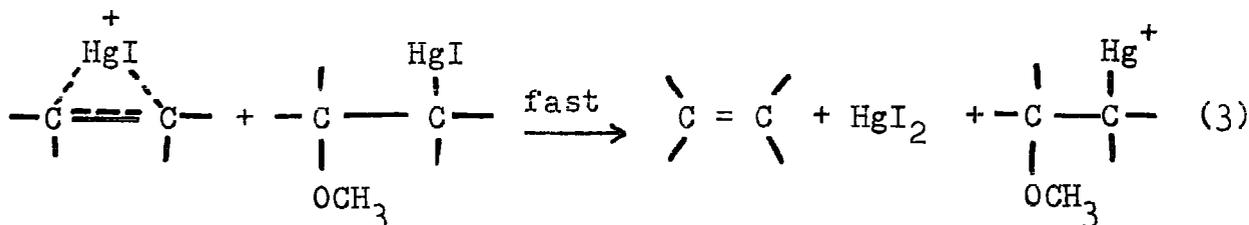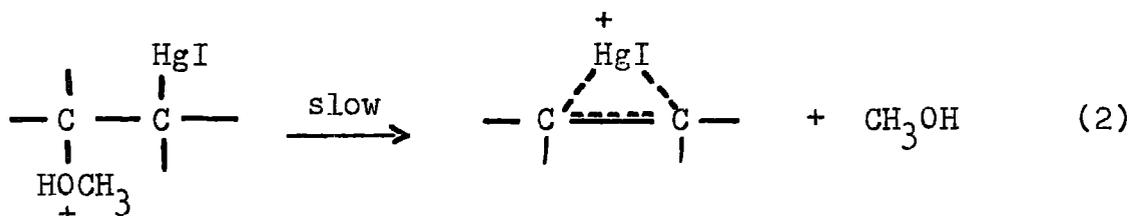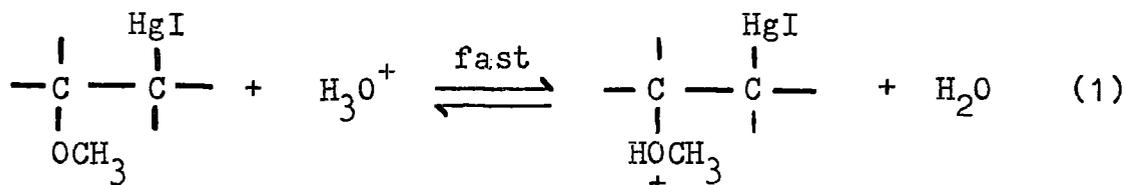
Equation (2) is the rate determining step and equation (3) comprises a series of fast steps.  The presence of a proton in the transition state is implied by the observed first-order dependance on the rate on perchloric acid concentration. Although the electron distribution in the transition state

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,

$$\left[ \begin{array}{c} \overset{|}{\underset{\pm}{C}} - \overset{HgI}{\underset{|}{C}} - \end{array} \right].$$
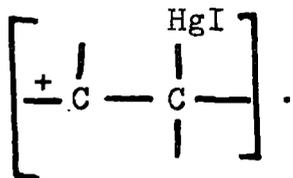
## Acetylene compounds of mercury

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]

$$C_2H_2 \; + \; acidic \; HgCl_2 \; \longrightarrow \; ClCH\!=\!CHHgCl$$
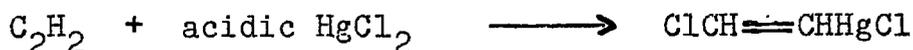
On bubbling dry ammonia through a solution of 2-chlorovinyl-mercuric chloride in chloroform bisdiaminodichloromercury, $(NH_3)_2HgCl_2$, slowly precipitates with the corresponding formation of the soluble bis(2-chlorovinyl)mercury.

$$2 \; (ClCH:CH)HgCl \; + \; 2 \; NH_3 \; \longrightarrow \; (NH_3)_2HgCl_2 + (ClCH:CH)_2Hg$$

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 <u>trans</u> isomer and the configuration is
retained on disproportionation to bis(2-chlorovinyl)mercury
m.p. 70°.    The <u>cis</u>-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.

$$ClCH:CHHgCl \xrightarrow{'AgOH'} ClCH:CHHgOH \xrightarrow{HX} ClCH:CHHgX$$
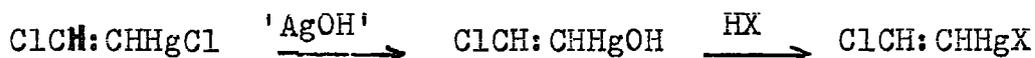
The corresponding iodide can be prepared from the chloride by
reaction of one molar equivalent of sodium iodide in absolute
alcohol :

$$ClCH:CHHgCl + NaI \longrightarrow ClCH:CHHgI + NaCl$$
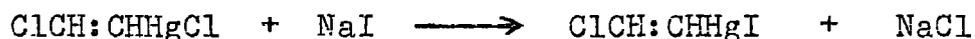
but if an excess of sodium iodide is used acetylene is
extensively evolved.

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]

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

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

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

$$ClCH:CHHgCl + 2 PPh_3 \longrightarrow C_2H_2 + (PPh_3)_2 HgCl_2$$
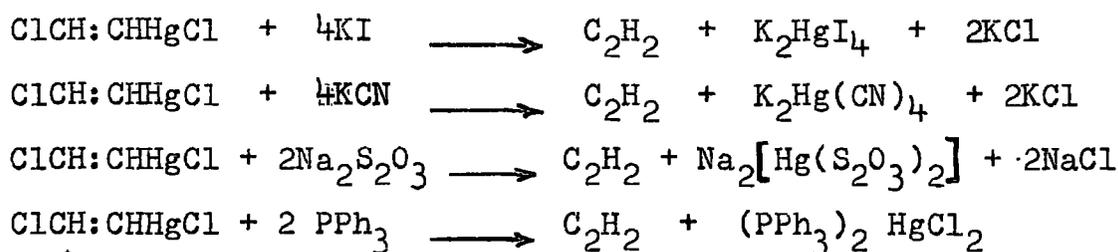
In the above cases acetylene is evolved and the mercury is bound as the stable anionic or neutral complex. Pyridine however forms a complex salt differing in this respect from ammonia which causes disproportionation.

$$ClCH:CHHgCl + py \longrightarrow [ClCH:CHHgpy]Cl \quad m.p. \ 76^O(dec.)$$
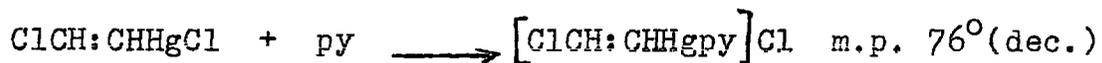
Mercuric salts do not always add across the carbon-carbon acetylenic linkage and many compounds have been prepared by passing various acetylenes into solutions of mercuric salts.[100] Brightly coloured solids can be obtained such as the yellow product from the addition of phenylacetylene to mercuric 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]

$$\text{EtHgCl} + \text{NaC!CPh} \xrightarrow{\text{8 hours}} \text{NaCl} + \text{EtHgC!CPh} \quad (70\%)$$
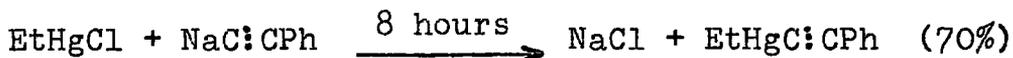
Phenylmercuric acetylides can be prepared in a similar manner.[104]

$$\text{PhHgCl} + \text{KC!CR'} \longrightarrow \text{KCl} + \text{PhHgC!CR'}$$

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

$$\text{MeHgX} + \text{CH!CMgBr} \longrightarrow \text{MgXBr} + \text{MeHgC!CH}$$

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]

$$\text{B\overset{i}{u}C!CH} + \text{HgI}_2 \longrightarrow (\text{B\overset{i}{u}C!C})_2\text{Hg}$$
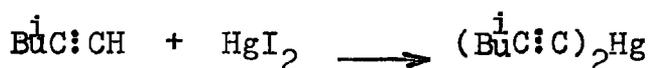
The above compound is also somewhat surprisingly formed from the stable tetraiodomercury anion.

$$\text{RC!CH} + \text{K}_2\text{HgI}_4 \longrightarrow (\text{RC!C})_2\text{Hg}$$

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

$$(\text{PhC!C})_2\text{Hg} + \text{HgCl}_2 \longrightarrow 2\text{PhC!CHgCl} \quad \text{m.p. } 320^\circ \text{ (dec.)}$$
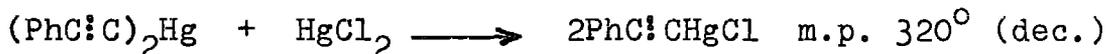
## Disproportionation of organomercury compounds

Cleavage reactions of the type

$$\text{R}_2\text{Hg} + \text{HgX}_2 \longrightarrow 2\text{RHgX}$$
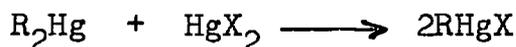
are rapid and the organomercuric halide is readily formed. Under certain conditions however this reaction can be reversed

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 tri-
phenylphosphine 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 aryl-
mercurials 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

$$Ar_2Hg \quad + \quad HgX_2 \rightleftharpoons 2ArHgX$$
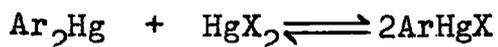
has been made.[55]   When arylmercuric iodides are refluxed with
excess alcoholic sodium iodide diarylmercurials are usually
formed according to the equation :

$$2ArHgI \quad + \quad 2NaI \rightleftharpoons Na_2HgI_4 \quad + \quad Ar_2Hg$$
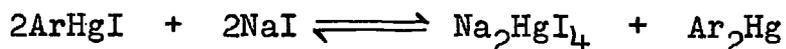
When the organic group is o-, m-, or p- tolyl, m- xylyl,
mesityl, $\alpha$ - or $\beta$ -naphthyl, the organomercuric iodide gives
solely the bis organomercury compound on refluxing with
sodium iodide.   Para-ethylphenylmercuric iodide gives a
mixture of starting material and disproportionation products
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 di-organomercury 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.

$$2 \ C_{10}H_{13}HgI + 2 \ NaI \ \rightleftharpoons \ Na_2HgI_4 + (C_{10}H_{13})_2Hg$$
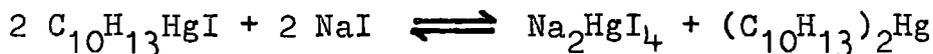
However on quenching the hot equilibrium mixture by pouring it onto ice-water only 1% of the disproportionation product was found, the product obtained was almost completely p-cymylmercuric iodide.

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]

$$2CH_2{:}CHCH_2HgI + 2KCN \longrightarrow (CH_2{:}CHCH_2)_2Hg + \tfrac{1}{2}K_2HgI_4 + \tfrac{1}{2}K_2Hg(CN)_4$$
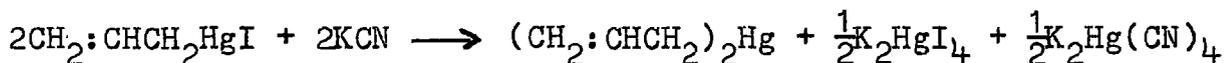
Small amounts of diallylmercury can be obtained with aqueous or alcoholic potassium iodide but potassium cyanide is the only reagent to react in the cold.

Equivalent quantities of alkali cyanides convert aryl-mercuric 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 phenyl-mercuric iodide, from which only starting material can be recovered, are the reactions shown below :

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

$$\text{PhHgCl} + \text{NaOMe} \xrightarrow[\text{reflux 3 hours}]{\text{MeOH}} \text{Ph}_2\text{Hg} \quad (34\%)$$
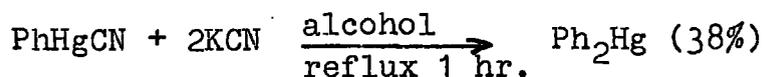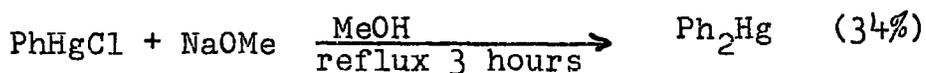
Alteration of the adverse solubility relationship or the position of equilibrium enables the isolation of diphenylmercury.

The reactions of bis(perchlorovinyl)mercury and perchloro-vinylmercuric 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 :

$$2CCl_2:CClHgCl + 2PPh_3 \longrightarrow (Ph_3P)_2HgCl_2 + (CCl_2:CCl)2Hg$$
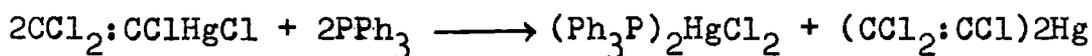
The latter can be obtained from carbomethoxymercuric chloride and triphenylphosphine.[115]

$$2ClHgCOOMe + 2PPh_3 \longrightarrow (Ph_3P)_2HgCl_2 + Hg(COOMe)_2$$
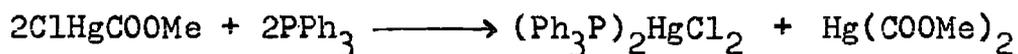
The carbomethoxymercuric chloride is formed from mercuric acetate according to the reactions :

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

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

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 $\alpha$-bromomercuriphenylacetic acid on reaction with

ammonia has been carried out by Reutov and co-workers.

Insoluble bisamino-dibromomercury is precipitated from chloro-

$$2Ph - \underset{\underset{COOR}{|}}{CH} - HgBr + 2NH_3 \longrightarrow \left(Ph - \underset{\underset{COOR}{|}}{CH}\right)_2 Hg + (NH_3)_2 HgBr_2$$
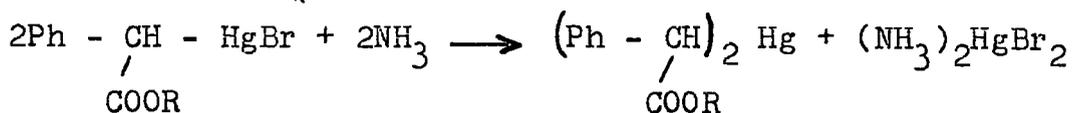
form solution as the disproportionation proceeds according to
the equation shown.    The kinetic results show that the reaction
is of second order with respect to both the organomercuric
salt[111] and ammonia.[112]    It was further found that the inductive
effect of a substituent X   (X = Cl, Br, H, 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 > iPr > n-nonyl > l-menthyl ⪢ t-Bu .
A critical examination of the results of Reutov's dispropor-
tionation studies has been made by Jenson and Rickborn.[116]
They criticize the mechanism postulated by Reutov :

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

$$HgBr_2 + 2NH_3 \; \overset{k_2}{\rightleftharpoons} \; \downarrow(NH_3)_2HgBr_2$$
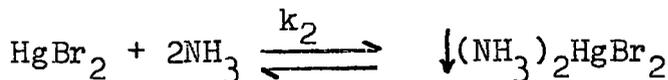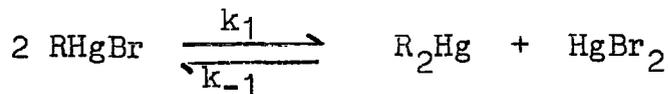
as being inconsistent with the observed kinetics.    They propose

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 :

$$RHgBr \; + \; NH_3 \; \rightleftharpoons \; RHg \underset{Br}{\overset{NH_3}{\diagdown}}$$

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

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

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

$$R-\underset{NH_3}{\overset{NH_3}{\underset{|}{\overset{|}{Hg}}}}-Br \; + \; RHgBr \; \xrightarrow{\text{slow}} \; R_2Hg \; + \; (NH_3)_2HgBr_2$$
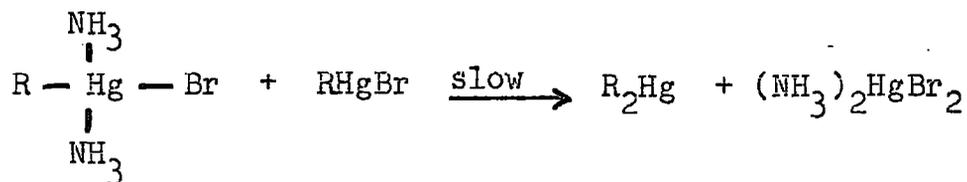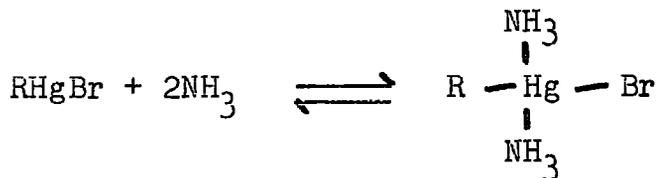
Without detailed kinetic evidence it is impossible to assign
a mechanism and Jenson and Rickborn conclude that a
reinvestigation of the kinetics is necessary.

# EXPERIMENTAL

# E X P E R I M E N T A L

## Preparation of starting materials

### Dimethylmercury

Dimethylmercury was prepared by the reaction of methyl-magnesium 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 bromo-methane 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.

$$Me_2Hg \ + \ HgCl_2 \longrightarrow 2MeHgCl$$
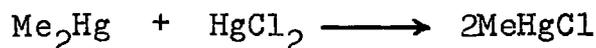
Dimethylmercury (34.3 gm., 1% excess) in ether (100 ml.) was added slowly from a dropping funnel to mercuric chloride (39.8 gm.) in ether (400 ml.).    The solution was stirred continuously and methylmercuric chloride crystallised from solution as large plates as the addition continued.    After addition 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 dimethyl-mercury 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 organo-mercury 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. Re-crystallisation 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°.

p-Tolylmercuric chloride was recrystallised from boiling xylene, m.p. 233°.

Trimethylphosphine

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.

Solvents

Benzene and diethyl ether 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 $400^{\circ}$ 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 $100^{\circ}$ 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 $25 \pm 0.1^{\circ}C$. 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)

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.

### Methyl(trimethylphosphine)mercury chloride, $[MeHgPMe_3]Cl$.

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 $-76^{\circ}$ when crystallisation slowly occurred.    The colourless crystalline solid melted with decomposition from $86^{\circ}$.  (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%).

### Methyl(triethylphosphine)mercury chloride, $[MeHgPEt_3]Cl$.

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$_{\circ}$ 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$^{\circ}$ 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 sub-
sequently 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$^{\circ}$ 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 $25^O$ 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 $\bigwedge$ (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 $25^O$ and all observed values of specific conductance were corrected for this.

# TABLE IV

Cell constant = 0.143     Thermostat temperature = $25^{\circ}C$

## 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. ($ohm^{-1}.cm^{-1}$) | $\Lambda$ ($ohm^{-1}.cm^{2}$) |
|---|---|---|---|---|---|---|
| 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 $\Lambda$ (mole$^{-1}\Omega^{-1}$cm.$^2$) against $\sqrt{C}$ (mole litre$^{-1}$)$^{1/2}$.
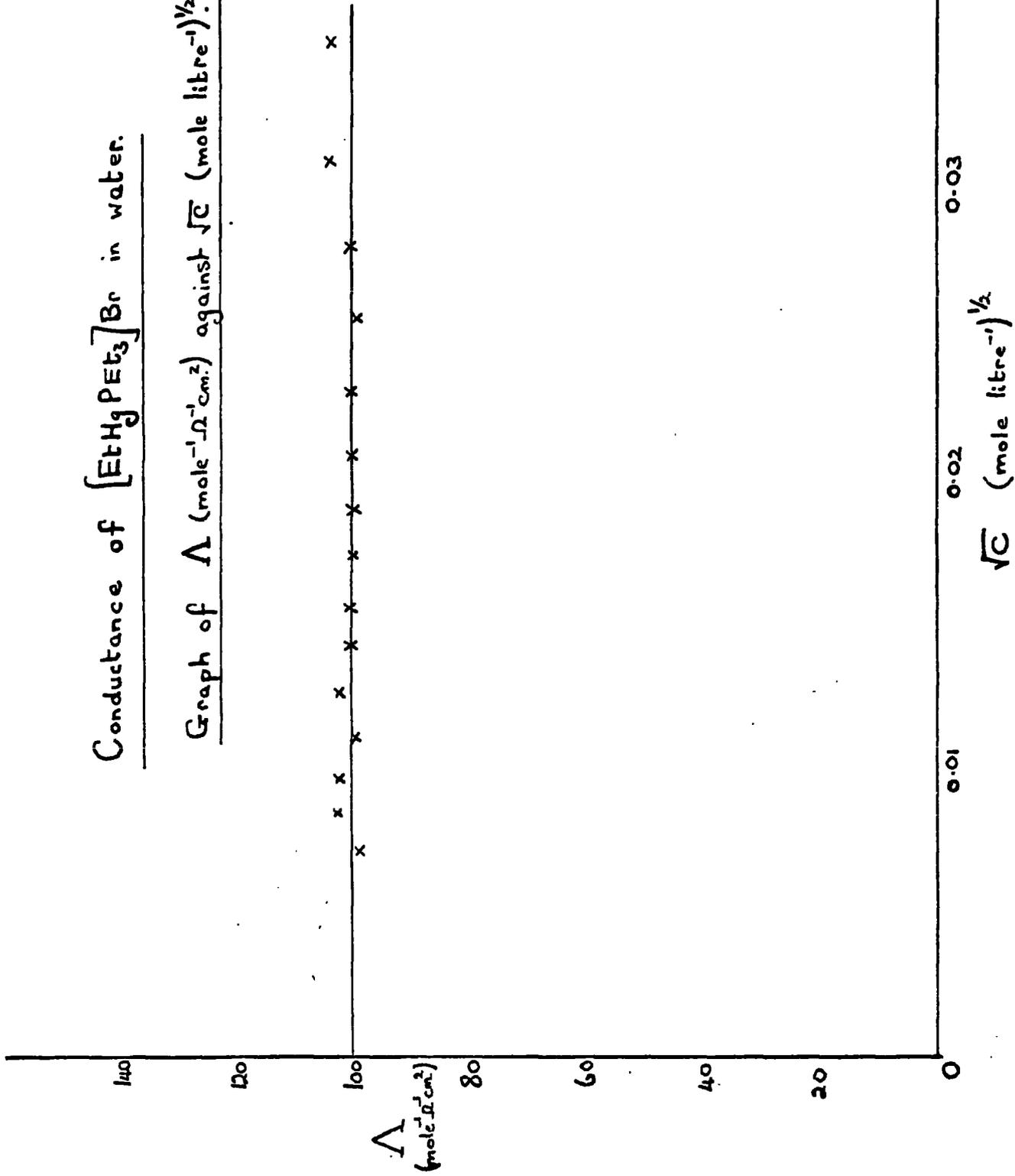
The latter values of equivalent conductance, $\Lambda$, are high due to increased experimental error in the determination of the resistance in this region. Extrapolation of the plot of $\Lambda$ against $\sqrt{c}$ gives the value of equivalent conductance at 'infinite dilution' $\Lambda_0$.

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

As $\Lambda_0 = \lambda_+ + \lambda_-$ where $\lambda_+$ and $\lambda_-$ 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 $40^o$, 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 $0^oC$, at which temperature the complex slowly crystallised as fine colourless needles, m.p. 121-124$^o$ 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.

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

### n-Butyl(trimethylphosphine)mercury iodide,

$$\left[Bu^nHgPMe_3\right]I.$$

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 $-20^{\circ}$ in an acetone $-CO_2$ bath. The complex slowly crystallised as fine colourless needles, m.p. $87-88^{\circ}$ 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 $215^{\circ}$. (Found: Hg, 50.0, $ClO_4$, by ion exchange, 25.1. $C_4H_{12}ClHgO_4P$  requires Hg, 51.3; $ClO_4$, 25.4%).

### Methyl(triethylphosphine)mercury perchlorate, $[MeHgPEt_3]ClO_4$

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 $137^{\circ}$. (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.

### Methyl(triphenylphosphine)mercury perchlorate, $[MeHgPPH_3]ClO_4$

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$^{\circ}$ 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.

## Preparation of methylmercuric tetrafluoroborate solution

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,

$$[MeHgPEt_3]BF_4$$
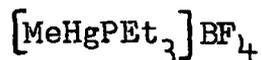
Addition of triethylphosphine (slight excess over 1 mol.) by means of a syringe against a counter current of nitrogen to an aqueous-methanolic solution of methylmercuric tetrafluoroborate in a two-neck 50 ml. flask purged with nitrogen resulted in heat evolution and the precipitation of a little metallic 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$^o$ (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

$$[MeHgPPh_3]BF_4$$
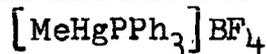
An aqueous methanolic solution of methylmercuric tetrafluoroborate was added to triphenylphosphine (1 mol.) in acetone in a two-neck flask. On concentrating to a very small volume the complex salt, m.p. 215-220$^o$, slowly crystallised. (Found: C, 40.7; H, 3.2. $C_{19}H_{18}BF_4HgP$ requires C, 40.4; 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 $190^{\circ}$.    (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(triethyl-
phosphine)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 $135^{\circ}$.
(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° _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°.

### 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° 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 $25^O$ 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 [PhHgPEt₃]NO₃ in methanol

| Volume [PhHgPEt₃]NO₃ 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$^{-1}$) | $\Lambda$ (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, $\Lambda$, against $\sqrt{C}$ the equivalent conductance for the salt at infinite dilution, $\Lambda_o$, is 86.6 ohm$^{-1}$cm.$^2$

Conductance of $[PhHgPEt_3]NO_3$ in methanol.

Graph of $\Lambda$ (mole$^{-1}$ $\Omega^{-1}$ cm.$^2$) against $\sqrt{c}$ (mole litre$^{-1}$)$^{1/2}$.
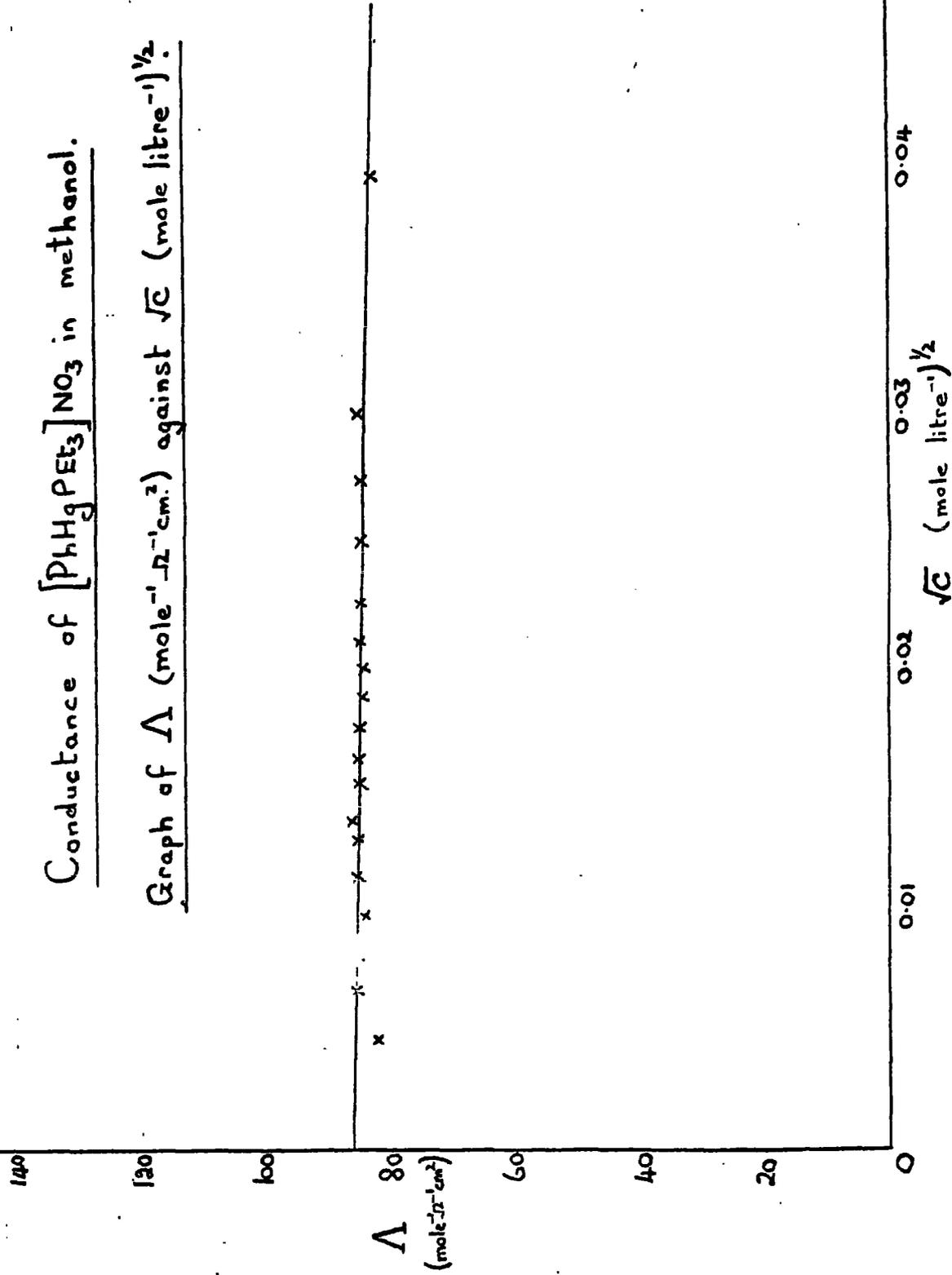
## Complexes of methylmercuric salts with nitrogen ligands

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 methyl-mercuric 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 $\nu$ (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 methyl-mercuric 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 $140^{\circ}$. (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 dichlorobis-triethylphosphinemercury, 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 triethyl-phosphine 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, $\Lambda$ , against $\sqrt{C}$ is shown.

### TABLE VI

### Conductance of $(Et_3P)_2HgCl_2$ in water

| Vol. added (ml.) | $C \times 10^{-5}$ (mole lit$^{-1}$) | $C \times 10^{-3}$ (mole lit$^{-1}$)$^{\frac{1}{2}}$ | $R \times 10^4$ (ohm) | $K \times 10^{-5}$ obs. ($\Omega^{-1}$cm$^{-1}$) | $K \times 10^{-5}$ ($\Omega^{-1}$cm$^{-1}$) | $\Lambda$ ($\Omega^{-1}$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 $\Lambda$ (mole$^{-1}\Omega^{-1}$cm$^2$) against $\sqrt{C}$ (mole litre$^{-1}$)$^{1/2}$.

$\sqrt{C}$ (mole litre$^{-1}$)$^{1/2}$

$\Lambda$ (mole$^{-1}\Omega^{-1}$cm$^2$)
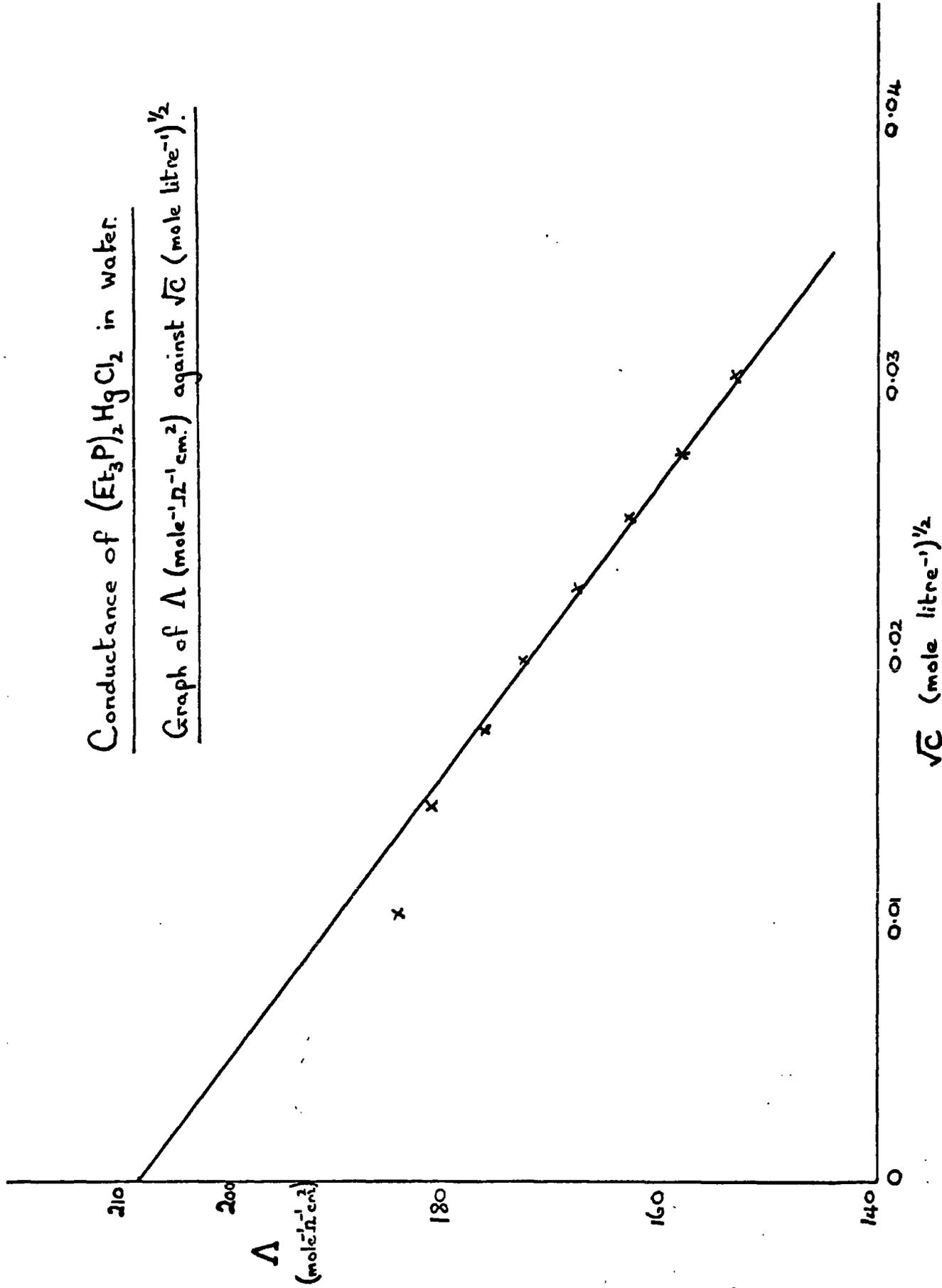
Extrapolation of the graph to infinite dilution gives a value of $\Lambda_o$ for the complex $= 208 \text{ ohm}^{-1}\text{cm.}^2$

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

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

$$\text{then } \tfrac{1}{2}(\text{Et}_3\text{P})_2\text{Hg}^{2+} = 27.7 \text{ ohm}^{-1}\text{cm.}^2$$

## 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 dibromobistriphenylphosphine-mercury, 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-iodobistriphenylphosphine-mercury (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 dichlorobis-
triphenylphosphinemercury (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-iodobistriphenyl-
phosphinemercury (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 dichlorobistriethyl-phosphinemercury (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 $\frac{1}{2}$ 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 dinitratobistriphenyl-
phosphinemercury, $(Ph_3P)_2Hg(NO_3)_2$, (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 $80^{\circ}$ 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$^{\circ}$, mixed m.p. 120-121$^{\circ}$. (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 0.1N 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$^{\circ}$C lit.[22] m.p. 115-7C$^{\circ}$ (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$^{\circ}$ mixed m.p. with starting material 275$^{\circ}$.

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$^{\circ}$ 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$^{\circ}$, 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 $= 1.011 \times 10^2$ ohm

Resistance, R, of 0.005NKCl $= 1.99 \times 10^2$ ohm

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

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

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

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

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

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

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

The cell constant, $\quad \dfrac{l}{a} = 0.143$ 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 $25^{o}$ 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) | $K \times 10^{-5} ohm^{-1} cm^{-1}$ |
|---|---|---|
| 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 $2.34 \times 10^{-5} ohm^{-1} cm^{-1}$ 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 $2.028 \times 10^{-5} ohm^{-1} cm^{-1}$

### Conductimetric titration of methylmercuric chloride against triphenylphosphine in methanol

Methanolic methylmercuric chloride solution (20 ml., 0.0092M) was placed in the cell and methanolic triphenyl-phosphine 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.$C \times 10^{-3}$ (mole.lit$^{-1}$) | $R \pm 10$(ohm) | $K \times 10^{-5}$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
$16.9 \times 10^{-5}$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 $c \times 10^{-3}$.

$K_{obs.} \times 10^{-5}$
$(\Omega^{-1} cm^{-1})$

Concentration of triphenylphosphine, c, $\times 10^{-3}$ (mole litre$^{-1}$)
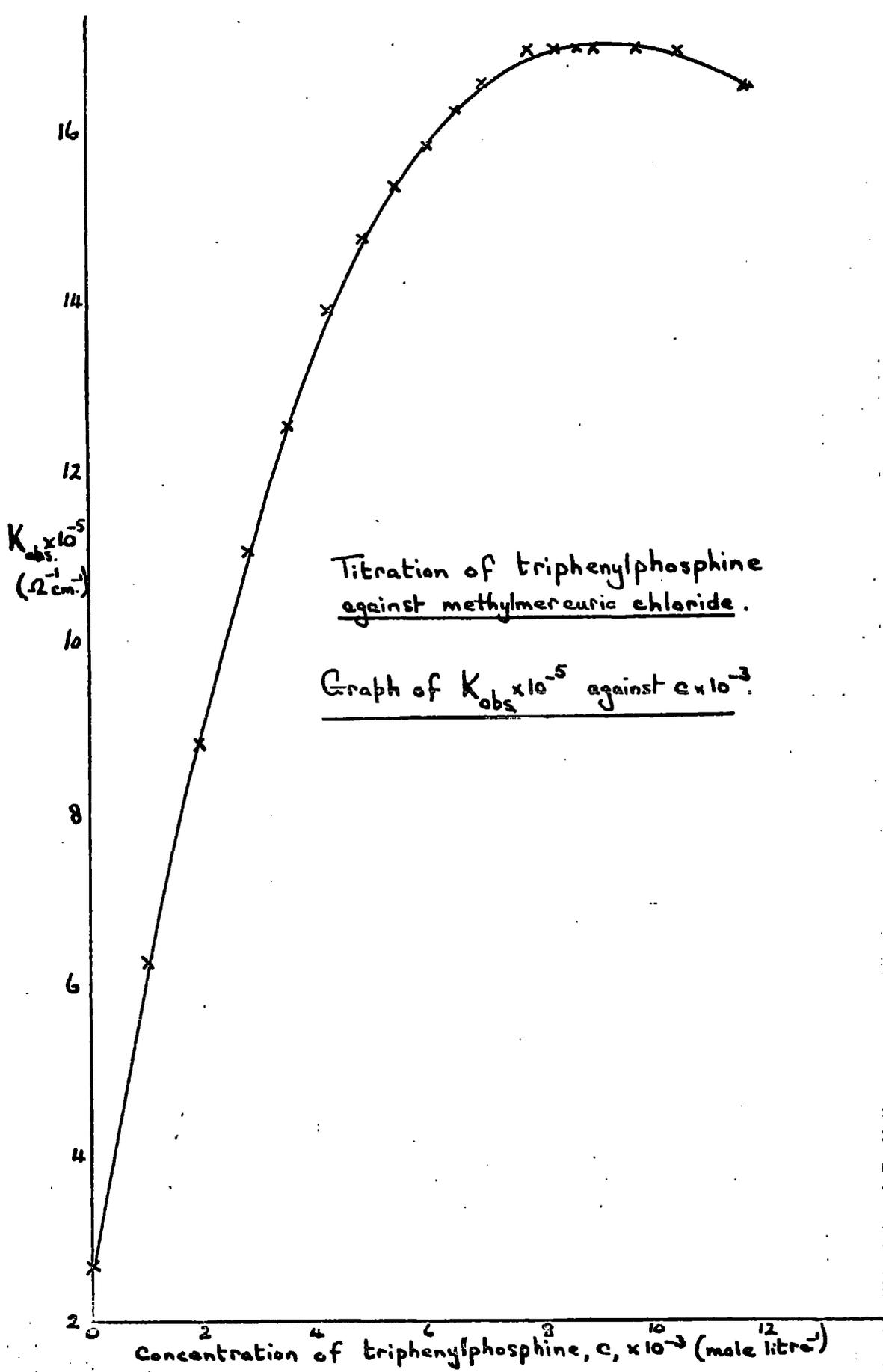
phosphine solution.    Maximum conductance occurred at a molar
ratio of phosphine to mercurial of 1:1.25.

### 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
$7.35 \times 10^{-5}$ohm$^{-1}$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

<u>Conductimetric titreation of PPh$_3$ against MeHgBr in methanol</u>

| 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.
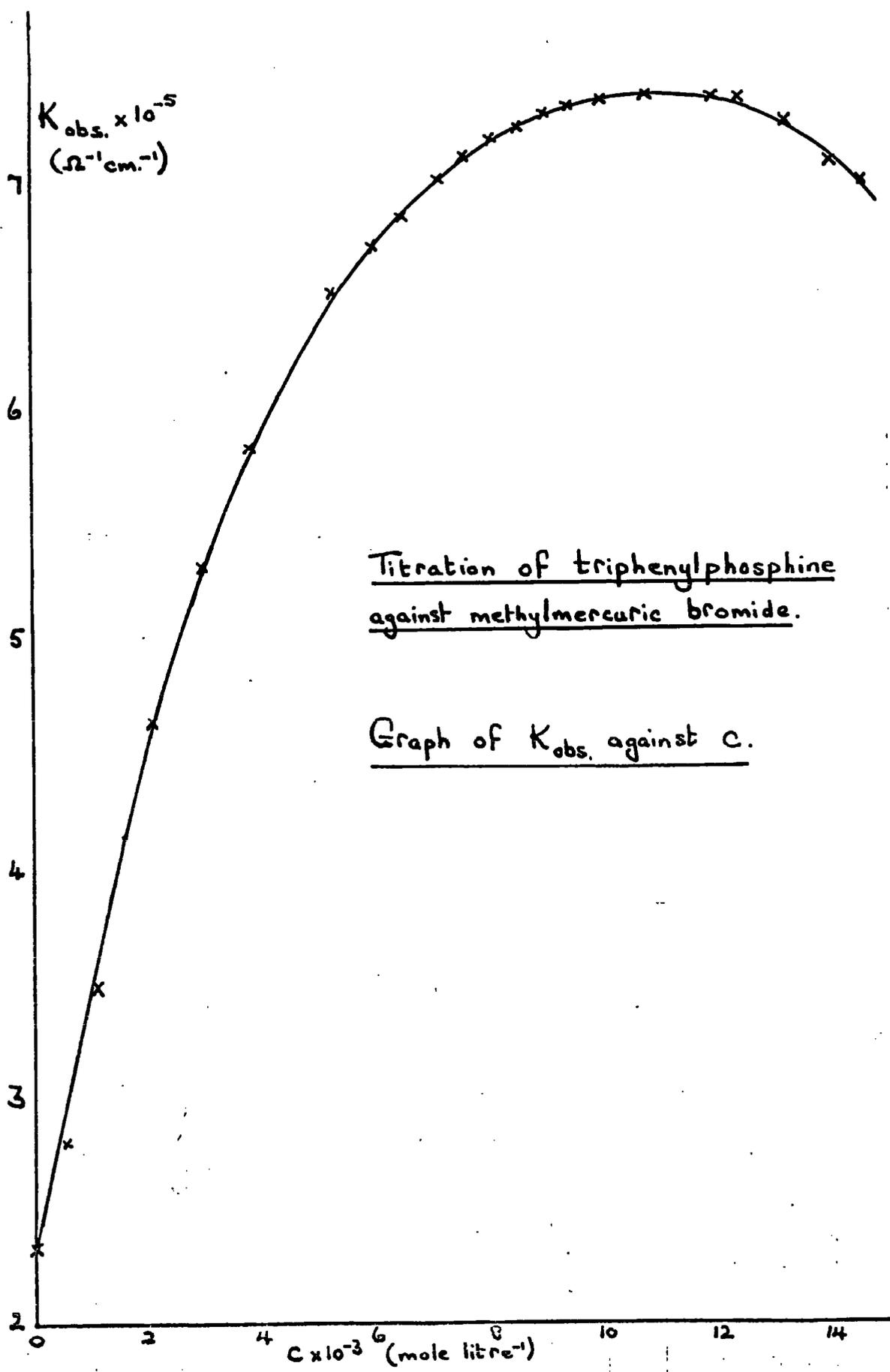
The maximum specific conductance of the solution of
$2.63 \times 10^{-5}$ohm$^{-1}$cm.$^{-1}$ was shown in a solution 0.01264M in
triphenylphosphine and 0.00435M in methylmercuric iodide
giving a molar ratio of phosphine to mercurial of 1:2.87 at
the point of maximum conductance.   The molar equivalence
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.) | $C \times 10^{-3}$ (mole lit.$^{-1}$) | $R \pm 10$(ohm) | $K \times 10^{-5}$(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 $C \times 10^{3}$.

$K_{obs.} \times 10^{-5}$
$(\Omega^{-1} cm.^{-1})$

$C \times 10^{-3}$ (mole litre$^{-1}$)
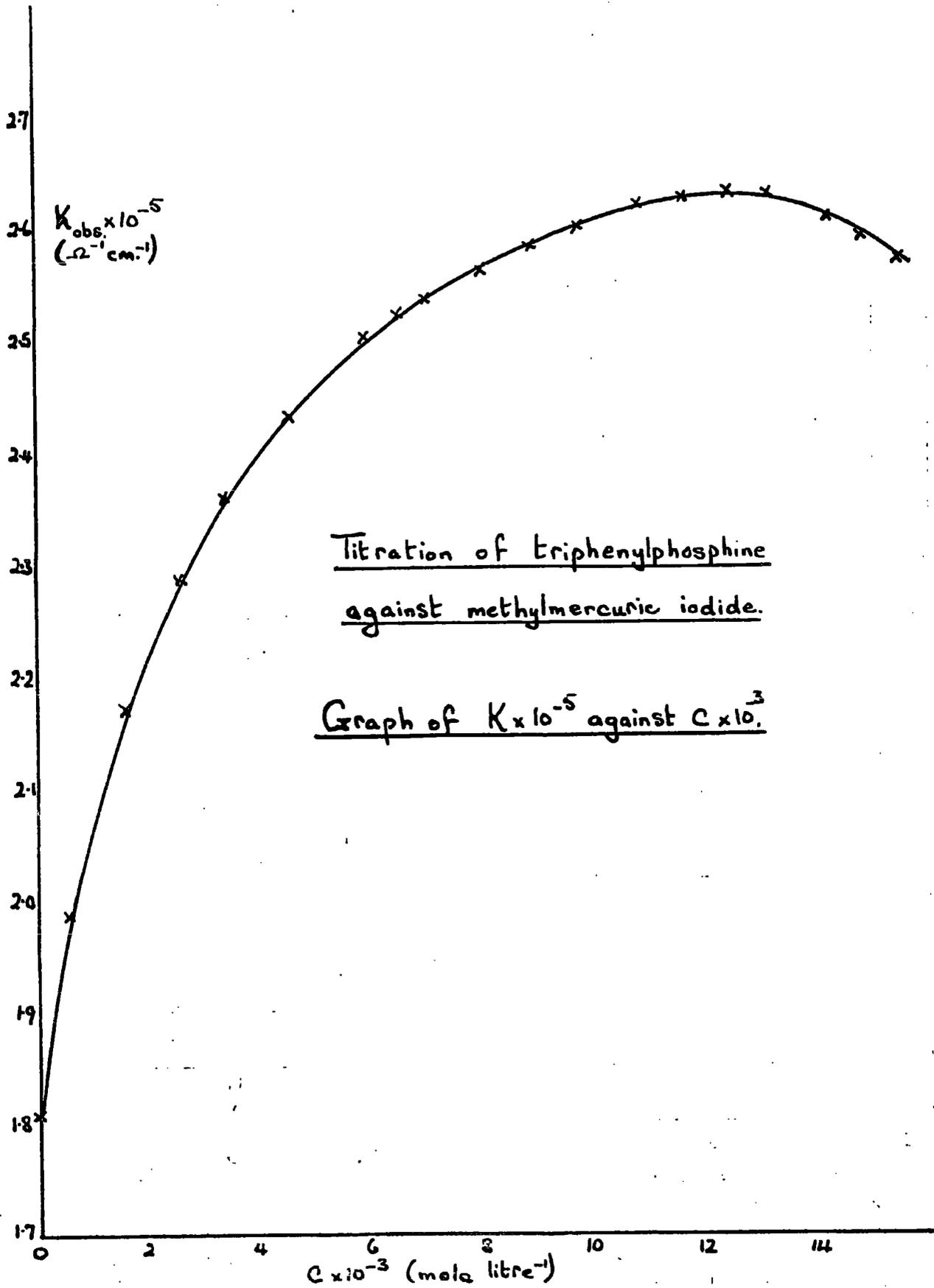
## Variation of conductance with time

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 |
| $\frac{1}{2}$ | 990 | 17.07 |
| 1 | 1000 | 16.90 |
| 1$\frac{1}{2}$ | 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 x 10$^{-5}$ ohm$^{-1}$cm$^{-1}$ | Time (hours) | R (ohm) | K x 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-tolyl-mercuric chloride (0.127M) was made up and 20 ml. placed in the cell.   The resistance of the solution was measured and tri-phenylphosphine 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 $\frac{1}{2}$ 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).
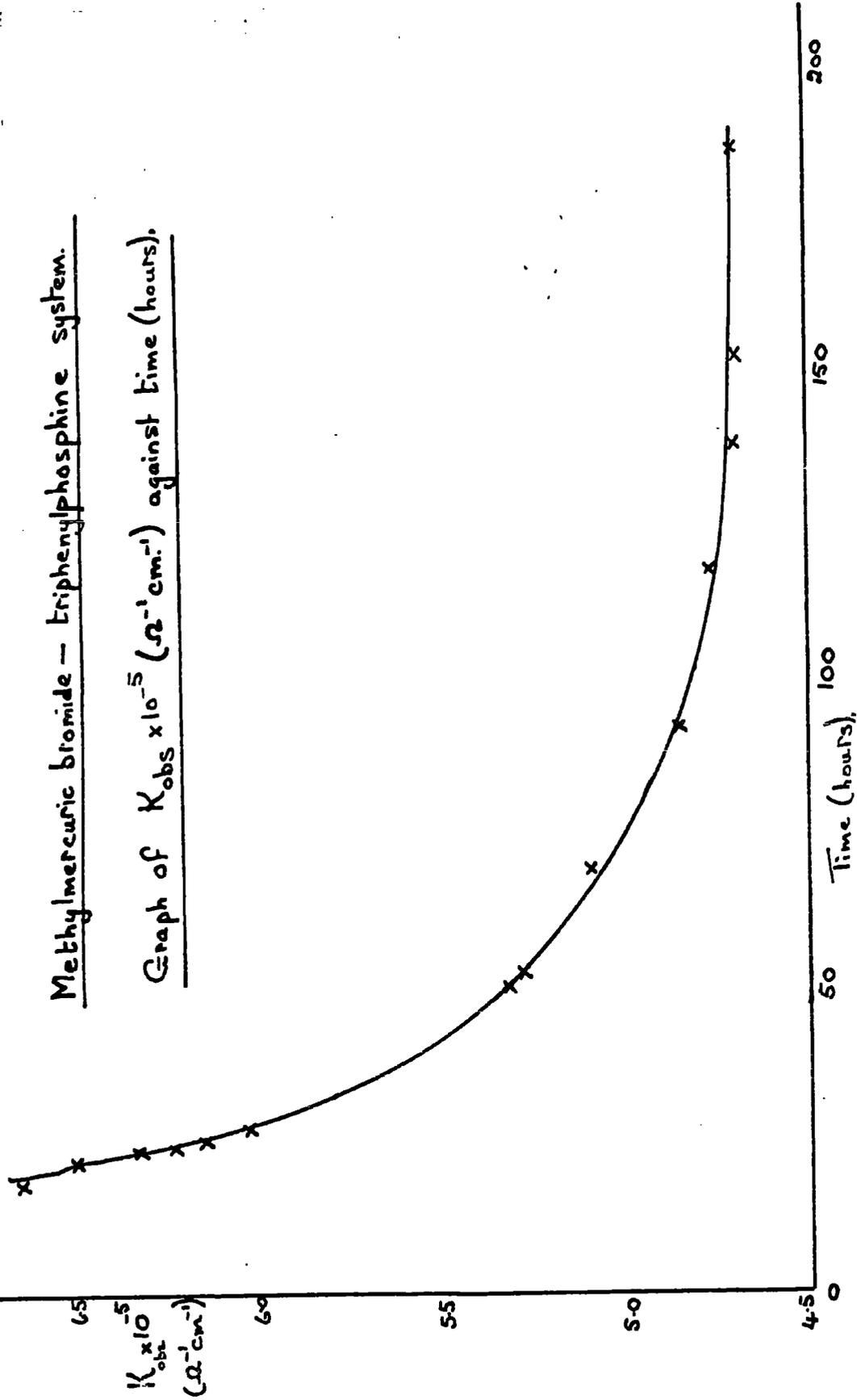
## TABLE XIII

Specific conductance, K, of the
purified acetone = $4.30 \times 10^{-6}$ $ohm^{-1}cm^{-1}$        Cell constant = 0.169

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

| Time (mins.) | Resistance, R, (ohm.) | $K \times 10^{-6}$ ($ohm^{-1}cm^{-1}$) |
|---|---|---|
| 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 = $2.633 \times 10^{-5}ohm^{-1}cm^{-1}$) 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).
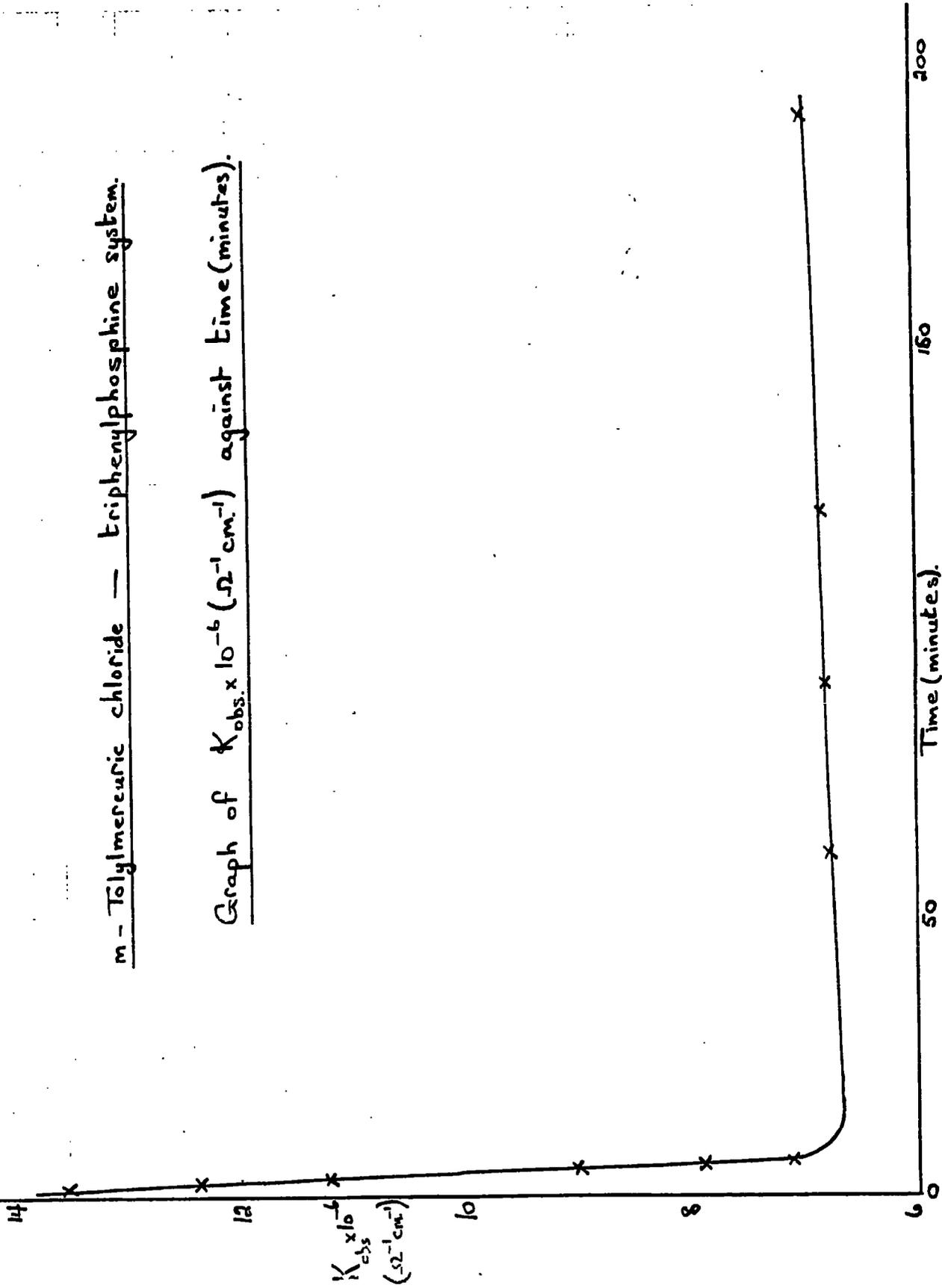
(7.75 ml., 0.02913M, 1 mol.).   The conductance increased
immediately on mixing the solutions, and the value of specific
conductance ($K = 17.16 \times 10^{-5} ohm^{-1} cm.^{-1}$) measured within about
ten seconds of mixing the reagents remained unchanged for 19
hours.   No disproportionation product was observed to crystal-
lise 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 dichlorobistriphenylphosphine-
mercury (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 $2\frac{1}{2}$ 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 $\underline{m}$-MeC$_6$H$_4$HgBr-PPh$_3$ system

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

m – Tolylmercuric bromide – triphenylphosphine system.

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

$K_{obs} \times 10^{-6}$ ($\Omega^{-1} cm^{-1}$)

5

4

3

2

0  1  2  4

Time (minutes).
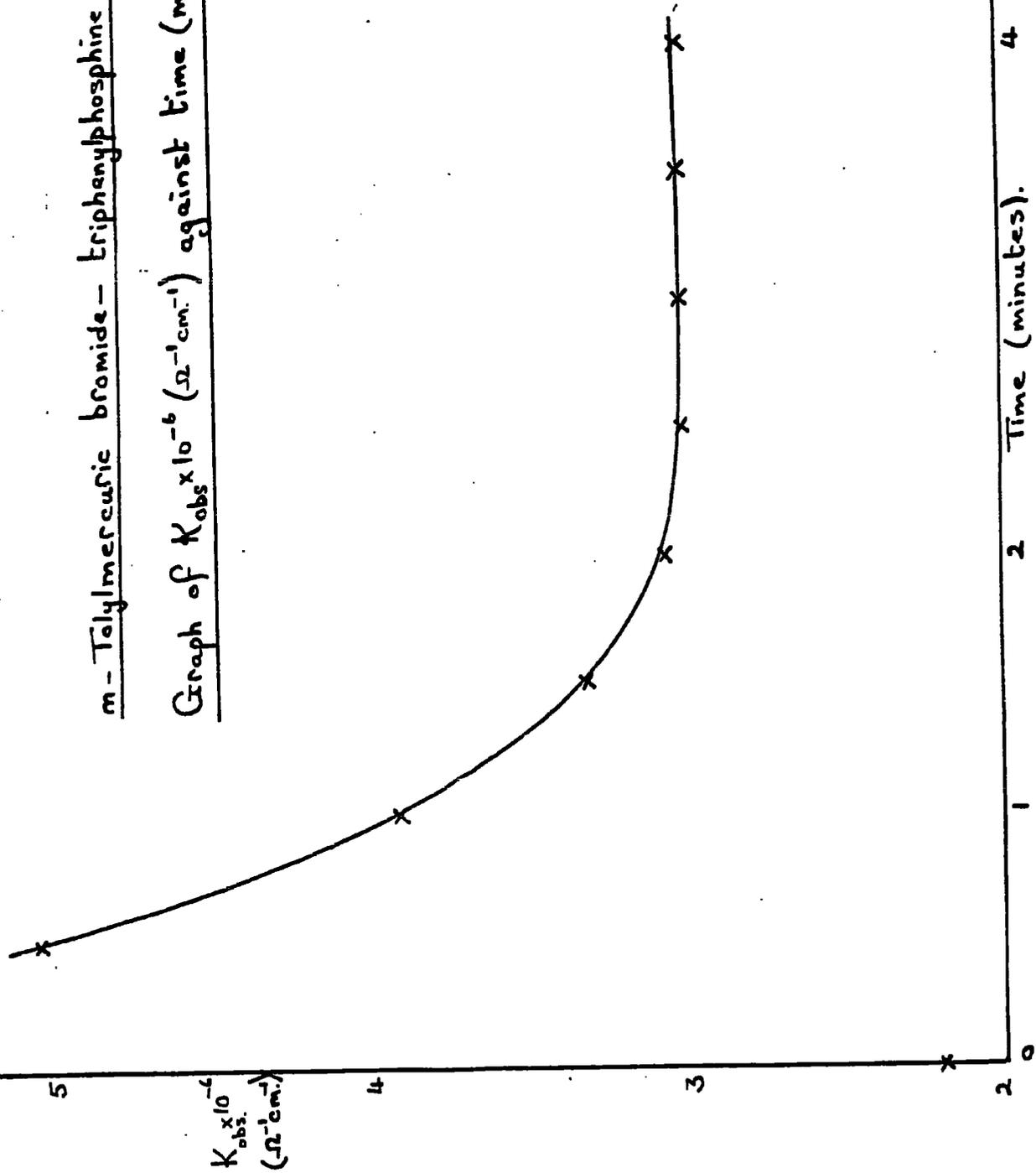
### Dichlorobistriphenylphosphinemercury and di-m-tolylmercury in methanol

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 $2.34 \times 10^{-5} ohm^{-1} cm^{-1}$. 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, $R \times 10^4$ (ohm) | $K \times 10^{-5} ohm^{-1} cm^{-1}$ ob. |
|---|---|---|
| 0 | 0.307 | 4.66 |
| $\frac{1}{2}$ | 0.282 | 5.07 |
| 1 | 0.264 | 5.42 |
| $1\frac{1}{2}$ | 0.251 | 5.70 |
| 2 | 0.240 | 5.96 |
| $2\frac{1}{2}$ | 0.232 | 6.17 |
| 3 | 0.224 | 6.38 |
| $18\frac{1}{2}$ | 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 $(m-CH_3C_6H_4)_2Hg$

Graph of $K_{obs} \times 10^{-5}$ against time (hours).
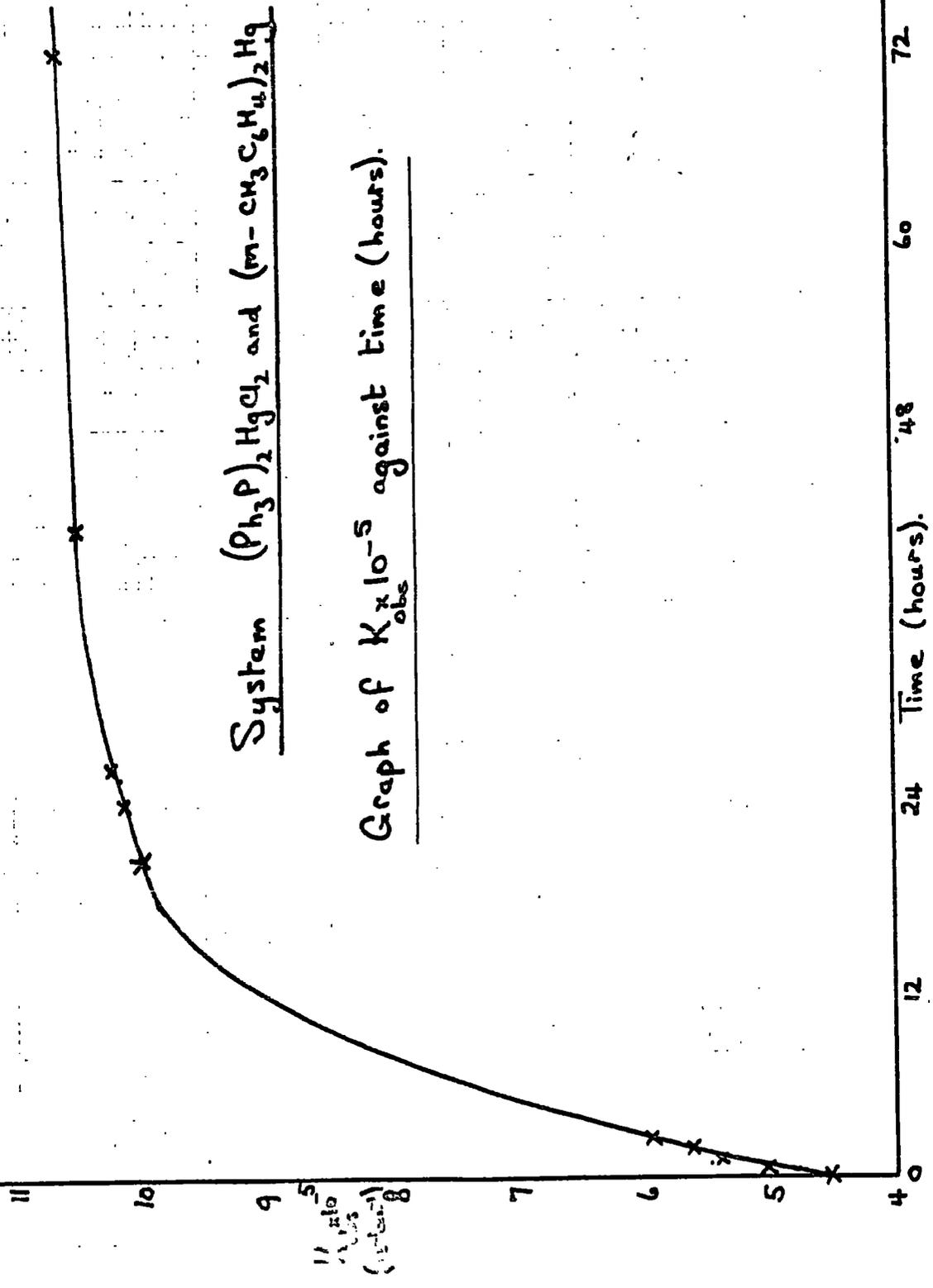
## Reaction of phenyl(triethylphosphine)mercury nitrate,

## $[PhHgPEt_3]NO_3$, 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 dibromobistriethyl-phosphinemercury (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 $lit^{-1}$) | $2700\overset{o}{A}$ | | $2800\overset{o}{A}$ | |
|---|---|---|---|---|
| | Opt.Den. | E | Opt.Den. | E |
| $3.481 \times 10^{-5}$ | 0.373 | 10,720 | 0.326 | 9,365 |
| $2.321 \times 10^{-5}$ | 0.248 | 10,690 | 0.219 | 9,434 |
| $1.161 \times 10^{-5}$ | 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 ($5.40 \times 10^{-7}$ mole)
in methanol (0.10 ml.), $[PhHgPEt_3]NO_3$ ($4.72 \times 10^{-7}$ 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 $2800\overset{o}{A}$ rose rapidly at first and then
became constant after 30 minutes at room temperature (ca. $25^{o}$)
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
$10.81 \times 10^{-5}$ mole $litre^{-1}$ NaI and $9.42 \times 10^{-5}$ 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 $368 \times 10^{-5}$ mole litre$^{-1}$, that of $(PEt_3)_2HgI_2$ fell to 3.83, 3.72, 3.39, 3.33 and $1.83 \times 10^{-5}$ 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
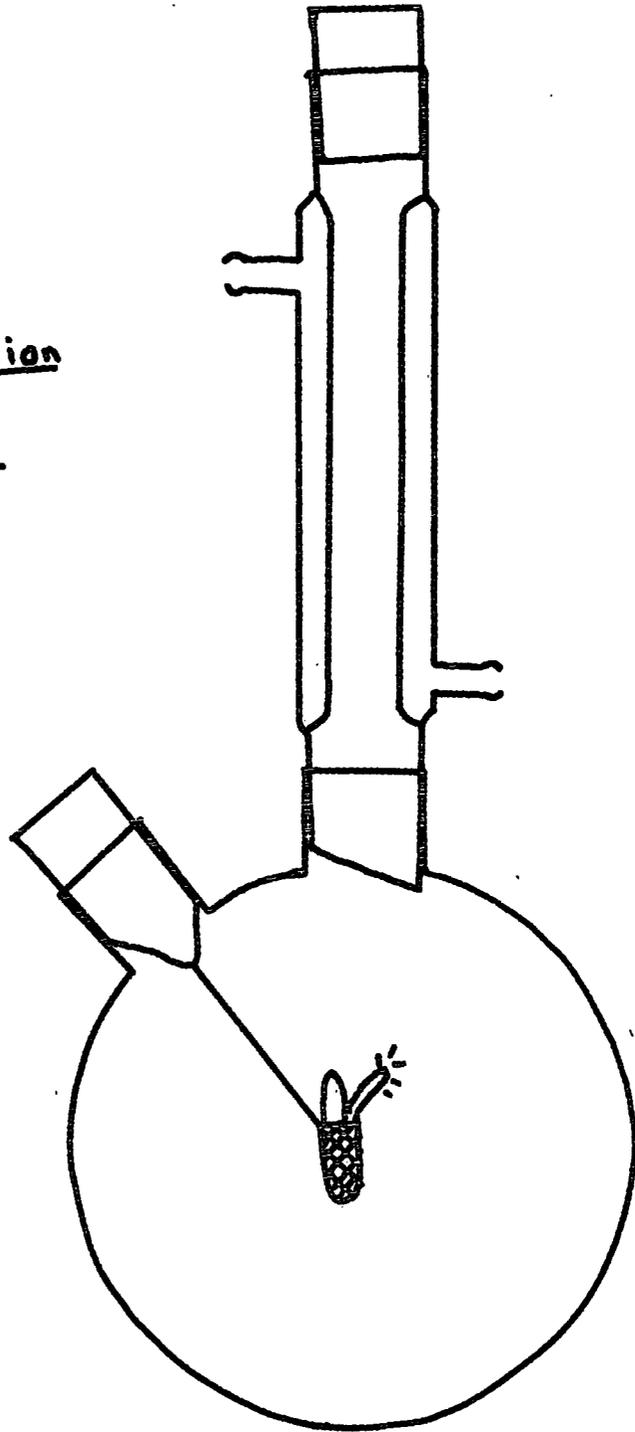
Combustion
flask

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 $60^\circ$, 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 $110^\circ$ for 45 minutes, cooled for 30 minutes in
a desiccator and weighed after 5 minutes 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

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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 organo-mercury 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.

<div align="center">

### Chromium

</div>

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% |
| $[MeHgPMe_3]Cl$ | $C_4H_{12}ClHgP$ | 14.5 | 3.70 | 14.7 | 3.73 |
| $[MeHgPMe_2Ph]Cl$ | $C_9H_{14}ClHgP$ | 27.8 | 3.60 | 27.5 | 3.66 |
| $[MeHgPEt_3]Br$ | $C_7H_{18}BrHgP$ | 20.3 | 4.35 | 20.5 | 4.50 |
| $[MeHgPMe_2Ph]I$ | $C_9H_{14}HgIP$ | 22.5 | 2.94 | 22.5 | 2.92 |
| $[EtHgPMe_3]Cl$ | $C_5H_{14}ClHgP$ | 17.6 | 4.13 | 17.4 | 4.23 |
| $[EtHgPEt_3]Br$ | $C_5H_{14}BrHgP$ | 22.5 | 4.71 | 22.5 | 4.75 |
| $[Pr^nHgPMe_3]Cl$ | $C_6H_{16}ClHgP$ | 20.3 | 4.54 | 20.2 | 4.60 |
| $[Pr^nHgPMe_2Ph]Cl$ | $C_{11}H_{18}ClHgP$ | 31.7 | 4.35 | 31.5 | 4.30 |
| $[Bu^nHgPMe_3]Cl$ | $C_7H_{18}ClHgP$ | 22.8 | 4.91 | 22.7 | 4.81 |
| $[Bu^nHgPMe_2Ph]Cl$ | $C_{12}H_{20}ClHgP$ | 33.4 | 4.67 | 33.4 | 4.74 |
| $[Bu^nHgPMe_3]I$ | $C_7H_{18}HgIP$ | 18.25 | 3.91 | 18.1 | 3.86 |
| $[MeHgbipy]NO_3$ | $C_{11}H_{11}HgN_3O_3$ | 30.45 | 2.55 | 30.4 | 2.55 |
| $[MeHgAsPh_3]ClO_4$ | $C_{19}H_{18}AsClHgO_4$ | 36.7 | 2.90 | 36.95 | 2.90 |
| $[MeHgPPh_3]$ $[Cr(NH_3)_2(SCN)_4]$ | $C_{23}H_{24}CrHgN_6PS_4$ | 34.8 | 3.05 | 34.9 | 3.15 |
| $*(Et_3P)_2HgBr_2$ | $C_{12}H_{30}Br_2HgP_2$ | 24.15 | 5.07 | $24.2\pm0.1$ | $5.13\pm0.14$ |

* 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%).

<u>Anion determination</u>

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

# D I S C U S S I O N

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 $(CCl_3)_2Hg$ 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 methyl-
mercuric nitrate in water.[29]  Pyridine forms a 1:1 complex
with p-tolylmercuric nitrate,[121] $[p-MeC_6H_4Hgpy]NO_3$, m.p. $210^{\circ}C$,
and also with 2-chlorovinylmercuric chloride, $[ClCH:CHHgpy]Cl$,
m.p. $76^{\circ}C$ 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 conducto-
metric titrations of triethylphosphine and phenyldimethyl-
phosphine 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]

$$2\ ClHgCOOMe + 2\ PPh_3 \longrightarrow (Ph_3P)_2HgCl_2 + Hg(COOMe)_2$$
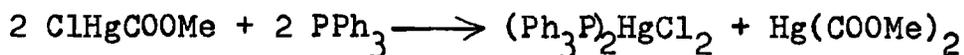
In a similar manner perchlorovinylmercuric chloride can be converted to the bis-mercurial.[108] By a presumably analogous reaction ammonia has been used to obtain bis-2-chlorovinyl-mercury from 2-chlorovinylmercuric chloride,[97] in contrast to pyridine which forms a salt, and a detailed kinetic study of the disproportionation reaction that occurs on addition of ammonia to a solution of an ester of $\alpha$-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 __alkyl__mercuric halides. Attempts to prepare similar complexes of aryl derivatives resulted in rapid disproportion-ation and isolation of the dihalo complex, $(R_3'P)_2HgX_2$, 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,
$\left[\text{MeHgPEt}_3\right]\text{Cl}$, m.p. 84-85$^\text{o}$C, on concentration. If, however,
the solution was allowed to stand at room temperature, large
prismatic crystals of the disproportionation product,
$(\text{Et}_3\text{P})_2\text{HgCl}_2$, m.p. 161$^\text{o}$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$^\text{o}$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 alkyl-
mercuric 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 crystallisa-
tion 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] $cm.^{-1}$ |
|---|---|---|
| $[MeHgPMe_3]Cl$ | $86^o$ | 528 s |
| $[MeHgPEt_3]Cl$ | $84-85^o$ | |
| $[MeHgPMe_2Ph]Cl$[d] | $95-97^o$ | 515.5 s |
| $[MeHgPEt_3]Br$ | $92-93^o$ [e] | 516 s[c] |
| $[MeHgPMe_2Ph]I$[d] | $107^o$ | 524 s |
| $[EtHgPMe_3]Cl$ | $86^o$ | 504 s |
| $[EtHgPEt_3]Br$ | $87^o$ | 508 m[c] |
| $[Pr^nHgPMe_3]Cl$ | $121-124^o$ | 504 m |
| $[Pr^nHgPMe_2Ph]Cl$[d] | $76-77^o$ | absent |
| $[Bu^nHgPMe_3]Cl$ | $107-108^o$ | 504 w |
| $[Bu^nHgPMe_2Ph]Cl$[d] | $86-88^o$ | |
| $[Bu^nHgPMe_3]I$ | $87-88^o$ | 517 s |

Notes: [a] with decomposition; [b] Nujol mull; [c] potassium
bromide disc; [d] darkens on exposure to light;
[e] lit.[110] m.p. $90-91^o$; 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
 $\nu$(C-Hg) region corresponding to that observed in the spectrum
of the bromide.    Thus, $\left[\text{MeHgPEt}_3\right]\text{BF}_4$ shows two absorptions at
532 cm.$^{-1}$ and 518 cm.$^{-1}$, the former being due to the $\nu$(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 $100^{o}C$, 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 $[MeHgPMe_3]Cl$ was sublimed under vacuum at $70^{o}C$ 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 $[MeHgPPhMe_2]I$ 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 $80^{o}C$ (below its melting point of $107^{o}C$) and the compound liquified to a viscous melt after thirty minutes. Dimethylmercury (85% of the theoretical for complete disproportionation) was recovered along with $(PPhMe_2)_2HgI_2$ 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-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 phenyl-dimethylphosphine 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 $[EtHgPEt_3]Br$ ($\Lambda_o$ = 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 $[MeHgPEt_3]Br$ ($\Lambda_o$ = 100.7 ohm$^{-1}$ cm.$^2$). As the ionic conductance of the bromide ion, $\lambda_o^-$, is 78.4 ohm$^{-1}$ cm.$^2$ this gives values of

ionic conductance, $\lambda_o^+$, for $[MeHgPEt_3]^+$ and $[EtHgPEt_3]^+$ of 22.3 and 22.1 ohm$^{-1}$cm.$^2$ respectively which is similar to those values of tetra-alkylammonium and other large ions in water at 25$^o$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 triphenyl- phosphine.   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 $17 \times 10^{-5}$ ohm$^{-1}$cm.$^{-1}$ was not reached until the molar ratio of PPh$_3$:Hg was 1.25:1.   Under similar conditions titration of triphenyl- phosphine against methylmercuric bromide gave a conductance maximum of $7.3 \times 10^{-5}$ 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 $2.6 \times 10^{-5}$ohm$^{-1}$cm.$^{-1}$ in a solution 0.0044 molar in mercury when the molar ratio of Ph$_3$P:Hg was 2.87:1.   The relative affinities of halide ions for the methylmercury cation would therefore appear to be  $I > Br > Cl$ and this is
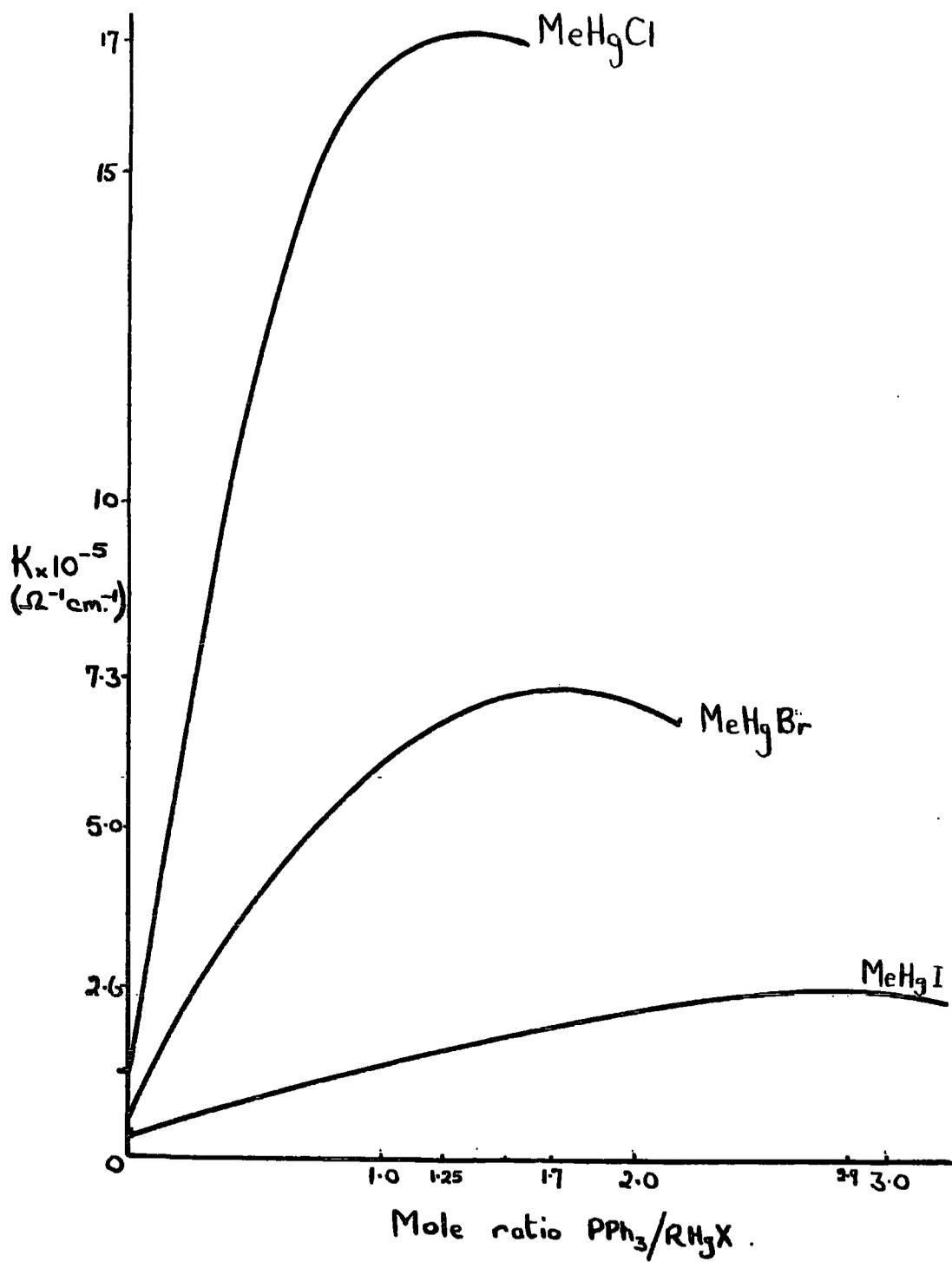
fig. (ix).

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

$$MeHgX + PPh_3 \rightleftharpoons [MeHgPPh_3]X$$
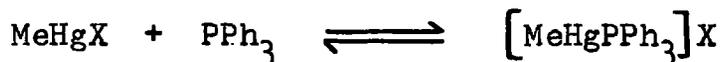
appears to favour the initial reactants to such an extent that the solubility of the complex salt is not exceeded. Furthermore, as the salt must have considerable ionic character, as is shown by the substantial increase in conductance in methanol, it should be most likely to precipitate from a non-polar 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, $(Ph_3P)_2HgCl_2$. 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 $[Pr^nHgPPhMe_2]Cl$ and $[Bu^nHgPPhMe_2]Cl$ 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 $[Bu^nHgPMe_3]I$ 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 $6^{o}C$ 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:

$$2\left[MeHgPPh_3\right]X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Me_2Hg + (Ph_3P)_2HgX_2$$
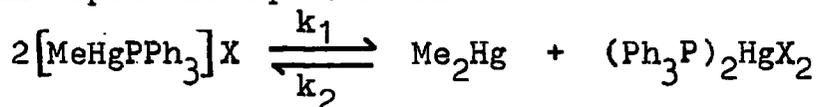
not being achieved rapidly (which appeared to be valid as the precipitate did not form immediately but after some hours and it was gradually deposited as refluxing continued) and that the rate of disproportionation and formation of $(Ph_3P)_2HgX_2, k_1$, is slow and rate determining.

## TABLE XXII

### Disproportionation of MeHgBr and PPh₃ 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,

$$RHgX + PR_3' \rightleftharpoons [RHgPPh_3]X \rightleftharpoons \tfrac{1}{2}R_2Hg + \tfrac{1}{2}(Ph_3P)_2HgX_2$$
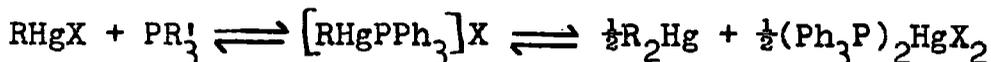
and the rate of formation of disproportionation products is claimed to be the rate controlling step in the disproportionation of esters of $\alpha$-bromomercuriphenylacetic acid by ammonia[116] which could well proceed by a similar mechanism to the above reaction.

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

## 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 |

initial reactants could become more significant thus reducing the concentration of $[RHgPPh_3]Br$ in solution. Secondly, an

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. $62^{\circ}C$, 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.   Methyl-
mercuric 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 infra-
red spectroscopic evidence.   Further, salts containing the
reineckate anion 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 triphenyl-phosphine 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, $(R_3'P)_2HgX_2$ 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, $(m-MeC_6H_4)_2Hg$. 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 $2\frac{1}{2}$ 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 $[m-MeC_6H_4HgPPh_3]X$ 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, $3.0 \times 10^{-6}$ 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, $2.2 \times 10^{-6}$ 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:

$$RHg\;X\;+\;PPh_3 \;\rightleftharpoons\; \left[RHgPPh_3\right]X \;\rightleftharpoons\; \tfrac{1}{2}R_2Hg + \tfrac{1}{2}(Ph_3P)_2HgX_2$$

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 $\left[EtHgPEt_3\right]Br$ and $\left[EtHgPMe_2Ph\right]Br$ 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 $\left[PhHgPEt_3\right]NO_3$ 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 $(PEt_3)_2HgBr_2$.

$$\left[PhHgPEt_3\right]NO_3 + NaBr \longrightarrow \tfrac{1}{2}Ph_2Hg + \tfrac{1}{2}(PEt_3)_2HgBr_2 + NaNO_3$$
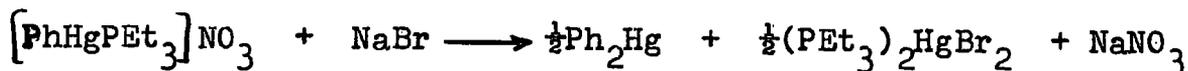
A similar reaction occurs with sodium iodide and this was followed spectrophotometrically. Solutions of $[PhHgPEt_3]NO_3$ and NaI in equimolar ratios were mixed and the reaction followed by tracing the increasing absorption at 2800Å due to the formation of the disproportionation product, $(Ph_3P)_2HgI_2$.

$$2[PhHgPEt_3]I \underset{-k_1}{\overset{k_1}{\rightleftharpoons}} Ph_2Hg + (PEt_3)_2HgI_2$$
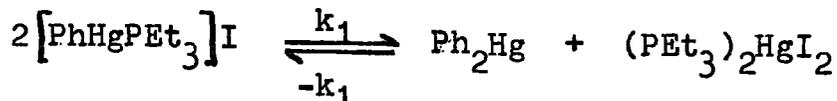
The optical density increased rapidly and became constant after 30 minutes at room temperature corresponding to 84.5% completion of the reaction. Within 4 minutes of the addition the concentration of di-iodide had reached 74.5% of the equilibrium value. Constant values of the rate constant, $k_1$, for 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 $[MeHgbipy]NO_3$.
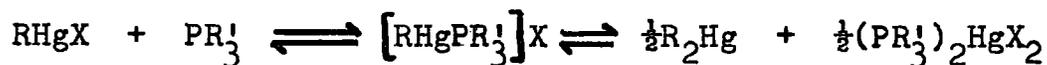
The rate of the disproportionation reaction was dependent upon the organic group attached to the mercury atom, anion, phosphine, solvent and temperature. The rate increased with increasing temperature and also with increasing dielectric constant of the solution, methanol > acetone > tetrahydrofuran > 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 $Me > Et > \underline{n}\text{-Pr} \simeq \underline{n}\text{-Bu}$.

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 $\alpha$-bromomercuriphenylacetic acid.

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The reversibility of the reactions:

$$RHgX \ + \ PR_3' \ \rightleftharpoons \ \left[RHgPR_3'\right]X \ \rightleftharpoons \ \tfrac{1}{2}R_2Hg \ + \ \tfrac{1}{2}(PR_3')_2HgX_2$$

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

$$R - Hg \overset{\displaystyle X}{\underset{\displaystyle PR_3'}{\Big\langle}}$$
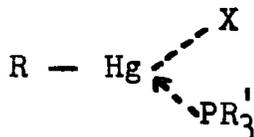
in the disproportionation transition complex. The idea of a 4-centre transition complex as postulated in the ammonia disproportionation, the reaction of $R_2Hg$ and $HgCl_2$,[124-5] and the cleavage of di-organomercurials with $HCl$[126] is also acceptable, but the actual structure of this complex is 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:

$$Me_2Cd + EtOH \longrightarrow MeCdOEt + MeH$$
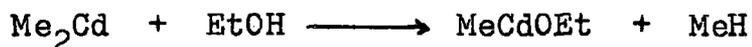
In the product, methylcadmium methoxide, the acceptor character of the metal is enhanced by the replacement of one of the carbon atoms by a more electronegative element, in this case oxygen, and the donor character of oxygen is similarly enhanced by attachment to a more electropositive element, cadmium. 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)
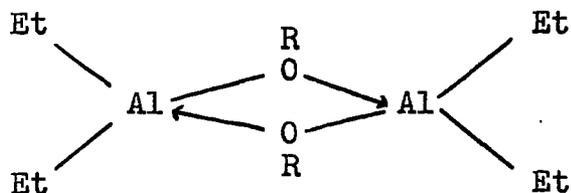


(i)

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

$$R - Cd \overset{\displaystyle \overset{R'}{\underset{\displaystyle O}{}}}{\underset{\displaystyle \underset{O}{\underset{R'}{}}}{}} Cd - R$$
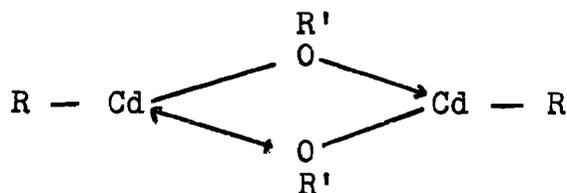
(ii)

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
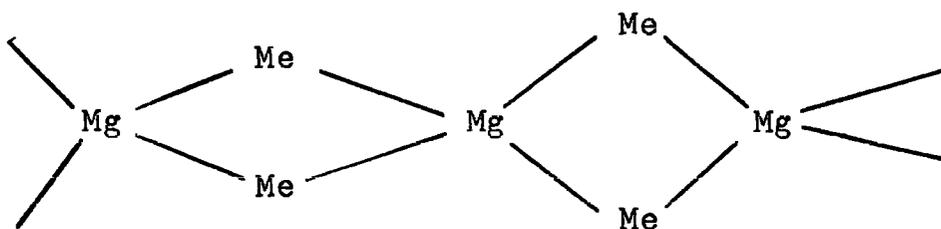


(iii)

distances indicate a more strongly bound polymer than dimethyl-
beryllium which explains the lower volatility of the magnesium
compound.

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
four co-ordinate in its compounds it is occasionally found in
a state of sp hybridisation in two covalent compounds such as

the monomeric di-<u>t</u>-butyl derivative and $\underline{sp}^2$ hybridised in

<u>three</u> 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.
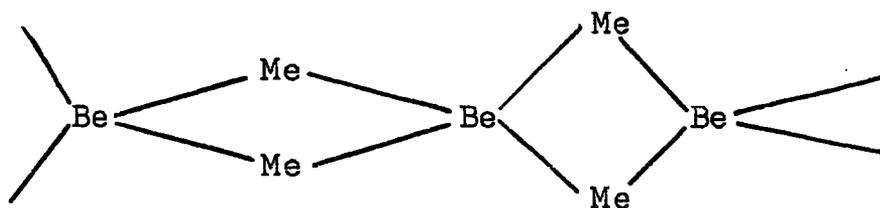


(iv)

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
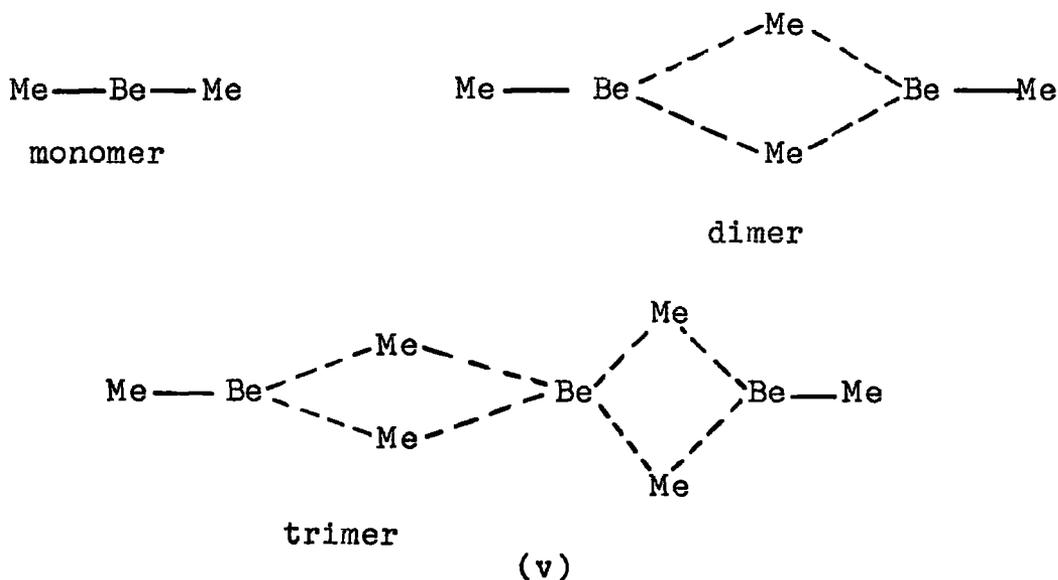
dimer



trimer

(v)

The polymer is broken into smaller units on heating and studies

of the vapour phase between 160-200° indicate that dimethyl-

beryllium 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, $Me_2Zn$, $44^O$;  $Me_2Cd$, $105.5^O$;  $Me_2Hg$, $92^O$.   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 electro-negativity trimethylamine forms a very stable 1:1 complex,[9] $Me_2Be \longleftarrow NMe_3$   m.p. $36^o$.   A slight degree of association is observed in benzene solution[10] (ca. 12%) and the complex is stable as a monomer[9] up to $180^o$.

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

$$Me_2Be \underset{\diagdown NMe_2 \text{—} CH_2}{\overset{\diagup NMe_2 \text{—} CH_2}{\bigg\langle}} \quad \begin{array}{c} | \\ | \end{array}$$
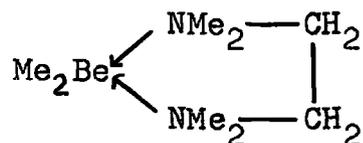
are known and the formation is possibly opposed by entropy effects.

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 trimethylphosphine 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
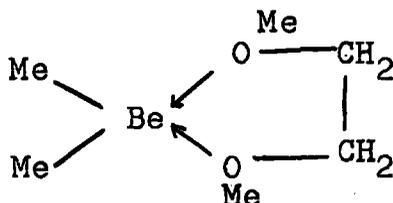


(vi)

sublimed at $70^{\circ}/0.06$ 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 trimethyl-amine and diethylberyllium, $(Me_3N)_2BeEt_2$, which dissociates above $-35^{\circ}$ 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 tri-phenylphosphine. 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 electro-negative 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 di-phenylzinc. Stabilisation of complexes of phosphorus and arsenic ligands by $d_\pi - d_\pi$ back-co-ordination 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'-tetra-methylethylenediamine 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-phenanthroline[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 bisdiphenylphosphino-ethane ($Bu^n$, 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

$$Me_2Zn \longleftarrow O \underset{CH_2}{\overset{CH_2}{<}} \bigg| \qquad and \qquad Me_2Zn \longleftarrow O \underset{CH_2}{\overset{CH_2}{<}} CH_2$$

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. $91^{o}$,
is obtained on mixing dimethylzinc and dimethoxyethane in 1:2
proportions. The 1:2 adduct

$$Me_2Zn \underset{O\ CH_2CH_2OMe}{\overset{O\ CH_2CH_2OMe}{<}} \quad \begin{matrix} Me \\ \\ Me \end{matrix}$$
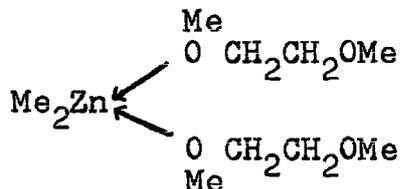
dissociates in solution to give a 1:1 compound, which is also
dissociated in solution, but can be crystallised on cooling to
give a low melting solid, m.p. $5.5^{o}$. Above $50^{o}$ this 1:1
complex disproportionates to dimethylzinc (b.p. $46^{o}$) and the
2:1 complex (b.p. $92^{o}$). The 1:1 chelate complexes

$$R_2Zn \underset{O-CH_2}{\overset{O-CH_2}{<}} \quad \begin{matrix} Me \\ \\ Me \end{matrix}$$
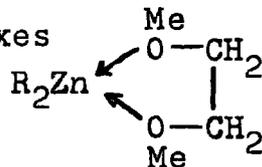
derived from bispentafluorophenyl- and diphenylzinc are much
more stable towards dissociation and ether is not lost
in vacuo at room temperature.[20]   The chelate complexes formed
between dimethylzinc and 1,4-dioxan and 1,4-thioxan,
figure (vii), are also stable to dissociation and molecular
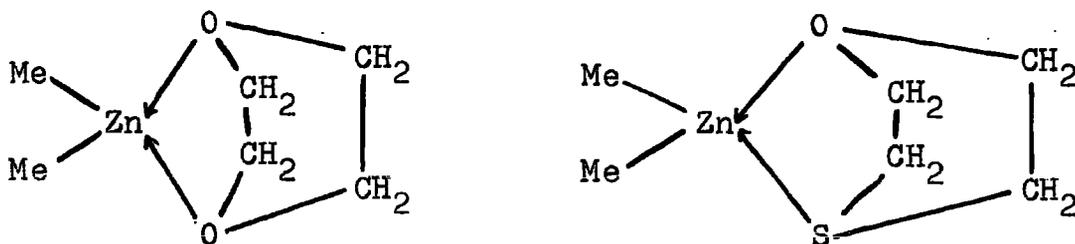


(vii)

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. $105^{\circ}$ and $(\underline{o}-MeC_6H_4)_2Zn(O_2C_4H_8)$, m.p. $69-71^{\circ}$
are also reported.[25,26]

## 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 dimethyl-
cadmium 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]
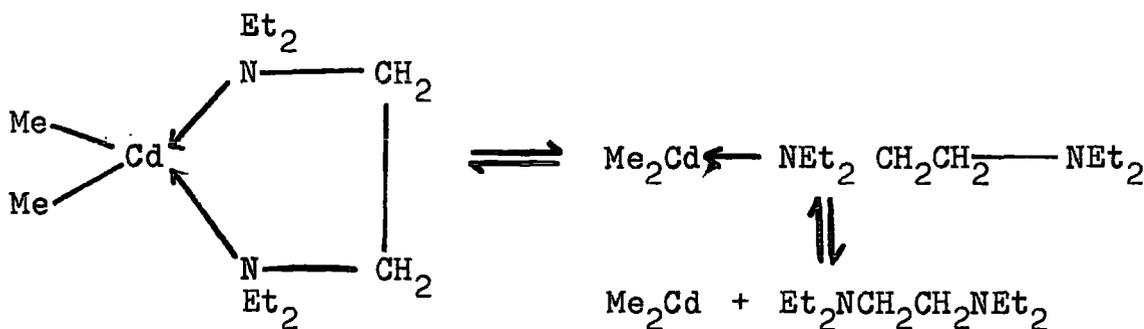


The bright yellow bipyridyldimethylcadmium complex,
decomposition from 120°, which loses dimethylcadmium on
pumping at room temperature[11] is also very much dissociated
in benzene solution.   In contrast the complex derived from
dimethylcadmium and 1,10 - phenanthroline, figure (viii) is



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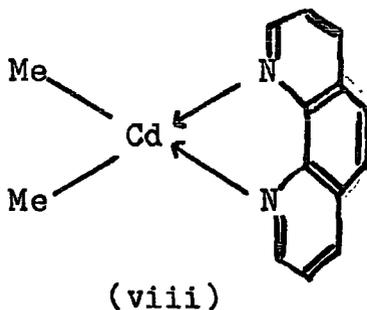
monomeric in benzene.[27]     Dimethylcadmium forms a 1:1 complex
with 1,4 - dioxan, figure (ix), m.p. 57°, which can be vacuum
sublimed.   In benzene solution, however, the complex is

almost completely dissociated.    This is in sharp contrast to
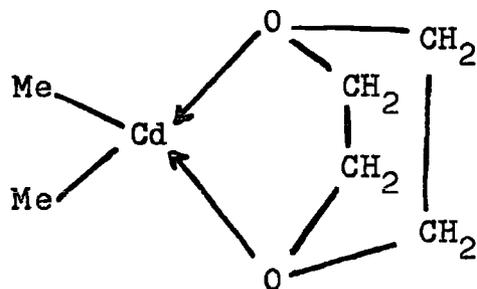


(ix)

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, triphenyl-
phosphine 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 evolved so rapidly from methanol and dimethyl-beryllium that the adduct $Me_2Be.MeOH$ is not observed and only the dimeric product, figure (x) is isolated.

$$
\begin{array}{c}
Me \\
O \\
Me\!-\!Be \qquad Be\!-\!Me \\
O \\
Me
\end{array}
$$
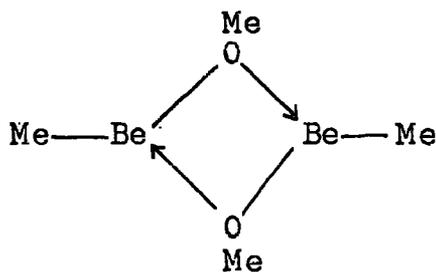
(x)

The compound is stable to $120^\circ$ 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 dimethyl-beryllium, 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 $44^O$ with evolution of methane and formation of a complex trimer, $(MeBe.NMe_2)_3$, m.p. $55-56^O$, for which a cyclic structure ha$ been postulated, figure (xi).

$$
\begin{array}{ccc}
& NMe_2 \longrightarrow BeMe & \\
\nearrow & & \searrow \\
MeBe & & NMe_2 \\
\searrow & & \swarrow \\
& NMe_2 \longrightarrow BeMe &
\end{array}
$$
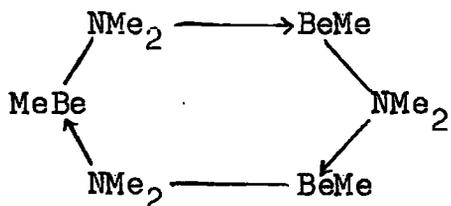
(xi)

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

$$Me_2Be + 2PhOH \xrightarrow[-70^O]{Et_2O} MeOH + Be(OPh)_2$$
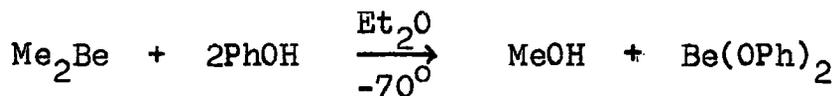
Dimethylberyllium reacts with both piperidine and morpholine to give the 1:1 adducts, $Me_2BeHNC_5H_{10}$ and $Me_2BeHNC_4H_8O$, respectively. Above $0^OC$ these compounds evolve methane but no molecular weight information for the products is given.[31] Above $20^O$ in the presence of excess amine a 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).
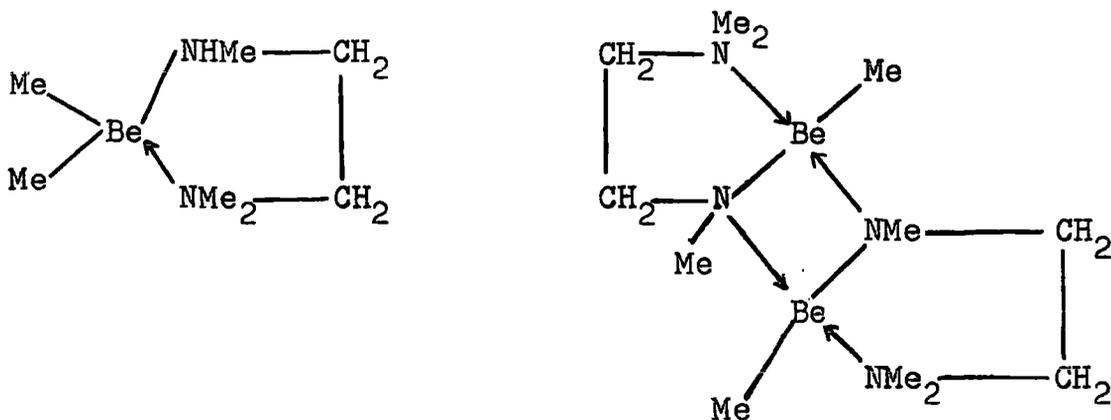


(xii)

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-isopropylberyllium reacts with one molar ratio of

methanol to give isopropylberyllium methoxide, (i-PrBeOMe)n
and propane. A similar reaction occurs with dimethylamine
and dimethylaminoisopropylberyllium,(i-PrBeNMe$_2$)$_n$, is formed.
With excess dimethylamine di-isopropyl- and di-t-butylberyllium
react in an analogous manner and yield trimeric bis-
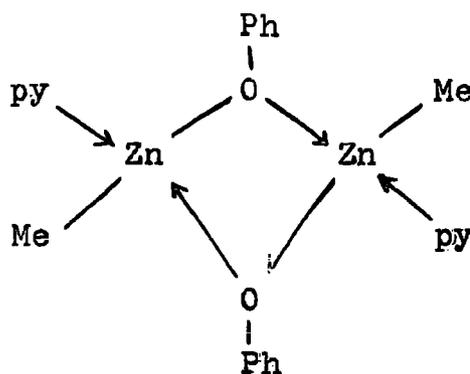dimethylaminoberyllium, $\left[Be(NMe_2)_2\right]_3$.

## 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$_2$CH$_2$NMe$_2$)$_2$, 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

$$
\begin{array}{ccccc}
 & & Ph & & \\
 & & | & & \\
 & & O & & Me \\
py & & \diagup \;\; \diagdown & & \diagup \\
 & \searrow Zn & & Zn \swarrow & \\
 & \diagup \quad \nwarrow & & \diagup \quad \nwarrow & \\
Me & & & & py \\
 & & O & & \\
 & & | & & \\
 & & Ph & &
\end{array}
$$

(xiii)

complexes have a substantial degree of co-ordinative saturation.

Thiols, $R'SH$ ($R'$ = Me, $Pr^n$ and Ph) reacted with dimethyl-
zinc 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,

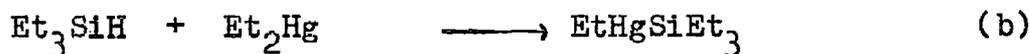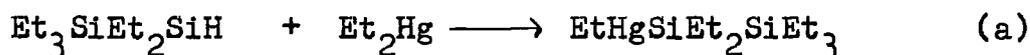$(MepyZnSBu^t)_2$, of the latter was also prepared.

On reaction of dimethylzinc with dimethylamine only bisdimethylaminozinc, $\left[(Me_2N)_2Zn\right]_x$ 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.
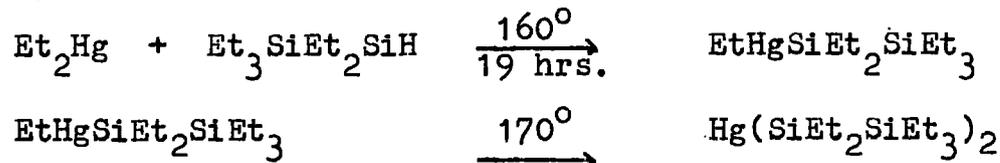
The reactions of the dialkyls of <u>cadmium</u> with molecules containing reactive hydrogen have been relatively little studied and dialkyl mercurials are stable even to water.

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,

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

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

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

were carried out under conditions varying from $85^o/6$ hours in (c) to $140^o/117$ 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:

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

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

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

EXPERIMENTAL

# E X P E R I M E N T A L

## 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 $65^{\circ}C$ to prevent significant loss of dimethylcadmium by co-distillation with ether. The temperature of the distillate remained below $37^{\circ}C$ 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 $50^{\circ}C$ solvent ether was distilled between $20^{\circ}$ and $40^{\circ}C$ at 20 cm. mercury pressure. The bath temperature was raised to $80^{\circ}C$ and dimethylcadmium distilled at $63^{\circ}$, $61^{\circ}$ and $57.5^{\circ}C$ 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. $63^{\circ}/19.0$ 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



A

B

C
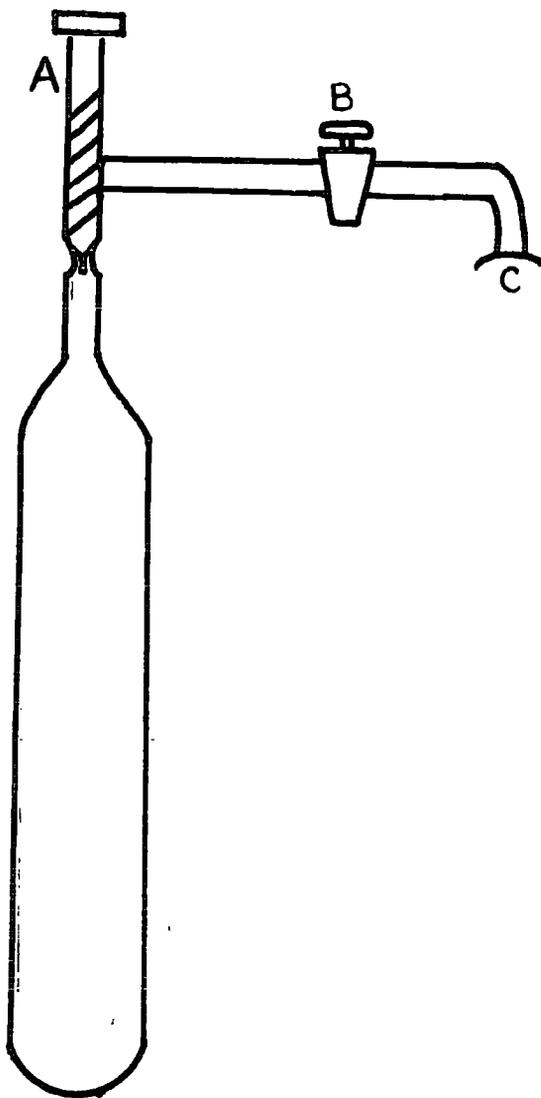
Dimethylcadmium  container

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 $-78^{\circ}$ 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 $70^{\circ}$, 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 $\nu$ (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 -$78^O$ 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 $100^O$. 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).

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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 $\gamma$ (Me $\rightleftharpoons$ 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 absorption 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 $-78^{\circ}$ 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 $10^{\circ}$ 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 $105^{\circ}$ 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$^{\circ}$ with an acetone -CO$_2$
bath when evolution of methane occurred. After 30 minutes
the solution was heated to about 40$^{\circ}$ 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 ⱱ(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$^o$
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.

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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 $-78^{\circ}$ 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 $150^{\circ}$ but did not melt below $300^{\circ}$. 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 methyl-cadmium(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
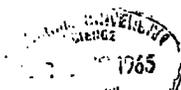
deposited. On completion of the reaction more hexane (30 ml.) was added and the solution boiled when all of the solid material dissolved. On cooling, the product crystallised as colourless prisms. On determination of the melting point in a sealed tube the compound turned brown over a long range, 30 - 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 $\nu$(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 $100^\circ$ 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 $60^o$ 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

# D I S C U S S I O N

The effect of replacing one methyl group of dimethyl-cadmium 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).
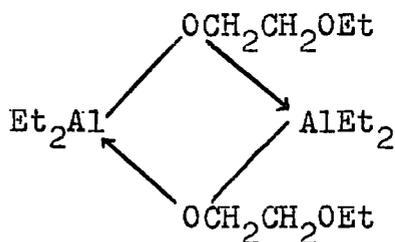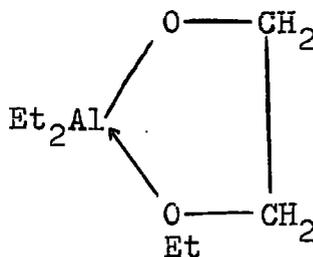


(xiv)                    (xv)

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

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

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

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

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]

$$(Me_2AlSMe)_2 + 2NMe_3 \rightleftharpoons 2Me_2Al(SMe)NMe_3$$
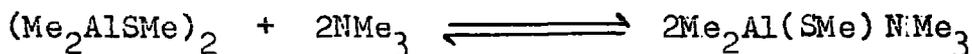
This indicates the comparable donor strength of the sulphur
and nitrogen atoms in the latter cases. A similar effect
involving pyridine is observed with tantalum <u>n</u>-alkoxides,[49]
$Ta(OR)_5$, which are dimeric in benzene solution but monomeric
in pyridine, probably due to co-ordination by solvent
yielding $Ta(OR)_5$ py. 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 $-76°$.

$$Me_2Cd + ROH \longrightarrow MeCdOR + CH_4$$
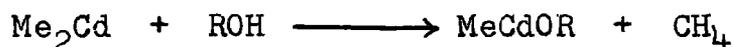
In contrast to the other alkoxides evolution of methane and corresponding formation of methylcadmium phenoxide did not occur until the solution was warmed to about $30°$. In no case was a co-ordination complex $Me_2Cd \longleftarrow O\overset{H}{\underset{R}{\diagdown}}$ isolated.

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 <u>four</u> such as $(Me_2GaOMe)_2$, figure (xvi) is

$$Me_2Ga \overset{OMe}{\underset{OMe}{\rightleftharpoons}} GaMe_2$$
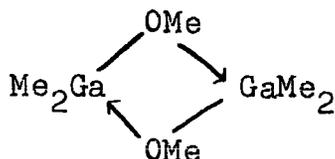
(<u>xvi</u>)

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

$$Me - Be \overset{OMe}{\underset{OMe}{\rightleftharpoons}} Be - Me$$
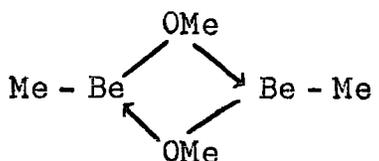
(<u>xvii</u>)

is not so surprising in this case as beryllium does in some cases exhibit stability in this state compared to that of $\underline{sp}^3$ hybridisation and <u>four</u> 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 _four_ 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
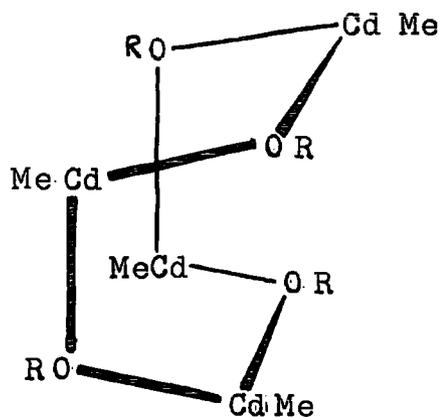


(xviii)

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 methyl-
cadmium 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
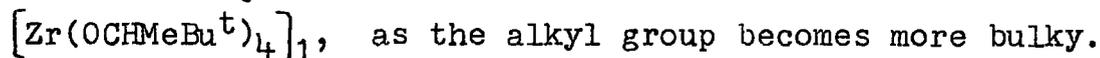in view of the many tetramers that have been observed among

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 prevent-
ing 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 :

$$\left[Zr(OCH_2CH_2CH_2CH_2Me)_4\right]_3, \quad \left[Zr(OCH(Me)Pr^i)_4\right]_2, \quad \left[Zr(OCMe_2Et)_4\right]_1.$$
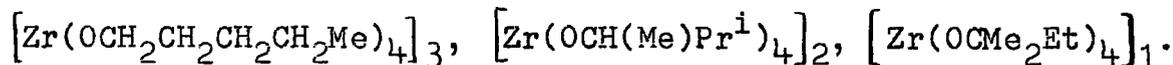
A similar decrease in association is observed in the series

$$\left[Zr(OCHMe_2)_4\right]_3, \quad \left[Zr(OCHEt_2)_4\right]_2, \quad \left[Zr(OCHPr^n)_4\right]_1,$$

$$\left[Zr(OCHMeBu^t)_4\right]_1, \quad \text{as the alkyl group becomes more bulky.}$$

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 $180^o$.

## TABLE II

### Reactions of methylcadmium compounds

| Compound | Reaction with : | | pyridine |
|---|---|---|---|
| | water | 2N.H$_2$SO$_4$ | |
| | 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.

$$2\text{MeCdOR} \xrightarrow{\text{heat}} \text{Me}_2\text{Cd} + \text{Cd(OR)}_2$$
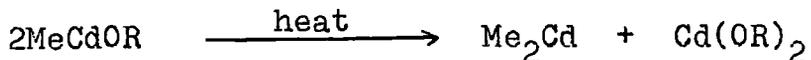
Dimethylcadmium was identified by infra-red spectrum taken on the gas liberated but the residue was not characterised. Similar disproportionation reactions on pyrolysis are observed for $(\text{MeBeOMe})_2$[29] and $(\text{MeZnOR})_4$, but not for $(\text{MeCdOBu}^t)_4$. In the latter case zinc[39] and cadmium derivatives react in a similar manner and liberate isobutene.

Reactions of dimethylcadmium with thiols

Dimethylcadmium reacts with methane thiol and thiophenol respectively at $-78^{\circ}$ 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] $[\text{Hg(SMe)}_2]_x$, $[\text{Hg(SEt)}_2]_x$ and $[\text{Hg(SBu}^t)_2]_x$ and the n-alkyl thiol derivatives of dimethylzinc,[39] $(\text{MeZnSR})_x$, which are also polymers. Although insoluble in organic solvents $(\text{MeCdSMe})_x$ 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 $(\text{MeCdSMe})_x$ does not cause the latter to dissolve and only bipyridyl was recovered from the solution. Similarly $(\text{MeCdSPh})_x$ 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)
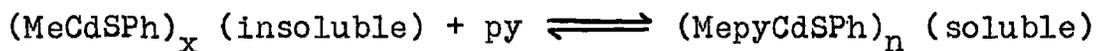
Such a reaction is analogous to the equilibrium obtained between trimethylamine and the dimeric aluminium and gallium compounds.

$(Me_2AlSMe)_2$ + $2NMe_3$ $\rightleftharpoons$ $2Me_2Al(NMe_3)SMe$
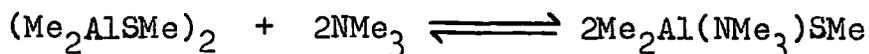
Thiol derivatives of non-transition metals have been relatively little studied but monomeric compounds of beryllium and gold are known. The product derived from 2 - amino - ethane thiol, $H_2NCH_2CH_2SH$, and $(Et_2AuBr)_2$ is monomeric,[61] figure (xix) in several solvents. This has
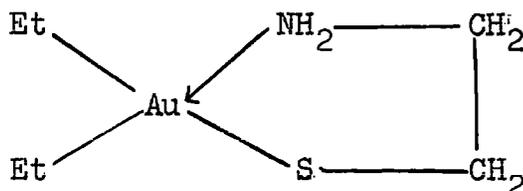


(xix)

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).



(xx)

- 218 -
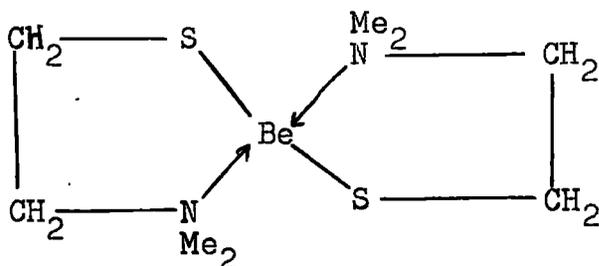
Branched chain thiols, $\underline{i}$-PrSH and $\underline{t}$-BuSH react with dimethylcadmium to give complexes which are soluble in organic solvents. Cryoscopic determinations of molecular weight in benzene solution, Table I, show that the complex derived from isopropane thiol is hexameric $(MeCdSPr^i)_6$ analogous to the corresponding zinc compound[39], while that derived from $\underline{t}$-butane thiol is tetrameric. The zinc derivative is a pentamer, $(MeZnSBu^t)_5$.

Methylcadmium($\underline{t}$-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.
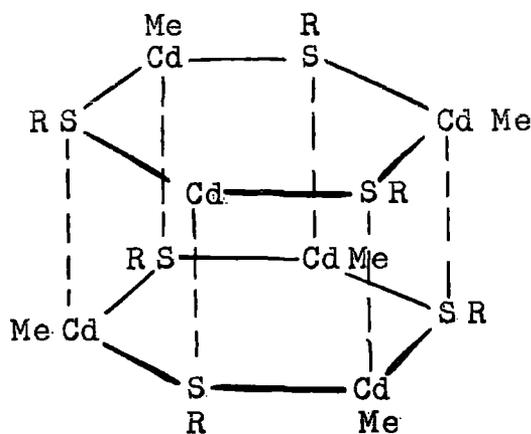


(xxi)

## TABLE III

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

| Compound | Cd-Me rock | $\nu$(Cd-Me) |
|---|---|---|
| Me$_2$Cd | 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$_2$Cd (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 $\nu$(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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